IX IBERO-AMERICAN CONGRESS ON MEMBRANE SCIENCE AND TECHNOLOGY

Santander- Spain, May 25-28, 2014

BOOK OF ABSTRACTS

IX IBERO-AMERICAN CONGRESS ON MEMBRANE SCIENCE AND TECHNOLOGY

May 25 – 28, 2014
Santander, Spain

http://citem2014.unican.es/

Advanced Separation Processes Group
Department of Chemical and Biomolecular Engineering
University of Cantabria

CITEM 2014 – IX Ibero-American Congress on Membrane Science and Technology
Book of abstracts

Editors: Alfredo Ortiz and Daniel Gorri

ISBN: 978-84-697-0397-7
Depósito legal: SA-299-2014

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WELCOME

It is our great pleasure to give you the warmest welcome to the IX Ibero-American Congress on Membrane Science and Technology (CITEM 2014) organized by the Advanced Separation Processes group, Department of Chemical and Biomolecular Engineering, of the University of Cantabria, Spain, and held at the CHIQUI hotel in Santander from May 25-28, 2014.

We have a great program ahead that will give us a unique opportunity to exchange points of view and covering the broad spectrum of topics in this exciting and extremely active field of membrane science and technology. We invited four recognized plenary speakers to broaden the scope of the program and generate discussion and new insights. The program covers more than 100 oral lectures and almost 115 posters presentations, from students and also from senior scientists in the field, giving an overview of the past and future developments in that specific fields. Moreover, a workshop on Membrane Technologies for Water Treatment will take place as part of CITEM 2014.

We would also like to encourage you to explore Cantabria and the city of Santander, because there are plenty of outstanding spots to visit and great opportunities to enjoy our magic culinary experience in the company of our renowned wines. The social program includes a welcome reception, a guided tour to Magdalena Palace, traditional Spanish northern "Tapas" tasting experience, conference cocktail dinner at the Casino of Santander and sightseeing in Santillana del Mar (Medieval Village and Altamira Cave location).

We would like to take the opportunity to express our sincere gratitude to the members of the organizing committee, scientific committee, and volunteers for their efforts and altruistic support at the expense of their own work. We are also very grateful to our sponsors and institutions for their highly valuable support. Finally we would like to thank all members of the membrane community for their contributions and help to make this conference a success.

We wish you a wonderful CITEM 2014 in Santander and hope you will have a great time!

Kindest Regards,

Alfredo Ortiz
Daniel Gorri

Chairs CITEM 2014

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PROGRAM

Sunday, 25th May 2014

Conference Room

14:00-19:00 h Registration

15:00-18:00 h Guided Walking Tour to Magdalena Palace. (Start at the entrance of Hotel Chiqui)

18:30-19.00 h Opening Session

19:00-20:00 h Plenary Lecture: **Prof. Bart van der Bruggen**. "The Potential of Electrodialysis for Sustainble Production and Recycling"

20:00-21:00 h Reception Cocktail

Monday, 26th May 2014

08:30-09:30 h Plenary Lecture: **Prof. Angel Irabien.** "Sustainable Membrane Processes and Products: Development and Innovation"

BLOCK 1

09:30-11:10 h **Session 1. Polymeric Membranes I** Chairman: **Mohamed Khayet**

Conference Room

09:30-09:50 h S1.1. "Preparation hollow fiber membrane by combination of thermally induced phase inversion and non-solvent induced phase inversion with green solvent". ***Naser Tavajohi Hassankiadeh***, *Zhaoliang Cui, Dong Won Shin, Ji Hoon Kim, Jong Geun Seong, Aldo Sanguineti, Vincenzo Arcella, Young Moo Lee, Enrico Drioli.*

09:50-10:10 h S1.2. "Experimental and molecular dynamics study of the effect of solvent on PES membrane morphology". *Arcadio Sotto,* ***Junkal Landaburu-Aguirre****, Arman Boromand, Jesus M. Arsuaga, Nerea Gonzalez.*

10:10-10:30 h S1.3. "Water reclamation in the steel industry by removing heavy metals with membrane technology and precipitation". ***Elena Piedra****, Jose R. Alvarez, Susana Luque.*

10:30-10:50 h S1.4. "Organosolv pretreatment for cellulose recovery from Quercus SPP sawdust for its ulterior use in membrane synthesis". ***Karla Ruiz-Cuilty***, *L. Ballinas-Casarrubias, Tania Saucedo, Guadalupe Nevárez-Moorillon, Laila Muñoz, G. Gónzalez-Sánchez.*

10:30-10:50 h S1.5. "Effects of thickness on PVDF membrane synthesized by the phase inversion process". ***Ana C. D. Morihama***, *J. C. Mierwza, G. Leocadio.*

09:30-11:10 h Session 2. Facilitated Transport membranes Chairwoman: **Isabel Coelhoso**

Santillana Room

09:30-09:50 h S2.1. "Separation and pre-concentration of low uranium (vi) content in water using bulk liquid and supported liquid membrane systems containing bis(2-ethylhexyl) phosphoric acid as carrier". *Angélica M. Candela Soto, Viola Benatti,* ***Cristina Palet Ballús***.

09:50-10:10 h S.2.2. "A novel liquid membrane process using a taylor flow regime". ***Alan Didier Pérez-Ávila***, *Javier Fontalvo.*

10:10-10:30 h S2.3. "Modulation of the transport of organic solutes through supported ionic liquid membranes by an external magnetic field". ***C. I. Daniel***, *P. Sebastião, Carlos A.M. Afonso, Pavel Izak, Carla A.M. Portugal, J.G. Crespo.*

10:30-10:50 h S2.4. "Improving performance of pervaporation membranes for biobutanol separation". ***Joanna Marszałek***, *Paulina Rdzanek, Władysław Kamiński.*

10:50-11:10 h S2.5. "Arsenic detection and removal from natural waters based on a polymer inclusion membrane system". ***Clàudia Fontàs***, *Rubén Vera, Enriqueta Anticó*.

09:30-11:10 h Session 3. Membrane Bioreactors I Chairman: **João Crespo**

Candil Room

09:30-09:50 h S3.1. "Improvement of sludge quality to control fouling in MBR". ***M. C. S. Amaral,*** *A. R. Alkmim, P. R. da Costa, P. B. Moser, L.S. França Neta, V. M. J. Santiago, A. C. Cerqueira.*

09:50-10:10 h S3.2. "Study of the influence of different variables on membrane fouling in submerged membrane bioreactors". ***Ana Urkiaga***, *Deiene Iturbe, Javier Etxebarria.*

10:10-10:30 h S3.3. "Membrane Fouling Behavior during the Performance of two Membrane Bioreactors: Resistance Analysis and Fouling Mechanisms". ***Liuba Domínguez***, *Manuel Rodríguez, Daniel Prats.*

10:30-10:50 h S3.4. "Fouling control in membrane bioreactors by sewage-sludge based adsorbents". ***V.M. Monsalvo***, *J. Lopez, J. Villamil, M.M. Somer, A.F. Mohedano, J.J. Rodriguez.*

10:50-11:10 h S3.5. "Role of the SMP and EPS in membrane bioreactors fouling". ***Eugenio Marín,*** *Jorge Pérez, Miguel Ángel Gómez.*

11:10-11:30 h Coffe Break

BLOCK 2

11:30-13:30 h Session 4. Polymeric Membranes II Chairman: **David Mecerreyes**

Conference Room

11:30-11:50 h S4.1. "VinyLoop: an innovative recycling solution to obtain high quality R-PVC for membrane production". ***Giovanni Piras.***

11:50-12:10 h S4.2. "Iron influence on uranium removal from water using cellulose acetate membranes doped with activated carbon". *Ruben Villalobos,* ***Karla Ruíz-Cuilty,*** *M. Elena Montero-Cabrera, V. Fierro, A. Celzard, V. Nevárez-Moorillón, H. Esparza, L. Ballinas-Casarrubias.*

12:10-12:30 h S4.3. "Extraction of propanol from aqueous solution by pervaporation process,with PDMS membranes". *S.Hamounil, O.Arous,* ***G.Nezzal.***

12:30-12:50 h S4.4. "Effects of polymer concentration on the characteristics and membrane distillation performance of nano-fibrous membranes". *M. Essalhi,* ***M. Khayet****.*

12:50-13:10 h S4.5. "Prediction of adhesion between the polymeric layers of composite hollow fiber membranes produced by simultaneous extrusion". *Felipe C. Cunha,* ***Frederico de A. Kronemberger****, Cristiano Piacsek Borges.*

13:10-13:30 h S4.6. "Desempenho de membrana PA12 preparada por inversâo de fases com partículas de dióxido de titânio na degradação do azul de metileno". ***Maria Teresa Pessoa do Amorim****, Eneida Sala Cossich, Rosângela Bergamasco.*

11:30-13:30 h Session 5. Inorganic Membranes Chairman: **Miguel Menéndez**

Santillana Room

11:30-12:00 h S5.1. Keynote: "Palladium membranes for hydrogen separation and membrane reactors". ***David A. Pacheco Tanaka.***

12:00-12:20 h S5.2. "MFI zeolite membranes: preparation and characterization". ***A. Garofalo****, L. Donato, O. Alharbi, E. Drioli, C. Algieri.*

12:20-12:40 h S5.3. "Study of two methods in the preparation of zeolite membrane (ZSM-5/alfa-alumina): rubbing and dip-coating". *Everton R. F. dos Santos, Marcílio M. Silva,* ***Meiry G. F. Rodrigues****, Lam Y. Lau.*

12:40-13:00 h S5.4. "Desempenho de um Sistema com Automação para Processos de Separação com Membranas Cerâmicas". ***Tellys Lins A. Barbosa****, Raquel Santos Silva, João U. L. Bezerra, Rodrigo Vieira Alves, Kepler Borges França, Hélio Lucena Lira.*

13:00-13:30 h S5.5. "Ceramic nanofiltration membranes in chemical and pharmaceutical applications". ***Stefan Duscher***. *INOPOR GMBH.*

11:30-13:30 h Session 6. Membrane Bioreactors II / Modelling and Process Simulation

Chairwoman: **Míriam. C. S. Amaral**

Candil Room

11:30-11:50 h S6.1. "Development of polymer inclusion membranes based on ionic liquids and laccase for application in biocatalysis and microbial fuel cells". *S. Haj Kacem,* ***S. Galai****, A. Pérez de los Ríos, F.J. Hernández Fernández, J. Quesada-Medina.*

11:50-12:10 h S6.2. "Submerged Membrane Bioreactor for water reuse and nutrients recovery in a Recirculated Aquaculture System". ***Isaías Negra-Jiménez****, Antonio Campos-Mendoza, Julio C. Orantes-Ávalos.*

12:10-12:30 h S6.3. "Effect of biofilm carriers on membrane permeability and organic matter and nitrogen removal in a submerged membrane bioreactor". ***Eduardo L. Subtil****, Ivanildo Hespanhol, José C. Mierzwa.*

12:30-12:50 h S6.4. "Analysis of the effects of ultrasound irradiation over effluent quality and membrane integrity in flat sheet microfiltration MBR system". ***Luz M. Ruiz****, G. Garralón, J. I. Pérez, M. A. Gómez.*

12:50-13:10 h S6.5. "Use of steady-state block modeling and genetic algorithms to optimize processes coupled with reverse osmosis membranes". ***José M. Gozálvez Zafrilla****, Asunción Santafé Moros*.

12:50-13:10 h S6.6. "Polymeric membranes application in petroleum industry hydrogen separation". ***A. Quesada Pérez****, A.R. Khan, S.M. Al-Salem*.

13:30-15:00 h LUNCH

BLOCK 3

15:00-17:00 h FLASH POSTER SESSION Chairwoman: **Ane Urtiaga**

Conference Room

15:00-15:05 h FPS.1. "Passive sampling of Zn(II) using a hollow fiber supported liquid membrane device". ***Eduardo Rodríguez de San Miguel Guerrero****, Erik A. Rodríguez Morales, Josefina de Gyves y Marciniak.*

15:05-15:10 h FPS.2. "Influencia del conformado sobre las propiedades de una membrana cerámica de bajo coste". ***Lorente, María M.***, *Mestre, S., Sánchez, E., Pérez-Fernández, O., Menéndez, M., Santateresa, E., Gozalbo, A.*

15:10-15:15 h FPS.3. "Synthesis of ceramic ion-exchange membranes with bipolar behavior for electrodialytic water splitting". ***M.C. Martí-Calatayud***, *M. García-Gabaldón, V. Pérez-Herranz, S. Sales, S. Mestre.*

15:15-15:20 h FPS.4. "Nutrient removal on sludge concentration by forward osmosis". ***Jaime Lora García***, *M. F. López-Pérez, E. Gonga Roselló, A. Abad Sempere.*

15:20-15:25 h FPS.5. "Morphological characteristics of the flocs and microfauna populations evolution during the adaptation of biomass in a submerged membrane bioreactor". *Aniceto Basalenque Rueda-Rocha,* ***Isaías Negra-Jiménez****, Renné I. López-Chacón, Abril Munro-Rojas, Julio C. Orantes-Ávalos.*

15:25-15:30 h Questions and Discussion FPS.1-5.

15:30-15:35 h FPS.6. "Membrane integration in biomedical microdevices". ***Magdalena Malankowska***, *Reyes Mallada, Pilar Pina, Ismael Pellejero, Miguel Urbiztondo.*

15:35-15:40 h FPS.7. "Synthesis and characterization of films of silver nanoparticles dispersed in poly(urethane urea) for the separation of petrochemical gases". ***Antoniel C. Carolino Campos***, *Dunieskys R. González Larrudé, Cecília Vilani, Ricardo A. F. Machado, Márcia Cerqueira Delpech, Deborah Vargas Cesar, Rodrigo Azevedo dos Reis.*

15:40-15:45 h FPS.8. "Biomimetic aquaporin membranes in forward osmosis applications". ***Claus Hélix-Nielsen***, *Irena Petrinic.*

15:45-15:50 h FPS.9. "Development of microporous TiO_2 doped silica membranes to enhance the hydrothermal stability for gas separation". ***Ghulam Mustafa***, *Jan Hoffman, Martin Bram, Dirk Enke.*

15:50-15:55 h FPS.10. "Permeability of propane and propylene in highly selective ionic liquid/polymer composite membranes". ***Raúl Zarca***, *Alfredo Ortiz, Daniel Gorri, Inmaculada Ortiz.*

15:55-16:00 h Questions and Discussion FPS.6-10.

16:00-16:05 h FPS.11. "Layer-by-Layer assembly of polyelectrolytes applied to obtain cation exchange membranes with monovalent ion selectivity". ***M. C. Martí-Calatayud***, *S. Abdu, J. E. Wong, M. García-Gabaldón, V. Pérez-Herranz, M. Wessling.*

16:05-16:10 h FPS.12. "Development of TiO_2 photocatalytic membranes for drinking water treatment". ***S. Sanches***, *C. Nunes, P. Passarinho, F. Ferreira, M.T. Barreto Crespo, J.G. Crespo, V.J. Pereira.*

16:10-16:15 h FPS.13. "Incorporation of vinylimidazolium based Ionic liquid in well-defined straight porous PBI membranes: Novel polymeric ionic liquid/PBI membranes for high temperature fuel cell applications". ***Parashuram Kallem***, *Adela Eguizábal, Maria Pilar Pina, Reyes Mallada.*

16:15-16:20 h FPS.14. “About the sustainability of the electrodialysis powered by photovoltaic solar energy”. ***C. Fernández-González***, *A. Domínguez-Ramos, R. Ibáñez, A. Irabien.*

16:20-16:25 h FPS.15. “Development of new electrolytes based on organic ionic plastics crystal supported on membrane nanofibres for their application in fuel cells”. ***Iván Merino***, *Mariana Díaz, Alfredo Ortiz, Inmaculada Ortiz.*

16:25-16:30 h Questions and Discussion FPS.11-15.

16:30-16:35 h FPS.16. “Evaluation of electrolyte mixtures rejection behavior using nanofiltration membranes using spiral wound and flat sheet configurations”. ***M. Reig***, *E. Licon, C. Valderrama, O. Gibert, A. Yaroshchuk, J.L. Cortina.*

16:35-16:40 h FPS.17. “Membrane based process for HCl and NaOH production from reverse osmosis brines”. ***Antía Pérez-González***, *Raquel Ibáñez, Pedro Gómez, Ana Urtiaga, Inmaculada Ortiz.*

16:40-16:45 h FPS.18. “Evaluation of the chemical resistance nanofiltration membranes applied in liquid radioactive waste”. ***Elizabeth E. de M. Oliveira***, *Edna T. R. Bastos, Júlio C. Afonso.*

16:45-16:50 h FPS.19. “Characterization of different type of fibers with PVDF for CO_2 absorption”. ***L. Gomez-Coma***, *A. Garea, A. Irabien, J.C. Rouch, J.,F. Lahitte, J.C. Remigy.*

16:50-16:55 h FPS.20. “Zeolite a / poly(1-trimethylsilyl-1-propyne mixed matrix membranes for CO_2/N_2 separation”. ***Ana Fernández-Barquín***, *Clara Casado-Coterillo, Susana Valencia, Ángel Irabien.*

16:55-17:00 h FPS.21. “Efficient oxygen production by means of advanced ceramic membranes based on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$”. ***J. Garcia-Fayos***, *S. Escolastico, L. Navarrete, S. Baumann, W.A. Meulenberg, J.M. Serra.*

17:00-17:05 h Questions and Discussion FPS.16-21.

17:05-17:30 h Coffe Break

17:30-19:30 h POSTER SESSION I

20:30 Traditional Spanish northern “Tapas” tasting

08:30-09:30 h Plenary Lecture: **Prof. João Crespo.** "Membrane Processes for Water Safety and Security"

BLOCK 4

09:30-11:10 h **Session 7. Workshop: Membranes for drinking water production**

Chairman: **Bart van der Bruggen**

Conference Room

09:30-09:50 h S7.1. "Donnan dialysis for safe drinking water supply: how can an "enemy" become a friend?". *Mafalda Lopes, João Crespo,* ***Svetlozar Velizarov.***

09:50-10:10 h S7.2. "Drinking water: single step ultrafiltration treatment of high turbid river water". ***Isadora A. Nagaoka****, Vanessa Brusius, André Lermontov.*

10:10-10:30 h S7.3. "Microbial regrowth in gravity-driven membrane filtration influences the water quality in terms of pathogen growth". ***J. Mimoso****, F. Hammes.*

10:30-10:50 h S7.4. "Combining nanofiltration with photolysis/TiO_2 photocatalysis as an hybrid process for water treatment". ***S. Sanches****, C. Nunes, A. Penetra, A. Rodrigues, V.V. Cardoso, E. Ferreira, M.J. Benoliel, M.T. Barreto Crespo, J.G. Crespo, V.J. Pereira.*

10:50-11:10 h S7.5. "Removal of pesticides from water with membrane processes". ***Fábio Merçon,*** *Alexandre L. de Azevedo Santos, Renata Cordeiro Machado.*

09:30-11:10 h **Session 8. Gas and vapor separation** Chairman: **Antonio Hernández**

Santillana Room

09:30-09:50 h S8.1. "Engineered membranes based on poly(ionic liquid)s for gas separation applications". *Liliana C. Tomé, David Mecerreyes, Carmen S. R. Freire, Luís P. N. Rebelo,* ***Isabel M. Marrucho.***

09:50-10:10 h S8.2. "CO_2 removal from anaesthetic gas circuits integrating enzymatic conversion and ionic liquid membrane extraction". *C. Martins,* ***L.A. Neves****, C.A.M. Afonso, I.M. Coelhoso, J.G. Crespo.*

10:10-10:30 h S8.3. "Development of exopolysacharide membranes for solvent dehydration". *Inês T. Meireles, Carla Portugal, João G. Crespo,* ***Isabel M. Coelhoso****.*

10:30-10:50 h S8.4. "Influence of reducing agent concentration via pore-plating in Pd membrane preparation over PSS support for H_2 separation". ***D. Alique****, R. Sanz, J. A. Calles, L. Furones.*

10:50-11:10 h S8.5. "Preparação e caracterização de membrana cerâmica de alumina impregnada com paládio". ***Mára Zeni***, *Tatiana Bisoto, Aline L. Schio, Camila Baldasso, Marcelo Godinho, Venina dos Santos, Carlos P. Bergamann.*

09:30-11:10 h Session 9. Membrane and surface modification Chairman: **Pedro Prádanos**

Candil Room

09:30-09:50 h S9.1. "Mixed-matrix electrospun nano-fibrous membranes for desalination". ***M. Khayet***, *M. Essalhi.*

09:50-10:10 h S9.2. "Design and characterisation of magneto-sensitive PVA hydrogel membranes". *Ana C. Manjua, Fabián Vaca Chávez, Pedro J. Sebastião, João G. Crespo,* ***Carla A. M. Portugal.***

10:10-10:30 h S9.3. "Development of membranes for desalination containing biocides for biofouling reduction". ***Helen C. Ferraz***, *Juliana A. Guimarães, Claudia Galinha, João Paulo S. G. Crespo, Cristiano P. Borges.*

10:30-10:50 h S9.4. "Chemistry modification of commercial reverse osmosis membrane to improve the resistance to oxidizing agents". ***Lucinda F. Silva***, *Maria L. Moreira, Ricardo C. Michel, Cristiano P. Borges.*

10:50-11:10 h S9.5. "Variation on processability of tunable membranes based on block-co-polymer/ionic liquids". *Ana Corres,* ***Thomas Schäfer****.*

11:10-11:30 h Coffe Break

BLOCK 5

11:30-13:30 h Session 10. Workshop: Waste water treatment and membrane fouling

Chairwoman: **Inmaculada Ortiz**

Conference Room

11:30-12:00 h S10.1. Keynote: "Current Industrial Wastewater Problems and Treatment Methods in Finland – The Focus Areas in Research". ***Riitta L. Keiski.***

12:00-12:20 h S10.2. "Electrodialysis powered by photovoltaic energy for industrial wastewater treatment". ***David Valero***, *Vicente García, Eduardo Expósito, Antonio Aldaz, Vicente Montiel.*

12:20-12:40 h. S10.3. "The role of liquid membranes in the valorization of hazardous spent pickling solutions". *J. Laso, V. García,* ***E. Bringas***, *A.M. Urtiaga, I. Ortiz.*

12:40-13:00 h S10.4. "Novel development of an efficient anti-fouling grafting to enhance the applicability of ceramic nanofiltration membranes in water treatment". ***Ghulam Mustafa***, *Kenny Wyns, Anita Buekenhoudt, Vera Meynen.*

13:00-13:20 h S10.5. "Study of the fouling in seawater ultrafiltration pretreatment process: mechanism and cleaning parameters". *Fatima Zohra Slimane, Selima Allouche, Ghofrane Ben Miled,* ***Nihel Ben Amar.***

11:30-13:30 h Session 11. Membrane Contactors and multifunctional reactors

Chairwoman: **Luisa Neves**

Santillana Room

11:30-11:50 h S11.1. "Succinic Acid Recovery by Membrane Contactor Extraction". *L. S. Moraes,* ***Frederico Kroenemberger****,H. C. Ferraz, A. C. Habert.*

11:50-12:10 h S11.2. "Evaluation of removal and recovery of ammonia from landfill leachate using membrane contactors". ***Wagner G. Moravia****, Natalie C. Magalhães, Míriam C. S. Amaral, Carolina D. Ferreira.*

12:10-12:30 h S11.3. "Ammonium removal by liquid-liquid membrane contactors in water purification process for hydrogen production". ***E. Licon****, M. Reig, P. Villanova, C. Valderrama, O. Gibert, J. L. Cortina.*

12:30-12:50 h S11.4. "Membrane reactor for transesterification of triglycerides: a simplified analysis of the coupled reactive separation process". *Dilson da Costa Maia Filho, Vera M. Martin Salim,* ***Cristiano P. Borges.***

12:50-13:10 h S11.5. "Transesterification with heterogeneous catalyst in membrane reactors". ***Claudia Nurra****, Sònia Abelló, Jorgelina Pasqualino, Michiel Makkee, Joan Salvadó, Carles Torras.*

13:10-13:30 h S11.6. "Evaluation of the Production of Biodiesel using a Liquid-Liquid Film Reactor packed with Hollow Fiber Membranes". *Nevardo Bello Yaya,* ***Luz Dary Carreño Pineda****, Paulo C. Narváez Rincón, Juan G. Cadavid Estrada, Alberto Claudio Habert.*

11:30-13:30 h Session 12. Fuel Cells/Batteries Electromembrane Processes

Chairwoman: **Silvia Álvarez**

Candil Room

11:30-11:50 h S12.1. "PVC-ionic liquid polymer inclusion membranes for their application in microbial fuel cells". ***V.M. Ortiz-Martínez****, M.J. Salar-García, F.J. Hernández-Fernández, A. Pérez de los Ríos, L.J. Lozano, C. Godínez.*

11:50-12:10 h S12.2. "High conductivity electrolytes based on polymerized ionic liquid and ionic liquid mixtures". ***Mariana Díaz****, Alfredo Ortiz, Inmaculada Ortiz.*

12:10-12:30 h S12.3. "Electrochemical reactors based on solid CsH_2PO_4 electrolyte membranes". ***Laura Navarrete****, Sonia Escolástico, Andreu Andrio, Vicente Compañ, Jose M. Serra.*

12:30-12:50 h S12.4. "Reverse electrodialysis: sustainable energy producer or consumer? how do we know it?". *Sylwin Pawlowski, João Crespo,* ***Svetlozar Velizarov.***

12:50-13:10 h S12.5. "Acid and base production in the desalination process by bipolar membrane electrodialysis: preliminary results". ***M. Reig****, E. Licon, M. Martínez, C. Valderrama, O. Gibert, J.L. Cortina.*

13:30-15:00 h LUNCH

BLOCK 6

15:00-17:00 h Session 13. Membrane applications for food and pharmaceutical processing

Chairwoman: **Carme Güell**

Conference Room

15:00-15:20 h S13.1. "Grignard functionalized ceramic nanofiltration membranes for affinity control and process intensification in solvent based liquid filtration". ***Pieter Vandezande****, Kenny Wyns, Sareh Rezaei Hosseinabadi, Ghulam Mustafa, Vera Meynen, Dominic Ormerod, Anita Buekenhoudt.*

15:20-15:40 h S13.2. "Development of microbial polysaccharide films for food packaging". *Ana R. V. Ferreira, Cristiana A. V. Torres, Filomena Freitas, Maria Reis, Vítor D. Alves,* ***Isabel M. Coelhoso.***

15:40-16:00 h S13.3. "Nanofiltration for sugar reduction in red and white grape must to produce low-alcohol wines". ***Camila M. Salgado****, Encarnación Fernández, Laura Palacio, Antonio Hernández, Pedro Prádanos.*

16:00-16:20 h S13.4. "Premix membrane emulsification to produce W1/O/W2 emulsions and microcapsules entrapping polyphenols". ***Montse Ferrando****, Rikkert Berendsen, Carme Güell.*

16:20-16:40 h S13.5. "Studies on polyphenols concentration by ultrafiltration (concentration and diafiltration modes) of an ethanolic extract of wood bark". ***Inês F. Mota****, Paula C. R. Pinto, José M. Loureiro, Alírio E. Rodrigues.*

16:40-17:00 h S13.6. "Increasing the angiotensing converting enzyme inhibitory activity of goat milk hydrolysates by cross flow filtration through ceramic membranes". ***F.J. Espejo-Carpio****, M.C. Almécija, A. Guadix, E.M. Guadix.*

15:00-17:00 h Session 14. Membrane for energy generation and CO_2 capture

Chairwoman: **Isabel Marrucho**

Santillana Room

15:00-15:20 h S14.1. "Integration of membrane new technologies for CO_2 removal from natural gas in offshore platforms". ***Cristiano P. Borges****, Rafael Aislan Amaral, Alberto C. Habert, Jailton F. Nascimento, Wilson M. Grava.*

15:20-15:40 h S14.2. "Playing with ionic liquid mixtures to design membranes with improved CO_2 separation performance". ***Liliana C. Tomé***, *Andreia S. L. Gouveia, Carmen S. R. Freire, Luís P. N. Rebelo, Isabel M. Marrucho.*

15:40-16:00 h S14.3. "ZIF-based mixed matrix membranes for CO_2 capture". ***Beatriz Zornoza***, *Javier Sánchez-Lainez, Mariolino Carta, Neil McKeown, Carlos Téllez, Joaquín Coronas.*

16:00-16:20 h S14.4. "Preparation and characterization of ionic liquid- polymer hybrid membranes for CO_2/N_2 separation". *Enrique Rodríguez-Fernández,* ***Esther Santos***, *Clara Casado-Coterillo, Ángel Irabien.*

16:20-16:40 h S14.5. "Hydrogen permeation throughLa5.5WO11.25-δ-La0.87Sr0.13CrO3 composites". ***S. Escolástico***, *C. Solís, R. Zanón, J.M. Serra.*

16:40-17:00 h S14.6. "Preparación de nuevas co-poli(benzoxazol-imida)s mediante transposición térmica y evaluación de sus capacidades en procesos de permeación de gases". *Bibiana Comesaña-Gándara, Ángel E. Lozano, José G de la Campa, Young M. Lee,* ***Javier de Abajo.***

15:00-17:00 h Session 15. Ultra and microfiltration Chairman: **Cristiano Borges**

Candil Room

15:00-15:20 h S15.1. "Evaluation of drinking water quality produced by ultrafiltration membranes in distribution systems". ***R. Álvarez-Arroyo***, *G. Garralón, F. Plaza, J.I. Pérez, M.A. Gómez.*

15:20-15:40 h S15.2. "Effect of different additives on the fabrication of hydrophilic polysulfone ultrafiltration membranes". ***Ana Urkiaga***, *Deiene Iturbe.*

15:40-16:00 h S15.3. "Evaluation of the membrane fouling in the separation of bovine serum albumin and lactoferrin mixtures by ultrafiltration". ***V. Valiño***, *M. F. San Román, R.Ibáñez, I. Ortiz.*

16:00-16:20 h S15.4. "Concentration of vinasse by microfiltration: bench and pilot scale". ***M.C.S. Amaral***, *L.H. Andrade, F.S. Santos, G.E. Mota, L.S.F. Neta, R.B. Carvalho.*

16:20-16:40 h S15.5. "Separation of cyclodextrins by complexation ultrafiltration". ***Fatma Ellouze***, *B. Sentier, N. Ben Amar, A. Deratani.*

17:00-17:30 h Coffe Break

17:30-19:30 h POSTER SESSION II

20:30 Conference Cocktail dinner at the Casino of Santander

08:30-09:30 h Plenary Lecture: **Prof. Claudio Habert.** "Integrating Membrane Separations in Some Energy/Fuels Production Processes"

BLOCK 7

09:30-10:50 h **Session 16. Biomedical membrane applications** Chairman: **Thomas Schäfer.**

Conference Room

09:30-09:50 h S16.1. "Controlled release of gemfibrozil from novel potential devices". ***L. Donato***, *L. Guzzo, E. Drioli , C. Algieri.*

09:50-10:10 h S16.2. "Development of funcionalized poly(etherimide) membranes for application in hemodialysis". ***Helen Conceição Ferraz***, *Alana Melo dos Santos, Alberto Claudio Habert.*

10:10-10:30 h S16.3. "Nutrients permeability through poly(ε-caprolactone) membranes applied for neural tissue engineering". ***Nazely Diban***, *Beatriz Gómez, Inmaculada Ortiz, Ane Urtiaga.*

10:30-10:50 h S16.4. "Removing endotoxins from solutions by membrane adsorber with L-histidine". ***Helen Conceição Ferraz***, *Karina Moita de Almeida, Eduardo Barbieri, Fernando Faria Fingola.*

09:30-10:50 h **Session 17. Composite membranes** Chairwoman: **Meiry G. F. Rodrigues**

Santillana Room

09:30-09:50 h S17.1. "Nanocomposite: new materials for catalytic membranes development". ***Jorge Macanás***, *Berta Domènech, Maria Muñoz, Dmitri N. Muraviev, Jean-Christophe Remigy, Jean-François Lahitte.*

09:50-10:10 h S17.2. "Hollow fiber polyurethane membranes to remove sulfur compounds from naphtha by pervaporation process". *Rafael A. Amaral, Cristiano P. Borges,* ***Alberto C. Habert.***

10:10-10:30 h S17.3. "Preparation, characterization and performance of PES membranes modified by binary metal oxides $Ti_{(x)}Zr_{(1-x)}O_2$ for wastewater filtration". ***Arcadio Sotto***, *Jeonghwan Kim, Jesús. M. Arsuaga, Ana Martínez, D. Nam, Patricia Luis, Bart Van der Bruggen.*

10:30-10:50 h S17.4. "Clay nanoparticles effects on performance and morphology of PVDF membrane". ***Ana C. D. Morihama***, *J. C. Mierwza, M. Anunciação.*

10:50-11:10 h **Coffe Break**

BLOCK 8

11:10-12:30 h **Session 18. Nanofiltration and reverse osmosis** Chairman: **Arcadio Sotto**

Conference Room

11:10-11:30 h S18.1. "Purification of polyphenols and sugars in bergamot juice by nanofiltration membranes". ***Carmela Conidi***, *Alfredo Cassano.*

11:30-11:50 h S18.2. "Up-scaling of nanofiltration hollow fiber membranes for sulfate removal". *Paula W. Teixeira, Jéssica C. N. Schner , M. Elizabeth F. Garcia, Jane H. Fujiyama-Novak, Nicolas R.J-D. Mermier, Alberto C. Habert,* ***Cristiano P. Borges****.*

11:50-12:10 h S18.3. "Phosphate recovery from tertiary treatment effluents using nanofiltration membranes". ***E. Licon****, M. Reig, M. Marin, C. Valderrama, A. Yaroshchuk, O. Gibert, J. L. Cortina.*

12:10-12:30 h S18.4. "Detection of damages on reverse osmosis membranes". ***Nuria Peña García****, Fernando del Vigo, Oscar Salmerón, S.P. Chesters.*

11:10-12:30 h **Session 19. Membrane characterization** Chairman: **Javier de Abajo**

Santillana Room

11:10-11:30 h S19.1. "Preparation and characterization of chitosan based anion-exchange membranes for alkaline media as alternative to nafion". ***Clara Casado-Coterillo****, Leticia García-Cruz, César Rubio, Carlos Téllez, Joaquín Coronas, Jesús Iniesta, Frank Marken, Vicente Montiel, Ángel Irabien.*

11:30-11:50 h S19.2. "Electrochemical characterization of a membrane manufactured by a bacterial exopolysaccharide". ***J. Benavente****, V. Romero, M.I. Vázquez, M.A. Reis, I.M. Coelhoso.*

11:50-12:10 h S19.3. "Characterisation of dense films: modelling transient permeation from time-dependent diffusivities". ***Carla Brazinha****, M.Sofia Fraga, Luís Trabucho, João G. Crespo.*

12:10-12:30 h S19.4. "Caracterización de una celda electrodialítica. Automatización y control del proceso". *José A. Ibáñez Mengual,* ***Ramón Valerdi Pérez****, Felipe Carbonell Bejerano.*

12:30-13.30 h Closing Ceremony

13:30-15:00 h LUNCH

15.30- 19.30 h Sightseeing in Santillana del mar (Medieval Village)

17:30-19:30 h POSTER SESSION I

Polymeric Membranes

P1.1 . "New blends of polyetherimide-polyimide for high pressure gas separation applications". ***Mónica de la Viuda***, *Lucia Escorial, Alberto Tena, Pedro Prádanos, Laura Palacio, Javier de Abajo, Ángel E. Lozano, Antonio Hernández.*

P1.2. "Conductivity of polymeric films based on supported ionic liquid-like phases". *Abel García-Bernabé, Andreu Andrio, Belén Altava, M.Isabel Burguete, Eduardo Garcia-Verdugo, Santiago V. Luis,* ***Vicente Compañ****.*

P1.3. "Effect of solvent in the precipitation bath of the PA6 nanocomposite membranes" ***Amanda M. D. Leite****, Rodholfo da S. B. Ferreira, Caio H. do O Pereira, Hélio L. Lira, Edcleide M. Araujo.*

P1.4. "Preparação e caracterização de membranas de polisulfona (PSf) com microcelulose (MCC) de eucalipto". ***Mara Zeni****, Diana Favero, Mikaela Lanfredi, Ana M.C. Grisa.*

P1.5. "New aromatic polyamides and polyimides bearing adamantane bulky groups". *Diego Plaza-Lozano, Mónica de la Viuda, Jong Geun Seong, Purificación Cuadrado,* ***Cristina Alvarez-Sancho****, Young Moo Lee, Antonio Hernández, Angel E. Lozano.*

P1.6. "Avaliação do efeito da argila em membranas de poliétersulfona". *Vanessa da N. Medeiros, Thamyres C. de Carvalho, Amanda M. D. Leite, Edcleide M. Araújo,* ***Hélio L. Lira****.*

P1.7. "Fluoride removal from waters by a polymeric membrane containing Aliquat 336". ***Enriqueta Anticó****, Adrià Casanovas, Clàudia Fontàs.*

P1.8. "Enatioselective sorption of D-L tyrosine in chitosan membrane". ***E. Andrés Takara****, Darío Díaz, C. O. Illanes, N. Ariel Ochoa.*

P1.9. "Poly(ionic liquids):tailoring the polymer properties for membrane applications". ***David Mecerreyes****.*

P1.10. "Optimización del proceso continuo en cascada, para la recuperación de solvente a partir de mezclas aceite de soja/hexano usando módulos de membranas espiraladas". ***L. Firman****, A. Ochoa, J. Marchese, C. Paqliero.*

P1.11. "Ultrafiltration of oil/water emulsion with PVDF/cation exchange resin membranes". *Martin Masuelli,* ***Leticia Firman****, José Marchese, Nelio A. Ochoa.*

P1.12. "Water electrolysis with Zirfon® as separator and NaOH as electrolyte". ***María José Lavorante****, Carla Yanina Reynoso, Juan Isidro Franco.*

Facilitated Transport Membranes

P1.13. "Ionic liquid-based membranes for syngas recovery from flue gases". ***Gabriel Zarca***, *Inmaculada Ortiz, Ane Urtiaga.*

P1.14. "Passive sampling of Zn(II) using a hollow fiber supported liquid membrane device". ***Eduardo Rodríguez de San Miguel Guerrero***, *Erik A. Rodríguez Morales, Josefina de Gyves y Marciniak.*

P1.15. "Supported ionic liquid membranes for the selective separation of metal ions". ***F.J. Hernández-Fernández***, *A. Pérez de los Ríos, L.J. Lozano, S. Sánchez-Segado, C. Godínez, J. Quesada-Medina, F. Tomás-Alonso.*

Modelling and Process Simulation

P1.16. "Ultrafiltration of municipal wastewater: study on fouling models and fouling mechanisms". *Jose L. Soler-Cabezas, Miriam Torà-Grau,* ***María-Cinta Vincent-Vela***, *Jose A. Mendoza-Roca, Francisco J. Martínez-Francisco.*

P1.17. "Fouling mechanisms in the ultrafiltration of whey model solutions". *María-José Corbatón-Báguena, Silvia Álvarez-Blanco,* ***María-Cinta Vincent-Vela.***

P1.18. "Implementation of membrane models on a cape-open tool to simulate a process including reverse osmosis stages". ***José M. Gozálvez-Zafrilla***, *Asunción Santafé-Moros, Miguel Sanchis-Sebastià, Joaquín Gomis-Fons.*

P1.19. "Mass transport kinetics of HCl and zinc chloride through diffusion dialysis and electrodialysis membranes". ***I. Ortiz Gándara***, *MF. San Román, I. Ortiz.*

P1.20. "Modeling and Simulation of Membrane Reactor for Biodiesel Production". Mario A. Noriega Valencia, Paulo C. Narváez Rincón, Nevardo Bello Yaya, Luz D. Carreño Pineda, Juan G. Cadavid Estrada, **Alberto Claudio Habert**.

P1.21. "Gas Permeation and Separation in Polymeric Hollow Fiber Membranes: Mathematical Modeling and Validation". ***S. Saeid Hosseini***, *Prodip Kundu, William B. Krantz, S. Mehrdad Roodashti, N. R. Tan.*

P1.22. "Analysis of the transport models governing permeation and separation of olefin/paraffin mixtures in polymeric membranes". *Sara Najari,* ***Seyed Saeid Hosseini***, *Nicolas R. Tan.*

P1.23. "Integration of economic and technical objectives for chemicals ultrapurification by reverse osmosis membrane cascades". *R.Abejón,* ***A. Garea***, *A. Irabien.*

Inorganic Membranes

P1.24. "Análise do comportamento de membranas cerâmicas para a filtração de vinhos brancos". ***Kélen Cristofoli***, *Danuza da R. Renosto, Venina dos Santos, Mára Zeni.*

P1.25. "Ceramic nanofiltration membranes". *Stefan Duscher,* ***Ernest Olasz***.

P1.26. "Fouling behaviour of textile wastewater model solutions treated by a ceramic UF membrane". ***M.I. Alcaina-MIranda***, *E. Alventosa-deLara, M.I. Iborra-Clar, S. Barredo-Damas.*

P1.27. "Influencia del conformado sobre las propiedades de una membrana cerámica de bajo coste". ***Lorente, María M.***, *Mestre, S., Sánchez, E., Pérez-Fernández, O., Menéndez, M., Santateresa, E., Gozalbo, A.*

P1.28. "Synthesis of ceramic ion-exchange membranes with bipolar behavior for electrodialytic water splitting". ***M.C. Martí-Calatayud***, *M. García-Gabaldón, V. Pérez-Herranz, S. Sales, S. Mestre.*

P1.29. "Síntese da membrana zeolítica (MCM-22/α-alumina) e sua aplicação no processo de separação de óleo / agua". ***Antonielly S. Barbosa***, *Antusia S. Barbosa, Meiry G. F. Rodrigues.*

P1.30. "Evolução da influência da temperatura de sinterizacão e eliminacão de tratamiento ácido da ɣ-alumina utilizada como soporte cerâmico para membrana zeolítica (MCM-22)". ***Antusia S. Barbosa***, *Antonielly S. Barbosa, Meiry G. F. Rodrigues.*

P1.31. "Remoção de óleo contaminante em efluentes aquosos utilizando membrana zeolítica (zsm-5/gama-alumina)". *Janaína R. Scheibler, Everton R. F. Santos, Antusia S. Barbosa,* ***Janaina C. Marinho***, *Meiry G. F. Rodrigues.*

P1.32. "Utilização da membrana zeolítica: (zeólita NAA/γ-Al_2O_3) no processo de separação de emulsão óleo/agua". ***Fabiana M. N. Silva***, *Everton R. F. Santos, Ana P. Araújo, Antusia S. Barbosa Meiry G. F. Rodrigues.*

P1.33. "Efeito de diferentes concentrações de sílica sobre a sintese da membrana zeolítica (zeólita γ/α-alumina)". ***Ana P. Araújo***, *André L. F. Brito, Rochélia S. S. Cunha, Mariaugusta F. Mota Meiry G. F. Rodrigues.*

P1.34. "Avaliação do tempo de tratamento hidrotérmico na síntese de membranas zeolíticas". ***Ana P. Araújo***, *André L. F. Brito, Mariaugusta F. Mota, Meiry G. F. Rodrigues.*

P1.35. "Influência do tipo de semente na síntese da membrana zeolítica ZSM-5/alfa-alumina". *Everton R. F. dos Santos, Mariaugusta F. Mota, Anna K. F. Sousa, Marcílio M. Silva,* ***Meiry G. F. Rodrigues***, *Lam Y. Lau*

Membrane Bioreactors

P1.36. "Fouling, the most serious problem in membrane bioreactors. how to characterize its magnitude?". ***Ana García***, *R. Martínez, C. Ramos, V. Diez.*

P1.37. "Effect of cyclic aeration on fouling in membrane bioreactors for cosmetic wastewater treatment". ***V.M. Monsalvo**, J. Villamil, J. Lopez, M.M. Somer, A.F. Mohedano, J.J. Rodriguez.*

P1.38. "Bio-lubricant production by pervaporation-assisted reaction". *Paola A. Borda Díaz, Alberto Claudio Habert, **Frederico de Araújo Kronemberger**.*

P1.39. "Nutrient removal on sludge concentration by forward osmosis". ***Jaime Lora García**, M. F. López-Pérez, E. Gonga Roselló, A. Abad Sempere.*

P1.40. "Effect of pure oxygen aeration in submerged membrane bioreactor under different mixed liquid suspended solids concentration". ***Eduardo L. Subtil**, Ivanildo Hespanhol, Karen Connery, Malcolm Fabiyi, Andre Rambor, José C. Mierzwa.*

P1.41. "Treatment of pharmaceutical industry wastewater in an anaerobic membrane bioreactor". ***Yasemin Kaya**, Ugur Golebatmaz, Ilda Vergili, Gulsum Yilmaz, A. Murat Bacaksiz, Z. Beril Gönder, Halil Hasar.*

P1.42. "Improving the performance of an aerobic membrane bioreactor (AMBR) with powdered activated carbon (PAC) addition in the treatment of pharmaceutical wastewater". *Yasemin Kaya, **Gulsum Yilmaz**, A. Murat Bacaksiz, Ugur Gölebatmaz, Z. Beril Gönder, Ilda Vergili.*

P1.43. "Morphological characteristics of the flocs and microfauna populations evolution during the adaptation of biomass in a submerged membrane bioreactor". *Aniceto Basalenque Rueda-Rocha, **Isaías Negra-Jiménez**, Renné I. López-Chacón, Abril Munro-Rojas, Julio C. Orantes-Ávalos.*

Biomedical Membrane Applications

P1.44. "Synthesis of polysulfone membranes for hemodialysis". ***Helen C. Ferraz**, Vivianne R. da Silva, Cristiano P. Borges, Alberto Claudio Habert, Roberto Bentes de Carvalho.*

P1.45. "Membrane integration in biomedical microdevices". ***Magdalena Malankowska**, Reyes Mallada, Pilar Pina, Ismael Pellejero, Miguel Urbiztondo.*

Composite Membranes

P1.46. "Síntese da membrana (Al-SBA-15/ZSM-5/α-alumina)". ***Janaína C. Marinho**, Everton R. F. dos Santos, Jocielys J. Rodrigues, Meiry G. F. Rodrigues.*

P1.47. "Preparação da membrana zeolítica compósita (ZSM-5/MCM-41/α-Al_2O_3) utilizando o método de mistura mecánica". ***Fabiana M. N. Silva**, Everton R. F. Santos, Meiry G. F. Rodrigues.*

P1.48. "Synthesis and characterization of films of silver nanoparticles dispersed in poly(urethane urea) for the separation of petrochemical gases". ***Antoniel C. Carolino Campos**, Dunieskys R. González Larrudé, Cecília Vilani, Ricardo A. F. Machado, Márcia Cerqueira Delpech, Deborah Vargas Cesar, Rodrigo Azevedo dos Reis.*

P1.49. “Synthesis of a new MOF for composite membranes”. ***María G. García***, *N. A. Ochoa, L. Palacio, P. Pradanos, A. Hernández.*

P1.50. “Biomimetic aquaporin membranes in forward osmosis applications”. ***Claus Hélix-Nielsen***, *Irena Petrinic.*

P1.51. “Composite membrane by deposition of acrylic acid plasma polymer”. *Betina Villagra Di Carlo, Elza Castro Vidaurre,* ***Alberto Claudio Habert.***

Mixed Matrix Membranes and Carbon Membranes

P1.52. “Carbon molecular sieve membranes for gas separation”. ***Sandra C. Rodrigues***, *Roger Whitley, José Sousa, Fernão D. Magalhães, Adélio Mendes.*

P1.53. “Design and characterization of mixed matrix membranes with ionic liquids for CO_2 capture”. *H.P. Andrade,* ***L.A. Neves***, *J.G. Crespo, I.M. Coelhoso.*

P1.54. “Study of the inclusion of carbon nanoparticles in polyurethane membranes for separation process”. ***Luz Dary Carreño Pineda***, *Alberto Claudio Habert, Rodrigo Azevedo dos Reis.*

17:30-19:30 h POSTER SESSION II

Gas and Vapor Separation

P2.1. "Pervaporation separation of methanol from MTBE using functionalized membranes based on polyelectrolyte surfactant complex". *H. Pahlavanzadeh, **S.S. Hosseini**, M. Tamaddondar, N. R. Tan.*

P2.2. "Development of microporous TiO_2 doped silica membranes to enhance the hydrothermal stability for gas separation". ***Ghulam Mustafa**, Jan Hoffman, Martin Bram, Dirk Enke.*

P2.3. "Preparation of flat sheet membranes by dual bath immersion precipitation technique for CO_2 removal from natural gas". ***Cristiano Piacsek Borges**, Daissy Marcela Angarita.*

P2.4. "Permeability of propane and propylene in highly selective ionic liquid/polymer composite membranes". ***Raúl Zarca**, Alfredo Ortiz, Daniel Gorri, Inmaculada Ortiz.*

Membrane and Surface Modification

P2.5. "Photo-modification with PEG/Al_2O_3 nanoparticles of polyethersulfone ultrafiltration membranes". *Jorge García-Ivars, **María-Isabel Iborra-Clar**, María-Isabel Alcaina-Miranda, José-Antonio Mendoza-Roca, Laura Pastor-Alcañiz.*

P2.6. "Enhancement in hydrophilicity of polyethersulfone membranes using Al_2O_3 nanoparticles". *Jorge García-Ivars, **María-Isabel Iborra-Clar**, María-Isabel Alcaina-Miranda, José-Antonio Mendoza-Roca, Laura Pastor-Alcañiz.*

P2.7. "Modification of nanofiltration membranes by radiofrecuency activated argon plasma". ***Miguel Montalvillo**, Francisco Javier Carmona, Laura Palacio, José Ignacio Calvo, Antonio Hernández, Pedro Prádanos.*

P2.8. "Layer-by-Layer assembly of polyelectrolytes applied to obtain cation exchange membranes with monovalent ion selectivity". ***M. C. Martí-Calatayud**, S. Abdu, J. E. Wong, M. García-Gabaldón, V. Pérez-Herranz, M. Wessling.*

P2.9. "Development of TiO_2 photocatalytic membranes for drinking water treatment". ***S. Sanches**, C. Nunes, P. Passarinho, F. Ferreira, M.T. Barreto Crespo, J.G. Crespo, V.J. Pereira.*

P2.10. "Synthesis and characterization of polysulfone membranes modified with nanoclay and polyethylene oxide". ***Raphael Rodrigues**, José Carlos Mierzwa, Chad D. Vecitis.*

Waste Water Treatment and Membrane Fouling

P2.11. "Combined ozone oxidation and membrane processes for water treatment". ***Fabiana Valéria da Fonseca***, *Felipe Rodrigues Alves dos Santos, Cristiano Piacsek Borges.*

P2.12. "Forward osmosis processes incorporating microfluidic separation stages for magnetic draw solutions recovery". ***R. Sanz,*** *J. Gomez-Pastora, E. Bringas, R. Ibañez, I. Ortiz.*

Membrane Contactors and Multifunctional Reactors

P2.13. "Catalytic membrane reactors for nitrate removal using low cost ceramic supports". *O. Pérez-Fernández, A. Grado, J. Herguido,* ***M. Menéndez****, M.M. Lorente, E. Sanchéz, S. Mestre, J. García, J.G. Berlanga.*

P2.14. "Pd-Ag membranes coupled to a two-zone fluidized bed reactor for propane dehydrogenation: effect of C_3H_8/C_3H_6 mixtures on H_2 permeation". *H. Montesinos, I. Julián, J. Herguido,* ***M. Menéndez.***

Fuel cells/Batteries and Electromembrane Processes

P2.15. "Membranas de SPEEK reforzadas con nanofibras de PVA y PVB para su uso en pilas de combustible: a) Microbianas (MFCs). b) Metanol directo (DMFC)". ***Vicente Compañ****, Sergio Mollá, Satish Kumar, Omar Solorza, Abel García-Bernabé.*

P2.16. "Incorporation of vinylimidazolium based Ionic liquid in well-defined straight porous PBI membranes: Novel polymeric ionic liquid/PBI membranes for high temperature fuel cell applications". ***Parashuram Kallem****, Adela Eguizábal, Maria Pilar Pina, Reyes Mallada.*

P2.17. "About the sustainability of the electrodialysis powered by photovoltaic solar energy". ***C. Fernández-González****, A. Domínguez-Ramos, R. Ibáñez, A. Irabien.*

P2.18. "Development of new electrolytes based on organic ionic plastics crystal supported on membrane nanofibres for their application in fuel cells". ***Iván Merino****, Mariana Díaz, Alfredo Ortiz, Inmaculada Ortiz.*

Membrane Applications for Food and Pharmaceutical Processing

P2.19. "Recovery of phenolic compounds from table olive wastewaters by means of membrane processes: pretreatment by ultrafiltration". *Carlos Carbonell-Alcaina,* ***Silvia Álvarez-Blanco****, Amparo Bes-Piá, José Antonio Mendoza-Roca, Laura Pastor-Alcañiz.*

P2.20. "Stability assay of a ceramic membrane reactor for the production of ace inhibitory peptides". ***F.J. Espejo-Carpio****, A. Guadix, E.M. Guadix.*

P2.21. "The contribution of the cake on the effective global pressure drop in nanofiltration". *C. Salgado, F.J. Carmona, L. Palacio,* ***A. Hernández****, P. Prádanos.*

P2.22. "Evaluation of nanofiltration for the concentration of bioactive compounds recovered from grape marc". ***Natalia Barbosa Eitel****, Ana P. Gil Cruz, Marlon de Oliveira Santos, Luiz F. Menezes da Silva, Suely P. Freitas, Lourdes M. C. Cabral.*

P2.23. "Active food packaging from pectin". ***F. Cruces****, E. Quiroga, J. Marchese, M. G. García.*

P2.24. "Membrane fouling caused by food grade emulsifiers during premix membrane emulsification". *J. Carmona, M. Ferrando,* ***C. Güell.***

P2.25. "Formulación y extracción de ácido láctico con niosomas de Span 80 modificados con SDS mediante microfiltración". *Roberto Fraile, Lara Roque, José M. Benito, María Olga Ruiz,* ***Isabel Escudero.***

Membrane for Energy Generation and CO_2 Capture

P2.26. "Zeolite a / poly(1-trimethylsilyl-1-propyne mixed matrix membranes for CO_2/N_2 separation". *Ana Fernández-Barquín,* ***Clara Casado-Coterillo****, Susana Valencia, Ángel Irabien.*

P2.27. "Direct osmosis process for power generation using salinity gradient: FO/PRO prototype investigation using hollow fiber modules". *Nicolas R. J.-D. Mermier,* ***Cristiano P. Borges.***

P2.28. "Efficient oxygen production by means of advanced ceramic membranes based on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$". ***J. Garcia-Fayos****, S. Escolastico, L. Navarrete, S. Baumann, W.A. Meulenberg, J.M. Serra.*

P2.29. "Optimization of the electrochemical properties of $Ln_{5.5}WO_{11.25-d}$ mixed proton-electronic conducting materials". ***S. Escolástico****, C. Solís, R. Zanón, M. Ivanova, W.A. Meulenberg, J.M. Serra.*

Ultra and Microfiltration

P2.30. "Hifh flux microfiltration membranes with silver nanoparticles for water disinfection". ***Fabiana Valéria da Fonseca****, Aline Marques Ferreira, Érica Barbosa Roque, Cristiano Piacsek Borges.*

P2.31. "Saline cleaning of two polymeric ultrafiltration membranes fouled with whey model solutions". *María-José Corbatón-Báguena,* ***Silvia Álvarez-Blanco****, María-Cinta Vincent-Vela.*

P2.32. "Cleaning of ultrafiltration membranes fouled with whey proteins with tensioactive and ultrasounds". *M.C. Vincent-Vela, M. Torà-Grau, J.L. Soler-Cabezas,* ***J.A. Mendoza-Roca****, F.J. Martínez-Francisco.*

P2.33. "Ultrafiltration fouling trend simulation of a municipal wastewater treatment plant effluent with model wastewater ". *María José Luján-Facundo, Beatriz Cuartas-Uribe,* ***José A. Mendoza-Roca****, Silvia Álvarez-Blanco.*

P2.34. “Decoloración de melazas azucareras mediante un proceso combinado de ultrafiltración con carbón activo”. *Marta Bernal, María Olga Ruiz, **José Manuel Benito**, Isabel Escudero.*

Nanofiltration and Reverse Osmosis

P2.35. “Evaluation of inhibition property of scale remover in offshore nanofiltration system”. ***T. N. Santos**, L. Yokoyama, C. P. Borges, F. B. Alvim, S. S. Ferreira.*

P2.36. “Nanotechnological Application in WAter DESalination (NAWADES)”. ***Marcel Boerrigter**, Anna Serra, Xavier Simón, Mirko Faccini.*

P2.37. “Evaluation of electrolyte mixtures rejection behavior using nanofiltration membranes using spiral wound and flat sheet configurations”. ***M. Reig**, E. Licon, C. Valderrama, O. Gibert, A. Yaroshchuk, J.L. Cortina.*

P2.38. “Separación y recuperación de compuestos de interés presentes en disoluciones diluidas y mezclas complejas mediante nanofiltración”. *Lydia Pérez, **José Manuel Benito**, Isabel Escudero.*

P2.39. “Diseño de un proceso combinado ultrafiltración/nanofiltración para la decoloración de vinazas industriale”. *Roberto Fraile, María Olga Ruiz, José Manuel Benito, **Isabel Escudero**.*

P2.40. “Membrane characterization by AFM and influence of operating conditions on the rejection of Cr(VI) from single aqueous solutions by nanofiltration (NF)”. ***J.A. Otero**, P. Díaz, P. González, E. Noriega, A. Otero-Fernández, A. Hernández.*

P2.41. “Analisis of lead (II) retention from single aqueous solutions by TFC aromatic polyamide nanofiltration (NF) membrane and characterization by XPS”. ***J. A. Otero**, S. Luguera, A. E. Sarabia, A. Otero-Fernández, A. Maroto-Valiente, L. Palacio, P. Prádanos.*

P2.42. “Membrane based process for HCl and NaOH production from reverse osmosis brines”. ***Antía Pérez-González**, Raquel Ibáñez, Pedro Gómez, Ana Urtiaga, Inmaculada Ortiz.*

P2.43. “Study of the direct fitting of a nanofiltration model using model solutions of different ionic complexity”. ***Irene Fernández-Fernández**, Asunción Santafé Moros, José M. Gozálvez Zafrilla.*

P2.44. “Removal of sulphate from wastewaters by nanofiltration”. ***Piia Häyrynen**, Junkal Landaburu Aguirre, Riitta L. Keiski.*

P2.45. “Removal of perfluorinated compounds from contaminated waters by nanofiltration and reverse osmosis”. ***Véronica García**, Ane Urtiaga, Inmaculada Ortiz.*

P2.46. “Applicability of combined Fenton oxidation and nanofiltration to the process wastewater of pharmaceutical industry”. ***Ilda Vergili**, Sezin Gençdal.*

Membrane Characterization

P2.47. "Chemical treatments of an electrodialysis membrane: Effect on ion transport numbers and conductivity". ***J. Benavente***, *B. Porras, V. Romero.*

P2.48. "Evaluation of the chemical resistance nanofiltration membranes applied in liquid radioactive waste". ***Elizabeth E. de M. Oliveira***, *Edna T. R. Bastos, Júlio C. Afonso.*

P2.49. "Surface and structural characteristics and permeation properties of porous polyvinylidene fluoride membranes prepared by phase inversion". ***J.I. Calvo***, *A. Hernández, L. Palacio, P. Prádanos, A. Bottino, A. Comite, C. Costa, A. Malfatto.*

P2.50. "Characterization of different type of fibers with PVDF for CO_2 absorption". ***L. Gomez-Coma***, *A. Garea, A. Irabien, J.C. Rouch, J.,F. Lahitte, J.C. Remigy.*

P2.51. "Preparation and electrochemical characterization of polymer inclusion membranes based on Aliquat 336". ***E. Anticó***, *V. Romero, M.I. Vázquez, C. Fontàs, J. Benavente.*

P2.52. "X-ray fluorescence spectrometry, a simple and non-destructive technique for membrane homogeneity testing". ***Clàudia Fontàs***, *Enriqueta Anticó, Ignasi Queralt.*

P2.53. "Tragacanth modified dense membranes". ***E. Andrés Takara***, *A. Martin Masuelli, Adolfo Acosta, José Marchese.*

P2.54. "Estudio del potencial zeta y corriente de flujo en membranas de ultrafiltracion en contacto con un tensoactivo aniónico". *Liliana Villafaña-López, Mario Ávila-Rodríguez, Ricardo Navarro Mendoza, Teresa I. Saucedo Medina,* ***Pilar González-Muñoz***.

P2.55. "Distribution of heavy metals Pb (II), Cd (II) and Cr (II) in Chitosan/PVA gel beads by SEM-EDX.". ***Omayra Almeida***, *Javier Guzmán, Juan M. García, Ricardo Conejo.*

P2.56. "Developing new polymeric inclusion membranes with increased stability in aqueous solution". *A.M. Rubio, F. Tomás-Alonso,* ***A.P. de los Ríos***, *F.J. Hernández-Fernández, S. Sánchez-Segado.*

Plenary Lectures

THE POTENTIAL OF ELECTRODIALYSIS FOR SUSTAINABLE PRODUCTION AND RECYCLING

B. Van der Bruggen

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Electrodialysis is a process with a long history, but relatively few large-scale applications. This is partly related to the process cost, which is typically high. This compromises the use of electrodialysis as a stand-alone process. However, the efficiency in salt removal combined with the flexibility of the process has pushed the process to new applications in integrated systems. Many of these are related to sustainable production and recycling. Its application in wastewater recycling will be explained as a key example of this new type of applications.

In addition, the use of bipolar membranes has opened yet another range of applications in sustainable processing with electrodialysis. Bipolar membranes have the feature of water splitting, which allows the separation of a salt into an acid and a base. Applications of electrodialysis with bipolar membranes will be shown in three categories: (a) for recovery of valuable compounds, such as the production of tetrapropyl ammonium hydroxide, L-ascorbyl-2-monophosphate (a substitute of vitamin C), glyphosate, morpholine and L-lysine; (b) for the production of salts from brines, which can be in combination with a fermentation reaction for the production of e.g., lactic acid, but can be also directly applied on industrial saline water, and (c) for advanced fractionation purposes, such as the separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electrodialysis coupled with chelation, separation of acids and metals such as cobalt and nickel, or the selective concentration of copper from a mixture of heavy metals in aqueous solution.

The sustainability of applications depends on the overall system, including the energy source used for the separation. Taking this into account, it can be concluded that electrodialysis with bipolar membranes is a viable method with a remarkable potential for those applications in which the added value of the purified streams is large.

SUSTAINABLE MEMBRANE PROCESSES AND PRODUCTS: DEVELOPMENT AND INNOVATION

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Membranes have been developed as an interphase for separation processes or as membrane products for different uses. Membrane technologies have been developed for the separation/concentration of components from a fluid phase or in order to integrate separation and reaction in the "so called" membrane reactors, but also membranes have been introduced as final products for example in construction, medical care, fuel-cells, etc.

In the nineties the word "sustainable" has been incorporated to the technical literature as an added value nickname to the technologies and we manage different "renewed unit operations", such as: sustainable distillation, sustainable extraction, sustainable absorption, etc. but the meaning of the sustainability qualification referred to a separation process, reactor or product remains unclear.

The first interpretation of sustainability in the membrane technology refers to the introduction of membrane processes for a sustainable industrial growth [1] as an innovative approach to the separation/concentration requirements in the process industries, the second interpretation for sustainable membrane technology is related to the sustainable use of natural resources: energy, water and raw materials [2].

Membrane products are related to different endusers and they may be certified according to standards as sustainable products following regulated procedures, for example in construction: a wide range of sustainable roofing membranes can be found in the market, they are suitable for flat, pitched or barrelled rooftops. Providing essential protection, these products guard structures against the dangers of water, root and climate damage, ensuring a long lifetime to the substrate.

With life expectancies of over thirty years, many of the products are fully recyclable and may be overlaid when replaced. Combined with a reliance on recycled and sustainable materials and an avoidance of harmful agents such as plasticisers, this market proven membranes offer superior protection with minimal environmental impact, and they are sold as sustainable membranes.

The presentation deals with the qualitative, semiquantitative and quantitative assessment of membrane processes and products taking into account the Supply Chain (SC) and the Life Cycle Assessment (LCA) respectively.

A set of environmental, economic and social indicators will be described in order to qualify membrane processes and products as sustainable, sustainability indicators allow a quantitative assessment of processes and/or products and need to be clarified in order to help decision making .

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Acknowledgements I thank to the Spanish Ministry of Economy and Competitiveness (MINECO) for funding the project ENE2010-14828.

MEMBRANE PROCESSES FOR WATER SAFETY AND SECURITY

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Water security is defined in the Millennium Development Goals (MDGs) as “access to safe drinking water and sanitation”, both of which have been recently recognized as human rights. While not part of most water security definitions yet, availability of and access to water for other human and ecosystem uses is also very important from a nexus perspective.

This lecture address the contribution of various membrane processes for water safety and security namely for enlarging access to water sources – water desalination, decontamination of water sources – and provide solutions for water treatment for recycle and reuse.

A particular emphasis will be given to the use of membrane bioreactors for water and wastewater treatment and also to the removal and degradation of micropollutants from water streams, using integrated advanced oxidation and membrane processes. Finally, the use and development of new membrane materials for water treatment will be discussed and needs / opportunities for materials’ research will be addressed.

INTEGRATING MEMBRANE SEPARATIONS IN SOME ENERGY/FUELS PRODUCTION PROCESSES

Alberto Claudio Habert

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As new raw materials source become options and challenges (typically the pre-salt natural gas and biofuels in Brazil), alternative solutions to several separation and purification problems in the energy and fuels producing processes are to be considered, and should be, technically and economically competitive, in addition to generate a minimal environmental impact. Introducing or coupling membrane separations with other operations are potential options and suggests new developments for membranes, modules and processes.
Some examples in gas phase separation such as those involving CO_2 removal, and in liquid phase separation, aimed at enhancing biofuels and related products production will be presented and discussed.

Polymeric Membranes

- **Oral session 1**
- **Oral session 4**

Preparation hollow fiber membrane by combination of thermally induced phase inversion and non-solvent induced phase inversion with green solvent

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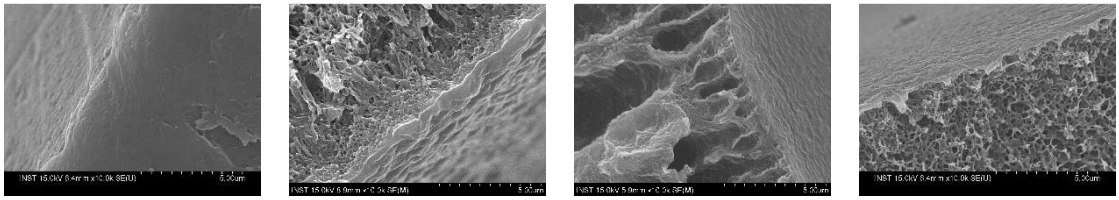
A green solvent was used to prepare PVDF hollow fiber membranes by combination of thermally induced phase separation (TIPS) and non-solvent induced phase inversion (NIPS). For the new solvent phase diagram was presented and the rate of solvent outflow comparison with quenching bath liquid inflow was calculated and compared at different preparation temperatures. The effect of different concentrations of non-solvent additive (glycerol 5 and 15 wt.%), polymeric additives (PVP 10k, PVP 55k, PVP 360k, PVP 1300k and PMMA) at different quenching bath temperatures (5, 15, 25 and 40 ^{o}C) on the morphology, roughness, mechanical properties, overall porosity, water permeability, polymorphism in the skin layer and polymorphism in the bulk of membrane structure were investigated. Because of contribution of two mechanisms in membrane formation by changing the preparation condition a variety of structure (i.e. dense, finger like, interconnected and spherulitic structure) were obtained. By using PVP NIPS process became dominant in the outer surface and by using glycerol NIPS process became dominant in the inner surface while by using PMMA there was no significant change in hollow fibers. Interestingly, the amount of β phase in skin layer of hollow fiber was changed by changing preparation condition while it remained constant in the bulk of membrane structure which shows potential of prepared hollow fiber membranes for controlling of the fouling by using piezoelectric properties of PVDF. This work represents the first step towards achieving a fundamental understanding of the effect of additive in combination of TIPS and NIPS for preparation PVDF hollow fiber membranes.



EXPERIMENTAL AND MOLECULAR DYNAMICS STUDY OF THE EFFECT OF SOLVENT ON PES MEMBRANE MORPHOLOGY

Arcadio Sotto[1], Junkal Landaburu-Aguirre[2], Arman Boromand[3], Jesus María Arsuaga[1], Nerea Gonzalez[1]

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Introduction

Immersion precipitation is one of the most popular method to synthesize asymmetric membranes because different morphologies can be obtained. In phase inversion immersion precipitation technique a homogeneous polymer solution becomes thermodynamically unstable after immersing it into a non-solvent coagulation bath. The solvent diffuses into the bath and the non-solvent diffuses into the polymer solution. Consequently, phase separation occurs forming a polymer rich phase and a polymer lean phase. [1]

Understanding the thermodynamics and kinetics of the precipitation process is crucial in order to understand the formation of different kind of membrane morphologies. The thermodynamic equilibrium composition of polymer solution is commonly studied with ternary phase diagrams. In addition, studies have been focused on understanding the effect of the casting solution composition on the membrane morphology. In this way, there is a wide range of experimental work reporting the effect of solvents [2,3], polymer concentration [4] and introducing polymeric and inorganic additives into the casting solution on the membrane morphology [5,6]. Besides the extensive experimental work available in literature, there is a lack in understanding the relationship between polymer chain configuration (molecular dynamidcs) and the final product functionality and properties. In this paper, experimental study of membrane formation mechanism is combined with modelling of molecular dynamics to achieve a better understanding of the effect of solvent on the membrane formation process and the membrane morphology.

Materials and Methods

Membranes were synthesized by phase inversion induced by immersion precipitation method. The casting solution was prepared using Polyehersulphone (PES, Solvay). Dimethylformamide (DMF), N-Methyl-2-Pyrrolidone (NMP) and Dimethylacetamide (DMAc) were the polymer solvents. The polymer concentration of the casting solution was 20%wt. The prepared films were immersed in a distilled water (non-solvent) bath for precipitation. For the thermodynamic study ternary phase diagrams were constructed by determining the cloud point of the casting solutions (20%PES and 80%wt solvent) by the titration method.The non-solvent solution consisted of 60%wt of solvent and 40% of distilled water. The morphology of membranes cross-section were observed by Scanning Electron Microscopy (SEM, XL-30, Philips, Eindhoven, the Netherlands). The manufactured membranes were further characterized for water flux using a cross-flow filtration set-up (SEPA II, Osmonics, membrane effective area of 139 cm^2).

Results and Discussion

As it can be observed in Figure 1, the casting solution PES/DMF needs the lowest percentage of non-solvent for the precipitation to occur. On the other hand, the casting solution PES/NMP needs higher non-solvent percentage for the precipitation to occur. These results were further compared with solubility parameter distance (Ra), where $Ra_{(PES/NMP)}$=2.147, $Ra_{(PES/DMAc)}$=3.087 and $Ra_{(PES/DMF)}$=4.755. As it can be observed, the

PES/DMF system shows the highest solubility distance parameter, which means that the polymer has the least affinity with DMF solvent. Figure 2 shows the images obtained by molecular dynamic simulations for the membranes formed using two different solvents. In case of low affinity between polymer and solvent (Figure 2 b) the simulation images show the formation of membranes with bigger pore size and less porosity than in the case of having a high affinity between polymer and solvent (Figure 2 a).

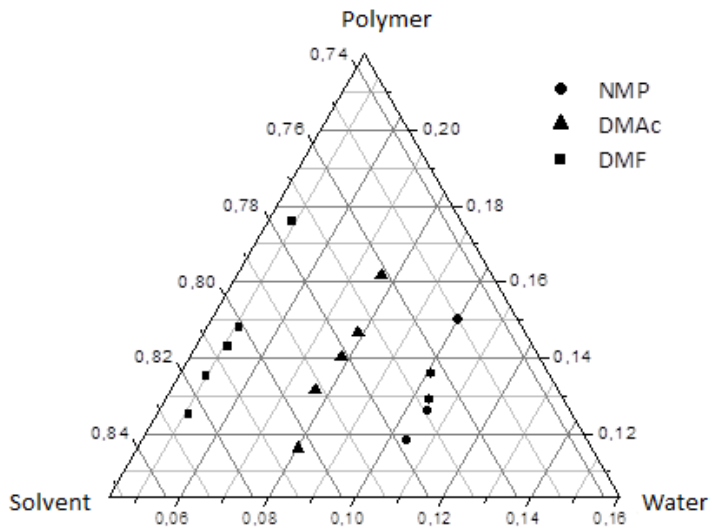

Fig 1. Ternary phase diagram using three different solvents: NMP, DMAc and DMF.

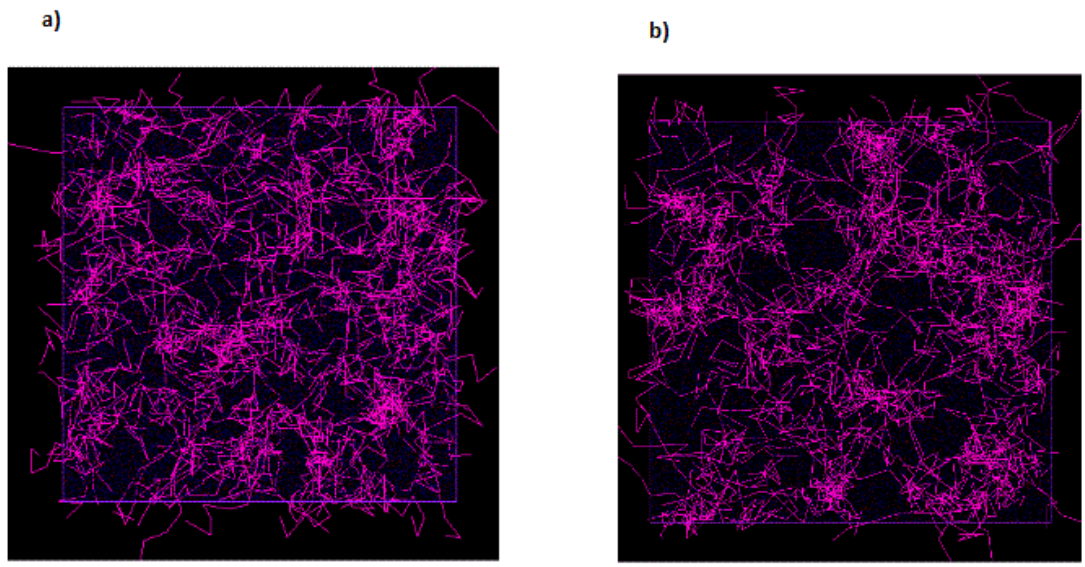

Figure 2. Molecular dynamic simulation of membranes when a) the polymer has high affinity with the solvent and b) the polymer has low affinity with the solvent.

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Water reclamation in the steel industry by removing heavy metals with membrane technology and precipitation

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Finishing lines in the steel industry use high amounts of water. The main pollutants in these streams that limit water reuse are heavy metals [1]. Heavy metals also present an environmental risk because of their toxicity and tendency to accumulate in living organisms [2]. The conventional process to treat these wastewaters is coagulation/flocculation followed by precipitation. These well-know techniques, however, do not achieve the required low metal concentrations needed for water reuse. Therefore, in this work a combination of a membrane treatment (for direct water reuse) followed by precipitation (of a higher concentration, but lower volumetric flowrate stream) is proposed.

The selected process waters contained mainly hexavalent chromium. All the membrane filtration experiments were carried out at the industrial site with pilot plant units.

The membrane filtration step included ceramic microfiltration or ultrafiltration as pretreatment for particle removal. Water recovery experiments were carried out with a nanofiltration membrane at different operating conditions. The concentrate of the nanofiltration step was subjected to reduction (of hexavalent chromium to trivalent chromium) and precipitation.

Pretreatment with a Novasep 150 kDa ultrafiltration membrane found to be the optimum choice. Average permeability was 84 L/hm^{2}bar and the permeate was free of particles. More open (i.e. microfiltration) membranes allowed the pasage of submicron particles and were, therefore, not appropriate. Among the reverse osmosis and nanofiltration membranes tested, the DowFilmtec NF90 gave the best results. At low pressure (10 bar), metal rejection was higher than 99.7% and no significant fouling was observed (the average flux was 92 L/hm^2). At higher pressure (30 bar) cleaning in place was required.

The concentrate of the nanofiltration step was mixed with ferrous chloride at pH 2-3 (adjusted with hydrochloric acid) to ensure hexavalent chromium is reduced to trivalent chromium. Then, other calcium hydroxide, the conventionally used chemical, or Nalmet 1689, a commercial mixture based on dithiocarbamate, were added to precipitate the metal.

Results were compared with the conventional process in terms of efficiency, water resue potential and costs.

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ORGANOSOLV PRETREATMENT FOR CELLULOSE RECOVERY FROM SAWDUST FOR ITS ULTERIOR USE IN MEMBRANE SYNTHESIS

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Agroindustrial wastes are accumulated every year in large quantities, causing an alarming environmental impact. Huge amounts of this residues are disposed outdoors annually worldwide, 140 million metric tons generated only from agriculture[1]. In Mexico, 3.9 millions of cubic meters of wood were destined to sawmills along the country only in the year 2011, generating sawdust, a lignocellulosic compound, constantly [1].

Lignocellulosic feedstock contains three main biopolymers: cellulose, hemicellulose, and lignin. Due to their chemical composition based on sugars, it could be utilized for the production of a number of value-added products [2]. Therefore, besides the environmental problems caused by their accumulation in the nature, the nonuse of these materials constitutes a loss of potentially valuable sources [2].

Many processing alternatives are being studied to efficiently recover these fractions. Cellulose is currently separated from lignocellulosic materials using non-environmentally friendly processes, such as kraft, sulfite and soda treatments, generating toxic wastes [3].

Obtaining a high yield of fractions depends on the pretreatment method. The goal of pretreatment is to remove as much hemicellulose and lignin as possible, while simultaneously keeping enough cellulose intact [4].

The ethanol organosolv process is among the pretreatment strategies currently being studied for the conversion of lignocellulosic biomass feedstocks. In this process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl, H_2SO_4) is used to break the lignin and hemicellulose bonds. Ethanosolv is a more convenient method than other pretreatments because it is safer than any other organosolv pretreatment and ethanol is less toxic than the other solvents, which can also be recovered easily through distillation, however, acid-catalyzed treatments have several limitations [5].

Inorganic salts were studied as a substitute in order to avoid these side effects, being by themselves less corrosive than acids and can be recycled [6]. The pretreatment process is more economically viable if inorganic salts in aqueous solution can be directly used in the pretreatment of the lignocellulosic biomass, this process would avoid further overliming in order to neutralize the hydrolyzate [5].

In recent studies of our group (xx), a comparison among diverse catalysts allows to improve the cellulose quality for its ulterior esterification and membrane production. For this objective cellulose crystallinity could be monitored by Differential Scanning Calorimetry and wide angle X-Ray scattering [7]. Cellulose adhesion is also a parameter which can be considered for ulterior esterification reactions [8].

For instance, the purpose of this work is to evaluate the organosolv treatment for Quercus *spp* sawdust for cellulose recovery. The evaluation considers an experimental design where temperature, contact time and catalyst concentration are varied in 3 levels each. This cellulose is valued for its thermal properties where high cristallinity acts as an indicator of the ulterior capacity in esterification reactions and membrane production.

Methodology

Quercus spp characterization. The material was pulverized to a particle size of 2.38 mm. The following methods were utilized to determine humidity: (TAPPI T1205-75) and extractives (ASTM-D-1107-96). To breakdown the bonds between cellulose, hemicellulose and lignin the

Puls method was adapted for 2g of each sample. Ashes were cuantified by the (TAPPI T211-om-02) method. To determine de fractions of cellulose and hemicellulose a High Efficiency Liquid Cromatoghaph Agilent 3100, was required using a column for carbohidrates (Aminex HPX 87H) and a ZORBAX C-18 for furfural and hydroximethyl furfural. To measure lignin the method (ASTM-D-1106-96) was the one utilized for the solid fraction and Ultra Violet Spectroscopy at 280nm for the soluble fraction of the lignin.

Pretreatment. 2 g samples of ground barley straw in 50% (w/w) aqueous ethanol were heated at 140, 160 and 180 °C for 60, 45, 30 and 15 min with a 0.05, 1 and 2 mol L^{-1} concentration of metal salts($FeCl_3$ and $AlCl_3$.). The ratio of liquor to-barley straw was constant in all of the experiments. The ethanosolv experiments were performed in 20ml metal reactors using an oil bath. After the ethanosolv pretreatment, the vessels were cooled in a water bath. Then the residual solid and liquor were separated through filtration (cotton fabric). The residual solid was washed with 100 mL 50% (w/w) aqueous ethanol. The washed residual solid was dried at 45 ◦C for 24 h and then characterized with the methodology previously described.

Thermal analysis. The DSC measurements were made using a differential scanning calorimeter (DSC 92-Setaram), with a controlled cooling accessory.

Results

Quercus *spp.* sawdust was characterized obtaining in % dry mass. Results are shown in table 1.

Table 1. Sawdust characterization. Results are in % w/w and standard deviation.

CELLULOSE		HEMI CELLULOSE		LIGNINE		EXTRACTIVES		ASHES		TOTAL	
37.9%	±4.9757	25.2	±3.02185	28.3	±3.6621	13.8	±1.1	0.36206	±0.05602449	105.6	±6.973

During ethanosolv treatment, original cellulose recovery ranges from 40-70% of the initial concentration, depending on the treatment conditions. Temperature and catalyst concentration play a fundamental role regarding cellulose crystallinity, ranging from 10-15% when mild conditions are employed. Cellulose with the lower order is required for more effectiveness during esterification process for membrane production.

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Acknowledgements To CONACYT for funding.

Effects of thickness on PVDF membrane synthesized by the phase inversion process

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Introduction: Poly(vinylidene fluoride) (PVDF) has become one of the most popular and usual polymer for membranes synthesis because of its affordable price, mechanical proprieties, chemical and thermal stability, radiation resistance and low superficial energy and dielectric constant ([1] and [2]). According MULDER (2003) the membrane thickness influences the membrane characteristics like mechanical strength and morphology and consequently the membrane permeation. MIERZWA *et al.* (2012) results showed that the membranes cast with a bigger thickness results in significant changes in the internal pore structure. These changes decreased membrane permeability due to an increased resistance for water flow. In order to understand the thickness influence on membrane performance, the main objective of this research was evaluate the thickness effect on the morphology and performance of three different types of PVDF membranes. Membranes were synthesized by the phase inversion process. Results from filtration tests were used for comparing membranes performance and Scanning Electron Microscopy to evaluate changes in membranes' pores morphology.

Key words: poly(vinylidene fluoride) membrane, thickness, performance, morphology.

Material and Methods: Polymeric solutions were prepared with poly(vinylidene fluoride) at 18%wt concentration dissolved in N-methyl-2-pyrrolidone solvent. Three different types of PVDF were used: Kynar®761, Solef®6012 and Solef®1015. All the chemicals were used as they were received. The solution was stirred using a mechanical stirrer for 24 hours at 50ºC until a homogenous polymeric solution were obtained. Membranes were cast by the phase inversion process. Each solution was spread onto a glass plate to produce a flat sheet membrane (casting temperature: 25ºC; casting knife: 110µm, 120µm and 130µm; casting speed: 0,04 m/s). The polymeric film was immediately immersed into the coagulation bath with demineralized water, as a non-solvent, at 25ºC during 2 minutes. From the coagulation bath, cast membranes were transferred to another bath (demineralized water at ambient temperature), for at least 24 hours to remove any residual solvent.

For performance evaluation, demineralized water flow tests were conducted using a laboratory-scale cross flow test cell. At least four different rectangular membrane samples (0,13 m x 0,09 m, with a net filtration area of 0,0077 m^2) from different membranes were tested. Based on the series resistance model, the permeate flux (J; [L. h^{-1}.m^{-2}.bar^{-1}]) and the clean membrane hydraulic resistance (R_M [m^{-1}]) were calculated. The porosity was determined by the difference between dry and wet membrane weight. The membranes thickness was measured by a micrometer. Membranes cross section images were obtained using the Scanning Electron Microscopy (SEM).

Results and Conclusions: Table 1 summarizes the results obtained for membrane performance and morphology. It can be noticed that the final thickness measurements were very similar, because of that the ANOVA test were performed to better understand these results. For Kynar®761 (F=1,66 and F_{crit}=3,89) and Solef®1015 (F=0,55 and F_{crit}=3,98) the statistic test results indicated that the hypothesis that the average thickness are equal can not be rejected at the 95% confidence level. In the Solef®6012 case (F=35,81 and F_{crit}=4,10), the statistic test results indicated that the hypothesis that the average thickness are equal can be rejected at the 95% confidence level, which means that at least two means that are significantly different from each other. Also, for Kynar®761/Solef®1015 the ANOVA test results indicated that the hypothesis that the average thickness are equal can not be rejected at the 95% confidence level (F=1,03 and F_{crit}=2,64).

It was expected that the final membrane had a 20% thickness reduction. However, as it can

be observed, the thickness reduction varied around 50% for Kynar®761 and Solef®1015 and from 44% to 70% for Solef®6012. It was realized that the Solef®6012 presents a further reduction and a different behavior compared to other polymers.

Table 1 PVDF membrane performance and morphology evaluation

Membrane type	Average permeate flux (L. $h^{-1}.m^{-2}.bar^{-1}$)	Median hydraulic resistance ($E^{+13}m^{-1}$)	Porosity (%)	Thickness (µm)	% reduction in thickness
Kynar®761-110µm	4,8	8,3	85,3	48,4	56
Kynar®761-120µm	8,4	7,8	67,5	50,4	58
Kynar®761-130µm	1,4	47,6	84,2	61,4	53
Solef®6012-110µm	3,6	8,7	63,3	33,2	70
Solef®6012-120µm	0,8	46,8	49,4	49,6	59
Solef®6012-130µm	0,7	59,8	50,1	73,0	44
Solef®1015-110µm	1,9	14,3	66,1	53,1	52
Solef®1015-120µm	9,7	3,4	47,6	57,6	52
Solef®1015-130µm	4,4	11,4	49,4	60,3	54

It can be observed that membranes cast with 120µm presented the best permeate flux in the case of the Kynar®761 and Solef®1015. However, for Solef®6012 the best permeate flux is for the membranes cast with 110µm. Thus, it is possible to establish a direct correlation between final thickness and membrane performance. Membranes with thickness ranging from 48µm to 60µm presents the same permeated flux for the case of Kynar®761 and Solef®1015.

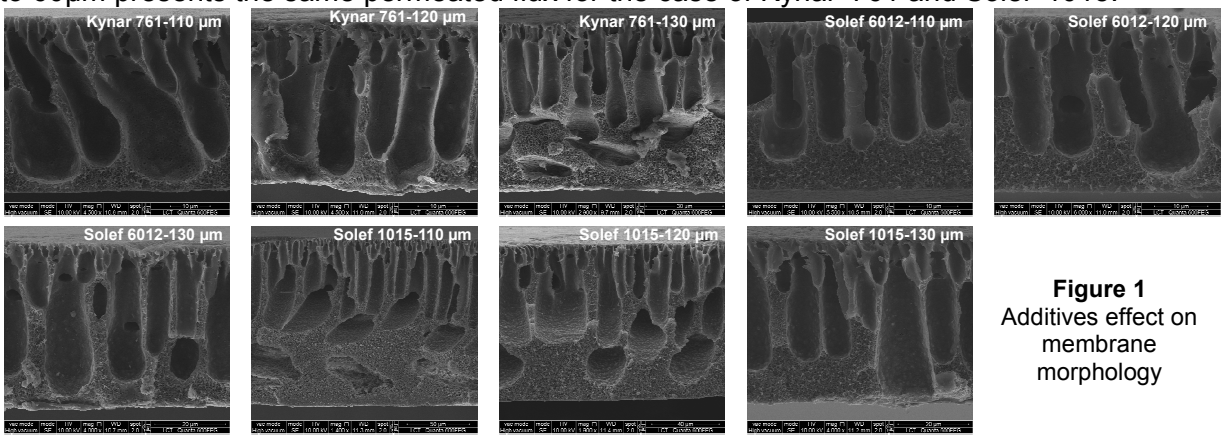

Figure 1 Additives effect on membrane morphology

Analyzing the results for membrane morphology, it is evident that the membrane porosity increased with decreasing membrane thickness, for all the polymers. It can be observed in SEM cross section images analysis (Figure 1) that membranes with morphology defined by a non dense structure, a thinner bottom layer with sponge-like structure and an intermediate layer with lengthy finger-like pores have best permeability results.

In this study, the influence of thickness on the performance of PVDF membranes has been evaluated. The results obtained suggest that the Kynar®761 and Solef®1015 polymers presents the same behavior. Membranes with these polymers present the same permeated flux for thickness varying around 50µm. The porosity results indicate that membrane performance seems to be associated to the changes in membrane internal morphology, less dense sponge-like structure and increased finger-like pores extension. Mechanical strength tests should be made to better understand the influence of the thickness.

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VINYLOOP: AN INNOVATIVE RECYCLING SOLUTION TO OBTAIN HIGH QUALITY R-PVC FOR MEMBRANE PRODUCTION

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Executive Summary
VinyLoop operates in Ferrara (Italy) a physical, solvent-based, recycling technology for difficult to recycle PVC waste. The purpose of VinyLoop is to recycle PVC composite waste which cannot be satisfactorily recycled by a grinding process, and to obtain an high quality R-PVC.
By this, valuable resources are prevent to be disposed in landfills or incinerated. Waste becomes a secondary raw material. Clients of VinyLoop R-PVC benefit from a high quality raw material which contributes to the improvement of the environmental footprint of their final products.

Focus On Innovative Technologies and Framework of VinyLoop
Recycling is widely seen as manner to save cost on raw materials in the first place. Regulations and voluntary commitments change the perception of recycled plastics derived from post-consumer waste. Recycling is a strategical end of life scenario. Even consumers are more and more aware of the recycled content.

Description of the VinyLoop Process
The VinyLoop process (a lot of details in www.vinyloop.com) separates the PVC compound from other materials (other plastics, rubber, metal, textile and others) by selective dissolution and filtration. It precipitates it into micro granules of PVC compound. The dissolution is a selective operation obtained by a solvent mixture and all non PVC compounds components remain insoluble. The filtration is used to separate the insoluble from the PVC solution by using sophisticated tools as also a particular centrifugal decanter. The precipitation stage is where, with the help of steam injection, the PVC compound is precipitated as granules and separated from the solvent. The solvent is recovered and reused. After a drying operation VinyLoop R-PVC is packaged to be sent to the customers. VinyLoop provides a readymade PVC compound that in most cases does not require further compounding.

VinyLoop as solution for membrane waste recycling

Materials with composite structures or post-consumer contaminated waste cannot be recycled in a traditional mechanical process by grinding and micronization for a new utilization in quite sophisticate applications. By using VinyLoop process the challenge of recycling membranes waste is possible and the R-PVC obtained a high grade quality material.

Figure 1: VinyLoop®-material calendered as a pond liner

VinyLoop as raw material in PVC membranes with lower impact

VinyLoop R-PVC compound is used for many applications. In addition to their strength specifications, also its good ability to be processed is of high importance. In 2012 the equipment manufacturer Leister together with Vinyloop performed a test which showed excellent results.
High quality welding seams can be produced with the VinyLoop material using different Leister welding machines. Given a specific application the welding machine can be chosen and its parameters developed. From the welding point of view VinyLoop is a suitable material for various applications.

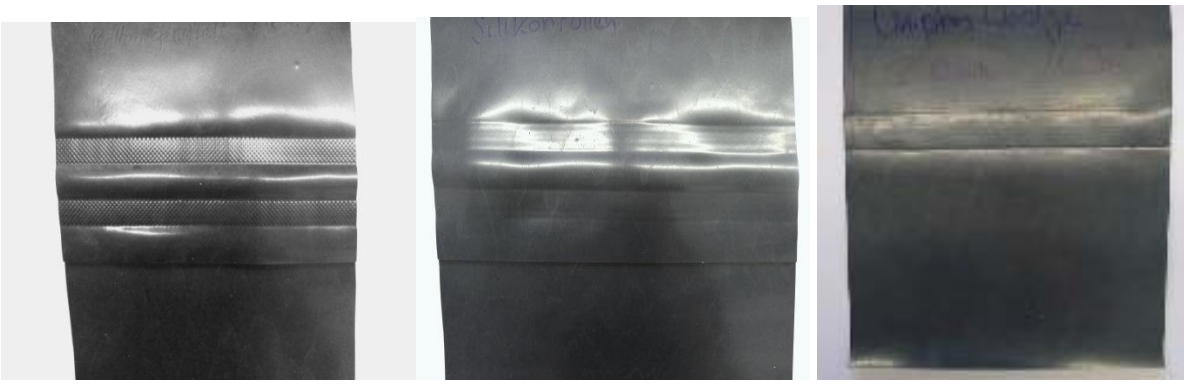

Figure 2: Welding seams produced with the TWINNY T and different pressure rollers (left: pressure roller with the maximum checkered surface, right: pressure rollers with medium checkered surface, right: silicon pressure rollers).

Low footprint
Valuable plastic is recycled by VinyLoop and allows it re-use in a new product. By this, valuable resources are prevent to be disposed in landfills or incinerated. Waste becomes a secondary raw material similar to virgin PVC compound. Clients of VinyLoop R-PVC benefit from a high quality raw material which contributes to the improvement of the environmental footprint of their final products.

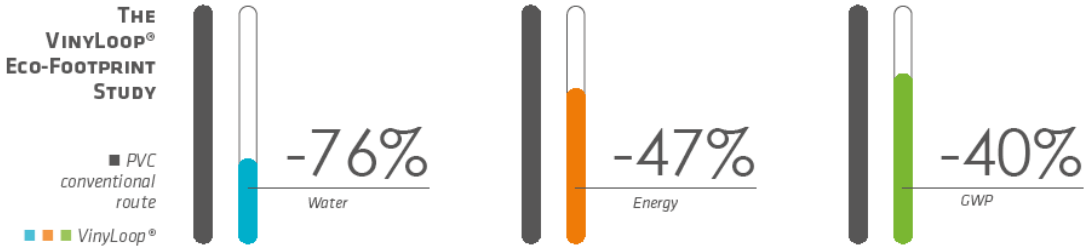

Figure 3: environmental performance of VinyLoop compared to conventional material.

With its environmental benefits in terms of energy saving and CO2 emission reduction, VinyLoop® R-PVC is an important resource to produce a lower environmental footprint and high technical/quality performance products.
A Life Cycle Assessment Study was performed to evaluate the environmental footprint of VinyLoop. Further it was compared to PVC Compound produced in conventional route. The methods of Life Cycle Assessment (LCA) as per ISO Standards of ISO1440-44 have been used in this study and it has been critically reviewed by DEKRA.

IRON INFLUENCE ON URANIUM REMOVAL FROM WATER USING CELLULOSE ACETATE MEMBRANES DOPED WITH ACTIVATED CARBON

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Uranium pollution in water is a matter of global concern, due principally to water scarcity for human consumption throughout the world. This actinide has been gradually introduced into ground water through mining and as natural mineral leaking. Uranium has toxic effects mainly in the urinary system. Other health risk is that uranium is converted into other high toxic radioactive species, which can cause cancer and other stochastic effects. Thus, based on a wide variety of studies, USEPA has set as maximum acceptable uranium level as 30 µg L-1 and 15 pCi L-1 (0.56 Bq L-1) for alpha particles [1].
In Mexico, NOM-127-SSA1-1994 fixes as the highest limit for alpha global radioactivity at 0.56 Bq L-1 [2]. Particularly, uranium pollution in water has been widely studied in the north part of the country [3]. Its concentration ranges from 0.03 to 1.34 Bq L-1. These levels are reached due to natural lixiviation mechanisms. Therefore, applicable and affordable separation techniques are necessary to diminish the health risk by eliminating or reducing uranium from surface and ground water. Regarding this situation throughout Chihuahua State, many osmosis plants for water purification have been established. Nevertheless, these techniques are quite difficult to preserve and maintain, due to their high energy and membrane replacement costs. Thus, it is desirable to develop high cost effective materials to improve water quality for consumption. In this regard, previous work has been done for ultrafiltration membrane development for uranium removal [4]. In this work, based on activated carbon capacity for uranium retention, a composite membrane with cellulose triacetate has been developed and tested in absence and presence of trivalent iron in synthetic water. Besides, iron loaded activated carbon has been used for membrane attainment and its effect is studied in membrane permeation processes.
Methodology. Two different approaches were adopted: adding iron chloride to the uranyl solution ($FeCl_3$ at 0.5, 1.0 and 2.0 ppm), and filtration of pure uranyl nitrate through composite membranes of CTA with activated carbon doped with iron. The original NC-100 carbon (Norit) was oxidized with nitric acid at 80º C, and stirred for 3 hours to obtain the main carbon identified as 3HNO. This carbon was impregnated with $FeCl_3$ dissolved in HCl at different times, 3, 6 and 24 hours, and the resulting materials were identified as Fe3H, Fe6H and Fe24H, respectively. The principal characteristics of AC were described as follows: 3HNO carbon, the raw carbon for all doped ones, was obtained by oxidation with HNO_3. Lactones, carboniles and phenolic groups were found, with a total of 1.5 meq/g acid groups and 0.72 meq/g of basic ones, giving up a final pH of 4.8.The filtrate was provided by uranyl nitrate dissolutions at very low concentration (1.2 ppm), with pH = 6-8. AC was added to CTA using a casting film process to obtain dense membranes.
Results Average uranium removal was 22 ± 3%. As it is has been observed, iron presence contributes to uranium filtration, dissolved or into activated carbon, obtaining 50% removal efficiency (%RE) for the best result (Table 1).

Table 1. Removal efficiencies for different CTA-FeAC membranes at three pH. Two independent replicates are shown. Standard deviations are calculated based on 3 radioactivity measurements.

SAMPLE	pH 6.0	pH 7.0	pH 8.0
3HNO	0.04 ± 0.01	0.10 ± 0.02	0.21 ± 0.04
	0.12 ± 0.02	0.08 ± 0.02	0.19 ± 0.03
Fe3H	0.30 ± 0.04	0.18 ± 0.03	0.20 ± 0.03
	0.36 ± 0.05	0.16 ± 0.02	0.23 ± 0.04
Fe6H	0.17 ± 0.03	0.18 ± 0.03	0.50 ± 0.07
	0.18 ± 0.04	0.16 ± 0.03	0.44 ± 0.06
Fe24H	0.39 ± 0.06	0.29 ± 0.05	0.15 ± 0.03
	0.36 ± 0.06	0.26 ± 0.04	0.16 0.03

From these data several points can be remarked:
1.pH has a significant effect for uranium rejection. Lightly basic media is the optimum when membrane Fe6H is used. Uranium rejection is the higher, around 50%, for that condition.
2.The lower rejection is attained for membrane 3HNO for all pH tested.
3.For membrane with the maximum iron concentration in the AC, lower pH is the best for uranium rejection.
These statements could be explained in terms of iron distribution. When it is well dispersed into AC, and the carbon is well distributed in the composite, the higher rejection is attained for basic pH. Taking into account the previous reported results [5], iron in carbon is forming oxi(hydroxides) which could be the principal responsible of uranium adsorption. As it was proposed [4], uranium complexes in the form of carbonate species could form with iron as Fe(III). These kind of compounds have been extensively reported in the use of adsorbents of uranium, such as iron oxides. In the case of Fe24H membranes, iron is agglomerated in AC surface [5]. This situation probably directs rejection process because iron effective surface concentration could be lower than in Fe6H membranes, as it was evidenced by SEM-EDS-SEM. As iron is not effectively interacting with uranium carbonate species, basic media does not favor uranium rejection.
Conclusions The principal parameter which directs uranium transport is pH, finding that in alkaline solutions, where uranium is forming high molecular weight compounds, it is trapped into membrane structure. AC plays also an important role during uranium transport. If it is well dispersed into the polymeric matrix, high %RE is attained, due to the high surface area available into the material. If AC conglomerates, uranium can go through membrane, increasing its permeability.

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Acknowledgements: To CONACYT for funding.

EXTRACTION OF PROPANOL FROM AQUEOUS SOLUTION BY PERVAPORATION PROCESS , WITH PDMS MEMBRANES

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Abstract

The objective of this study, is to investigate the separation in the first step, an alcohol from aqueous solutions ,with PDMS membranes,(made and traded) and establish it's performances thereof, under various operating conditions. This investigation is related to a national research project, to **CO_2 conversion**.

PDMS membranes are widely used for the separation of organic compounds, from hydro-organic mixtures; Polydimethylsiloxane, is one of the few hydrophobic polymers, which can give resistant films. It's high affinity for alcohol, characterized by it's good swelling, motivated the choice of this polymer, for our study.
The membrane film ,with thickness (**e),** is put in the pervaporation cell (jacketed), where the hydro-organic solution is introduced .,

The flow is assessed by weighing the pervaporat collected, during known times intervals. Pervaporat composition is homogenized, and determined by gas chromatographic analysis.

Performances are evaluated by total pervaporation flux (J), and separation factor (**α)**:

$$J = (m * e) / (s * t)$$

$$\alpha = (C (1-C)) / (C (1-C '))$$

J:total flux(kg.µm/h.m^2)
m:total mass permeate (kg);
C: concentration upstream ,
C': concentration downstream.
e: thickness of the membrane (µm); **s***: membrane active surface(m^2);
t: time between two pervaporat (h),samples.

To investigate performances of the PDMS membranes(two types) and to compare it, pervaporation experiments are carried out ,under variable conditions: mass fraction of propanol in the solution(05-20°/°); temperature(305-335°K);constant stirring speed(800 rev./min); constant solution rate(60ml/s).

Results show that the membranes made, are very effective. The pervaporat flux and the separation factor, increase with the concentration and the temperature. The mass transfer is expressed by a global model of dissolution-diffusion like principal mass transfer mechanism.

EFFECTS OF POLYMER CONCENTRATION ON THE CHARACTERISTICS AND MEMBRANE DISTILLATION PERFORMANCE OF NANO-FIBROUS MEMBRANES

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Electro-spinning is the most used technique for fabrication of nano-fibrous membranes. The system parameters such as the type and molecular weight of the polymer, polymer concentration, solvent type and polymer solution properties (viscosity, electrical conductivity and surface tension) and the electro-spinning process parameters such as the electric potential, flow rate of the polymer solution, distance between the metallic needle tip and the collector, ambient parameters (i.e. temperature and humidity in the electro-spinning chamber), both are affecting the characteristics of the nano-fiber and the nano-fibrous membranes [1-4].

In this study, the effects of the polymer polyvinylidene fluoride (PVDF) concentration on the characteristics and direct contact membrane distillation (DCMD) desalination performance of self-sustained electrospun nano-fibrous membranes (ENMs) have been studied. Different polymer concentrations ranging from 15 to 30 wt% were considered in the solvent mixture N,N-dimethyl acetamide and acetone, while all other electrospinning parameters were maintained the same [5].

The effects of the PVDF concentration on fiber diameter, thickness, water contact angle, inter-fiber space, void volume fraction, liquid entry pressure, mechanical and thermal properties of the ENMs were investigated.

Based on the minimum polymer concentration, which is the critical chain entanglement concentration, two groups of ENMs were identified: 1- beaded-ENMs and 2- bead-free ENMs. The critical chain entanglement concentration (C_e), which is the minimum PVDF concentration required for electrospinning beaded fibers, was found to be 17.05 wt%.

It was observed that the morphology of the beads changed from spherical to elongated or elliptical and their density decreased with increasing the PVDF concentration in the polymer solution from 15 to 22.5 wt%, while the amount of fiber formation was increased. The mean fiber diameter and the thickness of the ENMs were higher when using greater PVDF concentrations in the electrospinning solution.

In each group of ENMs, the inter-fiber space was reduced with increasing the PVDF concentration. However, due to the bead-free cohesive web of fibrous structure, the group of ENMs prepared with higher PVDF concentrations than 22.5 wt% exhibited higher void volume fractions and DCMD desalination performance than the other group of ENMs containing beads.

Among the prepared PVDF ENMs, the optimized membrane exhibiting the highest DCMD performance was prepared with 25 wt% PVDF concentration. This ENM exhibited a DCMD permeate flux of 43.7 kg/m^2.h and 38.9 kg/m^2.h for distilled water and 30 g/L NaCl feed aqueous solution operating at a feed temperature of 80 ºC and a permeate temperature of 20 ºC. The NaCl rejection factor was higher than 99.99 % [5].

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Acknowledgements: The authors gratefully acknowledge the financial support of the I+D+I Project MAT2010-19249 (Spanish Ministry of Science and Innovation) and Abengoa Water S.L.U. (Artículo 83: 320/2011, MEMsa and 85/2013, HOFI-MED-Plant). M. Essalhi is thankful to the Middle East Desalination Research Centre (MEDRC, Project 06-AS-02).

PREDICTION OF ADHESION BETWEEN THE POLYMERIC LAYERS OF COMPOSITE HOLLOW-FIBER MEMBRANES PRODUCED BY SIMULTANEOUS EXTRUSION

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The hollow-fiber membranes have their own niche market in some separation processes like gas separation, ultrafiltration, pervaporation and dialysis [2]. Furthermore, most of membranes are commercialized in a flat sheet shape. They therefore still have a great potential to expand their niche market. The hollow-fiber membrane advantages not only include the usual membrane advantages, such as energy saver (most of the time phase changes are not required), simplicity of operation and easy scale-up [1], but also includes higher packing density[1] modules, they are self-supporting (thanks to its cylindrical shape) and simplified module fabrication [2]. It is worth to mention that hollow-fiber modules could have packing density ten thousand times higher than flat sheet membrane modules [3]. Despite these evident advantages, hollow-fiber membranes are not common as flat sheet ones are, thanks to higher complexity of synthesis involved. Furthermore, this work deals with dual-layer hollow-fiber membranes synthesized by simultaneous extrusion process, which adds at least two main advantages [2]: (1) economy of high performance material and (2) avoiding a second step of depositing a selective layer upon the hollow-fiber membrane support. In this work, the selective layer is located on the inner surface of the hollow-fiber, which decreases significantly the possibility of external damage.

To investigate these composite hollow-fiber membranes, cloud points were determined for each polymer solution and related to Hansen solubility parameters, as well as the initial precipitation rate was determined in order to elucidate what happens in the very beginning of the contact between both polymeric solutions. These results were interrelated with the aim of studying the adhesion between composite hollow-fiber membrane layers. This work proposes that adhesion between these layers is intrinsically related to the very first moment of precipitation and it was observed that the initial precipitation rate can be used to predict adhesion or delamination between two distinct polymeric solutions in the dual layer hollow fiber synthesis.

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[1] Packing density is the rate between permeation area and module volume.

DESEMPENHO DE MEMBRANA PA12 PREPARADA POR INVERSÂO DE FASES COM PARTÍCULAS DE DIÓXIDO DE TITÂNIO NA DEGRADAÇÃO DO AZUL DE METILENO

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1. INTRODUCAO

O setor industrial, via de regra, ao mesmo tempo em que exerce forte demanda sobre este recurso, gera efluentes que podem causar fortes impactos ambientais e comprometer o uso. A indústria textil caracteriza-se por consumir grandes quantidades de água e por usar diferentes compostos quimicos, entre eles, diferentes tipos de corantes, detergentes e sais, que dependem do processo têxtil (tingimento, estamparia, acabamento etc) e da matéria prima utilizada (1). Estes efluentes podem ser caracterizados por meio de parâmetros físico-químicos e biológicos, tais como Demanda Química de Oxigênio, Demanda Bioquímica de Oxigênio, Carbono Orgânico Total, pH, cor e sólidos em suspensão, dentre outros. A cor normalmente é um dos parâmetros mais importantes, uma vez que, dentre os diversos tipos de corantes utilizados pela indústria têxtil, os corantes reativos são os mais utilizados e, no entanto, seu grau de fixação pode ainda ser considerado muito baixo (50 a 90%) (2).

Métodos tradicionais para o tratamento de efluentes têxteis incluem uma combinação de processos físico-químicos (coagulação/floculação) e biológicos (lodos ativados). No entanto, essas tecnologias têm se mostrado pouco eficientes, principalmente em relação à remoção de corantes, além de gerarem grandes quantidades de lodos.

Vários estudos mostram que a oxidação fotocatalítica pode ser uma alternativa para o tratamento de efluentes que possuem corantes reativos como o azul de metileno. O uso de dióxido de titânio (TiO2) em suspensão tem se mostrado um método promissor para a fotodegradação do azul de metileno devido à grande área superficial disponível para a reação [3]. Entretanto, uma etapa de separação sólido-líquido será necessária para remover o TiO_2. A incorporação de partículas de TiO_2 sobre a superfície de uma membrana poderia aliar a capacidade fotocatalítica dessas partículas para degradar corantes, sem a necessidade de uma etapa posterior de separação, com a capacidade da membrana em reter outros constituintes presentes no efluente.

Neste sentido, o objetivo deste trabalho foi avaliar a capacidade fotocatalítica de membranas preparadas com dióxido de titânio na degradação do corante azul de metileno.

2. MATERIAIS E MÉTODOS

2.1. Materiais

Poliamida 12 (PA12) (Rilsan) na forma de grânulos foi utilizada como polímero, e uma mistura 1:1 (volume) de ácido fórmico 99% (AnalytiCals) e diclorometano 99,5% (Panreac) como solvente. Água destilada a 10°C (± 2 °C) foi utilizada no banho de coagulação. Óxido de titânio (TiO_2) (degussa) foi utilizado como agente fotocatalítico e uma solução de azul de metileno para avaliação da capacidade catalítica.

2.2. Métodos

2.2.1. Preparação das Membranas por Inversão de Fases

Duas soluções foram preparadas para obtenção das membranas: PA12 12% (massa) e PA12 12% (massa) com 1% de TiO_2 (massa). À solução com TiO_2 foi adicionado 20 µL de Triton®X-100 (Sigma) para facilitar a dispersão das partículas. As soluções foram mantidas em banho de ultrassom até a completa dissolução do polímero.

As soluções poliméricas foram uniformemente distribuídas sobre uma placa de vidro com o auxílio de um bastão de vidro e submergida no banho de coagulação para a inversão de fases. Após a formação das membranas, estas foram mantidas em água destilada (à temperatura ambiente) por pelo menos 12 horas, para eliminação do solvente residual.

2.2.2. Avaliação da Capacidade Fotocatalítica

Partes das membranas produzidas (cerca de 3,0 cm^2) com e sem TiO_2 foram imersas em frascos contendo 15 mL de uma solução de azul de metileno, sob agitação, e expostas à claridade natural. Em intervalos regulares de tempo, amostras foram retiradas. Um outro frasco, sem membranas, foi submetido às mesmas condições (controle). A variação da concentração do azul de metileno ao longo do tempo foi avaliada por meio de um espectrofotômetro UV/Vis (Shimadzu TCC-240A). A faixa espectral analisada foi de 200 a 800 nm.

3. RESULTADOS E DISCUSSÃO

O azul de metileno é um corante orgânico bastante solúvel em água. Sua absorbâcia ocorre no comprimento de onda de 665,0 nm. A Figura 1 mostra os espectros das soluções de azul de metileno no início do experimento (1) e após 2 horas (2), bem como após duas horas de contato coma a membrana sem TiO_2 (3) e com a membrana com TiO_2 (4).

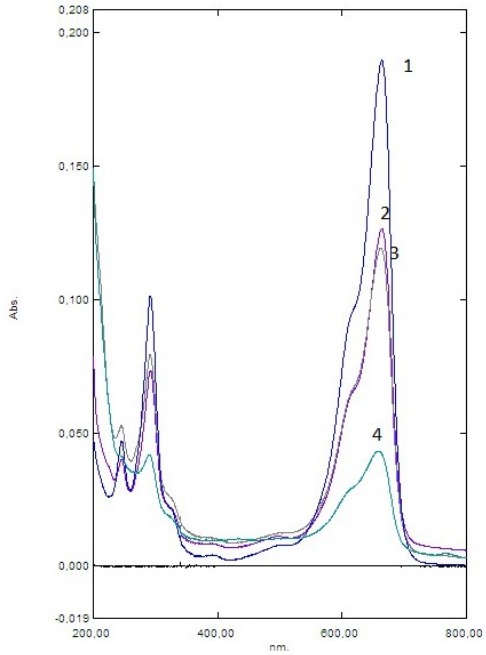

Figura 1- Espectro das soluções de azul de metileno

4. CONCLUSÃO

Os resultados mostram que a membrana produzida com TiO_2 foi capaz de diminuir a concentração do azul de metileno, indicando que esta tecnologia pode ser viável para o tratamento de efluentes têxteis. Outros experimentos serão realizados para avaliar o desempenho das membranas quanto ao fluxo de permeado e seletividade.

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Acknowledgements
Os autores agradecem ao CNPq pelo suporte financeiro.

Polymeric Membranes

- **Poster session 1**

NEW BLENDS OF POLYETHERIMIDE-POLYIMIDE FOR HIGH PRESSURE GAS SEPARATION APPLICATIONS

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Polymeric materials have been employed in many industrial fields including the purification of gas mixtures (GS). One of the most important drawbacks of polymeric membranes is their tendency to undergo plasticization, which leads to a loss of selectivity when used under high pressures. This is usually observed when the gas mixture to be processed includes a highly soluble gas as for example CO_2 [1]. Plasticization leads to a minimum in the permeability *vs* applied pressure plot. The subsequent increase in permeability is paired with a steeply decrease in selectivity [2].
Currently, there are about 600 trillion standard cubic foot (SCF) of natural gas only in the United States that cannot be processed due to its high content of CO_2 [3]. Natural gas is a complex mixture that produces (because it has carbon dioxide and other condensable gases) a fast plasticization at relatively low pressure in many of the polymeric materials used for its purification. Thus, the search of new materials less prone to undergo plasticization processes is a hot topic, impelled by the industry, in this field. There are several ways to minimize the effect of plasticizing gases in glassy membranes. In general, the most used route to reduce the plasticization effect consisted consists of cross-linking the material [4]. This route reduces the swelling of the membranes and prevents their plasticization. However, cross-linking is accompanied by a drastic reduction in permeability, which reduces greatly the productivity of the membranes.
In this work, a new and easy methodology to make plasticization-resistance GS membranes has been developed. It has consisted of making blends of aromatic polyimides (**PI),** having high GS productivity, with a set of aliphatic-aromatic copolymers (**PEO-PI**) formed by the reaction between a dianhydride and a mixture of aromatic diamine (same structure than that employed to make the PI homopolymer) and aliphatic diamine having polyethylene oxide chains, PEO, in its structure. The blends were made using different ratios between **PI** and **PEO-PI**. These polymers have the ability of losing the PEO chains at temperatures near 350 ^{o}C in nitrogen, and near to 275°C in an oxidizing atmosphere as air, giving materials with excellent gas productivity and a high plasticization resistance.

The aliphatic-aromatic copolymers showed gas permeation properties well below those observed for the fully aromatic polyimide. Nevertheless, the new generations of polymer- blend materials showed better gas separation properties, which depended on the employed **PI**/**PEO-PI** ratio. However, the materials obtained by partial pyrolysis (total removal of the polyethylene oxide moieties but taking care of using a temperature below the decomposition temperature of the aromatic polyimide) yielded polymeric membranes with good GS similar to those showed by the aromatic polyimide.

The density results showed that the blends that were heated to 390°C under N_2, had a density lower than that of the reference aromatic polyimide, what indicates that its fractional free volume fraction should be higher, and consequently its gas permeability should be more elevated.

Solubility test carried out for these membranes revealed that some kind of cross-linking was attained being this process dependent on the used atmosphere and also on the employed temperature. The gas separation properties carried out at high pressures also exposed that the membranes showed outstanding resistance to plasticization due to the commented cross-linking produced during the partial pyrolysis process.

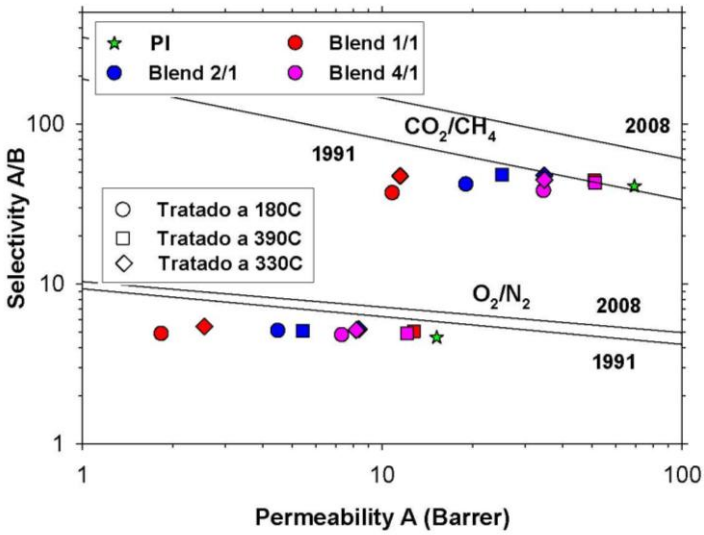

Figure 1. Permeability vs Selectivity for different couples of gases.

In conclusion, a new generation of partially pyrolyzed polymer blends, derived from a high gas productivity aromatic polyimide, has showed gas separation properties similar to the aromatic polyimide used for making the blend, but having a much higher plasticization resistance. In this way, this methodology has been able to produce in a very easy way gas separation membranes having a high plasticization resistance. Thus, these materials have a high potential to be used in industrial gas separation processes involving condensable gases.

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Acknowledgments
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CONDUCTIVITY OF POLYMERIC FILMS BASED ON SUPPORTED IONIC LIQUID-LIKE PHASES

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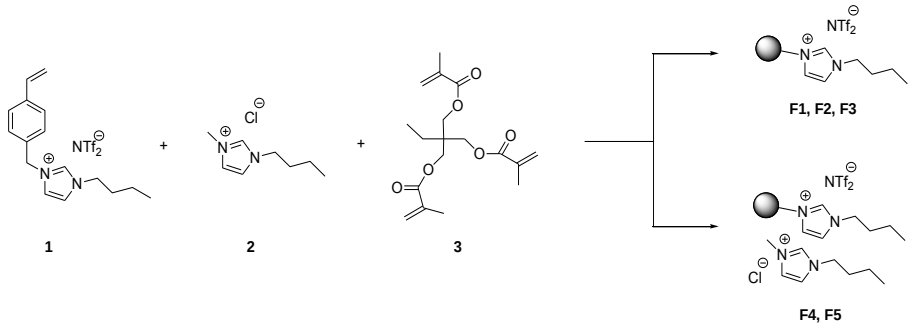
Abstract. The supported species can be obtained either by adsorbing ILs onto solid supports (Supported Ionic Liquid Phases or SILPs) or by covalently bonding IL-like fragments on the surface of the solid support (Supported Ionic Liquid-Like Phases or SILLPs). We have followed this last strategy for the preparation of different kinds of polymers (from gel-type to monoliths) containing surfaces functionalized with imidazolium subunits This has allowed us to demonstrate that, upon immobilization, ionic-liquid-like fragments appropriately transfer the properties of the bulk related ILs to the polymeric surfaces. An important application of ILs has been the preparation and stabilization of nanoparticles of many classes. In this regard we have analyzed the possibility of using SILLPs for the generation and stabilization of metal nanoparticles (NPs) as well as for the use of the corresponding supported systems as efficient heterogeneous catalysts. Recently poly(ionic liquid)s are attracting a growing interest to the application in various branches of science and technology. Moreover, ionic liquids containing NTf_2 as counterion, have attracted significant interest due to their unique physical properties such as high thermal and chemical stability, negligible vapor pressure, broad electrochemical window and high ionic conductivity[1]**.** The preparation of ionic liquid-type polymer brushes having different hydrocarbon chain lengths between the skeletal bonds of the main chain and imidazolium rings has been reported**.** Supported ionic liquid-like phases (SILLPs) have also been obtained by covalently binding IL-like moieties, such as alkylimidazolium cations, to either macroporous or gel-type polystyrene-divinylbenzene resins**.** On the other hand, polymers containing embedded ionic liquids inside their matrix can further improve their ionic conductivity[2]**.** Therefore, in order to improve the conductivity of poly(ionic liquid)s in this work we explored the possibility of immobilization of low-temperature ionic liquids absorved into the polymer matrices.

Experiments

Impedance experiments were carried out on four different samples at several temperatures lying in the range 273 K (0ºC) to 403 K (130ºC) and frequency window $10^{-1} < f < 10^{7}$ Hz. The measurements were performed with 100 mV amplitude, using a Novocontrol broadband dielectric spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface**.**



The sample of interest was placed between two stainless steel meshes coupled to the impedance spectrometer. The temperature was firstly twice gradually raised and lowered from 0 to 130ºC in 10ºC steps. Different scans have been collected to ensure the measurements reproducibility. The temperature was controlled by a nitrogen jet (QUATRO from Novocontrol) during every single sweep in frequency.

Results and Discussion

The results obtained for the SILLPs tested shown that conductivity is higher for the films containing both NTf_2 and Cl^- as anions.

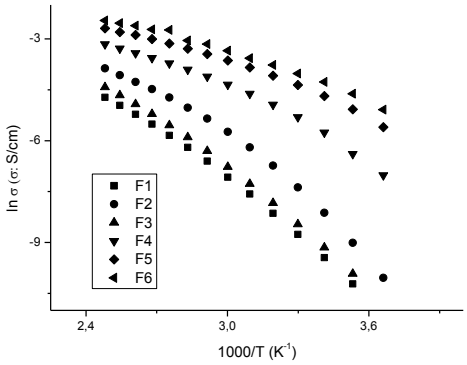


Fig. 1. Conductivity values as a function of the temperature for all samples.

Conclusions

In the present work, different SILLPs containing NTf_2 as counterion have been synthesized. The conductivity measurements have been performed as a function of the temperature in wet and dry atmospheres in order to study the influence of counterion on total conductivity.

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Acknowledgements. This research has been funded in the frame of Support Programme for Research and Development of the Polytechnic University of Valencia and the Ministry of Science and Innovation through the projects: 24761 and SP-ENE-20120718, respectively.

EFFECT OF SOLVENT IN THE PRECIPITATION BATH OF THE PA6 NANOCOMPOSITE MEMBRANES

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In recent years, polymeric membranes are widely used in industry fields, such as microfiltration, ultrafiltration, reverse osmosis and gas separation Among the several techniques to manufacturing porous polymeric membranes, the majority of membranes are prepared by phase inversion using pure polymers. In contrast to conventional phase inversion processes for manufacturing polymeric membranes, the use of nanocomposite is one of an alternative valuable ways of preparing microporous membranes and has particular advantages [1]. The significant improvement of barrier properties is often observed not only because of a tortuosity effect directly related to the shape, dispersion, and orientation of the nanofillers but also because of the strong interaction between the polymer chains and the nanofillers [2-4]. The structure of nanocomposites is known to play a major role in the enhancement of these properties. Depending on the process conditions and on the polymer/nanoclay affinity, intercalated and/or exfoliated structures are classically encountered. The melt process implies a polymer with nanoparticles under shear above the softening point of the polymer. It is generally recognized that the used processing conditions for melt process have a strong effect on the morphology of semi-crystalline polymer nanocomposites and thus may have significant influence on the barrier properties. Polyamide 6 (PA6) is usually selected for elaborating polymer nanocomposites because of the interesting properties associated with the possibility to extend the exfoliation [5]. The aim of this work it to obtain membrane from PA6/montmorilonite nanocomposites by phase immersion technique and to evaluate the presence of clay and solvent in coagulation bath in the membrane preparation The nanocomposite was produced by melting intercalation.

The results from X-ray diffraction of nanocomposite (Fig1) indicate that apparently all polymer/treated clay systems present exfoliated and/or partially exfoliated structure, due to the disappearance of characteristics peaks of clay when incorporated in the polymer matrix. The polyamide 6 has two inflection related to the crystalline planes of (200) and (002) of α phase in $2\theta = 20°$ and 23.7°, respectively. The reflection in 21.4^{o} of crystalline plane of (001) is related to the γ phase of the polymer and may also occur in the reflection at 10.8^{o}, consistent with the results found in the literature. In this case, it is possible to observe that the predominant crystalline phase of polyamide 6 is α. The PA6 is a semi crystalline polymer and the enlargement of the peaks indicates the presence of amorphous regions. As can be observed the presence of clay change the shape of these peaks, modifying the crystallinity of PA 6.

From SEM images it is possible to observe that the membrane of pure PA6 membrane (Fig.2a) presented a cellular structure with presence of small pores. With the presence of clay in the membrane (Fig2b) is possible to verify an increase in the amount of pores in the membrane surface, however the pores are small, with regular aspect and uniform. From Fig 2c it was verified that the presence of solvent in the coagulation bath change the morphology of the membrane, causing an irregularity in the pore shape. In this way it was possible to see that the presence of clay and solvent in the coagulation bath changed the morphology of the prepared membranes.

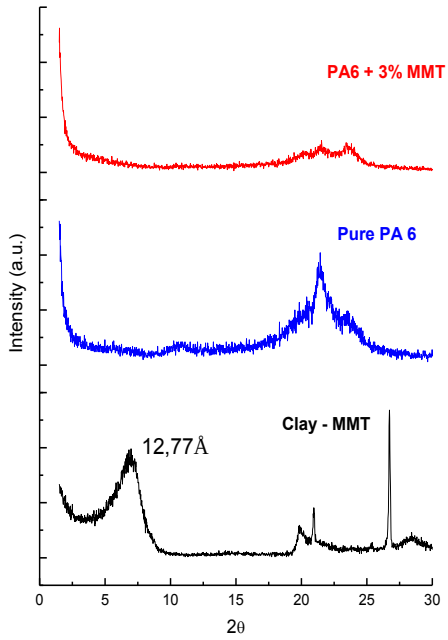

Figure 1: XRD of the MMT clay, PA6 and its nanocomposite with 3% of clay

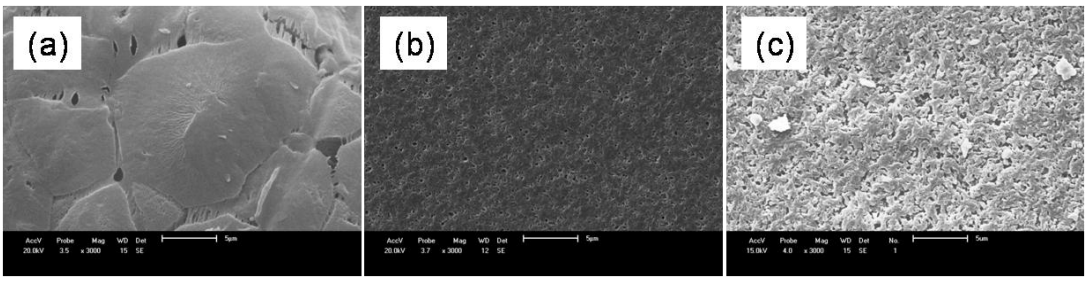

Figure 2: SEM images of PA6, PA6+3%MMT and PA6+3%MMT with 10% of solvent in the coagulation bath, respectively.

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Acknowledgements

The authors thank Bentonit União Nordeste (BUN), DEMa/ UFCG, CAPES / PNPD, MCT / CNPq and PRH-25/Petrobrás for the financial support.

Preparação e caracterização de membranas de polisulfona (PSf) com microcelulose (MCC) de eucalipto

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Introdução

Membranas poliméricas são cada vez mais estudadas, devido às suas aplicações industriais. Com a ampliação da área de compósitos poliméricos, são necessários materiais de reforço para aplicação em membranas, uma vez que estes podem contribuir nas propriedades mecânicas e de seletividade.

A celulose é um polímero caracterizado por regiões cristalinas entrecortadas por regiões amorfas [1]. A hidrólise ácida da celulose sob condições controladas obtém-se microcristais celulósicos que são compostos de feixes de cadeias de celulose e um arranjo linear rígido. Os fragmentos resultantes se agregam em microcristais que se apresentam como pós finos, chamados de microcelulose (MCC).

Modificações nas membranas de PSf são necessárias, a fim de melhorar suas propriedades. A adição de componentes orgânicos e inorgânicos à solução polimérica da membrana tem sido uma técnica bastante utilizada na preparação de membranas, e esta adição de componentes caracteriza as membranas compósitas [2-4].Neste trabalho são analisadas as propriedades das membranas de PSf com adição da carga de reforço MCC obtida pelo processo de hidrólise ácida,quanto a morfologia e no fluxo de água destilada dessas membranas.

Resultados e Discussões

Pela hidrólise realizada com os ácidos H_2SO_4 e HCl foi possível diminuir o tamanho das fibras de celulose eucalipto a tamanhos micrométricos. Atécnica de difração de raio X (DRX) foi utilizada com o intuito de avaliar o grau de cristalinidade das amostras (Fig. 1).

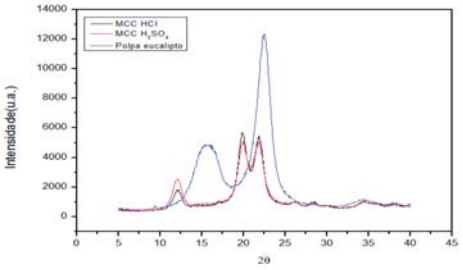

Figura1–Difratograma de raio X da polpa *Kraft* e da MCC de eucalipto, obtida pelo método de hidrólise ácida com agitação.

A cristalinidade da polpa *Kraft* de celulose eucalipto, de61,27%, aumentou após o tratamento químico para 74,66% com HCl e para 75,51%com H_2SO_4. Este aumento pode ser explicado pela remoção dos componentes amorfos (hemicelulose e lignina) e pelo rearranjo das cadeias de celulose na fibra após o tratamento químico (Tabela-1).

Tabela 1- Índices de cristalinidade (%) das MCC

Amostra	I_c eucalipto (%)
Polpa *Kraft* eucalipto	61,27
MCC HCl	74,66
MCC H_2SO_4	75,51

As membranas de PSf apresentaram área superficial com poucas fibras dispersas sobre a superfície da membrana evidenciando melhor interação fibra/polímero quando comparada a membrana sem carga de reforço. Na seção transversal a membrana com 0,2% de MCC apresentou estrutura porosa, com poros de uniformes (Figura-2).

A Figura 2 apresenta a morfologia por MEV das membranas de PSf sem carga de reforço e com carga de reforço com 0,2% de MCC.

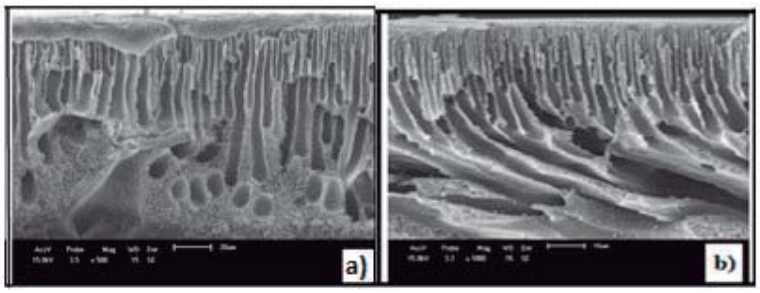

Figura 2- Micrografias(MEV) da membrana de PSf 18% NMP 50mL da seção transversal (x 500) a) sem carga de reforço b) com 0,2% MCC.

As membranas não permitiram fluxo de água até 2 bar como observado na figura 3a, podemos considerar que com a adição de 0,2% de MCC (figura 3b) o fluxo de água apresenta comportamento crescente ± 40% em relação a pressão. A membrana sem carga de reforço (Figura 3-a) apresenta menores valores de fluxo de água destilada,isto ocorre devido a adição da carga de reforço a MCC que modifica a estrutura da membrana e ao aumento da hidrofilia da membrana, comprovado pelo aumento do ângulo de contato, de 51,55° para 62,42°.

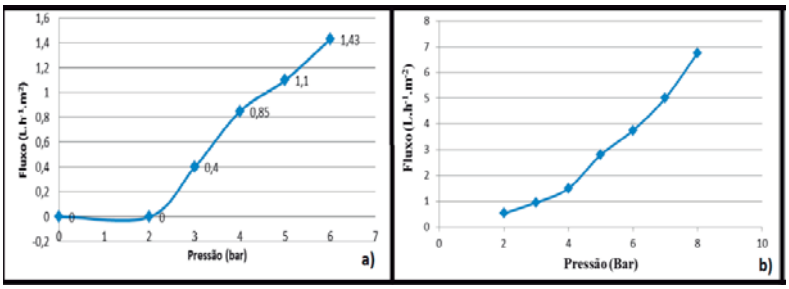

Figura 3 -Teste de Fluxo de água x pressão das membranas de PSf e NMP a) sem carga de reforço b)com 0,2% de MCC.

Conclusões

As membranas de PSf/ MCC apresentaram uma melhor resistência mecânica e um melhor fluxo de água permeada e hidrofilia devido a estrutura mais uniforme observada nos ensaios de microscopia(MEV), o que a torna mais resistente a elevadas pressões.

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NEW AROMATIC POLYAMIDES AND POLYIMIDES BEARING ADAMANTANE BULKY GROUPS

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This work reports the synthesis and characterization of a new diamine monomer with a spiro carbon in its structure and an adamantane bulky group (spiro-(adamantane-2,9'-(2',7'-diamino-fluorene) (SADAF), and a novel family of polyamides and polyimides, SADAF-PA and SADAF-PI, respectively, which were synthesized by reaction of the diamine with diverse diacid chlorides and dianhydrides. Polymer films of some selected polymers were prepared and measured as gas separation membranes.

Aromatic polyamides and aromatic polyimides are widely employed as gas separation materials. In particular, aromatic polyimides are considered as a class of polymers of high technological interest due to their good mechanical properties, excellent thermal stability, and high chemical resistance, glass transition temperature and fractional free volume, together with a high selectivity in gas separation. Furthermore, it is possible to obtain a wide variety of chemical structures by synthesis of new monomers or by simple modification of a certain monomer. Their gas permeation properties have been improved by modifying their chemical structure, for example, by introducing bulky side substituents that hinder the molecular packing and reduce the rotational mobility of the main chain.

The adamantane (tricyclo [3.3.1.1] decane) is a highly symmetric molecule that consists of three rigid cyclohexane rings in a chair-type conformation, relatively free of conformational stress. This conformation results in a high-volume structure that tends to inhibit the packing of polymer chains, thus decreasing the polymer packing and improving processability. Therefore, it is expected that the use of a new monomer having an adamantane bulky group conveniently placed in an aromatic diamine (Figure 1) will increase in a synergistic way the rigidity of the molecular chain and the fractional free volume of the obtained polymers causing also an improved solubility when compared with the reference structure not bearing the adamantane group.

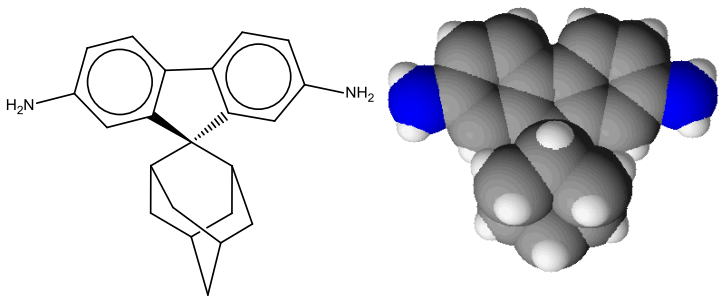

Figure 1. Molecular structure of SADAF (left) and its molecular model (right).

Main Conclusions of the work

A new diamine monomer with a spiranic sp^3 carbon in its structure, the spiro-(adamantane-2,9'(2',7'-diamino-fluorene) (**SADAF)** has been synthesized. On using this monomer, a set of aromatic polyamides and polyimides has been obtained.

All these polymeric materials showed excellent thermal stability, with decomposition temperatures near 500 °C, and high carbonaceous residue. Moreover, the glass transition temperatures were above 350 ^{o}C, suggesting high molecular chain rigidity.

WAXS patterns displayed a halo characteristic of structures with amorphous nature. The average d-spacing, which was estimated by Bragg's equation, indicated that the incorporation of adamantane groups into the polyimide brings about an increase of the intermolecular distances, which is going to influence the Fractional Free Volume and consequently the gas separation properties.

Polymers films made from aromatic polyimides and also from some aromatic polyamides showed good mechanical properties. The membrane derived from SADAF and 6F dianhydride also showed good gas separation properties, particularly for the gas pairs CO_2/CH_4 and O_2/N_2. The combination of a high permeability (35 barrer to CO_2 and 7 barrer to O_2) and an excellent permselectivity (CO_2/CH_4 and O_2/N_2 selectivity of around 50 and 6, respectively) produced materials with gas productivities close to the 1991 Robeson limit. It is expected that these results can be improved once the polymer synthesis, fabrication and post-thermal treatment of membranes are fully optimized. Particularly, these results suggest that the polymer structures obtained in this work are competitive with other polymers for industrial gas separation processes.

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The financial support of this work by the Spanish Ministry of Economy and Competitiveness (MAT2010-20668/MAT and MAT2011-25513/MAT) is greatly appreciated. This research was also supported by Korea CCS R&D Center, funded by the Ministry of Education, Science and Technology in Korea. Authors are indebted to the Spanish Junta de Castilla y León for the financing of this work through the GR-18 Excellence Group Action and project VA248U13. Authors also greatly appreciate the help provided by Sara Rodriguez in measuring gas separation properties.

AVALIAÇÃO DO EFEITO DA ARGILA EM MEMBRANAS DE POLIÉTERSULFONA

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O processo de separação por membrana é uma tecnologia atraente por ser um processo simples e eficiente, podendo ser efetuado sem de mudança de fase [1]. O crescimento dos processos de separação com membranas, embora recente, tem sido utilizado amplamente em processos tais como, purificação, fracionamento e concentração de uma grande variedade de indústrias [2]. Estes processos apresentam como principais atrativos, em relação aos processos convencionais de separação, o baixo consumo de energia, a redução do número de etapas em um processamento, a maior eficiência na separação e alta qualidade do produto final [3]. Em geral, o desempenho de uma membrana é caracterizado pelo fluxo permeado e pela retenção e passagem de espécies químicas. Nas operações governadas por diferenciais de pressão, tais como, a ultrafiltração e a microfiltração, a passagem de espécies para o permeado dependerá de suas dimensões ou massas molares médias. Nestes casos, removem-se partículas em suspensão e macromoléculas, tornando esta tecnologia competitiva, por exemplo no tratamento de água. O objetivo deste trabalho é produzir membranas de poliétersulfona (PES) e poliétersulfona/argila por meio da técnica de inversão de fases e avaliar a presença da argila na obtenção destas. A intercalação do polímero na argila se deu através da intercalação por solução.

A matriz polimérica utilizada foi o Poliétersulfona – PES e o solvente utilizado foi o Dimetilformamida (DMF) e a argila Brasgel PA empregada como nanocarga e denominada de MMT.

A Figura 1 apresenta as fotomicrografias de MEV da superfície das membranas planas do PES puro e dos nanocompósitos com a argila MMT nas proporções de 3 e 5%.

As membranas de PES puro apresentam-se com uma superfície pouco rugosa comparada à membrana com MMT 3% e 5%. Com o aumento usado nas imagens não foi possível observar poros na superficie para as membranas com PES puro. No entanto, é possivel observar alguns poros discretos para as membranas comPES/MMT 3% e PES/MMT 5%. Todas as composições apresentaram partículas sobre a superfície, indicando possivelmente polímero não dissolvido e/ou partículas de argila. Em algumas partes visualizam-se aglomerados dos mesmos. Segundo Liang [4], a presença destas partículas pode ser atribuído à fraca adesão entre PES e a cargas inorgânicas (montmorilonita).

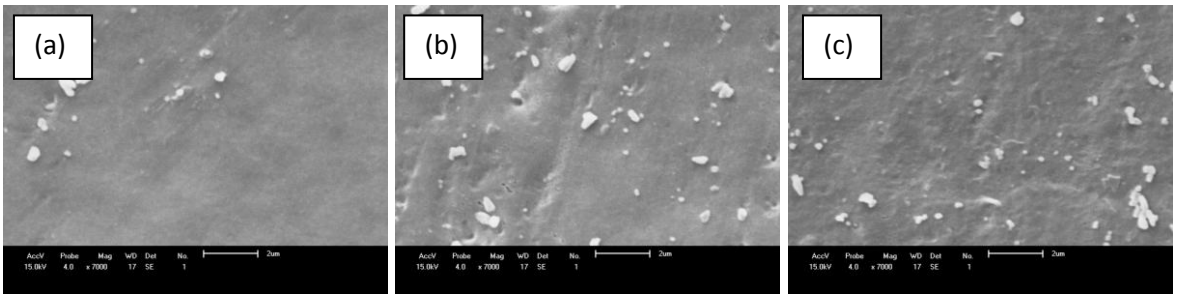
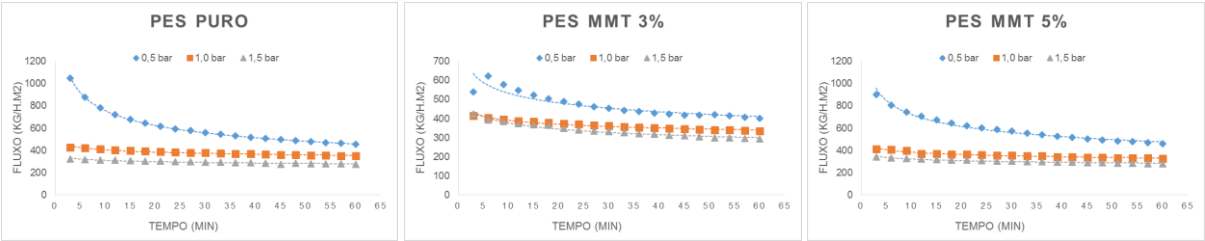


Figura 1: MEV das membranas de (a) PES puro, (b) PES/MMT – 3% e (c) PES/MMT -5%

Foi feita medidas de fluxo com água destilada para todas as composições em diferentes pressões de 0,5; 1,0 e 1,5 bar. Os gráficos dos fluxos em função do tempo estão na Figura 2. Observa-se que todas as composições apresentaram uma mesma tendência, o

qual começa com valores alto de fluxo e depois se estabiliza com tempos de aproximadamente 60 min. Para todas as membranas a pressão ideal foi de 0,5 bar, pois obteve-se uma melhor estabilização. Nas demais pressões, os fluxos foram menores, provavelmente por haver compactação dos poros.. Desta forma pode-se observar que quanto maior a pressão, maior é a compactação e menor o fluxo.

Ainda na Figura 2, verifica-se que o fluxo para a membrana de PES puro com 0,5 bar foi de aproximadamente 465 Kg/h.m^2, o que está consideravelmente acima do fluxo (214 Kg/h.m^2) do reportado pela literatura [5] para a membrana deste polímero. Nota-se que o fluxo mais alto é para a composição MMT 5%, isto sendo atríbuido, provavelmnete, a afinidade da argila com a água, visto que alguns autores indicam a necessidade de adicionar um agente hidrofílico, como aditivo, para melhorar a permeabilidade [1].



(a) (b) (c)

Figura 2: Gráfico do Fluxo de água destilada para a membrana de: (a) PES pura, (b) PES/MMT – 3% e (c) PES/MMT -5%

Logo, a incorporação da argila modificou a morfoloia superficial da membrana e aumentou a permeabilidade a água.

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Acknowledgements

Os autores agradecem à Bentonit União Nordeste (BUN), ao DEMa/UFCG, à CAPES/PROCAD/NF, ao PRH-25/ANP, à Petrobras, ao CTBrasil e à RENAMI, pelo apoio financeiro.

FLUORIDE REMOVAL FROM WATERS BY A POLYMERIC MEMBRANE CONTAINING ALIQUAT 336

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The presence of fluoride can be either beneficial or harmful for human health depending on its concentration in drinking water. At low concentration, fluoride is designed as an essential micronutrient which has a prominent role in the prevention of dental caries and facilitates the mineralization of hard tissues, while at higher levels, fluoride can have adverse impact on human health, causing dental or skeletal fluorosis. The standard level of fluoride in drinking water is 1.5 mg L^{-1} according to the WHO.

Extensive and widespread use of fluoride in different industries including aluminium refining, fertilizer and semiconductor manufacturing, glass and ceramic production has been found to be a reason for releasing large quantities of fluoride in the environment. Several technologies such as adsorption [1], precipitation-coagulation, electrodialysis, nano-filtration, reverse osmosis or Donnan dialysis [2] have been proposed for its removal.

In the present work we have prepared a polymer inclusion membrane based on cellulose triacetate (CTA) and Aliquat 336 as carrier to remove high levels of fluoride contained in waters. In a first stage, the effect of fluoride concentration has been investigated fixing as stripping phase a 0.1 M NaCl solution. It was observed that the transport from a 0.1 M fluoride solution was very slow. However, when dealing with 0.01 M fluoride as feed, the transport was possible, as it is shown in figure 1. However, as it can be observed, the transport stopped after a certain time, being not possible to completely remove all fluoride from the feed phase.

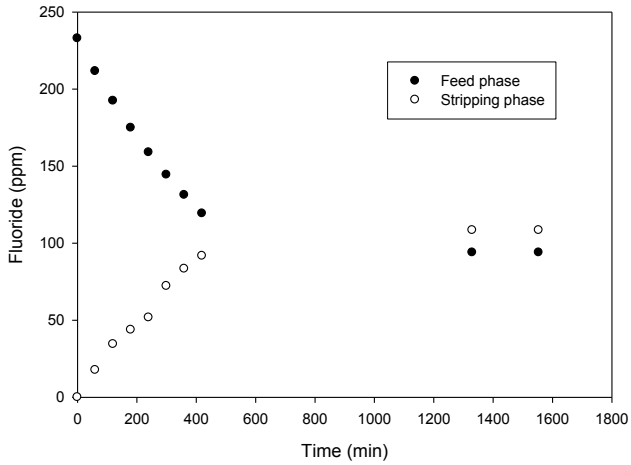

Fig. 1.Transient concentration curves in F^- transport experiments with a PIM consisting of 70% CTA and 30% Aliquat 336. Feed solution: 0.01 M fluoride (230 ppm) in milli-Q water; Stripping solution: 0.1 M NaCl.

In order to improve the membrane system efficiency different parameters are under study, such as the effect of NaCl concentration and the addition of a complexing agent such as aluminium in the receiving phase, as well as the PIM composition.

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ENATIOSELECTIVE SORPTION OF D-L TYROSINE IN CHITOSAN MEMBRANE

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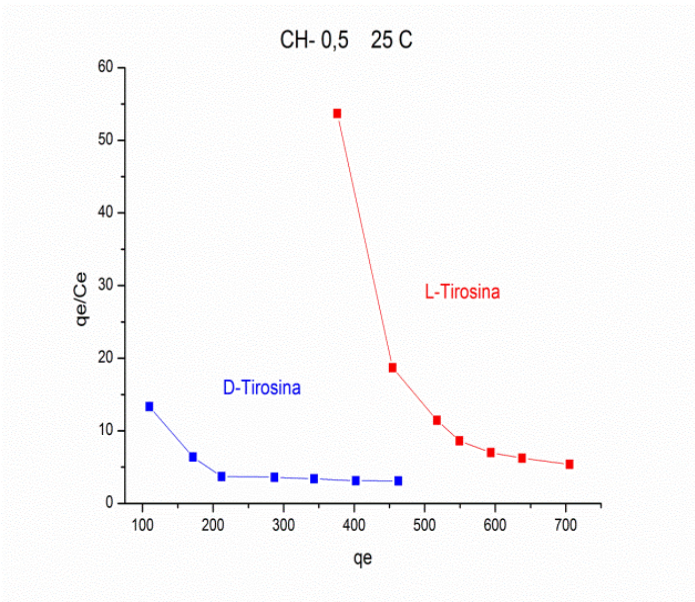
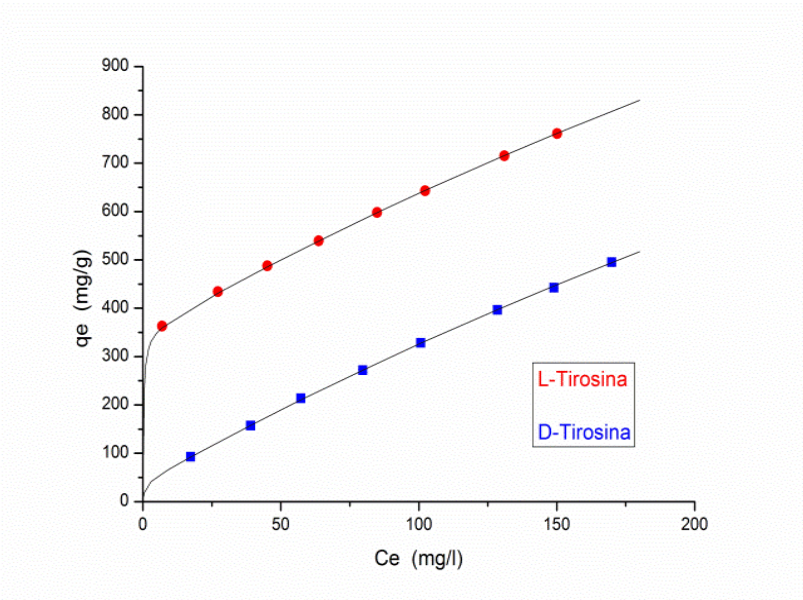
In this work a chitosan membrane (CH-0,5) was used for chiral separation by enantioselective sorption of Tyrosine (Tyr). The membrane was prepared from an acidic aqueous solution of 2% (p/p) of Chitosan containing 1% H_3PO_4 and then insolubilized by adding NaOH (0.5M). The study of D-L-Tyrosine in chitosan membrane was carried out using a racemic mixture of Tyrosine (0.25-2 mM) at 25° C and pH 5.6. Tyr sorption isotherms were determined by HPLC. Results from FITR measurements indicated that Tyr is present in chitosan matrix but no new covalent bond was formed.

As it shown in Figure 1A, Scatchard plots [1-2] indicated that the Tyr sorption is energetically heterogeneous for both enantiomers (D and L). Experimental data were fitted to bi-Langmuir model (Figure 1B) [3-5] and the resulting model parameters are shown in table 1.



(A)



(B)

Figure 1: (A) Scatchard Plots of *L*-Tyr (red) y *D* -Tyr (blue); *T* = 25 ºC. (B) *Bi-Langmuir Model (dot: experimental data, solid curve model fitting).*

Table 1: Parameters of Bi-Langmuir model fitting

D-Tirosina	q_s	k_s	q_{ns}	k_{ns}	R^2
M 0,5/25	39,73	1,5	2889	0,00115	0,9998
L- Tirosina	q_s	k_s	q_{ns}	k_{ns}	R^2
M 0,5/25	351	3,78	2887	0,001153	0,9997

It was found that Tyr sorption process is carried out by 2 kinds of sorption sites: selective and non selective. L-Tyr has 351 selective sites compared to 39.76 for D-Tyr. As it was expected, non selective sites were almost the same for both enantiomers. Selectivity = 46.7 of L-Tyr respect to D-Tyr was determined. More discussion will be presented in the full text.

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POLY(IONIC LIQUIDS):TAILORING THE POLYMER PROPERTIES FOR MEMBRANE APPLICATIONS

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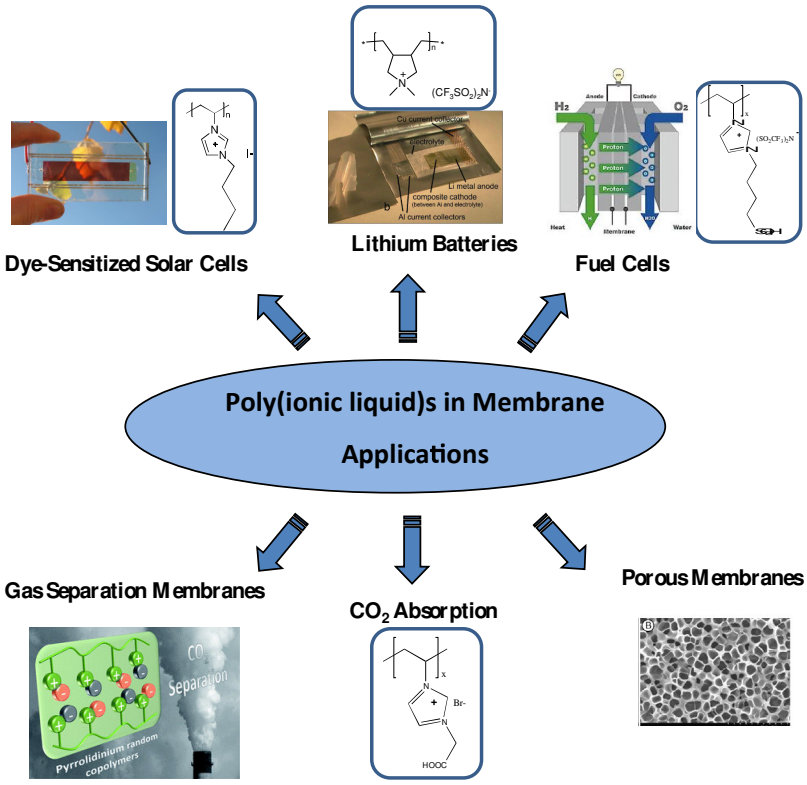
Poly(ionic liquid)s are a new type of materials which combine the properties of ionic liquids and polymers in a synergic way[1]. Poly(ionic liquid)s are finding new applications in classical fields such as energy[2], analytical chemistry, gas membranes[3], porous materials, or biotechnology. By using tools of a polymer chemist such as macromolecular engineering and ionic liquids chemistry, the materials properties can be easily tailored and adjusted to the specific applications. In this poster we will show some of our actual activities in the development of new poly(ionic liquid)s for membrane applications.



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Optimización del proceso continuo en cascada, para la recuperación de solvente a partir de mezclas aceite de soja/hexano usando módulos de membranas espiraladas

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Introducción En el proceso de producción de aceites vegetales, la primera etapa es la extracción del aceite a partir de la semilla. El solvente más utilizado es el hexano. La miscela obtenida tiene aproximadamente entre el 20-30 % de aceite. En el proceso convencional el hexano es eliminado por destilación y condensación. La tecnología de membranas brinda una alternativa atractiva frente al proceso convencional, presentando como ventajas: un menor consumo energético, reducción de efluentes, mejores condiciones de seguridad y equipamiento simple.
En este trabajo se propone optimizar un proceso continuo de recuperación de solvente en cascada usando módulos de membranas planas enrolladas en espiral, en donde las membranas empleadas en la construcción de los módulos son aquellas denominadas como PVDF-12SI, PVDF-10SI-1PC (preparadas en nuestro laboratorio) y SOLSEP 030306 (comercial).

Experimental La membrana asimétrica soporte (MA) de polifluoruro de divinilideno (PVDF), fue sintetizada utilizando el proceso de inversión de fases. La membrana compuesta (MC) fue preparada cubriendo la superficie de la MA con soluciones de goma siliconada (12% w/w siloc/hexano) y siloc-policarbonato (10%-1% w/w). Las experiencias de permeación se realizaron con una celda de extremo cerrado [1]. Las condiciones operacionales fueron: T: 30ºC, Δp=20 bar y velocidad de agitación de 500 rpm. La solución de alimentación fue preparada a partir de aceite crudo de soja y hexano (10-35 % p/p). El porcentaje de retención de aceite (R%) fue determinado analizando la concentración de aceite en el retenido (C_R) y permeado (Cp), mediante la aplicación de la siguiente ecuación: $\%R=(1-C_p/C_R)*100$ Dichas concentraciones fueron determinadas a través de un espectrofotómetro UV de absorción (Metrolab 330). Las corrientes de alimentación, permeado y retenido para cada etapa fueron determinadas mediante los balances de masa correspondientes.
En base a los resultados obtenidos de las experiencias de Permeación a escala laboratorio se diseñan dos procesos continuos en cascada con diferentes números de etapas basado en el proceso de diseño sugerido por Cheryan [2] como se muestra en la Figura 1 y 2. Para cada etapa se utilizan módulos de membranas espiraladas de PVDF-12 SI, PVDF-10SI-1PC ó SOLSEP 030306 espiraladas de área efectiva de 18 m^2.

Resultados y Discusión En la figura 1-a) se muestra el diagrama de flujo del modelo I del proceso en cascada de tres etapas para la recuperación de solvente. Luego de la extracción, la miscela aceite de soja/hexano de concentración C_A se alimenta a la primera etapa (TI) con un caudal de alimentación dado. De este modo se obtienen dos corrientes: el retenido (R_0), fase rica en aceite, y el permeado (P_0) fase rica en solvente. El P_0 se alimenta en la etapa TII, mientras que el R_0 se alimenta a la etapa TIII. La corriente de permeado de la etapa TII (P_1) es dirigida a la etapa de extracción de aceite; y la corriente de retenido del TIII (R_2) pasa a una etapa de evaporación, para una completa separación del aceite del hexano. Las corrientes R_1 y P_2 son recirculadas a la mezcla alimentada al proceso.
En la figura 2-b) se muestra el diagrama de flujo del modelo II del proceso en cascada de cuatro etapas para la recuperación de solvente. En este arreglo se parte del modelo I y se incorpora una cuarta etapa donde la corriente de retenido proveniente de la etapa III (R_2), es alimentada a

la etapa TIV, dando como resultado una corriente de permeado P_3, la cual es recirculada a la etapa TIII, y una corriente de retenido R_3 que es dirigida a una etapa final de evaporación.
En las figuras 1-b) y 1-a) se muestran la cantidad de módulos de membranas espiraladas necesarios en cada etapa. Se puede observar que las membranas sintetizadas en nuestro laboratorio poseen mejor performance que la membrana comercial.

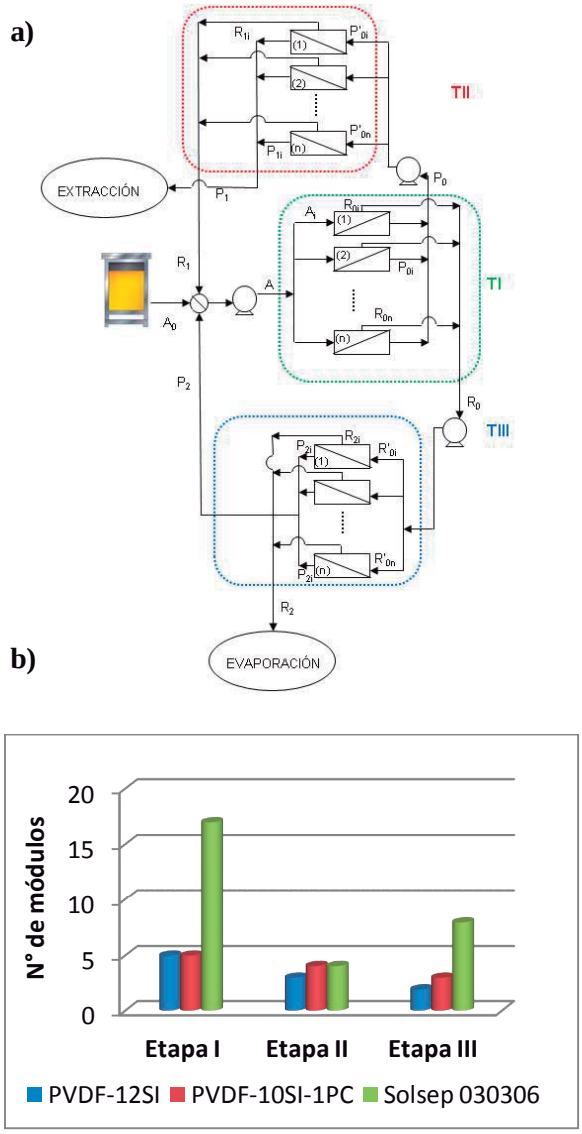

Figura 1. Modelo I a) Diagrama de flujo, b) Necesidad de módulos en función de las etapas planteadas

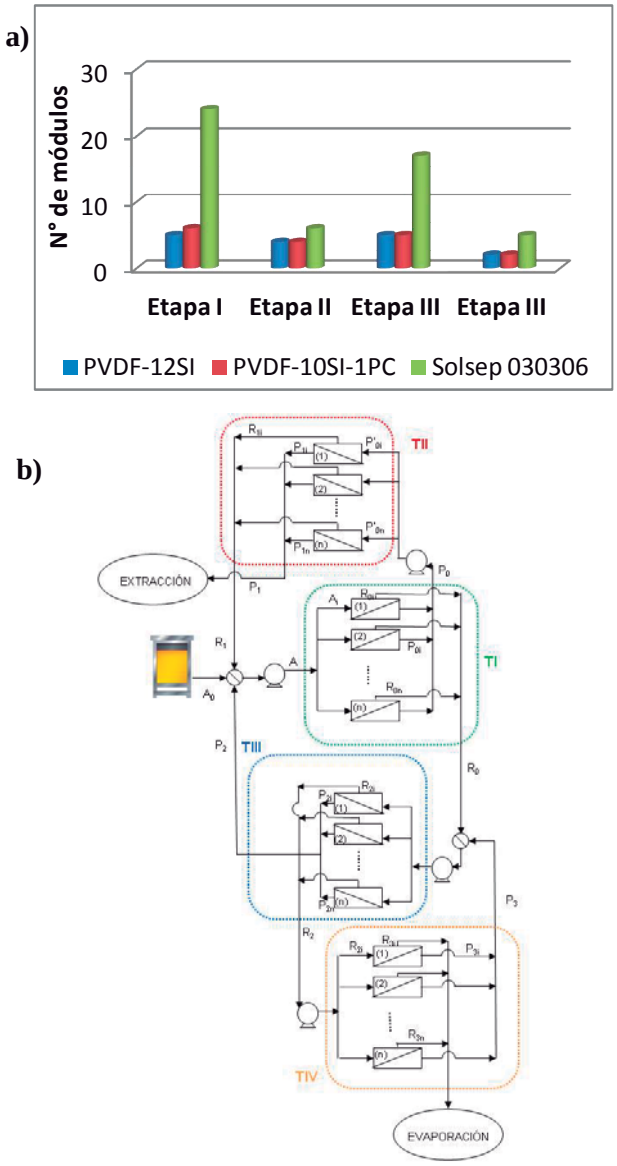

Figura 2. Modelo II a) Necesidad de módulos en función de las etapas planteadas, b)Diagrama de flujo

Estos sistemas híbridos de membranas/destilación, producen un importante ahorro energético frente al proceso convencional de recuperación.

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Ultrafiltration of oil/water emulsion with PVDF/Cation exchange resin membranes

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1- Objective

In this work, the preparation of PVDF charged membranes by adding resins to a polymeric solution is proposed. The effect of resin concentration on both the membrane structure and functional behavior has been analyzed. To evaluate their fouling behavior and performance, synthesized membranes were applied in oily emulsion treatment.

2. Experimental

Preparation and characterization of charged membranes: 20%w/w of Poly-vinylidene fluoride (PVDF) and 5%w/w of Polyvinylpyrrolidone (PVP) K30 are dissolved in 75% w/w of *N*,*N*-dimethyl-acetamide (DMAc), after that the ionic exchange resin is added to the solution. The mixture was cast onto the non-woven support using a film extensor. The solution was coagulated with bidistilled water at 25°C. Table 1 shows the membrane CER compositions.
Structural and functional membrane characteristics were determined by SEM images, tangential flow streaming potential measurements (SP), liquid-liquid displacement porosimetry (LLDP), charge density measurements (σ_0), and oil emulsion filtration experiments. Oil emulsion was obtained adding 0.1% Insignia® oil to distillated water at 500 rpm. The oil droplet average size was 2.5 µm. Chemical oxygen demand (COD) and oil content (OC) was measured by UV-Visible technique and oil content was evaluated by UV-vis spectroscopy.
To determine the reversible and irreversible membrane fouling, after oily emulsion filtration experiments, the membranes were mechanical cleaned with pure water for 1 hour at 67 KPa. Finally, the flow of pure water was measured and the reversible-irreversible resistances evaluated.

3. Results

Fig. 1 shows SEM images of PVDF-C20 membrane. There is a noticeable variation in the membrane structure from a finger-like morphology for a non-resin membrane (PVDF) to a more densified structure on the top layer for PVDFC20 membrane. Resin particles create zones of discontinuity in the polymeric solution, macrovoid spaces between resin particles, indicating a low adhesion between resin-polymer phases.

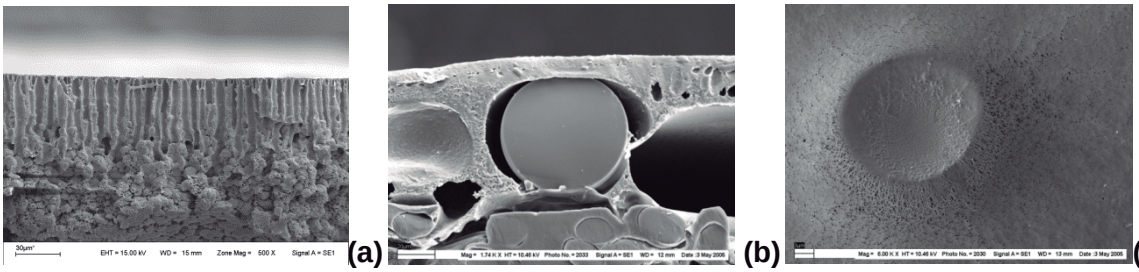

Fig.1-SEM images: a) PVDF cross section; b) PVDFC20 cross section, c) PVDFC20 surface.

Figure 2 illustrates the normalized flow decline of the oily effluent with prepared membranes. There is a more marked flux decline in the membrane with smaller amount of resin, indicating a higher fouling.

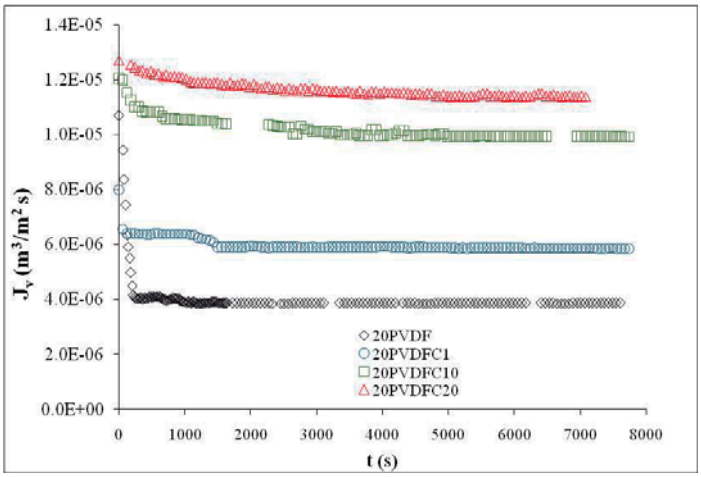

Figure 2- Flux decline with operational time

Table 1 resume the membrane characterization results: mean pore size (r_p), σ_0, initial permeate flux (J_{v0}), COD, oil rejection (OC%), water permeate flux (J_{v0}), intrinsic membrane resistance (R_M), membrane resistance of both reversible fouling (R_{Rev}) and irreversible fouling (R_{Irrev}), where the total membrane resistance is given by ($R_T = R_M + R_{Rev} + R_{Irrev}$).

Table 1 – Structural and functional properties of prepared membranes

Membrane	Relation (wt.) CER:PVDF	r_p(nm)	σ_0 (C/g) (pH=7)	OC%	COD ppmO_2	$J_{v0}10^5$ (m/s)	R_M $10^{-12}m^{-1}$	R_{Rev} $10^{-12}m^{-1}$	R_{Irrev} $10^{-12}m^{-1}$
PVDF	0:100	3.81	-10.0	95.15	98.32	1.07	6.26	2.67	7.43
PVDFC1	1:99	2.30	-13.0	97.86	86.12	0.80	8.36	1.07	1.42
PVDFC10	10:90	2.61	-15.0	98.03	74.96	1.20	5.58	0.61	0.19
PVDFC20	20:80	2.73	-18.0	98.62	71.75	1.27	5.28	0.25	0.03

4. Conclusions

PVDF membranes with different contents of ion exchange resins were prepared. The presence of resins created membranes with lower mean pore sizes due to the densification of top porous layer structure. The content of negative charges increases (at pH=7) with the increasing amount of resin, as a result of high surface conductivity. An increasing electrostatic repulsion due to the increase of resin content resulted in a permeate solution with lower both COD values and oil concentration. The ultrafiltration experiments showed a decrease on the total membrane resistance with the increasing amount of resin. The PVDFC20 membrane showed the best oily emulsion treatment performance; higher permeate flux (lower total membrane resistance), 98.6% of oil rejection and 71.75 ppm of chemical oxygen demand. There was practically not irreversible fouling, thus the membrane can be cleaned by washing with pure water.

Water electrolysis with Zirfon® as separator and NaOH as electrolyte

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Organic materials such as polymers could provide a good alternative to be used as separators in alkaline water electrolysis. For this process, the polysulfone family has good potential due to its excellent thermal, oxidative and hydrolytic stability, although hydrophobicity could be a relevant obstacle in a process where oxygen and hydrogen are obtained. In this research work a member of the polysulfone family, Zirfon® was studied. This material consists of a polysulfone matrix and zirconium oxide, in the form of powder. [1] The presence of zirconium oxide improves the wettability of the material, an important issue if the process includes the evolution of gaseous products as in water electrolysis. Zirfon® was tested in a crystal acrylic electrolytic cell with rectified blocks, which established the different distances between electrodes. The material selected for the cathode and the anode was stainless steel 316L- In this experience, 20% w/w NaOH was used as electrolytic solution at room temperature. The experiment was carried out applying a range of differential potential to the electrolytic cell. Six different distances between electrodes were studied: 7.5- 6.5- 5.6- 4.45- 4.25 and 3.10 mm. The control parameters were current, voltage and temperature. These parameters allowed us to calculate further parameters such as decomposition voltage, resistance and conductivity of the electrolytic solution. Resorting to this data set, it was possible to select the distance between electrodes where the best performance of the system is obtained.

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Acknowledgements

Authors want to thank the Defence Ministry for subsidizing this work through PIDDEF 21/11 and 22/11.

Facilitated Transport Membranes

- **Oral session 2**

SEPARATION AND PRE-CONCENTRATION OF LOW URANIUM (VI) CONTENT IN WATER USING BULK LIQUID AND SUPPORTED LIQUID MEMBRANE SYSTEMS CONTAINING BIS(2-ETHYLHEXYL) PHOSPHORIC ACID AS CARRIER

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The use of different separation techniques, and also pre-concentration systems, for uranyl ion are often employed prior to the determination step, i.e. solvent extraction [1,2] and ion exchange [2,3] are popular methods due to their easy applicability and also because they can perform separations and pre-concentrations in the same step [3]. Other separation processes such as membrane systems have been used for several years for the recovery and pre-concentration of uranyl ion. However, in most of these studies relatively high concentrations of Uranium (VI) are used, in the range between 20 mg/L and 1000 mg/L [2-9]. In this study the concentration of Uranium (VI) is around 0.100 mg/L and describes its recovery from nitric acid solutions by using Bulk Liquid Membrane (BLM) and Supported Liquid Membrane (SLM) systems. This work describes the transport of Uranium (VI) through both membrane systems using low concentration of bis(2-ethyl hexyl) phosphoric acid (D2HEPA) as carrier in kerosene solvent, which favors the removal of Uranium (VI) traces, with two different chemical systems called System 1 (S1) and System 2 (S2). The stripping used was a mixture of phosphoric acid and citric acid, which improves the removal of the Uranium (VI), and at different concentration levels for each chemical system [10]. In the case of SLM, the polymeric supports used were homemade Polysulfone membranes (PSf) and commercial Polyvinylidene Fluoride membranes (PVDF) from Millipore. The kinetics of the uranyl ion transport system was studied for up to 24 hours under fixed physical and chemical conditions. Maximum extraction values obtained were above 95% in all cases (with BLM and SLM), and recovery yields were in the range 57-79% for the BLM and 90% for the SLM.

The BLM and SLM systems are successful for the pre-concentration of trace uranyl ion, which leads to an improvement in the quantification of trace metals. Comparing both systems, SLM systems can be applied to real water samples with low concentration levels of uranyl ion for its suitable quantification, and with low consumption of reagents. Pre-concentration in both kinds of membrane systems are properly demonstrated in this study as show in Fig.1. [11].

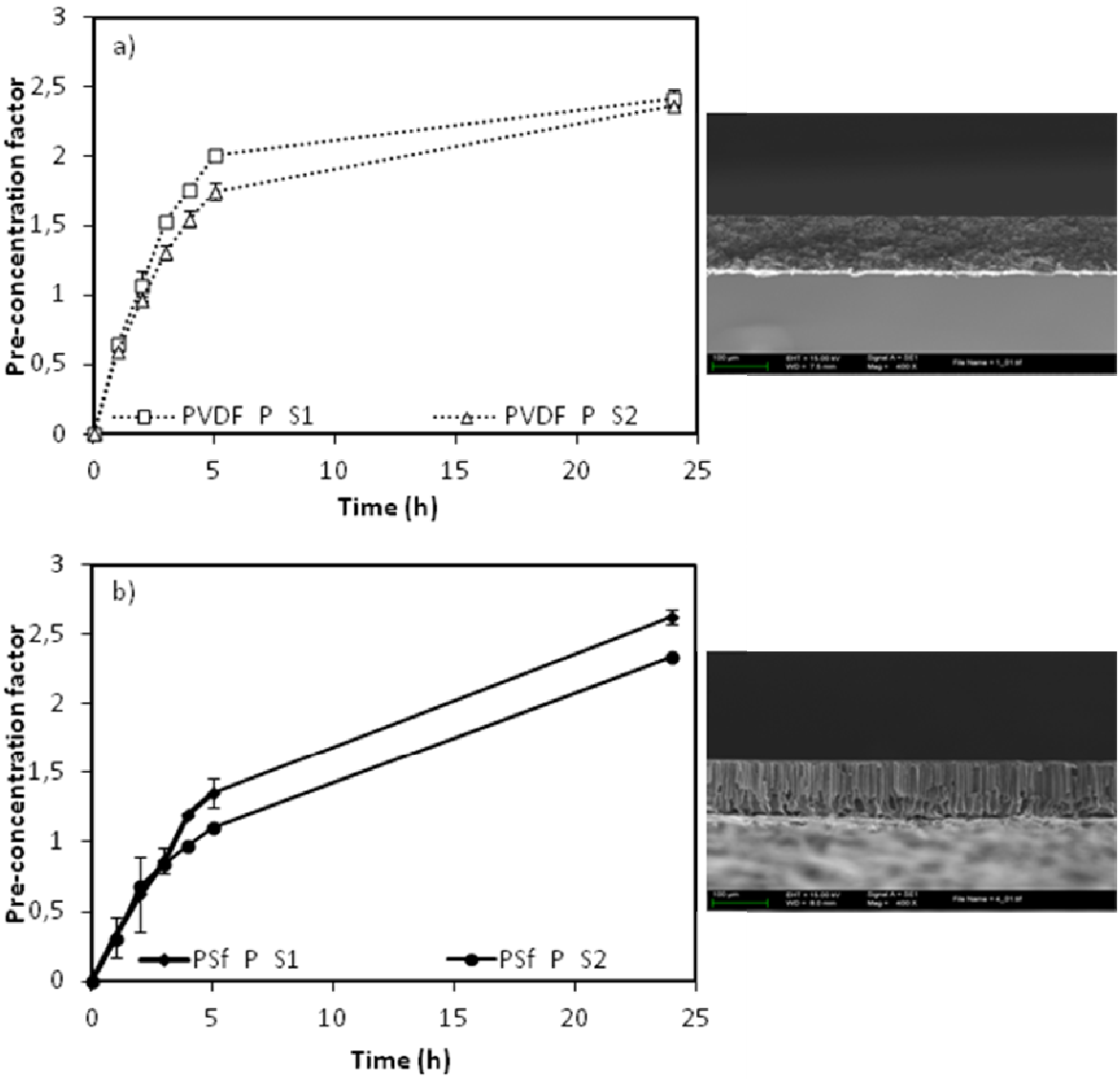

Fig. 1. Pre-concentration factor vs. Time (h) for both different chemical systems (S1 and S2) using Supported Liquid Membranes, with both membrane supports under study: a) PVDF and b) PSf.

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A NOVEL LIQUID MEMBRANE PROCESS USING A TAYLOR FLOW REGIME

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Separation processes using liquid membranes are advanced techniques for recovery, purification and abatement of substances in liquid or gas streams that has been extensively studied and that has been integrated to other separation or reactive processes [1]. Two kind of liquid membrane processes are attractive for industrial applications. The emulsion liquid membranes have received more attention than the supported liquid membranes, because in the former the mass transfer rate is higher and there is a better control on the liquid membrane losses. However, the emulsion in the liquid membrane can be easily broken, reducing the separation efficiency or, on the contrary the emulsion is very stable and consequently inhibits the phase splitting between the feed and strip phases [1]. Usually, in order to improve the emulsion stability, surfactants are used, hindering the phase separation and recovery. Also, surfactants pollute the feed or strip phases and they can reduce the mass transfer rate [2].

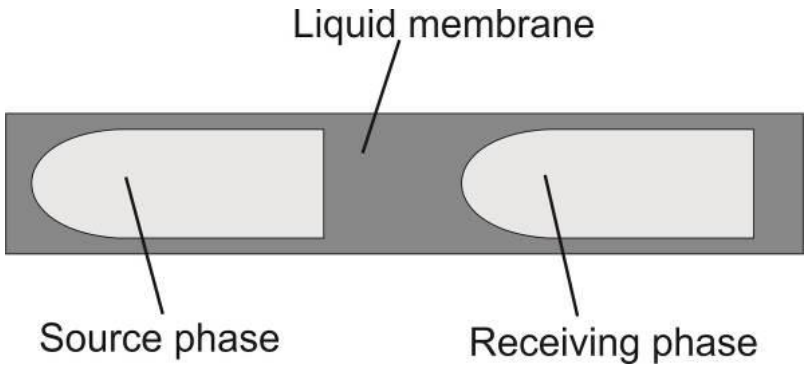

Figure 1. Diagram of a liquid membrane in the Taylor flow regime.

This work proposes a novel type of contact for liquid membranes by using the Taylor flow regime. Thereby, the feed and strip phases are located in the same tube in drops or Taylor "bubbles". The continues phase, that forms liquid slugs, constitutes the liquid membrane itself (Figure 1). The mass transfer start at the feed phase, continues through the liquid membrane and finishes at the strip phase. This work experimentally studies the removal level of lactic acid using the liquid membranes in the Taylor flow regime for removal of lactic acid at several flow rates of the source and receiving phases (1-3 mL/min) and analyses the effects that the drop length has on recovery. Lactic acid concentraciones between 50 g/L and 150 g/L were used in the aqueous solutions. The facilitated liquid membrane contains 0.8 mol/L of Trioctylamine (TOA) in Dodecanol.

The low layer thickness around the drops, the high liquid speed in this layer and the turbulence at the drop tail (von Kárman vortices) produce high mass transfer rates. This type of liquid membrane avoids the contact between the feed and strip phases and the use of surfactants overcoming the coalescence and improving the phase splitting. This kind of liquid

membrane preserves the advantages of conventional emulsion liquid membranes while overcomes the stability problems of emulsion systems.

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Acknowledgements

The finantial support of National University of Colombia under Code 19057 and COLCIENCIAS under project "Evaluación experimental de un reactor híbrido de fermentación para Bacterias Ácido Lácticas probióticas usando perstracción para la remoción simultánea del ácido láctico generado" are kindly acknowledged.

Modulation of the transport of organic solutes through supported ionic liquid membranes by an external magnetic field

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A new generation of ionic liquids, magnetic ionic liquids (MILs), has gained a growing interest due to their response to an external magnetic field [1]. The ability of these ionic liquids to switch reversibly their physicochemical properties and structural organization of their ionic network by changing the conditions of the applied magnetic field is particularly promising regarding the design of novel membrane based separation processes – e.g. magnetic responsive supported liquid membranes.

These membranes are expected to allow for an adjustable permeability and/or selectivity, contributing consequently for an improved transport of solutes through a fine tuning of the magnetic field conditions. In a recent work it was shown that it is possible to modulate the permeablity of CO_2, N_2 and air through supported magnetic ionic liquid membranes (SMILMs) by adjustment of the magnetic field conditions. It was observed that the permeability of these gases through these membranes increases in the presence of a magnetic field of 1.5 T, without changing membrane selectivity [2].

In the present work the membrane transport studies were performed to assess the influence of magnetic field on the transport of ibuprophen, in a enantiomeric mixture, within feed and stripping organic phases, through a SMILM prepared by immobilization of a quiral MIL, $C_{11}H_{21}BrCl_3GdN_2O$, into a microporous PVDF support.

Transport studies were conducted in the absence and presence of magnetic field with an intensity of 1.2 T. The results obtained showed an improvement of the ibuprofen permeation in the presence of an external magnetic stimulus with an increase of the diffusion coefficient in ~30 % as indicated below and shown in Fig.1.

$D_{eff\ (magnetic)} = 1.62 \times 10^{-7}\ cm^2/s$ and $D_{eff\ (non\ magnetic)} = 1.11 \times 10^{-7}\ cm^2/s$

The differences in the diffusion coefficient, Deff, induced by the magnetic field are in aggreement with the decrease of MILs viscosity with the magnetic field [3]. However, it was concluded that it cannot be only interpreted based on the magnetic dependence of MILs viscosity, but also it may rely on changes of molecular dynamics and the reorganization of MILs ionic network induced by the magnetic field[3]. The results obtained revealed that it is possible to modulate, in a non-invasive way, the transport of ibuprophen through SMILMs by suitable adjustment of the magnetic field conditions.

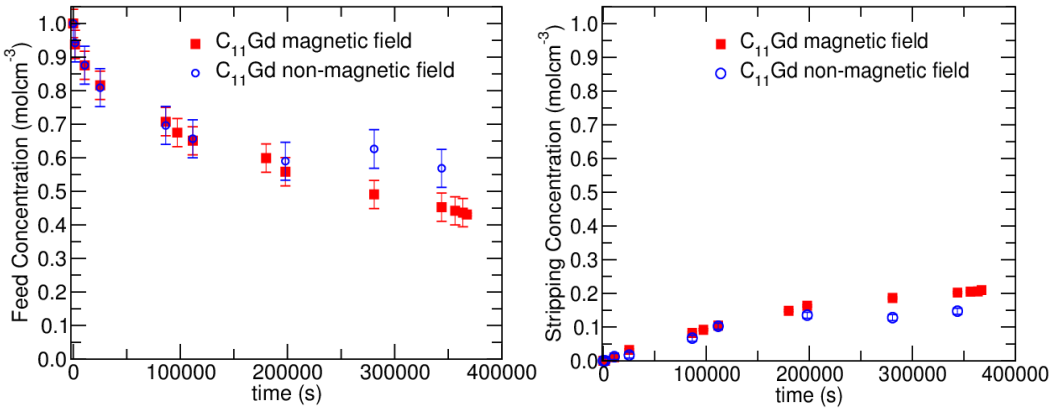

Fig.1. Profile of the normalized ibuprofen concentrations along the time in the organic feed and stripping phases

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Acknowledgments

The authors gratefully acknowledge the financial support from the European Research Action Network-ERANET, ERA-CHEM/0001/2008 Project (Portugal) and Project EUI 2008- 03857 (Spain). Carla Daniel also acknowledges the financial support of FCT-MCTES through the PhD grant SFRH/BD/81552/2011.

IMPROVING PERFORMANCE OF PERVAPORATION MEMBRANES FOR BIOBUTANOL SEPARATION

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Due to the increasing demand for energy, concerns about the limited supply of fossil fuels and the need to reduce global greenhouse gas emissions, biofuels are an attractive alternative to conventional fuels. Biobutanol has increased in popularity as it offers a range of advantages when compared with bioethanol: it has higher energy content, lower vapor pressure, it is less hygroscopic and easily miscible with gasoline. Being compatible with existing engines and refueling infrastructure, it is a perfect candidate to replace gasoline [1].

Biochemical process of biobutanol production involves ABE fermentation of biomass and subsequent separation and purification of n-butanol. The efficiency of the process is low due to the low concentration of butanol in the fermentation broth (approx. 2 wt. %) and the presence of other solvents such as acetone, ethanol and water. Purification and separation processes such as gas stripping, vacuum flash, liquid-liquid extraction, extractive fermentation, perstraction and membrane pervaporation [2] need to be intensified to improve the economics of biobutanol production.

Pervaporation (PV) is a novel membrane technique for liquid/liquid separation that is extensively studied to be used for butanol recovery from fermentation broth [3]. The advantage of transportation through PV membranes is that it follows the dissolution and diffusion mechanism instead of the vapor-liquid equilibrium as is the case in distillation. Pervaporation membrane performance can be defined by two parameters: permeation flux (J_i) and separation factor (α_i).

The aims of the present paper are to evaluate the performance of pervaporation membranes and select the best production technology. Studies on butanol concentration by pervaporation on a PERVAP 4060 commercial membrane and novel membranes with ionic liquids (ILs) are described. Model feed was an aqueous solution of three organic components: acetone (A), butanol (B) and ethanol (E) at 3:6:1 weight ratio. Butanol concentration in the feed ranged from 0.25 to 3 wt. %. The process was carried out under steady-state continuous flow conditions, and the pressure on the permeate side was 3 kPa. The experiments were carried out for 20, 40 and 60 dm^3/h feed flow rate at 50, 60 and 70°C.

Three types of hydrophobic membranes are used for PV, namely polymeric, inorganic and composite membranes. Membranes made from PDMS (polydimethylsiloxane) are most commonly used in n-butanol separation experiments [4]. Other types of polymeric membranes for butanol separation include PEBA (polyether block amide), PTFE (polytetrafluoroethylene), PP (polypropylene) and PTMSP (poly(1-trimethylsilyl-1-propyne)). Table 1 lists selected performance data for pure PDMS membrane of 200 μm in thickness and for PERVAP 4060 commercial composite membrane whose PDMS active layer is 2 μm.

Thin and relatively fragile polymeric membranes have high flux rates but low butanol selectivity, while thick membranes are structurally strong, have high selectivity values but operate at lower permeate flux rates. In brief, a high-performance polymeric membrane can be designed by reducing thickness and increasing selectivity at the same time, e.g. by incorporation of butanol-selective fillers.

Table 1. Permeate flux and separation factors (α) of feed components: A-acetone, B-butanol, E-ethanol for membranes studies in PV process (3 wt. % B, 50°C, 40 dm^3/h, 3 kPa)

Item	membrane	α_A	α_B	α_E	J_{tot}
		[-]	[-]	[-]	[kg/(m^{2}h)]
1	PDMS (200μm)	16.55	23.98	2.98	0.055
2	PERVAP 4060	5.27	6.55	3.47	1.295

Room-temperature ionic liquids (RILs), which are widely promoted as novel “green” solvents, can be used as fillers. Ionic liquids can be chemically designed to have high ability to extract butanol [5]. At the next stage, a supported ionic liquid membrane (SILM) with specific ionic liquids can be designed and used for pervaporative separation of biobutanol [6].

Several methods of ionic liquid immobilization in pervaporation membranes have been reported in literature. ILs may be incorporated by immobilization in pores, inclusion by additive coating, inclusion in polymer matrix, gelation of ILs, covalent binding of ILs or ion exchange [7]. In the present study pervaporation membranes with ionic liquids were created by mixing with PDMS and hardening by polycondensation. Hydrophobic ionic liquids used were 1-butyl-3methylimidazolium bis (trifluoromethylsulfonyl) imide and 1-hexyl-3-methylimidazilium hexafluorophosphate which can selectively separate butanol. The observed fluxes were relatively low due to additional resistance caused by the layer thickness. IL elution from the membrane structure, also reported elsewhere [8], was another problem. It would thus be advantageous to create an additional layer that would enclose the ionic liquid in the membrane and to reduce membrane thickness at the same time.

Several challenges must be addressed when designing membranes using ionic liquids. The most important problems include membrane thickness which decreases permeate flux, IL elution from the pores which affects membrane’s strength, minimum chemical modification of the filler’s structure due to the fact that IL’s properties may change after incorporation into the polymeric matrix. Improvement of the membrane structural strength is another problem. The obvious advantage is high butanol separation factor [9].

It must be borne in mind that efficiency of pervaporative removal of biobutanol is dependent both on factors related with the membrane and process operating conditions. The former group of factors includes thickness of the active layer, structure and size of membrane pores, adsorption capacity of fillers and modifications of membrane surface. Operating conditions which affect efficient energy use for the PV process are temperature and feed concentration as well as pressure on the permeate side. Comparison studies have shown that pervaporation is more energy efficient than other biobutanol separation processes, which encourages continuous improvement of pervaporation membrane design.

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Acknowledgements

The paper was financed from the Polish National Science Centre funds granted based on decision no. DEC-2012/07/B/ST8/03379.

ARSENIC DETECTION AND REMOVAL FROM NATURAL WATERS BASED ON A POLYMER INCLUSION MEMBRANE SYSTEM

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Arsenic is an element that occurs naturally in the earth's crust. It generally exists in low concentrations in many rock types and due to natural geochemical processes it can be found in groundwater. Nowadays, the main concern about As is its long exposure, because even low concentrations of arsenic, when ingested over a period of years, can result in a range of serious health problems taking into account that inorganic arsenic is a human carcinogen. Globally, over 130 million people are now estimated to be potentially exposed to arsenic in drinking water at concentrations above the World Health Organization (WHO) guideline value of 10 µg L^{-1}.

To perform in-situ arsenic screening, several kits are commercially available and they are normally based on Gutzeit method. They consist on the transformation of the whole arsenic present in the water sample to arsine gas which in turns reacts with the mercury bromide impregnated in a paper strip. The main drawbacks of this method are the formation of the toxic arsine and the use of mercury, which is very toxic as well.

Several technologies are available to remove As from waters, which include membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. However, the high operation and capital cost next to the high consumption of electrical energy limits its application. A possible alternative is the use of functionalized membranes in which the separation process is based on chemical pumping instead of physical rejection.

In this work we have developed a polymer inclusion membrane (PIM) system for the detection of As contained in waters. Moreover, the same system has shown to be a promising alternative to other removal technologies applied for this pollutant. PIMs are a type of functionalized membranes that can be tailor-made depending on the characteristics of the analyte to be transported. Normally PIMs consist of a polymer which provides mechanical strength, the carrier, which is the responsible of the extraction process, and sometimes also a plasticizer can be used to provide elasticity.

In the case of the detection method, we present a green and novel detection method for As screening in groundwater. The formation of a colored complex is the basis of the detection, but there is a previous preconcentration step involving a PIM made of poly(vinyl chloride) as polymer and Aliquat 336 as carrier [1]. Parameters affecting the system have been evaluated and the methodology has been validated. The proposed preconcentration method has been applied to standards containing As(V) in the range 20 to 120 µg L^{-1} in Milli-Q water with the molybdenum blue method used for measuring the concentration of As(V) in the stripping solution. Fig.1 shows the calibration curves obtained for the analysis of the As(V) standards with and without preconcentration using the PIM-device. From the slope of each calibration curve it can be stated that the sensitivity of the method using the PIM-based device is 17 times higher than that of the direct analysis.
The proposed method has been used to analyze natural waters from the Pyrenees region containing arsenic and the results obtained were in a good agreement with those obtained with ICP-MS.

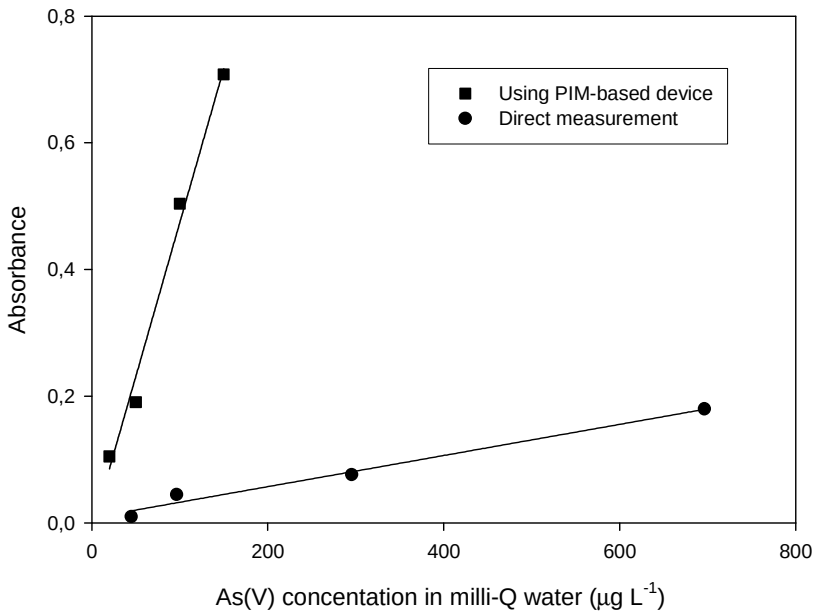

Fig. 1. Calibration curves obtained with and without the PIM preconcentration step. PIM: 69 PVC-31% Aliquat 336 (w/w). Feed solution: 100 mL of different As(V) concentrations in milli-Q water at pH=7; Stripping solution: 5 mL 0.1 M NaCl.

Moreover, the same membrane implemented in a spiral cell that allowed the continous flux of polluted water on one side, and 2 M NaCl solution in the other side, has successfully been used to remove As at µg L^{-1} levels from natural groundwater, showing its potential as a promising technology to be take into account.

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Facilitated Transport Membranes

- **Poster session 1**

IONIC LIQUID-BASED MEMBRANES FOR SYNGAS RECOVERY FROM FLUE GASES

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Some industrial processes perform a partial combustion of hydrocarbons in reductive conditions that generates a flue gas stream with high content of carbon monoxide and hydrogen, which are generally accompanied by nitrogen. In this work, the selective recovery of these valuable compounds, H_2 and CO, is sought as a means to reduce the environmental footprint of the industrial activity. To that end, we propose the combined use of ionic liquids and membrane technology. Room-temperature ionic liquids (RTILs) are liquid salts at ambient temperature entirely composed of highly asymmetric organic cations and organic or inorganic anions that can be combined to fine-tune the chemical and physical properties of these liquids regarding their use in a specific application. The fascinating and unique properties of RTILs, e.g. extremely low volatility, high thermal and chemical stability, non-flammability and excellent solvent properties, have attracted much attention towards these liquids as promising replacements for conventional organic molecular solvents in several fields, including gas separations [1].

In this work, we provide knowlegde on the transport properties of H_2, N_2 and CO through supported ionic liquid membranes (SILMs) prepared with an imidazolium chlorocuprate(I) ionic liquid. The permeability of H_2 employing these SILMs is faster than that of the other compounds due to its higher diffusivity, given the very small size of this molecule, therefore a H_2/N_2 selectivity of 11 was achieved [2]. In contrast, the CO/N_2 separation is very challenging owing to the similar properties of both compounds, namely, almost identical boiling point and size. Given that, a polymeric membrane capable to perform this separation is not available. For this purpose, we proposed the use of the reactive chlorocuprate(I) ionic liquid that improves the CO solubility over that of N_2, while providing a non-volatile medium to perform the separation and studied the thermodynamics and kinetics of this reactive system [3, 4]. The SILMs prepared with this RTIL provided an enhanced CO permeance flux due to a carrier-mediated trasnport that is complementary to the ordinary solution-diffusion transport mechanism through membranes. The reason of this additional trasnport mechanism is the selective and reversible formation of a CO-copper(I) complex that diffuses through the membrane until the permeate side where the reverse reaction occurs releasing the CO molecules. In this way, the use of the reactive SILMs prepared with the chlorocuprate(I)-based ionic liquid allows obtaining in one step a gas permeate stream with high content of both H_2 and CO, and low content of N_2.

Further work under study, is the development of composite membranes prepared with the same ionic liquid and either a polymer or a polymerized ionic liquid, in such a way that the RTIL is trapped within the polymeric chains during the casting process of the membranes. These type of membranes will enhanced the long-term stability of the membrane, thus overcomming one of the main concerns related to the use of liquid membranes.

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Acknowledgements

Funding to project ENE 2010-15585 from the Spanish Ministry of Economy and Competitiveness (MINECO) is gratefully acknowledged. Gabriel Zarca also thanks the MINECO for the FPI postgraduate research grant (BES-2011-046279).

Passive Sampling of Zn(II) using a Hollow Fiber Supported Liquid Membrane device

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Heavy metals enter aquatic systems by natural and anthropogenic sources; however, the anthropogenic inputs of some trace metals recently surpass the natural inputs affecting the organisms adversely due to their toxicity at relatively low levels.There are several forms in which these species can be dissolved in waters such as ionic, complex-ion, and organically bound states [1]. Different labile species of the metals may be taken up by aquatic organisms [2] and for that reason the measurement of labile heavy metal ions represents a matter of concern for resource managers and regulatory agencies.

In natural surface waters, the concentration of zinc is usually below 10 µg/L, and in groundwaters, 10–40 µg/L [3]. In tapwater, the zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings [4]. Zinc is most toxic to microscopic organism in the aquatic environment. Soluble species of zic are readily avalilable for biological reactions and, therefore, considered as most toxic. It has been shown that zinc in water is a better predictor of fish tissue contamination than zinc in either sediments or invertebrates [5].

Several techniques that rely on collecting discrete grab, spot, or bottle samples of water at a given time have been used during the past years for the measurement of heavy metals in aquatic ecosystems. However, to avoid the collection of large volumes of samples which analyses give only brief snapshots of the integrated dose of chemicals at the time of sampling, passive sampling techniques for monitoring organic and inorganic pollutants in water have been developed. [6, 7], among them some using hollow fiber supported liquid membranes (HFSLM) [8-10].

In the present work Zn(II) transport through an HFSLM device is studied employing the carrier Kelex 100 (7-(4-ethyl-1-methylocty)-8 hydroxyquinoline). The influence of different variables that affect the transport properties of the sampling module including some environmental factors are evaluated to contribute in the understanding of the methodological approach for speciation analysis and analytical determination of zinc(II) with such passive sampling modules.

The HFSLM module was assambled according to the procedure reported in reference 10 using as initial experimental conditions: donor phase: 100 mL 1×10^{-5} mol L^{-1} Zn(II) at pH 6.6 adjusted with 0.01 mol L^{-1} MES; acceptor phase: 6 µL 0.01 mol L^{-1} HCOOH at pH 2.2; membrane phase: 0.03 mol L^{-1} Kelex 100 in n-hexyl-benzene; agitation provided by orbital shaking. The time-depending profile of the preconcentration factor, E, defined as E = [Zn(II)]acceptor/[Zn(II)]initial donor, was measured. It was observed that after 4 h a constant value was obtained and further experiments were performed using this pertraction time.

The effect of pH of the donor solution on E was evaluated within the range 5.5-8.0. A plateau maximun value (E≈ 1200) was obtained above pH≈7.5. As for the effect of metal ion amount on E, a proportional relationship was observed (Figure 1), denoting the potentiality of the system for responding to the concentration of the analyte. As for the initial volume of the donor phase no variations in E were observed in the interval 100 – 1000 mL. This result is consistent with the operation of the module in negligible depletion conditions. Concerning the influence of the initial pH of the acceptor solution it was observed a strong dependence: at pH=1.0 the pertraction profile over time changes significatively in comparison to pH = 2.2. A constant value of E was attained at t > 20 h. In addition it was observed that the depletion

regimen changed from negligible to significative depletion (≈27%). The influence of interfering ions on E was evaluated with six different ions (Co (II), Cu (II), Ni (II), Cr (IV), Pb (II) and Cd (II)) at equal concentrations. Cu (II) and Pb (II) were those metals which caused an interference on Zn(II) transport.

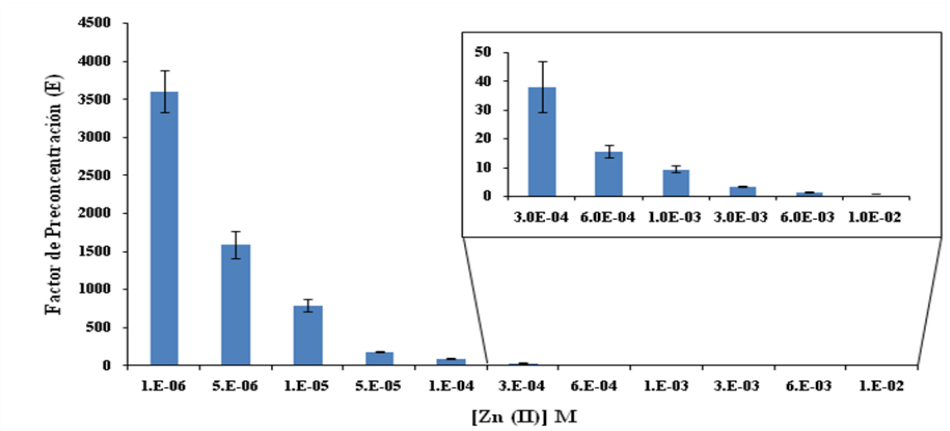

Figure 1. Effect of Zn(II) concentration in the donor solution on the the preconcentration factor, E.

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Acknowledgements

Support provided by CONACYT project 2011CB 167148 is highly appreciated. E.A.R.M. expresses his gratitude to CONACYT for the Ph.D. scholarship.

SUPPORTED IONIC LIQUID MEMBRANES FOR THE SELECTIVE SEPARATION OF METAL IONS

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Supported ionic liquid membranes (SILMs) have received growing attention during recent decades. The use of ionic liquids as liquid phase result in a stabilization of the liquid membrane and the possibility of designing membranes for different application by changing the ionic liquids compositions. Indeed, SLMs based on ILs have been applied to the selective transport of organic compounds such as amines, alcohols, organic acids, ketones, ethers, and aromatic hydrocarbons mixed gases and metal ions [1,2].

Previously, we reported the use of imidazolium and ammonium based ionic liquids in the absence of chelating agents for the selective liquid-liquid extraction of Zn(II), Cd(II), Cu(II), and Fe(III) from hydrochloride aqueous solutions [3]. It was found that the ionic liquid methyltrioctylammonium chloride, $[MTOA^+][Cl^-]$, allowed the almost complete removal of Zn(II), Cd(II), Fe(III) and Cu(III) from the aqueous solutions. In this work, supported ionic liquid membranes based on methyltrioctylammonium chloride were used in an extraction-stripping process for the selective extraction of Fe(III), Zn(II), Cd(II) and Cu(III). The influence of the composition of the receiving phase (milli-Q water or Na_2CO_3, 0.1M; or NH_3, 6M) in the extraction-stripping process was analysed. It was found that Milli-Q water and Na_2CO_3 allowed the recovery of Zn(II), Fe(III), reaching extraction factors (*EF*), defined as the ratio between the concentration of the target metal ion in the receiving and the feed phase, of up to 373 for Zn(II), using Na_2CO_3 as receiving phase at 48h and 9 for Fe(III), using Milli-Q water at 31h. The use of NH_3 (6M) allowed the recovery of Cd(II), with a EF of 15.1 at 24h. Therefore, by modifying the stripping composition, the selective separation of the target metal ions can be reached. It is worthy to highlight the remarkable stability of the obtained supported ionic liquid membranes [4].

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Acknowledgements

This work has been supported by Ministerio de Ciencia e Innovación de España (MICINN), ref. CICYT ENE2011-25188, and Fundación Séneca ref. 15260/PI/10.

Membrane Bioreactors

- **Oral session 3**
- **Oral session 6**

IMPROVEMENT OF SLUDGE QUALITY TO CONTROL FOULING IN MBR

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The membrane bioreactor (MBR) has been widely used due to higher pollutant removal efficiency, such as organic matter and nutrients, when compared to conventional processes for the industrial wastewater treatment. However, the fouling control is still a challenge for this technology. Regarding the minimization of membrane fouling in MBR, several strategies can be employed such as control of the filterability of sludge inside the MBR with use of membrane permeability improver or powdered activated carbon, in addition to improving hydrodynamics inside the BRM aimed to reducing polarized layer near the membrane surface, and others [1].

Some biopolymers have been developed to react with the biomass present in the BRMs. The biopolymers usually have a cationic network that reacts with the biomass. These biopolymers can be used as a tool for controlling and improving the sludge quality. Biopolymers are responsible for agglomerate of biological sludge flakes, dispersed fine particles in the environment and to reduce the concentration of SMP and EPS without causing damage to biological treatment and transfer of oxygen. The use of biopolymers will result in reduced interaction between the sludge with the membrane surface. This improvement could be reflected in a stable biomass and in the increase of membrane hydraulic permeability, the operational flux and reduction in the transmembrane pressure.

The aim of this study was to evaluate the long-term use of membrane permeability improver as an improving agent to sludge quality in the MBR in order to reduce the fouling potential in MBR. To evaluate the effect of improving agent two submerged hollow fiber MBR (PVDF membrane with average pore size of 0.04 µm and area of 0,9 m² and biological volume of 120L) were used for evaluate the improvement of sludge quality due the use of membrane permeability were used, one containing the sludge without the addition of membrane permeability improver and the other with continuous dosing of improver. The MBRs were operated with HRT of 8h and SRT 45 d. The membrane permeability improver of choice was a modified cationic polymer, MPE supplied by Nalco. The optimal dosage of flux improver was determined for both strategies. The optimal dosage was determined with a Jar test in which each vessel was filled with 2L of sludge and dosed with membrane permeability improver (100, 150, 200, 250, 300 and 500 mg/L for vessels 1 to 6, respectively). In order to determine an optimal improver concentration, sludge filterability and SMP and EPS concentrations were analyzed in terms of carbohydrates and proteins. An initial dosage corresponding to the optimal dosage was added, and the MBR was daily refilled with an amount of improver equivalent to the amount that was discharged in the excess sludge and biodegradable fraction (1%). The effect of the addition of the permeability improver was assessed by monitoring sludge filterability, SMP and EPS concentration, particle size and colloidal TOC.

The results showed a significant difference between the median values of filterability with and without 250 ppm of MPE addition. It was also found that the median values of filterability with the addition of MPE was significantly lower, whereas analysis using statistical hypothesis test, Mann-Whitney test for comparison of medians, at a significance level of 0.05 as observed in Figure 1, which infers the improvement of sludge quality by the addition of

improver. It was also possible to observe a significant difference between the median values of particle size. It was found that the particle size values are significantly greater when the addition of MPE. This same result was observed in YOON and COLLINS [2] study. The increased particle size changes the structure of the cake formed on the membrane surface, so that there is a uniform distribution of components throughout the layer formed, that will be responsable for the decreasing of membrane fouling and increases the performance of the process [3].

Table 1- Sludge quality with and without 250 ppm of MPE addition during the monitoring time

Parameter	Unit	Sludge BRM without MPE					Sludge BRM with MPE				
		average	median	mín	max	deviation	average	median	mín	max	deviation
Filterability	**s**	135	120	18	450	91	110	87	20	319	66
TOC colloidal	**mg/L**	12	6	0.3	75	17	11	5	1	63	14
SMP - carbohydrate	**mg/L**	15	14	6	30	8	13	11	9	21	4
SMP - DQO	**mg/L**	253	221	44	713	232	192	209	45	354	111
EPS - carbohydrate	**mg/L**	9	5	2	27	8	6	7	3	12	4
EPS - DQO	**mg/L**	142	113	21	291	123	103	89	34	182	61
Particle size	**µm**	28	28	26	33	2	32	32	23	42	5

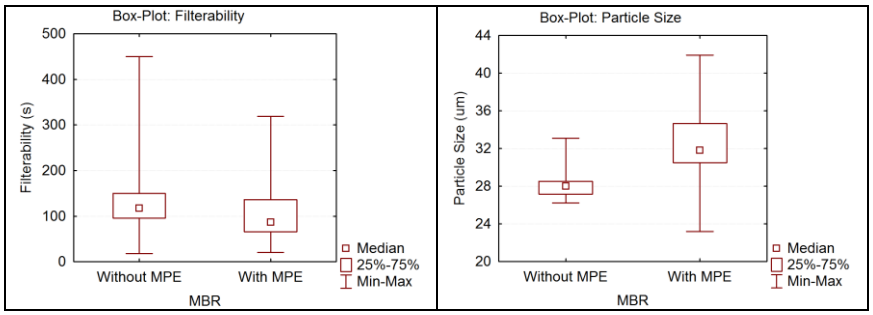

Figure 1 – Statistical analysis of filterability and particle size data of MBR sludge with and without 250 ppm of MPE addition

It can also be observed the colloidal TOC and SMP and EPS (in terms of COD and carbohydrate) decrease, which contribute to fouling control in MBR, since several studies suggest such substances as major contributors to fouling in MBR [4].

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Acknowledgements

The authors would like to express gratitude to: Petrobrás, CNPq, CAPES, FAPEMIG for their permanent support.

STUDY OF THE INFLUENCE OF DIFFERENT VARIABLES ON MEMBRANE FOULING IN SUBMERGED MEMBRANE BIOREACTORS

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Abstract

Submerged membrane bioreactor (SMBRs) processes for wastewater treatment are restricted by the membrane fouling [1, 2]. This fouling phenomenon during ultrafiltration is due to the interaction between the membrane material and the mixed liquor components. In fact, the process is strongly influenced by three factors: biomass and wastewater characteristics, operational conditions and membrane characteristics [3].

In this work, a design of experiments was carried out in order to optimize a submerged membrane bioreactor process. For that, the sludge retention time (SRT), mixed liquor suspended solids (MLSS), the ratio of soluble COD and particulate COD in the influent were studied as well as the influence they have in the membrane fouling as a result of the interaction between them. Table 1 shows the working range of each variable.

As a response of all these experiments, the concentration of extracellular polymeric substances (EPS) and the permeate flux were measured. EPS concentrations were determined as carbohydrate and protein, both measured colorimetrically by the methods of Dubois and Lowry, respectively [4].

All the experiments were performed with PVDF hollow fiber membranes which have an area of 1m^2 and a pore diameter of 0.4 µm. A synthetic wastewater was prepared to be used as the food source throughout this study, depending on the ratio of soluble COD and particulate COD. The pilot plant where all the experiments were carried out is shown in Figure 1.

The results of this work proved a direct relationship between the concentration of EPS and membrane fouling. When the synthetic wastewater had higher concentration of soluble COD than particulated, the membrane fouling was less pronounced. Moreover, high fouling potential was observed at high SRT. Regarding to MLSS, membrane fouling rates increased as the food to microorganism ratio (F/M) was increased.

This has been one of the different projects carried out by the Membrane Group of the Environmental Department of GAIKER. Other recently outstanding projects carried out in this field have been related to membrane autopsy, protein recovery from an industrial effluent and preparation of catalytic membranes.

Table 1. Working range of variables like SRT, MLSS and CODs/CODp.

Variable	Working Range
SRT, d	Low-high
MLSS, mg/L	8000-15000
CODs/CODp	<1; >1

Figure 1. Pilot plant of the submerged membrane bioreactor (SMBR) for wastewater treatment.

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Membrane Fouling Behavior during the Performance of two MBRs: Resistance Analysis and Fouling Mechanisms

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In this work, the filtration resistance of the mixed liquor, colloids + solutes and pellets obtained from two membrane bioreactors (MBRs) at different MLSS concentration was evaluated. The MBRs of 25 L each were equipped with micro (MF-MBR) and ultrafiltration (UF-MBR) submerged membranes and were fed with synthetic wastewater. They had the same filtration area (0.116 m^2) and the operational conditions were the same during 168 days of operation.

The results showed that in MF membrane, the filtration resistance decrease for the fractions of colloids + solutes and pellets while MLSS concentration increased from 3.3 to 14 g/L. In the case of mixed liquor, the resistance was very high only at 3.3 g/L and for the rest of MLSS was similar and showed low values. For the UF membrane occurred something similar, although the values of resistance were slightly lower at the lowest MLSS concentration. On the other hand, the relationship between EPS and filtration resistances was analyzed. The greatest filtration resistances were found at the lowest concentrations of bound and total EPS, and for the greatest soluble EPS concentrations.

In addition, the Hermia's model was applied to the experimental data obtained in the experiments. Results showed that for all MLSS concentrations and fractions filtered, data fitted the best for the mechanisms of cake layer formation and standard blocking.

Morever, from the slope obtained from each fitting of Hermia`s model, the specific resistance of the cake layer (α) of the 3 studied fractions for all MLSS was calculated (Figure 1).

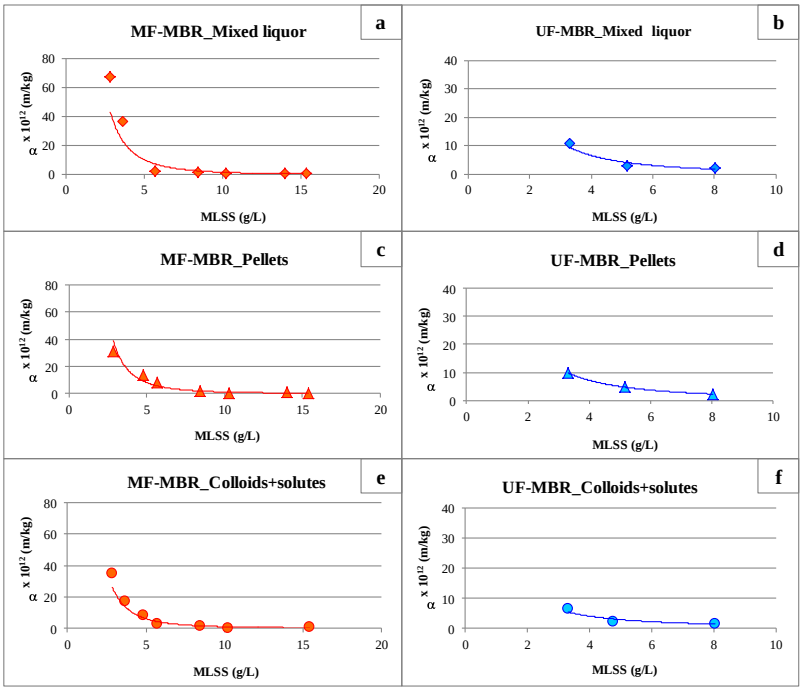

Figure 1. Influence of MLSS on specific cake resistance of the fraction analyzed in both membranes.

The results show similar trends for both MBRs and the fractions analyzed, that is, the greatest values of α were found at the lowest MLSS concentrations. The decrease in resistance when varying MLSS can be attributed to soluble EPS, due to the fact that they diminished in concentration as did the filtration resistance as MLSS increased. On the other hand, at the lowest values of MLSS, resistance was higher for MF membrane. At higher MLSS concentrations, the filtration resistance does not depend as much on membrane pore size.

The effect of the cake layer compressibility in both membranes was also studied, that is, the effect of the transmembrane pressure (TMP) on the specific resistance of the cake layer, because the mechanism of cake layer formation prevailed for all the experiments carried out. Table 1 shows the values of slopes, the y-intercept and the correlation coefficients of the curves, as well as the membrane resistance and the specific resistance of the mixed liquor at each pressure for both membranes.

Table 1. Parameters used to calculate the specific resistance of cake layer at different pressures for MF and UF membranes.

	PTM (bar)			
	0.1	**0.2**	**0.3**	**0.4**
	MF membrane			
Slope ($\frac{\mu \cdot \alpha \cdot MLSS}{2 \cdot A^2 \cdot PTM}$) $\cdot 10^{11}$	2.1	1.3	1.7	1.9
y-intercept ($\frac{\mu \cdot R_m}{A \cdot PTM}$) $\cdot 10^{6}$	6.2	1.4	4.9	4.9
R^2	0.996	0.989	0.997	0.997
$R_m \cdot 10^{11}$ (m^{-1})	1.8	2.8	4.2	4.9
$\alpha \cdot 10^{12}$ (m/kg)	**2.3**	**2.9**	**5.7**	**8.1**
	UF membrane			
Slope ($\frac{\mu \cdot \alpha \cdot MLSS}{2 \cdot A^2 \cdot PTM}$) $\cdot 10^{11}$	1.6	2.3	1.7	2.0
y-intercept ($\frac{\mu \cdot R_m}{A \cdot PTM}$) $\cdot 10^{6}$	11.3	9.5	8.1	7.9
R^2	0.988	0.997	0.979	0.999
$R_m \cdot 10^{11}$ (m^{-1})	3.3	5.5	7.0	9.1
$\alpha \cdot 10^{12}$ (m/kg)	**3.2**	**8.7**	**9.9**	**15.1**

Specific resistance increased when TMP increased, the values being higher for the UF membrane at all pressures studied. However, cake layer compressibility developed after filtering by the two membranes was similarly high, indicating that the cakes were very compressible.

Acknowledgements
This study was partially financed by the Ministry of Education via the projects “Treatment of superficial water and wastewater to obtain high quality effluents” (CTM2012-15348) and “Treatment and wastewater reuse for a sustainable management” (CONSOLIDER) (CSD200644), and by the Ministry of Environment via the project “Removal of organic micropollutants by MBR technology associated to nanofiltration” (124/SGTB/2007/3.1).

FOULING CONTROL IN MEMBRANE BIOREACTORS BY SEWAGE-SLUDGE BASED ADSORBENTS

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Powdered activated carbon (PAC) has been recently used to improve the performance of membrane bioreactors (MBR) treating domestic and municipal wastewaters. However, very few studies have been performed using industrial wastewaters. PAC is a relatively expensive material which has impeded to be a widely established technique for wastewater treatment. Thus, more cost-effective practical adsorbent-supports are being prepared from different wastes for their valorization. The use of sewage sludge as precursor for carbon materials with environmental applications has been studied recently [1,2]. Owing to its low initial cost, simplicity of design, high adsorption capacity and regenerability, sewage-sludge based adsorbents appeared to be a versatile and suitable alternative to the use of commercial PAC in MBR. In this work, wastewaters from a cosmetics industry have been treated in a submerged MBR. The presence of detergents, surfactants, oils, fats, and personal care products make difficult the biological treatment, which has been scarcely studied so far. The influence of the addition of PAC obtained from sewage sludge and commercial PAC over the fouling of membranes installed in a MBR treating cosmetic wastewater has been studied. The SMP adsorption capacity of commercial and prepared PAC, as well as, changes in the sludge characteristics and the development of fouling layers have been also evaluated.

Two 15 L MBR reactors were operated with commercial PAC (C-MBR) and biosolids-based PAC (B-MBR). A similar MBR was operated without PAC as control system. The reactors were inoculated with 8.6 $gVSS \cdot L^{-1}$ and operated during 140 days at room temperature. PAC-MBRs were supplemented with a PAC concentration of 1 $g \cdot L^{-1}$ at the start-up and operated at SRT and HRT of 30 and 2.6 d, respectively. MBRs were fitted with chlorinated polyethylene (PE) microfiltration flat sheet membranes (KUBOTA®) of 0.1 m^2 and a nominal pore size of 0.4 µm operated at constant permeate flux and specific aeration demand of 8 LMH and 1.5 $m^3 \cdot m^{-2} \cdot h^{-1}$, respectively. Membranes were submitted to a three-step cleaning protocol to know more about the foulant layers distribution [4]. The preparation method of PAC from biosolids (B-PAC) was performed according to the protocols described previously by Monsalvo et al. [1]. Commercial activated carbon (C-PAC) was purchased from Merck.

Fig. 1 shows the adsorption isotherms of carbohydrates and proteins into C-PAC and B-PAC. A maximum adsorption capacity of 130 and 143 $mg \cdot g^{-1}$ was obtained for carbohydrates with C-PAC and B-PAC, respectively. Proteins were efficiently adsorbed into C-PAC and B-PAC, reaching a maximum adsorption capacity of 634 and 570 $mg \cdot g^{-1}$, respectively. The addition of PACs can reduce the concentration of biopolymers, which can be deposited onto the membrane. Hence, the development of irremovable fouling can be mitigated, which would reduce the chemical cleaning frequency.

Time-course of TMP during long-term experiments is showed in Fig. 2a. An increase of the TMP was observed in all runs operating under subcritical permeate flux because of the occurrence of fouling (Fig. 2a). The sharp increase of TMP, known as TMP jump, observed in the control MBR and C-MBR is associated to the presence of foulants, which tend to self-accelerate. Although the presence of C-PAC delayed the “TMP jump”, which suggest that C-PAC effect over the sludge permeability disappears after some period of time, being necessary its replacement. B-PAC extended its beneficial effect for a longer period than C-

PAC. Thus, air-activation can be viewed as a simple way of valorisation of biosolids to inexpensive PAC, which can be effective for fouling mitigation in MBR.

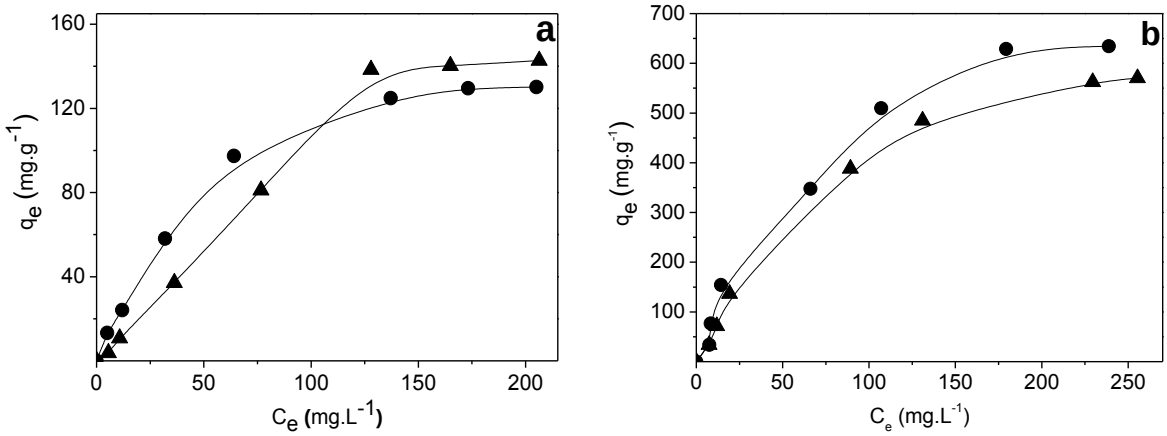

Fig. 1. Adsorption isotherm of carbohydrates (a) and proteins (b) onto C-PAC (circles) and B-PAC (triangles).

Fig. 2b shows the relative filtration distribution obtained in the control MBR and C-MBR. Significant differences were observed in the influence of each foulants layer along the evolution of fouling. The appearance of the gel layer, at TMP values in the vicinity of 9 kPa, caused the appearance of an easily reversible layer. Filtration resistance include membrane (9.3%), unstable layer (71.1%), easily reversible (17.1%) and hardly reversible (2.5%) resistance in the control MBR. The formation of the cake layer was identified as the main resistance cause leading to a filtration resistance of $1.9 \cdot 10^{13}$ m^{-1}. A similar total filtration resistance of $1.7 \cdot 10^{13}$ m^{-1} was reached in the C-MBR. Cake layer was also the main filtration resistance in C-MBR (71.1%), but hardly reversible layer contribution was reduced to 0.9%. Cleaning assay could not be carried out with the B-MBR since fouling layers were not observed after 10 d in operation. This suggests that the B-PAC have good properties to avoid the deposition of fouling substances.

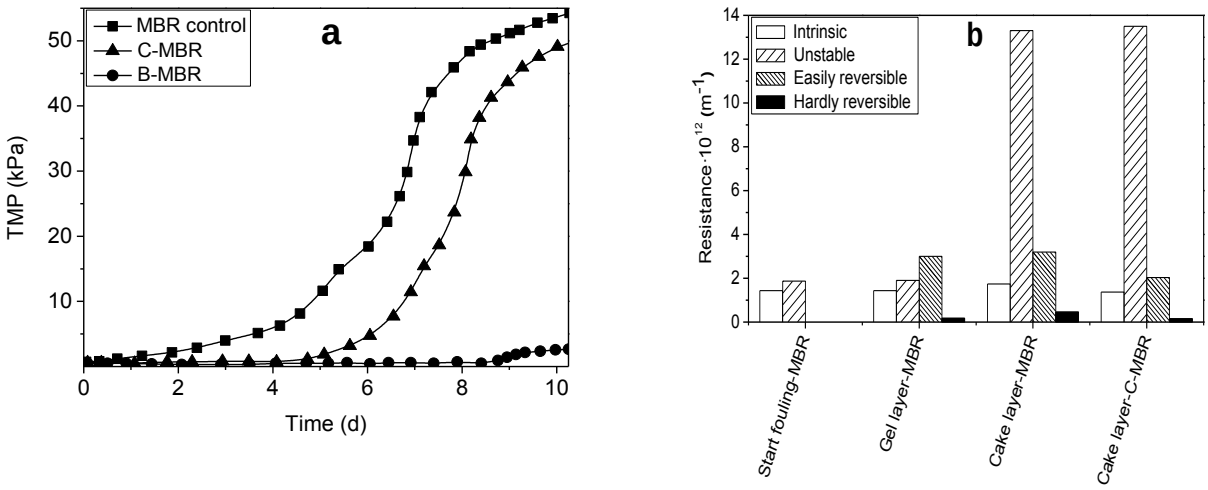

Fig. 2. Time-course of TMP during the long-term runs at 8 LMH (a). Resistance of each fouling fraction in the conventional MBR and C-MBR (b).

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Acknowledgements The authors greatly appreciate financial support from the Spanish MICINN and CM (REMTAVARES) through the projects CTM2010–15682 and S2009/AMB-1588, respectively.

ROLE OF THE SMP AND EPS IN MEMBRANE BIOREACTORS FOULING

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Membrane bioreactors (MBRs) are one of the most expanded technologies in waste water treatment within the past few years, reaching at the end of the last decade about 7600 plants of MBR around 200 countries of the world [1,2]. MBR have many advantages over usual treatments, standing out: a high quality effluent, reducing space and low sludge production [3]. Nevertheless, being yet a growing technology, it has many determining aspects and operational problems that restrict its use such as membrane fouling. It represents an added problem to the filtration process, which can increase the operational charge by energetic consumption and shortens the membrane average life [4]. This issue can be tackled from two different aspects, optimizing operational variables and studying the fouling mechanism.

This research has worked with both aspects, but focusing in the fouling mechanism, specifically in extracellular polymeric substances (EPS). EPS are excreted metabolites by microorganisms whose purpose is to protect the own microorganism from extreme environments. Different types of EPS can be distinguished according to the position they held inside the matrix of the microbial flocs. The soluble EPS, also called soluble microbial product (SMP), it's the soluble part which is out of the floc, while the EPS is the part bound to the cell [5]. The SMP and EPS composition is closely related with the type of water used and with the operational conditions of the wastewater plant [6].

The study has been carried out in an experimental installation located at Granada city. The installation was set up in pre-denitrification and is equipped with an MBR module with microfiltration technology (pore medium-sized of 0.4 µm). Analysis have been done for SMP as well as EPS, using the extraction method through centrifugation for SMP [1] and the precipitation method with ethanol at -20º C for the EPS [7]. Both cellular metabolism products have been characterized in its composition trough the analysis of proteins, carbohydrates and humic acids. In order to know their influence in membrane fouling, the retention times (SRT) have been sorted from 0 to 20 days, observing then the variations produced within cellular metabolites and how they affect membrane fouling and consequently transmembrane pressure (TMP).

The evolution of biopolymers of the SMP and EPS can be observed in figures 1 and 2 respectively.

Regarding biopolymers evolution it can be seen how at the beginning of the study there is accumulation in the activated sludge that reduces just as SRT is increased from 10 to 20 days. This is clearly shown in the total evolution of SMP, which is the sum of all the studied polymers. As in SMP, in EPS there was an initial raise of the total polymers amount, although this time, there was no reduction when SRT increased, instead it rises gradually. Approximately at the middle of the study a sharp drop due to the loose of activated sludge in the system takes place (and consequently a punctual drop of the SRT). As the SRT adjusted, the concentrations of biopolymers did it as well, achieving the same previous values to the loose of sludge.

Correlation between SMP or EPS with TMP was not observed. Yet, there was a clear relationship between the parameters within the first studied period (SRT= 0-10 days), where an increase of the SMP and EPS occurs, obtaining a correlation between TMP and SMP of 0.4505 and between TMP and EPS of 0.5773. Hence, it can be observed that these substances of the cellular metabolism affect the TMP and could be therefore the cause of the

membrane fouling. It is necessary to keep studying the evolution with new SRT and valuate the influence of other operational variables.

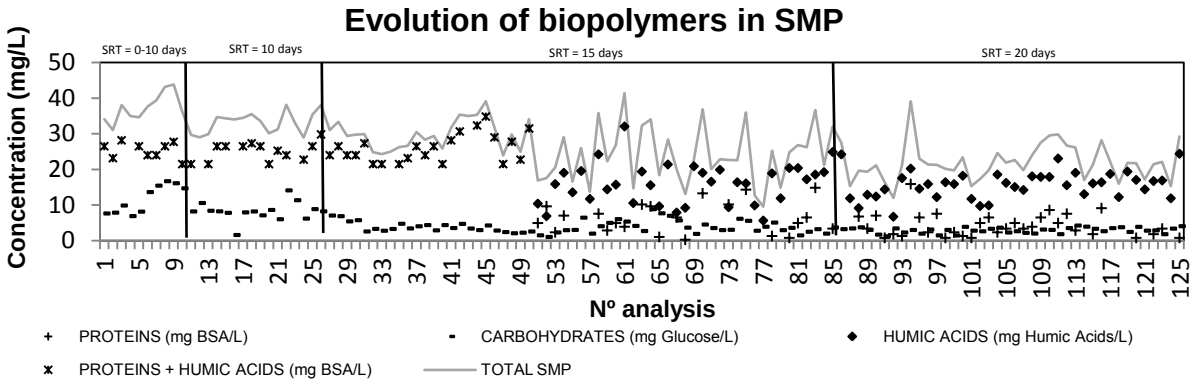

Figure 1: Evolution of biopolymers in SMP

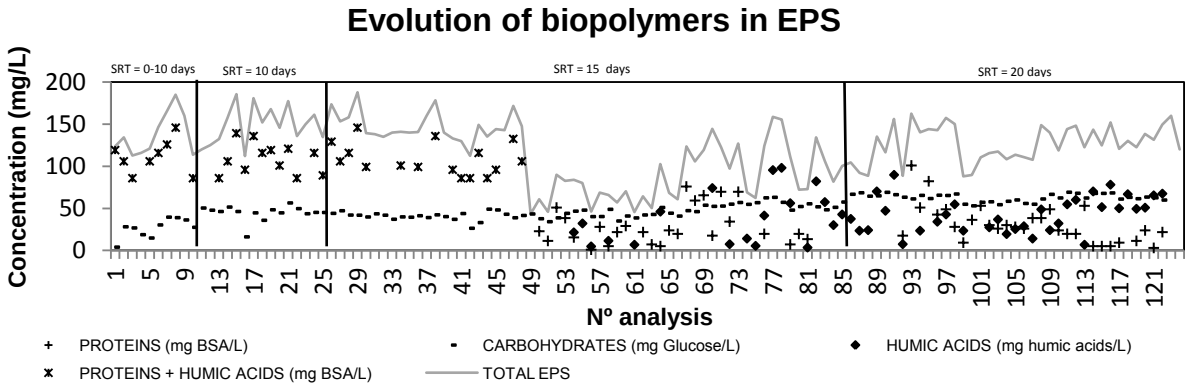

Figure 2: Evolution of biopolymers in EPS

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Acknowledgements

This research (NET 324936/1) was funded by the Andalusian Government (Andalusian Water Agency) with European Union funds (FEDER), and was conducted at the University of Granada, with the participation of EMASAGRA.

DEVELOPMENT OF POLYMER INCLUSION MEMBRANES BASED ON IONIC LIQUIDS AND LACCASE FOR APPLICATION IN BIOCATALYSIS AND MICROBIAL FUEL CELLS

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Laccase is an attractive enzyme (EC 1.10.) contributing in large spectrum of application such as such: biodegradation of phenols [1], decolourization of dyes [2], lignin-cellulose treatment [3] or recently as enzymatic cross-linking of alkyl resins in new generation of paints [4]. The desired industrial purpose is often difficult to achieve using the native form of the enzyme. Recent developments in enzyme engineering have revolutionized the development of commercially available enzymes as better industrial catalysts [5]. The use of ionic liquids (ILs) in biocatalysis has received growing attention due to the advantages they offer, such as the possibility of carrying out processes involving hydrolytic enzymes which are thermodynamically unfavourable in water, replacing the organic solvents (e.g. transesterification reaction), their ability to increase the solubility of organic substrates and to improve process performance increasing enzyme activity, stability and selectivity by assuring a comfortable medium for the enzyme [6].

The development of Polymer Inclusion Membranes based on Ionic Liquid and Laccase (PIMILLs) could be the solution for a wide range of laccase applications. For that, in first place, the activity of lacasse in a wide variety of ionic liquids were evaluated using the oxidation reaction of a laccase mediator ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) as reaction model. This study revealed that ILs based on the anion bis[(trifluoromethyl)sulfonyl]imide, [NTf_2], enhanced the laccase activity. Therefore, these ILs were used in the formulation of new polymer inclusion membranes based on ionic liquid and laccase, founding the highest activity in the oxidation of ABTS with the ionic liquids [Choline][NTf_2] and [emim][NTf_2]. The obtained enzyme-membrane derivates also showed a high operational stability, as it was found during several reuse assays. Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray (EDX) analysis was also used to evaluate the operational stability of these membranes. The developed polymer inclusion membranes based on ionic liquid and laccase have been used as biocathodes in single-chamber air-cathode Microbial Fuel Cells (MFCs), showing interesting voltage generation and wastewater COD removal.

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Acknowledgements (10 pt)
This work was partially supported by the MICINN ENE2011-25188 and SENECA Foundation 15260/PI/10 grants. Sihem Haj Kacem and Said Galai have fellowships from Erasmus Mundus EU Mare Nostrum Program. The authors thank Antonio Sánchez Amat from the Department of Genetics and Microbiology, Faculty of Biology, University of Murcia for his kind collaboration.

Submerged Membrane Bioreactor for water reuse and nutrients recovery in a Recirculated Aquaculture System

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Introduction.- The aquaculture have had recently an important worldwide growth. This growth needs the development of new technologies in order to get an efficient and sustainable production. The Submerged Membrane Bioreactors (SMBR) had been more and more used to treat water effluents in Recirculated Aquaculture Systems (RAS). These intensive aquaculture systems generate an organic matter and nutrients concentrated effluent, due to the non-used substances by the fishes. An alternative to recover and reuse these nutrients is to feed with them, in a SMBR, a heterotrophic microbial biomass [1], which could be used as a complementary food for the fishes [2]. Besides, the microfiltration membranes of the SMBR allows to get a solids-free and high sanitary effluent quality, which let it´s reuse for the aquaculture. The main porpoise of this work was to study in a lab scale SMBR, the assimilation efficiency of the residual organic matter and nutrients presents, by the biomass, in a RAS.

Materials and methods.- The pilot reactor, with a 70L volume, was equipped with a PVDF membrane module. It´s pore size was 0.14µm and it's filtration surface was FS=0.2m^2. Transmembrane filtration flux was J=7 L/m^2•h to guarantee sub-critic flux conditions [3]. Permeate was operated during 4600h without any membrane wash with 0.5 bar as a pressure limit criteria.

The SMBR was feed with waste sludge issued from the backwash of the primary solids filtration system of the RAS, of a tilapia (*Oreochromis sp*.) culture system. The fish culture density was 11kg/m^3, with fish sizes from 150 up to 400g each. Firstly the SMBR biomass was growth up to 5000 mg_{VSS}/L and stabilized. Thereafter the aquaculture waste sludge was feet at different organic loads (i.e. 0.05, 0.1, 0.2 y 0.3 kg_{COD}/kg_{VSS}•d), using acetic acid as a complementary substrate to guarantee a C/N=15 (as BOD/TKN). The air was supplied beneath the membrane module to avoid fouling, with a fine bubble diffusor to maintain dissolved oxygen concentrations, DO ≥ 2 mg/L. The SMBR worked out with a pH = 8 ±0.3 and a temperature, T = 25 ± 1 ˚C. The performed analysis were: COD_{Tot} and COD_{Sol}, TKN, N-NH_3, N-NO_3^- and P-PO_4^{-3} by spectrophotometric methods and VSS, TSS by standard methods.

Results.- The COD removal efficiency was always higer than 98%. The treated effluent was completely solids-free. However, during the 0.1 to 0.3 kg_{COD}/kg_{VSS}•d organic loads the permeate COD was different ($p<0.001$) from the soluble COD into the SMBR (Fig. 1). This range of organic loads results better to operate a SMBR since the relative increase of soluble COD into the reactor could lead to an increasing membrane fouling.

The ammonia nitrogen removal observed, for all the experimental conditions, was always higher than 99%, and the nitrate nitrogen removal remained between 8 and 25%. The nitrate nitrogen could be removed by a nitrification stage [3], however, since the tilapia tolerance to nitrate is hundreds of times higher than that to ammonia, and the aquaculture tanks remain in aerobic, with high DO concentrations (e.g. DO=5mg/L), there is no need to set up this stage in this case.

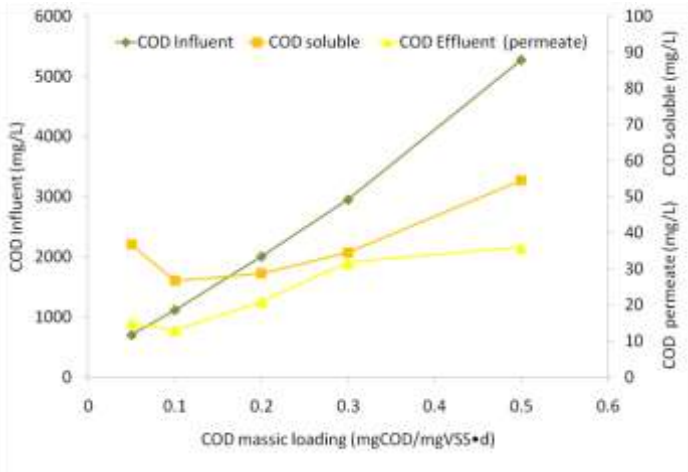

Figure 1 Soluble COD in the influent, soluble COD in the SMBR and permeate COD at different organic loads.

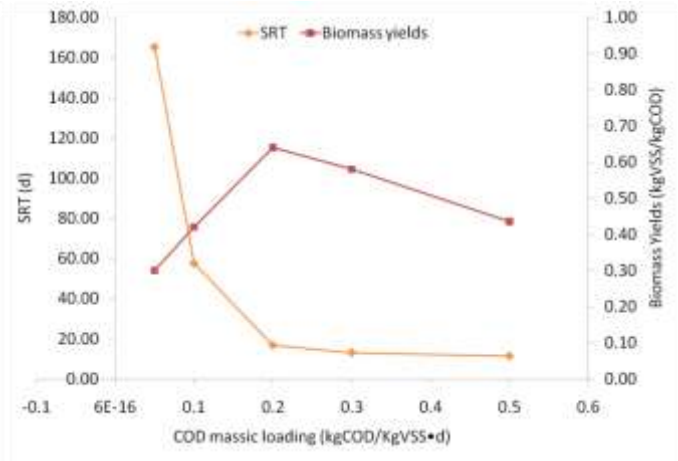

Fig. 2. Solids Retention Time (SRT) and Biomass Yields (Y) at different organic loads

The maximum substrate rate consumption estimated was 0.2 g_{COD}/g_{VSS}•d and the maximum specific biomass growth rate estimated was 0.1 g_{VSS}/g_{VSS}•d. The biomass yield production did not result linearly proportional to the organic load (Fig. 2), possibly due to the difference of the nutrients bioavailability, since the increase of the organic load was mainly in a particulate manner. The maximum biomass production rate observed was 506±10 g_{VSS}/kg of aquaculture sludge treated. In conventional suspended growth biological reactors the biomass production rates stayed between 415±5 [4] and over 1027±2 g_{VSS}/kg of aquaculture sludge treated [5]. The biomass production rate it is important if this biomass is going to be reused as a complement fish food in the aquaculture tanks.

Conclusions.- The operating conditions in the SMBR allows a high ammonia nitrogen assimilation, despite the different biomass production. Even during the high organic loading concentrations the SMBR the quality of the treated effluent guaranteed optimum aquaculture conditions.

Therefore, the SMBR can be used to treat the residual sludge in a RAS recovering the non-used organic matter and nutrients, by the fishes, due to its assimilation by the bacteria. Consequently the contaminant loading rejected to the environment is significantly reduced and the water can be reused into the system.

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Acknowledgements

Authors thakns to FORDECYT-CONACYT for the financial support and to the University of Montpellier 2 for the membrane module donation. First author thanks CONACYT for the postgraduate scholarship.

EFFECT OF BIOFILM CARRIERS ON MEMBRANE PERMEABILITY AND ORGANIC MATTER AND NITROGEN REMOVAL IN A SUBMERGED MEMBRANE BIOREACTOR

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Despite the potential benefits of MBR systems and the role they can play in water conservation and reuse, reduction in membrane permeability caused by fouling phenomenon, due to a complex membrane/biomass interaction, still remains one of the major drawbacks of MBR. Thus, some studies focused their attention on a hybrid system as an alternative to the conventional MBR, trying to combine the advantages of biofilm and MBR (BF-MBR) processes in order to overcome some of the limitations of C-MBR. In this context the influence of biofilm carriers in a MBR on the performance of organic matter and nitrogen removal and the influence on membrane fouling were evaluated. The study was carried out using two membrane bioreactor pilot-plants (Figure 1), working in parallel and gravity fed with domestic wastewater. The BF-MBR had 40% of its volume occupied with the carriers resulting in a specific surface area of 330 $m^2.m^{-3}$. During the evaluation period the total biomass concentration in the C-MBR and BF-MBR (suspended and attached biomass) were kept around 5540 ± 693 mg $MLSS.L^{-1}$ and 5186 ± 435 mg $MLSS.L^{-1}$, respectively. Flat sheet membrane modules were used for solid separation, and permeate was continuously withdrawn by a peristaltic pump operating with a cycle of 8 minutes filtration and 1.6 minutes relaxation.

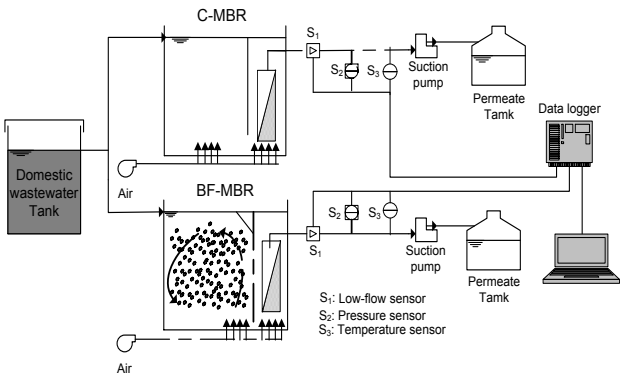

Figure 1: Pilot-plantsschemes, where S_1–low-flow sensor; S_2–pressure sensor, S_3–temperature sensor.

Regarding organic matter removal, no statistically significant differences were observed between C-MBR and BF-MBR (Figure 2), with average Soluble COD concentrations of 27 ± 9.0 $mgO_2.L^{-1}$ and 26 ±1.0 $mgO_2.L^{-1}$ and BOD concentrations of 6.0 ± 2.5 $mgO_2.L^{-1}$ and 6.2 ± 2.1 $mgO_2.L^{-1}$, respectively. On the other hand, the BF-MBR produced a permeate with lower ammonia and total nitrogen concentrations resulting in removal efficiencies of 98% and 73%, respectively, and an effluent with 0.9 ± 0.5 mg NH_4-N/L and 14 ± 3.1 6 mg TN-N/L. Higher TN removal in BF-MBR can mostly be attributed to multifunctional microbial reactions that take place in the developed biofilm, especially simultaneous nitrification and denitrification (SND), which plays an important role in nitrogen removal. Regarding membrane fouling, TMP was monitored at a constant flux condition of 10.2 ± 0.2 LMH for a C-MBR and 10.4 ± 0.3 LMH for BF-MBR. Figure 3 illustrates the TMP profile and fouling rate throughout the whole experiment. It can be observed in Fig. 3

that the TMP rate for C-MBR was higher than that for the biofilm membrane bioreactor resulting in a mean fouling rate for C-MBR and BF-MBR of 3.8 ± 1.2 L/m2.h.bar.d and 2.8 ± 0.1 L/m2.h.bar.d, respectively. As a result, the mean length of operational cycles increased by 7 days in BF-MBR compared to C-MBR.

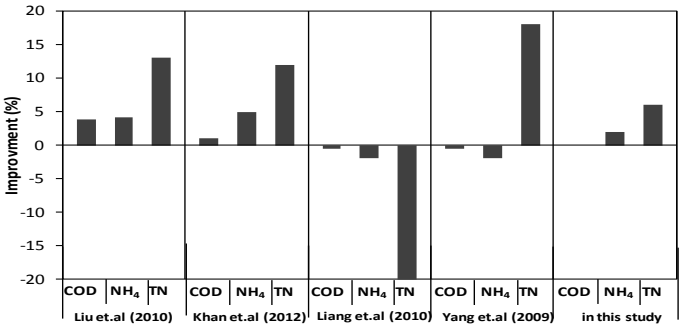

Figure 2: Efficiency improvement of organic matter and nitrogen removal in a BF-MBR compared to C-MBR.

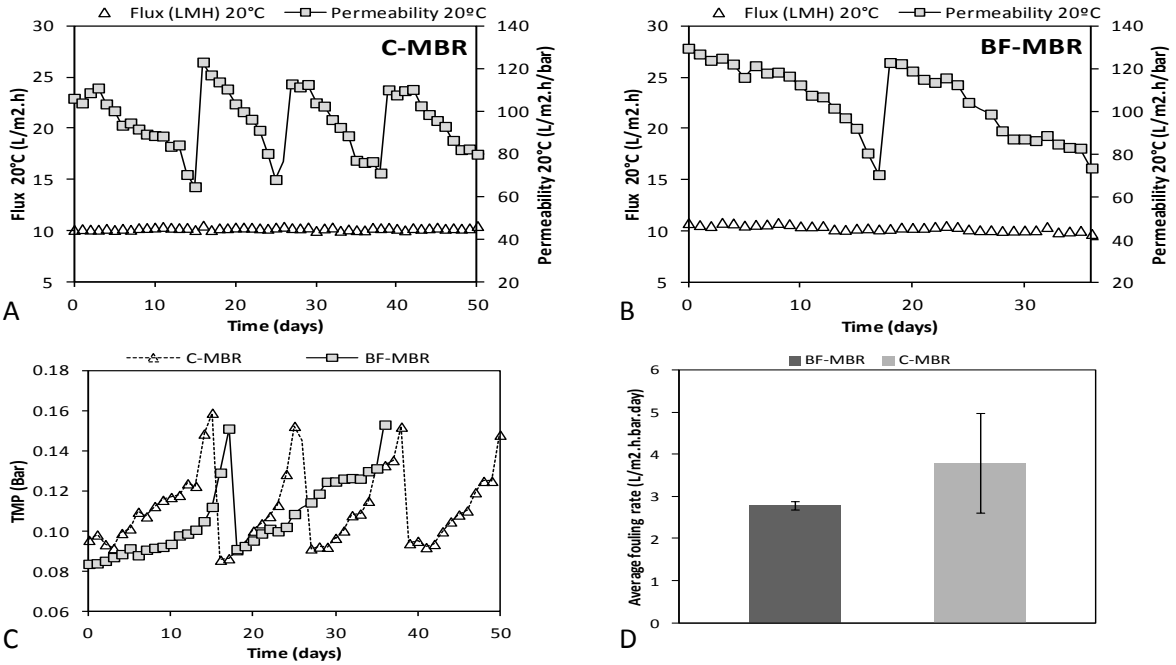

Figure 3: Membrane filterability during experimental period, where: (A) and (B) permeability; (C) Transmembrane pressure profile and (D) mean fouling rate.

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Acknowledgements

This work was suppported by a grant from the Counsel of Technological and Scientific Development (CNPq).

ANALYSIS OF THE EFFECTS OF ULTRASOUND IRRADIATION OVER EFFLUENT QUALITY AND MEMBRANE INTEGRITY IN FLAT SHEET MICROFILTRATION MBR SYSTEMS

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Membrane fouling is one of the main problems regarding the performance of membrane bioreactor (MBR) systems applied to wastewater treatment [1]. It constitutes an important impediment to the increasing application of this technology due to the largest operating costs [2, 3, 4] and for that reason, it is necessary to develop new mechanisms to control fouling. One of the most promising alternative cleaning methods is ultrasound (US) irradiation [5, 6], which can be applied as an unique method or combined to maintain adequate operational characteristics of the process [4, 7].

In this study, the performance of four MBR sonicated modules using immersed flat sheet microfiltration membranes and working in parallel (Figure 1) was analyzed and compared with a conventional MBR system in order to evaluate the effects of US irradiation over effluent quality, activated sludge solids concentrations and membrane integrity. Parameters such as TSS and VSS activated sludge concentrations and effluent COD concentration, turbidity, viscosity, colour or particle size distribution were analyzed, while others such as temperature, flux or transmembrane pressure (TMP) were continuously evaluated. In addition, scanning electron microscopy (SEM) and Fourier transformed infrared (FTIR) analyses were also carried out to check damage in the membranes surface. Tested US frequencies were 20, 25, 30 and 40 kHz and tested powers were 100, 200, 300 and 400 W. Moreover, different US on/off cycles were selected during the period of the study.

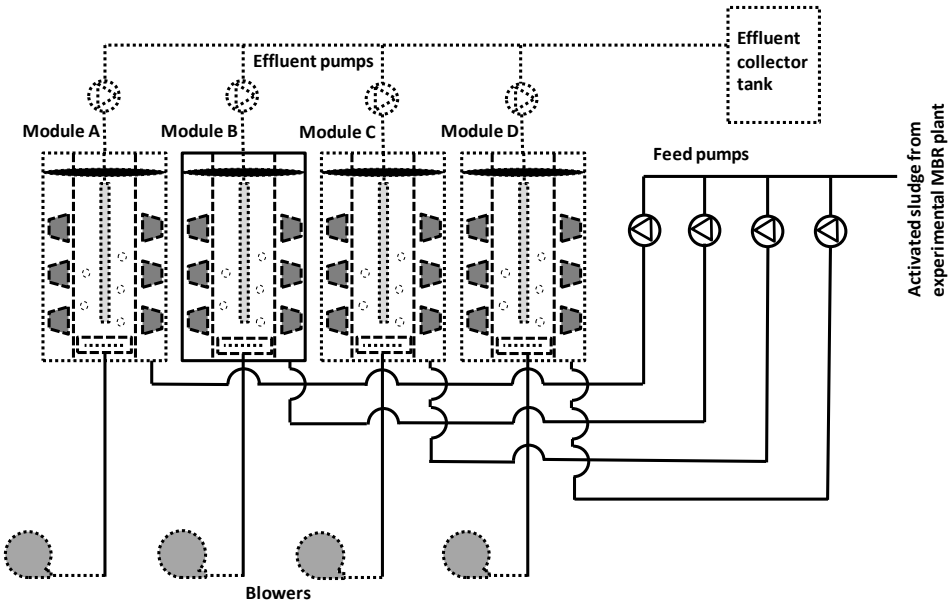

Figure 1. Schematic experimental setup.

Results showed that effluent quality was deteriorated when US irradiation was applied, especially at lower frequencies because as the sludge disintegration was enhanced, the amount of smaller particles able to pass through the membrane increased and subsequently, effluent parameters such as particles size distribution, COD concentration or turbidity also increased. Besides the effect of US irradiation over the activated sludge disintegration, the deterioration of effluent quality was also attributed to the fact that, at the tested conditions, membranes were damaged and their pore size was enlarged so, particles higher than the nominal membrane pore size appeared in the effluent, especially in the effluents from the modules which operated at lower US frequencies.

Regarding the operational parameters evaluated in this study, an increase in the temperature due to the US irradiation was observed inside the bioreactors, reaching values as high as 43 ºC while ambient temperature did not exceed 35 ºC. TMP readily increased when sonication was applied and the maximum allowable TMP was reached in no more than 20 days except for the module which operated at the lowest frequency, whose TMP was constant for almost 70 days. No significant differences in the FTIR profiles corresponding to the used membranes were observed comparing with that obtained for the clean membrane. However, SEM images showed that membrane integrity was damaged and the effect of the US irradiation over the membrane surface was more significant at lower frequencies.

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Acknowledgements

This study was supported by funds from the European Union and the Spanish Ministry of Economy and Competitiveness within the framework of the program INNPACTO (IPT-2011-1078-310000). It was conducted at the Department of Civil Engineering of the University of Granada with the collaboration of CADAGUA S.A.

Membrane Bioreactors

- **Poster session 1**

FOULING, THE MOST SERIOUS PROBLEM IN MEMBRANE BIOREACTORS. HOW TO CHARACTERIZE ITS MAGNITUDE?

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MBR and AnMBR processes appear to have a promising future in wastewater treatment. In spite of the advances made in membrane design, there are still some challenging issues with membrane bioreactor systems, in particular membrane fouling control [1]. Fouling remains the most significant factor limiting their cost effectiveness, it leads to flux decrease and transmembrane pressure increase, and its control requires chemicals, shortens the membrane lifespan and results in higher replacement costs [2]. In general, membrane fouling is closely bound to deposition of particles on the membrane surface forming a cake layer, macromolecules attachment and soluble molecules plugging and narrowing the membranes pores [3]. Fouling is inevitable but can be controlled to a certain extent, therefore there is great interest in studying the causes, characteristics, mechanisms and control measures of membrane fouling. Fouling can be characterized from filtration data obtained from specific lab trials or in full scale. Most of fouling test involved filtering a sample of the whole biomass or fractions such as washed biomass or supernatants in a stirred dead-end cell quantifying the fouling contribution of each fraction [4]. The chemical characterization of membrane foulant components has become the aim of many studies, however there are few comparative studies of the fouling resistances characterization methods.

Resistance is frequently measured by small-scale tests with deionized water. However, it has been suggested that the osmotic pressure could have an important contribution to filtration resistance in submerged MBRs, due to the gel structure and negatively charged functional groups of polymeric substances attached to the membrane surface [5]. Therefore, the effective resistance generated in situ sludge filtration could be not comparable to the one obtained with deionized water. On the other hand, results extrapolation to large scale and different operating conditions is problematic. Standardized and automatic methods that can be employed in situ without stopping the treatment process and without provoking fouling alteration will enhance the optimization of membrane bioreactors operation.

The proposed procedure for resistance measurement is based in the pre-compression critical flux method (PCCF) [6], allowing the determination of internal and external irreversible fouling resistances and its compressibility under different fouling conditions. The influence of effluent concentration on fouling resistance measurement and the fouling alteration provoked by ex situ measurement method are presented here.

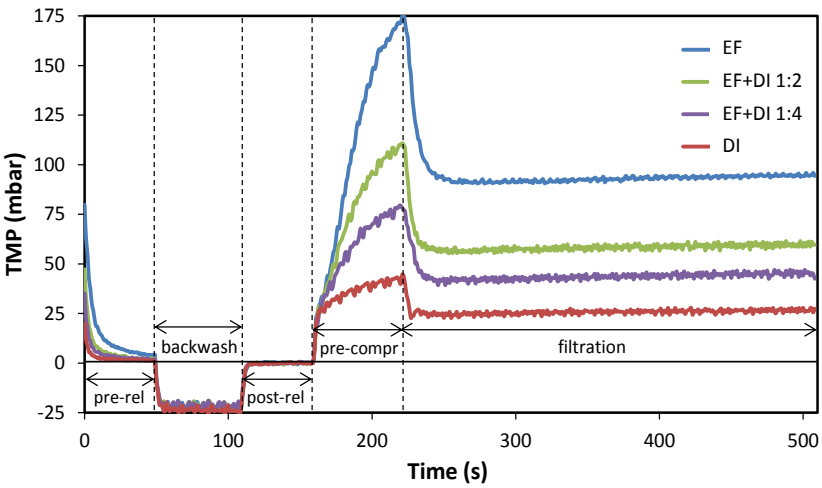

Figure 1. TMP profiles for 4.64 $l/m^2 \cdot h$ with effluent (EF), deionized water (DI) and 1:2 and 1:4 dilutions Pre-relaxation, backwash, post-relaxation and pre-compression and filtration steps are indicated.

The resistances obtained with effluent of an AnMBR pilot plant, with 1:2 and 1:4 dilutions of this effluent in deionized water, and with deionized water, were 10.0, 6.11, 4.48, $2.51 \cdot 10^{12}$ m^{-1}, respectively. Figure 1 shows the effect of concentration on TMP during filtration; however the backwash TMP does not change with the fluid employed to measure the resistance.

The effect of handling the membrane module for ex situ resistance measurement is shown in figure 2. Taking out the membrane module from the filtration tank and placing it in the vessel where resistance was measured ex situ, causes a fouling detachment and therefore a decrease in resistance, from 20.4 to $11.2 \cdot 10^{12}$ m^{-1}, despite the measurement was made with effluent. When the membrane module was again placed in the filtration tank, filtration resistance decreases once again to $8.3 \cdot 10^{12}$ m^{-1} as handling result.

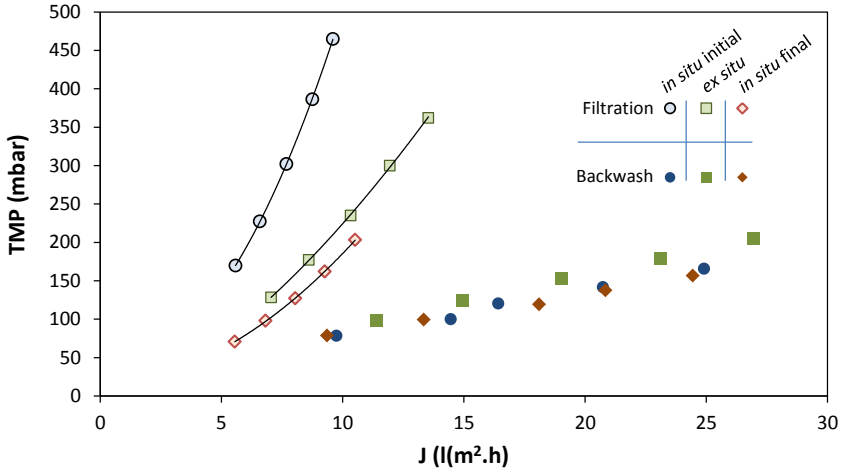

Figure 2. Resistance measurement in situ initial, before the membrane module was taken out for ex situ measurement, and in situ final, after the membrane module was replaced again.

It was confirmed that fouling resistance mesures performed ex situ with deionized water do not represent the effective resistance in the membrane bioreactor. On the one hand, permeate composition brings additional resistance and, on the other hand, membrane handling involves fouling detachment.

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Acknowledgements The authors gratefully acknowledge financial support provided by the Regional Government of Castilla y Leon (Ref. BU194A11-2) and the inestimable collaboration of Pepsico Iberia. C. Ramos is also grateful to Regional Government and European Social Fund (ESF) for his research personnel contract (PIRTU-2010).

EFFECT OF CYCLIC AERATION ON FOULING IN MEMBRANE BIOREACTORS FOR COSMETIC WASTEWATER TREATMENT

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The membrane fouling is a major obstacle for the wide application of membrane bioreactors (MBR) since the introduction of this technology. Air sparging is usually employed to mitigate fouling by constantly scouring the membrane surface. The tangential shear force generated by the air bubbling can prevent the deposition of large particles on the membrane surface. However, the tangential shear only has a limited effect on preventing the particle deposition of smaller particles [1]. Therefore, fine particles are preferentially deposited on the membrane surface in high aeration intensity MBR operation, resulting in a more compacted sludge cake, with high specific cake resistance. The cakes formed by fine particles are tightly attached to the membrane module and usually cause irreversible fouling. Sludge cakes formed under low aeration intensity are composed of more large particles, which are loosely attached and belongs to reversible fouling. The reversible fouling can be easily removed by physical cleaning, but irreversible fouling can only be removed by chemical cleaning. Under high aeration intensity, the shear force can break up the activated sludge flocs, causing the release of colloidal and soluble particles. In addition, high aeration reduces the cake layer formed on the membrane surface. With less protection from the cake layer, the membrane pore is more likely to be blocked by the soluble and colloidal particles. Due to the high energy cost and the irreversible fouling caused by the high aeration intensity, various works have reported about the aeration strategies [2]. Intermittent aeration, in which aeration is switched on and off alternatively has been previously studied, but the contradicting conclusions reported in previous studies make necessary to evaluate its effect in new cases. Therefore, the specific objective of this study is to investigate the influence of aeration intensity and cyclic aeration on the fouling behavior in a submerged MBR for cosmetic wastewater treatment.

A lab-scale MBR reactor (15 L) was inoculated with 8.6 $gVSS \cdot L^{-1}$ and operated during 140 days at room temperature. The MBR was operated at a constant SRT and HRT of 30 and 2.6 d, respectively. MBR was fitted with chlorinated polyethylene (PE) microfiltration flat sheet membranes (KUBOTA®) of 0.1 m^2 and a nominal pore size of 0.4 µm operated at a specific aeration demand (SAD) between 0 and 1.5 $m^3 \cdot m^{-2} \cdot h^{-1}$, and a constant permeate flux of 12 $L \cdot m^{-2} \cdot h^{-1}$ (LMH). Different aeration intensities were evaluated, working at different aeration times from 20 to 100% (constant aeration) and a constant SAD of 0.5 $m^3 \cdot m^{-2} \cdot h^{-1}$. The effect of the frequency of intermittent aeration cycles was also studied by applying different lengths of on:off aeration cycles from 1 to 30 min. For the sake of comparison, SAD and aeration time were kept constant at 0.5 $m^3 \cdot m^{-2} \cdot h^{-1}$ and 80%, respectively. To maintain the same air volume in these experiments, the duration of the runs was modified. Membranes were submitted to a three-step cleaning protocol to know more about the foulant layers distribution [3]. The critical flux was determined using the flux-step method purposed by Le-Clech et al. [4]. A step height of 2 LMH and a holding time of 20 min were chosen for the sake of comparison. Membranes were cleaned before of each critical flux test by soaking in 0.4%wt. sodium hypochlorite for 2 h range, achieving a permeability recovery of 90%. These tests were performed by duplicate to verify the results.

Fig. 1 shows the relationship between the critical flux and SAD. A high fouling rate was observed in the absence of air, which was partially mitigated by increasing the SAD. SAD values higher than 0.5 $m^3 \cdot m^{-2} \cdot h^{-1}$ did not lead to significant increases of the fouling rate and

critical fluxes about 12 LMH were obtained. Thus, the operation of the MBR at a SAD of 0.5 $m^3 \cdot m^{-2} \cdot h^{-1}$ is recommended for a cost-effective operation of the membranes.

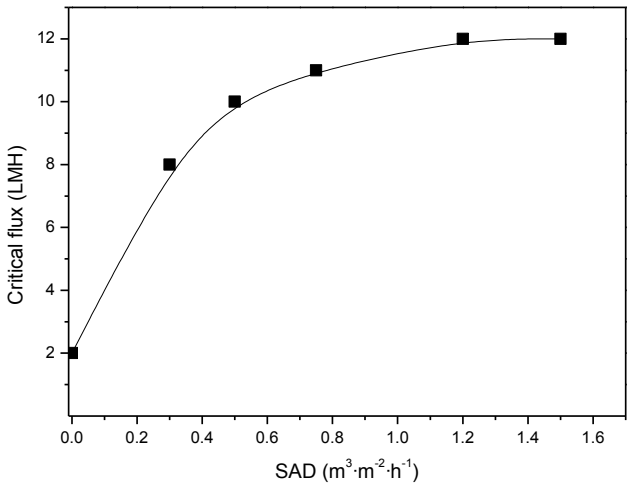

Fig. 1. Critical flux values obtained at different specific air demands.

Fig. 2a shows the evolution of TMP working at different aeration intensities from 20 to 100%. High aeration intensities led to an efficient control of fouling, which resulted in a negligible increase of TMP at higher intensities than 60%. As can be seen in Fig. 2b, the length of on:off cycles exerted an important effect over the TMP evolution. Cycles length of 15 min gave rise to an efficient control of TMP increase, which remain unaltered after 2 h. The formation of the cake layer was detected in the absence of air, reaching a filtration resistance of $2.2 \cdot 10^{13}$ m^{-1}.

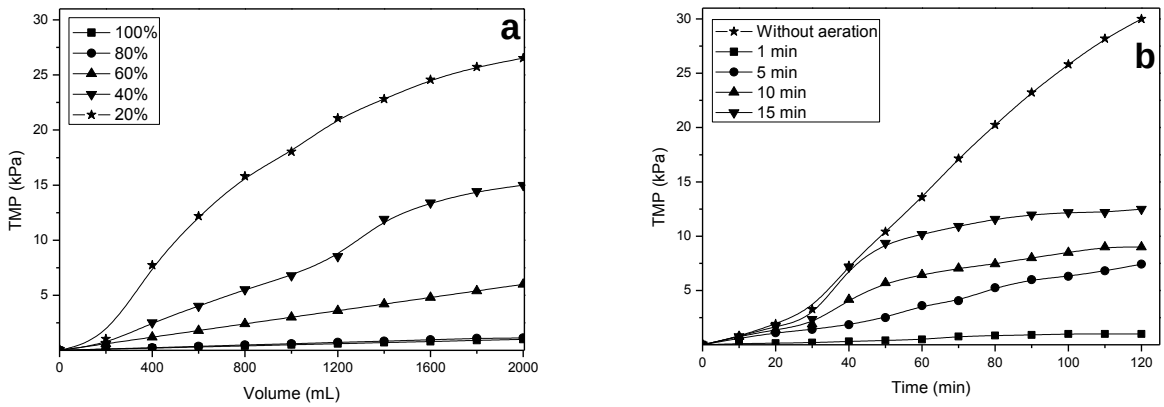

Fig. 2. Time-course of TMP operating at different aeration intensities (20 – 100%) (a), and different length of on:off cycles (0 – 15 min) at an aeration intensity of 20% (b).

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Acknowledgements The authors greatly appreciate financial support from the Spanish MICINN and CM (REMTAVARES) through the projects CTM2010–15682 and S2009/AMB-1588, respectively.

BIO-LUBRICANT PRODUCTION BY PERVAPORATION-ASSISTED REACTION

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The use of bio-lubricants has been an alternative to problems that results from the use of mineral lubricants. Today, approximately 50% of the waste lubricants are not properly disposed [1], causing pollution of soil, air, water and damage to many ecosystems.

Originated from plant raw materials, the main advantage of bio-lubricants lies in its biodegradability. In the raw material processing (lubricant precursor) industry, much energy is consumed in the reaction, separation and purification stages of products. For this reason, considerable effort has been devoted to the technology improvements to carry out these downstream process steps.

Promising bio-lubricant can be produced from the transesterification of castor oil biodiesel with trimethylolpropane (TMP) using a lipase from *Candida rugosa* as biocatalyst. However, the catalysts costs are still to be high to render the large-scale process viable. Knowing that transesterification is a reversible reaction, a pervaporation assisted- reaction was studied in this work, in order to shift the equilibrium by product removal, which in this case was methanol, aiming at the reduction of the catalyst usage.

Membrane separation processes has shown to be less consuming technology than conventional processes. A dense silicone (PDMS) membrane was selected to test films and hollow fiber separator coupled with the bioreaction. The effect of the molar ratio of the reactants and the level of water concentration on conversion time were evaluated. Permeate concentration was analized by Gas Chromatography (CG) and biodisel conversion was determined by Hight Performance Liquid Chromatography (HPLC).

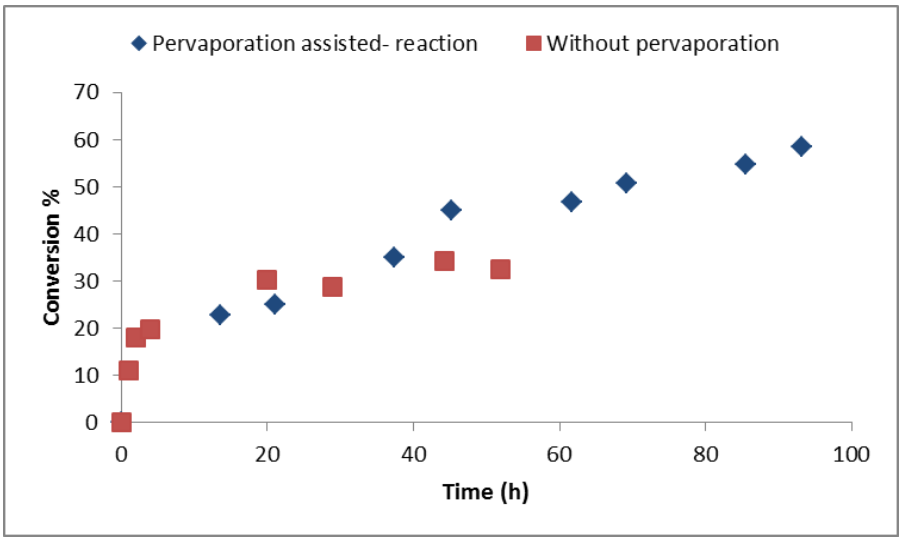

Figure1. Reaction biodiesel conversion with pervaporation and without pervaporation.

It was shown that keeping water concentration to 1% is required to maintain lipase activity. Methanol removal was affected by feed mixture mass transfer determined by system

viscosity and agitation. The improvement of coupling pervaporation can be demonstrated when a biodiesel conversion of 58% is obtained as compared to 33% of the equilibrium conversion according to Figure 1. It was possible to demonstrate that pervaporation assited-reaction is controled by its kinetics instead of its thermodynamics. This fact delayed the appearance of the equilibrium shifting for biodiesel conversion.

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Nutrient removal on sludge concentration by forward osmosis

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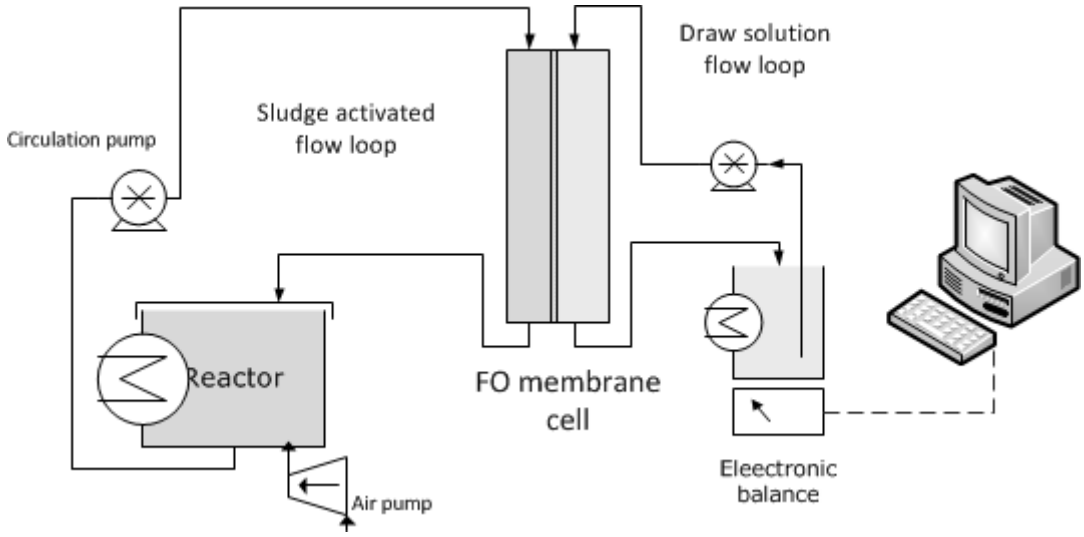
Conventional activated sludge process produces a large amount of high water-content sludge. Sludge dewatering is typically the final step for wastewater treatment plants (WWTP). The most common way to dewater sludge is to physically squeeze the water out of the sludge, including pressure filtration, belt press filtration, air drying, centrifugation and vacuum filtration. Although these conventional technologies are simple, major problems for application are that effluent of clarification process is difficult to achieve stringent regulations and sludge retention time (SRT) is long [1].

To address these problems different advanced methods have been proposed such asmicrowave irradiation, ultrasonication process, electro-dewatering technology, combining chemical conditions and filter and advanced oxidation process [2]. Although these methods may have high dewatering potentials, their application has been limited by problems such as high operation cost and secondary environmental pollution.

A novel process of sludge dewatering is forward osmosis (FO). FO is defined as the net movement of water across a selectively permeable membrane driven by a difference in osmotic pressure across the membrane. FO has been studied for a variety of applications such as volume minimization of sanitary landfill leachate, concentration of fruit juices, and desalting emergency water supplies for homeland security operations. The main advantage of using FO in water and wastewater treatment is the very low energy consumption rate, since no external pressure is required while rejecting a wide range of contaminants with possibly a lower membrane-fouling propensity than pressure-driven membrane processes have. The main challenges, however, exist in the manufacture of high performance FO membranes, the selection of easily separable draw solutions with a high osmotic pressure, and the optimization of process configurations to minimize concentration polarization (CP).

The aim of present work was focused on exploring the feasibility of applying FO to dewater a raw waste activated sludge from a WWTP, and simultaneously investigate the nutrient removal ability of this separation process.

The batch FO experiment setup for sludge dewatering is shown in next figure. The three major components of this setup are the cross-flow membrane cell, the draw solution flow loop, and the activated sludge flow loop. The draw solution flowed on the active layer of the membrane and the feed on the permeate side. Concurrent flow was used to minimize the shear force on the membrane. A flat-sheet cellulose triacetate (CTA) FO membrane from HTI OsMem with 34 cm^2 of effective area was used in all experiments. Draw solution (DS) was prepared by dissolving NaCl in deionized water (DI) to achieve 38±1 g/L, as a typical concentration of Mediterranean Sea. Besides, samples of activated sludge were collected at the secondary sedimentation tank of the WWTP located in the southern of Comunidad Valenciana in Spain. The sludge samples had a mixed liquor suspended solids (MLSS) concentration of 5200 mg/L, a mixed liquor volatile suspended solids (MVLSS) of 2500 mg/L and a soluble COD of 250 mg/L. Then in a reactor with a volume of 7 liters these raw sludge samples were added glucose, NH_4Cl and K_2HPO_4 solutions to produce synthetic sludge with different concentrations and a sludge retention time of ca. 20 days. For most testing conditions the temperature was controlled at 20±1.5 ºC, the cross-flow rate for the draw solutions was maintained at 4.0 L/min and the feed one was varied from 0.2 to 1 L/min.



The weight of draw solution was monitored over time by using an electronic balance in order to determine the volume of water transported through the membrane and to calculate the membrane flux. Following the time, sludge samples in reactor tank are collected to measure MLSS concentration and conductivity, while DOC, total nitrogen, NH_4^--N, total phosphorus and PO_4^{3-}-P were measured in the final flow of diluted DS. Every 24 hours of filtration through the membrane, the diluted DS was replaced by a fresh DS.

The research demonstrated the feasibility of applying FO on sludge concentration and provided high nutrient rejection. MLSS concentration reached 22,324 mg/L after 24 h from the initial MLSS concentration of 5200 mg/L. On the other hand, NH_4^-N removal was higher than of 95.8%, PO_4^{3-} -P of 97.5% and DOC of 99% in all FO tests.

The water flux evolution showed similar trends in all experiments, with a rapid decrease at the beginning followed by a smooth development. The highest water flux was observed with DI water (11.3 L/m^2 h) as feed solution. However, when activated sludge were used, the best water flux observed was 3.65 l/m^2 h. This flux reduction can be attributed to different issues such as membrane fouling caused by cake formation and concentration polarization at both sides of the membrane.

Hence, further studies in order to reduce membrane fouling are necessary; furthermore, the development of new draw solutions capable of increasing water flux would be convenient if the sludge dewatering process would be carried out on a larger scale.

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Acknowledgements (10 pt)

The authors gratefully acknowledge the support of Universitat Politècnica de València by the research program (PAID 05-12)

EFFECT OF PURE OXYGEN AERATION IN SUBMERGED MEMBRANE BIOREACTOR UNDER DIFFERENT MIXED LIQUID SUSPENDED SOLIDS CONCENTRATION

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Membrane bioreactor can used pure oxygen instead of air conventional to supplying oxygen to aerobic microorganism as an electron acceptor and keep the biomass in suspension. Besides the several advantages of pure oxygen, that specially include increased oxygen mass transfer, ability to treat high-strength wastewaters, reduced power requirements and improved biokinetics, some author has reported a positive impact in the fouling phenomenon when the MBR is operated with high dissolved oxygen concentration (Kim et al., 2006; Jin et al. 2006). In this paper, the performance of a Submerged Membrane Bioreactor operated with pure oxygen was evaluated with respect to membrane fouling under diferentt mixed liquid suspended solids concentration.

The study was carried out using four membrane bioreactor pilot-plants working in parallel and fed with synthetic effluent that was formulated to simulate petroleum refinery industry wastewater. Aeration was provided continuously by two fine bubble air diffusers. All reactors were made of fiberglass, with an effective volume of 203 L, with main characteristics showed in Table 1. Hollow-Fiber submerged ultrafiltration membrane modules, from Koch Membranes, were used for solid separation. Permeate was continuously withdrawn by a peristaltic pump operating with a cycle of 400 seconds of filtration and 30 seconds of backwash. Two operational conditions were established as function of Dissolved Oxygen (DO) concentration (2,0 mg O_2/L; Conventional Aeration CA; and 8,0 mg O_2/L; Pure Oxygen - PO) and two others as function of total suspended solids concentration (10 g MLSS/L - MBR_{10}; and 16 g MLSS/L – MBR_{16}). During role experiment the flow, transmembrane pressure, temperature, dissolved oxygen an pH were measured in real time and stored in a data logger. During steady-steady condition the influent and effluent wastewater characteristics were regularly monitory to COD, NKT, ammonia, nitrate, nitrite, and total phosphorus. Besides the monitoring of wastewater quality, were also characterized the sludge quality regarding Oxygen Uptake Rate (OUR), Soluble Microbial Product (SMP), Extracellular Polymeric Substance (EPS) and Time-To-Filter (TTF).

It took about 4 months (Figure 1) to attain steady state conditions in terms of Total Suspended Solids (16 and 10 g/l). Steady state conditions was reached on April, 4, 2012 and maintained for about two months. During this period the average solids concentration was maintained very close to the planned concentration for each pilot. The results shown (Table 2) that iMBR systems operated with DO concentrations above 7,0 mg O_2/L did not produce an effluent with statistically significant differences in relation to organic material (COD) nitrogen matter and total phosphorous. On the other hand the increase in DO concentration had a positive impact on the loss of permeability of membranes, characterized by the fouling rate, showing smaller fouling rates for systems operating with DO concentrations above 7.0 mg O_2/L. The filterability sludge test (TTF index) also confirmed better filterability condition for the sludge from the system PO-MBR, which showed values lower than five times those observed for the CA-MBR.

Table 1: Characteristics of each biological reactor during steady state period.

iMBR	MLSS[1] (g/l)	COD Load (kg/d)	F/M[2] (Kg COD/g.MLSS.d)	Sludge age (day)	DO (mg/L)
$PO\text{-}MBR_{10}$	10.6 ± 2.3	0.77	0.43	13	7.1
$CA\text{-}MBR_{10}$	10.8 ± 2.1	0.81	0.45	13	2.6
$PO\text{-}MBR_{16}$	15.6 ± 2.3	0.76	0.29	24	7.1
$CA\text{-}MBR_{16}$	15.5 ± 2.4	0.75	0.29	20	2.4

[1]Mixed liquor suspended solids;
[2]Food to microorganism ratio

Table 2: Characteristics of each biological reactor during steady state period.

Parameters	Inffluent	$PO\text{-}MBR_{10}$	$CA\text{-}MBR_{10}$	$PO\text{-}MBR_{16}$	$CA\text{-}MBR_{16}$	Unit
COD	842 ± 286	37 ± 72	51 ± 77	19 ± 72	26 ± 23	mg O2/L
NH_3-N	24.5 ± 7.7	2.5 ± 5.5	3.8 ± 5.9	2.5 ± 5.8	4.7 ± 7.5	mg N/L
NKT	41.6 ± 21.2	2.7 ± 3.6	7.8 ± 11.5	4.7 ± 4.2	7.4 ± 10.1	mg N/L
P-total	6.1 ± 3.5	2.0 ± 1.6	2.1 ± 1.6	2.1 ± 1.6	2.0 ± 1.5	mg P/L
SMP	-	12 ± 11	7.6 ± 6.2	11 ± 7.1	12 ± 17.4	mg COT/g SSV
EPS	-	30 ± 28	11 ± 7.1	29 ± 16	28 ± 17	mg COT/g SSV
TTF index	-	3.8 ± 2.2	11 ± 2.1	9.5 ± 5.1	48 ± 40	seconds/gMLSS
FR*	-	14.9 ± 1.3	15.4 ± 7.0	7.4 ± 3.0	15.8 ± 9.6	$L/m^2.h.bar.d$

*Fouling rate

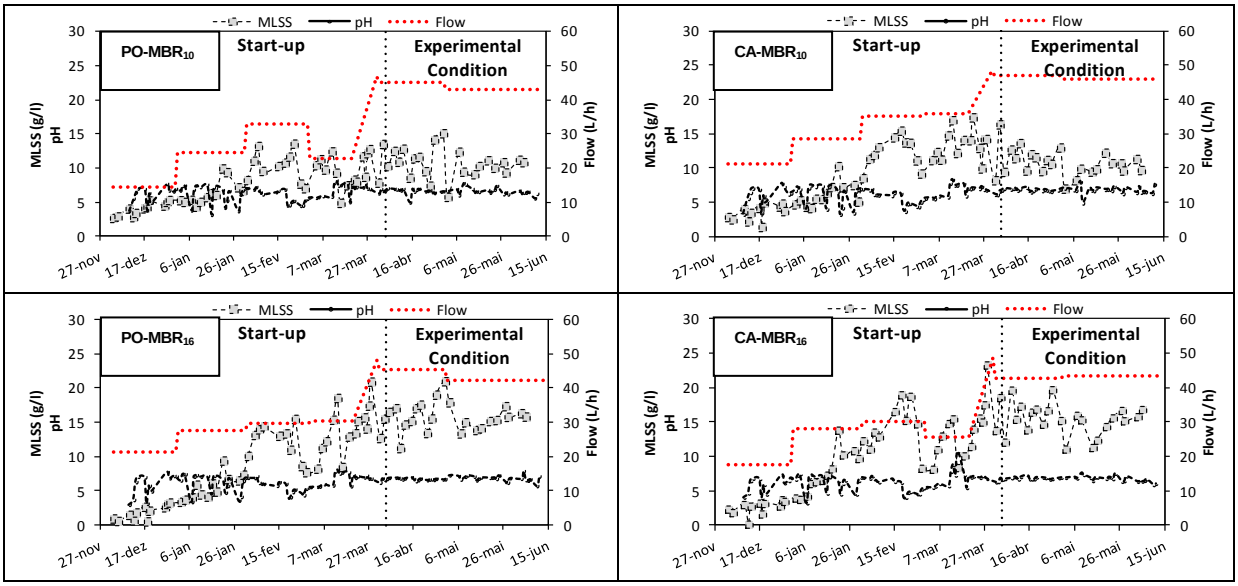

Figure 1: Temporal variation of MLSS, pH and flow during role experiment

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Acknowledgements

This work was suppported by a grant from the PRAXAIR In.

TREATMENT OF PHARMACEUTICAL INDUSTRY WASTEWATER IN AN ANAEROBIC MEMBRANE BIOREACTOR

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The pharmaceutical wastewater has high pollution potential with low biodegradability. Some studies have investigated the pharmaceutical wastewater in the literature and the biological treatment has been used in the most of these studies [1,2]. Conventional wastewater treatment processes are not sufficient for complete removal of pharmaceutical residues. Therefore, the removal of many of these pharmaceuticals during municipal wastewater treatment has been found to be incomplete due to their resistance against biological degradation [3,4]. Up to now, the advanced oxidation processes have been commonly examined to treat the pharmaceutical wastewater, but these processes are expensive and cannot be significantly applied to wastewater with high flow rates. Due to economic reasons, biologically treatment methods are indispensable in the treatment of strongly polluted wastewater.

While transformation of pharmaceuticals in the human body and in other mammals has been studied extensively, the microbial degradation of such compounds, its degradation pathways and products, have rarely been investigated and are largely unknown. In recent years, in parallel with developments in membrane technology and related knowledge increase; systems that membrane modules are submerged in biological systems – known as Membrane Bioreactor (MBR) were developed alternatively to conventional activated sludge systems. MBRs have an important place in domestic and industrial wastewater treatment especially due to the disinfection property. Anaerobic MBRs have received considerable attention in recent years because they offer high quality effluents efficiencies and complete retention biomass, regardless its settling and granulation proporties [5].

In this study, anaerobic treatability of etodolac chemical synthesis wastewater from pharmaceutical industry and removal of etodolac pharmaceutical active substance and metabolites are aimed. In this context, an Anaerobic MBR reactor was inoculated with granule sludge of an up-flow anaerobic sludge blanket reactor treating the beer industry wastewater (Figure 2). A flat sheet membrane module, had a total area of 66 cm^2. Microfiltration membrane with pore sizes of 0.05 µm (FM MP005- Microdyn-Nadir GmbH) was placed on the module. Firstly, the full characterization of the wastewater and Biochemical Methane Potential (BMP) tests were carried out for a better understanding of anaerobically degradation. Anaerobic MBR reactor was operated at pH:7, temperature: 35^oC, 4 L of reactor volume and infinite sludge retention time. Chemical Oxygen Demand (COD) was increased to 2500 mg/L, 5000 mg/L, 7500 mg/L, 10000 mg/L, and 15000 mg/L. Hydraulic retention times (HRTs) were determined as 12.0, 15.6, 22.9, 21.4 and 27.6 days, with increasing COD. Organic Loading Rate (OLR) values were also found as 0.21, 0.32, 0.47 and 0.54 kg KOİ/m^3.d. Fluxes were decreased with an increase in COD and fouling as 2.1, 1.6, 1.1, 1.18 and 0.9 L/m^2.h (Figure 2).

Etodolac and COD removals were found as 20-60% and 85-90% respectively. System performance was deteriorated with increasing COD to 15000 mg/L and COD removal rate decreased to 60%. Sulphite inhibition was likely the reason of the system deterioration.

Ozonation of the wastewater is suggested as pre-treatment for the effective operation of Anaerobic MBR reactor with wastewaters having high COD and sulphite concentrations.

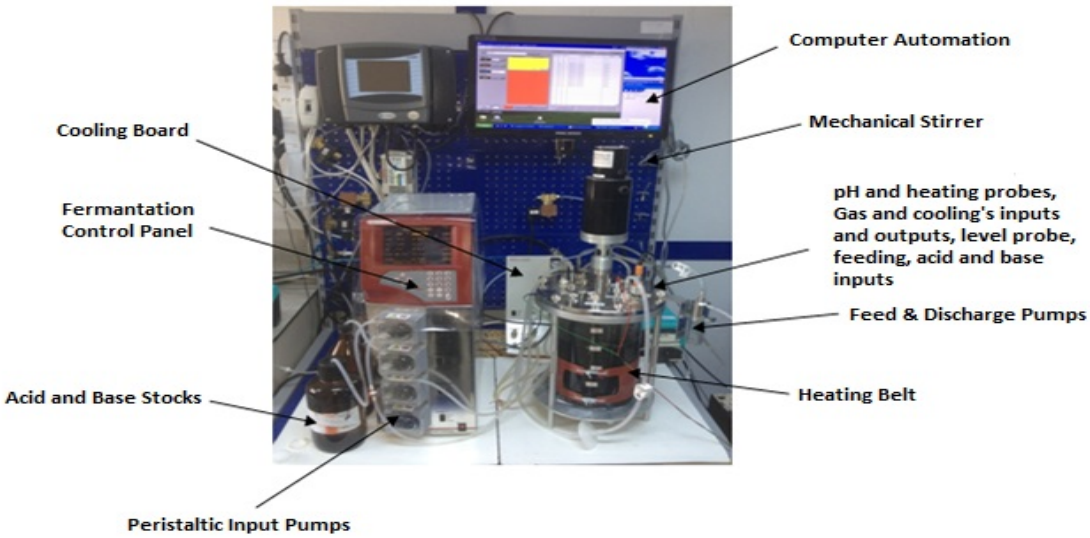

Figure 1: Anaerobic MBR reactor system

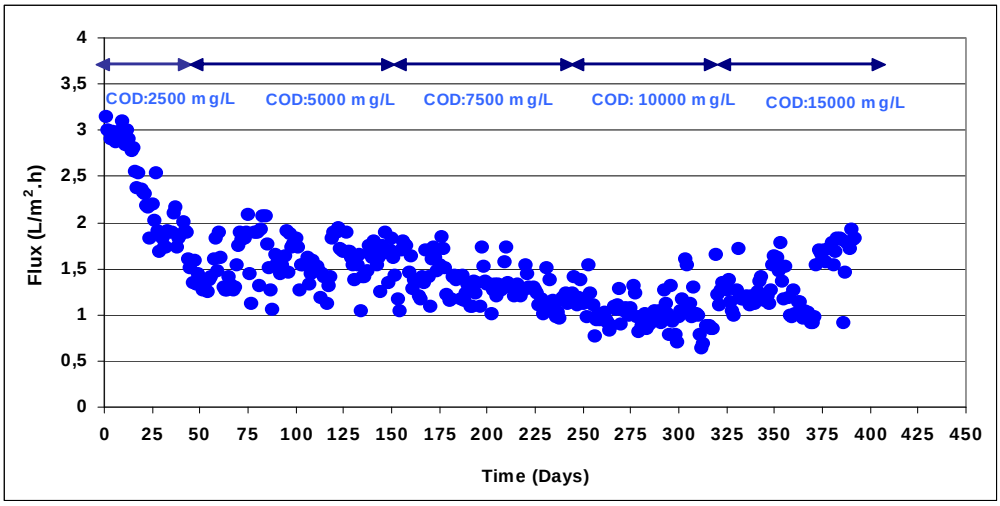

Figure 2: The flux decline during the operation anaerobic MBR reactor

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Acknowledgements

The work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK) under Grant no. CAYDAG-111Y078.

IMPROVING THE PERFORMANCE OF AN AEROBIC MEMBRANE BIOREACTOR (AMBR) WITH POWDERED ACTIVATED CARBON (PAC) ADDITION IN THE TREATMENT OF PHARMACEUTICAL WASTEWATER

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Wastewater from the pharmaceutical wastewater contains residuals of the synthesized pharmaceutical active matter, solvents and intermediates. Many of them can not be completely removed due to non-biodegradable and toxic matters in wastewater treatment plants therefore they are capable of entering into the environmental ecological cycle. As conventional water and wastewater treatment processes are unable to act as a reliable barrier towards some pharmaceutical wastewater, it is necessary to introduce and apply additional advanced treatment technologies [1]. Hybrid MBR processes including advanced oxidation processes ($UV/O_3//H_2O_2$) and adsorption processes (powdered activated carbon-PAC) are used to prevent pharmaceutical matters dispersion in the environment via incompletely treated wastewater. PAC in combination with MBR process increases the removal efficiency by adsorbing non-biodegradable, toxic and inhibitory organic matters [2]. The submerged membranes do not become clogged as almost all organics are removed by PAC and the role of the membrane is only to retain the PAC and other suspended solids. The energy requirement is very low and there is no major sludge problem [3]. In addition, membrane fouling is decreased by the addition PAC because some of the large molecular weight organic matters, which is responsible for the membrane fouling [4].

The aim of this work to introduce the removal of real pharmaceutical process wastewater belongs to production of etodolac pharmaceutical active matter by direct addition PAC into AMBR (hybrid PAC-AMBR system). The effects of organic loading rate (OLR) on the AMBR performance and membrane fouling on presence of PAC was also investigated at an infinite SRT. The membrane fouling was analyzed with Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and Fourier transform infrared spectroscopy (FT-IR) analysis. Extracellular polymeric substances (EPSs), soluble microbial products (SMPs), zeta potential and surface properties (hydrophobicities) were also preformed to explain their variation with OLR.

The wastewater used in this work was obtained from a pharmaceutical industry based on chemical synthesis manufacturing pharmaceutical active matter in Gebze, Turkey. The wastewater belonging to production of etodolac active matter was generated from equipment cleaning. The values of COD and etodolac was 18000 mg/L and 511 mg/L, respectively in the wastewater. The laboratory scale AMBR system schematically shown in Fig.1 was used in this study. The system made a cylindrical plexiglas, with a working volume of 7 L, was employed a submerged kestamid frame module. Polyethersulfone (PES) microfiltration membrane (FM MP005-Microdyn-Nadir GmbH) was used. A nominal pore size of membrane is 0.05 µm and the membrane module has an effective surface area of 74 cm^2. WAC i600 M200 (Eurocarb Products Ltd, Bristol, UK) was used as the PAC (pore size=200 mesh).

AMBR system was operated 3 different OLRs ranging from 1 to 2 kg $COD/m^3.d$ at infinite SRT of 145 days. The effect of OLR in the presence and absence of PAC was monitored. AMBR reactor was operated without PAC addition in (OLR: 1 kg COD m^{-3} d^{-1}) for 20 days. After 20 days, 2 g/L PAC was added to AMBR and OLR was increased gradually in the above operating conditions. PAC addition was repeated as 2 g/L for each time the OLR. As

seen in the Figure 2, flux decreased from 9 to 5 L/m^2.h during the 20 days (without PAC addition and OLR: 1 kg COD/ m^3.d). Flux increased to 14 L/m^2.h depend on PAC addition in the OLR 1 kg COD/ m^3.d. But, flux decreased to 8.2 L/m^2.h at the end of 30 days. When addition of PAC, flux reached to 5.5 L/m^2.h in the OLR 2 kg COD/ m^3.d.

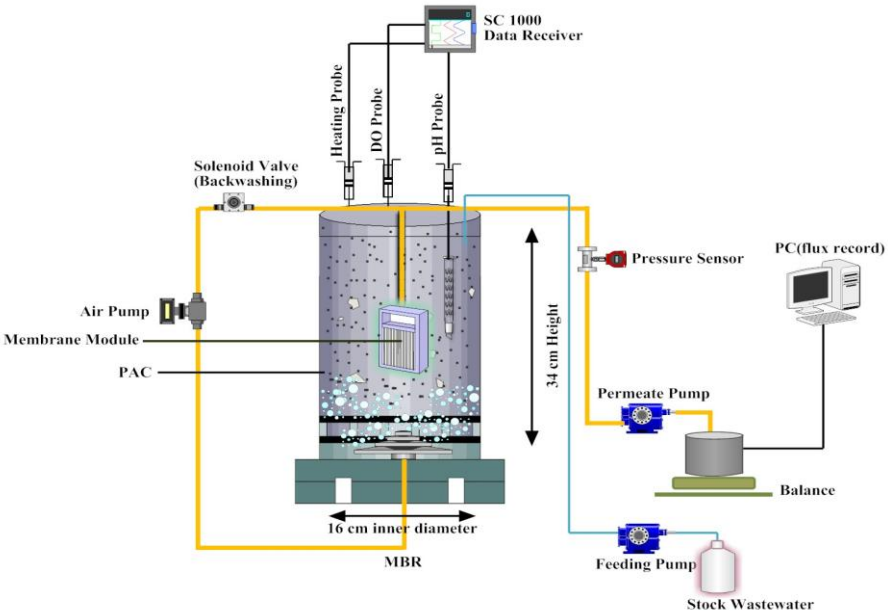

Figure 1: Schematic diagram of hybrid AMBR-PAC system

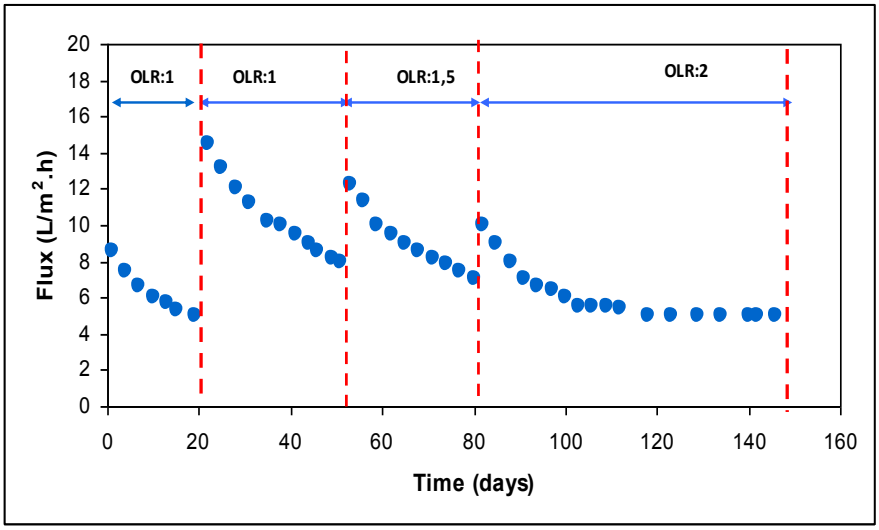

Figure 2: Flux decline in AMBR-PAC system for different OLR values

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Acknowledgements

This work was supported by the Research Fund of the Istanbul University (Project number: 4239).

Morphological characteristics of the flocs and microfauna populations evolution during the adaptation of biomass in a Submerged Membrane Bioreactor

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Introduction.- The BRM constitute a technology that can achieve very low effluent concentrations, facilitating reuse given the quality of the treated water, completely free of suspended particles and low amount of pollutants in soluble form [1]. Large numbers of studies have been focused at the filtration process of MBR [2], however has not been fully studied the biological aspects, in special with microfauna populations and floc´s morphology. Although recent research haven´t found a clear relationship between microfauna populations at steady state with the depuration and filtration efficiency of a MBR, if could be related with processes of stabilization and adaptation of the biomass. On the other hand, the morphological characteristics of the flocs and the filaments abundance have been related with the efficient in the filtration process.

Objective.- This work studies the floc´s morphology and the microfauna populations of the biomass, during its adaptation process to the MBR operational conditions, and its relationship with soluble microbial products (SMP), by their importance with the performance of the filtration process.

Materials and methods.- A laboratory scale MBR was used and it was operated for 110d until get MBR operation conditions. The reactor was inoculated with activated sludge from a traditional wastewater treatment plant and was feeded with acetate´s based substrate with a ratio C/N/P of 150/15/1. The reactor, with a volume of 70l, was operated at pH = 8 ± 0.3, T = 20 ± 1°C and DO ≥ 2 mg/L; the microfiltration module is made of PVDF, with pore diameter of 0.14µm, preventing the membrane fouling by hydrodynamics forces. Were followed the operation parameters: COD, SSV, depuration efficiency (Ef.) and mass organic load (CO). It was determined average size, form, structure and firmness from the flocs, and counts from the microfauna groups in the biomass were made and their relative abundance (AR) was calculated.

Results.- The results show that the biomass adaptation could be divided in two phases: (i) Adaptation phase, where the reactor showed low Ef., and a more pronounced decline in the CO, also increased production of SMP represented by the $COD_{soluble}$ in the reactor, that was corresponded by lower magnitude increments in the $COD_{permeate}$, in this phase were observed dominant populations of sessile ciliates (up to 05% of AR), this agrees with the found in conventional activated sludge systems in periods of instability or adaptation [6,7]; (ii) Stabilization phase, where the reactor showed a better Ef.(Fig. 1), with a stabilization of CO which presented an asymptotic behavior and $COD_{soluble}$ lower one without being corresponded by $COD_{permeate}$. In this phase were observed two consecutive dominant populations: crawling ciliates (up to 65% of AR) and then testate amoeba (up to 73 of AR).

The flocs´s morphological characteristics were related with the observed phases in the reactor, showing in the adaptation phase (i) a low flocculation process where the flocs lost cohesion forming weak dispersed units releasing soluble particles and macromolecules in suspension represented by $COD_{soluble}$; during the stabilization phase (ii) existed a tendency to enhance the flocculation process.

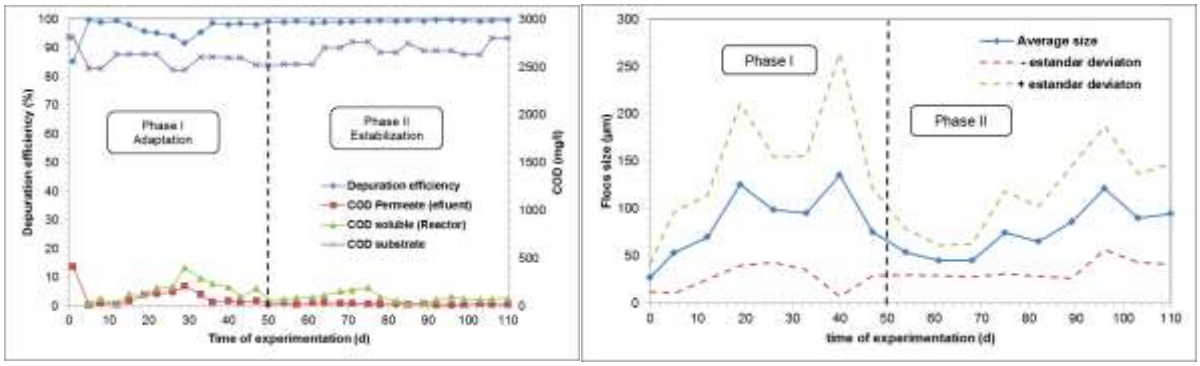

Fig. 1: Depuration efficiency vs $COD_{soluble}$ and $COD_{permeate}$(left). Average floc size (right)

The flocs´s size increase during the adaptation phase, at the beginning of the stabilization phase the flocs´s size decreased and was observed a most uniform floc size (i.e. the standard deviation decreased). The decreasing of the flocs size coincides with the increment of rotifers populations, as well as a lower $COD_{soluble}$ one. The rotifer populations and have been associated with changes in morphology fllocs [8] and for their feeding habits.

Conclusions.- The results show that the adaptation process of the biomass to MBR operation conditions is divided in two phases: Adaptation phase where exists a low depuration efficiency and an increase in the production of SMP; and the stabilization phase, where show a stabilization of the operational parameters, better depuration efficiency and a lower SMP production. These phases were related with the morphological characteristic of the flocs and microfauna populations. The understanding of the adaptation and stabilization processes will allow to design better operational strategies that improve the depuration efficiency and prevent the production of foulant particles (SMP) for increase the performance of the filtration process.

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Acknowledgements

Authors thakns to the University of Montpellier 2 for the membrane module donation. First author thanks CONACYT for the postgraduate scholarship.

Inorganic Membranes

- **Oral session 5**

PALLADIUM MEMBRANES FOR HYDROGEN SEPARATION AND MEMBRANE REACTORS.

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Global interests in developing the hydrogen economy are generating an important research activity for optimization of hydrogen production processes. Due to the high hydrogen flux and exclusive perm-selectivity, palladium (Pd)-based membranes have received a growing interest for the separation and purification of hydrogen as well as in catalytic membrane reactors in hydrogen-related reactions such as methane steam reforming (MSR) or water gas shift (WGS).

Pure Pd membranes are often damaged by hydrogen embrittlement due to the α-β phase transition of palladium hydride which occurs at below the critical temperature (293 °C) and pressure (2 MPa). This phase transition is accompanied by a considerable lattice expansion (ca. 3.5%) and the resulting internal stress generates defects. Resistance to the embrittlement of palladium membrane can be improved by alloying with silver and controlling the palladium particles as nanometer size [1-3]; Fig 1 shows a thin Pd supported membrane and a pore filled (PF) membrane (dark); in the PF type, nanosize Pd particles areg cloged in the nano-porous of a ceramic support.

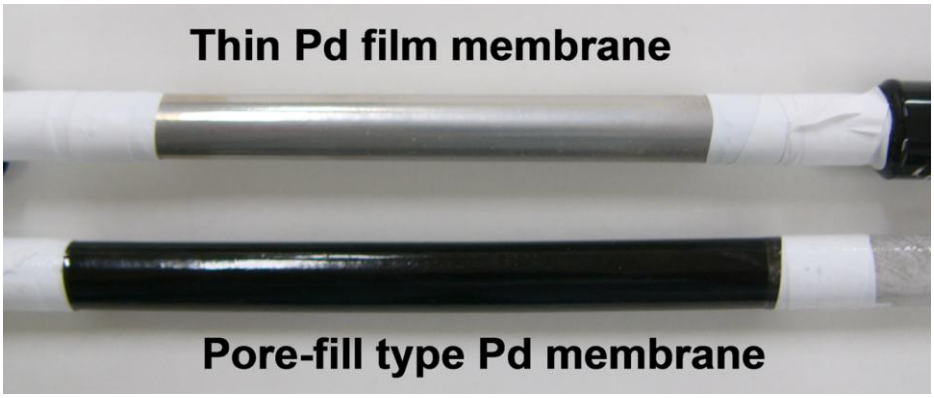

Fig. 1.- Soported and pore filled Pd membranes.

Since the permeation flux is inversely proportional to the membrane thickness, development of supported membranes with a thickness of less than 5 μm have been intensively studied in order to attain high hydrogen flux and to minimize the material cost. The choice of support is of critical importance in the preparation of thin and defect-free palladium membranes. Surface roughness and the presence of large pores inhibit the deposition of thin palladium membranes. The porous supports can improve the mechanical strength of thin palladium membrane but they may impose resistance to hydrogen permeation particularly when the pore size is very small. Commercial porous ceramics with asymmetric configuration are often used as the support. It is important to consider the thermal compatibility of Pd and the supports for practical applications in hydrogen recovery using Pd membranes carried out at the temperature of more than 650 °C [4] . One of such examples is hydrogen recovery from methane reforming gas, where the reaction is highly endothermic and requires elevated temperature i.e., more than 600 °C [5].

In this presentation, recent advanced in the preparation of supported Pd-alloy membranes will be presented; in addition, the application of membrane reactors for hydrogen production will be discused.

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Acknowledgements

The author would like to thank to People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement n° 267200.

MFI ZEOLITE MEMBRANES: PREPARATION AND CHARACTERIZATION

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In the last years, zeolite membranes have attracted a lot of interest in industrial and academic fields owing to their crystalline structure and to their uniform pore diameters close to molecular size of different species. Considering these characteristics, they can be used in many liquid and gas separation processes. Besides, for their high thermal and chemical stability, they can also replace polymeric membranes in applications that require strong operating conditions like high temperature and presence of aggressive organic solvents [1]. The high costs and poor reproducibility in the synthesis step represent a limiting factor for their development at industrial level. Until now, only LTA and T zeolite membranes were commercialized for organic solvent dehydration by pervaporation and permeation processes [2].

Self-standing zeolite layers are difficult to synthesize, therefore zeolite membranes are usually prepared on porous supports of alumina or stainless steel [1]. The most common methods for their preparation are the *in situ* and the secondary growth. The last one consists of two different steps: seeding and growth of zeolite crystals on the support. Decoupling zeolite nucleation from crystals growth, it is possible to control the conditions of each step independently and thus to obtain a higher reproducibility compared to the *in situ* method. Different seeding procedures are used to cover the support with crystals and the more controllable one is represented by the filtration of a zeolite aqueous suspension through the support [3]. In particular, the cross-flow mode, combining support tilting and rotation with the filtration, allows a more uniform and homogeneous coverage with zeolite seeds when membranes are prepared on tubular supports [4, 5].

In the present work, supported MFI zeolite membranes were synthesized by secondary growth method. For the first time the new cross-flow seeding procedure was employed for the preparation of membranes having this topology. The influence of several seeding parameters (support pore size, crystals pore size and zeolite slurry concentration) was studied to optimize the membranes quality.

After the synthesis, the membranes are gas tight. The synthesis was carried out in presence of the organic template, therefore, calcination was required in order to remove it. Membrane post treatments like new cross-flow and dip coating with polydimethylsiloxane [6] were also performed with the aim to seal the membrane defects due to the calcination step.

Morphology of the zeolite layer was evaluated by scanning electron microscopy, while, crystal topology was examined by X-ray diffractometry.

Furthermore, transport properties like flux and selectivity were also investigated before and after calcination by permeation tests of single gases and pure water and by direct contact membrane distillation in order to evaluate the membranes performance and their potential applications in different membrane processes.

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Acknowledgements
The authors gratefully acknowledge the support of the King Abdulaziz City for Science and Technology (KACST) for funding the research Project 895/33 entitled “Preparation and Characterization of Zeolite Membranes for Water Treatment”.

STUDY OF TWO METHODS IN THE PREPARATION OF ZEOLITE MEMBRANE (ZSM-5/ALFA-ALUMINA): RUBBING AND DIP-COATING

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Introduction

supported zeolite layers have attracted intensive research efforts due to their potential applications as separation membrane, catalytic membrane reactor, chemical sensor, electrode, opto-electronic device, low dielectric constant material for use as electrical insulator, protection or insulation layer or as host for the organization of functional guest molecules [1]. Zeolites are crystalline microporous aluminosilicates. It is built up by a three dimensional network of SiO_4 and AlO_4 [2]. This paper reports the synthesis of zeolite ZSM-5 membrane using two different methods of secondary growth: rubbing and dip-coating. Zeolite ZSM-5, porous support (α-alumina) and zeolite membrane were characterized by X ray Diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

Support preparation: Home-made α-alumina disks: Support disks were prepared by pressing commercial α-Al_2O_3 powder (Almatis) in a custom-made mold with the aid of a hydraulic press (4 tol), followed by sintering at 1200 °C for 1 h. **Membrane preparation: Synthesis of zeolite membrane ZSM-5/α-Al_2O_3 – Rubbing:** In this method an amount (0.5 g) of ZSM-5 zeolite was rubbed (sown) on the surface of the ceramic support. This membrane precursor was then immersed in a clear mixture having the following composition: 1.0 SiO_2:0.4TPAOH: 27,6H_2O was then placed inside teflon-lined stainless steel autoclaves and hydrothermally treated at 175 ºC for 70h. **Synthesis of zeolite membrane ZSM-5/α-Al_2O_3 – Dip-coating:** In this method the surface of the ceramic support was seeded using a dispersion containing 5% of seeds of zeolite ZSM-5. The support was immersed in this dispersion for a period of 1 minute and then dried at 60 °C/min. This procedure was repeated three times. This membrane precursor was then immersed in a solution having the following composition: 1.0 SiO_2:0.4TPAOH: 27,6H_2O, was prepared for the synthesis of zeolitic membrane. It was then placed inside teflon-lined stainless steel autoclaves and hydrothermally treated at 175 ºC for 70h. **After synthesis - drying and calcinations:** The supported membranes were removed from the synthesis solution after 24 h and 60ºC of synthesis of membrane zeolite rubbing and dip-coating, thoroughly washed with distilled water and then heat treated in air at 550ºC for 20h. **Characterization: XRD:** The X-ray diffraction (XRD) measurements were performed in a Shimadzu XRD-6000 equipment with Cu Kα radiation (40kV, 30mA) in the 2θ range of 2.0°– 50°. **SEM: the samples were** covered with a thin layer of gold and the powder samples were fixed in the alumina sample holder by an adhesive carbon tape. The micrographs needed to analyze the morphology of the samples were obtained through a scanning electron microscope Philips XL 30 EDAX.

Results

The XRD patterns of the samples are shown in Figure 1.

Figure 1. Diffractograms of the samples synthesised (A, B, C and D) and calcined (a, b, c, d): (A/a) porous support (B/b) zeolite ZSM-5 (C/c) ZSM-5/membrane Rubbing (D/d) ZSM-5/membrane Dip Coating.

The diffraction pattern of the zeolite membrane (ZSM-5/α-alumina) is a combination of the XRD patterns of the porous support and the powder of the zeolite particles. A comparison with a standard powder diffraction pattern of (MFI) [3] confirms that the zeolite layer on the support consists of pure ZSM-5 zeolite. The heat treatment (calcination) provided evidence that there were no changes in the structure of the zeolite membrane (ZSM-5/α-alumina) for two methods (rubbing and dip-coating).
Representative SEM images of the samples are shown in Figure 2.

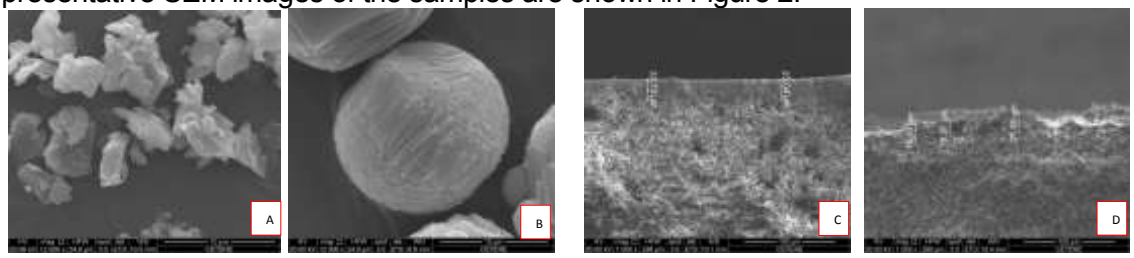

Figure 2. Micrographs: (A) porous support and (B) zeolite ZSM-5 (C) ZSM-5/membrane Rubbing and (D) ZSM-5/membrane Dip Coating.

The micrographs (Figure 2A) show a typical structure of the support α-alumina with particles agglomerated and uniforms in size. The results (Figure 2B) show that the samples consist of clusters and/or aggregates of crystals, presenting a hexagonal shape, characteristic of ZSM-5 zeolite. The presence of amorphous phase is not detected on the surface of the crystals, in agreement with the results found in the literature [4]. It can be seen (Figure 2C) that the growth of ZSM-5 seeds on the porous α-alumina support results in an apparently continuous polycrystalline ZSM-5 layer (≅ 23μm thick). The cross section view (Figure 2D) shows the formation of a heterogeneous ZSM-5 layer (≅ 21.86, 18.37 and 16.33μm thicks) and observed the formation of an interface porous support/zeolitic film and the morphology of the support itself.

Conclusions

Zeolite membrane (ZSM-5/α-alumina) have been prepared by rubbing and dip-coating methods. The XRD results confirm the successful formation of the zeolite membranes by two methods, but rubbing method showed more crystalline and XRD patterns of the zeolite layer more homogeneous than dip-coating method.

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Acknowledgements

The authors would like to make special acknowledgements to Petrobras for their financial support.

Desempenho de um Sistema com Automação para Processos de Separação com Membranas Cerâmicas

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A água produzida (AP) é a água aprisionada nas formações subterrâneas que é trazida à superfície juntamente com petróleo e gás durante as atividades de produção desses fluidos. Entre os aspectos da AP que merecem atenção estão os seus elevados volumes e a complexidade da sua composição. Esses aspectos fazem com que o gerenciamento da AP requeira cuidados específicos, não apenas relacionados com aspectos técnicos e operacionais, mas, também, os ambientais. Como consequência, o gerenciamento da AP resulta em custos consideravelmente elevados e que representam um percentual significativo dos custos de produção [1]. Atualmente, os campos da Bacia de Campos produzem 1 barril por dia de água para cada barril de petróleo produzido. Esta relação é inferior à média mundial obtida na literatura de referência (Instituto Francês de Petróleo E Society of Petroleum Engineers), que aponta para valores entre 3 e 5 barris de produção de água para cada barril de petróleo produzido [2]. O presente trabalho avaliou o desempenho um sistema automático para processo de separação por membranas cerâmica (PSM), mais especificamente membrana cerâmica de alumina com tamanho de poros de 1μm, no tratamento de águas oleosas. O trabalho foi dividido em duas etapas: testes em escala de bancada e em escala piloto. Nos testes em escala de bancada foi realizado dois ensaios, o primeiro para determinar o fluxo do permeado com água dessalinizada, como mostra a figura 1. O segundo ensaio foi realizado com efluente sintético (emulsão), nos testes com efluentes sintéticos realizou-se a estabilização das emulsões a partir de um emulsificante em função da concentração de óleo. As bateladas em escala de bancada foram realizadas em fluxo cruzado (cross-flow), e sem o auxilio de um sistema de limpeza para mostrar a influência do óleo na obstrução dos poros, com isso, diminuído o fluxo do permeado como pode ser observado na figura 2. Para os experimentos de bancada foram definidos os seguintes parâmetros: pressão 3kgf/cm^2, a concentração da emulsão óleo/água foi fixada 100mg/L, o STD e SST é aproximadamente 5.000 e 250mg/L, respectivamente. No teste em escala piloto foi avaliado o desempenho do sistema automático em função da eficiência da membrana cerâmica no tratamento de águas oleosas. A batelada no sistema automático teve como agente de limpeza a injeção de *Ar comprimido* no sentido contrário ao do fluxo de permeação (*backpulse*) no intuito de remover o óleo na superfície e no interior dos poros da membrana, e obter a recuperação no fluxo do permeado. A batelada no sistema piloto obedeceu às mesmas características do experimento de bancada no que se referem aos parâmetros pressão, concentração da emulsão óleo/água, STD e SST. Contudo, para o sistema piloto foram fixadas algumas variáveis de processo: pressão de *backpulse* 2kgf/cm^2, intervalo entre limpezas e tempo de duração das mesmas foi de 15min e 10s, respectivamente. O desempenho do sistema automático para processos de separação com membranas cerâmicas pode ser observado na figura 3.

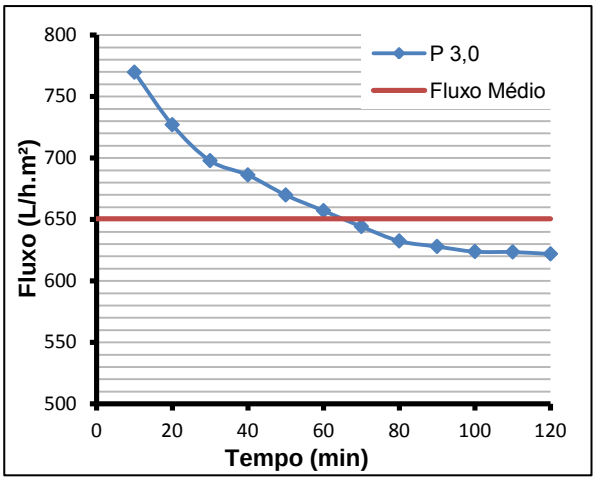

Figura 1: Fluxo permeado da membrana de alumina em função do tempo. Ensaio realizado com água dessalinizada, para uma pressão 3kgf/cm^2.

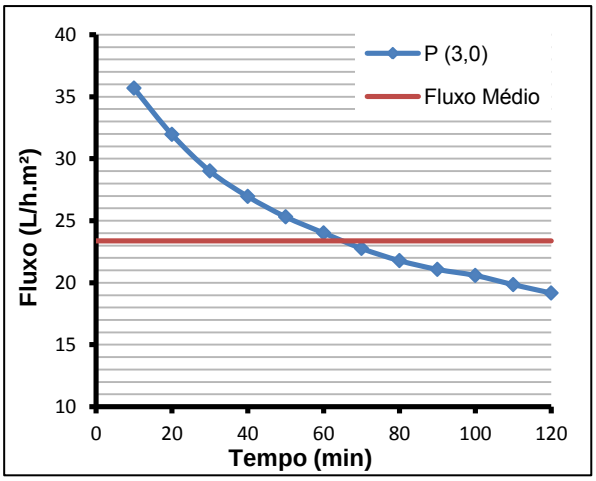

Figura 2: Fluxo permeado da membrana de alumina em função do tempo. Ensaio realizado com emulsão óleo/água concentração de 100mg/L, para uma pressão 3kgf/cm^2.

Na figura 1 verifica-se a queda do fluxo com água pura este comportamento se deve a hidratação da membrana, uma vez que a membrana tem uma superfície hidrofílica, camadas de água adsorvem fisicamente nesta superfície provocando uma redução no fluxo permeado. Após este fenômeno o fluxo tende a estabilização a partir de 90min.

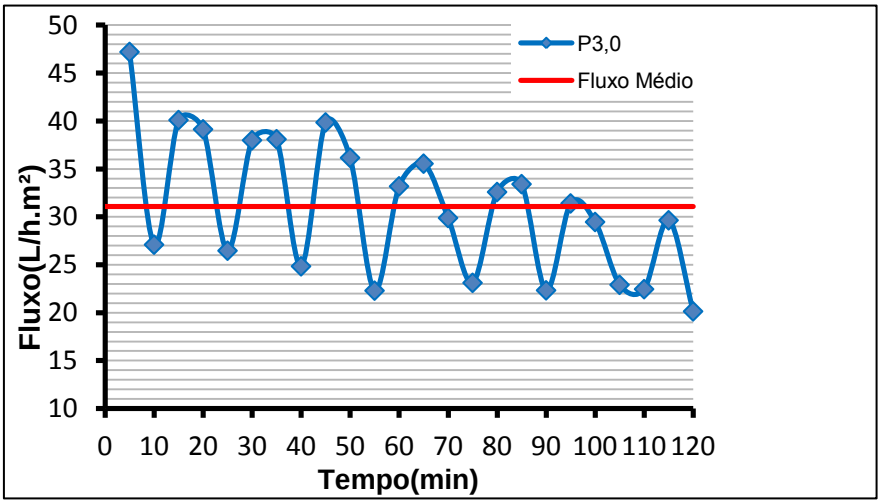

Figura 3: Experimento realizado com sistema piloto mostra a influência do *backpulse* no fluxo do permeado em função do tempo, considerando que o intervalo entre as limpezas foi de 15min e a duração de cada limpeza foi fixada em 10s, e tendo como agente de limpeza *Ar comprimido.* Experimento realizado com emulsão óleo/água concentração de 100mg/L, para uma pressão 3kgf/cm^2.

Pode-se observa na figura 2 a influência do óleo na queda acentuada do fluxo do permeado, comparando o fluxo médio dos ensaios de bancada podemos verifica uma redução de aproximadamente 90% do fluxo. Na figura 3, mostra embora ocorra a redução do fluxo do permeado, o *backpulse* proporcionaou uma recuperação no fluxo de aproximadamente 25%. Isto mostra que o sistema automático para processos de separação com membranas cerâmicas, e tendo com agente de limpeza a injeção de *Ar comprimido* é eficiente na estabilização do fluxo permeado.

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Ceramic nanofiltration membranes in chemical and pharmaceutical applications

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Ceramic membranes for microfiltration and ultrafiltration are state of technics since decades. Since nearly six years, Inopor GmbH has enlarged the field of applications for ceramic membranes by inventing ceramic nanofiltration membranes into the market. Actually, Inopor GmbH is the only supplier delivering ceramic nanofiltration membranes with a cut-off range of 450 Dalton. With that membrane, the advantages of a ceramic membrane, like e.g. chemical and thermal stability, are combined with a very low cut-off range.

Actually, the ceramic nanofiltration membranes of Inopor GmbH are already used in many applications and the range of applications is still growing. Typical applications for this membrane are:

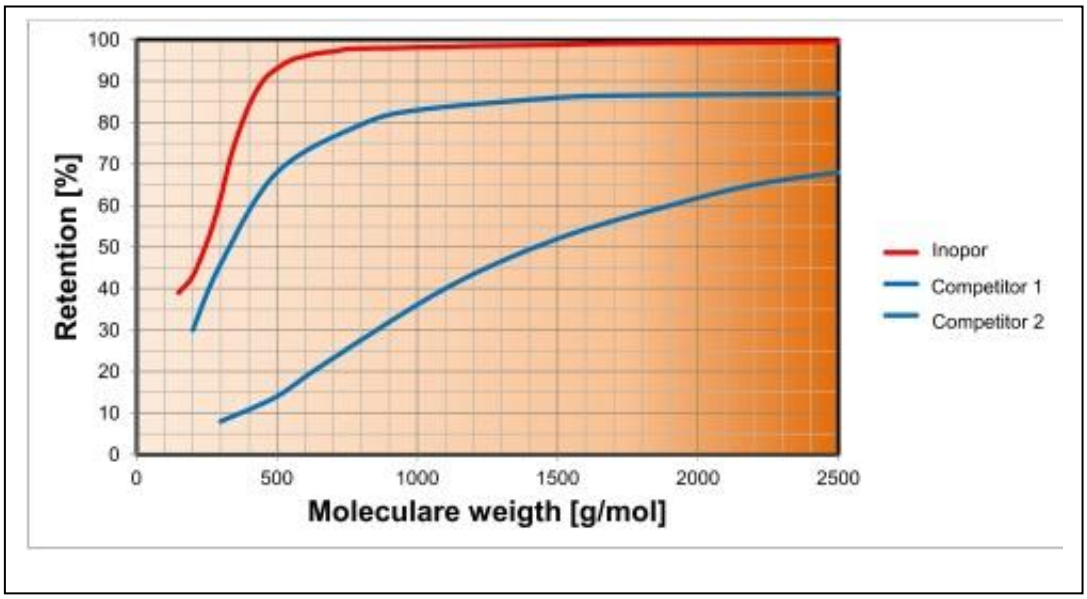
- Production of inuline
- Production of isocitric acid
- Production of acetic acid
- Various treatments of milk and milk derivates
- Separation of peptides
- Cleaning of acids and caustics

For example, combined with other membrane processes, it has been shown, that acetic acid can be produced with Aceto Bacter bacteria, cleaned up with ceramic nanofiltration membranes and concentrated with further membrane processes up to 30% .

Another typical application is the separation of pharmaceutical products out of waste waters; it has been shown, that waste water can be treated in a very effective way with ceramic nanofiltration membranes; further more trials all around the world are running.

Another application, which was developed by Inopor with partner companies is the separation of peptides out of organic solvents.

Inopor GmbH is a supplier and manufacturer of ceramic membranes, located at Veilsdorf (Germany). All membranes are produced by Inopor GmbH at Veilsdorf; typical material for membranes and membrane supports are TiO_2 and Al_2O_3, as well as ZrO_2 and SiO_2.



Pic 1.: Cut-Off range of Inopor ceramic nanofiltration membranes

Inorganic Membranes

- **Poster session 1**

Análise do comportamento de membranas cerâmicas para a filtração de vinhos brancos

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Com o desenvolvimento crescente na área de tecnologia de membranas, novos usos para estas estão ganhando espaço nas indústrias vinícolas. Por um lado, para se obter produtos com características aceitáveis pelo consumidor e que sejam viáveis às indústrias, há a necessidade de se ter materiais filtrantes cada vez mais resistentes, com durabilidade que permita uma vazão contínua, com custo baixo e ao mesmo tempo mantenha as características organolépticas e físico-químicas dos vinhos inalteradas durante o processo de filtração. Por outro lado, a questão de se produzir alimentos e bebidas com o conceito de alimento seguro, tem levado a utilização de membranas cerâmicas pelas indústrias vinícolas para se obter vinhos livres de leveduras e, em alguns casos, isentos de determinadas bactérias em função da porosidade que as membranas podem apresentar [1, 2]. As membranas cerâmicas despertam um maior interesse, pois apresentam algumas vantagens quando comparadas com as poliméricas, como: alta inércia química frente a ambientes agressivos (tanto ácidos como básicos), resistência a altas ou reduzidas temperaturas, vida útil mais longa, facilidade de limpeza, entre outras vantagens [3-5].

Materiais e Métodos

Neste trabalho são analisadas as propriedades de membranas cerâmicas tubulares de α-alumina, produzidas pela TECNICER do Brasil Ltda. As membranas cerâmicas tubulares monocanal foram testadas para uso na filtração de vinho branco. O sistema foi mantido entre 20 ±0,5°C, em uma planta piloto de microfiltração e pressões de 0,5 a 3,5 bar.

Resultados

Foram avaliados os fluxos de permeado para o vinho branco em diferentes pressões, como é mostrado na Figura 1, onde é possível verificar que a pressão de 0,5 bar apresenta valores de fluxo semelhante à pressão de 3,5 bar, sendo que em menores pressões o volume de permeado permanece constante por mais tempo, ocasionando variação no período de tempo avaliado. Fato que se for observado nas demais pressões, o declínio do fluxo de permaeado é muito mais acentuado no mesmo intervalo de tempo.

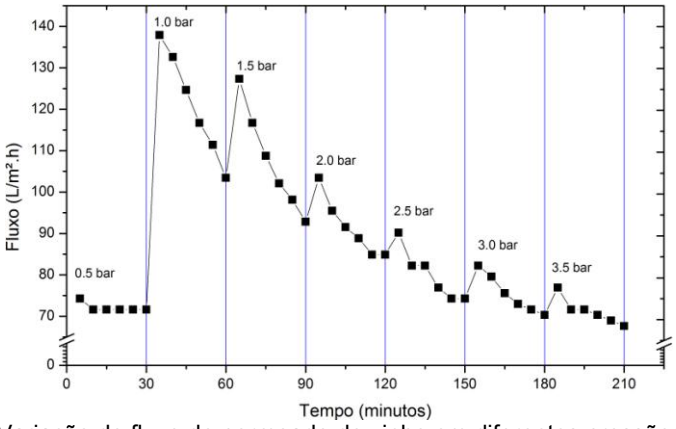

Figura 1: Variação do fluxo de permeado de vinho em diferentes pressões e tempo.

Foi avaliada a diferença no valor do fluxo de vinho permeado de acordo com o período de compactação da membrana que antecede a filtração, ou seja, 24 horas antes e 3 horas antes (Figura 2).

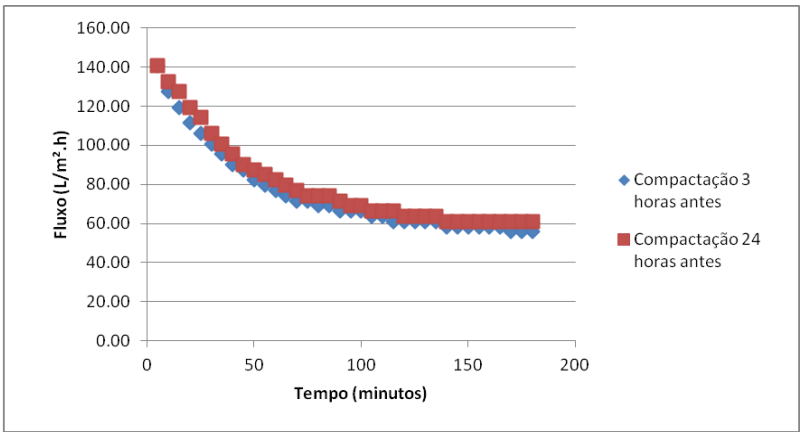

Figura 2: Fluxo de vinho permeado em função dode acordo com o período de compactação da membrana.

É possível observar na Figura 2, que a compactação da membrana por um período 24 horas antes da utilização da membrana permite o aumento do fluxo de vinho branco permeado em aproximadamente 3% em 180 minutos.

O fluxo de permeado diminui, consideravelmente, com o tempo de processamento em todos os ensaios realizados, tornando estável a partir de 120 minutos. Este comportamento pode ser atribuido à matriz complexa do vinho após a fermentação alcoolica, a qual possui moléculas de soluto como ácidos orgânicos, sais, polifenóis, bem como, colóides e partículas de tamanho consideraveis como leveduras, precipitados orgânicos e restos celulares [6].

Em ambos ensaios de compactação, a turbidez inicial do vinho, 620 NTU, foi reduzida para valores inferiores a 0,40 NTU, o que indica um produto límpido e sem a presença de sólidos suspensos no vinho, como mostra a Figura 3.

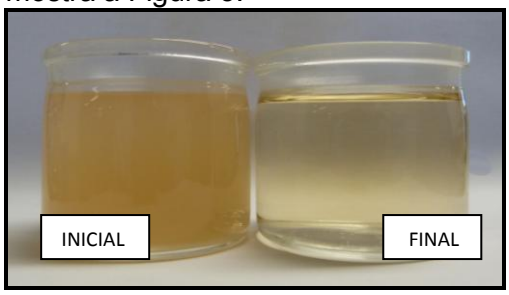

Figura 3: Comparação do aspecto visual da amostra de vinho branco antes e após a filtração por membrana cerâmica.

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Acknowledgements

Os autores agradecem à Universidade de Caxias do Sul, ao CNPq e à Vinícola Salton.

CERAMIC NANOFILTRATION MEMBRANES

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Inopor ® GmbH is one of the leading manufacturer of ceramic membranes and the world only supplier of patented real ceramic nanofiltration membranes with a cut-off of 450 Dalton. Ceramic Inopor ® nanofiltration membranes are successfully used in various applications and branches around the world.

Ceramic nanofiltration membranes from Inopor ® GmbH can be used e.g. for:

- Separation of pharmaceutics.
- Beverage filtration.
- Separation of milk ingredients.
- Separation of proteins.
- Cleaning of acids and caustics.
- Removal of multivalent ions.

Inopor ® GmbH is driven by innovation and performance. Next to a multitude of high quality membranes, Inopor ® Gmbh offers to its customers:

- Membrane housing.
- Lab and field trials.
- Layout of membrane plants.
- Start-up and service of membranes plants.
- Competences in other membrane processes (e.g. reverse osmosis, electrodialysis).

	Material	Mean pore size	Cut - off	Open porosity
Microfiltration inopor® micro	α-Al_2O_3	800 nm		40% - 55%
		600 nm		
		400 nm		
		200 nm		
		100 nm	200 kD	
		70 nm		
	TiO_2	400 nm		
		250 nm		
		200 nm		
		100 nm	200 kD	
	ZrO_2	110 nm		
Ultrafiltration inopor® ultra	γ-Al_2O_3	10 nm		30% - 55%
		5 nm	7500 D	
	TiO_2	30 nm		
		10 nm		
		5 nm	8500 D	
	ZrO_2	3 nm	2000 D	
Nano-filtration inopor® nano	SiO_2	1.0 nm	600 D	30% - 40%
	TiO_2	1.0 nm	750 D	
		0.9 nm	450 D	

Ceramic membranes

FOULING BEHAVIOUR OF TEXTILE WASTEWATER MODEL SOLUTIONS TREATED BY A CERAMIC UF MEMBRANE

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Introduction

Effluents from textile industry are known to be environmentally problematic because of its high dye, salt and organic matter content. Membrane technologies like nanofiltration (NF) or ultrafiltration (UF) are employed to treat such effluents with satisfactory results [1]. Nevertheless, the well-known phenomenon of membrane fouling is still a matter of great concern. Accurate study of this phenomenon is therefore necessary to achieve a better understanding of the process and, consequently, be able to reduce it. The purpose of this research was to evaluate the performance of an UF ceramic membrane during the treatment of different model solutions simulating textile wastewater. The solutions ranged from single-component to four-component solutions, in order to study the influence of each component and their combinations on membrane fouling, analyzing as well the different resistances contributing to flux decline in each case.

Materials and methods

A tubular ceramic UF membrane with 7 channels (INSIDE CéRAM^{TM}) was used to filter the solutions. It had a molecular weight cut-off of 150 kDa, an active layer of ZrO_2-TiO_2 and an effective area of 132 cm^2. The reagents used for preparing the solutions were a reactive dye (Reactive Black 5, RB5), NaCl, carboxymethyl cellulose sodium salt (CMC) and starch. All of them are used in processes of the textile industry [2]. Table 1 shows the composition of each solution as well as their conductivity and Chemical Oxygen Demand (COD).

Table 1. *Composition and characteristics of the model solutions used.*

Component	Solution						
	1	2	3	4	5	6	7
[RB5] (mg/L)	100	100	0	100	100	0	100
[NaCl] (g/L)	0	2.5	0	0	2.5	0	2.5
[CMC] (mg/L)	0	0	300	300	300	0	300
[Starch] (mg/L)	0	0	0	0	0	1500	1500
Parameter							
Conductivity (µS/cm)	98.8	5050	70.8	137.8	5430	24.5	5400
COD (mg/L)	100	106	310	493	454	1520	1821

Experiments were conducted in a cross-flow UF system, at constant operating conditions (25 °C, 3 m/s and 3 bar) and constant concentration mode. The evolution of normalized flux (Jp/Jw, where Jp is the permeate flux and Jw the initial deionized water flux) was monitored during the whole experiments (8h) in order to assess the fouling behaviour of each model solution. RB5 retention was evaluated by means of the dye rejection coefficient (R_{dye}); moreover, the rejections of salt (R_{salt}) and organic matter (R_{org}) were determined through conductivity and COD measurements. Aiming at a further fouling analysis, the resistance-in-series model [3] was used to determine the percentage contribution of membrane resistance (Rm) and fouling resistance (Rf) to the total (Rt). Furthermore, the contribution of Rf was divided into a hydraulically reversible resistance (Rrev), easily removed by rinsing, and a hydraulically irreversible resistance, only supressed by chemical cleaning.

Results and discussion

The results of the filtration experiments are presented in Figure 1. Regarding the rejection of salt and organic matter, R_{salt} and R_{org} were <4% and >90% in all the cases, respectively.

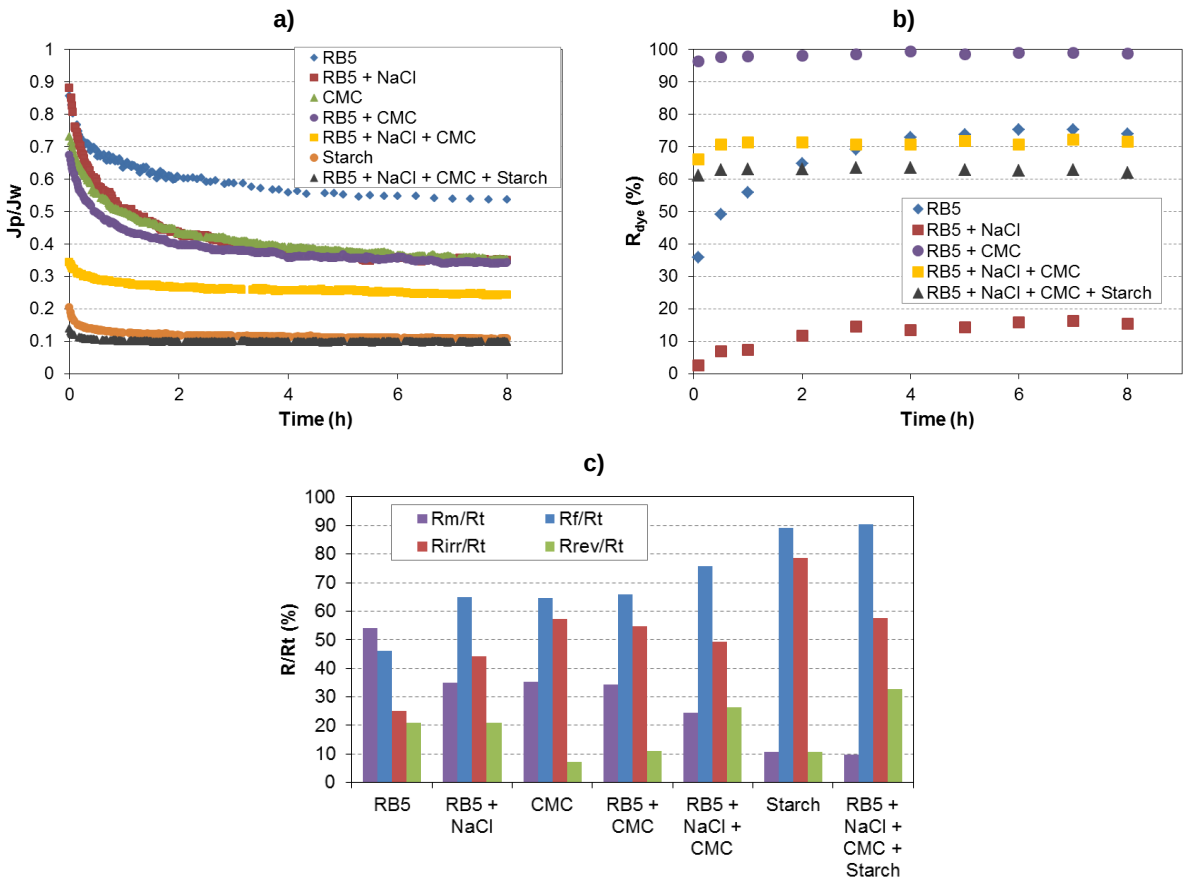

Figure 1. *Evolution of a) normalized permeate flux and b) dye rejection coefficient. c) Contribution of the different resistances to the total (Rm+Rf=Rt; Rirr+Rrev=Rf)*

As it can be seen from Figure 1a, flux noticeably decreased when starch was present in the solution, as Jp was less than 20% of the initial water flux since the beginning of the experiment. This indicates rapid initial pore blocking [4]. The addition of salt to the solutions seems to negatively affect both flux and dye rejection, probably due to electrostatic membrane-solutes interactions [5]. However, despite the presence of salt, R_{dye} increased by adding CMC. Due to its high molecular weight CMC is likely to be retained by the membrane forming a layer on the surface which hinders the passage of dye molecules. It is evident from Figure 1c that fouling phenomenon was severe in all cases (except for the RB5 solution) since Rf contribution was much higher than Rm, especially when starch was present in the solution (Rf/Rt around 90%). Regarding the nature of fouling it was observed that it was mainly irreversible, especially in the presence of organic matter like CMC and starch, which means that membrane permeability could only be recovered by chemical cleaning.

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Acknowledgements

This work was supported by the “Ministerio de Ciencia e Innovación” through the project ref. CTM2009-13048 and the “Ministerio de Educación” through the FPU grant ref. AP2009-3509.

INFLUENCIA DEL CONFORMADO SOBRE LAS PROPIEDADES DE UNA MEMBRANA CERÁMICA DE BAJO COSTE

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Las membranas cerámicas empleadas habitualmente en la industria se centran en composiciones basadas en alúmina, circona, titania o una combinación de éstos óxidos. Aunque estas membranas presentan unas elevadas prestaciones, como resistencia mecánica, química (pH extremos, medios oxidantes…), térmica, etc., su elevado coste limita las aplicaciones en las que se emplean [1]. Si se dispusiera de membranas cerámicas de bajo coste con unas prestaciones aceptables podrían ser utilizadas en un mayor número de procesos, como tratamientos terciarios, reactores biológicos de membranas, etc.

En el presente trabajo se han desarrollado membranas cerámicas de bajo coste mediante dos métodos de conformado empleados habitualmente en la industria cerámica (prensado y extrusión) [2], manteniendo constante tanto la composición de las membranas (basada en una mezcla de arcilla, chamota y carbonato cálcico) como la temperatura máxima de cocción y modificando el tiempo de permanencia a la misma. Mediante un diseño factorial de experimentos 2^2 se ha estudiado la relación entre las propiedades de las membranas cerámicas obtenidas y las citadas variables de operación durante su síntesis (Ver codificación en la tabla 1).

Las respuestas analizadas han sido: contracción lineal, absorción de agua, pérdida por calcinación, densidad aparente en cocido, diámetros característicos, d_{max} y d_{50} (obtenidos mediante el método de punto de burbuja), permeabilidad al aire y permeabilidad al agua. En la tabla 2 se muestra la influencia que las diferentes variables ejercen sobre las propiedades de estudio, codificadas como porcentajes respecto al valor medio. Se observa que el el tipo de conformado ejerce mayor influencia sobre las propiedades de las membranas que el tiempo de permanencia a T_{max} o la interacción de ambos factores. Por otro lado, las propiedades que se ven más influenciadas por el tipo de conformado son la contracción de cocción y la permeabilidad al aire y al agua, siendo la pérdida por calcinación la única que no se ve influenciada por el ninguna de las variables, ya que solamente depende de la composición de la membrana.

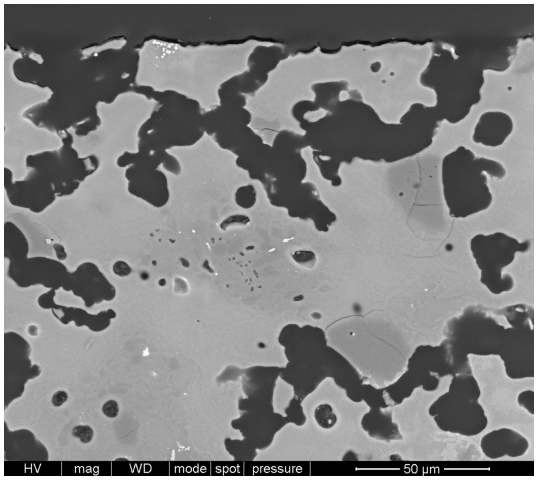
Adicionalmente, se ha evaluado la resistencia mecánica en cocido, la distribución de tamaños de poros (mediante porosimetría de mercurio) y la microestructura de las membranas obtenidas con el tiempo de permanencia de 60 minutos. La resistencia mecánica en cocido de las membranas conformadas por extrusión (405 ± 20 kg/cm^2) es superior a las de prensado (327 ± 14 kg/cm^2) y los resultados de la distribución de tamaños de poro siguen la misma tendencia que el resto de propiedades (prensado: d_{50}=7,7µm, ε_a=29,5%; extrusión: d_{50}= 4,3µm, ε_a=13,6%). Finalmente, la observación de la microestructura mediante microscopio electrónico de barrido (figura 1) muestra que, al analizar en sección la zona correspondiente a la superficie de las membranas, aquellas obtenidas mediante extrusión poseen una capa superficial que interrumpe la conectividad de los poros con la superficie de la membrana. Este hecho y la menor porosidad de las muestras obtenidas mediante extrusión, explican la menor permeabilidad observada en las muestras extruidas.

Tabla 1. Correspondencias de las variables en la matriz de diseño.

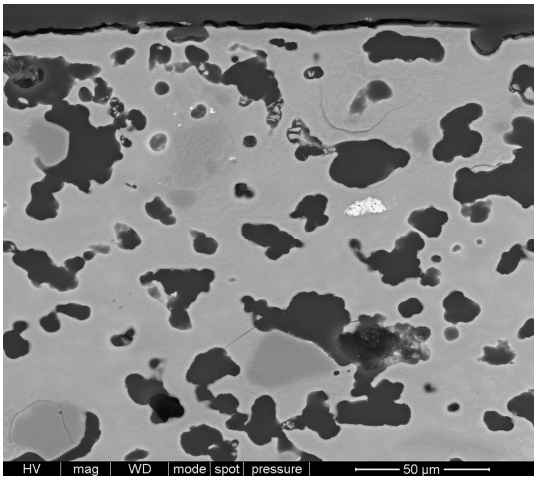
Variables	Niveles	
	-1	+1
Conformado (C)	Prensado	Extrusión
Tiempo permanencia (t) [min]	6	60

Tabla 2. Resultados del diseño de experimentos 2^2.

		Efectos de las variables (%)		
Propiedad	Valor medio	C	t	Cxt
Contracción lineal (%)	1,5	167	73	40
Absorción de agua (%)	18,1	-28	-12	-4
Pérdida por calcinación (%)	13,33	0	0	0
Densidad aparente (g/cm^3)	1,77	7	4	2
d_{50} (µm) [PB]	4,1	-79	55	-20
d_{max} (µm) [PB]	8,1	-70	70	-20
P_e aire ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	567500	-142	78	-63
P_e agua ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	6032	-168	90	-73



a) Prensado



b) Extrusión.

Figura 1. Microestructura de las membranas conformadas con diferentes métodos y con un tiempo de permanencia de 60 minutos (Método: microscopio electrónico de barrido).

Conclusiones

▪ Las membranas conformadas por extrusión presentan menor porosidad y permeabilidad, debido a la diferencia en el principio de conformado y a la capa superficial formada durante el proceso de extrusión.

▪ Al aumentar el tiempo de permanencia a la máxima temperatura, aumenta la densificación de las membranas, disminuyendo su porosidad y permeabilidad.

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Agradecimientos

Los autores agradecen al Ministerio de Ciencia e Innovación el apoyo recibido para el desarrollo de esta investigación (Plan Nacional de Investigación Científica, Desarrollo e Innovación Tecnológica 2008-2011, subprograma INNPACTO, IPT-2011-1069-310000).

SYNTHESIS OF CERAMIC ION-EXCHANGE MEMBRANES WITH BIPOLAR BEHAVIOR FOR ELECTRODIALYTIC WATER SPLITTING

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Bipolar ion-exchange membranes are composed of an anion- and a cation-exchange membrane casted together. When these membranes are submitted to an intense electric field, the splitting of water molecules to form OH^- and H^+ ions occurs at the interface between both membranes, as shown schematically in Fig. 1. The use of bipolar ion-exchange membranes has increased the potential application of electrodialysis for the production of acids and bases from salts. Hence, these membranes can be the key to zero-emission processes, such as the treatment of reverse osmosis concentrates by bipolar electrodialysis [1]. However, one of the main limitations of bipolar ion-exchange membranes is the requirement of stability and durability under extreme pH conditions and high operating current densities.

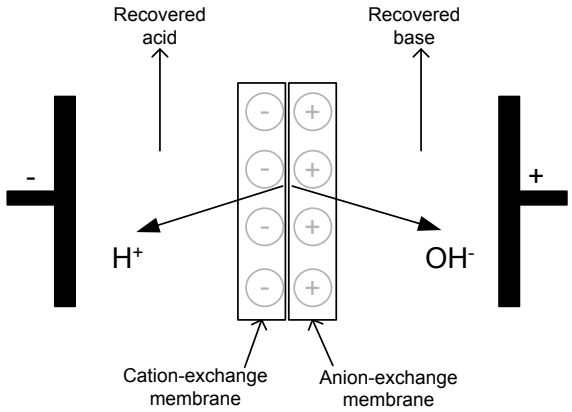

Fig. 1. Schematic diagram of an electrodialysis cell composed of a bipolar ion-exchange membrane arranged between two working electrodes.

The synthesis of ceramic membranes with ion-exchange properties could solve the conventional limitations of polymeric membranes, since ceramic materials have higher chemical stability. In the present study we synthesized ceramic supports from alumina, kaolin and starch using a procedure described in a previous work [2]. Then, hydrous zirconium dioxide (HZD) was infiltrated in the internal voids of the sintered supports by means of direct precipitation. HZD exchange anions in acidic conditions [3]:

$$ZrO_m(OH)_n(OH_2)^+ + An^- \rightleftarrows ZrO_m(OH)_n(OH_2)^+An^-$$

However, HZD has amphoteric properties and can also be used as cation-exchanger in basic conditions:

$$ZrO_m(OH)_nO^- + Cat^+ \rightleftarrows ZrO_m(OH)_nO^-Cat^+$$

The electrochemical behavior of the synthesized ceramic membranes was determined by means of measuring the current-voltage curves with 0.1M NaCl solutions. The curves obtained exhibit the typical behavior of bipolar ion-exchange membranes (see Fig. 2). When

the first limiting current density (i_{lim1}) is reached, the supply of counter-ions to the membrane surface is limited by diffusion. As a consequence, the resistance of the membrane system increases and a plateau is formed in the curves. However, under intense concentration polarization conditions, the catalytic dissociation of water is enhanced and the current density increases drastically for currents above i_{lim1}. The generation of H^+ and OH^- ions is verified by the pH variation registered in each compartment of the electrodialysis cell. Although the pH of the side compartments is affected by the electrode reactions, the sharp pH decrease in the central compartment occurring when the i_{lim1} is surpassed confirms the catalytic activity of HZD. Finally, at very high current densities, limitations in the water transport from the electrolyte to the membrane active sites can reduce the dissociation of water. This occurs when the second limiting current density (i_{lim2}) is reached.

In conclusion, the infiltration of HZD in ceramic porous supports could be a promising approach to obtain ceramic membranes with properties typical of bipolar membranes. These membranes do not have the stability problems related to the interface layer of polymeric bipolar membranes, since they are not composed of two different membrane layers casted together. Moreover, the increased chemical resistance of ceramic materials against extreme pH conditions is also an important advantage of the synthesized ceramic membranes.

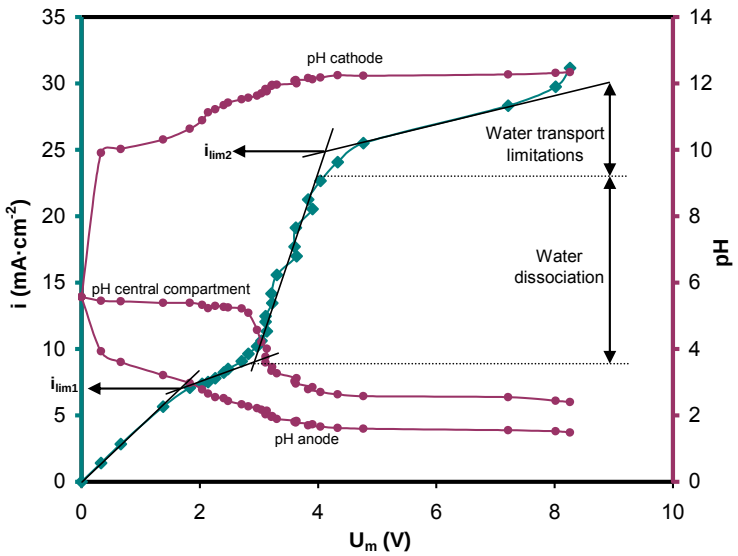

Fig. 2. Current-voltage curve obtained for 0.1M NaCl with the ceramic membrane obtained after six HZD infiltration cycles.

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Acknowledgements

M.C. Martí-Calatayud is grateful to the Universitat Politècnica de València for a postgraduate grant (Ref. 2010-12). This work was supported by the Ministerio de Economía y Competitividad (Spain) with the project number CTQ2012-37450-C02-01/PPQ and CTQ2012-37450-C02-02/PPQ.

SÍNTESE DA MEMBRANA ZEOLÍTICA (MCM-22/α-ALUMINA) E SUA APLICAÇÃO NO PROCESSO DE SEPARAÇÃO DE ÓLEO / ÁGUA

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Introdução

O uso de membranas zeolíticas representa uma modernização em processos químicos, permitindo a minimização de custos operacionais, redução da demanda energetica e tempo de processamento [1].

Objetivo

Assim, o presente estudo teve como objetivo desenvolver a síntese da membranas zeolíticas MCM-22 com aplicação na separação de emulsões de água / óleo.

Experimental- Preparação do Suporte: suporte em formato de discos foram preparados por prensagem de pó comercial α-Al_2O_3 (Almatis) num molde feito por medida com o auxílio de uma prensa hidráulica (4 toneladas), seguido por sinterização a 1200 °C durante 1 h. **Preparação da membrana** - Síntese de membrana zeolítica MCM-22: Neste método, um grama de zeólita MCM-22 foi friccionado (semeadas) sobre a superfície do suporte de cerâmica. A mistura resultante clara com a seguinte composição: 0,511SiO_2: 0,039 NaOH: 0,024 Al_2O_3: 0,6 HMI: 23,06 H_2O foi adicionado a autoclave de aço inoxidável revestido de teflon e tratada hidrotermicamente a 150 ° C durante 10 dias. **Após a síntese:** As membranas suportadas foram removidas da solução de síntese, após 10 dias de síntese, foram lavadas com água destilada e depois secas a 60 º C durante 1h.

Resultados

A Figura 1 mostra o resultado da análise de DRX, na varredura de 2θ de 0 a 50º, da zeólita MCM-22, do suporte cerâmico e da membrana zeolítica MCM-22.

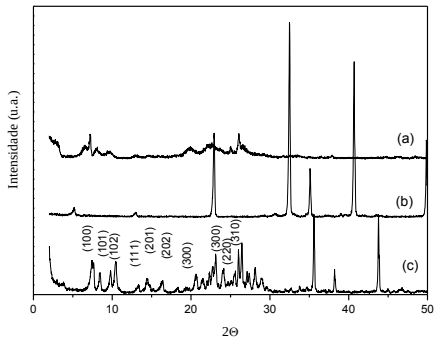

Figura 1. Difratogramas das amostras: (a) zeólita MCM -22 (b) suporte poroso (c) membrana zeolítica MCM-22.

Atráves da análise de XRD , verificou-se que a amostra obtida (Figura 1a) mostrou os picos característicos de material do tipo MCM-22 nas regiões correspondentes às 2θ = 12-25 ° e 2θ = 26-29°, sem a presença de impurezas. Observou-se também indexado como os picos (001) e (002) que são característicos da topologia MWW de acordo com a literatura [2] . Observa-se a formação de picos característicos de óxido de alumínio , na região correspondente ao 2θ = 25-45 ° (Figura 1b) , o que confirma que a amostra tem a estrutura cristalina de α-alumina (JCPDF cartão nº 10 - 0173) .Este resultado está de acordo com os resultados relatados na literatura [3] . Na Figura 1 (c), foi observada a presença de fases cristalinas relacionadas a zeólita MCM-22 e o suporte cerâmico (α-alumina) , que mostra a formação da membrana zeolítica MCM-22.

A Figura 2 mostra imagens das amostras: suporte cerâmico (α-alumina) e membrana zeolítica MCM-22 obtidas por microscopia eletrônica de varredura (MEV).

De acordo com a micrografia do suporte cerâmico (Figura 2a), observa-se uma microestrutura heterogênea com regiões de grãos grandes e regiões de grãos pequenos de formas irregulares, e a presença de poros. Este comportamento também foi observado [4].

(a) (b)

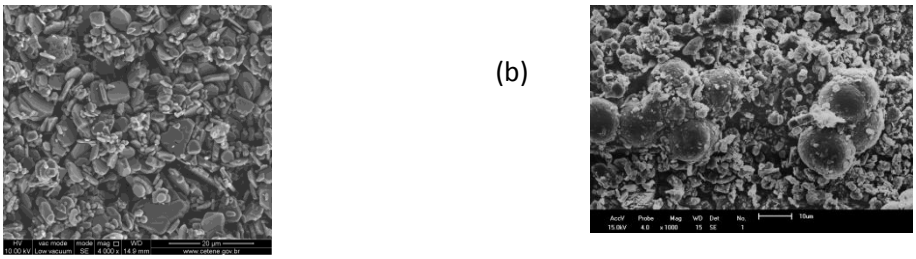

Figura 2. Micrografias: (a) suporte poroso e (b) membrana zeolítica MCM-22.

Por microscopia eletrônica de varredura (Figura 2), observa-se a existência de duas morfologias diferentes na superfície da membrana zeolítica MCM-22, podem ser visto a formação de um filme zeolítico composto de cristais de MCM-22, e a morfologia do suporte cerâmico (α-alumina), a imagem exibida por esta camada é de acordo com [5].
A Figura 3 apresenta a concentração de óleo na corrente de permeado em função do tempo para o disco α-Al_2O_3 e membrana zeolítica (MCM-22/α-Al_2O_3).

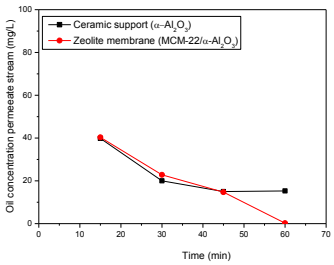

Figura 3. Gráfico da concentração de óleo no fluxo permeado do suporte cerâmico (α-Al_2O_3) e membrana zeolítica (MCM-22/α-Al_2O_3).

Analisando as medições de fluxo de óleo no permeado (Figura 3), pode observar-se que a membrana zeolítica MCM-22, obteve uma percentagem mais elevada de remoção de óleo, no início do processo, em comparação com o suporte cerâmico (α-alumina) . Este fato pode ser explicado devido à camada de zeólita MCM-22, depositado na superfície do suporte cerâmico (α-alumina), o que aumenta a eficácia do processo de separação. A partir da Figura 3, podemos ver que a membrana zeolítica MCM-22, apresentaram percentuais de remoção equivalentes aos padrões exigidos pela Resolução 392 do CONAMA (CONAMA, 2007).

Conclusões

O padrão de XRD mostrou que a membrana zeolítica MCM-22 não mostraou nenhuma evidência de outras fases caracterizadas como impurezas. A micrografia da membrana zeolítica MCM-22 mostrou a formação de uma camada de zeólita sobre o suporte cerâmico, que partículas esféricas cresceu na superfície do suporte cerâmico. A membrana zeolítica MCM-22 conseguiu uma redução significativa da concentração de óleo no permeado, mostrando assim, que tem o potencial para esta aplicação.

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Agradecimentos

Os autores agradecem à Petrobras pelo apoio financeiro a esta pesquisa.

EVOLUÇÃO DA INFLUÊNCIA DA TEMPERATURA DE SINTERIZACÃO E ELIMINACÃO DE TRATAMIENTO ÁCIDO DA ɣ-ALUMINA UTILIZADA COMO SOPORTE CERÂMICO PARA MEMBRANA ZEOLÍTICA (MCM-22)

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Introdução

A utilidade da ɣ-alumina baseia-se na combinação favorável de propriedades físicas, texturais, térmicas e químicas para ser utilizada como suporte na preparação de membranas zeoliticas [1]. Atualmente, vários métodos para a síntese de ɣ-alumina são relatados na literatura [2], que envolve principalmente processamento complicado como tratamentos ácidos e temperatura de sinterização elevada. Este trabalho consiste em sintetizar ɣ-alumina para utilização como suporte de membrana zeolítica do tipo MCM-22/ɣ-alumina, avaliando a eliminacão do tratamento ácido previo, assim como tambêm a influência da temperatura de sinterizacão.

Experimental

Síntese da alumina: A síntese da alumina foi realizada por decomposição térmica do sulfato de alumínio ($Al_2(SO_4)_3.16H_2O$) P.A, em forno mufla, a uma temperatura de 1000°C, utilizando taxa de aquecimento de 5ºC/min e patamar de 2 horas.

Preparação do suporte cerâmico: Preparou-se 200 ml de dispersão com a seguinte composição: 40% de alumina obtida anteriormente; 0,2% de PABA ácido para-amino benzóico (dissolvido em álcool); 0,5 % de ácido oléico (lubrificante) e 59,3 % de álcool etílico. Moeu-se a mistura durante 1 hora em um moinho de bolas e então colocou-se na estufa por 24 horas a 60ºC; umidificou-se com 7 % de água, deixou-se repousar por 24 horas. Pesou-se 3 g do material e colocou-se no molde. A prensagem foi realizada com 4 toneladas.

Estudo térmico (sinterização): O material prensado foi submetido a sinterização a várias temperaturas: 900 °C, 950 °C, 1000 °C e 1100 ºC com taxa de aquecimento de 5 ºC/min por 1 hora.

Sintese da membrana zeolítica: Neste método foi realizada uma mistura mecânica (manualmente) dos dois sólidos: zeólita MCM-22 (sintetizada com 10 dias de tratamento hidrotérmico) e o suporte cerâmico (ɣ-alumina) obtido anteriormente. Após a mistura mecânica foi realizada uma nova presangem mecânica com 4 toneladas por 10 segundos e em seguida a membrana foi levada à mufla a 900 ºC com taxa de aquecimento de 5 °C/min durante 1 hora.

Resultados

Na Figura 1 está apresentado o difratograma do material sintetizado a partir do sulfato de alumínio. Os resultados obtidos a partir da porosimetria de mercúrio da ɣ-alumina são apresentado na Tabela 1.

Analisando o difratograma na Figura 1, é possível observar os picos característicos e bem resolvidos indicando a formação da fase ɣ-alumina (ficha padrão JCPDS Card No. 10 - 0425).

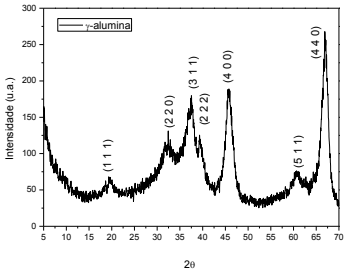

Figura 1. Padrão de difração de raios x do material sintetizado a partir do sulfato de alumínio.

Tabela 1. Propriedades da ɣ-alumina.

Fase	Diâmetro médio dos poros (μm)	Porosidade (%)
ɣ-alumina	0,02	37,95

De acordo com o valor de diâmetro médio do poro, a ɣ-alumina, pode ser classificada como material de ultrafiltração, conforme a literatura [3].

Na Figura 2 mostra o difratograma de raios X do estudo térmico realizado no suporte cerâmico e na Figura 3 o difratograma da membrana zeolítica.

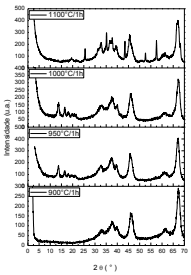

Figura 2. Difratograma do tratamento térmico realizado no suporte cerâmico.

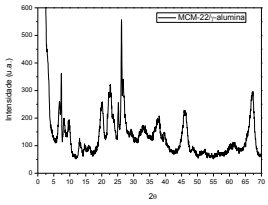

Figura 3. Difratograma da membrana zeolítica MCM-22/ɣ-alumina.

Na Figura 2 mostra a influência da temperatura de sinterização no suporte cerâmico, podendo indicar que: Na temperatura de 900 ºC é possivel obter a fase da gama alumina pura com 1h de sinterização, nas temperaturas de (950 e 1000 ºC) foram formadas as fases (gama e teta), e para temperatura de 1100 ºC foram formadas as fases (alfa e gama). Segundo [4], acima de 900 – 950 ºC, observa-se a formação da fase alumina teta, o aquecimento acima de 1000 ºC dá início à formação da fase α. Sendo assim fica explica a escolha do suporte sinterizado a temperatura de 900 °C para utilização na síntese da membrana zeolítica, um suporte puro e livre de impurezas. Os picos relativos para os padrões de DRX da membrana zeolítica MCM-22/ɣ-alumina demostrado na Figura 3 sintetizada atraves da mistura mecânica, apresentam picos característicos àqueles encontrados para a zeólita em pó MCM-22 [5] juntamente com os picos característicos dos suportes cerâmicos observados na Figura (1), o que indica que a membrana zeolítica típica MCM-22 foi obtida com exito.

Conclusões

É possível obter a ɣ-alumina com elevado grau de pureza, a partir do sulfato de alumina, sem uso de um tratamento ácido, como tem sido encontrado na literatura. Alem disso, o tratamento térmico de sinterizacão utilizando 900 °C por 1 hora, mostra-se efetivo na obtenção da ɣ-alumina sem presença de otras fases. A membrana zeolítica foi obtida com exito.

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Agradecimentos

Os autores agradecem a CAPES pela bolsa de doutorado e a Petrobras pelo apoio financeiro.

REMOÇÃO DE ÓLEO CONTAMINANTE EM EFLUENTES AQUOSOS UTILIZANDO MEMBRANA ZEOLÍTICA (ZSM-5/GAMA-ALUMINA)

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Introdução

As membranas inorgânicas podem ser descritas como um material assimétrico poroso formado por macroporos com sucessivas camadas finas depositadas sobre o suporte. O suporte proporciona resistência mecânica a membrana [1,2]. Os processos de separação por membranas, apresentam-se capazes de tratar efluentes com elevados teores de óleo em emulsão, competindo com tecnologias de tratamento mais complexas [3]. O objetivo deste trabalho foi sintetizar a membrana zeolítica utilizando o método de mistura mecânica e avaliá-la na remoção da emulsão óleo/água, em relação ao suporte (γ-Al_2O_3).

Experimental

Obtenção da alumina: inicialmente foi realizada a decomposição térmica do sulfato de alumínio ($Al_2(SO_4)_3.16H_2O$) P.A, em forno mufla, a uma temperatura de 1000°C, utilizando taxa de aquecimento de 5ºC/min por 2 horas. **Preparação do suporte ceramic poroso:** Preparou-se 200 ml de dispersão com a seguinte composição: 40% de alumina obtida anteriormente; 0,2% de ácido para-amino benzóico (dissolvido em álcool); 0,5 % de ácido oléico (lubrificante) e 59,3 % de álcool etílico. Moeu-se a mistura durante 1 hora em um moinho de bolas e então colocou-se na estufa por 24 horas a 60ºC. **Preparação da Zeólita:** Preparam-se três soluções: (A) diluindo a sílica em água; (B) dissolvendo aluminato de sódio e hidróxido de sódio em água; (C) dissolvendo o brometo de tetrapropilamônio (TPABr) em água, e adiciona-se cerca de 20 gotas de H_2SO_4 98%. As soluções B e C à solução A. A mistura reacional foi colocada em autoclaves de aço inoxidável com cápsula interna de teflon. A temperatura de cristalização empregada é de 150ºC durante 7 horas. **Preparação da membrana zeolítica ZSM-5/γ-Al_2O_3:** Foi utilizado o método de mistura mecânica. Então, 1,5g da zeólita ZSM-5 foi adicionada a 1,5g da γ-alumina em pó. A mistura foi feita mecanicamente, e inserida em um molde de aço inox, onde foi prensada com 4ton por 2 minutos. Logo após a membrana foi submetida a um tratamento térmico a 550°C por 4 horas. **Teste de separação da emulsão óleo/água em sistema contínuo:** Para testar a capacidade de remoção de óleo da membrana em sistema contínuo, uma emulsão óleo/água a 600 ppm foi passada através da membrana, a um fluxo de 5mL.min^{-1}. As amostras do permeado foram coletadas a cada 10 minutos, em um tempo total de 40 minutos e posteriormente quantificadas pelo método do clorofórmio.

Resultados

A análise de difração de raios (DRX) foi feita no suporte gama-alumina, na zeólita ZSM-5 e na membrana zeolítica ZSM-5/gama-alumina.

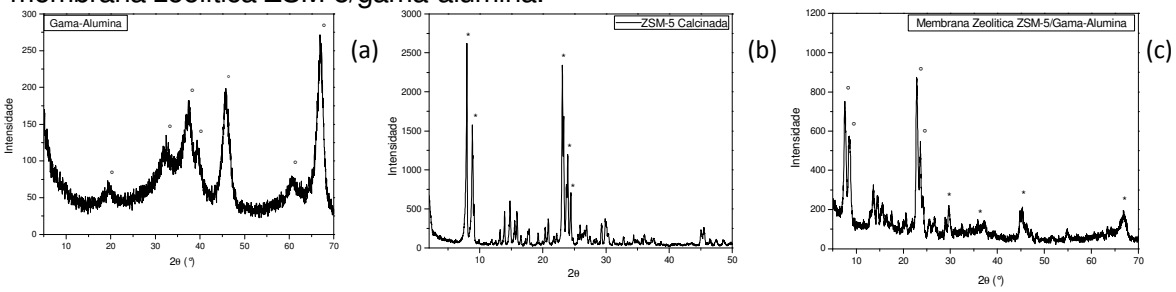

Figura 1. Difratograma das amostras: (a) suporte cerâmico poroso (γ-Al_2O_3)**,** (b) zeólita ZSM-5, (c) membrana zeolítica (ZSM-5/γ-Al_2O_3).

A partir da análise das Figuras 1(a, b) pode-se observar a formação dos picos específicos da zeólita da γ-alumina, bem como os picos caracteristicos da estrutura zeolítica ZSM-5. A Figura 1(c) apresenta a confirmação da formação da estrutura da membrana zeolítica (ZSM-5/α-alumina), realizada neste trabalho em decorrência da mistura mecânica.

Separação emulsão óleo/água em sistema contínuo

A Figura 2 apresenta a concentração da emulsão permeada na membrana e no suporte, em relação ao tempo, enquanto na tabela 1 é possível observar o comportamento de remoção da membrana e do suporte, em percentual. A partir desta análise, foi possível observar que a membrana zeolítica (ZSM-5/γ-Al_2O_3) apresentou uma capacidade de remoção de 99,97%, obtendo um excelente resultado em relação a Resolução CONAMA 357/2005, que estabelece para o descarte em corpos receptores, um limite de óleos e graxas na água produzida de até 20 mg/L [4]. Enquanto que para a remoção usando apenas o suporte não obteve um resultado satisfatório, comprovando que a presença da zeólita ZSM-5 foi essencial para o processo de separação.

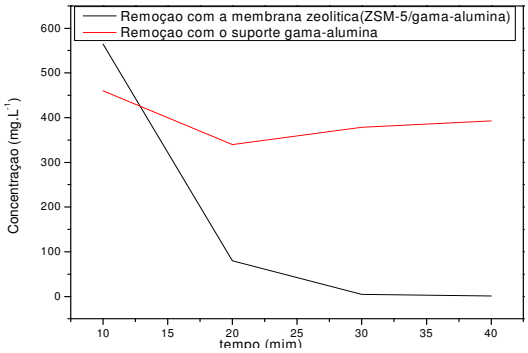

Figura 2. Concentração da emulsão (óleo/água) em função do tempo

Tabela 1. Percentual de remoção da membrana ao logo do tempo

Tempo	10min	20min	30min	40min
Remoção Membrana (ZSM-5/γ-Al_2O_3)	5,95%	86,83%	99,97%	99,85%
Remoção suporte (γ-Al_2O_3)	23,35%	56,23%	63,1%	65,44%

Conclusões

A capacidade de remoção da membrana zeolítica (ZSM-5/γ-Al_2O_3) em remover óleo em emulsões aquosas, analisada neste trabalho e observada pela elevada qualidade do permeado, que apresentou uma alta eficiência resultando na remoção de 99,97% da concentração inicial de óleo, como esperado, quando comparado ao suporte(γ-Al_2O_3), que removeu 65,44% da concentração inicial. A remoção eficiente da membrana zeolítica foi maior devido a porosidade adquirida pela membrana a partir da presença da zeólita ZSM-5.

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Agradecimentos

Os autores agradecem a CAPES pelo apoio financeiro e bolsa de mestrado concedida, e em especial à Petrobras pelo apoio financeiro a esta pesquisa.

UTILIZAÇÃO DA MEMBRANA ZEOLÍTICA: (ZEÓLITA NaA/γ-Al_2O_3) NO PROCESSO DE SEPARAÇÃO DE EMULSÃO ÓLEO/ÁGUA

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Introdução

Apesar de existirem tecnologias para tratamentos de efluentes oelosos da indústria petrolífera, elas possuem um alto custo e são mais restritas ao serem utilizadas [1, 2]. São crescentes as pesquisas por novas alternativas para solucionar este problema. O processo de separação óleo/água com membranas oferece uma nova opção para se enfrentar estes desafios [3]. Os processos de separação por membranas zeolíticas estão sendo muito usados na indústria química, substituindo as técnicas convencionais de separação por apresentarem vantagens como, baixo consumo de energia, vida útil longa, ocupação de pouco espaço físico e facilidade de limpeza [4]. Muito interesse tem sido despertado nas aplicações em processos industriais usando as membranas zeolíticas, devido à sua estrutura cristalina e seus diâmetros de poros estreito. Portanto, este trabalho tem como objetivo a síntese da membrana zeolítica (zeólita NaA/γ-Al_2O_3) e avaliar seu potencial na remoção de emulsão óleo/água.

Experimental

Obtenção da alumina: inicialmente foi realizada a decomposição térmica do sulfato de alumínio ($Al_2(SO_4)_3.16H_2O$) P.A, em forno mufla, a uma temperatura de 1000°C, utilizando taxa de aquecimento de 5ºC/min por 2 horas. **Síntese do suporte cerâmico (γ-Al_2O_3):** Preparou-se 200 ml de dispersão com a seguinte composição: 40% de alumina obtida anteriormente; 0,2% de PABA ácido para-amino benzóico (dissolvido em álcool); 0,5 % de ácido oléico (lubrificante) e 59,3 % de álcool etílico. Moeu-se a mistura durante 1 hora em um moinho de bolas e então colocou-se na estufa por 24 horas a 60ºC; umidificou-se com 7 % de água, deixou-se repousar por 24 horas. Pesou-se 3 g do material e colocou-se no molde. A prensagem foi realizada com 4 ton. **Síntese da Zeólita NaA:** Composição do gel de síntese da zeólita NaA: $4{,}62Na_2O:1Al_2O_3:6SiO_2:180H_2O$. **Gel de semente (D):** Preparam-se três soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); Envelhecimento de 24 horas; após o envelhecimento obtém-se o gel de semente (D). **Mistura reacional (E):** Preparam-se duas soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); adiciona-se (D) a (E). Agita-se por 20 min. A mistura reacional foi colocado em autoclaves de aço inoxidável com cápsulas internas de teflon. A temperatura de cristalização empregada é de 100ºC por 7 horas. **Síntese da Membrana Zeolítica (Zeólita NaA/γ-Al_2O_3):** Para a preparação da membrana zeolítica Zeólita NaA/γ-Al_2O_3**,** foi realizada uma mistura mecânica (manualmente) dos dois sólidos: zeólita A e o suporte cerâmico (γ-Al_2O_3). Após a mistura mecânica foi realizada uma prensagem mecânica com 4 toneladas por 2 minutos e em seguida a membrana foi levada à mufla a 550ºC com taxa de aquecimento de 5°C/min durante 4 horas. **Preparação da emulsão óleo/água:** A emulsão com concentração de 500 ppm foi obtida utilizando óleo lubrificante da marca Lubrax. Esta foi preparada sob agitação intensa 17000 rpm durante 20 minutos, para garantir formação da emulsão óleo/água.

Resultados

Nas Figuras 1 (a, b, c) são apresentados os difratogramas de raios X das amostras.

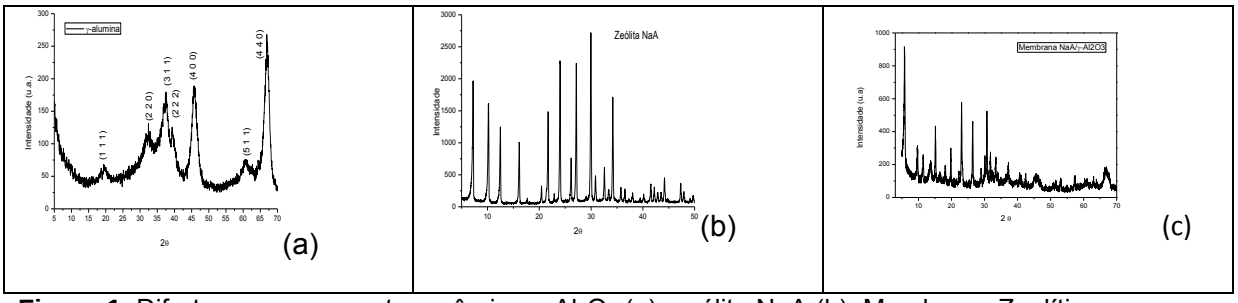

Figura 1. Difratogramas: suporte cerâmico γ-Al_2O_3 (a); zeólita NaA (b); Membrana Zeolítica.

A partir do difratograma (Figura 1a), é possível observar os picos característicos e bem resolvidos da fase γ-alumina. Com o auxílio da biblioteca do ICDD-JCPDS (International Centre for Diffraction Data) foi identificado a presença de picos indicando a formação da fase γ-alumina (ficha padrão JCPDS Card No. 10 - 0425). O difratograma (Figura 1b) evidencia a formação da zeólita A. De acordo com dados da literatura [5], trata-se da fase zeolítica NaA (zeólita LTA), que é formada geralmente em meios reacionais com baixas razões SiO_2/Al_2O_3. É possível identificar duas fases distintas como sendo as constituintes da estrutura da membrana zeolítica: NaA e γ-alumina (Figura 1c). Os picos apresentados pelo difratograma da membrana zeolítica revelaram a existência de estruturas cristalinas, com picos bem definidos, indicando que elas apresentam alta cristalinidade.

Na Figura 2 e Tabela 1 estão apresentados os resultados de Remoção de óleo em função do tempo.

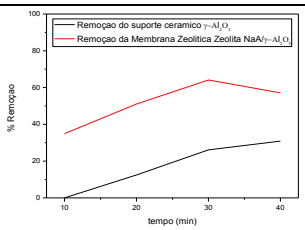

Figura 2. Concentração da emulsão óleo/água em função do tempo.

Tabela 1. Percentual de remoção do suporte cerâmico e membrana ao longo do tempo.

Tempo (min)	10	20	30	40
% Remoção (γ-Al_2O_3)	0	12,46	26,12	30,89
% Remoção Membrana (NaA/γ-Al_2O_3)	34,93	51,06	64,09	57,11

Conforme os dados avaliados na Figura 2 e Tabela 1, observa-se um aumento da remoção na emulsão óleo/água com o tempo, atingindo para o suporte cerâmico (γ-Al_2O_3) um valor máximo de 30,89% e para a membrana zeolítica (zeólita NaA/γ-Al_2O_3) um valor máximo de 64,09%. Ao comparar os resultados verifica-se que a membrana zeolítica apresentou uma melhor eficiência. Pode-se explicar este fato em função da modificação da porosidade do material, uma vez que o suporte cerâmico é composto somente pela fase γ-alumina e a membrana zeolítica é composta por duas fases: a zeólita NaA e a γ-alumina.

Conclusões

A formação da membrana zeolítica utilizando o método de mistura mecânica foi confirmada, evidenciando que após o processo da mistura mecânica e calcinação sua estrutura foi preservada, apresentando uma leve diminuição de seus picos característicos. Baseado no ensaio de remoção de óleo, pode-se concluir que a membrana zeolítica evidenciou uma maior eficiência na remoção de óleo quando relacionado com o suporte (γ-Al_2O_3).

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Agradecimentos

Os autores agradecem a CAPES pela bolsa concedida e a Petrobras pelo apoio financeiro.

EFEITO DE DIFERENTES CONCENTRAÇÕES DE SÍLICA SOBRE A SINTESE DA MEMBRANA ZEOLÍTICA (ZEÓLITA Y/α-ALUMINA)

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Introdução

As membranas zeolíticas são preparadas comumente através da síntese hidrotérmica, conduzindo ao crescimento de um filme de zeólita sobre um suporte poroso. Neste caso, o suporte cerâmico entra em contato com o gel precursor da zeólita em uma autoclave a uma determinada temperatura e por certo tempo e em condições adequadas, os cristais crescem para formar uma camada relativamente contínua de zeólita [1]. Este trabalho investiga a influência da variação da concentração da sílica sobre a preparação das membranas zeolíticas (zeólita Y/α-alumina), via método de crescimento secundário – rubbing.

Experimental

Preparação do suporte ceramico (α-alumina): conforme descrito na referência [2]. **Síntese da zeólita Y:** A síntese hidrotérmica foi baseada em [3]. **Gel de semente (D):** Preparam-se três soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); Envelhecimento de 24 horas; após o envelhecimento obtém-se o gel de semente (D). **Mistura reacional (E):** Preparam-se duas soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); adiciona-se (D) a (E). Agita-se por 20 min. A mistura reacional (E) assim preparada é colocada em autoclaves de aço inoxidável com cápsulas internas de teflon. A temperatura de cristalização empregada é de 100ºC por 7 horas. Para avaliar a influência da concentração da sílica na mistura reacional, a proporção dos reagentes foi variada de 10 a 14 com intervalos de 2 moles. A composição padrão: $4{,}62Na_2O:Al_2O_3:10SiO_2:180H_2O$.

Síntese da membrana zeolítica (Y/α-alumina): As membranas zeolíticas foram sintetizadas utilizando o método secundário – rubbing, onde as sementes de zeolita Y foram friccionadas na superfície do suporte cerâmico e em seguida seguiu para o tratamento hidrotérmico, onde a mistura reacional foi preparada conforme descrito na seção síntese da zeólita Y conforme referencia [2].

Resultados

Os difratogramas das zeólitas Y com variação na concentração de sílica estão apresentados nas Figuras (1a, b, c).

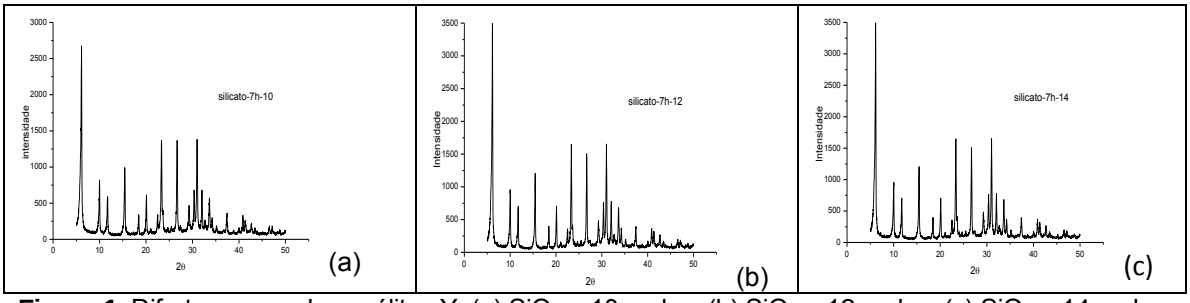

Figura 1. Difratogramas das zeólitas Y: (a) SiO_2 = 10 moles; (b) SiO_2 = 12 moles; (c) SiO_2 = 14 moles.

Os resultados de DRX indicam que os picos formados nos difratogramas (Figuras 1 (a, b, c) das amostras, correspondem aos valores de 2θ de 6,2º; 10,3º; 12,5°; 15,8°; 17,6°; 20°; 21,7°; 26°; 27,9°; 31° e 34°, que de acordo com o padrão obtido no IZA (International Zeolite Association) [4] e com a ficha JCPDS 43-0168, são picos típicos da zeólita Y sódica (NaY). Não foi observada a formação de picos adicionais referentes a fases indesejadas para essas amostras, as mesmas possuem picos intensos e bem definidos. Verifica-se que ocorre um aumento na intensidade dos picos quando a concentração de SiO_2 aumenta de 10 para 12. Contudo, no intervalo de 12 para 14 não são observadas modificações consideráveis na intensidade dos picos. Nesse intervalo provavelmente as espécies alcançaram o máximo da taxa de reação no processo de cristalização e um aumento da quantidade de silíca já não altera a estrutura do produto zeolítico [5].

Os difratogramas das membranas zeolíticas (Y/ α-alumina) com variação na concentração de sílica estão apresentados nas Figuras 2 (a, b, c).

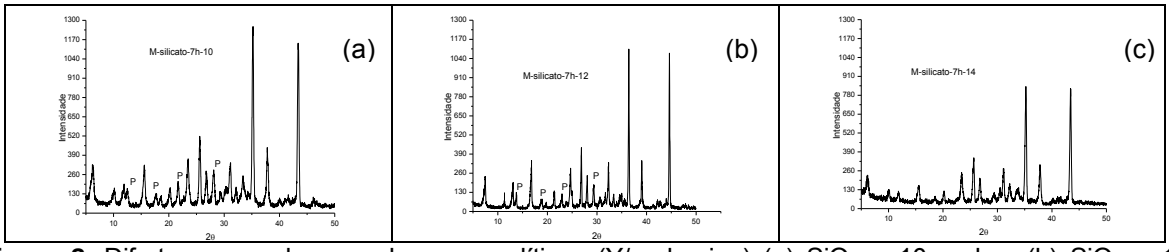

Figura 2. Difratogramas das membranas zeolíticas (Y/α-alumina) (a) SiO_2 = 10 moles; (b) SiO_2 = 12 moles; (c) SiO_2 = 14 moles.

Pela análise dos difratogramas verifica-se que em todas as amostras (Figuras 2 (a, b, c)) identifica-se a presença de picos característicos da alumina em 2θ = 26°; 35,5°; 37,8° e 43,4°, de acordo com a ficha JCPDS 10-0173 e também de picos referentes a zeolita Y em 2θ = 6,2º; 10,3º; 12,5°; 15,8°; 17,6°; 20°; 21,7°; 27,9°; 31° e 34°. Porém nas amostras (Figura 2a) e (Figura 2b), além de picos da alumina e da zeólita Y aparecem também picos da zeólita P (GIS), mas para a amostra M-silicato-7h-14 (Figura 1c) não há a presença dessa impureza, ou seja, para as razões SiO_2/Al_2O_3 iniciais menores que 14 outra fase zeolítica foi formada no tratamento hidrotérmico de síntese da membrana zeolítica.

Conclusões

Baseado nos resultados obtidos por DRX houve influência da concentração de sílica (10, 12 e 14 mols) na síntese da membrana. A zeólita Y foi formada para todos os valores de concentração de sílica (10, 12 e 14 mols). Porém, a membrana zeolítica Y foi formada com sucesso somente para concentração de sílica com valor de 14 mols. Para os outros dois valores de concentração de sílica (10 e 12) além da fase Y apareceu outra fase (zeólita P).

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Agradecimentos

Os autores agradecem a CAPES pela bolsa de doutorado e a Petrobras pelo apoio financeiro.

AVALIAÇÃO DO TEMPO DE TRATAMENTO HIDROTÉRMICO NA SÍNTESE DE MEMBRANAS ZEOLÍTICAS

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Introdução

Dentre as membranas inorgânicas microporosas, membranas zeolíticas constituem uma tecnologia promissora não só para processos de separação e reatores de membrana, mas também para campos mais incipientes [1]. As membranas zeolíticas são preparadas em forma de finas camadas sobre um suporte cerâmico poroso de forma a se obter altos fluxos. Para a formação dos suportes das membranas zeolíticas são semeados com cristais zeolíticos de tamanho nanométrico. Os suportes semeados são colocados dentro de uma solução de síntese após a secagem e sob condições hidrotérmicas as sementes crescem para uma membrana zeolítica densa [2]. Este trabalho tem como objetivo a avaliação do efeito do tempo de tratamento hidrotérmico na síntese de membranas zeolíticas (zeólita Y/α-alumina).

Experimental

Preparação do suporte ceramico (α-alumina): conforme descrito na referência [3]. **Síntese da zeólita Y:** A composição padrão: $4{,}62Na_2O:Al_2O_3:12SiO_2:180H_2O$. A síntese hidrotérmica foi baseada em [4]. **Gel de semente (D):** Preparam-se três soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); Envelhecimento de 24 horas; após o envelhecimento obtém-se o gel de semente (D). **Mistura reacional (E):** Preparam-se duas soluções: (A) diluindo o hidróxido de sódio em água e acrescentou-se o aluminato de sódio; (B) dissolvendo silicato de sódio em água e adiconando a (A); adiciona-se (D) a (E). Agita-se por 20 min. A mistura reacional (E) assim preparada é colocada em autoclaves de aço inoxidável com cápsulas internas de teflon. A temperatura de cristalização empregada é de 100ºC por 7 horas e 24 horas. **Preparação da membrana zeolítica:** As membranas zeolíticas foram sintetizadas utilizando o método secundário – rubbing, onde as sementes de zeolita Y foram friccionadas na superfície do suporte cerâmico e em seguida seguiu para o tratamento hidrotérmico, onde a mistura reacional foi preparada conforme descrito na seção síntese da zeólita Y de acordo com a referencia [3].

Resultados

Os resultados de DRX das amostras são apresentados nas Figuras 1 e 2.

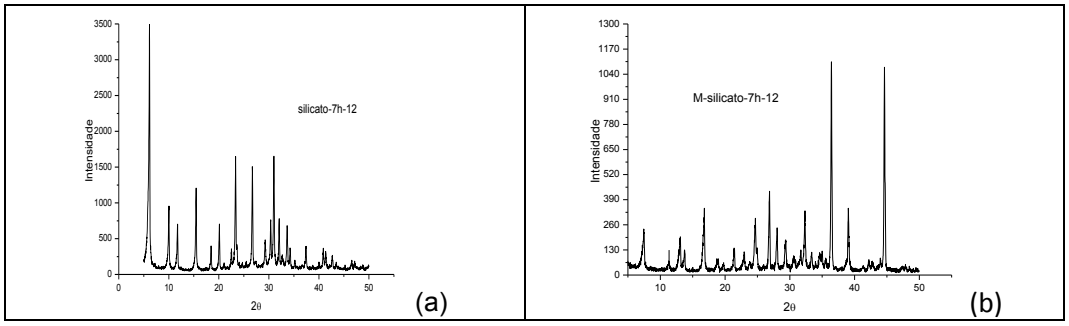

Figura 1. Difratogramas das amostras (tempo de tratamento hidrotérmico= 7 horas): (a) zeólita Y e (b) membrana zeolítica (Y/α-alumina).

Os picos formados no difratograma da amostra silicato-7h-12, (Figura 1a) correspondem aos valores de 2θ de 6,2º; 10,3º; 12,5°; 15,8°; 17,6°; 20°; 21,7°; 26°; 27,9°; 31° e 34°, que de acordo com o padrão obtido no IZA (International Zeolite Association) [5] e com a ficha JCPDS 43-0168, são picos típicos da zeólita Y sódica (NaY).

Pela análise dos difratogramas identifica-se a presença de picos característicos da alumina em 2θ = 26°; 35,5°; 37,8° e 43,4°, de acordo com a ficha JCPDS 10-0173 e também de picos referentes a zeolita Y em 2θ = 6,2º; 10,3º; 12,5°; 15,8°; 17,6°; 20°; 21,7°; 27,9°; 31° e 34°, além de picos da alumina e da zeólitas Y aparecem também picos da zeólita P (GIS). De acordo com Liu at al. (2013) [6], as zeólitas NaP e NaA são fases competitivas que se fazem presentes junto com produtos zeolíticos do tipo NaY.

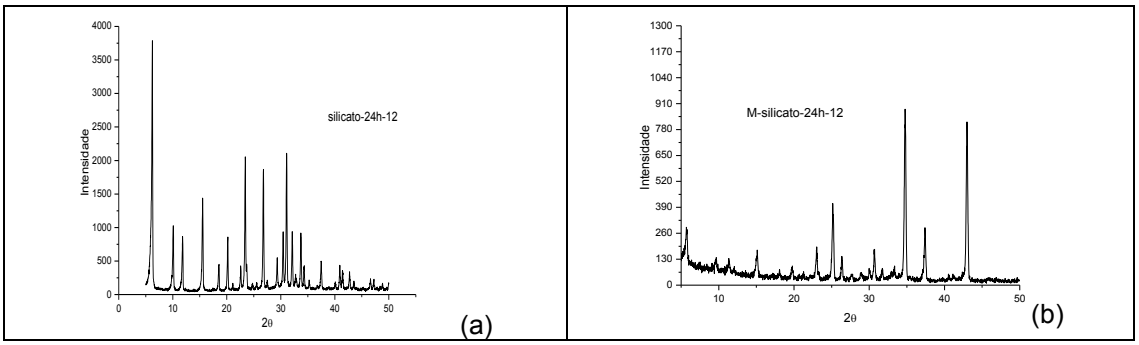

Figura 2. Difratogramas das amostras (tempo de tratamento hidrotérmico= 24 horas): (a) zeólita Y (b) membrana zeolítica (Y/α-alumina).

A análise dos difratogramas em comparação com a ficha JCPDS 43-0168 mostra que a amostra (Figura 2a) apresentou picos caracteríticos da zeolita Y sem a presença de impurezas. Verifica-se a formação da alumina e da zeólita Y com tempo de tratamento hidrotérmico de 24 horas.

Conclusões

A caracterização por DRX dos materiais (zeólita Y e membrana zeolítica) permitiu comprovar que o tempo de tratamento hidrotérmico é um fator importante no controle da síntese dos materiais. Evidenciando que o tempo de síntese de 24 horas é o tempo ideal para a síntese.

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Agradecimentos

Os autores agradecem a CAPES pela bolsa de doutorado e a Petrobras pelo apoio financeiro.

INFLUÊNCIA DO TIPO DE SEMENTE NA SÍNTESE DA MEMBRANA ZEOLÍTICA ZSM-5/α-ALUMINA

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Introdução

As membranas zeolíticas constituem uma classe de membranas inorgânicas microporosas onde cristais de zeólitas crescem em forma de filme contínuo sobre um suporte meso ou macroporoso, de geometria plana ou tubular [1]. Os fatores que afetam a qualidade de uma membrana zeolítica são: mistura reacional, matéria prima, temperatura e tempo de cristalização, a posição do suporte poroso na autoclave, o pré-tratamento do suporte, tratamento da membrana zeolítica após cristalização [2]. O método de crescimento secundário para formação das membranas zeolíticas é destinado a cobrir a superfície do suporte cerâmico com uma camada de sementes de zeólita [1]. Este trabalho visa compreender o efeito do tipo de semente de zeólitas ZSM-5 na síntese da membrana zeolítica ZSM-5/α-alumina via método de crescimento secundário - Rubbing.

Experimental

Síntese do suporte cerâmico: a alumina foi fornecida pela ALMATIS em forma de pó. Prepararam-se 200 ml de dispersão com a seguinte composição: 40 % de alumina; 0,2 % de ácido para-amino benzóico (dissolvido em álcool); 0,5 % de ácido oléico e 59,3% de álcool etílico. A mistura foi moída em um moinho de bolas durante 1 hora e então, foi colocada na estufa por 24 horas a 60 ºC; umidificou-se com 7 % de água, deixou-se repousar por 24 horas. Pesou-se 1 g do material que foi compactado e prensado. A prensagem foi realizada com 4 toneladas por 3 minutos e o material prensado foi submetido à sinterização a 1400 ºC a uma taxa de 5ºC/min, permanecendo por mais 4 h após atingir a temperatura. O suporte cerâmico (α-alumina) foi obtido na forma de disco com 1mm de espessura e 20mm de diâmetro. **Síntese das membranas zeolíticas:** Foram utilizadas três sementes distintas: a primeira foi a zeólita comercial ZSM-5 fornecida pela Zeolyst nomeada ZSM-5 (Zeo), a segunda foi uma zeólita ZSM-5 obtida a partir de um subproduto gerado da síntese em laboratório baseada na literatura [3] denominada (ZSM-5 (Sub)) e a terceira foi uma zeólita ZSM-5 sintetizada em laboratório baseada na literatura [4] nomeada ZSM-5 (Lab). A síntese da membrana zeolítica consistiu em preparar soluções contendo 0,5 g da semente (três diferentes tipos) e 5 ml de água destilada. Estas sementes foram friccionadas (semeadura) sobre a superfície do suporte cerâmico (α-alumina) [5]. Após essa etapa o suporte semeado foi levado para estufa para secagem por 12h a 60°C. Em seguida este suporte semeado foi adicionado à mistura reacional (solução clara) com composição química: $1SiO_2$–0,4TPAOH-$27,6H_2O$, então o produto (solução clara + suporte cerâmico) foi colocado em cadinho de teflon que foi inserido em autoclave de aço inoxidável e o conjunto foi levado para a estufa a 175°C iniciando o tratamento hidrotérmico por 70 horas. A membrana zeolítica foi removida do cadinho de teflon, lavada até o pH neutro e posteriormente seca em estufa a 60°C durante 24h. **Calcinação:** A calcinação em mufla com as condições de 550°C durante 20h e posteriormente submetida a caracterização.

Resultados

As propriedades das sementes são apresentadas na Tabela 1.

Semente ZSM-5	Cristalinidade (%)	SiO_2/Al_2O_3	Área Externa (m^2/g)
Zeo	100	30	99
Lab	95	30	82
Sub	73	-	-

Nota-se que para a semente ZSM-5 (Zeo) a cristalinidade é maior (100%), quando comparada com a cristalinidade obtida para semente ZSM-5 (Lab) e para a semente ZSM-5 (Sub). O tipo de semente favorece a formação de fases zeolíticas conduzindo a fases mais cristalinas. A relação SiO_2/Al_2O_3 é a mesma tanto para a semente (Zeo quanto Lab) e as áreas externas são bem próximas.

As membranas zeolíticas (ZSM-5/α-alumina) utilizando os diferentes tipos de sementes obtidas estão apresentadas nas Figuras 1 (a, b, c).

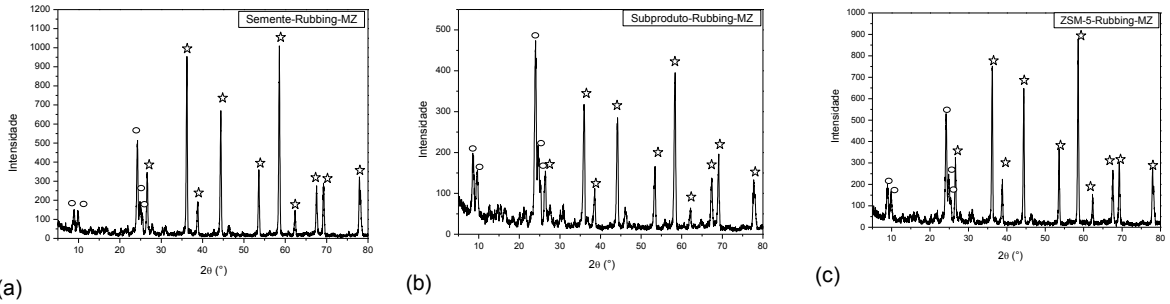

Figura 1. Difratogramas das membranas zeolíticas: (a) ZSM-5 (Zeo), (b) ZSM-5 (Sub), (c) ZSM-5 (Lab), via método de crescimento secundário – rubbing.

Observa-se nos difratogramas das diferentes sementes (Figuras 1a, b, c) a formação da zeólita ZSM-5, uma vez que há presença dos picos característicos do grupo MFI em 2θ = 7 - 9º e 23 - 25º. A partir da análise das Figuras (2a, b, c) observa-se a formação dos picos específicos da zeólita ZSM-5 (o) juntamente com os picos da α-alumina (*), confirmando a formação das estruturas das membranas zeolíticas (ZSM-5/α-alumina). Para se determinar a melhor semente utilizada para a síntese da membrana zeolítica, determinou-se a cristalinidade das membranas baseada no somatório das intensidade dos picos característicos dos difratogramas de raios X das Figuras (2a, b, c). A amostra padrão considerada foi a semente ZSM-5 (Zeo) (100% cristalinidade). Os resultados de cristalinidade foram 99% para a membrana zeolítica (ZSM-5 (Lab)/α-alumina) e 52% para a membrana zeolítica (ZSM-5 (Sub)/α-alumina). As diferenças nos resultados de cristalinidade das membranas zeolíticas são devido às diferenças das propriedades das sementes. Os valores da razão SiO_2/Al_2O_3 e a área externa da semente (Sub) devem ser inferiores aos das sementes (Zeo e Lab).

Conclusões

O efeito dos tipos de sementes na síntese das membranas zeolíticas foi investigado. A cristalinidade da membrana zeolítica (ZSM-5(Sub)) apresentou uma cristalinidade bem inferior as membranas zeolíticas (ZSM-5(Zeo) e ZSM-5(Lab)/α-alumina) que pode ser explicado em função das suas propriedades.

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Agradecimentos

Os autores agradecem a Petrobras pelo apoio financeiro dado a esta pesquisa.

Modeling and Process Simulation

- **Oral session 6**

USE OF STEADY-STATE BLOCK MODELING AND GENETIC ALGORITHMS TO OPTIMIZE PROCESSES COUPLED WITH REVERSE OSMOSIS MEMBRANES

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In many situations in which membranes are integrated in a process, membrane optimization can not be separately performed because of the following reasons:

- The recirculation of the permeate streams influences the composition of the membrane feed streams.
- The cost function for the whole process is a result of the costs derived from the membrane units and those from the other units.
- Complex problems are usually multiobjective ones, that is, there can be more than one (usually competing) objectives.

Genetic algorithms can be used as optimization techniques very suitable for multiobjective problems [1]. However, depending on the software used for the process simulation, the interconnection between the process simulator and the genetic algorithm code can be extremely difficult or even impossible.

In this work, we proposed an approach integrating modular modeling of units and genetic algorithms in the same computational environment. Modeling using blocks is a way to rapidly evaluate or optimize different system configurations. Using this approach, the model is implemented in a function asigned to a block with input and output ports related with the input and output streams of the physical units. One possible tool to implement the model of the process is the Simulink® application integrated in the Matlab® environment. This toolbox has a graphic interface to rapidly connect the blocks by means of signals. This application is used in many engineering applications and has a great potential for chemical process engineering applications.

In our work, we created a steady-state model of a process that includes reverse osmosis membranes to recycle a stream to the process. Fig. 1 shows the Simulink diagram for this process. For the membrane stage, a reverse osmosis model considering concentration polarization and drop of pressure along the vessels was used. One computational issue that appears in the model process development is the existance of algebraic loops; therefore, a suitable selection and initialization of the cut streams must be performed. Another issue is the correct definition of the optimization problem with the selection of decision variables and relevant fitness functions. Fig. 2 shows an example of calculation flow to obtain the fitness values from the decision variables. Another problematic issue is that same combination of the decision variables lead to non-physical situations during the application of the genetic algorithm. For example, a low feed flow or a very high pressure can lead to a non-physical solution for which the concentrate flow is negative. To avoid this situation, previous calculations can be performed using a simple model based on the use of the stage recoveries as decision variables with an approximate estimation of the pressure needed in order to calculate energetic costs. After this previous optimization, the results can be used to set restrictions for the pressures to be optimized, previously to the use of the most accurate model.

To perform the optimization, we used an implementation of the NSGA-II genetic algorithm. These algorithm has been previously used to optimized RO processes [2]. The application of this algorithm to a configuration of a rinsing process with regeneration like the one studied in [3] led to a Pareto frontier (Fig. 3). Points belonging to this frontier shows not only a solution, but a set of good feasible solutions of process design and operation.

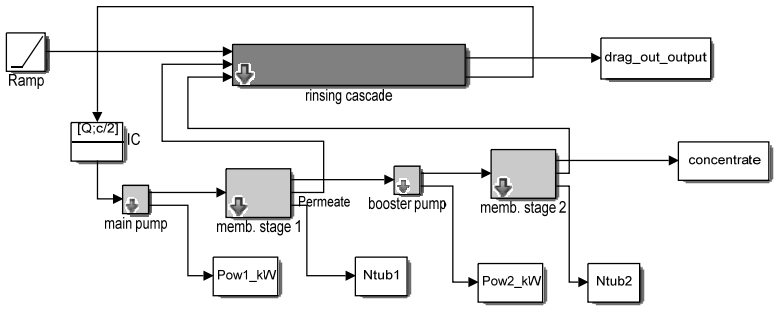

Fig. 1. Flowsheet of a rinsing process coupled with regeneration using membrane stages.

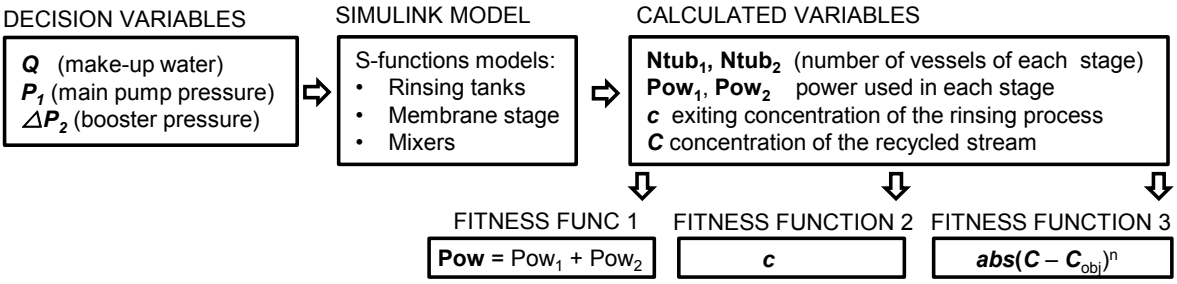

Fig. 2. Calculation flow to obtain the fitness values from the decision variables.

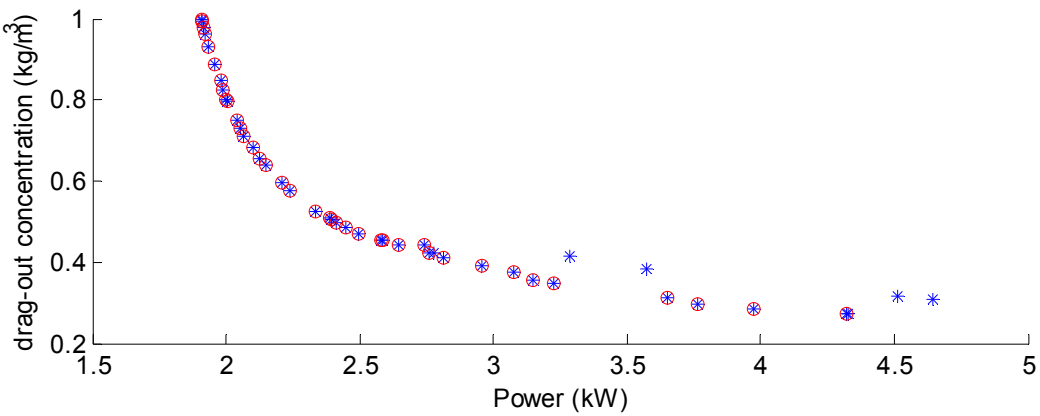

Fig. 3 Pareto frontier obtained using the genetic algorithm NSGA-II.

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Acknowledgements

The Spanish Ministry for Science and Innovation (Project OPTIMEM CTM2010-20248) is kindly acknowledged.

POLYMERIC MEMBRANES APPLICATION IN PETROLEUM INDUSTRY HYDROGEN SEPARATION

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Abstract

Hydrogen is a utility produced in petroleum refineries for a number of processes, namely diesel, naphtha and kerosene hydrotreating units, vacuum gas oil hydrocracking and atmospheric residue desulphurisation (ARDS). In addition, hydrogen is becoming more expensive due to its demand as a clean fuel. Furthermore, the implementation of more stringent environmental regulations forces the petroleum industry to adapt more efficient methods of hydrogen recovery with minimal fuel consumption. In light of the above, the Kuwait Institute for Scientific Research (KISR) has established a membrane technology group with the aim of developing and transferring technology of modern membrane applications applied in the petroleum industry. Hence, this work was initiated in order to implement polymeric membranes – which present themselves as a cheap option for gas separation – in Kuwait's petroleum refineries. A polyamide membrane (ε = 0.3, S = 95.4% at 308 K, prepared by casting) was chosen to be modelled in accordance to typical operating conditions. The permeability was estimated for a hydrogen/carbon dioxide mixture (50/50% mol basis) with a flow rate of 10 m^3/s, representing most refinery applications. The *Carman-Kozeny* fluid dynamic packed bed equation was used to estimate the pressure drop (ΔP, Pa/m) across the cross-flow geometry of the membrane configuration. It was observed that ΔP estimations (2.3×10^9 Pa/m) represent an obstacle for gas separation due to its order of magnitude, forcing the recommendation of inter-cooling compressor installation. In addition, hydrogen recovery in the permeate fraction ranged between 5×10^{-9} to 1.5×10^{-8} (mol/s m^2 Pa) with a flow rate range of 5 to 15 m/s. This demonstrates the sensitivity of hydrogen recovery and need to control gaseous mixture flow rates.

Keywords: Polyamide Membrane, Petroleum Refinery, Carman-Kozeny Equation, Hydrogen.

Modeling and Process Simulation

- **Poster session 1**

ULTRAFILTRATION OF MUNICIPAL WASTEWATER: STUDY ON FOULING MODELS AND FOULING MECHANISMS.

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Ultrafiltration (UF) with hollow fiber membranes is a proven membrane technique that can achieve high water quality standards as a tertiary treatment in municipal wastewater treatment plants (MWTPs) [1][2]. However, UF has an important drawback, membrane fouling, which causes losses of productivity and increases operation costs.

In order to study membrane fouling mechanisms, several models were used to fit permeate flux decline vs. time. The experimental tests were carried out with model solutions that consisted of bovine serum albumin (BSA, a protein) and dextran (a carbohydrate). These model solutions are commonly used to model secondary effluents from MWTPs [3,4]. BSA and dextran concentrations were adjusted to 15 mg/l and 5.5 mg/l, respectively. These concentrations were chosen according to previous studies that revealed that the fouling trend of the simulated wastewater and the secondary effluent of a MWTP were very similar. Three different transmembrane pressures (TMPs) and three different crossflow velocities (CFVs) were tested in the experiments performed with the UFCM5 Norit X-flow® hollow fiber membrane. Membrane material was PES/PVP, its MWCO was 200 KDa, its diameter was 1.5 mm and its configuration is inside-out. The models considered in this study are shown in Table 1.

Table 1. Models equations.

Model	Flux decline Equation	Eq.
Hermia's models adapted to cross-flow filtration	$-\frac{dJ}{dt} = K_{CF}(J_P - J_{Pss})J_p^{2-n}$	Eq. 1
Belfort's empirical model	$\mathrm{J} = \mathrm{J}_0 \cdot \exp\left\{\frac{-\mathrm{t}}{\mathrm{A} + \mathrm{B} \cdot \mathrm{t}}\right\}$	Eq. 2
Modified Belfort's model	$\mathrm{J} = \mathrm{J}_0 \cdot \exp\left\{\frac{-\mathrm{t}}{\mathrm{A} + \mathrm{B} \cdot \mathrm{t} + \mathrm{C} \cdot \mathrm{t}^2}\right\}$	Eq. 3
Modified quadratic complete blocking	$\mathrm{J} = \mathrm{J}_{\mathrm{pss}} + \left(\mathrm{J}_0 - \mathrm{J}_{\mathrm{pss}}\right) \cdot \mathrm{e}^{-\left(\mathrm{A} \cdot \mathrm{t} + \mathrm{B} \cdot \mathrm{t}^2\right)}$	Eq. 4
Logarithmic inversed model	$\mathbf{J} = \mathbf{A} + \frac{\mathbf{B}}{\mathbf{ln}(\mathbf{C} \cdot \mathbf{t} + \mathbf{D})}$	Eq. 5
Double exponential model	$\mathbf{J} = \mathbf{A} \cdot \frac{(\mathbf{B} + \mathbf{e}^{\mathbf{C} \cdot \mathbf{t}})}{(\mathbf{D} + \mathbf{e}^{\mathbf{E} \cdot \mathbf{t}})}$	Eq. 6
Tangent inversed function	$\mathbf{J} = \mathbf{J}_{\mathbf{pss}} + \frac{\mathbf{A}}{\mathbf{tan}(\mathbf{TMP} \cdot \mathbf{t} + \mathbf{0.017})}$	Eq. 7

Hermia´s model in Table 1 considers different fouling mechanisms depending on the value of n: n=2 complete blocking, n=1 intermediate blocking, n=1.5 standard blocking, n=0 gel layer formation. In Table 1, J is the permeate flux, J_0 is the initial permeate flux, J_{pss} is the steady-state permeate flux, t is time and A, B, C, D, E are empirical constants.

The fitting accuracy of the models was determined in terms of the R-squared (R^2) and standard deviation (SD) (Table 2).

Table 2. Models fitting accuracy: R^2 and SD values (in brackets).

	Operating conditions		Model					
Test Id.	**TMP (MPa)**	**CFV (m/s)**	**Intermediate blocking**	**Gel layer formation**	**Belfort quadratic**	**Double exponential**	**Tangent inversed**	**Logarithmic inversed**
1	0.10	0.50	0.93 ($4.3\cdot10^{-6}$)	0.93 ($4.3\cdot10^{-6}$)	0.99 ($3.1\cdot10^{-6}$)	0.98 ($1.9\cdot10^{-6}$)	0.98 ($2.3\cdot10^{-6}$)	0.99 ($1,4\cdot10^{-6}$)
2	0.10	0.75	0.92 ($2.5\cdot10^{-6}$)	0.93 ($2.3\cdot10^{-6}$)	0.98 ($2.4\cdot10^{-6}$)	0.94 ($2.2\cdot10^{-6}$)	0.96 ($1.7\cdot10^{-6}$)	0.98 ($1,2\cdot10^{-6}$)
3	0.10	1.00	0.95 ($3.9\cdot10^{-6}$)	0.91 ($5.5\cdot10^{-6}$)	0.99 ($2.7\cdot10^{-6}$)	0.99 ($1.4\cdot10^{-6}$)	0.98 ($2.7\cdot10^{-6}$)	0.99 ($1,6\cdot10^{-6}$)
4	0.15	0.50	0.96 ($4.6\cdot10^{-6}$)	0.90 ($7.5\cdot10^{-6}$)	0.99 ($4.2\cdot10^{-6}$)	0.99 ($1.6\cdot10^{-6}$)	0.98 ($2.4\cdot10^{-6}$)	0.99 ($1,2\cdot10^{-6}$)
5	0.15	0.75	0.94 ($3.9\cdot10^{-6}$)	0.92 ($4.9\cdot10^{-6}$)	0.99 ($2.8\cdot10^{-6}$)	0.99 ($1.5\cdot10^{-6}$)	0.98 ($1.8\cdot10^{-6}$)	0.99 ($1,3\cdot10^{-6}$)
6	0.15	1.00	0.89 ($7.4\cdot10^{-6}$)	0.94 ($5.4\cdot10^{-6}$)	0.98 ($6.4\cdot10^{-6}$)	0.98 ($3.2\cdot10^{-6}$)	0.93 ($5.8\cdot10^{-6}$)	0.99 ($1,7\cdot10^{-6}$)
7	0.20	0.50	0.96 ($6.5\cdot10^{-6}$)	0.87 ($1.2\cdot10^{-5}$)	0.96 ($8.5\cdot10^{-6}$)	0.99 ($3.3\cdot10^{-6}$)	0.97 ($5.4\cdot10^{-6}$)	0.99 ($1,9\cdot10^{-6}$)
8	0.20	0.75	0.97 ($3.0\cdot10^{-6}$)	0.89 ($6.9\cdot10^{-6}$)	0.98 ($3.3\cdot10^{-6}$)	0.99 ($1.9\cdot10^{-6}$)	0.99 ($1.4\cdot10^{-6}$)	0.99 ($1,1\cdot10^{-6}$)
9	0.20	1.00	0.97 ($3.9\cdot10^{-6}$)	0.83 ($1.1\cdot10^{-5}$)	0.97 ($5.6\cdot10^{-6}$)	0.98 ($3.1\cdot10^{-6}$)	0.96 ($4.8\cdot10^{-6}$)	0.99 ($2,4\cdot10^{-6}$)

The author's logarithmic inversed model was the model that fitted the best to the experimental data except in the case of the tests 2 and 3. For these two tests, the model that fitted the best was the Belfort quadratic model. Although Hermia´s models fitted worse than the above mentioned models, the analysis of Hermia´s models is interesting because it allows identifying the fouling mechanisms occurring for each experimental condition. Among Hermia´s models, the intermediate pore blocking was the predominant fouling mechanism except in the case of tests 2 and 6. For these tests the fouling mechanism was gel layer formation.

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Acknowledgements

The authors of this work wish to gratefully acknowledge the financial support from the Generalitat Valenciana through the program "Ayudas para la realización de proyectos I+D para grupos de investigación emergentes GV/2013".

FOULING MECHANISMS IN THE ULTRAFILTRATION OF WHEY MODEL SOLUTIONS

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One of the major drawbacks in the ultrafiltration (UF) processes used in dairy applications is permeate flux decline due to membrane fouling. To overcome this problem, the determination of the optimum operating conditions to perform UF processes with a minimum fouling and the prediction of permeate flux decline with time are of a great interest. Two mathematical models widely used in the literature are Hermia's models and their adaptations to crossflow UF (Eq. 1) [1, 2] and resistance-in-series models (Eq. 2) [3, 4], because they can predict experimental data with high accuracy. A combined model based on the Hermia's models of complete blocking and cake formation was also proposed (Eq. 3) [5].

$$-\frac{dJ}{dt} = K\left(J - J_{SS}\right)J^{2-n} \qquad \text{Eq. 1}$$

$$J = \frac{\Delta P}{\mu\left(R_m + R'_f\left(1 - exp(-bt)\right) + R_c\right)} \qquad \text{Eq. 2}$$

$$J = \alpha J_{\text{complete blocking model}} + (1-\alpha)J_{\text{cake formation model}} \qquad \text{Eq. 3}$$

In these equations, J is the permeate flux, J_{ss} is the permeate flux when the steady-state is achieved, K is the Hermia's models fouling parameter, n is the Hermia's models parameter that describes the fouling mechanism (complete blocking (n = 2), intermediate blocking (n = 1), standard blocking (n = 1.5) and cake formation (n = 0)), ΔP is the transmembrane pressure, μ is the viscosity of the feed solution, R_m is the resistance of the new membrane, R'_f is the resistance due to fouling phenomena (adsorption and concentration polarization), b is the rate at which fouling phenomena occurs, R_c is the cake resistance and α is the pore blocking parameter and t is the filtration time.

The aim of this work is to investigate the fouling mechanisms that take place during the UF of several whey model solutions. For this purpose, Hermia's models adapted to crossflow UF, a combined model based on the complete blocking and cake formation equations and a resistance-in-series model were used.

Experiments were carried out in an UF pilot plant using three different membranes: a ZrO_2-TiO_2 monotubular membrane (TAMI Industries, France), a flat-sheet polyethersulfone (PES) membrane (Microdyn Nadir, Germany) and a flat-sheet permanently hydrophilic polyethersulfone (PESH) membrane (Microdyn Nadir, Germany). Their molecular weight cut-offs (MWCOs) are 15, 5 and 30 kDa, respectively. Whey model solutions that contained BSA (1 % w/w), BSA (1 % w/w) and $CaCl_2$ (0.06 % w/w in calcium) and a whey protein concentrate (WPC) with a protein content of 45 % (22.2 g/L) were used as feed solutions during the fouling step at 2 bar, 2 m/s and 25 ºC.

The results obtained showed that experimental data did not fit well to the standard blocking model for all the membranes tested, because solute molecules are larger than membrane pores and thus, they cannot penetrate inside the porous structure. The Hermia's model adapted to crossflow UF that corresponded to the highest fitting accuracy in terms of regression coefficient (R^2) and standard deviation (SD) was cake formation for all the

membranes tested when feed solutions were BSA and BSA and $CaCl_2$ solutions. When WPC solutions were used, the highest accuracy was achieved with the complete blocking model for the polymeric membranes and the incomplete blocking model for the ceramic membrane. However, more accurate fittings (R^2 from 0.969 to 0.993) were obtained when the combined model and the resistance-in-series model were considered.

The values of model parameters for the best fitting models are shown in Table 1. As it can be observed, as MWCO increased, the value of the parameters decreased. In addition, comparing BSA and BSA and $CaCl_2$ solutions for the polymeric membranes, the values of the model parameters increased when calcium was added to the feed solution. This is due to the fact that calcium and other salts favour protein agglomeration and decrease their solubility. Thus, fouling is more severe when BSA and $CaCl_2$ and WPC solutions were used as feed solutions.

Table 1. Values of model parameters for the best fitting models.

MWCO (kDa)	Feed solution	Resistance-in-series model			Combined model		
		$R'_f \cdot 10^{-13}$ (m^{-1})	$b \cdot 10^4$ (s^{-1})	$R_c \cdot 10^{-13}$ (m^{-1})	K_c (s^{-1})	$K_{cg} \cdot 10^{-6}$ ($s \cdot m^{-2}$)	α
5	BSA	-	-	-	83.519	2.050	0.349
	BSA+$CaCl_2$	-	-	-	112.731	7.287	0.312
	WPC	1.877	6.392	2.792	-	-	-
15	BSA	-	-	-	30.042	2.012	0.288
	BSA+$CaCl_2$	1.253	4.250	1.015	-	-	-
	WPC	1.789	3.664	1.713	-	-	-
30	BSA	-	-	-	7.757	1.212	0.312
	BSA+$CaCl_2$	-	-	-	17.858	4.766	0.805
	WPC	0.487	2.951	1.330	-	-	-

K_c: complete blocking model parameter
K_{cg}: cake formation model parameter

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Acknowledgements

The authors of this work wish to gratefully acknowledge the financial support from the Spanish Ministry of Science and Innovation through the project CTM2010-20186 and the Generalitat Valenciana through the program “Ayudas para la realización de proyectos I+D para grupos de investigación emergentes GV/2013”.

IMPLEMENTATION OF MEMBRANE MODELS ON A CAPE-OPEN TOOL TO SIMULATE A PROCESS INCLUDING REVERSE OSMOSIS STAGES

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Process simulators are a useful tool for evaluating different configurations of chemical processes and developing new ones. Process simulators include many standard units (equilibrium reactors, distillation towers, etc.) that the engineer can parameterize adapting them to their own process. Usually, the engineer does not need to include physical or thermodynamic data when the compounds are included in the simulator databank. Besides, the simulator includes several thermodynamic models to obtain the properties of mixtures or to perform flash calculations. However, some unit operations are very specific and very material dependent, so there are serious difficulties to define them as general units to be parameterized. That is the case of membrane processes. To face the problem, simulators include the possibility to define user units that liable to be integrated in the process flowsheet to interact with the units integrated in the simulator. To do so, it is necessary to know how the stream information is defined, to correctly interchange information through the unit ports. In a previous work [1], we showed how to implement a simple membrane process model in CHEMCAD simulator using the VisualBasic interface. However, many engineers are not familiar with Visual Basic; and CHEMCAD is a commercial software that cannot be affordable for small applications [2].

In this work, we show the possibility to perform calculations of processes including RO membranes using the freeware environment COCO with models developed in MATLAB. COCO software is based on computer aided process engineering open (CAPE-OPEN) that is a standard for communication between software components. In the COCO environment, the flowsheeting is performed by COFE. The model of the user units is developed in MATLAB Matlab (or alternatively in Scilab which is also freeware) and the units interchange data with the COFE environment (Fig. 1). The communication is possible thanks to software applications developed by AmsterCHEM [3].

As a case of study, we developed a RO unit to be used in the rinsing process, whose COFE flowsheet we show in Fig. 2. In this process, the RO membrane unit recycles water with low salt concentration to the last tank unit were solids coming from the previous tank are rinsed.

The membrane model includes the solution-diffusion model equations to explain volumetric flux and solute permeation as function of pressure, concentration. An iteration is performed to take into account the effects of the difference of osmotic pressure developed on the permeate flux and to account for polarization effects. These equations, valid for a local position of the membrane, are integrated together with a model for pressure charge to obtain the performance of a vessel unit containing several modules in series. The possibility to use robust solvers and many mathematical procedures constitutes one of the strong points of the MATLAB programming. It is important to mention that we must check if the components used are defined, should not be this case, they must be included in the property database using the TEA server provided with COCO. Finally, the membrane stage unit is defined by including the number of vessels and modules per vessel as parameters, together with solution diffusion parameters and other necessary parameters that can be experimentally obtained for any specific membrane.

Once the membrane model is included any typical process simulator capabilities can be used in the COFE environment. As an example, we show a parametric study of the effect of the pressure used in the process on the concentration of the final tank.

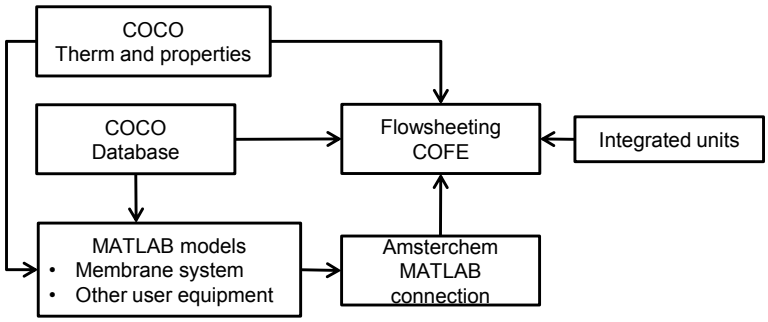


Fig. 1 Communication between models in the COCO environment.

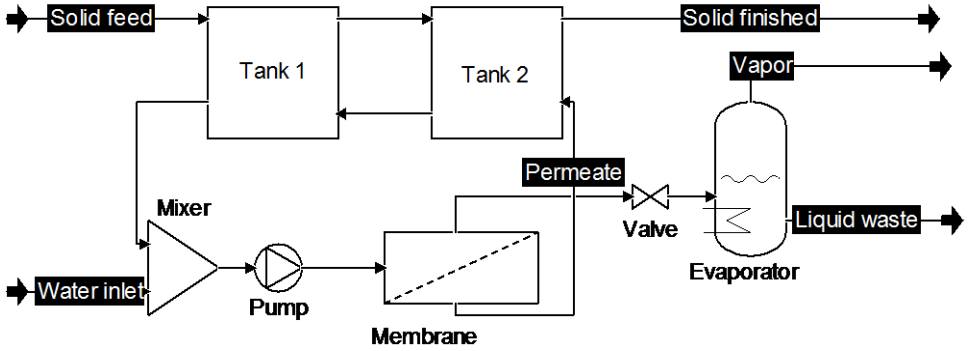
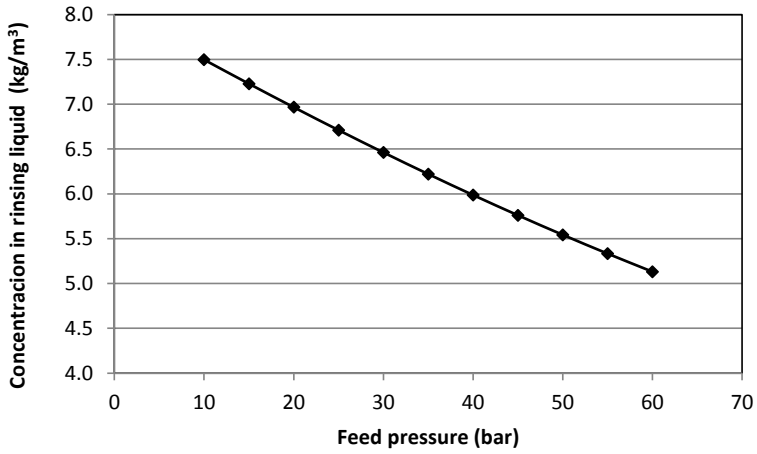


Fig. 2 Flowsheet of rinsing process coupled with membrane for water recycling.



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Acknowledgements

The Spanish Ministry for Science and Innovation (Project OPTIMEM CTM2010-20248) is kindly acknowledged.

MASS TRANSPORT KINETICS OF HCL AND ZINC CHLORIDE THROUGH DIFFUSION DIALYSIS AND ELECTRODIALYSIS MEMBRANES

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Hot-dip galvanizing consists of covering the surface of iron or steel pieces with a reactive zinc layer that provides oxidation protection. This process is carried out by immersion of the metallic pieces in a bath of molten zinc. During the whole process, spent pickling solutions (SPS) coming from stages such as washing, pickling or galvanizing itself are generated. Among other substances, SPS contain high concentrations of zinc, iron and HCl. The increasingly stringent regulations regarding the discharge of acids and metals into the environment, and the increasing demand upon the recycling/reuse of these effluents after proper treatment, have focused the interest of the research community on the development of new approaches for the recovery of acid and metals from these industrial wastes [1,2].

The difficulty underlying the development of recovery processes is associated to the physicochemical complexity usually encountered in hydrochloric acid effluents, where the main species are present as anionic species, such as zinc chlorocomplexes; as a result it is difficult to select one universal method for the treatment of this type of effluents. Membrane techniques are considered to be simple, effective and sustainable because of large and well-defined area of contact, compactness and reduced size of equipment, no need of chemicals addition, easy scale-up [3]. Among them, Diffusion Dialysis (DD) and Electrodialysis (ED) are membrane separation processes with demonstrated applications in the recovery of valuable compounds from liquid matrices. The basic element of these technologies is an ion-exchange membrane having in its structure electrically charged sites, which facilitate the transport of counter-ions while the co-ions are rejected. If an anion-exchange membrane is used, the anions can permeate the membrane freely but the cations will be retained by the membrane. The protons, however, can pass the anion-exchange membrane in spite of their positive charge because they are transported by a tunnelling mechanism. Thus, the acid could be removed from the complex solutions [4].

Diffusion dialysis (DD), using anion exchange membranes, is an attractive method for acid recovery that was first applied industrially in the late 1950s. The driving force for this process relies on the difference in chemical potential of the species on either side of a membrane and as such the only external power required is that needed to circulate the solutions [4,5]. Electrodialysis membrane technology is an electromembrane process where combinations of ionic membranes are placed between a pair of electrodes. Under the influence of an applied dc electric field, ions move in the direction of the opposite charged electrode. Electrodialysis membrane technology enables not only separation of acid but also its concentration to high enough values to recycle the acid to be further used in the pickling bath [6].

This work reports the comparative study of the membrane mass transport kinetics of HCl and Zn species from a feed solution that simulates the composition of spent pickling solution by means of DD and ED. Mass balances of the permeating species were developed obtaining the mathematical models and characteristic parameters. The overall mass transfer coefficient in DD membranes in a continuous dialyzer with co-currently parallel-flow in both channels has been calculated using the Michaels equation [7]. The membrane mass transport coefficient and the mass transfer coefficients in the liquid films were also determined. On the other hand, the Nernst–Planck equation that accounts for the contributions of the concentration driving force and the migration of ions as a result of the electric field, has been used to describe the mass transport of HCl and Zn through ED membranes. The diffusion

coefficients of both species, zinc anionic complexes and protons did not remain constant within the whole range of experimental variables, and their variation with the membrane concentration was described by means of an exponential equation $D_i = D_0 \cdot \exp(-\tau \cdot C_m)$, that was incorporated into the mathematical model [6]. The mathematical model also incorporates the distribution of zinc chloride (cationic and anionic) species as a function of the process conditions. The experimental behaviour was satisfactorily described with the mathematical model and parameters thus providing a useful tool for the design of the separation process.

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Acknowledgements

Financial support from the project CTQ2011-25262 (Ministerio de Economía y Competitividad-MINECO/SPAIN and FondoEuropeo de Desarrollo Regional-FEDER) is gratefully acknowledged.

MODELING AND SIMULATION OF MEMBRANE REACTOR FOR BIODIESEL PRODUCTION

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Biodiesel is an important renewable fuel whose production has been limited mainly by high residence times in the reaction and separation sections due to the presence of soaps and high viscosity gels. Intensified processes for biodiesel production have been studied using different technologies. This work studies the possibility of reducing this problem by implementing a falling film reactor (FFR) integrated whit hollow fiber membranes. This reactor takes advantage of both systems: while production of biodiesel using a FFR is characterized by high reaction rates and productivity and a positive effect on separation stages because interfacial mass transfer area is achieved without mixing, the integration of a membrane system allows it increase the yield to fatty acid methyl esters as well as the simultaneous purification of the biodiesel obtained. In this work a mathematical model to predict the behavior of falling film reactor assisted by membranes was developed. The model describes a reactor as a non-equilibrium two phases reactor and the flux through the membrane with the transport equations of Ultrafiltration. A sensitivity analysis was performed to understand the operation of the membrane reactor and identify the main variables of the system. The model predicts the appropriate operating conditions range for experimental evaluation. Simulation of the process allows us to conclude that there is a strong drag effect exerted by methanol on the glycerol and that the conversion and yield in the reactor increase when the biodiesel and glycerol flux through the membrane rise, but they decreases when the flux of methanol increases, indicating that the amount of methanol fed to the reaction system is a main operating variable because it has strong influence on the transport through the membrane. The evaluation of the reaction in the FFR with membrane showed an increment on biodiesel yield in comparison to the FFR without membranes, although molar ratio methanol to oil increases in order to compensate the methanol that permeates through the membrane.

Gas Permeation and Separation in Polymeric Hollow Fiber Membranes: Mathematical Modeling and Validation

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Gas separation using membranes has turned into an important industrial process. Prediction and analysis of permeation and separation in gas separation membranes require appropriate mathematical models in order to provide accurate information about the process performance. Non-ideal effects are among the parameters that their incorporation into the models can highly affect the validity of the predictions. These include pressure losses within the membrane module, real behavior of the gas molecules in the mixture, concentration polarization, temperature change due to permeation and its subsequent effect on the permeation performance, and temperature-, pressure- and concentration-dependence of the fluid viscosity are among the major parameters that determine deviations from ideal conditions. To our best understanding, despite numerous studies focused on this subject and various models presented in the literature, no specific study could be identified encompassing the role and influence of all these parameters in a single model [1-3].

The main objective of this study is to develop a comprehensive model that accounts for non-ideal parameters in order to improve the accuracy of the prediction of the permeation and separation performance in asymmetric hollow fiber membranes. Fundamental equations based on the permeation, mass transfer and momentum equations were considered for permeation of feeds comprising binary and ternary gas mixtures. Then the effect of real gas behavior was included by considering fugacity coefficients and using the SRK equation of state. The effect of concentration polarization was considered by accounting for the relationship between the bulk and membrane surface concentrations. The temperature drop due to permeation was considered through calculation of the Joule-Thomson coefficient and its effect on the equations. The effects of pressure drop on both the shell and lumen side of the hollow fibers was accounted for by using the governing equations of fluid mechanics. The effects of temperature, pressure and concentration dependency of the fluid viscosity were accounted for at both the low and high pressure ranges. All these parameters and their effects were appropriately accounted in a model that was solved using MATLAB codes. The influence of non-ideal effects on the module efficiency was investigated and verified using available experimental and/or plant data from various processes. Sensitivity analysis was carried out in order to determine the extent of influence of each effect on the module performance. The results and findings in this study can be used for effective analysis and prediction of gas separation membrane performance for practical applications.

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Analysis of the transport models governing permeation and separation of olefin/paraffin mixtures in polymeric membranes

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Large capital expense and enormous energy cost imposed by conventional separation technologies for the separation of olefin/paraffin mixture has necessitated the need for alternative separation techniques [1]. In recent decades, membrane technology is recognized as an alternative technology owing to the improved economy of the process, lower energy consumption and smaller equipment footprint. Polymeric membranes can often exhibit desirable selectivity thus have been used extensively as candidates for olefin/paraffin separation and other similar applications [2]. Althogh polymers possessing large free volume have higher permeation rates, as in the case of rubbery polymers, achieving high separation efficiencies can is a tedious task due to the high permeation rates for both olefin and paraffin [1]. Substantial researches to explore various polymeric membranes have indicated that polyimides can offer higher separation performance compared to conventional membranes [1, 3-6]. Permeation in polymers is determined by both thermodynamic (sorptive) and kinetic (diffusive) factors. In this regard, development of advanced polymeric membranes requires a through understanding about the issues affecting the transport of penetrants in the membrane, and particularly in case of olefins and paraffins.

Modeling binary gas transport in glassy membranes have been usually accomplished using Fick's first law without much attention for taking into account the effect of presence of both component and the resulting effects on transport properties. This may be erroneous specially when bulk fluxes are not negligible. Bulk flow model describing a binary gas permeation system as a ternary mixture of two penetrants and a polymer was consequently proposed by some researchers to overcome this problem [3, 7-8]. In spite of it's wide applicability in membrane transport modeling, results have shown that this model was not able to predict some permeation data in polyimides [9]. This discordance can possibly be related to the fact that the flux of each species in a binary mixture depends on the gradient of concentration of the other as well as itself which is not accounted for in the model [10]. Maxwell-Stefan approach which was originally developed to describe multi-component diffusion has been proposed to assess this issue in several studies [11-13].

The main purpose of this study is to provide an in depth analysis and evaluation on the benefits and limitations of bulk flow and Maxwell-Stefan models for predicting the transport properties and performance of several polyimide membranes for olefin/paraffin separation. In addition, the influence of thermodynamic and kinetic coupling contributions on the membrane performance will be addressed. To this end, dual-mode sorption model was employed to calculate pure gas sorption using the available sorption data in the literature. Permeability of each component has been subsequently obtained using the fluxes calculated by the mentioned transport models using MATLAB codes. Modeling results revealed that choosing a proper transport model for a given polymer is of great importance since bulk flow model failed to predict even the trend of selectivity in one case. Despite predicting the trend, Maxwell-Stefan model underestimated experimental data of selectivity. As a result, coupling effect of diffusion coefficients which has been accounted for in the Maxwell-Stefan equations, seemed to have a paramount influence on transport studies in polyimdes. Moreover, considering thermodynamic coupling effects leaded to remarkable alterations while kinetic coupling effects caused negligible changes in the model predictions. Results of the present examination can be used to assess the eligibility of two well-known transport models to predict the ability of polyimide membranes in the propylene/propane separation.

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INTEGRATION OF ECONOMIC AND TECHNICAL OBJECTIVES FOR CHEMICALS ULTRAPURIFICATION BY REVERSE OSMOSIS MEMBRANE CASCADES

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Electronic chemicals, which are the chemicals and materials used to manufacture and package semiconductors and printed circuit boards, require extreme low content of metallic impurities to avoid reliability problems due to loss of oxide integrity or shortening of minority carrier lifetime. Ultrapurification processes become necessary to achieve these exigent limits from technical grade chemicals. Among all the ultrapurification alternatives (distillation, adsorption, ion exchange, membrane technologies), reverse osmosis emerges as the most desirable technology according to environmentally friendly criteria, as auxiliary chemicals are not needed and zero effluent generation can be achieved by commercialization of the retentate streams to non-electronic purposes.
Multistage process becomes indispensable to achieve the exigent electronic grades. Integration of the several stages by recirculation of retentate streams to previous stages, configuring a membrane cascade, is considered an effective way to combine a high removal of metallic impurities with a high recovery rate [1-3].
The problem of the design of reverse osmosis networks has been considered from the optimization techniques by generation of the configurations and their optimization with mass and energy integration or multi-objective optimization, mainly for desalination units of seawater in order to minimize costs and energy consumption or to maximize permeate production and economic profit [4, 5].
The present work is focused on the multiobjective optimization of multistage reverse osmosis membrane cascades applied to the ultrapurification of chemicals for the semiconductor industry (hydrogen peroxide was chosen as case study). The membrane systems are formulated adding product quality metrics to economic criteria to result a bi-criteria nonlinear programming (NLP) problem.
The aim of the work is the analysis of the influence of the quality of the product over the economically optimum membrane systems by means of multiobjective optimization when product quality metrics were added to economic criteria. Furthermore, the integration of both criteria is also considered by the application of an economic optimization within the framework of quality-dependent prices.
The mathematical model for integrated countercurrent membrane cascades is based on overall and solute (metallic impurities) material balances and the Kedem- Katchalsky transport equations. The general scheme of a n-stage integrated countercurrent membrane cascade with implementation of bypass stream in the last stage is depicted in Figure 1. The use of bypass streams has been demonstrated as an effective way to reduce the costs of advanced membrane-based separation systems when the margin between the final product requirements and the obtained product is significant.

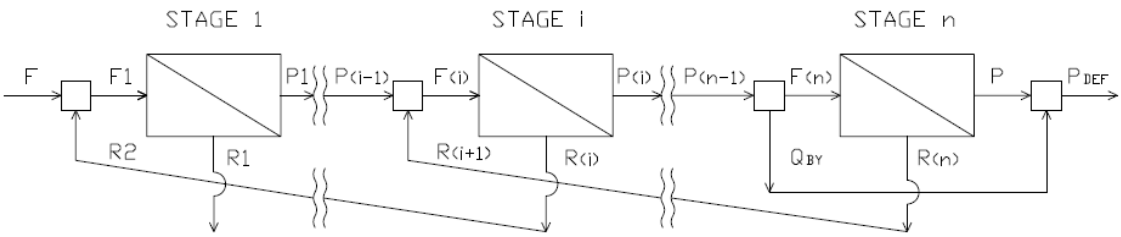

Figure 1. General scheme of a n-stage integrated countercurrent membrane cascade

The economic profit of the process (Z) is defined as the difference between total daily revenues and costs. More detail about the economic terms can be found in the previous work [6]. The product quality is formulated as a dimensionless safety factor (SF), defined as the quotient between the limit concentration (fixed by SEMI Standard limiting requirements) and the product concentration.

As illustrating case of study, an industrial-scale system is designed to treat an annual target of 9000 tons of technical grade peroxide in order to produce each electronic SEMI Grades (from 1 to 5) by membrane cascades. The reverse osmosis membrane selected for the process is the BE model from Woongjin Chemical, which is a polyamide membrane used in previous studies [6, 7].

Five different quality-dependent price models are proposed to illustrate the case study: linear, parabolic, exponential, sigmoidal and bisigmoidal relationships between product quality and price. Figure 2 shows the results of production of Grade 1 chemical by a three-stage membrane cascade considering the exponential dependence for the product price.

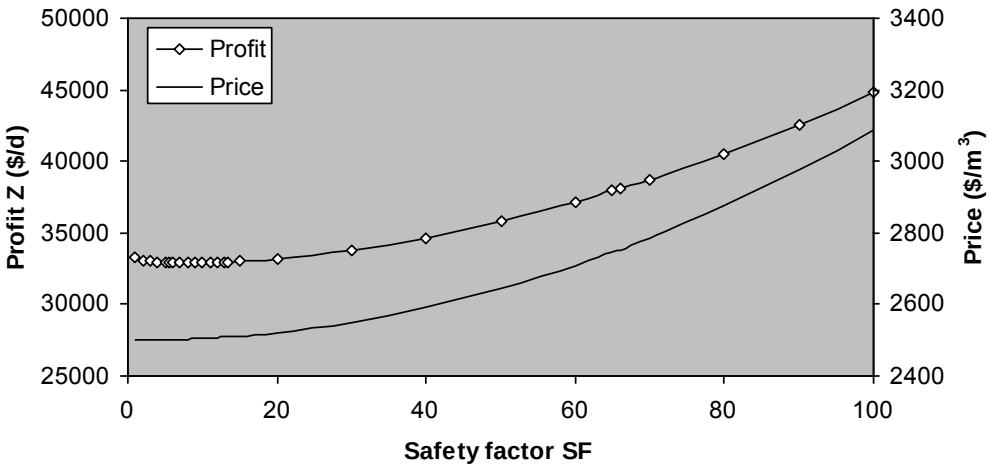

Figure 2. Economic optimization under consideration quality-dependent prices.

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Acknowledgements

This research has been financially supported by the Ministry of Science and Innovation of Spain (MICINN) through the projects CTQ2010-16608 and ENE2010-14828.

Membranes for Drinking Water Production

- **Oral session 7**

DONNAN DIALYSIS FOR SAFE DRINKING WATER SUPPLY: HOW CAN AN "ENEMY" BECOME A FRIEND?

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The contamination of groundwater sources with arsenic is a matter of great concern worldwide, because of its negative impact on the human health and on the ecosystems. The integration of ion exchange [1] membrane transport and separation of a target hazardous ion with an appropriate method for its removal can prevent the drawbacks associated with direct application of physicochemical and/or biological processes for drinking water treatment, and provide an environmentally friendly means of removing or recovering of a target ion [2]. In prior research, the arsenate transport from single arsenate-containing model solutions across anion-exchange membranes was systematically studied both theoretically and experimentally [3]. A possible limitation of applying anion-exchange membranes for arsenate separation in practice is when sulphate is present as an accompanying anion. This is due to the strong competition between arsenate and sulphate transport in such a case. Therefore, the aim of this research was to develop a novel strategy to deal with this problem. The performance of different Donnan dialysis operating regimes (with or without arsenic precipitation in the stripping compartment) was investigated and compared.

Methods

Three anion-exchange membranes were tested, a monovalent anion-perm-selective membrane Neosepta ACS, an open polymer matrix (300 D) and alkali resistant Neosepta AXE 01, both manufactured by Tokuyama Soda (Japan) and a PC 200 D membrane from PCA-GmbH (Germany). The experiments were carried out in a two-compartment membrane cell provided with a circular window, where a flat-sheet membrane piece (exposed area, A = 11.3 cm^2) was placed. The membrane was fixed between the two half-cells of the apparatus and the feed (equimolar mixtures of arsenate and sulphate in their sodium forms) and the stripping (sodium chloride, sodium sulphate or ferric sulphate) containing solutions (136 mL each) were placed in the respective compartment of the cell. The experiments were initiated when stirring in each compartment was started with a rate of 700 rpm. The tests were operated for up to 72 h. Samples were periodically withdrawn from both compartments and the transient arsenic, sulphur and sodium concentrations in the two compartments were analyzed by ICP-AES. Conductivity and pH were also followed.

Results and Discussion

For all tested membranes either no preferential (in the low arsenate/sulphate concentration range < 1 mmol/L) or preferential transport of sulphate to the stripping compartment (in the arsenate/sulphate concentration range of 50 mmol/L) was documented when chloride was used as the "driving" counter-ion. Therefore, a new strategy to overcome the sulphate preferential transport over arsenate was developed and validated using the very sulphate as the "driving" counter-ion according to the Donnan dialysis principles. Through this novel approach, arsenate in the treated water is replaced by a non-toxic anion as sulphate, which, on its side, is not anymore strongly competing with arsenate transport from the treated water to the stripping solution across the membrane. Moreover, since the arsenic levels relevant to drinking water sources contamination are most frequently in the concentration range of less than 0.1 mmol/L (equivalent to ~0.75 ppm of As), arsenate substitution by sulphate should (in most cases) not lead to secondary contamination of the treated water by this anion since its maximum allowed level is much higher 250 ppm. The driving force for arsenate transport across the membrane can be additionally enhanced by

using ferric sulphate in the stripping solution due to the arsenic precipitation by iron. The process performance is illustrated in Figure 1.

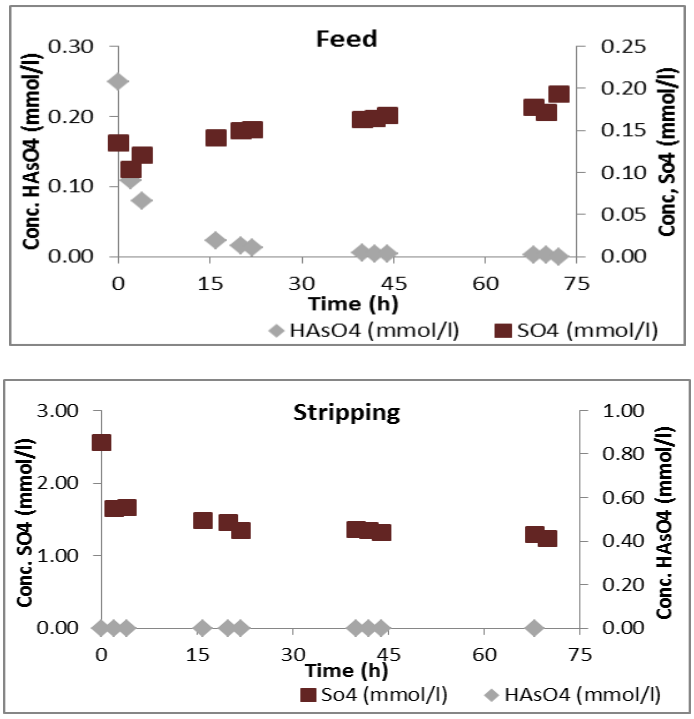

Figure 1. Time course variation of arsenate and sulphate concentrations in the feed and stripping solutions. AXE 01 membrane was used under batch Donnan dialysis conditions. The experiment was performed with an initial concentration of 2.6 mmol/L of $Fe_2(SO_4)_3.7H_2O$ in the stripping compartment.

As it can be observed in Figure 1, at an about of 1 order of magnitude sulphate excess in the stripping compartment, the process can be efficiently performed, thus eliminating completely the arsenate from the treated water by exchanging it for sulphate. At the same time, arsenate on its arrival into the stripping solution is efficiently precipitated by iron (no soluble As was detected).

Conclusions

- It has been demonstrated that Donnan dialysis can be successfully applied for removal of arsenate from sulphate-containing water streams.
- For the first time, by using the very sulphate as the “driving” counter-ion for arsenate counter-transport, it has been shown that this separation problem can be solved successfully.
- When Donnan dialysis is combined with simultaneous arsenic precipitation in the stripping compartment, its performance can be further improved both in terms of arsenic removal efficiency and process kinetics.

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Acknowledgements

Mafalda Lopes is a PhD student at DQ/FCT/Universidade Nova de Lisboa, Portugal.

DRINKING WATER: SINGLE STEP ULTRAFILTRATION TREATMENT OF HIGH TURBID RIVER WATER

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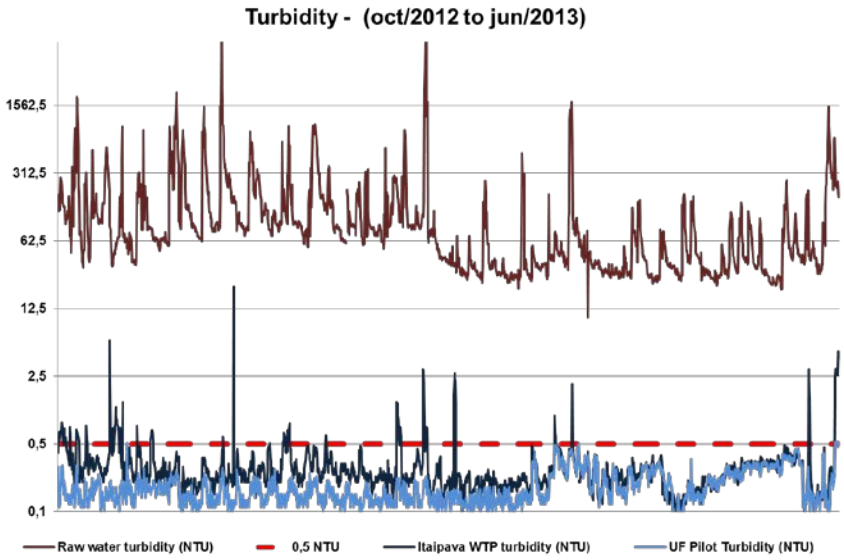
The conventional treatment to produce potable water is a physical-chemical process. Depending on the water quality the chemical consumption can be very high and hard to reach the requested water quality. Brazilian legislation is getting more strict so the sanitary companies are looking for new alternatives to be able to meet the parameters. Aiming to evaluate technically and economically the membrane process it was installed a pilot plant in Rio de Janeiro state to treat difficult river water.

The results were favorable to membrane technology as the turbidity values acquired were always lower than 0.5 NTU, value defined by Brazilian Law (2914/2011 from Healthy Ministry). The operational costs were also evaluated, while the ultrafiltration were USD 35,867.00 and USD 179,646.00 for 20 lps and 100 lps, respectively, the conventional were USD 117,699.00 and USD 388,174.00.

Table 1 – Turbidity during piloting.



The pilot demonstrated that a single unit operation without coagulant dosing can be used to produce high quality product water regardless of the feed water quality. The pilot data will be used to design a membrane system with the same capacity as the existing plant.

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Microbial regrowth in gravity-driven membrane filtration influences the water quality in terms of pathogen growth

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Introduction One of the main purposes of water treatment worldwide is to avoid microbiological contamination of drinking water. The major problems associated with this, are, mainly, related with the danger for consumer health [1]. Gravity driven membrane filtration (GDM) is a water treatment process which provides good perspectives for application since that it achieves stable water fluxes and is carried out in a dead-end mode without any cross-flow, backflushing or disinfection. Although membrane processes, such as this, are used for the production of drinking water and can, in theory, produce bacterial-free drinking water [2], they do not retain dissolved compounds (nutrients for bacteria). Therefore, bacteria ultimately regrow because of the ideal conditions (excess nutrients and low bacterial concentration) in the permeate water. These occurrences are identified in several studies and neglected in others, however, the issue has not been addressed in detail. Also, there are indications that under certain conditions, indigenous bacteria growing in the permeate tank can outcompete pathogens, such as, E.coli and provide safer drinking water [3]. In this study, we focus on the GDM process which has the particularity of being a slow system, mainly, used in developing countries and where concerns of contamination of drinking water with pathogens are high. The purpose of this research is to assess to what extent do the indigenous bacteria growing in the permeate tank affect pathogen growth (E.coli) and improve the drinking water provided by the GDM system.

Materials and methods Filtration was done using a ultrafiltration membrane (100 kDa cut-off) for 5 hours and regrowth was measured during this period and the remaining stand-still period of 18 hours in the permeate tank (one cycle of operation). Total cell count measurements were conducted with 30 minutes interval using flow cytometry and E.coli count was done using selective medium plates. The feed waters used were surface water and wastewater effluent and the microbial communities and pathogens (E.coli) introduced as inocula in the permeate tank came from the same sources. In the end of each cycle all the permeate containers were changed in order to avoid biofilm formation on the surfaces.

Results and discussion Three operation cycles were performed under controlled, temperature and nutrient conditions. The results obtained with surface water used, both as feed and as inocula in the permeate, are shown in Figure 1.

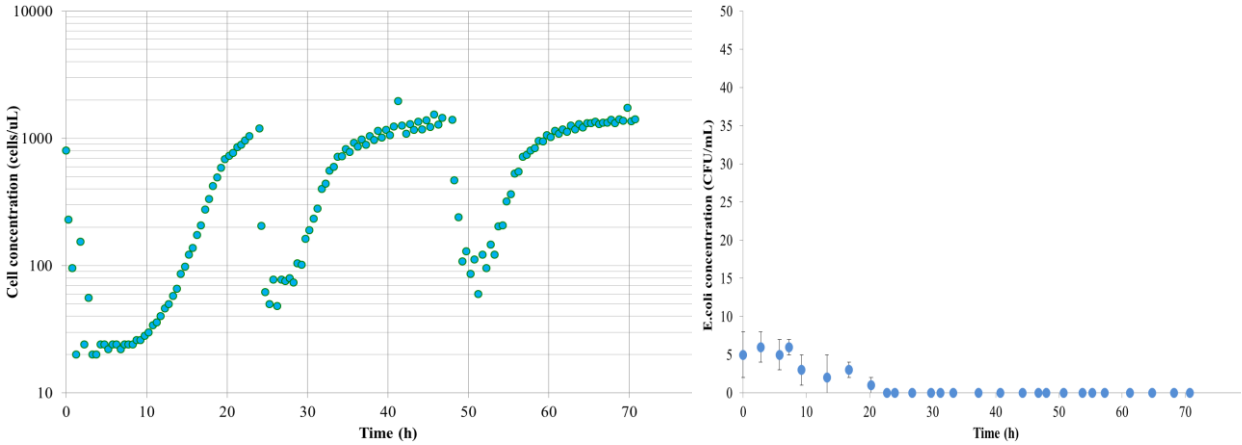

Figure 1: Measured cell concentration (cells/µl), left, and E.coli counts, right, in the permeate tank of the GDM filtration system after three cycles of operation with surface water used, both as feed and as inocula in the permeate.

The first cycle is the determinant one, when the major adaptation of the microbial communities present in the permeate tank takes place. The influence of dilution is visible in the first five hours for the total cell counts but not for the E.coli counts. However, the fast disappearance of E.coli (reaching 0 CFU.mL^{-1} after the first cycle of operation) is visible and this is clearly linked to the lack of fitness for competition of resources under these conditions. The following cycles show very stable patterns of regrowth and no counts of E.coli. Another experiment was ran in parallel using wastewater effluent, both as feed and as inocula in the permeate. The results obtained are shown in Figure 2.

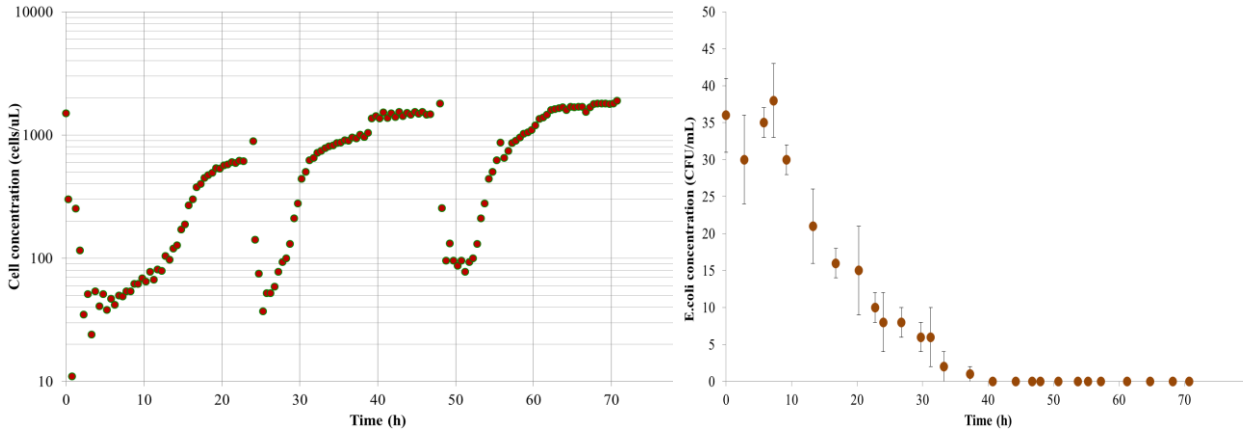

Figure 2: Measured cell concentration (cells/µl) and E.coli counts in the permeate tank of the GDM filtration system after three cycles of operation with wastewater effluent used, both as feed and as inocula in the permeate.

It is possible to observe that even though the conditions, in terms of nutrient availability and variability, change drastically (due to the significant differences between surface waters and wastewater effluent) the regrowth pattern is very similar to the previous experiment, with the main adaptation occurring in the first cycle and relative stability achieved in the following cycles. However, there are increased numbers of E.coli as a starting point and the higher amount of nutrients provided could benefit pathogenic growth [3]. This was not the case in this experiment, with the E.coli counts lowering steadily after the consecutive cycles and reaching 0 CFU.mL^{-1} after 40 hours of operation. It should be noticed that other tests for pathogens, such as, Enterococci, Vibrio cholera and Total coliforms were done in the end of both experiments and they were negative.

Conclusion It was shown that the characteristics of regrowth in GDM filtration systems under controlled conditions are significantly stable and can provide conditions where pathogens, such as E.coli, cannot outgrow the remaining microbial communities. The main changes occur during the first cycle of contamination of the permeate tank, when the microbial communities have to adapt to the new temperature and batch growth and afterwards the regrowth pattern is very stable. When there is a lower amount of E.coli as a starting point, its disappearance occurs during the first cycle of operation and in the case of a higher contamination in the beginning, it happens during the second cycle. This is a very important contribution to the understanding of the concept of water stability during treatment and distribution without disinfection, especially for membrane systems.

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COMBINING NANOFILTRATION WITH PHOTOLYSIS/TIO_2 PHOTOCATALYSIS AS AN HYBRID PROCESS FOR WATER TREATMENT

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Nanofiltration has demonstrated high potential towards the removal of a wide range of organic micropollutants such as pesticides and endocrine disrupting compounds [e.g. 1]. Nevertheless, there are some challenges related with its application: fouling development and formation of a retentate that needs further treatment and/or disposal [2].

In this study, the integration of nanofiltration with low pressure (LP) ultraviolet (UV) direct photolysis or titanium dioxide (TiO_2) photocatalysis was evaluated in terms of its potential to address these challenges and remove environmental relevant pesticides (atrazine, isoproturon, diuron, alachlor, pentachlorophenol, and chlorfenvinphos) and hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) from water. Two configurations that combine these technologies, taking place sequentially or simultaneously in a single module were assessed.

In the sequential treatment, LP/UV direct photolysis or photocatalysis using suspended TiO_2 nanoparticles took place in an irradiated tank to achieve degradation of the target micropollutants spiked in surface water collected after sedimentation. Then, a nanofiltration unit equipped with a spiral-wound Desal 5DK membrane was subjected to applied pressure. In another configuration, the processes occurred simultaneously. In this configuration, TiO_2 was immobilized by reactive magnetron sputtering at the top surface of a ceramic membrane, composed of non reactive Al_2O_3 and TiO_2, forming a reactive layer.

The removal of atrazine, diuron, isoproturon, and estrone was improved by applying the sequential integrated process relatively to single nanofiltration, with global removals often higher than 90% (Table 1). Moreover, this integrated process remarkably reduced in 98% the extremely high endocrine disrupting activity of the surface water collected after sedimentation spiked with the hormones.

Fouling development was not noteworthy in the sequential treatment since the decrease in permeability was not higher than 8%. The retentate was much less concentrated in the majority of the target compounds, which suggests that the combined treatment might reduce the costs associated with the treatment/disposal of retentate. Furthermore, the integration of these two technologies even demonstrated the ability to remove UV photolysis by-products, a major drawback of this kind of process [3].

The presence of the TiO_2 thin film on the membrane surface improved the removal of the target compounds up to approximately 15% due to the reduction of the membrane molecular weight cut-off. The scanning electron microscopy image showing a TiO_2 thin film obtained by magnetron sputtering evidenced the homogeneity of the films composed of vertically aligned TiO_2 nanostructured columns (Figure 1).

Table 1 Comparison of the effectiveness of nanofiltration and the sequential integrated treatment towards the removal of the target compounds; removal of the compounds from retentate attained during the sequential integrated treatment.

Compound	Removal (%)		Removal from retentate (%)
	Nanofiltration	Sequential integrated treatment	
Atrazine	75	>99	99
Isoproturon	36	95	49
Diuron	40	97	>93
Alachlor	96	>99	>86
Chlorfenvinphos	99	99	95
17β-Estradiol	84	85	>86
17α-Ethinylestradiol	90	94	>71
Estrone	77	95	>94
Estriol	94	91	69
Progesterone	93	98	>95

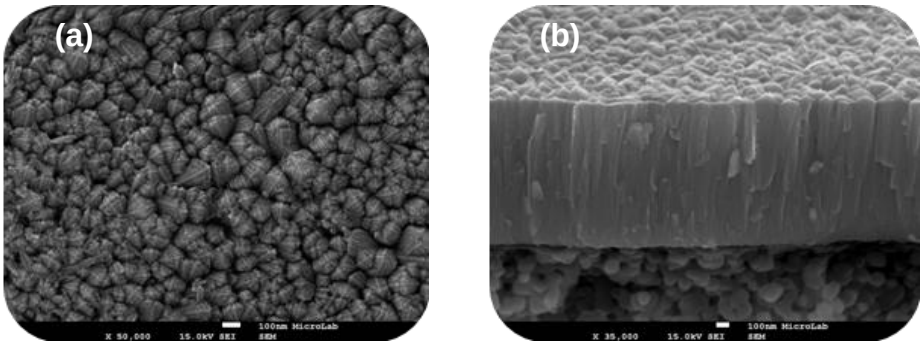

Figure 1 Scanning Electron Microscopy image of the **(a)** top view and **(b)** cross-section of the TiO_2 thin film developed on the surface of a commercial ceramic membrane by reactive magnetron sputtering.

Data obtained highlight the potential of the integration of nanofiltration and UV processes to remove the target compounds while overcoming drawbacks related with the application of nanofiltration - fouling development and retentate production.

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Acknowledgments

Financial support from Fundação para a Ciência e a Tecnologia - through the project PTDC/AMB/66024/2006, the grant PEst-OE/EQB/LA0004/2011, and the fellowships SFRH/BD/72 244/2010, SFRH/BPD/94303/2013, and BPD/26990/2006 is gratefully acknowledged.

REMOVAL OF PESTICIDES FROM WATER WITH MEMBRANE PROCESSES

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Recently, a group of water contaminants has attracted the interest of researchers. These contaminants are denominated emerging micropollutants and are characterized by being organic molecules found in very low concentrations, originating from human activity and persistent in conventional water and wastewater treatment. These substances are present in many products consumed in modern life, such as pharmaceuticals, veterinary products, food packaging, hygiene products and pesticides. The risk of presence of emerging micropollutants in water supply is associated with the endocrine disruptors and reproductive systems of humans and animals.

In the present work, pesticides were studied. In the last years, environmental concern with the intensive use of pesticides has increased significantly, mainly because of the adverse effects of these pollutants in soil and especially to aquatic organisms. Contamination of water by pesticides is a problem that afflicts many nations.

Two classes of commonly used pesticides in agriculture were studied: organophosphates and pyrethroids. Glyphosate is one of the most used organophosphate pesticides. Several studies in vivo and in vitro revealed the mutagenic and carcinogenic potential effect of glyphosate [1] as well as its impact on aquatic life [2]. Aminometyhylphosphonic acid (AMPA) is a metabolite from glyphosate. Studies indicate that the toxicity of AMPA shows equal or superior to glyphosate [3].

Pyrethroids are a class of less persistent pesticides than organophosphates [4]. Deltamethrin and beta-cyfluthrin emerge in the current market as the most commonly used assets in crop protection and pest control and domestic vectors. Despite being less harmful to the environment, pyrethroids can have harmful effects to the environment due to increased use of this pesticide and also because of the possible adverse interactions with the environment. Figure 1 shows the structural formulas of the contaminants studied in this work.

Conventional wastewater treatment processes are ineffective in removing pesticides for drinking water. Due the molecular size of pesticides nanofiltration and reverse osmosis are indicates for their removal from water [5,6].

By these facts, the objective of the present was the removal of glyphosate, AMPA, deltamethrin and beta-cyfluthrin from aqueous solutions using commercial nanofiltration membranes and reverse osmosis.

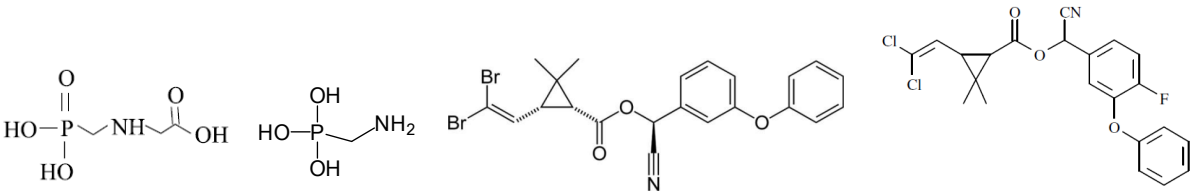

Figure 1 – Structural formula of contaminants.

Glyphosate and AMPA were derived from Sigma Aldrich. Beta-cyfluthrin and deltamethrin were provided by Bayer. Commercial reverse osmosis membrane model 4040-X201 was manufactured by TSA Trisep Corporation and commercial nanofiltration membrane NF90-2540 was manufactured by Membranes Filmtec – Dow Chemical Company. Ion chromatograph model ICS 3000 was manufactured by Dionex. High performance liquid chromatograph (HPLC) model HPLC1100 was manufactured by Agilent.

The experimental setup consisted in a batch system with flat membrane and tangential flow. Permeation area of 116.9 cm^2, capacity of 10 L and maximum operation pressure of 50 bar. The experiments employed aqueous solutions containing one or more studied contaminants (glyphosate, AMPA, beta-cyfluthrin and deltamethrin). Samples of glyphosate and AMPA were analyzed by ion chromatography while the samples of beta-cyfluthrin and deltamethrin were analyzed by HPLC.

In a first step it was evaluated the removal of glyphosate and AMPA in aqueous solution by reverse osmosis. In this step it was used the commercial membrane TSA-4040-X201 manufactured by Trisep Corporation. Initially, were performed experiments with solutions of glyphosate at concentrations ranging from 5 to 50 $mg.L^{-1}$ under a pressure of 30 bar. It was observed an increase in permeate concentration as a function of feed concentration, with rejection ranging between 94.8 and 95.6%. Then, it was studied the influence of pH with a glyphosate solution at a concentration of 50 $mg.L^{-1}$ and pH varying from 3 to 11. The operating pressure was maintained at 30 bar. There was a decrease in rejection with increasing pH. This behavior becomes from the change in net charge of glyphosate as a function of the ionization groups with pH increasing. The used polyamide membrane has an isoelectric point at pH 3.2 [7], and glyphosate has an isoelectric point at pH 2.2 [8]. Thus, the increase in pH favors the predominance of anionic form of glyphosate, which increases the rejection due to the electrostatic interactions of the negatively charged ionic species of glyphosate with the negative surface of the membrane. Following, it was analyzed the effect of operating processes variables. No significant effect of the operating pressure (10 to 30 bar) or feed flow (0.5 to 1.0 $L.min^{-1}$) on membrane rejection was observed. However, pressure significantly affects the permeate flow, leading to an approximate flow limit of 10 $L.h^{-1}.m^{-2}$. In the last experiments, solutions containing a mixture of glyphosate and AMPA were tested. No significant variations between rejections of these compounds, which were around 93%, for both, were observed. This result can be explained by the fact that both compounds have similar characteristics regarding the effects of sieving and electrostatic repulsion between ions in solution glyphosate and AMPA and polyamide membrane.

In a second group of experiments, it was studied the removal of beta-cyfluthrin and deltamethrin by reverse osmosis and nanofiltration in a comparative study. The experiments were performed with aqueous solutions of these contaminants at concentrations between 5 and 100 $mg.L^{-1}$ and pressure of 5 bar. It was used the reverse osmosis membrane TSA-4040-X201 manufactured by Trisep Corporation and nanofiltration membrane NF90-2540 manufactured by Filmtec Membranes. First it was evaluated the removal of beta-cyfluthrin. It was found that, in the studied concentration range, there was no significant difference between the processes of nanofiltration and reverse osmosis, resulting in rejections over than 99.97%. However, the porous structure of nanofiltration membrane provides a higher permeate flow rate (30.1 $L.h^{-1}.m^{-2}$) than the reverse osmosis membrane (4,6 $L.h^{-1}.m^{-2}$). Similar results were obtained when testing aqueous solutions of deltamethrin, where the two processes provided rejections of 99.99%, and with the permeate flux of nanofiltration (31.3 $L.h^{-1}.m^{-2}$) higher than reverse osmosis (3.9 $L.h^{-1}.m^{-2}$).

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Acknowledgements
CAPES/Nanobiotec for support

Gas and Vapor Separation

- **Oral session 8**

Engineered membranes based on poly(ionic liquid)s for gas separation applications

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New strategies for the use of energy from renewable resources, non-fossil fuels and carbon capture and storage are being developed at a large scale. In particular, research targeted at designing advanced materials with the ability to efficiently separate specific gases has been undertaken by the scientific community. Taking into account the extremely broad range of chemical and structural possibilities of ionic liquid (IL) chemistry, and the undeniable engineering advantages of membrane, there has been growing interest in poly(ionic liquid)s for gas separation [1] since this new class of functional polymers combines some of the exceptional and unique properties of ILs with the macromolecular architecture and improved mechanical stability of polymers [2].

In this communication, we will present a perspective of straightforward strategies for designing new efficient gas separation membranes based on poly(ionic liquid)s and their composites with ionic liquids [3-5]. The aim is not only to show the versatility of these ionic materials in the development of improved gas separation membranes but also their easy preparation. We here focus on pyrrolidinium-based polycations combined with a highly performant carboxilates, cyano and fluorinated-containing anions. Due to the promising data obtained, it is foreseen that the prepared poly(ionic liquid)-based membranes will play a especial role as alternative efficient materials for gas separation membranes.

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Acknowledgements

Liliana C. Tomé is grateful to FCT (Fundação para a Ciência e Tecnologia) for her PhD grant (SFRH/BD/72830/2010). Isabel M. Marrucho and Carmen S. R. Freire acknowledge FCT/MCTES (Portugal) for contracts under *Investigador FCT 2012*. This work was supported by FCT through the projects PTDC/QUI-QUI/121520/2010 and PTDC/EQU-FTT/1686/2012.

CO_2 REMOVAL FROM ANAESTHETIC GAS CIRCUITS INTEGRATING ENZYMATIC CONVERSION AND IONIC LIQUID MEMBRANE EXTRACTION

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In typical anesthesia processes, a gas mixture composed by 70% of nitrous oxide (N_2O), 30% of oxygen and 1-8% of halogenated hydrocarbons (HHCs) is administrated to patients. After the patient exhales, the carbon dioxide (CO_2) (approximately 5%) should be removed to values down to 0.5% in order to be possible to recirculate it to the patient. Although N_2O is the most common gas used in anesthesia, there are significant medical advantages on the use of Xenon, such as the decrease of risk of hypoxia, a rapid anesthesia induction, it can be totally excreted by pulmonary way, among others.[1] However, the main limitation for the generalized use of Xenon in anesthesia processes is its high cost, and due to this, the use of Xenon is limited to neurosurgery or for patients with respiratory pathologies. The usual technology for capturing CO_2 from an anesthesia circuit is based on soda lime. However, there are some disadvantages such as the possibility of reaction with anesthetic agents and production of toxic compounds. Moreover, it is necessary to replace soda lime on a regular basis, which represents an expensive cost for the hospital. Therefore, it is important to develop efficient and compact separation technologies for capturing CO_2 from anaesthetic gas streams, in particularly when an expensive gas such as Xenon is used.

In recent years, ionic liquids (ILs) have been proposed due to their high affinity towards CO_2, providing new opportunities for gas separation and enrichment. Ionic liquids are compounds consisting entirely of ionic species, with an organic cation and an inorganic or organic anion. The physical and chemical properties of ILs may be tuned according to the cation and anion present in their structure. Among the unique properties of these compounds, one of their most interesting properties is that they present a negligible vapor pressure.[2]

This work proposes an innovative process for efficient removal of CO_2 from anesthetic gaseous streams of Xenon, using supported ionic liquid membranes that combine the ability of ionic liquids (ILs) to solubilize CO_2 with the use of the enzyme carbonic anhydrase, which catalyzes the conversion of CO_2 to bicarbonate, as shown in Figure 1.

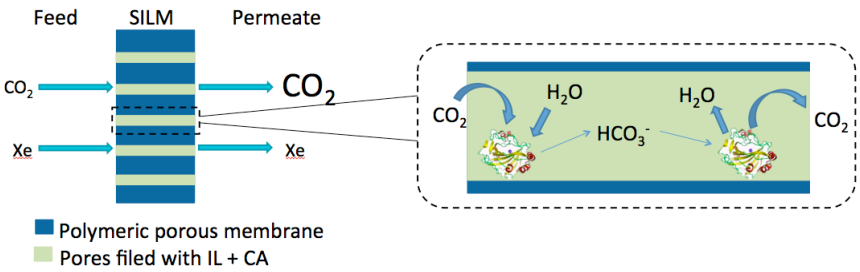

Figure 1. Schematic representation of the proposed concept.

CO_2 and Xe solubility and diffusivity coefficients in different pure ionic liquids and ionic liquids containing carbonic anhydrase enzyme in a very low concentration ($0.1 mg_{enzyme}/g_{solvent}$) were determined at 30ºC. Due to the fact that the biocatalytic activity is very sensitive to enzyme hydration, the water activity of the solvent was controlled. The results obtained showed that, depending on the water activity of the ionic liquids, the CO_2 solubility coefficient increased up to 30%, even for the low enzyme concentration used. The CO_2 diffusion coefficient remains practically constant in the presence of the enzyme, and it increases with an increase in water activity, which may be related with ionic liquid viscosity decrease.[2]

Supported liquid membranes containing ionic liquid and ionic liquid with enzyme were also prepared, and CO_2 and Xe permeability was measured at 30ºC. It was observed for all water activity values, that the CO_2 permeability and CO_2/Xe ideal selectivity is higher when the enzyme is present. It was also observed that when using a higher value of enzyme concentration, both CO_2 permeability and CO_2/Xe ideal selectivity increase. These results suggest that, for CO_2 capture from anaesthesia circuits, the enzymatic reaction may be used to enhance the performance of supported ionic liquid membranes at a controlled water activity.

On going work is focused on the use of hollow fiber membrane contactors, in contrast with the flat geometry of supported ionic liquid membranes, due to their high specific area, enabling the development of compact medical devices for recycle of anesthetic gases.

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DEVELOPMENT OF EXOPOLYSACHARIDE MEMBRANES FOR SOLVENT DEHYDRATION

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Solvent dehydration has a high economic and environmental relevance in the pharmaceutical, fine-chemistry and chemical industry. Among the available techniques, hydrophilic pervaporation is attractive due to its relative simplicity and lower energy input, as compared to other methods. Hence, many efforts have been devoted to the development of new pervaporation membranes for solvent dehydration based on biopolymers, namely natural polysaccharides [1-2].

An exopolysaccharide (EPS) produced by a microbial culture using a glycerol by-product stream from biodiesel production [3] was used in this study. The biopolymer was purified from the complex fermentation media using two methods: dia-ultrafiltration and dialysis. These techniques were used in order to remove compounds (small peptides and salts) that interfere with the membrane-forming ability of the biopolymer. The polymer composition in terms of proteins, salts and sugars was analysed for the two methods of purification.

Then, the biopolymers obtained by the two methods, were used to prepare hydrophilic dense membranes, using 1.5 % w/v of EPS dissolved in water. After this, 0.1 %w/v of Genipin was added to the aqueous solutions and stirred during 1h, followed by adjusting of pH value to 11 by NaOH solution. The solutions were casted and let to dry at 30ºC to form the membranes, which were characterized and compared in terms of their structure, mechanical properties and resistance to organic solvents and acids.

According to the results, the biopolymer obtained by dialysis presents a higher concentration of proteins and a lower content of salts than the biopolymer obtained by dia-ultrafiltration. Both types of membranes produced are dense and hydrophilic, resistant to most organic solvents, such as, ethanol, toluene, tetrahydrofuran, dichloromethane, acetone, ethyl acetate and also to aqueous acetic acid solutions up to 20%(w/w) of water. However, the membranes prepared using diafiltration are not as brittle as those prepared by dialysis.

The membranes developed, in particularly the one obtained by diafiltration, exhibit a high potential for ethanol dehydration, since a water/ethanol selectivity of 140 for 10.0 wt% water concentration in the feed was achieved. Experiments for acetic acid dehydration by pervaporation are under development in order to compare the performance of the membranes for acid conditions. Future work includes the optimization of membranes with enhanced water resistance and water selectivity in order to explore the promising results of this exopolysaccharide for solvent and acids dehydration.

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This work was supported by Fundação para a Ciência e Tecnologia (FCT), Portugal, through project PEst-C/EQB/LA0006/2013.

Inês Meireles acknowledges FCT for the PhD fellowship SFRH/BD/ 80699 /2011.

INFLUENCE OF REDUCING AGENT CONCENTRATION VIA PORE-PLATING IN Pd MEMBRANE PREPARATION OVER PSS SUPPORT FOR H_2 SEPARATION

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Purification processes represent a key technology for developing a sustainable hydrogen economy. In this context, palladium membranes appear as a promising alternative for hydrogen separation apllications as well as membrane reactor, due to the potential to reach a completely pure hydrogen stream and increase the conversion rate [1].
The major challenge of these systems is the reduction of the Pd thickness in order to increase the hydrogen permeate flux and decrease the overall cost of the membrane, maintaining a good thermal and mechanical stability. One alternative consists on preparing composite membranes formed by a thin Pd layer supported over a porous support [2]. However, the surface properties of this support determine the quality of the Pd layer and the minimum thickness to obtain a totally defect-free membrane [3]. Different techniques have been employed to incorporate the Pd layer, although the electroless plating (ELP) presents relevant advantages such as the capability to be used on both conducting and non-conducting surfaces with different geometries, the absence of electrodes and external sources of electricity and, consequently, low equipment and operational cost [4]. In order to achieve homogeneous and ultrathin Pd layers by ELP, several authors have proposed modifications of the conventional procedure, including the use of osmosis to facilitate the penetration of the plating solution inside the pores or the preparation of pore-fill type membranes. In this context, a new procedure was developed in our group to prepare composite Pd membranes directly over PSS tubular supports in one single step, denoting the process as electroless 'pore-plating' (ELP-PP) [5]. The process basically consisted on feeding both plating solution and reducing agent, hydrazine, from opposite sides of the support. In this way, the chemical reaction is forced to take place inside the pores. The result is the formation of a thin palladium layer around the external surface of the support as well as in the more external pores of PSS. In the present work, the influence of hydrazine concentration in the morphology of the Pd layer and permeation properties has been studied: 1.0 M (MB-01), 0.2 M (MB-02) and 0.05 M (MB-03). In the first case, a totally dense membrane with a reasonable low thickness cannot be obtained, while totally dense membranes were achieved by reducing the hydrazine concentration. Figure 1 shows the external surface and cross-section of the membranes MB-02 (0.2 M, Figure 1a and b) and MB-03 (0.05 M, Figure 1c and d). As it can be seen, an external and continous Pd layer was achieved in both cases. However the incorporation of Pd inside the pores was clearly different for each experimental condition. Higher hydrazine concentration (0.2 M) generates an apparently dense external Pd layer with thickness around 5 μm (from SEM images), while a certain amount of Pd is incorporated inside the pores up to 20-30 μm in depth, wich yieds a medium gravimetric thickness of t_m=8.8 μm. On the other side, a thinner external Pd layer of about 2.5 μm is obtained for the lowest hydrazine concentration (0.05 M), although the penetration of the Pd inside the pores increases up to 115 μm, which gives a medium thicknes of t_m=16.0 μm. In the last case, some pores can still be observed on the external surface, although this fact does not imply a low quality of the membrane. The Pd particles deposition provokes the complete filling of the narrow pores at the first stages of the process, while the hydrazine agent can pass through the largest pores, partially filled, until the external surface, where it reacts with the Pd solution. In this manner, all pores of the PSS support can be closed in spite of the external Pd film is not apparently continuous.

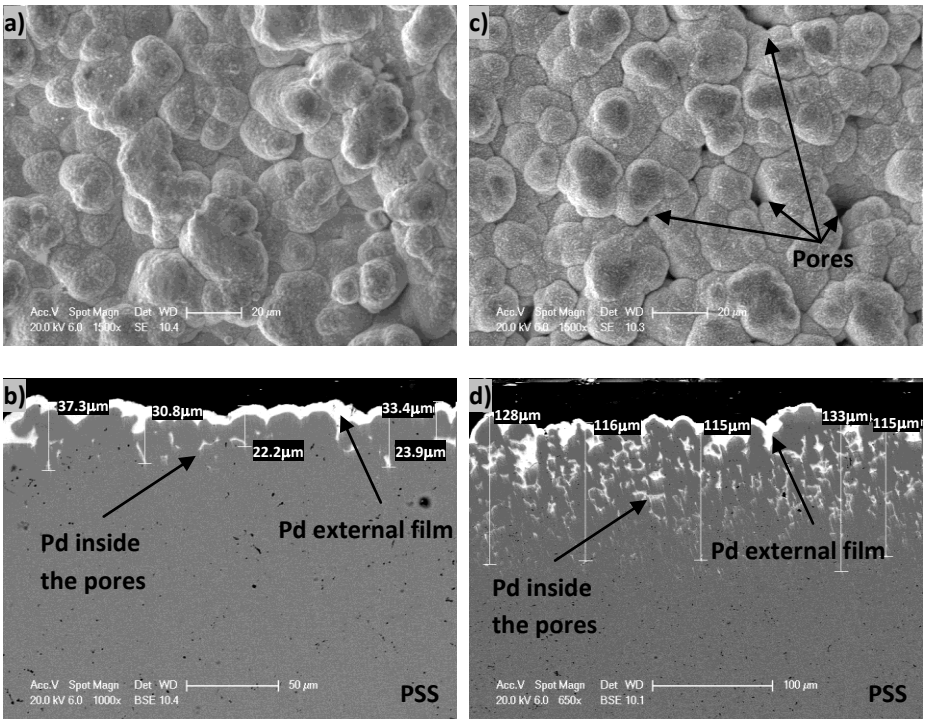

Figure 1. SEM images of the membranes prepared with different hydrazine concentration: 0.2 M (a, b) and 0.05 M (c, d).

Pure gas permeation measurements of both nitrogen and hydrogen were performed for both membranes (MB-02 and MB-03). From these data, it can be concluded that a completely dense membrane was achieved, since no nitrogen was detected in the permeate side in the entire range of experimental conditions (T=350-450ºC and ΔP=0-2.5·10^6 Pa). Figure 2 shows the hydrogen permeation fluxes. At these conditions, a H_2 permeance of k=1.0-1.6·10^{-9} mol/m^2·s·Pa$^{0.5}$ and an activation energy of E_a=17.9 kJ/mol were calculated for MB-02, while these values are reduced until k=9.60·10^{-10}-1.15·10^{-9} mol/m^2·s·Pa$^{0.5}$ and E_a=8.2 kJ/mol for MB-03. This fact is probably due to an adittional resistance to the permeation process in this membrane as the Pd increases inside the pores.

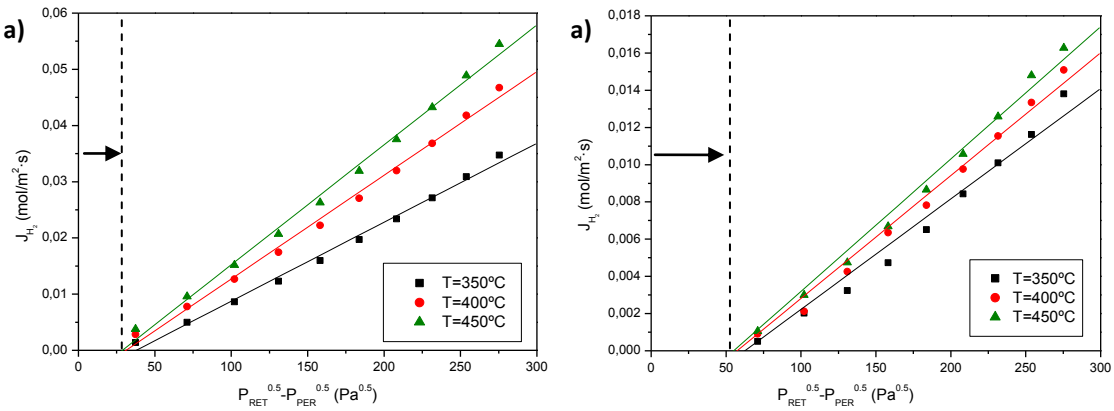

Figure 2. H_2 permeation experiments of the membranes prepared with different hydrazine concentration: a) 0.2 M and b) 0.05 M.

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Preparação e caracterização de membrana cerâmica de alumina impregnada com paládio

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Introdução

Devido ao aumento da emissão de dióxido de carbono (CO_2) e metano (CH_4) na atmosfera, sabe-se da necessidade de separar e capturar estes gases para contribuir na diminuição do efeito estufa. Estes gases têm gerado preocupação com questões ambientais. Tal fator, associado ao esgotamento de reservas de fontes fósseis de energia intensifica a pesquisa de novos métodos para separar e capturar estes gases e permite a recuperação de hidrogênio (H_2), como fonte de energia renovável e livre de poluentes [1].

Os métodos mais utilizados para separação de gases são: destilação criogênica, absorção e adsorção [2]. No entanto, um método que vem se mostrando promissor, devido a facilidade de instalação, operação e ampliação além de baixo consumo de energia é o processo de separação por membranas (PSM) [3].

Neste trabalho membranas inorgânicas tubulares de α-alumina impregnadas com paládio foram preparadas através da técnica *electroless plating*, para a deposição metálica sobre a superfície externa do suporte cerâmico [4, 5, 6]. Tal técnica tem como agente redutor o hipofosfito de sódio, responsável pela redução de Pd^{2+} para Pd^0 e que promove a uniformidade da camada ativa (catalisadora) por meio da formação de uma película com estrutura de grãos finos.

A técnica *electroless plating* consiste de três etapas: sensibilização e ativação, onde preparam a membrana ativando-a com íons de paládio afim de promover na terceira etapa, deposição metálica, melhor aderência e uniformidade.

Resultados e Discussão

A caracterização morfológica das membranas de alumina impregnada e não impregnada com paládio foram analisadas por *Field Emission Scanning Electron Microscopic* (FESEM) na seção transversal, conforme as Figuras 1 e 2.

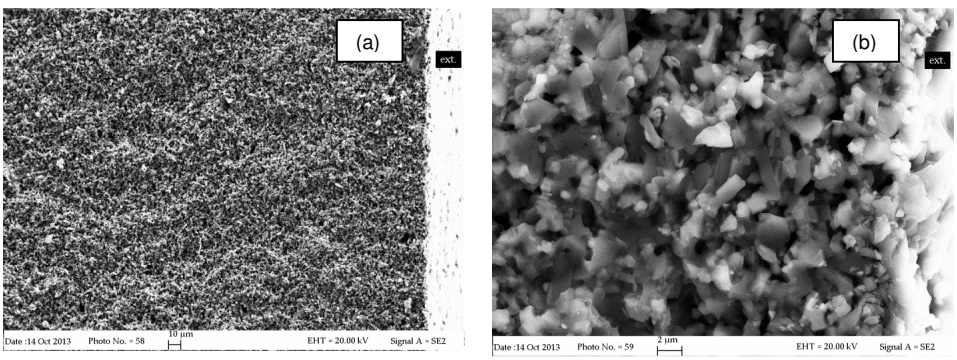

Figura 1- Micrografia (FESEM) da membrana cerâmica ampliada 1000x (a) e 10000x (b).

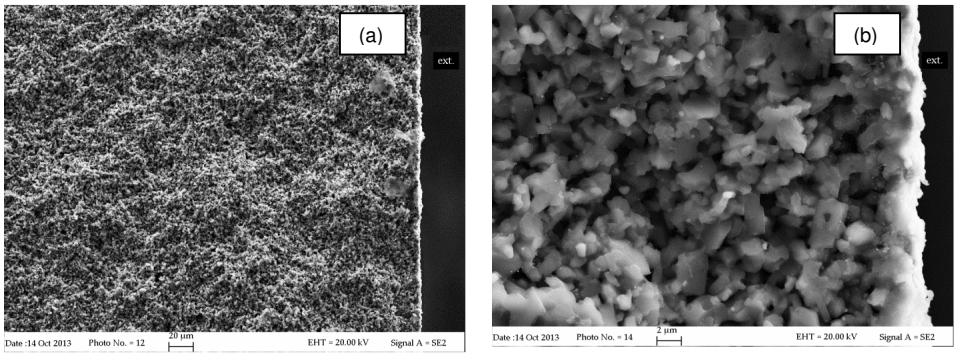

Figura 2 - Micrografia (FESEM) da membrana cerâmica com impregnação de paládio ampliada 1000x (a) e 10000x (b).

Paralelo ao FESEM foram realizadas as análises de EDS das amostras e observou-se exclusividade de alumina (Al) (Figura 3 (a)), enquanto após a deposição de paládio através da técnica *electroless plating* verificou-se a presença do metal (Figura 3 (b)).

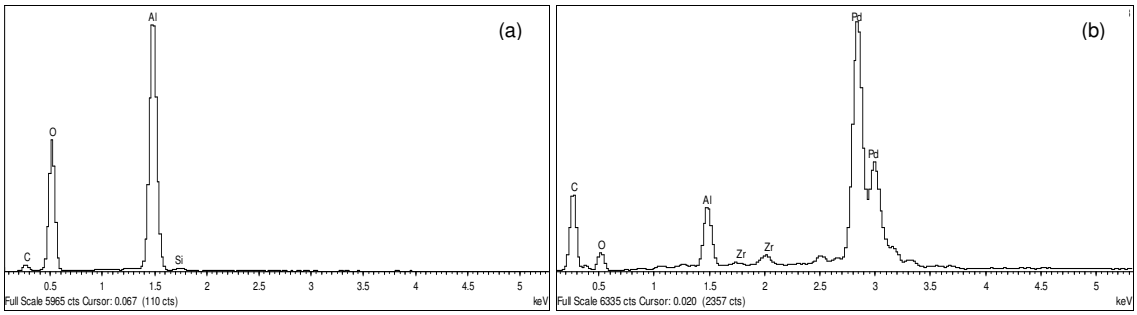

Figura 3 – Análise de EDS (a) membrana cerâmica sem impregnação de paládio e (b) membrana cerâmica com uma impregnação de paládio.

Conclusões

A solução de deposição promoveu a interação das partículas de metal com o hipofosfito de sódio, o que permitiu a aderência eficaz do metal paládio sobre a membrana porosa de α-alumina. Contudo, tal camada mostrou-se não uniforme e tal fato acarreta necessidade de realizar uma sequência de deposições metálicas. Testes preliminares de permeação de gases vêm sendo realizados para verificação da permesseletividade da membrana impregnada com paládio, como CO_2, CH_4, N_2 e H_2.

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Agradecimentos

Os autores agradecem a UCS, a UFRGS, ao CNPq, a CEEE e ao Professor Aldo Bottino (Unige – Genova Itália) pela análises de FESEM.

Gas and Vapor Separation

- **Poster session 2**

Pervaporation Separation of Methanol from MTBE Using Functionalized Membranes Based on Polyelectrolyte Surfactant Complex

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Pervaporation is playing an increasingly vital role in liquid/liquid separation processes due to its great cost and energy efficiency; however, the main limitation of this process is the usual trade-off between flux and selectivity of membranes. Asymmetric polymeric membranes having selective layers comprised of polyelectrolytes/surfactant complex systems have demonstrated high performance for separation of polar/non-polar mixtures [1-3].

In this research study, pristine and mixed matrix polyelectrolyte surfactant complex (PELSC) composite membranes were fabricated using sodium cellulose sulphate salt (NaCS) and hexadecylpyridinium chloride (HDPC) as polyanion and cationic surfactant, respectively. Poly (acrylonitrile) (PAN) ultrafiltration (UF) membranes with surface pore sizes (less than 45 nm) were synthesized through an optimization of dope solution concentration, coagulation bath temperature and coagulant composition. PELSC selective layer was fabricated onto the as-prepared supports through layer-by-layer assembly of dilute electrolyte solutions for initial deposition steps followed by deposition of concentrated ionic solutions. In addition, nanocomposite PELSC membranes containing different amounts of SiO_2 nanoparticles were fabricated for the first time by solution casting method. The effects several fabrication (number of deposition steps and nanosilica content in PELSC membranes) and operational parameters (feed temperature and concentration) were investigated for pervaporation separation of MeOH/MTBE.

The results revealed that increasing the number of deposition steps from 3 to 7, results in higher fluxes and lower selectivities for pristine membranes contacting an azeotropic feed solution (14.3 wt.% MEOH at 51 °C). Also, increasing the temperature and MeOH concentration of the feed led to simultaneous increase in flux and selectivity of pristine PELSC membranes. As for a pristine PELSC membrane composed of 3 bilayers of dilute solutions and 3 bilayers of concentrated ones, the flux and selectivities were 0.76 kg/m^2.hr and 61.34 at 25 °C which changed to 1.55 kg/m^2.hr and 83.45 at 51 °C, respectively. Also, increasing feed concentration from 5 wt.% to 40 wt.% MeOH at 51 °C led to a rise in pervaporation separation index (PSI) from 15.00 kg/m^2.hr to 117.18 kg/m^2.hr for a PELSC membrane composed of 3 dilute and 7 concentrated bilayers.

For mixed matrix PELSC membranes, increasing nanosilica content of the membrane from 2 wt.% to 10 wt.% increased the flux from 1.23 kg/m^2.hr to 1.62 kg/m^2.hr at 51 °C and reduced the selectivity from 88.83 to 65.86 using a feed mixture containing 14.3 wt.% MeOH at 51 °C. Investigation of the effects of feed temperature on a mixed matrix PELSC membrane containing 2 wt.% nanosilica revealed that there was a trade-off between flux and selectivity. Increasing feed temperature from 25 °C to 51 °C changed the flux and selectivity from 0.74 kg/m^2.hr and 101.02 to 1.23 kg/m^2.hr and 88.83 respectively for a 2 wt.% nanosilica PELSC membrane using an azeotropic feed mixture.
The findings in this study demonstrate high opportunity for effective and high performance separation of MeOH/MTBE mixtures using proposed membranes with considerable potentials for industrial applications.

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Development of microporous TiO_2 doped silica membranes to enhance the hydrothermal stability for gas separation

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The progress in the field of gas separation by membranes has been very fast. Membranes are the most decisive part of the gas separation technology. It has attracted maximum attention in terms of research and development. Efforts to correlate the basic structure with permeability and selectivity have resulted.

Inorganic micro porous membranes have narrow pore size distributions with pore diameters less than 1 nm, depending on the sol-gel synthesis route applied (colloidal or polymer), particle size, rate and extent of hydrolysis and condensation. Supported microporous membranes consist of asymmetric structures with a macroporous support, intermediate layers and a microporous selective top layer providing the selectivity. In general, the main transport resistance is in the top layer and, therefore, this layer should exhibit low thickness to achieve high fluxes and combined with sufficient stability (especially hydrothermally stable for power plant fuel gasses separation applications) for better techno-economical evaluation.

In the present work, supported microporous inorganic gas separation membranes with multiple interlayers were synthesized by conventional dip coating. Well defined gradient of pore sizes in the interlayers and gas separation membrane was realized by sequentially dipping a macro porous support of α-Al_2O_3 (80-150 nm) in sol solutions with descending order of sol particle sizes as γ-Al_2O_3 colloidal sol for interlayers with mesopores (2-50 nm), polymeric SiO_2 and different TiO_2 doped SiO_2 sols for functional layers with microspores (< 1 nm). The sols were prepared by acid catalyzed hydrolysis of alkoxides (precursors) using different synthesis routes (colloidal and polymeric) and polymeric composite sols were synthesized using different methods like single step, two step, and direct method depending upon the molar ratio of water/alkoxides.

Emphasis is put on preparation conditions of the sols especially the composite sols (TiO_2 doped silica sols) in order to identify the main factors governing the performance of the processed membranes.

Synthesized sols as well as membranes were characterized by XPS, FT-IR, XRD, permporometry and single gas permeation test. Consequently, the proposed process has made it possible to prepare membranes with good selectivity and permeation rates for fossil fuel gases. Investigation of hydrothermal stability of TiO_2 doped silica membranes in comparison to pure silica membrane is in progress. The obtained results will be useful for future modifications of microporous inorganic membranes dealing with improved performance in separation, purification, and conversion technology.

Acknowledgements

We are grateful to Dr. Wilhelm Albert Meulenberg and Dr. Tim Van Gestel for kind help to interpret the obtained data scientifically. We also acknowledge Forschungszentrum Juelich for the financing of this research.

PREPARATION OF FLAT SHEET MEMBRANES BY DUAL BATH IMMERSION PRECIPITATION TECHNIQUE FOR CO_2 REMOVAL FROM NATURAL GAS

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The increase on energy consumption has made necessary the exploration of natural gas, even in wells that once were considered unfeasible, due to high levels of carbon dioxide (CO_2). The use of membrane separation processes to separate this compound from methane has been established as an attractive alternative, as it offers several advantages compared to traditional methods, based on absorption with amines. These benefits range from versatility and less waste production to scalability and ease of operation.

The objective of this paper is to manufacture flat sheet membranes of poly(ethersulfone) (PES), by dual bath immersion precipitation technique to be used in carbon dioxide separation from methane. In this technique, the traditional phase inversion precipitation process is modified through immersion in two successive coagulation baths, allowing a better control of the anisotropic membrane morphology.

So far, this technique has been focused on manufacturing hollow fiber membranes. However, flat sheet membranes might be arranged in spiral-wound modules, characterized by a higher manufacturing productivity, as well as better performance when applied to processes that involve larger pressure differentials.

In order to better understand the membrane formation the polymer solution precipitation was investigated, relating different variables of membrane formation to the membrane transport properties. The polymer solution was prepared with a base polymer (PES), solvent (NMP) and one non-solvent (water, glycerol or 2-methyl-2,4-pentanediol (MPD)). The polymer non-solvents were also used as precipitation bath. For each polymer non-solvent the solution miscibility was determined by cloud point tritation. The precipitation velocity of the polymer solution after immersion in the precipitation bath was followed by light transmission. The final membrane morphology was observed by scanning electron microscopy (SEM) and the transport properties were determined by pure gas permeation.

The influence of factors, such as film casting thickness and immersion time in the first bath, in both morphology and transport properties were evaluated. The best gas permeation performances was obtained when MPD was the first coagulant and water the second, related to decrease of the skin thickness, which has been verified through SEM. It was possible to achieve CO_2/N_2 selectivity of 51.3, very close to the ideal selectivity of the material (55), showing the feasibility of the technique in the production of anisotropic membranes. It was also observed presence of macrovoids in the membrane cross section, which formation is influenced by the casting thickness and exposure time to the environment before immersion in the first precipitation bath.

A mathematical model was also developed to estimate the thickness of the formed skin and the amount of superficial pores, presenting a good correlation with experimental results.

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PERMEABILITY OF PROPANE AND PROPYLENE IN HIGHLY SELECTIVE IONIC LIQUID/POLYMER COMPOSITE MEMBRANES

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The recovery of olefin from catalytic cracking, steam cracking units and paraffin dehydrogenation off-gasses has been traditionally carried out by cryogenic distillation. These operations are capital and energy intensive due to the low relative volatilities of the components. For this reason in recent years the development of an alternative process is becoming increasingly important. Among a number of different separation technologies, membrane technology appears as an attractive solution.

Recently the use of facilitated transport polymer/ionic liquid/silver salt composite membranes has been proposed [1]. In these membranes a selected ionic liquid embedded in a suitable polymer matrix improves gas permeability while silver cations react selectively and reversibly with the olefin reaching high selectivities. Composite membranes allow process intensification thanks to their operational simplicity and flexibility, high selectivity and permeability and low energy requirements.

In this work permeation experiments using constant volume time-lag method were performed in order to obtain diffusivity and solubility parameters of propylene and propane in PVDF-HFP polymer matrix and ionic liquid/polymer composite membranes. These results combined with facilitated transport experimental data obtained from our previous works [1] will allow the development of a mathematical model able to describe the behavior of the facilitated transport mechanisms of propylene through the composite membrane and estimate the unknown facilitated transport parameters.

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This research was supported by the Ministry of Education and Science under the project CTQ2012-31639 (MINECO, SPAIN-FEDER 2001-2013).

Membrane and Surface Modifications

- **Oral session 9**

MIXED-MATRIX ELECTROSPUN NANO-FIBROUS MEMBRANES FOR DESALINATION

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Nanotechnology is a wide field of applied science focused also on the design, synthesis and application of nanomaterials in desalination and wastewater treatment with improved treatment efficiencies in order to meet the ever-increasing demand for potable water. This is because nanomaterials exhibit a number of key physical, chemical and antibacterial properties. Among the various types of engineered nanomaterials that are under active research and development, nanofibrous materials are receiving extensive research interest for applications in diverse fields as biosensors, optical and chemical sensors, drug delivery carriers, antibacterial materials, reinforced nanocomposites, affinity membranes, etc. This is due to their important and interesting characteristics including a very high surface area to volume ratio, tunable void volume fraction and inter-fiber space, flexibility in surface functionalities, good mechanical performance and malleability to construct a wide variety of nanofiber based materials including beaded, ribbon, porous, and core-shell nanofibers [1,2].
Electro-spinning or electro-static spinning is the most popular and preferred technique for fabrication of nano-fibers. Synthetic and biopolymers, polymer blends, melts, nanoparticle or drug-impregnated polymers, and ceramic precursors have been successfully used to produce electro-spun nanofibers [1].
It was observed that the following parameters and processing variables affect the morphological nanostructure of electro-spun fibers [3-6]:
- System parameters such as the type and molecular weight of the polymer, polymer concentration, solvent type and polymer solution properties (viscosity, electrical conductivity and surface tension).
- Process parameters such as the electric potential, flow rate of the polymer solution, distance between the metallic needle tip and the collector, ambient parameters (i.e. temperature and humidity in the electro-spinning chamber), motion of the collector and heat-treatment.
Recently, we have fabricated different types of mixed-matrix electrospun nano-fibrous membranes for desalination by the non-isothermal process membrane distilaltion (MD). Interesting results were obtained when using fluorinated surface modifying macromolecules (SMMs) in the hydrophilic host polymer polysulfone (PS), polytetrafluoroethyelene (PTFE) nanoparticles in PS and carbon-based nanomaterials such as multi-walled carbon nanotubes (MWCNTs) in hydrophobic host polymers such as polyvinylidene fluoride (PVDF). The effects of the concentration of these nano-additives on the bulk and surface characteristics of the nano-fibers as well as on the final electrospun nano-fibrous membranes (ENMs) and their MD performance when used in desalination will be presented. The observed advanced MD performance, mechanical and thermal efficiency of the ENMs confirmed that these membranes are attractive for desalination by MD process [7].

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Acknowledgements: The authors gratefully acknowledge the financial support of the I+D+I Project MAT2010-19249 (Spanish Ministry of Science and Innovation) and Abengoa Water S.L.U. (Artículo 83: 320/2011, MEMsa and 85/2013, HOFI-MED-Plant). M. Essalhi is thankful to the Middle East Desalination Research Centre (MEDRC, Project 06-AS-02).

Design and characterisation of magneto-sensitive PVA hydrogel membranes

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The structural and topographical design of surfaces assumes a high importance in the performance of several membrane based processes. A suitable combination of the surface topography and chemical characteristics may generate membranes with extreme hydrophilic or hydrophobic properties [1]. Membrane hydrophilic/hydrophobic character and surface topography itself (*e.g.* roughness) are important parameters in separation processes, since it may regulate solute interactions to the membrane surface and thus fouling, fluid dynamics and ultimately mass transport [2]. Also, these membrane surface properties are quite relevant in the performance of biocatalytic processes, membrane sensors and biomedical devices (*e.g.* tissue scaffolds). The efficiency of these processes is intemately related with the mode that specific molecules (*e.g.* proteins) or cells sense the surface and the impact that it may produce on their activity [3]. The ability to adjust the surface chemical and topographic design, *in situ*, in a non-invasive and reversible mode is forseen as an important membrane functionality that may contribute for the development of membrane based processes with improved effciency.

Aiming the design of magneto-sensitive hydrogel membranes for biocatalytic and medical applications, polyvinyl alcohol (PVA) membranes with embedded magnetic responsive particles, such as magnetite Fe_3O_4, were prepared in the absence and presence of an external magnetic field. As shown in Fig 1. (a) and (b), the use of a low magnetic field (< 0.1 T) allowed for a complete allignment of the particles towards the magnetic field direction.

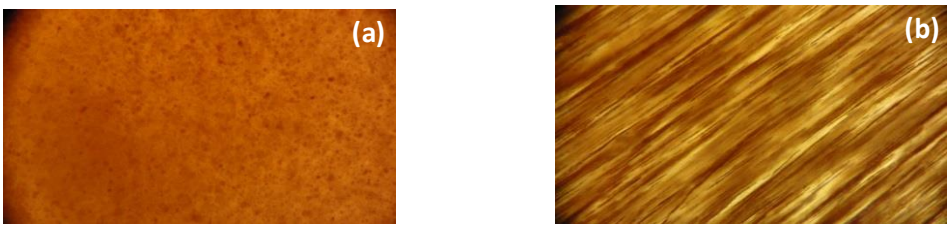

Fig.1. Polyvinyl alcohol membranes containing 1 % of magnetite (Fe_3O_4) particles prepared in the **(a)** absence and **(b)** presence of a magnetic field of 0.05 T. These images were acquired by optical microscopy, using an objective of an amplification of 4x and the photo was acquired using a zoom of 362 mm.

The magnetic behaviour of these hybrid gel membranes incorporating oriented and randomly distributed particles was characterized by contact angle analysis in the absence and presence of an external magnetic field and proton NMR relaxation technique. The contact angle analysis revealed that the magnetic content, particles allignment and dispersion degree affect the topographical properties of these membranes. Moreover, as shown in Fig.2, the presence of an external magnetic field generates a decrease of the glycerol contact angles at these membrane surfaces. Therefore, it was possible to conclude that the

membranes prepared by suitable combination of these parameters are capable to switch their structural characteristics when exposed to distinct magnetic field conditions.

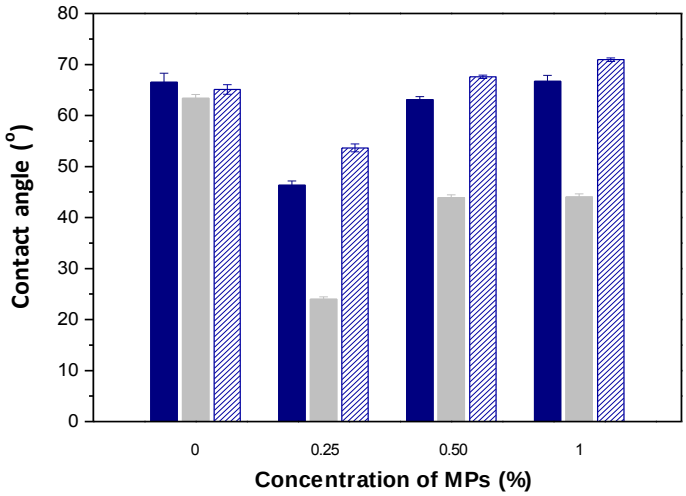

Fig.2. Variation of glycerol contact angle for PVA membrane surfaces presenting different concentrations of oriented magnetite (Fe_3O_4) particles (MPs) in the absence (dark blue), presence (light grey) and 1 min after removal (patterned bar) of an external magnetic field with an intensity of 0.07 T applied in orthogonal direction relatively to the membrane surface.

Proton NMR relaxation analysis were performed in order to establish a comprehensive relation between the magnetic induced structural changes and the molecular dynamics of the polymer chain within the membrane matrix. The results obtained evidence the presence of a specific relaxation mechanism associated to the presence of the magnetic component that is observed on the high Larmor frequency region of the spin-lattice relaxation time (T_1) dispersion.

Mass transport studies are under development in order to evaluate the influence of magnetic allignment of the magnetic particles on the permeability and selectivity of the membranes to target solutes, particularly those of interest for biomedical applications (*e.g.* O_2, CO_2, sugars, salts) and infer the ability to modulate the mass transport parameters by adjustment of the external magnetic field conditions.

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Acknowledgements: The authors aknowldeges the finantial support from FCT-MEC (Portugal) through the research project EXPL/CTM-POL/1117/2012.

DEVELOPMENT OF MEMBRANES FOR DESALINATION CONTAINING BIOCIDES FOR BIOFOULING REDUCTION

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Reverse osmosis (RO) and nanofiltration (NF) processes stand out as a feasible and safe separation technique in water treatment and reuse of wastewater mainly for desalination of brackish or salty water. RO and NF presents advantages compared to other desalination processes [1], but a serious drawback is the flux decline caused by the irreversible adsorption of foulants onto the membrane surface. Fouling formation increases operating costs, since it generates higher demand of energy, decreases the intervals between chemical cleaning and significantly reduces the lifetime of the membranes [2,3]. Fouling is function of several parameters such as the feed stream characteristics, hydrodynamic conditions of the system and membrane characteristics. Many routes have been examined to mitigate fouling problem [5-7]. Surface modification is considered as the most interesting way to prepare fouling-resistant membranes by changing surface-foulant affinity or surface morphology [4,8-10]. Incorporating biocides to the RO membrane surface layer provides an additional mechanism of reducing biofouling. Natural biocides such as bee glue (propolis) and clove oil, focuses of this study, exhibit recognized antimicrobial activity (11,12).

Polyvinyl alcohol (PVA) and natural biocides (propolis extract – PE and clove oil – CO) were incorporated into commercial reverse osmosis (RO) and nanofiltration (NF) membranes by dip coating technique. The effect of the surface modification of membranes were studied in terms of surface properties, using scanning electron microscopy (SEM, JSM-5300 JEOL), atomic force microscopy (NanoWizard AFM, JPK Instruments), streaming potential measurements (SurPass Electro-kinetic Analyze, Anton-Parr), contact angle analyzer (KSV goniometer), 2D fluorescence spectroscopy (Cary Eclipse, Varian), and performances tests on membrane systems fed with a solution containing the bacterium *Pseudomonas fluorescens* (13525, American Type Culture Collection).

Results showed that after PVA covering, Root mean square roughness (RMS) showed a greater reduction, from 64 (BW30) to 17 nm (PVA/CO-covered BW30). The contact angle of water on modified membranes decreases after biocide addiction (from 76º for PVA-coated to 62° for PVA/PE-coated and 69° for PVA/CO-coated). Upon coating, the isoelectric point of the membranes shifts to basic values. The behavior of the PVA/PE-coated membranes is very different from the others and might be caused by presence of polar groups.

Table 1. Membrane surface characterization.

Membrane	RMS (nm)	Contact angle (º)	Isoelectric point (IEP)
BW30 (uncoated)	63.5 ± 2.5	19.7 ± 0.6	4.8
PVA-coated BW30	21.5 ± 2.4	75.5 ± 0.6	5.4
PVA/PE-coated BW30	42.2 ± 16.9	62.0 ± 0.1	3.5
PVA/CO-coated BW30	17.0 ± 2.4	68.7 ± 1.5	6.1

2D fluorescence analysis indicated that PVA/CO-coated BW30 membrane was less prone to irreversible fouling by *P. fluorescens* after long-term test (150 hours).

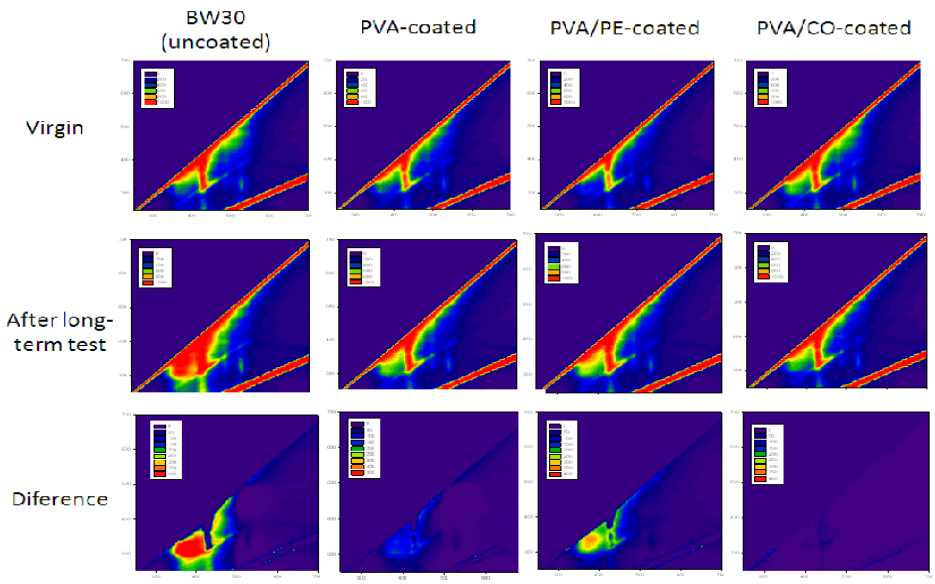

Figure 1. 2D Fluorescence spectra of the uncoated and coated membranes, before and after the long-term test, and their subtraction of the spectra.

During a dead-end fouling test, the rate of flux decline was slower for coated than for uncoated membranes. The anti-fouling property for the PVA/CO-covered NF90 membrane was enhanced greatly. The stabilization of the permeate flow at 20% of the initial value and after the test showed a flow recovery of 65% and a salt rejection of 96%.

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Acknowledgements

The authors thank to CNPq and Capes for scholarships and Instituto de Biologia Experimental e Tecnológica (IBET, Portugal).

Chemistry Modification of Commercial Reverse Osmosis Membrane to Improve the Resistance to Oxidizing Agents

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The Membrane Separation Processes (MSP) has been widely used for water desalination as an alternative to produce potable water. Reverse Osmosis (RO) and Nanofiltration are the most used processes for water desalination and much research attention has been focused on better process performance. However, the membrane fouling is still the most serious drawback. In order to avoid or minimize fouling in RO membranes it is necessary several steps of water pre-treatment. Oxidizing biocides as chlorine and its derivatives leads to degradation of the active skin layer of the polyamide (PA) thin-film-composite (TFC) membranes [1]. This work reports surface modification of a commercial TFC RO membrane (BW30-Dow Filmtec) in order to improve its resistance to chlorine. It was evaluated two modifications: one covering the commercial membrane with a poly(vinyl alcohol) (PVA) membrane and another by a composite membrane containing powdered activated carbon (PAC) in a matrix of PVA. PVA was chosen as a polymeric matrix due its suitable properties like high hydrophilicity and feasibility to form dense films and PAC was used as load in the polymeric composite according its well known characteristics of an effective adsorbent material.

PVA membranes were prepared by casting 1%wt. aqueous solution of hydrolyzed PVA 99%. Chemical and physical stability of PVA membranes were provided by crosslinking reaction with glutaraldehyde (GA), mainly because this compound reacts in mild temperatures [2]. Composite PVA/PAC membranes were prepared like the methodology described for PVA membranes. Adsorption isotherms were taken both for the adsorbent (PAC), PVA membranes and PVA/PAC composite membranes. The achieved results showed that the adsorbent material (PAC) remains with high adsorption capacity for NaClO (1250mg/g) even imbibed in PVA matrix. Surface coating method has been widely used to modify the surface properties of the aromatic polyamide TFC membranes. In this work we applied a dip-coating method by using a flat-sheet of commercial RO membranes samples and PVA or PVA/PAC solutions, in order to modify the PA layer properties, mainly the chlorine resistance.

This study compares the performance of the original commercial membrane and the modified ones in an oxidant chlorine medium (NaClO 300 mg/L, NaCl 2,000 mg/L, pH 9.5). The exposure time and the chlorine concentration were monitored and taken in terms of ppm.h (ppm chlorine concentration solution exposed to membrane for a fixed time in h). ATR-FTIR and TGA analysis confirmed the crosslinking reaction between GA and PVA besides the influence of PAC in the PVA matrix of the composite membrane. SEM images of the original and modified membranes were used to evaluate the surface coating of the membranes. The salt rejection (NaCl) and water permeability were measured during more than 100 h period. Figure 1 shows the effect of exposure time on the NaCl rejection and Figure 2 on the hydraulic permeability.

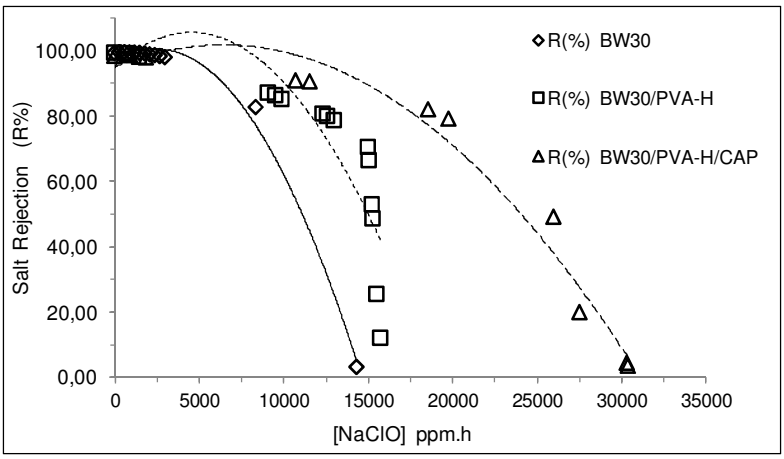

Figure 1 - Effect of exposure time (ppm.h) on salt rejection of the tested membranes

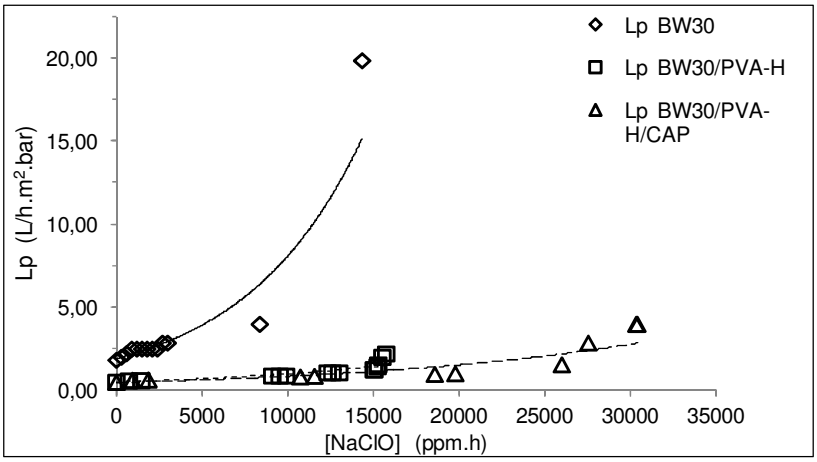

Figure 2 - Effect of exposure time (ppm.h) on hydraulic permeability of the tested membranes

Both surface modifications have effectively demonstrated the increase for the chlorine resistance of the commercial RO membrane from 1,000 ppm.h to more than 15,000 ppm.h. The results suggest the use of these membranes to protect RO membranes in presence of chlorine, avoiding their degradation and reducing the formation of biofouling, the main cause of reduction in permeate flow rate [3].

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Acknowledgements

The authors thank the National Council for Nuclear Energy (CNEN), Chemical Engineering Program (PEQ/COPPE/UFRJ) and Macromolecule Institute (IMA/UFRJ) for providing financial and technical support for the development of this work.

VARIATION ON PROCESSABILITY OF TUNABLE MEMBRANES BASED ON BLOCK-CO-POLYMER/IONIC LIQUIDS

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The development of selective capture techniques for flue gases such as CO_2, H_2S or SO_2 as well as organic vapours has become an important issue in recent years due to the increasing demand to reduce green house gas emission. Membrane separation processes may be an option for this task as long as they can easily be tuned according to the separation needs. One approach being considered is the use of low-volatile solvents, such as ionic liquids, in membrane separation barriers.

A common strategy to combine both ionic liquids and membranes is the use of supported ionic liquid membranes (SILMs) which - although widespread - reveal severe disadvantages under actual operating conditions, such as little stability, limited control of the IL content as well as instabilities during solute uptake. An alternative approach which might overcome these drawbacks is the incorporation of ionic liquids in non-porous polymeric matrices, similarly to what is commonly done with plasticizers. The concept consists of using a non-porous polymer matrix as a base material into which ILs can be incorporated as a second phase. Hereby, the aim is not only improving both permeability and selectivity of the blend membrane, but also maintaining the overall machanical properties of the bulk membrane material. Such a modular approach would allow conveniently adapting the blend membrane to particular separation tasks without changing the mechanical properties of the membrane[1].

We here report on two different techniques on preparing such non-porous mixed-matrix-membranes: (1) a solvent casting method, and (2) a thermal compression process. Our aim was not only to prove the feasibility of the concept, but also to understand how the ionic liquids interacted with the base polymer. For this purpose, we resorted to characterization techniques such TGA in order to verify the stability of the blend membranes; FTIR-ATR and ^{13}C solid NMR for elucidating interactions taking place between the base polymer and various ILs; DSC, DMTA and X-Ray diffraction in order to detect how and to what extent the structure of the co-polymer was affected once the IL had been incorporated.

The synthesized membranes were compared with regard to their mechanical stability as well as their permeability to sample vapours and gases. Hardly any variation in terms of permeability was observed as a function of the membrane processability, however, it could be proven that the IL determined significantly the overall membrane properties.

Both membrane formation methods provided similar results with regard to interactions between IL and polymer, as well as mass transport properties. This means that either membrane processing method may be chosen for obtaining IL/polymer blend membranes, depending on the particular application.

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Acknowledgements

We gratefully acknowledge the ERC Starting Grant 209842-MATRIX (T. Schäfer).

Membrane and Surface Modifications

- **Poster session 2**

PHOTO-MODIFICATION WITH PEG/Al_2O_3 NANOPARTICLES OF POLYETHERSULFONE ULTRAFILTRATION MEMBRANES

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Polyethersulfone (PES) is an attractive material for ultrafiltration membrane formation due to their pressure resistance, heat resistance, mechanical strength and excellent chemical and thermal stability. However, its inherent hydrophobic nature causes important fouling on the membrane surface, which leads to a gradual decline of permeation flux and frequent membrane cleaning (Zhu et al., 2014).

Many investigations have demonstrated that increasing membrane surface hydrophilicity could effectively minimize membrane fouling and thus, achieving the desired membrane properties (Hua et al., 2008; Peeva et al., 2012). Thus, there are growing interests in developing hydrophilic PES membranes with high antifouling capability and filtration properties before their practical use. Several methods can be used to improve the hydrophilicity of PES membranes, such as blending, coating, adsorption, surface chemical or plasma treatment, surface grafting, etc. (Lalia et al., 2013; Ahmad et al., 2013). Among these methods, surface modification via UV-grafting is a very interesting technique due to its relatively low investment cost, low temperature, and simplicity (Qiu et al., 2006).

The aim of this work is the evaluation of the surface properties and the permselective performance of several PES membranes modified with UV light in the presence of two hydrophilic additives with different nature. A charged-neutral polymer (polyethylene glycol of 400 Da (PEG 400)) and an inorganic compound (aluminium oxide (Al_2O_3)) were selected to modify the membrane and improve the surface hydrophilicity of the PES membranes. The effect of these additives and their concentration in photo-modified PES ultrafiltration membranes were evaluated in terms of chemical structure, morphology, surface characteristics, permeability and fouling resistance.

Pristine PES ultrafiltration membranes were prepared via phase-inversion method with N,N-dimethylacetamide (DMA) as solvent and deionized water as non-solvent. Experiments were carried out in an UF pilot plant using a flat membrane module with 100 cm^2 of effective area (RAYFLOW X100, supplied by TECHSEP). Membrane permeability tests were performed with deionized water at a constant cross-flow velocity of 2.08 m/s, 25 ºC, and at transmembrane pressures (ΔP) ranging from 50 to 400 kPa. Hydraulic permeability and membrane intrinsic resistance were obtained using Darcy's law. After that, three cycles of PEG ultrafiltration and rinsing test were performed in order to evaluate the antifouling properties of the prepared membranes. PEG of 35 kDa was used as a feed solution with a concentration of 5 g/L. Membrane surface hydrophilicity was determined in terms of membrane porosity (ε), surface roughness (S_q) and water contact angle (WCA). Structure and morphologic changes of such membranes were analysed through FTIR-ATR spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

The results indicated that PES membranes were successfully modified and their hydrophilicity increased. It was also observed a strong dependence between WCA and S_q. Fig. 1 shows the results for both parameters at different PEG/Al_2O_3 concentrations. When

PEG/Al_2O_3 content increased, WCA decreased as well as S_q increased. In addition, membrane porosity was higher in the grafted membranes in comparison with unmodified PES membrane. The presence of the additives in membrane surface and its chemical structure was demonstrated by FTIR-ATR analyses. These results were corroborated by SEM and AFM analyses. In fouling/rinsing experiments, grafted PES membranes with 2 wt% PEG and 0.5 wt% Al_2O_3 presented the lowest total flux loss (only 20% of the initial flux) of all the membranes tested and then, the best antifouling properties. Therefore, the incorporation of PEG/Al_2O_3 nanoparticles as additives improved the hydrophilic character of the PES membranes.

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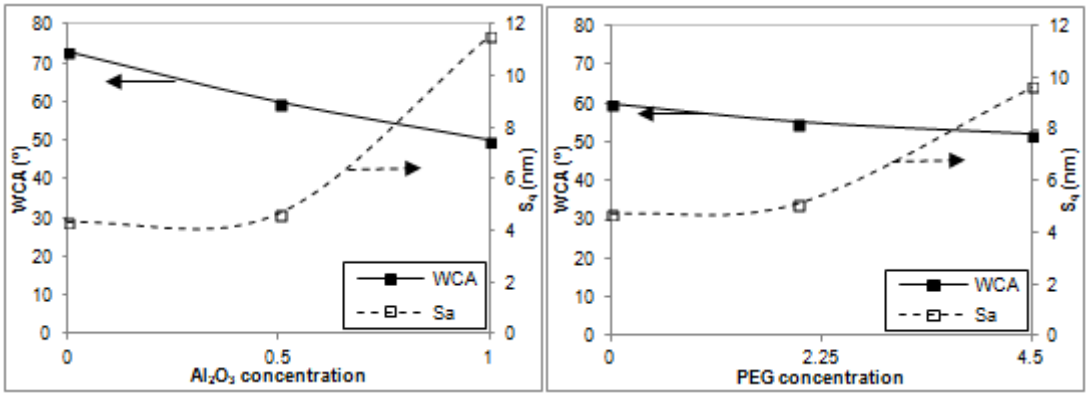

Fig. 1. Water contact angle (WCA) and surface roughness (Sq) at different additive concentration when PEG concentration was 0 wt% (left) and when Al_2O_3 was 0.5 wt% (right).

Acknowledgements

The authors of this work wish to gratefully acknoledge the financial support of CDTI (Centre for Industrial Technological Development) depending on the Spanish Ministry of Science and Innovation. The authors also thank the Center for Biomaterials and Tissue Engineering (Universitat Politècnica de València) for contact angle measurements and BASF (Germany) for supplying the polymers used.

ENHANCEMENT IN HYDROPHILICITY OF POLYETHERSULFONE MEMBRANES USING Al_2O_3 NANOPARTICLES

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Ultrafiltration (UF) is a pressure-driven membrane separation process which is employed to separate macromolecules, proteins, colloids and suspended particles from different solutions. This technique has been applied to different industries, such as beverages, dairy, water production and wastewater treatment, among others [1].

Phase-inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric UF membranes [2,3]. When substrate is immersed in the coagulation bath, the solvent in the casting solution film is exchanged with non-solvent presented in precipitation media, starting the phase separation. The prepared asymmetric membranes have a dense top layer and a porous substructure containing macrovoids, pores and micropores. Membrane formation is controlled by the composition of the casting solution, the coagulation bath temperature and the presence of organic/inorganic additives, among others variables [4,5]. However, UF membranes have serious problems caused by fouling. Generally, an increase in hydrophilicity improves the antifouling properties of the membrane [1]. Several researchers have studied the hydrophilization of UF membranes materials using inorganic additives [4,6]. The incorporation of inorganic compounds in the polymer casting solution during the phase-inversion process, such as titanium dioxide (TiO_2) or aluminium oxide (Al_2O_3), results in a higher membrane hydrophilicity and permeability and even control the membrane surface properties. Therefore, membranes show an antifouling behaviour that allows a reduction of cleaning cycles and an increase in membrane lifetime.

In this work, the effect of nano-sized Al_2O_3 in asymmetric polyethersulfone ultrafiltration membranes was evaluated in terms of morphology, contact angle, surface roughness, and permeability. These membranes were prepared by phase-inversion method induced by immersion precipitation with N,N-Dimethylacetamide (DMA) as solvent and deionized water as non-solvent. Likewise, the influence of the polymer concentration in the casting solution was studied in the same terms.

Experiments were carried out in an UF pilot plant using a flat membrane module with 100 cm^2 of effective area. Membranes were characterized in terms of hydraulic permeability with deionized water and molecular weight cut off (MWCO) with PEG solutions. MWCO profiles were constructed by measuring the separation values of PEG solutes of varying molecular weights [6]. Membrane characterization experiments were performed at transmembrane pressures ranging from 50 to 400 kPa and at a flow rate of 300 L/h. PEG retention was analyzed by refractive index. After the permeability tests, prepared asymmetric membranes were subjected to a series of fouling and hydraulic cleaning experiments to evaluate their antifouling properties. PEG of 35 kDa was used as a feed solution with a concentration of 5 g/L. Equilibrium water content (EWC), membrane porosity (ε), surface roughness (S_a) and water contact angle (WCA) were also studied to determine the membrane hydrophilicity. Structural changes of prepared membranes were analysed through microscopic observations (SEM, AFM).

The results demonstrated that the incorporation of Al_2O_3 nanoparticles improved the hydrophilic character of the PES membranes. These results were corroborated by WCA and S_a analyses (Table 1), where the hydrophilization of the membrane surface was evident when Al_2O_3 was incorporated. EWC and membrane porosity also presented higher values when Al_2O_3 was added, whereas pore sizes were not affected. SEM images showed that the size of finger-like cavities also increased in comparison with unmodified membranes. Fig. 2 shows the evolution of the total flux loss with filtration time (2 h), where fouling degree of the original membrane and modified membranes can be compared. At low PES concentration (15 wt%), the best results were achieved when Al_2O_3 content was 0.5 wt%. At high PES concentration (20 wt%), similar total flux loss was obtained for PES/Al_2O_3 membranes, where PES4 presented the lowest total flux loss and the highest solute rejection. Therefore, PES membranes with 0.5 wt% Al_2O_3 presented the best antifouling properties.

Table 1. Membrane composition, solute rejection, water contact angle, and roughness parameter for all prepared polymeric membranes.

Membrane	Composition of casting solution (wt%)			PEG 35kDa rejection (%)	Water contact angle (º)	Average surface roughness (S_a)
	P	DMA	Al_2O_3			
PES0	15	85	---	91.25	75.9 ± 1.1	3.09
PES1	15	84.5	0.5	96.37	69.6 ± 2.8	3.42
PES2	15	84	1.0	91.63	54.2 ± 1.8	5.46
PES3	20	80	---	92.50	72.9 ± 1.5	2.75
PES4	20	79.5	0.5	100.00	65.3 ± 2.0	2.98
PES5	20	79	1.0	93.54	56.7 ± 3.1	3.16

P, polymer; Membrane area = 100 cm^2; Temperature = 25 ºC; Coagulation Bath Temperature (CBT) = 18 ºC.

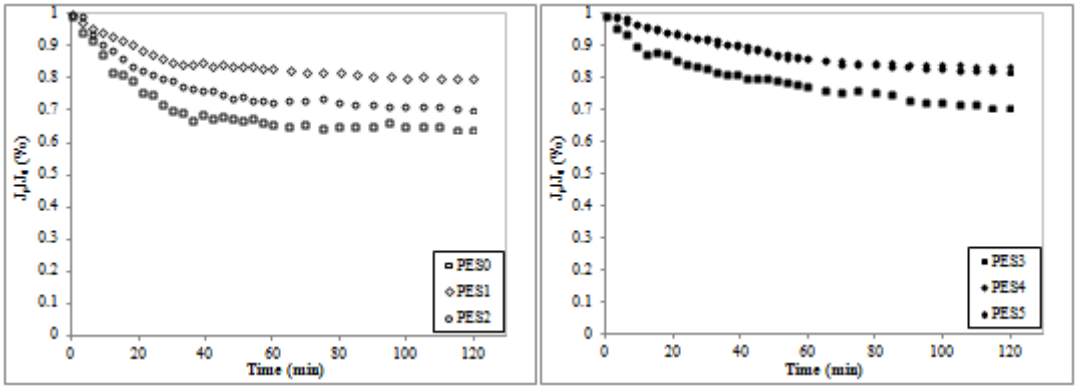

Fig. 1. Flux loss (J_p/J_0) in PEG ultrafiltration of PES membranes with a polymer concentration of 15 wt% (left) and of 20 wt% (right), with and without additive (25 ºC, 200 kPa, 2.08 m/s)

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MODIFICATION OF NANOFILTRATION MEMBRANES BY RADIOFRECUENCY ACTIVATED ARGON PLASMA

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The efficiency of membrane separation processes can be increased by using techniques of surface modification of the active layer. New applications in nanofiltration, in the fields of biotechnology and pharmaceutical industry for example, require hydrophilic membranes with improved fouling resistance. One way to achieve this is by the technique of surface modification by plasma. Because of its versatility, this technique is widely used with polymer membranes for applications such as biomedicine, gas separation, pervaporation of organic compounds, antifouling or electrochemistry [1]. In general, plasma modification applied to nanofiltration and reverse osmosis membranes, is used to increase the performance of the filtering process. Firstly this increases the permeability and selectivity, but it also increases hydrophilicity and reduces fouling. The aim of this work is to test how the structural and functional characteristics of a nanofiltration membrane change when it is modified by plasma. Argon was used to produce the plasma, with different exposure times and the changes in the membrane are analyzed as a function of exposure time. Different characterization methods such as hydraulic permeability, impedance spectroscopy of the system membrane-saline solution (water-KCl solution), and AFM, SEM and EDX techniques were used to evaluate the physicochemical and structural changes produced by the ionized gas.

The parameters studied as a function of the time of plasma treatment are the topographical changes, the membrane roughness, the elemental chemical composition, the permeability and the conductivity of an ionic solution inside the pores. The results are analyzed by different models to explain possible changes produced by the plasma, such as the effects of devastation, cross-linking or grafting onto the polymer.

A commercial nanofiltration membrane (Desal HL) was used, with a polyamide selective layer on a polysulfone support, manufactured by Osmonics SA (Vista, CA, USA). The treatment was carried out with an Argon cold plasma device activated by radiofrequency. The samples were subjected to different exposure times between 20 and 160 minutes.

The results of permeability measurement show an increase until the 60 min treatment, stabilization between 60 and 100 min, and a decrease between 100 and 160 min. The AFM and SEM images show a devastation of the surface in the first time interval and a densification at large time. As an example in Figure 1 the structure of the surface of the membrane is shown without change, and for two times of treatment. As it is clearly seen at 20 min, the surface shows a deterioration of the active layer while for very long times a dense structure appears again.

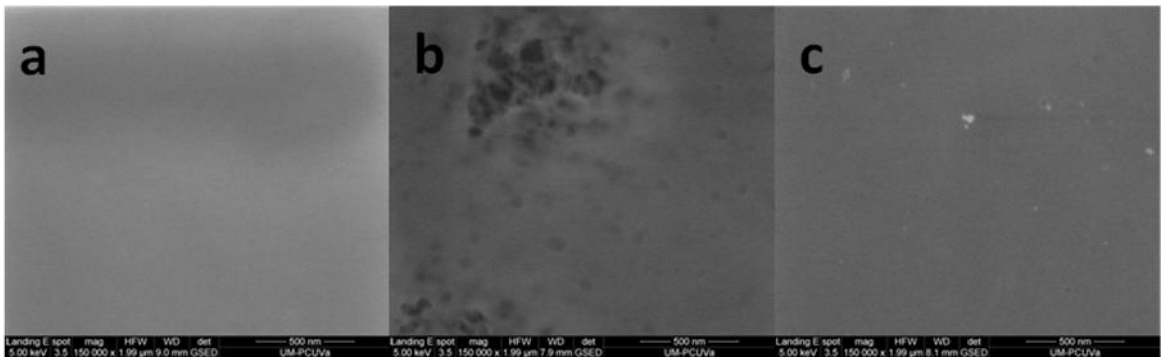

Figure 1: Images of the active surface membranes for: (a) new membrane, (b) 20 min treatment and (c) 160 min treatment.

EDX results show an increase in percentage of S and a decrease of the N content with the treatment time, which suggests a decrease in the content of the polyamide in the active layer (which provides N) and more presence of polysulfone (which provides S). Note that in this type of technique, the power of penetration of the electrons, allows detecting not only the elements on the surface layer but also those in inner layers that are also accounted for to evaluate the elemental percentage of the different atoms that form the chemical structure of the polymers.

Conductivity measurements inside the pore when these are occupied by KCl solution were performed using a previously described model [2]. The results as a function of exposure time show a maximum of pore conductivity in the active layer during the first 20 minutes, when SEM images show a maximal devastation, followed by a gradual decrease of conductivity. This behavior might be associated with a decrease in the thickness of the polyamide active layer and an increase of pore radius, followed by a cross-linking for higher treatment times. This could lead to a strong densification of the surface. This modification mechanism would explain the changes in topography, in chemical composition, in permeability and in pore conductivity.

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Acknowledgements

Authors would like to thank the “Ministerio de Ciencia e Innovación (MCINN)” for the financial support of this work within the frame of the “Plan Nacional de I+D+I” through the research projects, CTQ2012-31076 and MAT2011-25513. We also are grateful to the projects: VA248U13 of the Junta de Castilla y León.

LAYER-BY-LAYER ASSEMBLY OF POLYELECTROLYTES APPLIED TO OBTAIN CATION EXCHANGE MEMBRANES WITH MONOVALENT ION SELECTIVITY

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Ion exchange membranes are used in electrodialysis cells for desalination purposes. These membranes are polymeric films with fixed ionic groups that enable the permeation of electrolyte ions with opposite charge (counter-ions) through the membrane structure and reject ions with the same charge sign (co-ions), which are retained in the feed compartment. There is recently an increased interest in synthesizing ion exchange membranes with advanced functionalities to expand their use to more demanding processes. For example, the use of monovalent ion selective membranes is desired in metal ion recovery operations or for energy conversion purposes [1,2].

The present study investigates the possibility of imparting monovalent ion selectivity on cation exchange membranes [1]. We modified the commercial cation exchange membrane CMX using the Layer-by-Layer (LbL) assembly of polyelectrolyte multilayers. The membranes were sequentially immersed in polycation (polyethylenimine, PEI) and polyanion (poly(styrene sulfonate), PSS) solutions. The surface of the membranes terminated with a layer of PEI is likely to be positively charged, so that this coating may induce stronger repulsive forces toward multi-charged cations, as represented schematically in Fig. 1.

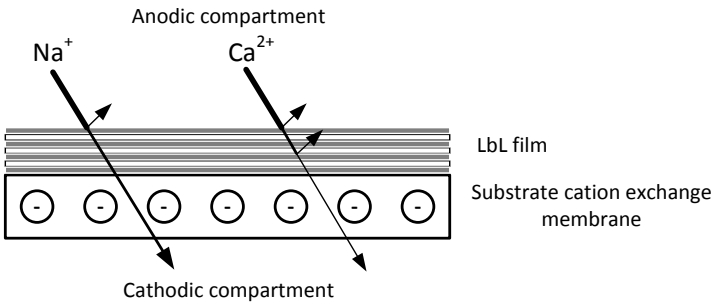

Fig. 1. Schematic representation of rejection of cations on multi-bipolar structure of the LbL layers atop of a cation Exchange membranes.

The progress of polyelectrolyte deposition was monitored and characterized by means of X-ray photoelectron spectroscopy (XPS) and contact angle measurements. XPS results confirm a progressive increase in the content of nitrogen at the surface of membranes having a top layer of PEI. This can be attributed to the increased amount of positively charged amine groups. On the other hand, membranes terminated with a PSS layer show a higher content of sulphur, due to the presence of sulfonate groups.

The electrochemical behavior of the membranes was investigated by galvanostatic permselectivity experiments, current-voltage curves and electrochemical impedance spectroscopy measurements using equimolar mixtures of NaCl and $CaCl_2$ as the electrolyte. Coating of the $(PEI/PSS)_N$ LbL multilayers on CMX membrane caused only moderate

variation of the ohmic resistance of the membrane systems. Nonetheless the polyelectrolyte multilayers had a substantial influence on the monovalent ion permselectivity of the membranes. As shown in Fig. 2, the membrane with only one PEI layer (N = 0.5 bilayer) already showed higher permeation of Na^+ ions ($P_{Ca^{2+}}^{Na^+}$ > 1). Permselectivity comparable to that of a commercial monovalent-ion-permselective membrane was obtained with only 6 bilayers of polyelectrolytes.

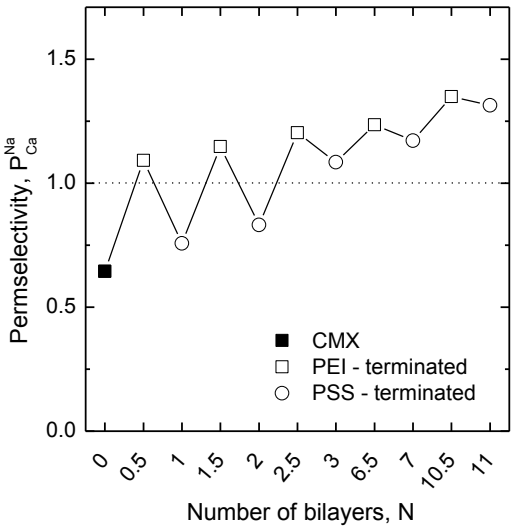

Fig. 2. Measured permselectivities between sodium and calcium of the modified CMX membranes as a function of the number of PEI/PSS bilayers.

Double layer capacitance obtained from impedance measurements showed a qualitative indication of the divalent ion repulsion of the membranes. Moreover, another interesting finding was observed: at overlimiting current densities, water dissociation occurred at membranes with PEI-terminated layers and increased with the number of layers, while it was nearly absent for the PSS-terminated layers [1]. Hence LbL layers also allow switching on and turning off water splitting at the surface of ion exchange membranes.

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Acknowledgements

The authors from Germany acknowledge support through the German Research Foundation (DFG) grant – SFB 985 “Functional Microgels and Microgel Systems”. M.C. Martí-Calatayud is grateful to the Universitat Politècnica de València for his postgraduate (Ref.:2010-12) and visiting scientist grant (PAID-00-12). M. Wessling appreciates financial support from the Alexander-von-Humboldt Foundation.

DEVELOPMENT OF TiO_2 PHOTOCATALYTIC MEMBRANES FOR DRINKING WATER TREATMENT

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Titanium dioxide (TiO_2) is a reference catalyst in promoting an efficient degradation and mineralisation of a multitude of organic compounds present in drinking water sources [e.g.1]. Such ability may reduce membrane fouling, a critical phenomenon in membrane processes, if TiO_2 could be immobilized on the membrane surface, forming a photoreactive layer. The decrease of membrane permeability could be attenuated due to the photodegradation of the organic components responsible for fouling. Furthermore, the irradiation of the membrane by an ultraviolet (UV) source may also reduce the concentration of organic compounds in the retentate, reducing the need to further treat/dispose the retentate.

Magnetron sputtering became the number one choice for the deposition of a wide range of industrially relevant coatings due to its ability to produce high-purity and high-quality well-adhered functional films even at heat-sensitive and large surface area substrates [2]. One of the most significant industrial applications of magnetron sputtering is the production of self-cleaning glass containing a thin TiO_2 layer.

In the present study, two methodologies - pulsed direct current (DC) reactive magnetron sputtering and a chemical methodology - were used and compared in terms of their potential to immobilize TiO_2 on the surface of a nanofiltration ceramic membrane. Magnetron sputtering conditions were optimized in terms of the distance to the target and sputtering time. The morphology and composition of the membranes developed were evaluated and compared in terms of: 1) membrane selectivity, using a dead-end cell; 2) photocatalytic activity of the TiO_2 thin films, using a solar simulating laboratory device equipped with an UV source emitting in the UV range (290-400nm). Membrane selectivity and photoactivity were evaluated using two environmentally relevant pesticides - diuron and chlorfenvinphos. These water micropollutants present different molecular weight and are better degraded by TiO_2 photocatalysis compared to direct photolysis using solar light [e.g. 3].

Figure 1 presents the thin TiO_2 films obtained by magnetron sputtering and the chemical methodology employed.

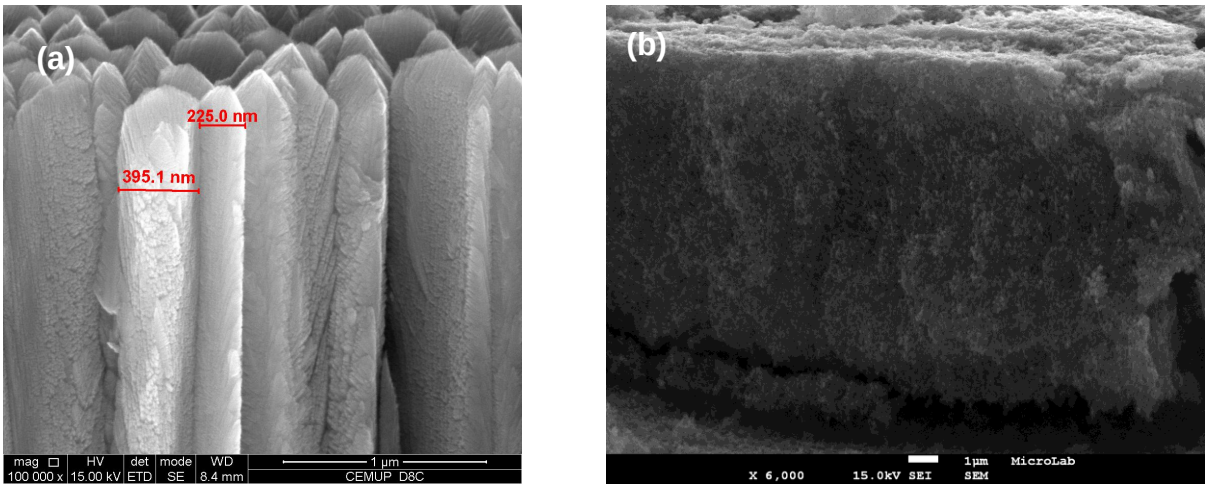

Figure 1 Scanning Electron Microscopy image of the cross-view of the TiO_2 layer attained by **(a)** reactive magnetron sputtering and **(b)** a chemical method developed on the surface of a commercial ceramic membrane composed of alumina and non-reactive TiO_2.

While defined vertically aligned nanocolumns of the catalyst were obtained by magnetron sputtering, a TiO_2 layer with very different and non-defined morphology was attained using the chemical method. Furthermore, an homogeneous distribution of the catalyst was attained by magnetron sputtering. Anatase nanocrystals, the most reactive form of TiO_2, were detected at different sputtering conditions. Similar photocatalytic activity towards the selected compounds was, however, observed using both immobilization strategies addressed (70-80% removal).

The rejection of diuron and chlorfenvinphos was higher when the membrane modified by magnetron sputtering was applied relatively to the membrane modified by the chemical methodology. Significant differences in the rejection of these compounds were not observed in the membrane modified by sputtering relatively to the unmodified membrane.

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Acknowledgments

Financial support from Fundação para a Ciência e a Tecnologia - through the project PTDC/AMB/66024/2006, the grant PEst-OE/EQB/LA0004/2011, and the fellowships SFRH/BD/72 244/2010, SFRH/BPD/94303/2013, and SFRH/BPD/26990/2006 is gratefully acknowledged.

Synthesis and characterization of polysulfone membranes modified with nanoclay and polyethylene oxide

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The addition of inorganic nanoparticles in the polymeric dope solution is one of the most innovative approaches for obtaining high performance composite membrane [1]. In order to understand the effect of inorganic nanoparticles additives on membranes performance, this work evaluated the use of clay nanoparticles and Polyehtilene Oxide (PEO) as additives for polysulfone (PSf) ultrafiltration membranes synthesis.

Some researchers examined the use of clay minerals and clay-like materials, such as montmorillonite, as the inorganic component to modify the membrane surface [2,3]. These clays are hydrophilic, have a high cationic exchange capacity and are easily expansible. Membranes prepared with clay in the casting solution showed improved hydrophilicity as well as increased thermal and mechanical resistance due to changes in the structure formation. There are also organic components used as pore forming agents, like polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), PEO, glycerol, alcohols or di-alcohols [4]. These components can also be used as additives, lowering the chemical potential of the coagulation bath and changing the inflow of water on the phase inversion step. In this study, modified and unmodified PSf membranes were prepared via phase inversion method in order to evaluate their flux, hydrophilicity and internal structure.

Twenty different solutions were prepared: one solution without any modifier, seven solutions with clay concentrations varying from 1.0 to 5.0% (polymer wt%), three solutions only with PEO in different concentrations (no clay) and twelve solutions with different concentrations of clay and PEO. These solutions were prepared by the dissolution of PEO, dispersion of clay and then addition of 18 wt% PSf in 200 mL of NMP at room temperature. The solutions were kept under stirring for 24 hours and then went through ultrasonic bath for degasing before being cast. Membranes were cast using a casting bar with 100 µm thickness in an automatic film applicator at speed of 1 cm/s. Membranes were obtained through the phase inversion process, submerging the glass plate with the solution film in deionized water bath. After this, they were kept in deionized water for 24 hours to remove residual solvent.

Membrane permeability was evaluated using a laboratory-scale cross-flow ultrafiltration unit fed with deionized water, under a pressure of 1 bar at room temperature. Hydrophilicity was estimated by measuring the contact angle of a sessile drop using a goniometer. Membrane Thickness, porosity and solution viscosity were also measured. Samples of clay membranes were analyzed using SEM images in the efforts to correlate the results of permeability and hydrophilicity with structural modifications. T

The use of nanoclay and PEO improved membrane performance comparing to the neat membrane. Among pure clay membranes, 1.5% clay concentration had highest permeability (3.8 times the control one). PEO by itself increase permeability (around 14 times the control). The combination of PEO and clay increased the flux 22 times compared to control (4.5% clay and 5% PEO). Membrane hydrophilicity, measured by contact angle, showed there was no direct correlation between contact angle and permeability. PEO addition increased membrane thickness and average porosity Table 1 shows the average results of permeability, contact angle, membrane thickness and porosity

Considering the SEM images, the analysis of the superficial images didn't have a satisfying level of definition to evaluate surface pore diameter and distribution. However, the analysis of internal structure provided significant data for analysis. The use of nanoclay changed internal structure even in lower concentrations. The structure tended to become

from finger-like form to sponge-like form as the concentration of clay increased. Membranes with nanoclay had a finger-like structure from the top to the bottom. 4 and 5% nanoclay membranes had a structure with narrow fingers and a bottom predominantly with sponge-like structure with macrovoids on the bottom layer.

Table 1 Results of the filtration experiment and contact angle measurement

	PS-0	PS-1	PS-2	PS-3	PS-4	PS-5	A0	A1	A3	A5
Permeability ($L/m^2.h.bar$)	14,4	44,1	48,1	31,5	31,2	33,5	55,5	146,4	188,7	192,2
Contact Angle (^{o})	78,4	75,2	73,1	76,8	75,4	75,2	81,8	81,3	72,9	71,0
Porosity (%)	65,2	72,9	75,7	64,5	64,2	61,4	0	0	0	0
Thickness (µm)	60,8	58	55,1	60,4	52,5	53,8	51,1	53,5	61	59,2
	B1	**B3**	**B5**	**C0**	**C1**	**C3**	**C5**	**Z1**	**Z3**	**Z5**
Permeability ($L/m^2.h.bar$)	126,4	205,0	228,8	22,9	115,5	182,2	319,3	207,9	206,7	237,4
Contact Angle (^{o})	80,9	73,4	72,7	76,4	70,0	64,8	64,6	78,4	79,9	77,0
Porosity (%)	63,2	52,6	52	63,9	70,2	66,3	62,2	59,7	64	58,7
Thickness (µm)	58,2	63,2	63,3	55,8	62,8	62,6	65,5	55,9	63,3	64,7

PS-X: X% of Nanoclay

AX: 1.5% Nanoclay, X% PEO / BX: 3% Nanoclay, X% PEO / CX: 4.5% Nanoclay, X% PEO / ZX: X% PEO

Considering the SEM images, the analysis of the superficial images didn't have a satisfying level of definition to evaluate surface pore diameter and distribution. However, the analysis of internal structure provided significant data for analysis. The use of nanoclay changed internal structure even in lower concentrations. The structure tended to become from finger-like form to sponge-like form as the concentration of clay increased. Membranes with nanoclay had a finger-like structure from the top to the bottom. 4 and 5% nanoclay membranes had a structure with narrow fingers and a bottom predominantly with sponge-like structure with macrovoids on the bottom layer.

The possible explanation for this structure alteration resides in the fact that adding clay in higher concentrations makes the chemical potential in the casting solution lower compared to ultrapure water (enthropy increases), which makes the inflow of water in phase inversion occur faster, causing an instantaneous demixing and formation of macrovoids on the bottom layer.

The next step in this research will focus on a more detailed membrane performance evaluation in terms of rejection and physical properties as well as the presence of residual clay on the final membranes. The analysis of these parameters will help to better understand the role of nanoclay and PEO on the morphology and performance of obtained membranes.

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Waste Water Treatment and Membrane Fouling

- **Oral session 10**

CURRENT INDUSTRIAL WASTEWATER PROBLEMS AND TREATMENT METHODS IN FINLAND – THE FOCUS AREAS IN RESEARCH

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Water pollution is a major threat to our health, environment and the quality of life. The releases of hazardous and toxic compounds existing in wastewaters into the ecosystem are a significant source of pollution, eutrophication and perturbations of aquatic life and a threat to human health. Effluents contain typically heavy metals, nutrients and organic compounds that are mutagenic, carcinogenic, teratogenic or otherwise toxic, e.g. toxic organic compounds, and thus may be harmful to human health. For example heavy metals are detrimental to human health already in small quantities and they have a tendency to accumulate in the environment. Nitrogen and phosphorus compounds are essential for life but their excess discharge to the environment can cause eutrophication and health effects to humans if they are present in e.g. drinking water. These compounds can be found e.g. from mining, chemical, metallurgical, agricultural or sewage wastewaters in high quantities. Rapid industrialization along with the population explosion has led to a serious increase in the consumption of pharmaceuticals. Amoxicillin is one of the most important and widely consumed pharmaceutical globally. It has been reported in waste discharge streams and also in surface waters. Pesticides are widely utilized in agriculture and their presence in waters create environmental hazards.

Effective techniques for treating hazardous, toxic and highly concentrated organic compounds in wastewaters are a necessity of today. Advanced oxidation processes, e.g. photocatalysis and catalytic wet oxidation have been found to be effective techniques in the abatement of organic load existing in wastewaters. In recent years, membrane separation has received a lot of attention due to its performance and reliability in operation for the removal of heavy metals, organic pollutants and other large molecules from wastewaters from dairy industries and pharmaceutical industries. Nanofiltration is a relatively new wastewater treatment process compared to other membrane processes such as reverse osmosis, ultrafiltration and microfiltration. For example high sulfate and arsenic contents in discharges from the mining wastewaters have been a well-known problem worldwide and moreover, sulfate scaling is an inherent problem in all the steps of a desalination process leading to precipitation on the desalination equipment, e.g., tubes, membranes, etc. To overcome this problem, nanofiltration membranes have recently been employed.

This presentation aims at providing information of the research done in Finland on the removal of harmful compounds from industrial wastewaters discharged from e.g. real mines and other industries. The aim of the research has been to find out new environmentally benign solutions for the purification of aqueous effluents or to adopt existing technologies to new fields, e.g. mining industry, technologies that have earlier been used successfully in other application areas. The role of the Finnish research funding organizations is discusses as well.

ELECTRODIALYSIS POWERED BY PHOTOVOLTAIC ENERGY FOR INDUSTRIAL WASTEWATER TREATMENT

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Food industries such as almond industry generate large volumes of wastewater in their processes and common techniques are not always efficient for treating this kind of effluents. In addition, almond industry has a high relevance in Spain (especially the southeast of the country) as it is the second producing country in the world. Wastewater from this sector has high concentration values of suspended solids, COD, turbidity, color and conductivity, so they must be treated before discharging in order to satisfy the discharge limits established by existing legislation. Electrocoagulation (EC) and Electrooxidation (EO), which can be powered by PV energy, have been proposed as suitable techniques to remove the main pollutants [1-3]. Nevertheless, these techniques neither remove ions nor decrease water conductivity. For this reason, when conductivity is high, a different technique must be applied to decrease it.

Electrodialysis (ED) is an electrochemical technique widely employed for the desalination of brackish water [4], the purification/concentration of effluents and the recovery of substances with a high added value from industrial effluents. In addition it is a clean technique, easy to implement and able to be powered by photovoltaic cells, increasing its "green" character and turning it into a sustainable technique for desalinaton purposes. In this case, the application of ED, after EC and EO treatment, in order to reduce conductivity from almond industry wastewater has been studied.

In this work, a method for controlling membrane fouling due to organic matter in wastewater has also been developed. To this aim, an electrodialyzer has been modified in order to allow voltage drops at the membranes to be measured and control its fouling. Moreover, the relationship between these voltage drops and membrane fouling or organic matter passing through membranes has been studied.

After the optimization of the ED system, the treatment of the wastewater was performed under different experimental conditions and values permiting the water dumping to the sewage system or reuse were achieved. The ED treatment has been performed at both, laboratory and pre-industrial escale and powered by photovoltaic energy. In both cases the system decreased conductivity until 0.5 mS cm^{-1}, and a water that can be dumped into sewage system was generated.

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THE ROLE OF LIQUID MEMBRANES IN THE VALORIZATION OF HAZARDOUS SPENT PICKLING SOLUTIONS

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Hot-dip galvanizing is the most extensively used surface treatment to protect steel pieces against corrosion. During the process, spent pickling solutions (SPS) are generated during several stages such as washing, pickling or galvanizing itself. These effluents are of environmental concern because they contain, among other substances, high concentrations of zinc (20-120 g L^{-1}), iron (100-130 g L^{-1}) and hydrochloric acid (1-6 mol L^{-1}) [1,2]. Resource efficiency by means of valorization practices is a key strategy to reduce the environmental impact of processes that utilize non-renewable materials and produce hazardous effluents. The selective separation of zinc from SPS would reduce the toxicity of the effluent and would facilitate the recovery of metallic zinc by electrodeposition, a component of high added value. This may be attained by means of liquid membrane based processes. Liquid membrane technology incorporating selective carriers takes advantage of the benefits derived from the facilitated transport of a solute versus others resulting from the coupling between chemical reaction and mass transport phenomena. The combination of liquid membranes and membrane contactors (membrane-based solvent extraction, MBSX) is a promising alternative to obtain a stream that contains mainly zinc and to embrace the aimed resource efficiency (Figure 1).

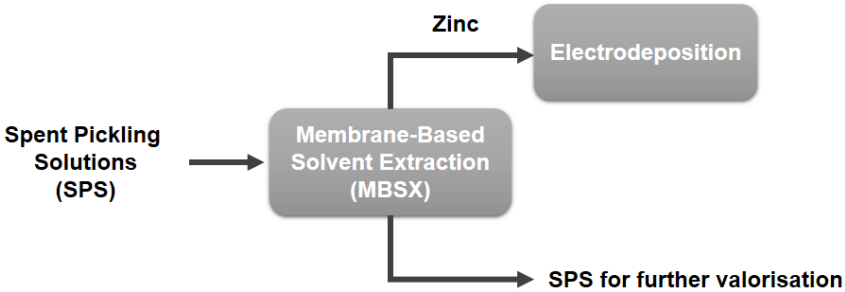

Figure 1. Recovery of zinc from SPS by means of Selective Liquid Membranes.

The selective separation and recovery of zinc from SPS by means of MBSX can be carried out using two configurations: Non-Dispersive Solvent Extraction (NDSX) and Emulsion Pertraction Technology (EPT). These configurations differ in the way of contacting the fluid phases and the number of the membrane contactors involved [2,3] and can exhibit different selectivity towards zinc versus other compounds such as iron. In the NDSX configuration, the extraction and back extraction are conducted in two different membrane modules. This fact allows the non-dispersive contact between feed/organic solutions and between organic/stripping phases. In the EPT configuration, the extraction and back extraction are conducted in a single membrane module. The non-dispersive contact occurs between the feed and the pseudo-emulsion prepared by dispersing the stripping solution into the organic solution.

This work reports the technical performance of NDSX and EPT for selectively extract zinc over iron from SPS. The main objective was to assess the experimental conditions that benefit the selective extraction of zinc over iron and its recovery in the stripping phase. The considered parameters were process configuration,i.e. NDSX and EPT, the extractant concentration (20% (v/v), 50% (v/v) and 100% (v/v)) and the phase volume. The experiments

were performed employing tributylphosphate (TBP) as selective extractant and tap water as stripping agent.

The results showed that the extraction of zinc was benefited by the use of EPT, increasing TBP concentration and increasing the volume of stripping phase compared to the volumen of the feed phase. However, the use of EPT and the increase of extractant concentration and stripping volume also enhanced the transport of iron to the organic phase, which may affect negatively the selectivity of the process. This work concludes the need of compromising the effect of the experimental parameters on the extraction of zinc over iron. The obtained results suggest that using NDSX configuration and the introduction of a purge system where the stripping phase is replaced will allow to obtain higher percentages of zinc extraction.

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Acknowledgements

Financial support of the Spanish Ministry of Economy and Competitiveness under the project CTQ2012-31639 (FEDER 2007-2013) and under Juan de la Cierva programme, and of the company is gratefully acknowledged.

NOVEL DEVELOPMENT OF AN EFFICIENT ANTI-FOULING GRAFTING TO ENHANCE THE APPLICABILITY OF CERAMIC NANOFILTRATION MEMBRANES IN WATER TREATMENT

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Water is an extremely valuable commodity for society but also for industry. Therefore, adequate processing of water (cleaning and recycling) is essential. Membrane technology can be a flexible and viable long-term strategy for treatment of water. However, widespread use of membranes for water treatment is hindered due to fouling caused by the impurities present in the water. Particularly, natural organic materials (NOM) strongly reduce the membranes performance especially for NF membranes. **Fouling** is a major drawback and an unsatisfactorily resolved problem of membrane technology up to today, not only for water treatment but for all other membranes applications.

Fouling of membranes (both polymeric and ceramic membranes) is caused by surface properties including hydrophilicity and charge. Therefore, we have developed **smart surface functionalization to decrease the fouling tendency drastically**. In this study, focus is on two approaches for surface functionalization of ceramic NF membranes using Grignard reagents and Phosphonic acids. Both techniques are applied to commercial TiO_2 NF membranes manufactured by Inopor GmbH Germany. Systematic studies were carried out to explore the potential of surface functionalization for fouling reduction, the correlation between foulants chemical properties and membrane surface, and ultimately how the type of functionalization relates to the fouling resistance. This way, a methodology to tailor surface functionalization on TiO2 nanofiltration (NF) membranes is being developed, to reach a desired set of properties to diminish fouling.

The fouling tendency of the membranes (with and without fouling-resistant functionalization) was tested by doing filtrations using model foulant solutions and real waters. Experimental results revealed that grafting of NF TiO_2 membranes by the mentioned techniques definitely decreases their fouling tendency. Importantly, **methyl functionalized membrane** (Grignard method) exhibited a significantly lower propensity to foul throughout all measurements. **This functionalized membrane proved to be non foulable for humic acids,** the major part of NOM in water. All the results shown can be elegantly explained taking into account the chemical structure of functionalized membrane and foulants. Moreover, chemical cleaning experiments showed that all functionalized groups are stable in basic media up to pH 10 and allowed for proper cleaning of the functionalized membranes at lower pH than unmodified membranes.

Acknowledgements

We are grateful to the European Commission (grant number: 180909) and VITO (Flemish institute of technological research) for the financing of this research. We also acknowledge the FP7 CeraWater project partners for the fruitful discussions on the model foulants, and the fouling procedure.

STUDY OF THE FOULING IN SEAWATER ULTRAFILTRATION PRETREATMENT PROCESS: MECHANISM AND CLEANING PARAMETERS

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Nowadays ultrafiltration is well used in several industrials applications: food processing industries, pharmaceutical industries,… Recently, ultrafiltration has been recognized as a competitive pre-treatment for reverse osmosis system compare with conventional ones. The problem of UF applications is the fouling and the incapacity to predict it and to anticipate, avoid or inhibit its establishment by regulating the cleaning parameters. To handle this problem, the treated case is the ultrafiltration of a seawater pretreatment system prior to reverse osmosis system. In a first stage, we investigated the fouling mechanism using the classical fouling models established by Hermia and the combined models of Bolton. The pilot designed for the purpose is equipped with a hollow fiber membrane cross flow module (100 kDa, S=4.2 m^2). Experiments were made using the methodology of experimental design varying 5 parameters: the filtration time which varied between 30 and 60 min, the backwashing flow rate (15, 17.5, 20, 22.5 and 25 L/min), the backwashing duration (10, 20, 30 and 40 second), the backwashing frequency (1, 2, 3 and 4 stops by backwashing cycle simulating the relaxation), and the hypochlorite concentration (0, 2, 4.5, 7 and 10ppm). Each experiment was 600 min duration.

The fouling mechanisms responsible of the permeate flux decline was investigated using the flux expressions of Hermia and Bolton models and the 60 mn experiments data. The results show (based on the values of the least square [1]) that the blocking pores model had the lower least square values, suggesting it as the best model to describe the fouling and that the use of sophisticated models like the combined models [2], [3] and [4] is not useful.

Concerning the experimental design plan, we did a screening study and from the results, we can draw the following remarks:

- the difference in trans-membrane pressure decreases as the NaClO concentration increases, showing a better effect on removing fouling. Besides, the NaClO concentration increases has no effect on the permeate quality.
- the filtration duration has a significant effect on the time at which begins the fouling (considered as the time at which the PTM increases without decreasing after a backwash). When increasing the filtration duration from 30 to 60mn, the establishment of the fouling is delayed.
- three factors appear to have an effect on the net permeate production response, the functioning duration, the backwashing duration and the flow rate. Functioning at 60 min gives a greater net permeate production. As the backwashing duration increases, the net permeate production decreases. The backwashing flow-rate has a slight influence where it gives a better response at 15 and 17.5 L/min rather than at 22.5 or 25 L/min. The NaClO rate and the backwashing frequency don't show any effect on the net water production.

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Acknowledgements
The authors would like to acknowledge the financial support of the Tunisian company of electricity and gas (STEG) and Mr. Heddaji Mondher.

Waste Water Treatment and Membrane Fouling

- **Poster session 2**

COMBINED OZONE OXIDATION AND MEMBRANE PROCESSES FOR WATER TREATMENT

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Ozone is a powerful oxidant compound and it is applied to disinfection and/or to remove pollutants in the water treatment processes, reacting with a wide range of recalcitrant compounds without waste production. This technology has drawbacks such as high cost for ozone generation, high oxygen demand caused by low oxygen conversion and ozone losses due to the high mass transfer resistence in the gas dispersion. Membrane contactor devices are used as a physical barrier to separate two fluids, for example in gas/liquid systems, without phase dispersion and it can improve the ozonation process efficiency.

In a membrane contactor the diffusion occurs through the gas/liquid interface as in conventional process. However, the fluids are separated by the membrane, resulting in higher interfacial area than conventional process. Other advantagens include independent control of fluids flow rates and better control of the mass transfer, improving the ozonation efficiency.

This work investigated transfer of ozone to the liquid phase by a polypropylene membrane contactor and in a conventional bubbling reactor. The ozonation process was conducted with pH ranging from 2 to 7 in both bubbling reactor and membrane contactor processes. The influence of liquid and gas flow rates on the overall mass transfer resistance was evaluated, indicating that the best configuration is a non-wetting membrane. The polymer degratation by ozone was also investigated through FTIR, TGA and DSC analyzes.

The inicial permeate flux of ozone was higher at pH 7, reaching the equilibrium concentration at 30 min in the fed tank. However, saturation of the liquid phase was observed in the stream leaving the contactor. It was observed an increase in the overall mass transfer coefficient with the liquid flow rate, but very little influence of the gas flow rate. The analysis of the membrane after the contact with ozone did not indicate a signifficant change in the polymer properties.

FORWARD OSMOSIS PROCESSES INCORPORATING MICROFLUIDIC SEPARATION STAGES FOR MAGNETIC DRAW SOLUTIONS RECOVERY

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Water has always been one of the most important natural resources for society development, since it is used not only for consumption, but also for agricultural, industrial and recreational purposes. As a consequence of extensive water requirements for human activities, ensuring water supply has become one of the most challenging problems in our era.

Several research groups have focused their efforts towards the development of new water treatment technologies able to minimize the current worldwide water deficit. In particular, pressure-driven membrane separation processes such as reverse osmosis (RO) offer several benefits which make them to prevail over other technologies. In spite of RO reports high removal efficacies for a wide range of undesirable compounds from aqueous solutions, the high energy supplies needed to produce the hydraulic pressure turns RO into a non-viable option in many cases.

Currently, a promising pressure-driven membrane technology namely forward osmosis (FO) is acquiring relevance for water reclamation. In FO the solvent flows spontaneously through a semi-permeable membrane only as a result of osmotic pressure difference between two solutions: a diluted solution known as Feed Solution (FS) and a concentrated one usually referred as Draw Solution (DS). As high osmotic gradients lead to the high water fluxes, further research should be conducted to define novel solutes to formulate DS capable of producing higher osmotic pressures than typical solutes (i.e inorganic salts, alcohols, sugars, etc.) but minimizing at the same time, the back flux of the solutes through the membrane. As a result of solvent permeation the DS becomes diluted so that it is necessary to couple a non-energetically extensive DS recovering stage to avoid the decrease of the osmotic gradient. Recently, many scientifics has focused their attention on magnetic nanoparticles (MNPs) as support of different functional compounds useful for the development of different applications in areas such as biomedicine, catalysis, adsorption and water treatment. In general, MNPs exhibit enhanced physical and chemical properties, i.e. magnetic permeability, chemical reactivity, surface area, as compared to macroscopic materials and thus, their integration in existing technologies could lead to processes energetically and economically more efficient.

This work aims at the assessment of integrated forward osmosis processes based on the use of draw solutions formulated with magnetic nanoparticles functionalized with moeities able of providing osmotic gradients similar to those reported for conventional draw solutions. In addition, the reconcentration of the draw solutions by the application of an external high gradient magnetic is theoretically evaluated. Figure 1 depicts a flow diagram of the integrated forward osmosis process incorporating a magnetic separation stage:

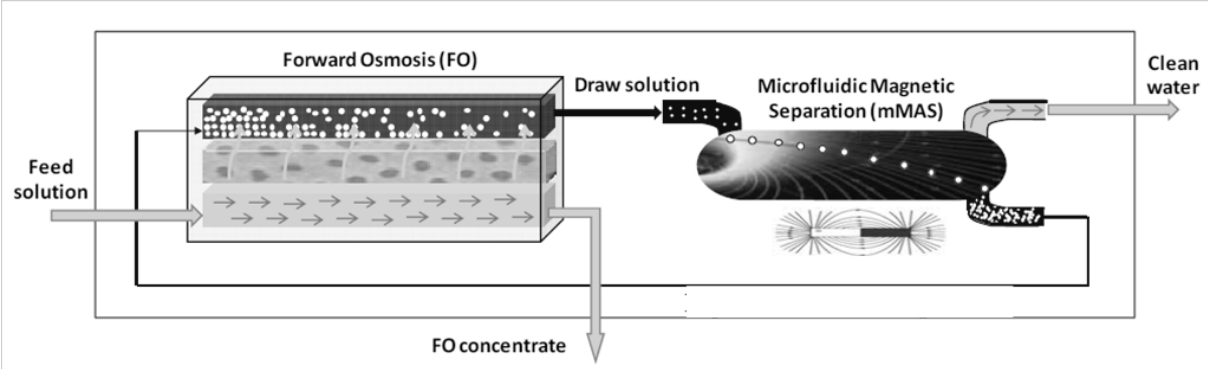

Figure 1. Integrated forward osmosis processes with magnetic separation stages.

The methodology proposed consits of three different stages:

1) Initially aqueous draw solutions formulated with imidazolium chloride-based Room Temperature Ionic Liquids (RTIL) and N-[(3-Trimethoxysilyl) propyl] ethylenediamine triaceticacid trisodium salt have been selected to evaluate the water flux and the solute back flux through commercial cellulose triacetate (CTA-ES) forward osmosis membranes.

2) In a second stage magnetite cores obtained by a co-precipitation method have been functionalized with those draw solutes which showed the better performance in stage 1. RTIL's were grafted on the solid surface after reaction with the linker (3-Chloropropyl) triethoxysilane whereas N-[(3-Trimethoxysilyl) propyl] ethylenediamine triaceticacid trisodium salt was directly supported on the solid surface. The effective osmotic pressure gradient provided by the partial solubility of the surface-grafted groups of this MNP's were tested using CTA-ES membranes and through the evaluation of the water flux. In additon the osmolality of the draw solutions was quantified and correlated with the permeability results.

3) In the third stage, a continuous flow method capable of separating MNP's inside a microchannel is proposed. The advantages of this method lie in the possibility of controlling the movements of the particles under the influence of an external magnetic field and the continuous nature of the separation process, thus avoiding a possible aggregation of the MNP's. Particle motion is predicted using computational fluid dynamic (CFD) techniques based on a Lagrangian tracking method, being the separation efficiency evaluated through the particle trajectories inside the microfluidic separation device.

Water fluxes obtained as a result of DS formulated with RTILs present, in some cases, high values than the obtained with sodium chloride. Furthermore, a correlation between the osmotic gradient and the molecular weight and chemical structure of RTILs was obtained. The best results were obtained with N-[(3-Trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt supported over magnetite.

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitiveness under the projects CTQ2012-31639 (FEDER 2007-2013) and CTM2011-23912 is gratefully acknowledged**.**

Membrane Contactors and Multifunctional Reactors

- **Oral session 11**

Succinic Acid Recovery by Membrane Contactor Extraction

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The importance of organic acids to the industry has been grown, due to their recent use in the production of biodegradable polymers [1]. For this specific application, it is preferred to use raw materials obtained from renewable sources, increasing the demand for organic acids produced by fermentation. However, the exploitation of the fermentative route in a large scale still relies on the improvement of the product recovery process [2]. Various methods have been proposed, including membrane contactor extraction, which appears to be technically and economically promising. Membrane extraction consists of a liquid-liquid operation using an organic compound as the extraction agent. Membrane acts as a contactor, providing a high contact area between phases. Unlike conventional extraction, phases do not disperse in each other [3]. Extraction and re-extraction of the organic acid can be coupled in the same experimental system. In case of an industrial application, the acid would be removed from the fermentation broth and further purified in just one step. This work aims at studying the membrane extraction process of succinic acid, investigating both the extraction to the organic phase and the re-extraction into a new aqueous phase. The objective is to obtain purified acid, improving efficiency using hollow fiber modules as contactors.

To recover succinic acid (initial concentration in aqueous phase: 0,4 mol/L), the extractants evaluated were the primary alcohol 1-octanol, the primary amines Primene JM-T® (C16-C22) and Hexadecylamine, the tertiary amines Tris(2-ethylhexyl)amine and Trioctylamine, the quaternariumm ammonium salt Aliquat 336® and the phosphate Tributyl phosphate. Because amines are viscous and corrosive, 1-octanol was used as diluent. The extractant concentration in the organic phase was set in 0,25 mol/L.

Preliminary liquid-liquid extraction tests were performed in order to evaluate the performance of the extractants. Results are presented in Table 1. The best result was obtained for the extractant containing trioctylamine (TOA).

Table 1. Succinic Acid Liquid-liquid Extraction.

Extractant	Extraction (%)
1-Octanol (Pure Diluent)	18.1
Primene JM-T® in 1-Octanol	48.9
Hexadecylamine in 1-Octanol	55.3
Tris(2-ethylhexil)amine in 1-Octanol	17.3
Trioctilamine in 1-Octanol	61.8
Aliquat 336® in 1-Octanol	23.7
Tributyl Phosphate in 1-Octanol	17.1

The extraction with membrane was evaluated using a system with two coupled non-porous cellulose acetate hollow fiber modules, allowing simultaneously extraction and re-extraction. For these tests, the extractant flows inside the fibers while the aqueous phases flow externally to the fibers.The extent of recovery of acid is shown in Figure 1.

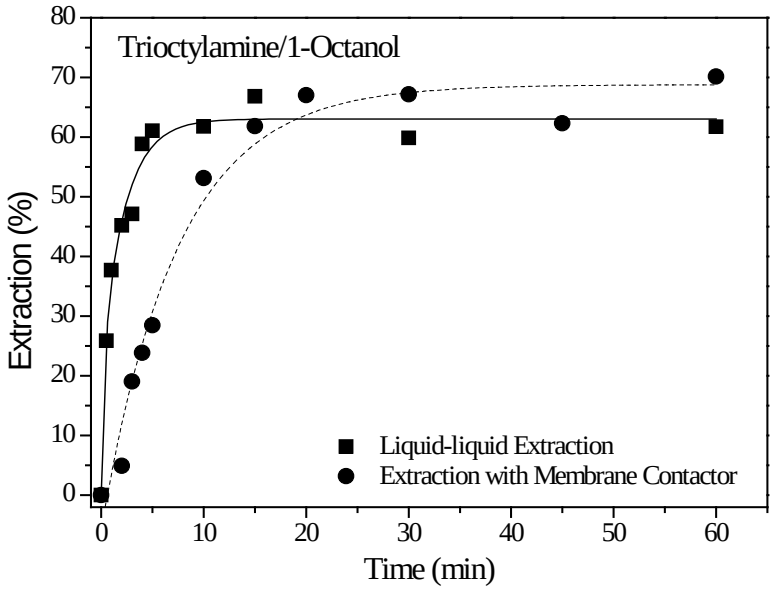

Figure 1: Comparison between Liquid-liquid and Membrane Contactor Extraction.

The result obtained for exctraction with membrane contactor was similar to that obtained by direct contact. However, the presence of the membrane affects the extraction kinetics, slowing the process.

Coupling extraction and re-extraction steps rises the total amount of acid recovered from the feed by shifting the equilibrium of the extraction. Thus, the total recovery of the acid from the feed can be five times higher than the single extraction. Those promising results indicate a good potential for the proposed process.

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EVALUATION OF REMOVAL AND RECOVERY OF AMMONIA FROM LANDFILL LEACHATE USING MEMBRANE CONTACTORS

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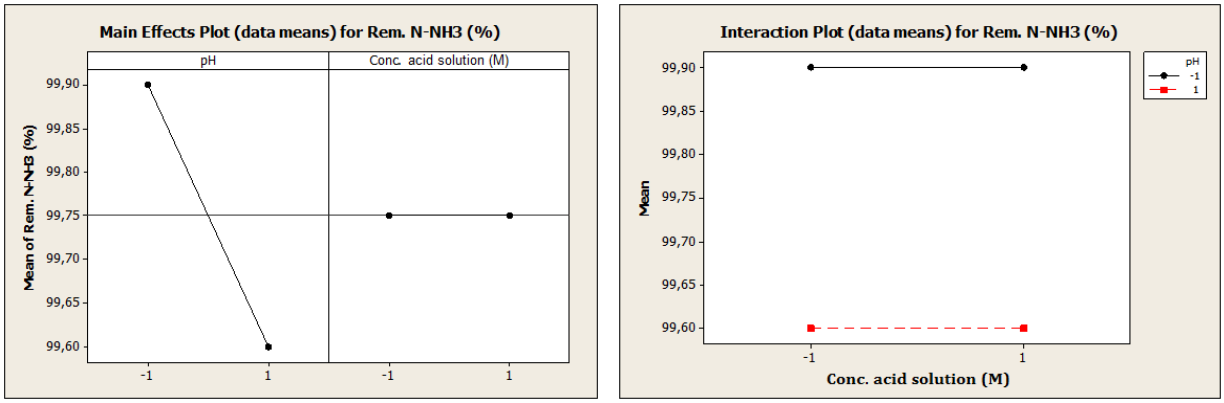
Ammonia is one of the main pollutants that are released into natural receiving waters through improper discharge of domestic and agricultural wastewater. At the end of an effluent treatment is desirable to have a very low ammonia concentration for two reasons: this substance is highly toxic to most species of fish and it may be oxidized by nitrifying microorganisms producing nitrites and nitrates that are undesirable to beings human [1]. High concentrations of ammonia can be found in landfill leachate, whose inadequate allocation brings health, economic and environmental problems, which makes it necessary to treat before release into water courses. Furthermore, ammonia is an important input for fertilizer industries. In order to remove and recover the present ammonia in landfill leachate and thus make it suitable for disposal in relation to this component effluent, with maximum concentration of total ammonia nitrogen (TAN) of 20.0 mg L^{-1} according with legal regulations, membrane contactor technology configuration liquid-gas-liquid can be used, since it offers a large surface area that facilitates rapid separation of the ammonia present in the effluent and subsequently reaction with a liquid absorbent, such as e.g. a solution of sulfuric acid, producing a byproduct: ammonium sulfate. In this context , this study aimed to evaluate some operating parameters of the conditioning factors pH (10 and 12) and concentration of sulfuric acid solution (0.1 and 0.4 M) to obtain high values of removal efficiency and recovering ammonia from the use of membrane contactors. For the tests , the leachate was previously microfiltered (submerged microfiltration module of hollow fiber type), for retention of suspended solids and minimizing fouling in membrane contactor, which permeate was used as feed for passage through the membrane contactor (Minimodule X50 Liqui-Cel®-1.0 x 5.5, area of 0.18 m^2 and the membrane material of polypropylene PP). Samples collected throughout the trials were analyzed in terms of TAN [2]. FTIR analysis were carried out to evaluate ammonia solution composition. The tests performed and their respective settings and results can be seen in Table 1.

Table 1 - Parameters and their values for each test conducted in membrane contactor module to optimize the removal and recovery of ammonia.

Test	pH	Conc. acid sol. (mol L^{-1})	Removal of TAN (%)	Recovery of TAN (%)	Ammonium sulfate (% m/m)
1	10	0,4	99,9	87,0	12,8
2	10	0,1	99,9	79,1	41,2
3	12	0,4	99,6	83,7	12,7
4	12	0,1	98,6	88,6	43,1

Obs.: $V_{leachate}/V_{acid\ solution}$=1,5; Flow rate ($L.min^{-1}$) = 0,5; Time = 6 h

The influence between the effects of the factors pH and concentration of the acid solution were assessed for response variable removal efficiency of total ammonia nitrogen, whose main effects graphics and interaction between the assessed parameters can be viewed in Figure 1.



(a) (b)

Figure 1 - (a) Graphics of main effects and (b) interaction of the factors pH and concentration of the acid solution as a function of the response variable efficiency of TAN removal

According to the graphics of main effects and interaction, one realizes that there is a difference in the influence of the pH factor in relation to the factor of concentration of the acid solution, because for both studied concentration values the response of ammonia removal was the same (in around 99.75%), indicating that this factor does not exert great influence on the removal efficiency of ammonia. Similar results were observed by Hasanŏglu *et al.* [3], who evaluated the same parameters in a solution of ammonia nitrogen. Already in pH 10 (-1) and 12 (1), the removal efficiencies showed a very small difference in their values, 99.9% and 99.6%, respectively. According to the results of Table 1, the recoveries of ammonia obtained in acidic solutions, corresponding to tests 2 and 4, were 88.6% and 79.1%, respectively, to yield 12.6 mg L^{-1} and 1.2 mg L^{-1} of TAN in the leachate at the end of each test, thus having fulfilled the legal requirements. In both trials, the percentage of ammonium sulfate in acid solution was very high compared to the values found in the marketed product (21% of $N\text{-}NH_4^+$ and 24 % $S\text{-}SO_4^{2-}$), indicating that both configurations adopted in this study (tests 2 and 4) may be used to remove and recover ammonia from leachate. However, as there is no significant difference in the influence of the concentration of the acid solution on the removal of ammonia, the use of an acid solution of concentration of 0.1 M, for removal and recovery of ammonia, and adjusting the pH of the leachate is recommended the value equal to 10, with a view to reducing the costs of the process. Thus, the results presented extremely promising in terms of the operating system and ammonia removal as confirmed by FTIR results. The sharp reduction of ammonia allowed the framework of the leachate to the standards required by legislation and high recovery of ammonia produced a by-product of high commercial value, ammonium sulphate, adding value to the landfill leachate.

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Acknowledgements

The authors thank DCTA/CEFET-MG, DESA/UFMG and CNPq for their support and resources granted.

AMMONIUM REMOVAL BY LIQUID-LIQUID MEMBRANE CONTACTORS IN WATER PURIFICATION PROCESS FOR HYDROGEN PRODUCTION

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Hydrogen is considered a clean energy source since only water vapor is obtained during its combustion. However, production of H_2 from water by electrolysis is limited by water quality requirements in terms of ionic conductivity [1]. The use of membrane distillation has been postulated as an attractive solution to achieve this objective, nonetheless the presence of aqueous ionic species with the potential of change to a gaseous phase are limiting its performance [2, 3]. In this work a liquid-liquid membrane contactor (LLMC) was evaluated to remove ammonia traces from water for electrolysis hydrogen production. Three operational parameters were evaluated: the feed flow rate, the initial ammonia concentration in the water stream and the pH of solution. Synthetic aqueous solutions with ammonium concentration of 5 to 25 ppm and a sulfuric acid as stripping solution (pH=2) were feeded to the LLMC (Liqui-cel X30) in countercurrent and open loop configuration with flow rates between 0.16 and 1.3 L/min and the pH of the feeding solution was set between 8 and 11. The ammonia concentration of the permeate was determined during the experiments with a selective ammonia electrode (HACH 51927). The ammonium removal efficiencies were calculated from the experimental data and the results were used to validate a 2D numerical model solved by COMSOL Multiphysics, which was developed considering advection-diffusion equation inside a single fibber of the lumen with laminar flow conditions and liquid gas equilibrium in the membrane-solution interface. According to both, experimental data and numerical predictions, the hollow fiber membrane contactor technology is a suitable alternative to remove ammonium from water and to feed the membrane distillation unit in order to fullfil water quality requirements for electrolysis-based hydrogen production. There was not found any clear dependance in the initial amonium concentration for the range evaluated. As can be seen in Figure 2, the amonium removal was clearly affected by the solution pH. It can explained with the pH dependance of the equilibrium between the ammonia gas and ammonium ions, making it the driving force responsible for the separation process inside the membrane. The other important parameter to be taken into account is the flow rate which affects the residence time of the solution inside the LLMC (see Figure 3).

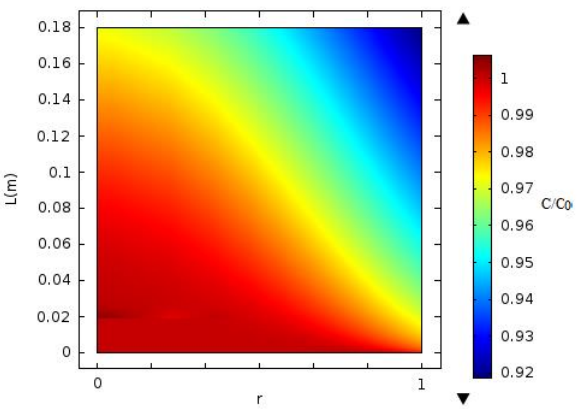

Figure 1. Concentration field in the LLMC inside a single fiber of the lumen side, were L and r represent coordinates with the radial one normalized with the inner radius of the fiber.

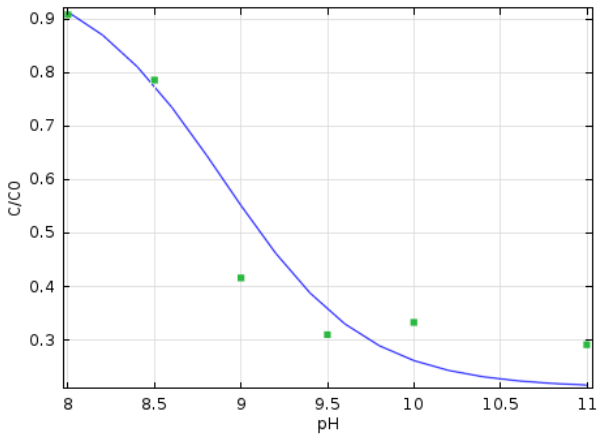

Figure 2. Numerical simulation (blue line) and experimental concentration (green dots) at the exit of the LLMC for several pH values with constant flow rate.

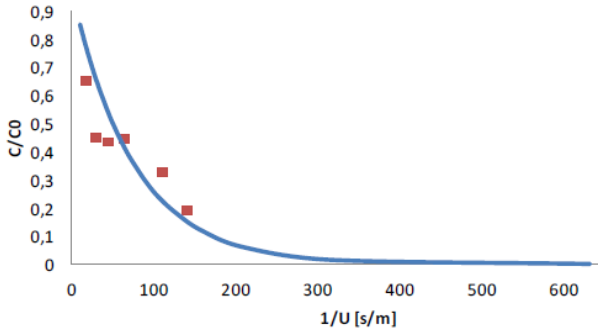

Figure 3. Numerical simulation (blue line) and experimental concentration (red dots) at the exit of the LLMC for several flow rate values with constant pH.

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Acknowledgements

This study has been supported by the ZERODISCHARGE project (CPQ2011-26799) financed by “Ministerio de Economía y Competitividad” and the Catalan government (project ref. 2009SGR905). The work of Edxon Licon was supported by the National Council of Science and Technology of Mexico (CONACYT) within the scope of fellowship reg: 213775. The authors also thank to A. Gali, E. Larrotcha and E. Marzo, project leaders of the Greenlysis project from CETaqua, for their support and help on the study.

Membrane reactor for transesterification of triglycerides: a simplified analysis of the coupled reactive separation process.

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In the transesterification reaction triglycerides are converted in glycerol and in a mixture of fatty acid alkyl esters (FAAE). These two products can be applied as raw materials for further synthesis or directly used as high value-added useful chemicals [1]. Actually, the main use of this reaction is to produce biodiesel, employing conventional reactors, such stirred tank reactor, with methanol and refined vegetable oil as reagents and strong soluble basic as homogenous catalyst. However, there are several drawbacks in this process: a) requires the use of highly refined oils, b) there are mass transfer and immiscibility limitations, c) Incomplete conversion, and d) wastewater generation (at least 3.0 L / L of biodiesel).

Process intensification technologies are been developed in order to overcome the problems, using either novel reactors or coupled reaction/separation processes [2,3]. The use of membranes integrated to reactors is one of the most promising approaches, allowing reaction and separation simultaneously [4].

This work evaluated membrane contactor applied to byproducts extraction from transesterification medium. An anionic resin (Amberlyst 26 OH) was applied as catalyst of the transesterification reaction. The membrane reactor has of two compartments of 0.4 L separated by a microporous membrane. The reaction medium included the heterogeneous catalyst, triglyceride, ethanol and the reactions products, while water was use as extraction phase. Both sides of the membrane reactor were kept under mechanical stirring. The permeate flux of glycerol and ethanol were determined periodically. The reaction conversion was evaluated by the free and total glycerol concentrations.

The overall and local mass transfer coefficients for glycerol extraction were determined using different membranes, which allows identifying the rate-controlling step. A simplified mass transfer model was developed and the simulated results showed the possibility to reduce 98.4% of glycerol content in reaction medium using 0,45 μm microporous cellulose acetate membrane. Removal of glycerol also shifts the reaction equilibrium increasing the triglyceride conversion by 18%. This results demonstrates the potencial of coupling transesterification and membrane contactor to simplifying and reducing the purification steps of the process. A better process performance was related to high conversion obtained by shifting the reaction equilibrium to the product side.

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TRANSESTERIFICATION WITH HETEROGENEOUS CATALYST IN MEMBRANE REACTORS

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Homogeneous-based catalyzed transesterification is the reaction commonly used for biodiesel production from vegetable oils/fats [1]. In this process in order to separate glycerol from biodiesel, sedimentation is typically used and its supernatant is washed to remove rests of glycerol and catalyst [2]. Although homogeneous processes for biodiesel production are fast and display high conversion, they are still not very cost-competitive with petroleum-based processes [4,5] as the catalyst cannot be reused and must be neutralized after the reaction. Therefore, an important amount of water is needed, and consequently, undesired reactions like saponification are present [3]. An alternative is the use of heterogeneous catalysts, which can also be immobilized on/in membranes. It will prevent water consumption and soap formation and gives process intensification opportunities (coupling separation and reaction) with increasing reaction performance.

In this work, three aspects for transesterification of sunflower oil with methanol were studied: reactions in batch using inorganic catalysts, catalyst immobilization on polymeric membranes and membrane separation tests in combination with reaction. Polymeric membranes (relatively cheap in respect to inorganic ones) were used since the maximum operation was only up to 60ºC.

Two types of catalysts were studied: Strontium Oxide (a strong base) and Amberlyst 15 (a strong acid). The strontium oxide was by far the preferred catalyst. The optimal transesterification condition was a 12:1 molar ratio of methanol to oil with the addition of 3% SrO catalyst. Complete conversion was observed within 3 hours. In filtration experiments, where unreacted triglycerides were rejected, the effect of membrane pore size was investigated. Preliminary experiments were performed with oil, methanol, glycerol and biodiesel for separated and later in combination with the transesterfication a membrane with filtration with opening up to the 0.2 microns membrane gave the best results.

In summary, sunflower oil biodiesel (FAME) was produced combining transesterification and separation processes in a polymeric membrane reactor using heterogeneous catalysts.

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Acknowledgements

Project ENE2011-22761 (MINECO). European Regional Development Funds (ERDF, FEDER Programa Competitividad de Catalunya 2007-2013).

Evaluation of the Production of Biodiesel using a Liquid-Liquid Film Reactor packed with Hollow Fiber Membranes

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Intensified processes for biodiesel production have been studied using different technologies. Among the technologies assessed, polymeric and ceramic membranes have been widely investigated. Membranes have been evaluated for separation and purification of the product, mainly to remove free and bonded glycerol, as well as media for simultaneous reaction and separation and support for heterogeneous catalysts. Carbon and ceramic membranes are the most studied, regarding some limitations exhibited by polymer membranes, most of them related to chemical and mechanical resistant.

This study presents some results of the experimental evaluation of a continuous process for biodiesel production in a falling film reactor (FFR) using a semi-structured packing which includes hollow fiber membranes. In a first step, avalilable commercial membranes were tested for chemical resistance to NaOH and Methanol. Membranes with the best performance were made from polyethersulfone (PES). They were chosem for the tests ina FFR.

In this reactor methanolysis and glycerol separation occur simultaneously, shifting the reaction equilibrium to the product side, increasing conversion of oil and yield to methyl esters (FAME) compared to reactor packed without membranes. A bench-scale (5 kg/h production capacity) FFR was designed, constructed and tested. Permeate flux of each component individually and in the reactant mixture were determined inside the FFR using the semi-structured packing and the usual reaction conditions (Fig. 1). Results showed that the semi-structured packing including PES is suitable to perform the simultaneous reaction and separation, with good selectivity to glycerol permeation. The evaluation of the reaction in the FFR using the semi-structured packing including PES hollow fiber membranes showed an increment on biodiesel yield in comparison to the FFR without membranes, although molar ratio methanol to oil increases in order to compensate the methanol that permeates through the membrane (fig 2-3).

Conclusions:

It is possible to transform *Jatropha Curcas* oil in biodiesel by methanolysis in a LLFR packed with hollow fiber membranes, increasing the conversion and yield in comparison to a LLFR. PES membranes show good chemical and mechanical resistance to NaOH and methanol at operation conditions in a LLFR. Methanol to oil molar ratio, length, area and position of the membranes into the reactor have to be evaluated in order to optimize the process.

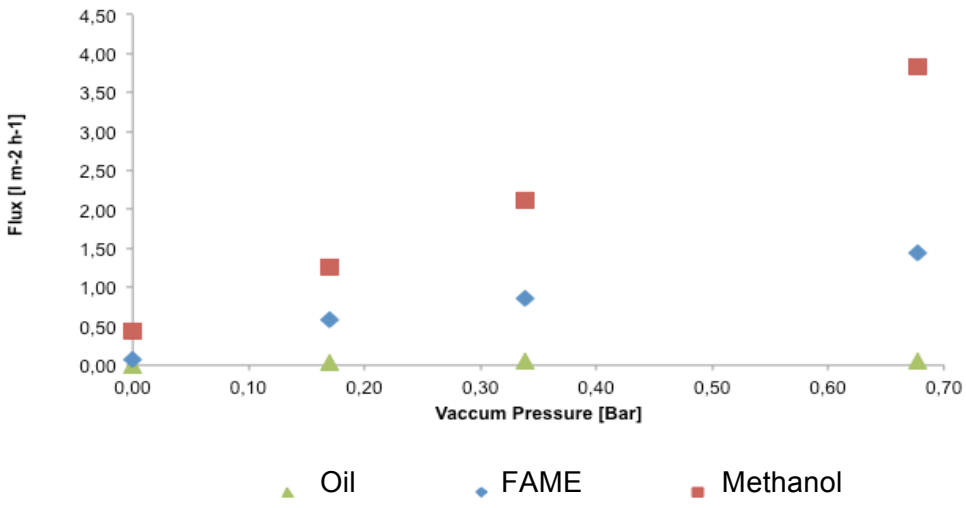

Figure 1. Flux v.s Pressure for PES hollow fiber membranes

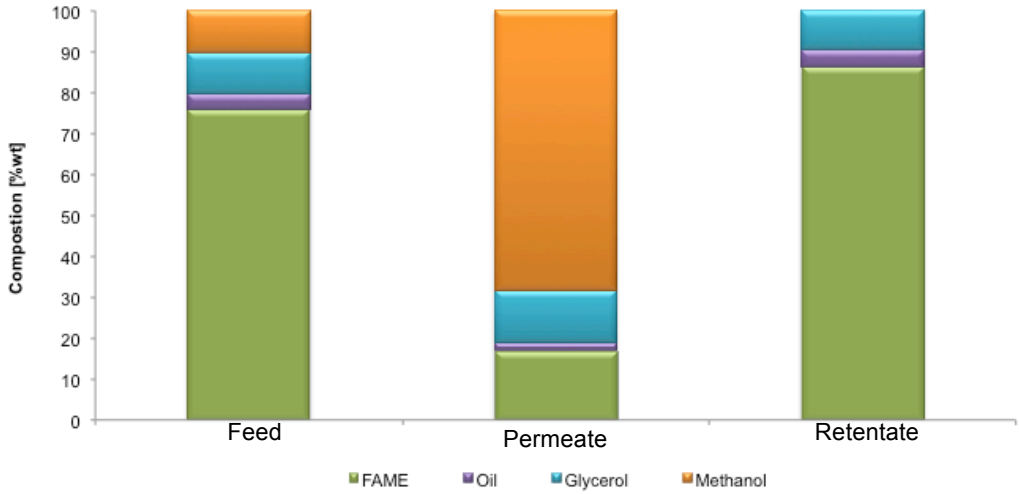

Figure 2. Quaternary Mixture Mass Composition. 15% wt Permeate – 85% Retentate. Vacuum Pressure 0,7 bar; Temperature 55°C

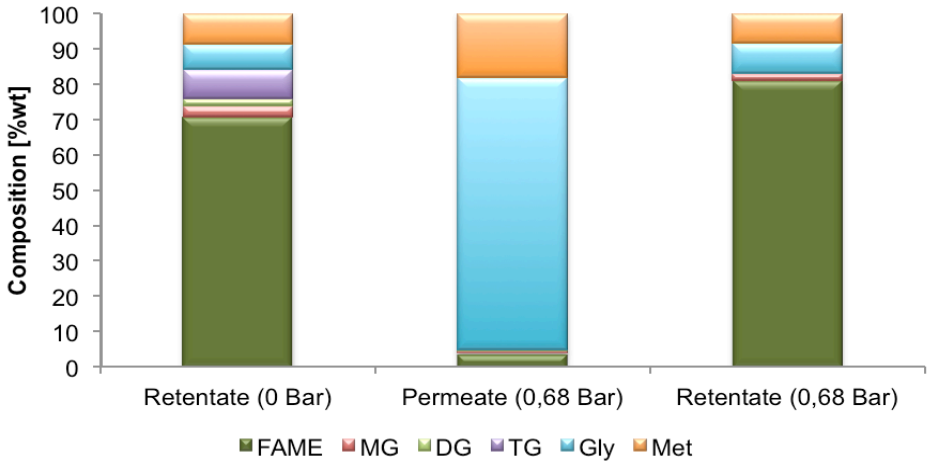

Figure 3. Mass Composition LLFR – PES membranes. Oil Flow 9.0 g/min; Vacuum Pressure 0,7 bar; Temperature 55°C; Molar rate Methanol: Oil) 6:1; Catalyst 0,75% wt (Oil). MG: Monoglycerides, DG: Diglycerides, TG: Triglycerides, Met: Methanol.

Membrane Contactors and Multifunctional Reactors

- **Poster session 2**

CATALYTIC MEMBRANE REACTORS FOR NITRATE REMOVAL USING LOW COST CERAMIC SUPPORTS

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Polution of surface and ground water by nitrates, caused by agriculture and farming, constitutes a health problem which is not well solved with the existing technologies. An alternative technology, still to be developed, is based in the use of a catalytic process, nitrate hidrogenation, using a suitable catalyst. According to the following reaction, only gaseous nitrogen is produced:

$$NO_3^- + 2{,}5\ H_2 \rightarrow \tfrac{1}{2}\ N_2 + 2\ H_2O + OH^-$$

Compared with the reverse osmosis technology, this process would have the advantage of avoiding the production of a retentate with a high nitrate concentration.
A large amount of literature is available on the development of suitable catalysts for nitrate hidrogenation, being those based on Pd/Cu or Pd/Sn over a variety of supports the most widely employed catalyst. The procedure was patented by Sell et al. [1] and the developments in the last decades were reviewed by Barrabés and Sa [2]. Some previous research has shown the feasibility of using a membrane, with the catalyst deposited on the pore surface, in flow-through configuration, i.e. flowing all the feed through the membrane, where the reaction is produced by effect of the catalyst.
This project aims to the development of a catalytic membrane using a low cost ceramic membrane as support. As a main difference, instead of the ceramic membranes employed in previous research [3,4], which are based on high cost materials (such as high puritiy alumina), we have developed low cost ceramic membranes with traditonal ceramic raw materials and natural organic compounds as pore generating additive. The obtained membranes have been employed as support for the deposition of Pd, Cu or Pd-Cu mixtures, by the method of incipient wetness. Samples were calcined and reduced with CO.
A laboratory scale plant has been employed for testing these membranes. As is shown in figure 1, the water to be treated was saturated with a mixture containing hydrogen and CO_2 (molar ratio 2:1) in an absorption tower with Raschig rings, then flows through the membrane. Treated water was recirculated to the feed storage deposit, which simulates the operation in a discontinuos reactor. Samples are taken at the membrane exit and analyzed by UV-vis absorption with standard reactive kits.
A comparison between five membranes, with 1 wt% Pd, 1 wt%Cu or Pd-Cu (1+1 wt%), is shown in figure 2. This figure shows the change of conversion with dimensionless time ($Q.t/V_o$), which informs on how many times the solution has permeated through the membrane. It is clear that the combination of Pd and Cu provides a sinergic effect, which increases greatly the catalyst activity. Pd or Cu alone have quite low activity. There is not a significant difference if Pd and Cu impregnation was done with or without intermediate reduction.
The effect of flowrate has also been tested. As it may be expected, an increase in the liquid flow rate decreases the nitrate conversion per pass. The relationship between reaction rate and nitrate conversion has been studied. Although this relationship should be independent of liquid flowrate, an effect of residence time has been observed.

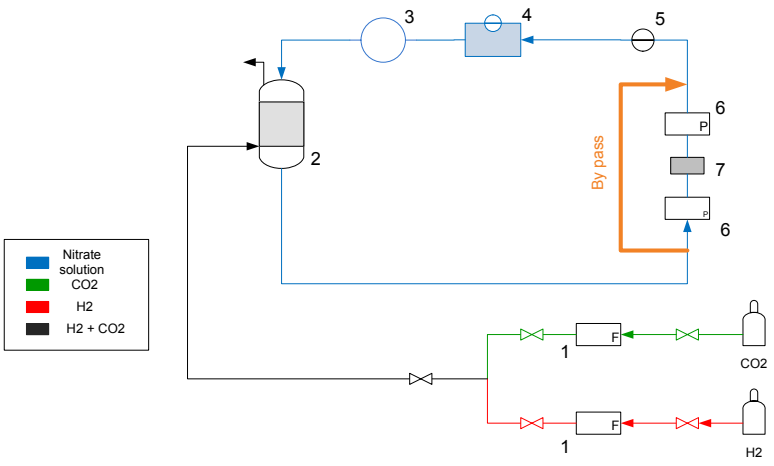

Figure 1. 1: Gas flowmeter; 2: Absorber; 3: Pump; 4: feed storage; 5: Septum; 6: Pressure meter; 7: Membrane module

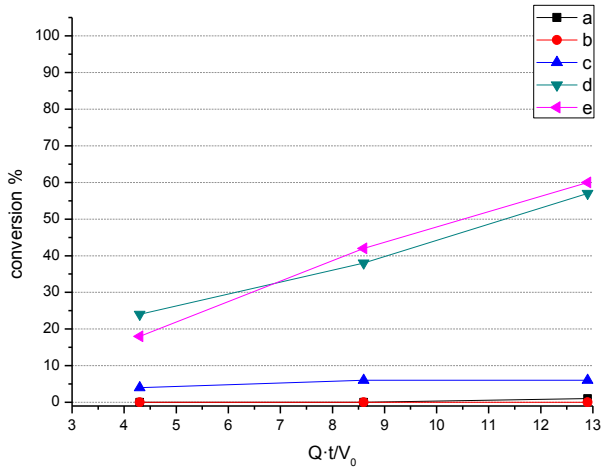

Figure 2. (a) Pd; (b) Cu 4 impregnations 5 $g{\cdot}L^{-1}$ each; (c) Cu 1 impregnation 20 $g{\cdot}L^{-1}$; (d) CuPd impregnation, Cu and Pd separately, without intermediate reduction; (e) CuPd impregnation, Cu and Pd separately, with intermediate reduction. Initial nitrate concentration: 100 ppm.

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Pd-Ag MEMBRANES COUPLED TO A TWO-ZONE FLUIDIZED BED REACTOR FOR PROPANE DEHYDROGENATION: EFFECT OF C_3H_8/C_3H_6 MIXTURES ON H_2 PERMEATION

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Membrane reactors (MR) allow simultaneous reaction and separation in a single unit. The potential advantages of MR are the reduction of downstream separation costs, the reduction of capital costs or the improvement of yields and selectivity in reactions limited by the equilibrium [1]. MR configurations that use inorganic membranes, often based on palladium or alloyed Pd thin layers for hydrogen production or extraction, are among the most extensively investigated ones.

The production of light olefins by alkane dehydrogenation is limited by the thermodynamic equilibrium. The use of MR would enhance alkane conversion by a selective removal of hydrogen from the reaction media. Hydrogen removal results in an equilibrium shift towards the production of olefins. However, hydrogen permeance through Pd-based membranes may be affected by the presence of light hydrocarbon species.

In a recent work, Medrano et al. [2] used a novel membrane reactor concept to produce propylene by catalytic propane dehydrogenation (PDH) in the presence of Pt-Sn based catalyst. Main drawbacks of the considered reaction were its high endothermicity, equilibrium conversion, side reactions and tendency to coke deposition over the catalyst surface. The combined effect of a low acidity support with a highly selective catalyst, together with the use of a novel auto-regenerative reactor concept coupled to a Pd-Ag membrane, leaded to a successful performance of PDH with increased conversion rate and steady-state operation at usual reaction temperatures.

The novel auto-regenerative reactor concept, i.e. Two-Zone Fluidized Bed Reactor (TZFBR), consisted of a catalytic gas-solid fluidized bed with two gas injection points, as described elsewhere [3]. Propane was fed through an immersed gas distributor, whereas an oxidizer (diluted O_2) was fed through the distributor located at the bottom of the bed. The catalytic PDH took place within the upper region of the bed leading to coke deposition as byproduct over the catalyst surface. Oxygen was used to burn coke deposits and to regenerate the catalyst within the lower bed zone. The characteristic axial mixing of solid that usually takes place in a fluidized bed allowed the steady-state operation without net catalyst deactivation. Additionally, a Pd-Ag membrane immersed in the upper bed zone improved propane conversion by selectively removing H_2 from the reactive atmosphere, thus, shifting reaction equilibrium towards propylene production.

Although experimental results were satisfactory, the increase of the yield to propylene due to the equilibrium shift was not in agreement with the permeation capacity of the membrane at similar H_2 pressure drop conditions. Membrane characterization tests showed higher hydrogen permeation at different H_2/Ar ratios than at reactive conditions, i.e. H_2 in a mixture of alkanes (C_1 – C_3) and light olefins, with the same H_2 molar fraction in the feed gas. These results motivated the present study.

This work evaluates the effect of the contents of propane/propylene mixtures (main reaction compounds) on the hydrogen permeation through Pd-based membranes for propane dehydrogenation. The commercial membranes used in this work were dense Pd-Ag membranes supported on porous stainless steel, provided by REB Research®. The two tubular membranes used were 178 mm long with an external diameter of 3.17 mm and a thickness of Pd-Ag layer of 76 µm. The effective permeation area of the two membranes used in our set-up was 30.4 cm^2. The bottom-end of the membrane was sealed whereas the top-end consisted of a standard 3/16" stainless steel tube for connection to a vacuum pump. A scheme of the experimental set-up is shown in Figure 1.

The experimental characterization of the dense Pd membranes was carried out performing several permeation tests with different $C_3H_8/C_3H_6/H_2/Ar$ volumetric compositions at typical PDH operational temperatures, ranging from 525ºC to 575ºC. Results showed that the transient hydrogen permeation decreases in the presence of C_3 species due to coke deposition over the Pd-Ag layer. It was found that membrane coking was more sensitive to propylene than to propane.

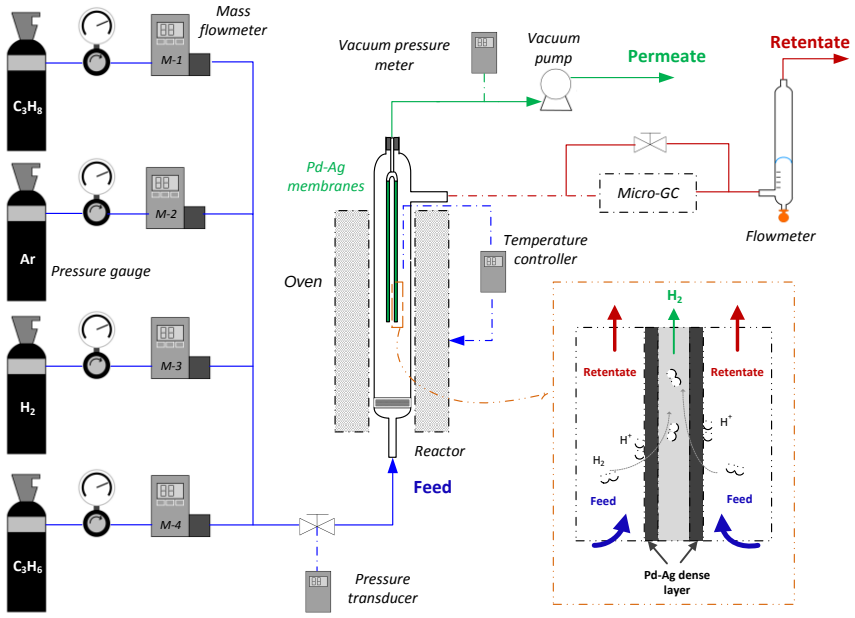

Figure 1. Set-up for measuring H_2 permeation in a simulated reaction environment.

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Fuel Cells / Batteries Electromembrane Processes

- **Oral session 12**

PVC-IONIC LIQUID POLYMER INCLUSION MEMBRANES FOR THEIR APPLICATION IN MICROBIAL FUEL CELLS

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The called Microbial Fuel Cells (MFCs) is a green technology which produces electricity from organic matter. This system uses microorganisms to transform the chemical energy into electrical power. Using wastewater as source of organic matter we can generate electricity while treating water in order to reduce its Chemical Oxygen Demand (COD) [1]. To make this technology feasible, new materials must be found to replace the conventional ones.

One of the key factors of these devices is the separator. The aim of this work is to develop and characterize new PVC-ionic liquid polymer inclusion membranes and to studying the suitability of their application as proton exchange membranes in Microbial Fuel Cells in replacement of the commercial separators (Nafion®, Ultrex®) in order to reduce their cost and improve their efficiency.

Ionic liquids are organic salts that remain liquid at room temperature [2]. Normally, they are formed by an organic cation and a polyatomic inorganic anion or an organic anion. In the present work, a mixture of polyvinyl chloride (PVC) and ionic liquid was used to prepare the proton exchange membranes. The ionic liquids selected for this study were: (i) 1-methyl-3-octylammonium chloride [MTOA][Cl], (ii)1-methyl-3-octylimidazolium hexafluorophospate [OMIM][PF_6], (iii) triisobutyl(methyl)phosphonium tosylate [$P_{14,14,14,1}$][TOS], (iv)1-ethylpyridinium bis[(trifluoromethyl)sulfonyl]imide [EPy][NTf_2], and (v) tributylmethylphosphonium methylsulphate [$P_{4,4,4,1}$][$MeSO_4$]. All the membranes were prepared at 70% w/w of ionic liquid and 30% w/w of PVC.

In a first step, all the membranes were used as separators in MFCs fed with wastewater to evaluate their performance in terms of power and COD removal. The set-up selected to carry out this study consisted of a single-chamber air-cathode MFC [3] which main components were the developed membrane, graphite granules as anode and a Pt/carbon cloth as cathode [4].

To carry out the electrochemical characterization of the membranes two different techniques were used: Frequency Response Analysis (FRA) and Chronoamperometry (AC) both in a two-electrode configuration with an HCl solution (1M) as a proton source. The former technique allows the measurement of the internal resistance (R), with which the proton conductivity is calculated according to the following expression:

$$\sigma = \frac{L}{R \cdot A}$$

where σ, L, A and R are the ionic conductivity ($S.cm^{-1}$), the thickness (cm), the cross-sectional area (cm^2) and the resistance (Ω) of the membranes, respectively.

With the AC technique it is possible to determinate the total ionic transport number (t_{ionic}) with the polarization curves (I *vs* t) and the Wagner equation:

$$t_{ionic} = \frac{I_0 - I_e}{I_0}$$

where t_{ionic}, I_0 and I_e are the total ionic transport number, the current intensity at t=0 hour and the current intensity at the end of the polarization measurement, respectively. The results show that the voltage values reached with the [MTOA][Cl] membrane are similar to those obtained with Nafion®, followed by [omim][PF_6] and [$P_{14,14,14,1}$][TOS] membranes.

The FRA for the membranes analyzed shows that the proton conductivity of [MTOA][Cl], [$P_{14,14,14,1}$][TOS] and [EPy][NTf_2] membranes are high. The AC proves that all the membranes have a high ratio ionic/total conductivity, being this parameter almost 100% for the polymer inclusion membrane based on [MTOA][Cl].

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This work has been supported by Ministerio de Ciencia e Innovación de España (MICINN), ref. CICYT ENE2011-25188, and Fundación Séneca ref. 15260/PI/10. V.M. Ortiz-Martínez and M.J. Salar-García and have fellowships from the Spanish Ministry of Economy and Competitiveness.

HIGH CONDUCTIVITY ELECTROLYTES BASED ON POLYMERIZED IONIC LIQUID AND IONIC LIQUID MIXTURES

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Proton Exchange Membrane Fuel Cells (PEMFCs) are considered one of the most promising power technologies due to their high energetic efficiency and low environmental impact. However, there are still some technical and economic obstacles that hinder their commercialization. One of the issues that must be addressed is the development of high proton conducting membranes under anhydrous conditions which allow working at temperatures above 80 ºC and reduce the system complexity. Ionic liquids have been attracting increasing interest in this field because of their unique properties such as high conductivity in anhydrous conditions, high thermal and chemical stability, negligible vapor pressure and a large electrochemical window [1]. Nevertheless, most of these electrochemical devices require solid electrolytes. The polymerization of ionic liquid monomers is an innovative technique toward achieving this quality, but this strategy usually results in a decrease in conductivity because the mobility of the ions is reduced and the glass transition temperature increases [2]. In order to improve the ionic conductivity it is important to maintain the fluidity at the electrolyte which can be reached by the incorporation of non-polymerizable ionic liquid in the structure [3].

In this work, electrolytes consisting in poly(ionic liquid)/ionic liquid mixtures (figure 1) were developed for H_2/O_2 fuel cells without external humidification. For this purpose, the ionic liquid monomer 1-(4-sulphobutyl)-3-vinylimidazolium trifluoromethanesulphonate [HSO_3-BVIM][OTF] was mix the ionic liquid 1-(4-sulphobutyl)-3-methylimidazolium trifluoromethanesulphonate [HSO_3-BMIM][OTF] and photopolymerized. In order to improve the mechanical stability, glycerol dimethacrylate was added as cross-linker agent. The obtained polymers are flexible and transparent and provide high conductivities even under anhydrous conditions.

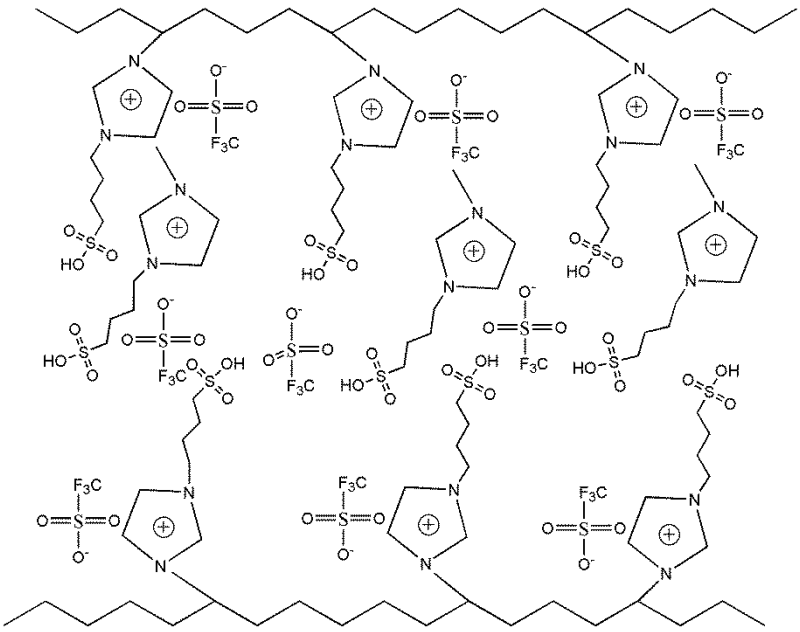

Figure 1. Poly ([HSO_3-BVIM][OTF])/ [HSO_3-BMIM][OTF] mixtures

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Acknowledgements

This research was supported by the Ministry of Education and Science under the project CTQ2012-31639 (MINECO, SPAIN-FEDER 2001-2013). Mariana Díaz also thanks MINECO for the FPU fellowship (AP2012-3721).

Electrochemical Reactors based on Solid CsH_2PO_4 Electrolyte Membranes

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CsH_2PO_4 has emerged as the new generation of fuel cells electrolyte membranes able to work at moderate temperature (200 - 300 ºC)[1]. Crystalline CsH_2PO_4 transforms to a cubic phase showing superprotonic conductivity when the temperature is increased above 230 ºC [2]. The low operation temperature of this material allows the possibility to use cheap materials for the stack construction, reducing the cost of the device. This temperature ranges meets the requirement for a series of very appealing electrochemical reactions, making possible the use of electrocatalyst with negligible or very low loading of precious metals. Moreover, the synthesis method avoids thermal treatments and long periods of calcination for the single phase manufacture, reducing the production costs. The fuel cell has to be manufactured using electrodes compatibles with the electrolyte and actives for the oxidation and recombination of hydrogen in the anode and cathode respectively. the same way, electrolysis can be performed using CsH_2PO_4 and doped cesium phosphates as electrolytes. Co-electrolysis can also be performed for the production of syngas.

In the present work different symmetrical cells (using the same anode and cathode) have been measured in order to check the influence of pH_2O and operation temperature. When the temperature is higher than 240 ºC, there is not a significant change in the electrolyte conductivity (0.015 $S\cdot cm^2$ at 240 ºC and 0.037 $S\cdot cm^2$ at 250 ºC). More important is the water partial pressure influence on the electrolyte conductivity changing from $3.96\cdot10^{-4}$ $S\cdot cm^2$ at 0.025 atm to 0.015 $S\cdot cm^2$ at 0.3 atm of water (Figure 1).

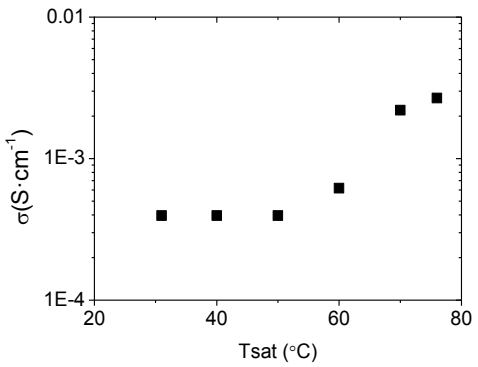

Figure 1: CsH_2PO_4 electrolyte conductivity as function of the water saturator temperature.

Carbon Gas Diffusion Layer (GDL) has been employed as electrode and different catalysts have been incorporated by impregnation in order to improve the hydrogen reaction. Some of the materials infiltrated in the Carbon GDL, are Cu, Zn and Pt. The infiltration of the different catalyst has ben checked by means of FESEM analysis, showing nanoparticles around 40 nm. The electrolyte conductivity has been recorded by means of Electrochemical Impedance Spectroscopy (EIS) obtaining values of 0.04 $S\cdot cm^2$ in fuel cell mode. The influence of hydrogen partial pressure and oxygen on the fuel cell power has been tested as well.

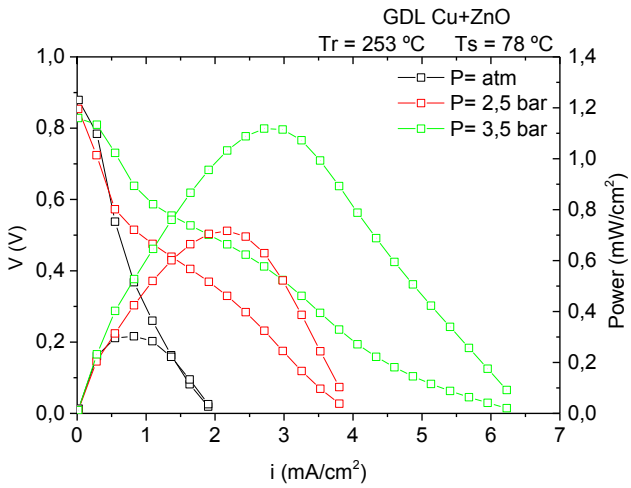

Figure 2: i-V and P-i curves for the CsH_2PO_4 fuel cell with GDL infiltrated by Cu and ZnO.

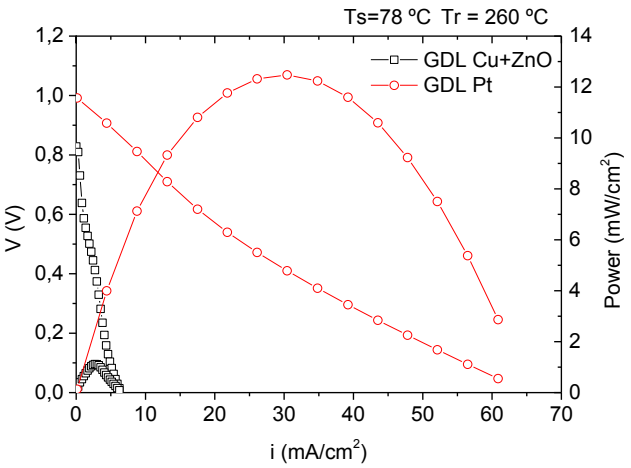

Figure 3: Comparative of i-V and P-i curves for the CsH_2PO_4 fuel cell with GDL infiltrated by Cu and ZnO and Pt.

Finally, the influence of the total pressure in the system was studied. The fuel cell Power density was increased six times changing the pressure from atmospheric (1 bar) to 4.5 bar absolut pressure (Figure 2). The maximun Power density obtained for the fuel cell measured with Cu and Zn was 1.2 mW/cm^2 whereas the fuel cell obtained with Pt and tested at the same conditions reached values of 12 mW/cm^2 (Figure 3).

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Acknowledgements

Funding from Spanish Government (MINECO) ENE2011-24761 grant is kindly acknowledged.

REVERSE ELECTRODIALYSIS: SUSTAINABLE ENERGY PRODUCER OR CONSUMER? HOW DO WE KNOW IT?

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Power generation from salinity gradients can be achieved by controlled mixing of concentrated and dilute electrolyte solutions in a reverse electrodialysis (RED) operation mode [1]. The main limitation for improving the process efficiency is usually associated with the electrical resistance offered by the dilute saline stream compartment, so optimization of the fluid dynamics conditions and ionic mass transfer this compartment is required [2]. However, intensifying the hydrodynamic conditions leads also to higher pressure drop and more energy demand for pumping, which ultimately can lead to a negative net power balance of the process. Therefore, the in RED stacks with different number of cell pairs in order to identify the optimal working regime allowing for obtaining a maximal possible net power density.

Methods

An electrodialysis EDR-Z-Mini unit (MEGA a.s.), constituted by up to 10 cell pairs (10 AMHPES and 11 CMH-PES membranes of the Ralex type, separated by dedicated 0.8 mm thick spacers) stacked between two titan electrodes with a platinum layer, was used. Model solutions of NaCl, as well sea water and river water, were used as working solutions. Power generation was recorded in an open circuit voltage (OCV) mode using a homogeneous $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox couple as the electrodes rinse solution. An AUTOLAB potentiostat/galvanostat, coupled with a 10 A current booster, was applied to study the transport phenomena in a two-cell pairs module through chronopotentiometric analyses [3].

Two pressure transducers (Druck, PDCR 910) were mounted at the stack inlet and outlet. The pressure was registered automatically every second during two minutes in each case. In such a way, the experimental pressure drops at different linear flow velocities were obtained. These data were compared with simulations of a recently developed mathematical model, considering all possible partial pressure drops inside the stack [4].

Results and Discussion

The maximum power density, with the RED stack with 0.8 mm spacers, obtained for model saline solutions of 30 g/L vs. 1 g/L of NaCl, was equal to 0.51 W/m^2. A similar power density (0.45 W/m^2) was obtained when Atlantic Ocean water (taken from the Lisbon coast area) and Tagus river water, were used as the concentrated and dilute saline stream, respectively. The generated power was strongly dependent of the flow rates of the two streams and this effect was more pronounced for the side of the low salinity stream.

Under-limiting current chronopotentiometric measurements were performed to explain quantitatively the reasons for such behavior. The data obtained for total and non-ohmic resistances in the RED stack with 0.8 mm spacers operated at different linear flow velocities without the mesh (“open channel”), and with the mesh (“with spacer”) are presented in Figure 1. The presence of a mesh increased the stack total resistance (Fig. 1 a), due to its “shadow” effect on the membranes used. It is important to note that although the mesh did reduce the non-ohmic resistance (Fig. 1 b), this effect was relatively modest.

It was also found that with an increasing linear flow velocity, the power needed for pumping increases faster than the gross power density, which eventually results in negative net power densities (Figure 2) The modeling results showed that for the same linear flow velocity in the compartments and, therefore, for the same fluid dynamic conditions for the ionic transfer through the membranes, the net stack power decreases when the cell pair number increases (from 50 to 200 cell pairs as illustrated in Figure 2).

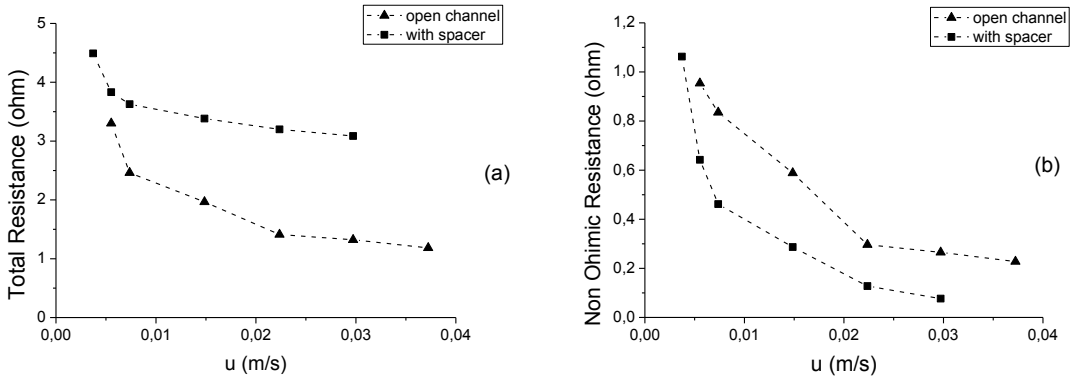

Figure 1. Resistance results obtained by chronopotentiometric analysis in the underlimiting current-range, over the central cation-exchange membrane in a two-cell pairs RED stack configuration with an 1 g/L NaCl solution. (a) Total resistance; (b) Non-ohmic resistance.

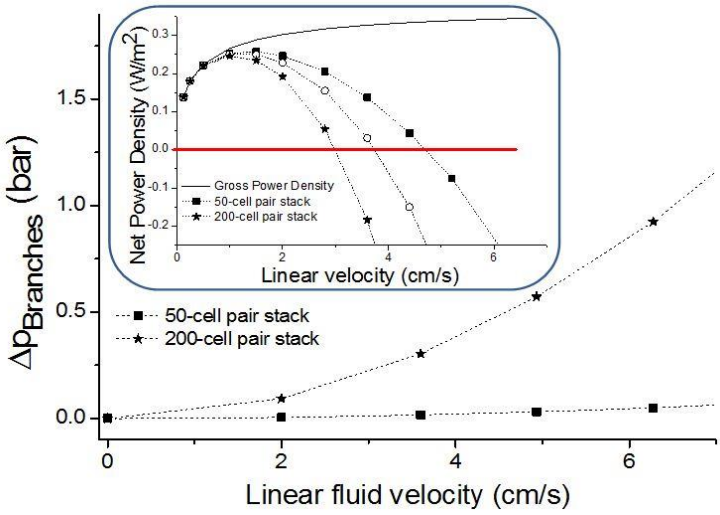

Figure 2. Model values for net power density for a) 50- and b) 200-cell pair stacks (with 3 inlets and 3 outlets; and with branch ratio of 0.122) in function of the average linear flow velocity. The value of the gross power density for an inter-membrane distance of 0.8 mm is presented.

Conclusions

- The main resistance, in the investigated RED stacks was ohmic and located in the diluted saline stream compartment.
- The presence of spacers reduced the diffusion boundary layer thickness, but also leads to a membrane "shadow" effect, which was dominant in the case studied.
- For simulated large-scale stacks, the partial pressure drop in the branches becomes dominant. Therefore, at identical hydrodynamic conditions, the net power density decreases when the number of cell pairs increases.

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Acknowledgements

Sylwin Pawlowski acknowledges *FCT-MEC*, Lisbon, Portugal for his PhD grant SFRH/BD/68649/2010.

ACID AND BASE PRODUCTION IN THE DESALINATION PROCESS BY BIPOLAR MEMBRANE ELECTRODIALYSIS: PRELIMINARY RESULTS

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The aim of this work is to study the valorization of reverse osmosis desalination brines as acid and base by using bipolar membrane electrodialysis process. An experimental lab-scale pilot plant was used where the membranes stack used was PCCell ED 64-004 (PCCell GmbH, Germany). The dimension of the cell is 0.11x0.11m. It is a 4 chamber system with an active membrane area of 0.0064 m^2 per membrane. The stack configuration is composed of three cell triplets; each cell triplet has one cationic exchange membrane (PC-SK), one anionic exchange membrane (PC Acid 60) and one bipolar membrane. Each cell triplet has three compartments: for diluted, acid, base. Moreover, there are two electrodes rinse compartments that form a single circuit located at the cell ends. Thus, the pilot plant was working by means of 4 circuits: the electrode rinse, acid, basic and diluted. Each of them has a pump, pressure, temperature, flow and conductivity sensors. Furthermore, pH of the dilution solution during the experiment was monitored by a pHmeter in the diluted circuit. A power supply device was used to establish an electrical current density in the stack.
Preliminary experiments with NaCl as feed solution were carried out in recirculation configuration in order to test the stack and to find the optimal operation conditions. Some experiments were carried out at different conditions of current density and voltage (9V, 0.4kA/m^2 and 6V, 0.1kA/m^2) to evaluate the effect of these parameters. In turn, different initial acid and base concentration (0.05M and 0.1M) were used to determine their influence on the final concentration of HCl and NaOH obtained. Finally, the NaCl initial concentration was varied from 50 to 200 g/L. Results corroborated that the electrodialysis with bipolar membrane is a suitable method for desalinating NaCl while producing NaOH and HCl [1]. Furthermore, with regard to the effect of current density and voltage, it was found that the higher they were, the higher NaOH and HCl concentration were obtained [2] (Figure 1). Moreover, initial acid and base concentrations had no a substantial effect on the overall of the performance (Figure 2). Finally, concerning the effect of feed salt solution concentration, it was found that an increase of NaCl let to an increase of acid and base concentration (Figure 3).

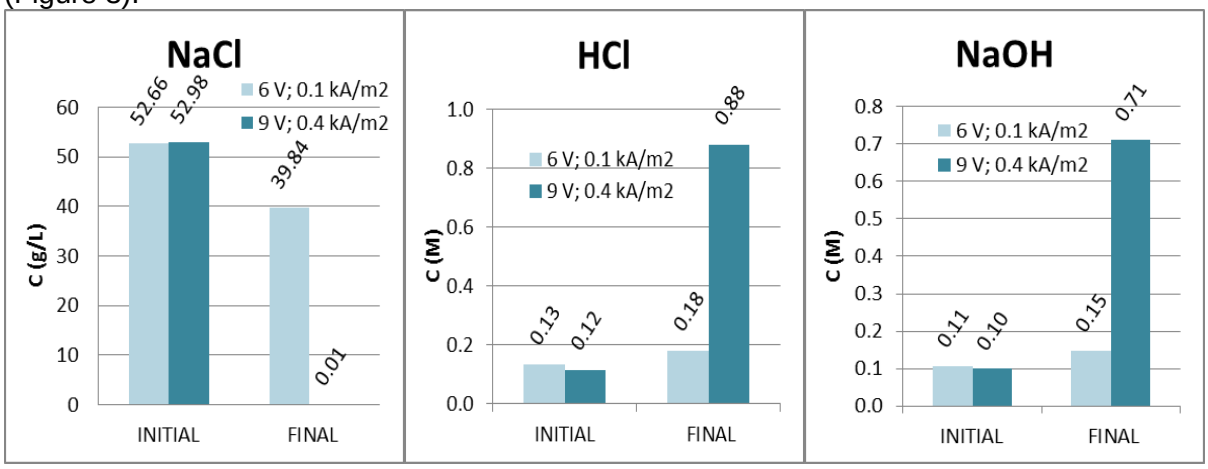

Figure 1. Salt, acid and base concentration at the initial and final time under different voltage and current densities

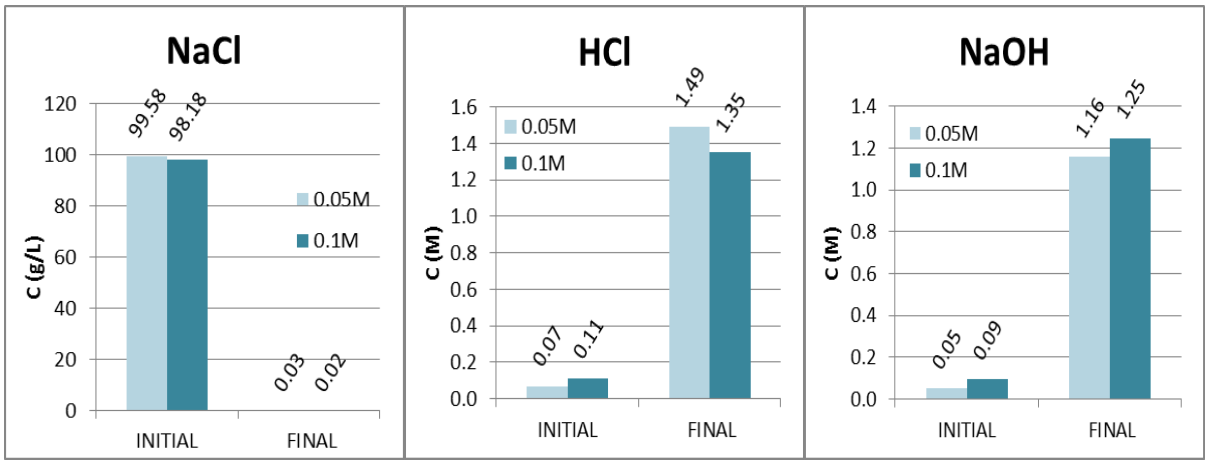

Figure 2. Salt, acid and base concentration at the initial and final time under different initial concentration of HCl and NaOH

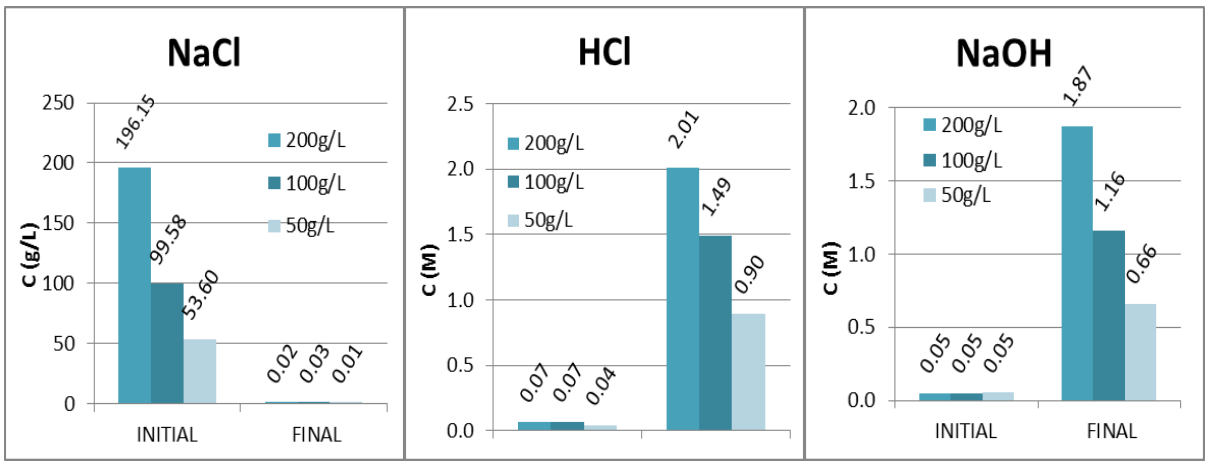

Figure 3. Salt, acid and base concentration at the initial and final time under different initial concentration of NaCl

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Acknowledgements

This research was supported by the ZERO-DISCHARGE project (CTQ2011-26799) financed by “Ministerio de Economía y Competitividad” and the Catalan Government (Project Ref. 2009SGR905), Spain. The work of Mònica Reig was supported by the Spanish Ministery within the scope of the grant BES-2012-051914

Fuel Cells / Batteries Electromembrane Processes

- **Poster session 2**

Membranas de SPEEK reforzadas con nanofibras de PVA y PVB para su uso en pilas de combustible: a) Microbianas (MFCs). b) Metanol directo (DMFC)

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Resumen

El desempeño de una pila de combustible microbiana (MFCs) está determinado principalmente por la actividad catalítica de los electrodos, la cual depende de la naturaleza del catalizador, de las propiedades mecánicas y de transporte de protones y de la baja permeabilidad al oxígeno de la membrana empleada como poli electrólito (PEM). Por otro lado en pilas de combustible de metanol directo (DMFC), la permeabilidad al combustible (metanol) y la posibilidad de trabajar a temperaturas por encima de los 100ºC, nos limita la selección de buenos materiales para que hagan de separador entre ánodo y cátodo [1]. El material estándar empleado básicamente en este tipo de pilas de combustible ha sido el Nafion® pero dicho polímero además de su elevado coste, presenta una limitación importante como es su elevada permeabilidad al oxígeno que desde el aire exterior atraviesa la membrana en las MFCs y la elevada permeabilidad al metanol en las pilas del tipo DMFC, así como la imposibilidad de utilizar las membranas Nafion por encima de los 100ºC ya que su temperatura de transición vítrea (Tg) se encuentra alrededor de los 100ºC. Un material prometedor para emplearse por encima de los 100ºC es el SPEEK (poly-ether-ether-ketone sulfonado), ya que dicho material es un buen conductor de protones y su Tg se encuentra alrededor de los 200ºC. Aunque es conocido que el principal problema que presenta este material es su solubilidad en agua y por tanto es preciso estabilizarlo para emplearlo como PEM en pilas de combustible. En este sentido, mezclas de SPEEK con PVA (polyvinyl alcohol), material hidrofilico, han sido preparadas y hemos observado que por encima del 25% wt% de PVA las membranas son completamente estables en agua hirviendo y presentan una conductividad aceptable. Por otro lado, mezclas de SPEEK con un polímero hidrofóbico tal como el PVB (polyvinyl butyral), han sido preparadas y hemos comprobado que por encima de un 30%wt de PVB las membranas también tenían un comportamiento estable en agua hirviendo. La medida de las propiedades barrera al metanol y oxígeno han sido excelentes mientras que la conductividad los protones era baja en comparación al comportamiento de las membranas de Nafion. Sin embargo, el uso de nanofibras de SPEEK-PVB obtenidas mediante electrohilatura nos ha proporcionado un incremento notable en la conductividad protónica de dichas membranas. Es por ello, por lo que en este trabajo se ha procedido a la obtención de membranas compuestas basadas, por un lado, en

nanofibras de SPEEK-PVB embebidas en una matriz de polímero de SPEEK-PVA y posteriormente se ha efectuado una caracterización completa de dichas membranas para estudiar su uso en MFCs y en DMFC[2-4]. Para ello hemos caracterizado nuestras membranas en una simple cámara microbiana de pila de combustible (SCMFCs) usando una disolución salina de sodio enriquecida con una bacteria inocula como biocatalizador. Por otro lado, hemos efectuado la caracterización en monocelda usando como combustible metanol a diferentes concentraciones (2 y 4 M) y a diferentes temperaturas (80, 100 y 120ºC). Los resultados han mostrado que los desempeños en MFCs generan una densidad de potencia alrededor de 800mW/m^3 las membranas de SPEEK-35PVA y de 725mW/m3 las membranas de SPEEK-35PVB. Mientras que en DMFC los resultados obtenidos proporcionaron una densidad de potencia de 80 mW/cm^2 y una permeabilidad al metanol de 9.5 x10^{-6} cm^2/s las membranas de SPEEK-35PVA mientras que en el caso de SPEEK-35PVB la permeabilidad fue de 2.2x10^{-7} cm^2/s. Por otro lado, una caracterización electroquímica mediante espectroscopia de impedancias (EIS) revela que las resistencias internas totales (Rint) de las membranas de SPEEK-35PVA y SPEEK-35PVB son entorno a 1465 y 1140 Ω, respectivamente[4,5]. Los resultados encontrados muestran claramente una llamada de atención debido al bajo coste de este tipo de membranas en el uso de obtención de energía mediante su uso como pilas de combustible microbianas o de metanol directo (MFCs y DMFC).

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Acknowledgements

Los autores agradecen al CINVESTAV-IPN por conceder una beca para la obtención de su tesis doctoral a uno de los autores (KSK), así como al CONACYT, con la ayuda referencia 75/2012 para financiar parte del trabajo aquí desarrollado. Por otro lado el grupo español ha sido financiado bajo el Programa de Investigación y Desarrollo de la Universidad Politécnica de Valencia y por el Ministerio de Ciencia e Innovación a través de los proyectos: 24761 y SP-ENE-20120718, respectivamente.

Incorporation of vinylimidazolium based Ionic liquid in well-defined straight porous PBI membranes: Novel polymeric ionic liquid/PBI membranes for high temperature fuel cell applications.

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This paper aims to development of Polybenzimidazole (PBI) and Ionic liquid membranes for High Temperature Proton Exchange Membranes for Fuel Cell applications (HTPEMFCs). Today acid doped PBI (PBI/H3PO4) membranes are presented as the only material that meet the US DOE targets for HTPEMFCs under no humidification [1].

An alternative to provide conductivity to these membranes is the use of protic ionic liquids which could avoid the problems related with corrosion and endurance of the phosphoric acid doped PBI [2-5].

Straight porous Polybenzimidazole (PBI) membranes with well-defined porosity and pore diameter were prepared by micro transfer moulding technique. The porosity of the prepared membranes is around 30% with 15 to 20 microns pores. In this research we introduced the Ionic liquid 1-H-3-Vinyl imidazolium bis(trifluoromethanesulfonyl) Imide in a straight porous polymeric polybenzimidazole (PBI) membrane which is acts as a support to prepare PIL (Polymeric Ionic Liquid) based membranes. PBI/PIL membranes have been synthesized with and without cross linker (Divinyl benzene) by ultra-violet radiation-induced polymerization [6]. The influence of cross linker amount on membrane properties has been evaluated. The polymerization was confirmed by ATR-FT IR spectroscopy and we study thermal properties, ionic conductivities and stability properties of prepared PBI/PIL membranes. Polymerization strongly depends on the viscosity of monomeric ionic liquid and the irradiation time.

The conductivity of membranes increases with temperature and conductivity of membrane achieved 22.79 mS/cm at 200ºC in the absence of cross-linker. The long term stability of these membranes at high temperatures shows no decline in conductivity indicating promising membranes for HTPEMFCs applications.

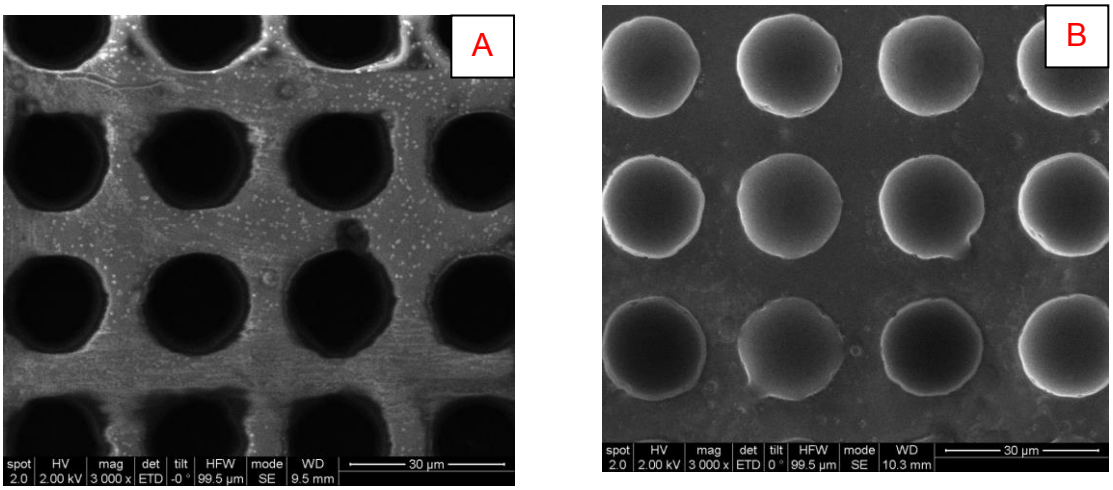

Fig: A.SEM analysis of porous PBI Membranes B. SEM analysis of porous PBI with PIL loading

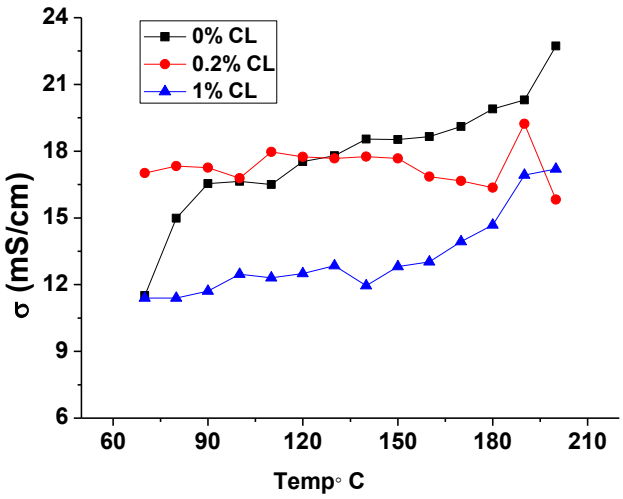

Fig: Conductivity measurement of PBI/PIL membrane with the influence of Cross linker

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Acknowledgement:

The authors express their gratitude to EUDIME (The Erasmus Mundus Doctorate in Membrane Engineering) for the economic support and Laboratory of Advanced Microscopies LMA, and Institute of Nanoscience of Aragon INA at University of Zaragoza for all the facilities.

ABOUT THE SUSTAINABILITY OF THE ELECTRODIALYSIS POWERED BY PHOTOVOLTAIC SOLAR ENERGY

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Desalination is a viable alternative capable to supply the fresh water needed in the modern world and to reduce the water stress suffered in many countries. However, the obtaining of fresh water from seawater (SW) and brackish water (BW) is energy intensive. The specific energy consumption (SEC) and the high salts concentration in the generated brines compromise the environmental sustainability of the selected process. The integration of renewable energies with desalination can palliate the consequences from the SEC, especially at isolated locations. Apart from thermal-based technologies, two main options are considered for the desalination of SW and BW: Reverse Osmosis (RO) and Electrodialysis (ED). Both the pressure gradient in RO and the electrical field in ED can be directly supplied by renewable energies such as wind power and photovoltaic solar energy. Even if RO-PV is the preferred option between current available plants (31% of the worldwide capacity from renewable powered stations [1]), ED-PV presents some advantages worthy of consideration for a larger market implementation. From a technical point of view, ED does allow a simpler operation and maintenance as well as adaptation to intermittent energy inputs when compared to RO [2,3]. Consequently, the aim of this work is to describe the current sustainability of ED-PV as an alternative technology to RO-PV for drinking water purposes, considered as reference technology. The main barriers of a larger implementation of ED-PV are identified as well.

From an environmental point of view, ED, no matter the source of the power, requires an SEC ranged between 0.6-4 $kWh \cdot m^{-3}$ which still falls in the conventional figures for RO. Therefore, any marginal improvement has a large impact because the total power of PV modules is reduced. On the other hand, from an economy perspective, in the case of ED-PV of brackish water, we developed a time trend (2005-2050) of the water cost obtained from an ED plant connected to the grid power (ED-Grid) or directly powered by photovoltaic modules (ED-PV) in a sunny area with access to BW. Assuming a continuity of the increasing local electricity cost, and the decrease of the ion exchange membranes and photovoltaic investment costs, under the most favorable conditions, ED-PV could be potentially cheaper against ED-Grid before 2020. Under the worst conditions, 20 to 30 additional years would be necessary. Finally, we identified the three main barriers for ED-PV: i) technical barriers, related to the matching of the intermittent output of the renewable energy with the water demand, ii) techno-economic barriers associated with the efficiency and performance of membranes and solar modules, and iii) economic barriers associated with the initial investment in ion exchange membranes and photovoltaic modules leading to a relatively high cost of the treated water. Economic figures of RO-PV will be also provided, together with a comparison of social issues.

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Acknowledgements

Financial support from MICINN under project CTM 2011-23912 is gratefully acknowledged. The author C. Fernandez-Gonzalez thanks the Ministry of Education for a FPI grant BES-2012-053461.

DEVELOPMENT OF NEW ELECTROLYTES BASED ON ORGANIC IONIC PLASTICS CRYSTAL SUPPORTED ON MEMBRANE NANOFIBRES FOR THEIR APPLICATION IN FUEL CELLS

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Due to the limited energy resources available based on fossil fuel, as well as increasing environmental concerns, in recent decades the development of new technologies and alternative energy sources are emerging. In this context, fuel cells represent an attractive future option due to their high energy efficiency and low environmental impact. Notwithstanding these advantages, it has some problems with the conduct proton electrolyte such as durability, cost, operating temperature, and water and heat management. [1]

Salts with rotatory phases and/or plastic crystalline phases in their solid states, called Organic Ionic Plastic Crystals (OIPC), are attractive materials for high proton conducting electrolytes because of their ideal property set, which includes excellent thermal and electrochemical stability, plastic mechanical properties, fast ion transport and great flexibility in terms of chemical design.

Thus, in the present work, Guanidinium triflate (GTf) doped with triflic acid (HTf) has been selected because their high proton conductivity. [2] With the aim of forming a suitable electrolyte film to be installed in a fuel cell; solid-state composite membrane electrolytes incorporating different polymer nanofibres (PVDF and PBI) combined with acid doped GTf were prepared. Thus, composite materials exhibit high thermal, mechanical and electrochemical stability producing thin, flexible and structurally homogeneous electrolytes. [3]

Test fuel cell experiments through polarization curves were carried out in order to evaluate the performance of the membrane electrolyte in the electrochemical device. The influence of cell temperature and gas humidification has been analyzed reaching very promising power and current densities under anhydrous conditions. Furthermore, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), impedance spectroscopy, and scanning electron microscopy (SEM) were followed to characterize membrane electrolyte properties.

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This research was supported by the Ministry of Education and Science under the project CTQ2012-31639 (MINECO, SPAIN-FEDER 2001-2013).

Membrane Applications for Food and Pharmaceutical Processing

- **Oral session 13**

GRIGNARD FUNCTIONALIZED CERAMIC NANOFILTRATION MEMBRANES FOR PROCESS INTENSIFICATION IN SOLVENT BASED LIQUID FILTRATION

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A new membrane market is arising within chemical related industries where many in-process separation problems may be tackled efficiently and elegantly by using chemically stable membranes. In particular, organic solvent nanofiltration (OSN) which enables separation of solvent-based mixtures at the molecular level and in a non-thermal way by simply applying a pressure gradient over a nanoselective membrane, offers great perspectives towards wide application in the process industry as it provides a facile, energy-efficient and scalable alternative to conventional separation technologies such as distillation, liquid-liquid extraction or chromatographic purification [1]. OSN cannot be considered a mature technology yet, but it definitely holds enormous potential in solvent intensive pharmaceutical and chemical synthesis processes, where it may be used for concentration, purification and fractionation of valuable target molecules, as well as for recycling of spent solvents, residual reactants or homogeneous catalysts.

A number of dedicated polymer-based OSN membranes and modules are available on the market. Due to their wide chemical resistance and high temperature stability, ceramic NF membranes have the potential to take a significant market share in the area of solvent filtration. However, nanoporous transition metal oxide membranes are intrinsically hydrophilic, resulting in poor performance in non-polar solvents. By exchanging OH-groups with other functional groups, the surface properties of ceramic membranes may be tuned towards specific solvents or solutes.

At VITO, tubular ceramic membranes are being functionalized with organic groups using a novel grafting method based on the use of Grignard reagents. This proprietary functionalization method results in the creation of a direct, non-hydrolysable bond between the membrane surface and the metal atom, and offers a versatile route towards ceramic membranes with tunable surface properties [2,3].

In this work, ceramic membranes were grafted with various organic groups (e.g. alkyl, phenyl) to change their affinity towards specific target solvents and/or solutes. The surface modifications markedly affect the performance of the membranes in OSN. The measured solvent fluxes (water to hexane) and solute rejections (PEGs, polystyrenes, Ru-Binap, etc.) emphasize the importance of membrane surface polarity. They also point to the amphiphilic character of the grafted membranes, originating from the presence of both organic groups and residual OH-groups at the membrane surface. Comparing the performance of native hydrophilic and grafted, hydrophobized membranes suggests a clear competition between solvent-membrane and solute-membrane interactions. Similar effects were also found using

test mixtures consisting of PEG solutes with the same size but different polarity, i.e. fully methyl-capped, partially methyl-capped and non-capped PEGs. All results appear to open a path towards tailor-made membranes [4].

Meanwhile, the potential of the grafted membranes has been evaluated on real solvent streams, aiming at catalyst recovery, solute concentration or solvent recycling. Moreover, functionalized ceramic membranes with attractive anti-fouling properties have been prepared, as demonstrated recently on various industrial waste waters. The innovative grafting method has recently been scaled up to 19-channel elements of 50 cm length and proven to be also applicable to more open, MF/UF-type ceramic membranes.

Moreover, recent work has opened perspectives for these functionalized ceramic membranes towards efficient, intensified synthesis of active pharmaceutical ingredients (APIs). Many reaction, for instance macrocyclisations, are to be performed in very dilute conditions to avoid side-reactions, hence achieve a viable product yield and selectivity. This requirement results in a very high solvent usage and demands large reactors to produce just a small amount of product. Hence, while macrocycles are becoming more and more common as APIs (biological activity, bio-availability, etc.), commercial production of such compounds remains problematic. At VITO, an efficient process for this kind of reactions that by their very nature must be performed at a low concentration has been recently developed. The process relies on OSN to create a dilute reaction environment and recycle the solvent. Using this novel, patented 'Volume Intensified Dilution' (VID) technology [5], the solvent usage required to carry out such reactions can be significantly reduced. This in turn translate into large decreases in process mass intensity (pmi), as well as environmental impact, risks and hazards, footprint and process costs.

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Acknowledgements

The authors acknowledge support by the Agency for Innovation by Science and Technology in Flanders (IWT) for the Strategic Basic Research (SBO) project FunMem4Affinity – Exploration of Functional Ceramic Membranes for Affinity Control in Organic Solvent Nanofiltration (2012-2014), and by the European Commission for the FP7 project CeraWater – Fouling Resistant Honeycomb Nanofilters for Efficient Water Treatment (2012-2015).

DEVELOPMENT OF MICROBIAL POLYSACCHARIDE FILMS FOR FOOD PACKAGING

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Nowadays, many researchers have driven their attention to the use of natural/bio-based polymers as new materials to replace or reduce the use of petrochemical-based plastics. This is due to the fact that the later are non-degradable and non-totally recyclable, which causes an extremely negative environmental impact.
Films of different polysaccharide materials have been studied to tackle this problem, including, chitosan, starch, alginate and carrageenan, mainly because polysaccharides are biodegradable, nontoxic and widely available [1].

Microbial polysaccharides are better alternatives to others recovered from animals or plants, because they are independent on climate and season of the year, being only dependent on microbial cultivation parameters which may be easily controlled. Some microbial polysaccharides have been studied to produce biodegradable films with potential final use on packaging materials, which is the case of gellan, kefiran and xanthan [2].

In this work, FucoPol, an exopolysaccharide, produced by Enterobacter A47 strain grown in a bioreactor with glycerol, a surplus from biodiesel production, as carbon source, was used to produce biodegradable films. FucoPol is a high molecular weight heteropolysaccharide, composed mainly of neutral sugars (fucose, galactose and glucose) in nearly equimolar proportion. The presence of glucuronic acid, as well as pyruvyl and succinyl groups, confer the polymer an anionic character. Both product and process are innovative and were patented [3].

FucoPol revealed the capacity to produce cohesive and dense films when in presence of citric acid. The films are quite transparent and with a good physical integrity, although presenting a high hydrophilic character being completely soluble in water.
The mechanical properties revealed a low tensile strength at break (3.10 MPa), a high elongation at break (55 %) and a Young Modulus of 2.8 MPa, which are characterisitic of a material with a rather low stiffness and a high plasticity.

Regarding the barrier properties, in what concerns the water vapour permeability the results show a value similar to other polysaccharides (1.01×10^{-11} mol/m s Pa) such as corn starch when similar driving force is applied [4]. Regarding the single gas permeability (CO_2 and O_2), it was much lower than that of water vapour. However, FucoPol films demostrated a higher permeability to CO_2 (42.70×10^{-16} mol m/m^2 s Pa) than to O_2 (0.69×10^{-16} mol m/m^2 s Pa). This behaviour is also characteristic of films obtained from polysaccharides, such as starch or chitosan.

Due to the observed ductile mechanical properties, hydrophilic character and good barrier properties to gases, the most promising application of these films may be as an inner layer in a multilayered film for packaging material. Ongoing work is focused on the optimization of blends and bi-layered FucoPol/chitosan films in terms of water resistance, mechanical properties, antimicrobial activity and permeability to gases (e.g. O_2 and CO_2). It is intended to design packaging materials to extend shelf life of specific food products (e.g. fruits or cheese).

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NANOFILTRATION FOR SUGAR REDUCTION IN RED AND WHITE GRAPE MUST TO PRODUCE LOW-ALCOHOL WINES

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Over the last years, due to global warming, observations from various world winemaking regions have provided evidence of modified vine development and fruit maturation patterns. Among the most important climate change-related effects there is an increased grape sugar concentration that leads to high wine alcohol levels [1]. Premature grape harvest and winemaking should affect the final wine quality, because the acidic and phenolic maturity should not be fully achieved [2] leading to more acid and less colored wines. A commendable oenological practice establishes that the quality of wines depends essentially on the maturity of phenolic components contained in the grape berries [3].Therefore, in order to produce a full flavored wine, the harvest should be carried out in the optimum ripeness of the fruits and then an adequate control of sugars in musts can be very useful to keep the alcohol degree of the resulting wines within the desired range. One of these mild and highly specific technologies is the use of membrane processes, such as nanofiltration (NF) for controlling the concentration of sugars in the must before fermentation.

The aim of the present study is to analyse the NF technique to reduce the alcohol content of wines approximately 2 degrees by controlling the sugar content of the grape must before its fermentation. The NF membrane used was a KMS SR3 Spiral Wound Module (SWM), made and commercialized by Koch Membrane Systems. The treated musts came from two Spanish varieties of grapes, a white one (*Verdejo*) and a red one (*Garnacha*). For the white must two NF processes were carried out: a single-stage NF process and a two- stage one, in order to observed differences in the process. In the case of the red must only a two-stage NF was analyzed. For the white must two NF methods were carried out: a single-stage process and a two- stage one. During the single-stage NF of white must intermittent backflush due to the osmotic pressure effect was tested in order to analyze its influence on the membrane fouling. The mixture of the final permeate (P2) with the first retentate (R1) in the two- stage process or of the permeate (P1) with untreated must (C) in a single-stage process, provides a grape must chemically similar to the original must but with a lower sugar content. Figure 1 describes briefly the NF procedures, mixture and fermentations carried out for the Garnacha red must (a) and for the Verdejo white must (b and c). Finally, sensory evaluation of the resulting wines, on the basis of the acceptance of the sensory descriptors colour, odour, flavour, persistence and overall liking was conducted with a panel of volunteer consumers. The sensory data collected were subjected to PCA analysis in order to see which the favorite wines were.

After the assessment of the different NF techniques studied, the main following conclusions were raised:

- All the filtration processes and stages follow a typical and expected kinetics of permeate flux decrease, but backflushing had an undesirable effect because it increased the pace of flux decay by disturbing the cake stabilization on the membrane.
- Alcohol degree reduction was achieved for the red wines produced by the two-stage NF process (i.e. G2NF1 and G2NF2). In the case of white wines only the wine

originated from the single-stage NF (V2NF) process had the appropriate alcohol degree content

- Sensory evaluation and PCA analysis showed that none of the wine samples was particularly preferred by the consumers, showing that there were no significant differences between the control and the filtered wines.
- NF did not affect significantly the odour and colour of the resulting red wines, since the G2NF1 had the highest colour and odour acceptance.

All in all, it can be said that among the processes studied, the best NF technique is the two-stage process without backflushing. This technique allows not only an appropriate sugar content reduction, but the mixture (P2+R1) promotes a higher recovery of polyphenolic compounds (i.e. color). Besides it minimizes volume losses since the retentate of the first stage is used for the appropriate blend of must.

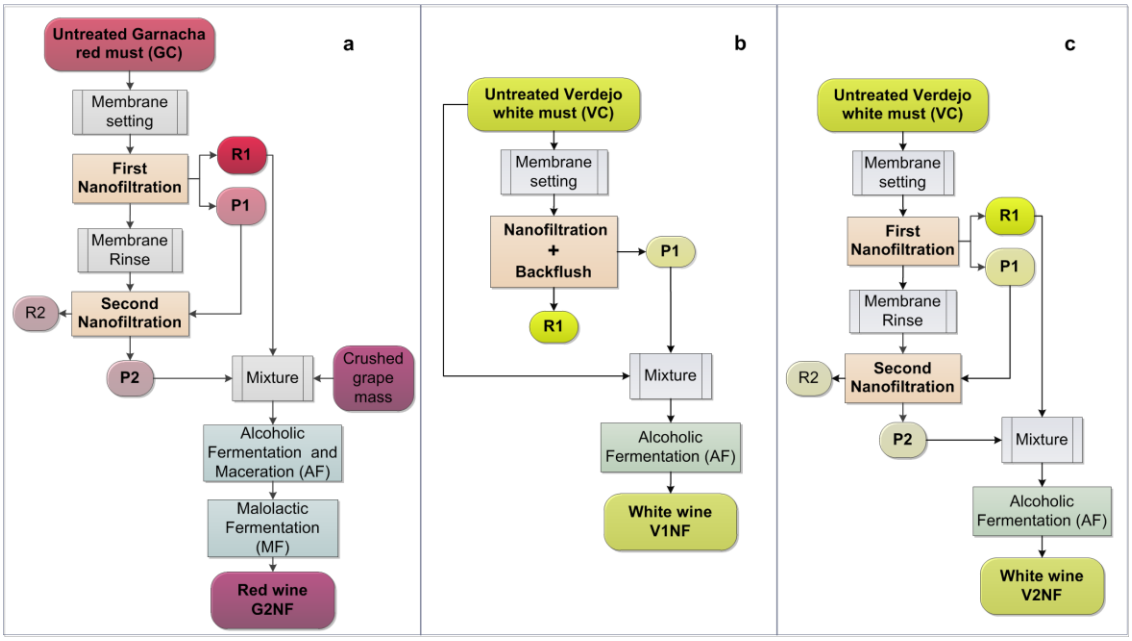

Figure 1. Scheme of the Nanofiltration procedures carried out for the grape musts and ulterior fermentations.a) Garnacha red must two–stage NF b) Verdejo white must two-stage NF and c) Verdejo white must single-stage NF

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Acknowledgements

Authors would like to thank the “Ministerio de Ciencia e Innovación (MCINN)” for the financial support of this work within the frame of the “Plan Nacional de I+D+I” through the research projects, CTQ2012-31076 and MAT2011-25513. We also are grateful to the projects: VA248U13 of the Junta de Castilla y León.

C. Salgado wants to thank the Spanish Ministry of Education for the grant they gave to her within the frame of the “Plan Nacional de Investigación Científica, Desarrollo e Innovación Tecnológica 2008–2011” (FPU grant: AP2010-5769) to complete her PhD.

PREMIX MEMBRANE EMULSIFICATION TO PRODUCE W1/O/W2 EMULSIONS AND MICROCAPSULES ENTRAPPING POLYPHENOLS

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Premix Membrane Emulsification (PM) has received increasing attention over the last years because of the low energy consumption, the better control of droplet size distribution and the mildness of the process. In Premix ME, first a coarse emulsion is made and successively pushed through a membrane. Passing the coarse emulsion through the membrane, the droplets break up into smaller ones [1].

Premix ME has been reported to be specially suitable for producing double emulsions, such as water-in-oil-in-water (W1/O/W2) emulsions. Double emulsions, in which small water droplets contained within larger oil droplets are dispersed in an aqueous continuous phase, are used as delivery systems of water soluble bioactive molecules. Double emulsions are normally produced using a two-step procedure: (i) a W1/O emulsion is produced by homogenizing water, oil and a hydrophobic emulsifier; (ii) a W1/O/W2 emulsion is then produced by homogenizing the W1/O emulsion in water containing a hydrophilic emulsifier. The mild conditions of premix ME are especially useful for the second emulsification step in order to prevent the rupture of the emulsion structure.

Polyphenols, plant metabolites with a wide range of beneficial effects on human health, are sensitive to several factors, such as temperature, oxygen, light, pH, enzymes, etc., which can reduce their bioavailability. Encapsulation in emulsions or in solid microcapsules has been suggested as a method to protect polyphenols during storage, processing and further digestion. W1/O/W2 emulsions, in which the inner water phase contains polyphenols, and microcapsules obtained by spray drying from W1/O/W2 emulsions were investigated as carriers of polyphenols.

To produce the W1/O/W2 emulsions we followed a two-step process: i) a single W1/O emulsion containing a commercial grape seed extract, rich in procyanidins, in the water phase was obtained by rotor-stator homogenization that led to a mean droplet size of the inner droplets of ca. 2.6 µm and ii) W1/O/W2 emulsions were produced by Premix membrane emulsification. Polyglycerol polyricinoleate (PGPR) was used to stabilize the inner interface (W1/O) while two different protein-polysaccharide complexes (whey protein isolate (WPI) with carboxymethyl cellulose (CMC), and WPI with gum Arabic (GA)) were applied to increase the barrier properties of the external interface (O/W2) [2]. For producing microcapsules, maltodextrin (MD) was added as a wall material to the W1/O/W2 emulsions that were subsequently spray-dried.

The mean droplet size of the outer W1/O/W2 emulsions stabilized with WPI-CMC and WPI-GA was 7.5 and 10.4 µm m, respectively. The emulsions were stable over a storage period of 14 days at several pH values (5, and 7). In terms of encapsulation of polyphenols , we observed that it was reduced from 88 - 96% in coarse emulsions (cycle 0) to 70% - 83% after 3 cycles of Premix ME.

The microcapsules obtained by spray-drying, with a mean particle size of 20 µm, became W1/O/W2 emulsions after resuspension in water, showing that spray-drying preserved the typical compartmented structure of double emulsions.

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Acknowledgements

The authors would like to acknowledge the Dirección General de Investigación, projects CTQ2010-16724/PPQ and CTQ2011, for providing financial support.

STUDIES ON POLYPHENOLS CONCENTRATION BY ULTRAFILTRATION (CONCENTRATION AND DIAFILTRATION MODES) OF AN ETHANOLIC EXTRACT OF WOOD BARK

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This work was developed within a project aiming to screen for processes and products for a global valorisation of pulp and paper side-streams and integration of biorefinery concept in these industries. Bark of woody species is considered a by-product in these industries and usually is burned to energy recovery. *Eucalyptus globulus* bark has a high content of polyphenolic components that can be used as anti-oxidant and bioactive agents in several application fields. In a previous work, an ethanol/water (52/48, % v/v) extract of *Eucalyptus globulus* was produced at optimized conditions focusing total phenolic compounds (TPC) (assessed by Folin-Ciocalteu method), leading to a biological active extract [1]. This is a rather complex extract containing 16% of total carbohydrates (TC), 38% of TPC, 32% of proanthocyanidins (Pac) and 36% of formaldehyde condensed tannins (fcT) and a concentration of total solids of 7.9 g/L. Aiming to promote the enrichment of polyphenols (TPC, Pac and fcT) rather than other compounds such as carbohydrates, membrane nanofiltration and ultrafiltration (concentration and diafiltration mode) were attempted. Figure 1 represents the experimental sequence for membrane processing of *E. globulus* bark extract.

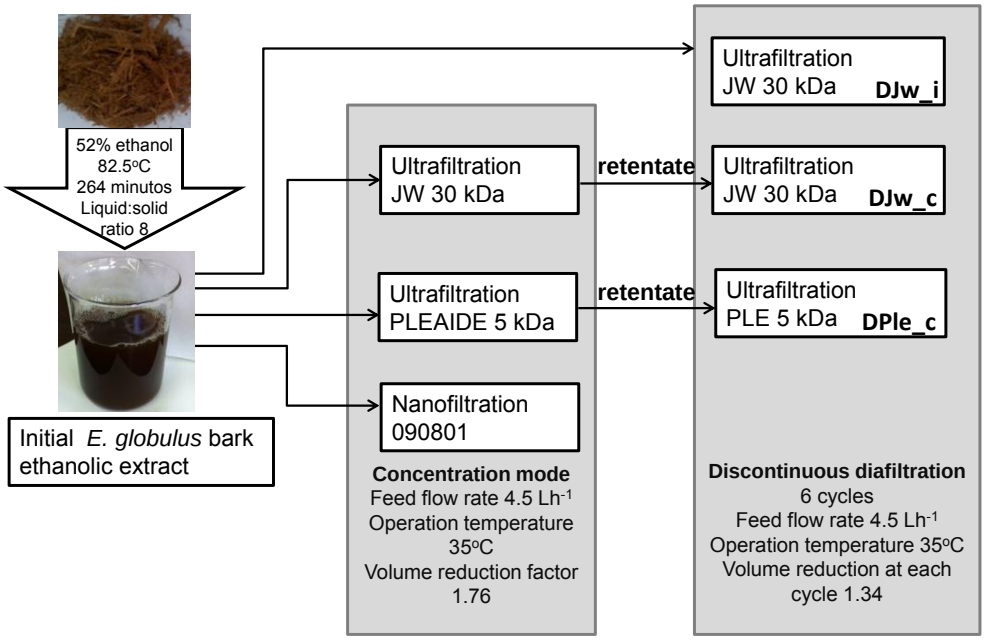

Figure 1 – Membrane processing approaches for concentration of polyphenols from *E. globulus* bark

Three commercial membranes were selected to perform the extract concentration and the final product composition was assessed. Membrane cleaning cycles required by each membrane were also studied. A discontinuous diafiltration mode of operation was conducted in order to accomplish further enrichment of the extract on polyphenolic fraction and,

simultaneously, to decrease the ethanol content to about 10% v/v, turning it able to further refining by adsorption on polymeric nonpolar resin.
Concentration experiments were carried out to a volumetric concentration factor of 1.76, with retentate recycling and permeate removal at constant TMP, feed flowrate and temperature. The membranes selected were the UF membranes JW (GE Osmonics, cut-off 30 KDa) and PLEAIDE (Orelis Environment, cut-off 5KDa) and the NF polyamide-based membrane (SolSep). Among the studied membranes, JW showed the best permeate flux performance. Membrane rejections were assessed concerning all the parameters studies for each membrane. JW revealed to be more selective to compounds of phenolic nature in detriment of TC. The content of TPC, Pac and fcT in the retentate produced by JW membrane increased by 2%, 19% and 28% relative to initial extract, with a simultaneous decrease of TC. In order to achieve higher concentration of polyphenols and, simultaneously to decrease the ethanol %, three approaches based on diafiltration were carried out using water for volume replacement; two diafiltrations with the membrane showing the best performance in the concentration process - JW membrane - using as feed 1. the initial extract (DJw_i) and 2. JW concentrate (DJw_c). And a third diafiltration with PLEAIDE membrane using the respective concentrate as feed (DPle_c) – Figure 1.
Six discontinuous diafiltration cycles were conducted and the different compositions of retentates and permeates obtained at the end of each cycle were assessed. Figure 2 shows the retentate composition concerning the relevant parameters.

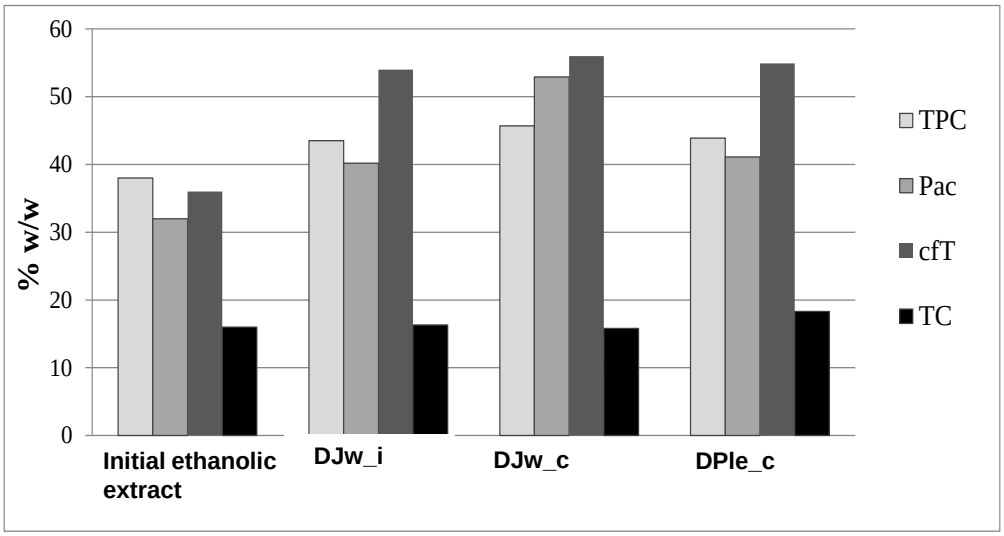

Figure 2 - Composition of the initial extract and final retentates from diafiltration.

After the sequence of concentration and diafiltration processes, the best performance was found for JW membrane, with a final retentate composed by 46% of TPC, 53% of Pac and 56% of fcT. The sequential process of concentration and diafiltration was successfully applied to fractionate and increase the initial polyphenolic content of the bark ethanolic extract (increment of 55-65% concerning Pac and fcT) revealing the potential of this technology to be integrated in biorefining processes for bark valorization.

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Acknowledgements Project BIIPP No.11551 - Integrated Biorefinery in Industry Pulp and Paper. This work was co-financed by FCT and FEDER under Programme COMPETE (Project PEst-C/EQB/LA0020/2013).

INCREASING THE ANGIOTENSING CONVERTING ENZYME INHIBITORY ACTIVITY OF GOAT MILK HYDROLYSATES BY CROSS FLOW FILTRATION THROUGH CERAMIC MEMBRANES

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Milk protein hydrolysates have been described as an important source of bioactive peptides [1], i.e., peptides which exert a physiological effect beyond their nutritional value. One of the most interesting bioactivities is the inhibition of angiotensing converting enzyme (ACE). This enzyme take part into two important mechanisms of blood pressure regulation, producing an increase in blood pressure [2]. Therefore, inhibiting ACE cause a decrease in blood pressure. Currently, some of the drugs employed in hypertension treatment are based in ACE inhibition, however, these medicines present adverse side effects. In contrast, food derived peptides with ACE inhibitory activity have not shown any side effects, even at high concentrations [3]. Consequently, these peptides might be included in food formulas to help in the control of hypertesion.

Milk protein hydrolysates are a complex mixture of peptides including some without any ACE inhibitoy activitym. Then, it would be desirable to obtain hydrolysates enriched in active peptides in order to produce a purified product which can be used as functional ingredient. To this regard, membrane technology would be very useful. Organic membranes have been used previously at lab scale to fractionate the hydrolysates obtaining significant improvement in the inhibitory activity of the hydrolysates [4], [5]. Despite of the advantages in terms of chemical resistance, pH and T limits and operating lifetimes, ceramic membranes have been rarely employed in hydrolysates purification [6]

The objective of this work was to study the purification of ACE inhibitory peptides from goat milk hydrolysates using ceramic membranes. To this end, three channel membranes Inside Céram (Tami) of 15 and 50 kDa with a length of 0.25 m and a filtration area of 0.0094 m^2 were employed. The hydrolysate fed in both cases was 2 L of casein hydrolysate produced after 3 h of reaction at 50ºC using a mixture of subtilisin and trypsin (5%). The hydrolysate was concentrated at 50ºC, 1 bar of transmembrane pressure and a cross-flow velocity of 3.3 m/s which assure the turbulent flow in membrane channels. The ACE inhibitory activity of the fractions was evaluated in the retentate and permeate fractions by a spectrophotometric assay [7]. After the filtration, the membrane was cleaned with NaOH to recover its permeability. The cleaning efficiency index which represents the percentage removal of the fouling resistance after the cleaning procedure was determined.

In both filtrations, a volume reduction factor of 3 was reached after 5.8 and 5.2 h of operation for 15 and 50 kDa membranes, respectively. In the two filtrations, the flux decreased constantly and no stationary flux was reached. At the end of the process the permeate flux decreased around 50 and 60 % for 15 and 50 kDa membranes. Regarding the protein concentration of the fractions, the results obtained in the experiments were also similar. The retentate fraction was greatly enriched in proteins while the permeate presented a lower values of protein concentrations. However, the inhibitory activity of the retentate fractions worsened significatively. In contrast, the permeates, with lower protein concentration, presented an increase in the ACE inhibitoy activity of 15 and 30 % for 15 and 50 kDa membranes. That point toward an enrichment of inactive peptides in the retentate fractions whereas the inhibitory peptides would cross the membrane and they would be recovered in the permeate. After the filtration, the membrane was subjected to a cleaning protocol which

recovered the permeability of the membranes almost completely, reaching a 97% removal of the fouling resistance.

In conclusion, filtration through ceremic membrane is an adequate method for purifying ACE inhibitory peptides. The best results were found for the filtration through 50 kDa which improved 30% the ACE inhibitory activity of the permeate fraction. Despite of the drop in the flux obtained during the process, the membrane was recovered satisfactory.

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Acknowledgements

This work was funded by the project P07-TEP-02579 from the Consejería de Economía, Innovación, Ciencia y Empleo of Junta de Andalucía, Spain. F.J. Espejo-Carpio also acknowledges the postdoctoral fellowship support from the Consejería de Economía, Innovación, Ciencia y Empleo of Junta de Andalucía.

Membrane Applications for Food and Pharmaceutical Processing

- **Poster session 2**

RECOVERY OF PHENOLIC COMPOUNDS FROM TABLE OLIVE WASTEWATERS BY MEANS OF MEMBRANE PROCESSES: PRETREATMENT BY ULTRAFILTRATION

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The residual wastewater from the fermentation process of olives has a high salt concentration and chemical oxygen demand (COD); part of this organic matter corresponds to phenolic compounds. The presence of these phenolic compounds in olive brine residue is one of the major problems in its management. This brine is treated in wastewater treatment plants (WWTP) or in evaporation lagoons. In WWTP the phenolic compounds reduce the efficiency of the biological processes due to their antimicrobial action [1]. Furthermore, most of these phenolic compounds are degraded to quinones, their oxidized forms, which are hardly biodegradable.

Thus, the separation of this phenolic fraction improves the performance of the WWTP and allows the recovery of phenolic compounds for further applications. The major phenolic compounds present in olive brine are hydroxytyrosol and tyrosol. They have a strong antioxidant activity, which makes them very valuable for the food, cosmetic and pharmaceutical industries [2].

In this work membrane processes have been investigated to recover the phenolic compounds from table olives wastewaters. A nanofiltration (NF) process has been considered to recover and concentrate the phenolic compounds. In order to improve the performance of the NF process, a pre-treatment with ultrafiltration (UF) was investigated. The aim of the UF process was to separate phenolic compounds from organic matter and decrease the fouling of the NF membrane.

The UF laboratory plant was an automatic plant that can regulate transmembrane pressure, cross flow velocity and temperature. A Rayflow membrane module from Orelis (France) was used. This module was configured to work only with one membrane in cross-flow mode. Two flat sheet polymeric membranes from Microdyn Nadir (Germany) were tested: a hydrophilic membrane of polyethersulfone (PESH) with a molecular weight cut-off (MWCO) of 30 kDa (Nadir UH030) and a membrane of polyethersulfone (PES) with a MWCO of 5 kDa (Nadir UP005). The total active surface for each membrane was 0.0125 m^2.

For the UF process feed samples were olive brine from a table olive packing plant. Due to the high suspended solid content, a filtration step with a 60 µm filter was previously carried out. For each run the total volume of the feed sample was 5 L. Tests were performed at three different transmembrane pressures (1, 2 and 3 bars) and three different cross flow velocities (2.2, 2.9 and 3.7 m/s) during 2.5 hours. After this period, the steady state was achieved. Temperature was kept constant at 25 ºC. During the test, permeate and retentate were recycled back to the feed tank. Permeate flux was monitored with a precision balance from Kern (Germany) and the collected data were recorded with a data acquisition system. Feed and permeate samples were characterised. Turbidity was measured with a Dinko turbidimeter (Spain) and dissolved COD with Hach Lange kits (Germany). The concentration of total phenolic compounds was determined by the Folin-Ciocalteu method and total antioxidant activity (TAA) by the 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) method.

After each run, the membrane was cleaned with citric acid (1% p/v) and NaOH (pH 11). A permeability recovery higher than 90% was required before beginning the following test.

Table 1 shows the steady state permeate flux for both membranes and some of the operating conditions. Permeate flux was low for both UF membranes. At 2 and 3 bar steady state permeate flux was similar for both membranes, but the 30 kDa membrane was much more difficult to clean, and showed a severe flux decline, which is typical of internal pore fouling.

Table 1. Steady state permeate flux for both membranes and some of the operating conditions.

Operating conditions		Permeate flux (L h^{-1} m^{-2})	
TMP* (bar)	Cross flow Velocity (m s^{-1})	30 kDa	5 kDa
1	2.2	26.64	13.73
1	2.9	31.81	12.87
2	3.7	34.98	34.48
3	3.7	37.05	35.26

* TMP: Transmembrane pressure

UF pretreatment was able to reduce turbidity by more than 99% in all the runs. Figure 1 shows dissolved COD removal for both membranes and some of the operating conditions tested. The highest COD removal (50%) was obtained with the 5 kDa membrane at 3 bar and 2.2 m/s. The permeability of phenolic compounds trough the membranes was lower at 1 and 2 bar than at 3 bar. Phenolic compounds rejection varied between 0 and 45%, depending on the membrane and operating conditions. For the operating condition that showed the highest COD removal total phenolic compounds rejection was around 20%. The permeate streams maintained between 80-90% of the TAA.

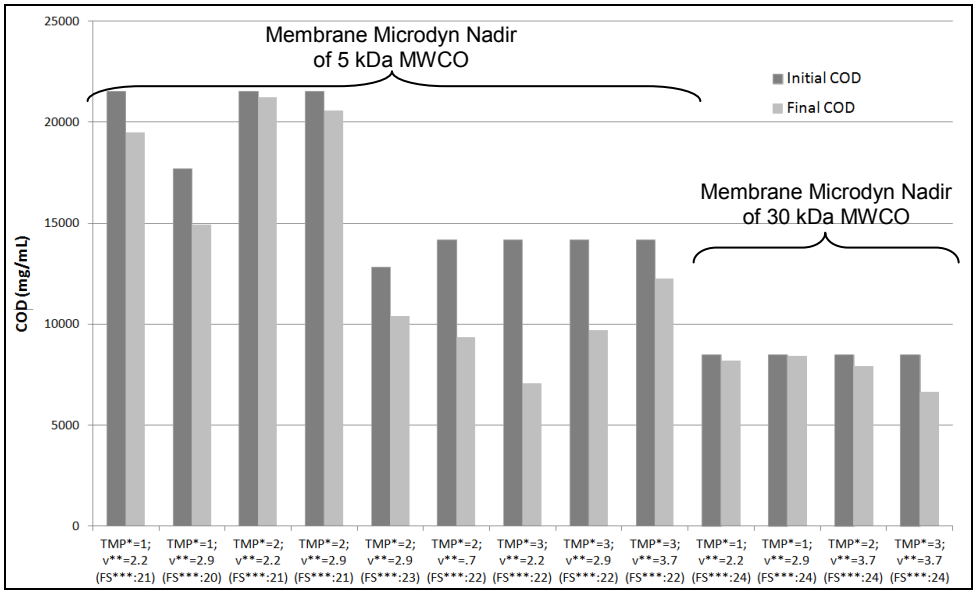

Figure 1. Dissolved COD removal for both membranes and some of the operating conditions for some different feed samples (*TMP: Transmembrane pressure (bar), **v: cross flow velocity (m/s), ***FS: Feed sample)

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Acknowledgements

The authors of this work wish to gratefully acknoledge the financial support of CDTI (Centre for Industrial Technological Development) depending on the Spanish Ministry of Economy and Competiviness.

STABILITY ASSAY OF A CERAMIC MEMBRANE REACTOR FOR THE PRODUCTION OF ACE INHIBITORY PEPTIDES

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Hypertension is a major worldwide heath problem since it is the main risk factor for cardiovascular diseases which, according to World Heath Organization, were responsible for 17.3 million of deaths in 2008. Currently, hypertension patients are treated with drugs such as captopril, which inhibit angiotensing converting enzyme (ACE) originating a decrease in blood pressure. Just in the USA, these antihypertensive medicaments represent an annual costs of approximately $15 billion [1]. Moreover, adverse effect such us hypotension, increased potassium levels, reduced renal function, cough, angioedema, skin rashes have been described for these drugs [2]. Food derived peptides with ACE inhibitory activity have shown in vivo activity and no side effect, therefore, they might be a good alternative to synthetic ACE inhibitory drugs.

The use of membrane reactor for the production of ACE inhibitory peptides from food proteins have been studied previously. However, most of the studies used organic membranes as a separation media [3], [4]. However, ceramic membranes present better characteristics which allow a wider operational range and better resistance to cleaning. Consequently, inorganic membranes show longer operational lifetimes without losing efficiency.

The objective of this study was to evaluate the time evolution of the performance of a ceramic membrane reactor for the hydrolysis of goat milk protein. In preliminary studies, goat milk hydrolysates were produced in batch hydrolysis in order to select the one with the highest ACE inhibitory activity. Subsequently, the hydrolysate was fractionated by size exclusion chromatography in order to identify the molecular size fraction with better ACE inhibitory activity. Based on that previous results, the best hydrolysate was selected to develop the membrane reactor operation using a membrane with a molecular size cutoff suitable for purifying the most active fraction. According to this, 2 L of skimmed goat milk (28 g protein/L) was hydrolysed with a mixture of subtilisin and trypsin (5%). The reaction was carried out at 50 ºC and pH 8.The degree of hydrolysis was determined by pH-stat method. During the hydrolysis reaction, the content of the reactor was pumped through a 15 kDa membrane (Inside Céram, Tami) at a transmembrane pressure of 1 bar and a cross-flow velocity of 3.3 m/s. Retentate was recirculated and filtrate was continuously removed. Goat milk was feed to the reactor at the same flow of permeate in order to maintain the reactor volume. The ACE inhibitory activity of the permeate was evaluated during the reaction time by a spectrophotometric assay [5] and protein concentration was determined by the BCA method.

In the first 2 hours of operation, the permeate flux reached a steady value around 45 $L/(h \cdot m^2)$. The protein content of the permeate increased up to a constant value of 13 g/L. With respect to the ACE inhibitory activity, a stationary inhibition of 78 % was obtained.

However, after 4 hours of operation, a sharp decrease permeate flux took place. Some visible changes occurred in the reactor: pH became totally uncontrollable and the reaction medium increased its viscosity and color. At this moment, the operation was stopped in order to avoid permanent damages in the membrane due to an excessive fouling. A possible cause of this undesirable phenomena could be the development of Maillard reactions, which could be solved by removing the lactose content in the original feed by means of diafiltration. Other

possibility is the accumulation of non-hydrolysable long peptidic chains, which should be purged out of the system.

To conclude, using a reactor membrane seems a promising method for producing ACE inhibitory peptides from goat milk proteins. Although, further research should be made in order to extend the operational time of the membrane reactor.

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Acknowledgements

This work was funded by the project P07-TEP-02579 from the Consejería de Economía, Innovación, Ciencia y Empleo of Junta de Andalucía, Spain. FJ Espejo-Carpio also acknowledges the postdoctoral fellowship support from the Consejería de Economía, Innovación, Ciencia y Empleo of Junta de Andalucía.

THE CONTRIBUTION OF THE CAKE ON THE EFFECTIVE GLOBAL PRESSURE DROP IN NANOFILTRATION

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Three nanofiltration membranes have been analyzed for their application for the retention of sugars from red grape must in order to produce wines, after fermentation, with a reduced alcohol degree. . These membranes are: NF270 from Dow – Filmtec; HL from GE Water & Process Technologies and KMS SR3 from Koch membrane systems.
The influence of low and high molecular weight compounds in fouling and retention have been studied in detail [1]. The procedures used are general and could be applied in other filtration fouling problems.
Here, fouling is analyzed by using a synthetic solution (containing the typical LMW of natural must, namely glucose, fructose, malic and tartaric acids, potassium, sodium, calcium and magnesium. and a commercial red must). The analysis of the flux decay and retention of sugar in musts shows that, two of the three membranes studied, HL and SR3 are appropriate to reduce the content of sugar of red must. Specifically SR3 shows the best passage of sugar and less fouling.

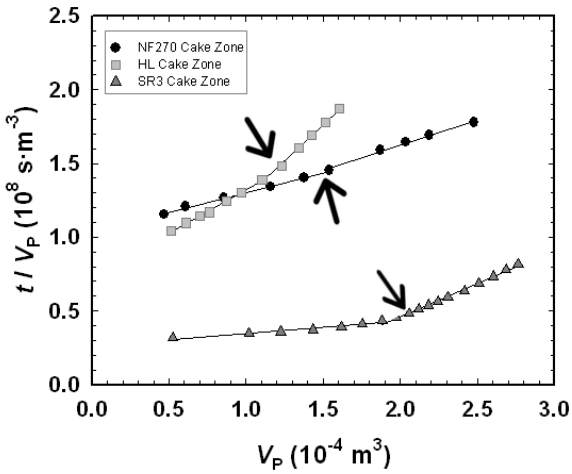

Figure 1. Flux kinetics for three nanofiltration membranes. Arrows point to the change in cake kinetics from fast to slow flux decay.

The cake fouling kinetics when high molecular weight compounds are present is shown in Figure 1 for the SR3 membrane during must nanofiltration. The kinetics includes two main consecutive steps (changing at the arrows in Figure 1) after a short initial pore blocking step (not shown in Figure 1). These main consecutive kinetics steps in flow decay are:

1. A cake deposition phase with increasing compression until arriving to compaction followed by

2. A slower kinetics once the cake is completely well assembled. Here, the retention of low molecular weight compounds, such as sugars, arrives to a maximum and ulterior increases in effective pressure happen through the membrane itself.

As shown in Figure 2, the change from the first cake kinetics to the second one happens when the osmotic pressure across the cake opposes the hydraulic pressure drop and the influence of the cake resistance has arrived to its maximum. Afterwards the cake is quite similar to the membrane and cake and membrane increase their effective pressure at the same pace.

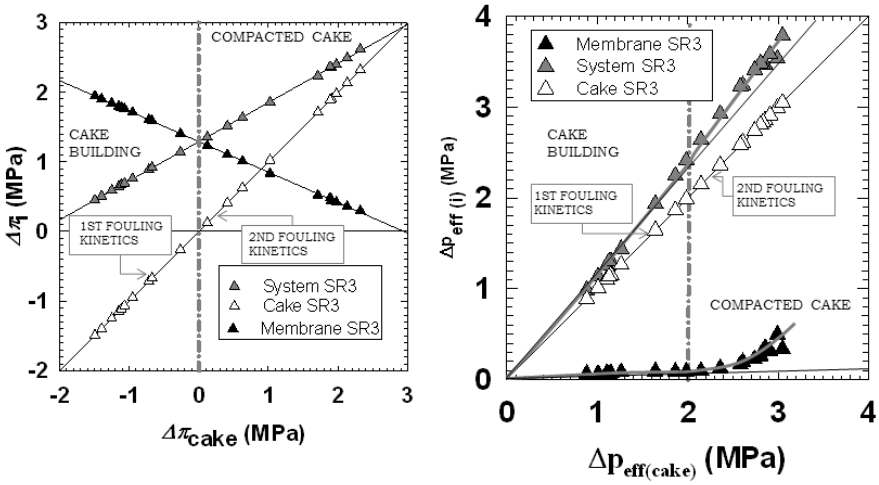

Figure 2. Osmotic pressure and effective pressure of membrane and membrane system as as a function of the corresponding pressure drop through the cake. The vertical line corresponds to the maximum resistance to flux due to fouling, arrival to a plateau in retention and change to a second slower cake kinetics.

It has been proven, for the three membranes that the evolution of sugars retention and the effective pore size converge to the effective pore size of the cake after compaction.

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Acknowledgments

We are indebted to the Spanish Junta de Castilla y León for the financing of this work through the GR-18 Excelence Group Action and project VA248U13 also to the Ministry of Economy and Competitiveness in Spain for their economic support (MAT2011-25513, MAT2010-20668 and CTQ 2012-31076).
C. Salgado wants to thank the Spanish Ministry of Education for the grant they gave her within the frame of the “Plan Nacional de Investigación Científica, Desarrollo e Innovación Tecnológica 2008-2011” (FPU grant: AP2010-5769) to complete her PhD.

EVALUATION OF NANOFILTRATION FOR THE CONCENTRATION OF BIOACTIVE COMPOUNDS RECOVERED FROM GRAPE MARC

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One of the goals of modern researches is to reclassify industrial wastes, above all the derived from natural sources, into subproducts in order to reduce the adequate treatment costs. Regarding the grape juice industries, the main waste generated and also of the highest volume is the marc, basically consisting of skins and seeds [1]. Due to its high chemical and biochemical oxygen demand, the inappropriate disposal of this waste presents serious environmental constraints [2]. However, this co-product stands out for its rich phenolic composition and great antioxidant potential, which can be recovered as an alcoholic extract [3-6]. This recovery could increase its value and therefor, reduce the costs of its treatment for the proper environmental disposal. Phenolic compounds are known to be easily degraded in the presence of inadequate oxygen concentrations, pH, temperature and other inadequate conditions [7]. The aim of this study, therefore, is to evaluate the application of nanofiltration to concentrate the hydroethanolic extract obtained from red wine marc (Chardonnay). The nanofiltration (NF) was chosen due to its characteristics: energy savings, selectivity, separation of thermolabile compounds and simplicity of operation [8].

A semipilot using a 30% hydroethanol solution for extraction was performed. The grape marc, previously hydrated during 1 hour at 30°C, suffered the extraction with 30% ethanol, pH 4.0 adjusted with citric acid, in proportion of 9:1 solvent: substrate during 120 min at 50°C under a mechanical stirring of 48 rpm. The nanofiltration was carried out in duplicate in a spiral wound polyamide membrane modules system with a filter area of 2,5 m^2. The processes was conducted at 40°C with applied pressure of 12 bar in the system, which was previously determined by evaluation of the limiting flux at 20°C, 30°C and 40°C, under a fed batch until a volumetric concentration factor (VCF) of at least 10 was reached (Figure 1). The permeate stream was fully collected and its flux measured in $kg.h^{-1}m^{-2}$ every 5 minutes. Samples of the streams were collected and submitted for analyzes of antioxidant activity, using an eletron transfer methodology (ABTS) [9,10] and an hydrogen atom transfer methodology (ORAC) [11] and, of total phenolics (TP) [12 modified by 13].

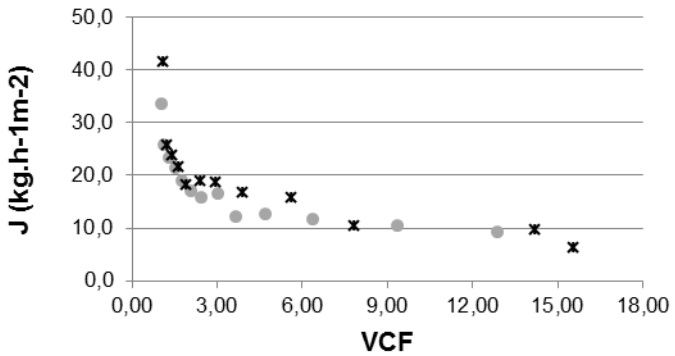

Figure 1 – Permeate Flux (J) depending on the Volumetric Concentration Factor (VCF) of both processes

The nanofiltration process proved itself as an efficient system for bioactive compounds concentration reaching VCF of 12,9 and 15,5 (Table 1).

Table 1 – Bioactive compounds and antioxidant capacity *in vitro* from the NF Streams

Stream	Process 1			Process 2		
	ABTS[1]	ORAC[2]	TP[3]	ABTS[1]	ORAC[2]	TP[3]
Feed	3,50 +0,07	4,46 + 0,22	43,93 + 1,10	3,67 + 0,10	4,88 + 0,01	43,93 + 0,99
Permeate	0,34 + 0,03	0,38 + 0,38	4,19 + 0,31	0,19 + 0,06	0,53 + 0,03	2,30 + 0,18
Retentate	37,64 + 0,46	47,87 + 2,31	415,34 + 20,26	40,43 + 1,69	43,20 + 3,61	421,17 + 3,54
VCF	12,90			15,54		

[1] ABTS- antioxidant capacity expressed in µmol Trolox equivalent.g^{-1} by the ABTS methodand [2] ORAC - antioxidant capacity by ORAC method; [3] TP–Total Phenolics expressedin galic acid equivalent.$100g^{-1}$

The retention coefficients for the phenolic compounds and antioxidant capacity measured by the ABTS and ORAC methods were on average 99% (Figure 2).

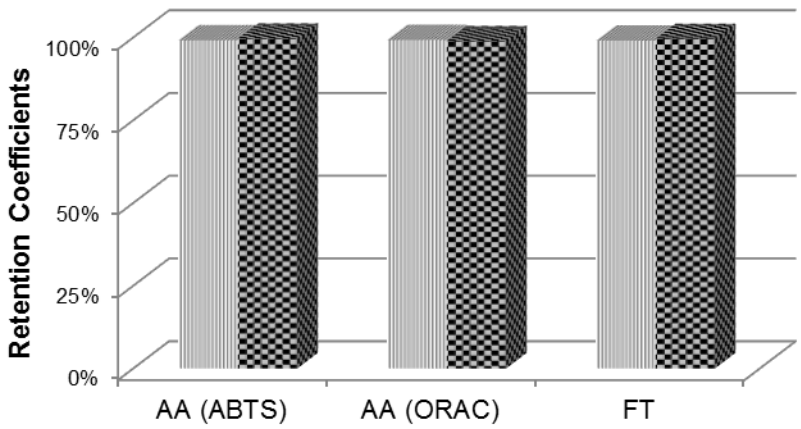

Figure 2 – Rentention Coefficient of Both Processes

The results confirmed that using a 30% hydroethanol solution for extracting bioactive compounds from the grape marc and their subsequent concentration with NF could be an interesting alternative for aggregate value in such a costly waste.

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Acknowledgements

The authors want to thank the *Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)* for the studentships granted.

ACTIVE FOOD PACKAGING FROM PECTIN

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Introduction

Pectin is one of the main components of the plant cell wall chemically constituted by poly α1-4-galacturonic acids. According to its degree of esterification with methanol, pectin can be classified as high methoxyl pectin or low methoxyl pectin. In food industry, pectin is listed as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA). Due to its biodegradability, biocompatibility, edibility, and versatile chemical and physical properties, pectin is a suitable polymeric matrix for the elaboration of active food packaging. Active packaging possesses active ingredients in the packaging material and/or uses functionally active polymers. When the packaging system has antimicrobial activity, the packaging limits or prevents the microbial growth [1-3]. This work presents results about pectin film formation and characterization. Standars such as ASTM D882-02 for tensile properties of thin plastic sheeting; ASTM F372-99-03 for Water Vapor Transmission Rate (WVTR), and ASTM D 6002-96-R02 for biodegradability were used. Migration of the active component was also evaluated. Results showed active food packaging from pectin were sthrenght resistant as well as flexible; highly permeable to water vapor and successful fresh food preserver.

Materials and Method

Pectin (Pec) from citrus peel (≥ 74 % galacturonic acid, 6.7 % methoxyl groups, Sigma-Aldrich) and Glycerol (Gly) as plasticizer (≥ 99,5 %, Biopack) were used to prepare pectin filmogenic solutions. The solutions were prepare by adding pectin at 2 wt.% and glycerol 1 vol.% in destilled water. Then biodegradable packaging films were prepared by wet casting of the aqueous solution on a flat plate and later drying in an oven at 60 °C during 24 h. Plasticized films were then processed to perform characterization techiques. Benzoic acid (BA, Sigma-Aldric) was used as the active component of films. It was added to the filmogenic solution of PecGly before casting. Once the solution was homogeinized, casting and dying procedure was applied in order to obtain active films. Nomenclature used to refer to those films were PecGly and PecGlyBA for common and active packaging film, respectively.

Results and discussion

Results showed PecGly-1% BA presented best mechanical performance as long as it depicted highest tensil sthrength value (σ) as well as elastic module (E). Elongation at break (‰ε) was half of PecGly value, however, it represents a good flexibility for this film. The appearance of a fibrous-like structure when BA was incorporated within the pectin matrix could be responsible for the polymer matrix reinforcement. WVTR showed pectin packaging has higher water vapor permeability than synthetic polymers. However, the presence of BA reduces WVTR of film packaging. Furthermore, antimicrobial activity of BA was evaluated through migration experiences following the Codex Alimentarius (CA) procedure. The amount of BA migrated to the food simulant was measured through UV-Vis technique at 273 nm. It was determined BA diffuses from membrane matrix to food simulant at a rate of 0.032 mg/dia. Finally, biodegradability assays were performed placing two samples of each film, PecGly and PecGlyBA, respectively, in an organic compost. Results showed a total degradation in a time lower than a week.

Conclusion

Pectin from citrus peel is a biodegradable polymer able to form resistant as well as flexible films for food packaging. Benzoic acid was used as the active component in the packaging material. It was demostrated the active component was responsible for mechanical

reinforcement, water vapor transmittion decreases as well as it diffuses to preserve fresh food.

Table 1. Properties of PecGly films at different concentration of BA

BA (%p/p)	σ (MPa)	% ε	E (MPa)	WVTR (g/m^2 day)
0	17,24	30,34	180	373
1	30,10	15,94	496	141
10	13,50	4,50	483	-
20	10,25	1,02	217	-
30	2,22	0,90	275	-

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MEMBRANE FOULING CAUSED BY FOOD GRADE EMULSIFIERS DURING PREMIX MEMBRANE EMULSIFICATION

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Many foods currently in the market are based on emulsions. Some emulsification methods used by the industry, such as mixers, require a high-energy input to produce emulsions with a high polydispersity of droplet size, which is often correlated with a poor stability of the emulsions. Others, such as high pressure homogenizers produce monodisperse emulsions at the expense of a high-energy requirement [1]. A novel technology that combines low energy inputs and production of monodisperse emulsions is membrane emulsification (ME). Moreover, ME is able to produce droplets in the micron size range using small amounts of emulsifier, which is very interesting from the manufacturer point of view [2]. ME process can be carried out either directly or in premix mode. In both systems, the final droplet size is very dependent on the flow through the membrane [3]. During premix ME the whole emulsion is pushed through the membrane pores and membrane fouling occurs, mainly when proteins are employed as emulsifiers. One of the best ways to reduce fouling in premix ME is a correct optimization of process conditions, which consists basically in applying the minimum number of cycles to obtain a monodisperse emulsion, optimize the selection of the membrane and the type and concentration of the emulsifier [4].

In this work we have produced oil-in-water (O/W) emulsions based on lemon essential oil stabilized with food-grade emulsifiers: Tween 20, whey protein isolate (WPI), sodium caseinate (NaCAS) and Arabic gum (AG) by premix membrane emulsification. The main goal of the work is to study the effect of using different emulsifiers at different concentrations in the final droplet size of the emulsion, the flux and membrane fouling. All the O/W emulsions prepared in this work had an oil (lemon essential oil) load of 20 % w/w, they were stabilized with either 1, 2 or 10% (w/w) of food grade emulsifier and produced by premix membrane emulsification. The first step of the premix ME consisted of preparing a coarse emulsion by rotor – stator. Then, the coarse emulsion underwent three cycles of emulsification through a nylon, nitrocellulose ester or inorganic membrane. Fluxes during emulsification (for nylon and nitrocellulose ester membranes) and droplet size distribution after each emulsification cycle were measured as process parameters. Emulsification using the inorganic membrane was not characterized regarding fluxes, since the rate of the process was too fast to be measured with the available equipment. Details on the membranes and process conditions are presented in Table 1.

From the results obtained in this study (Table 2), we can confirm that premix membrane emulsification produces monodisperse O/W emulsions, with span values lower than one in most of the cases. As can be seen in Table 2 the droplet size of the emulsions after three emulsification cycles depends on the type of membrane, its pore size and the type and amount of emulsifier, as reported previously by Vladisavljević et al. [5]. When proteins or Arabic gum are used to stabilize the emulsions the flux decreases after each emulsification cycle, which is attributed to fouling caused by these compounds. Fouling will reduce the size of the pores or block some of them, decreasing the flux at constant pressure. When comparing the fluxes obtained when proteins or Arabic gum are used to stabilize the emulsions with the ones obtained for Tween 20, it is clear that this emulsifier is more convenient regarding the efficiency of the process, however, the use of emulsifiers with film forming properties, like WPI, NaCAS and AG has a positive impact for the production of solid microcapsules, reducing the amount of wall building material that has to be added before drying.

Table 1. Membranes en process conditions employed.

Membrane	Pore size of the membrane (μm)	Membrane configuration	Type of membrane	Wettability	Working pressure (MPa)
Nylon	0.8	Flat	Organic	Hydrophilic	0.7
Nitrocellulose ester	0.8	Flat	Organic	Hydrophilic	0.7
Inorganic	1.0	Tubular	Inorganic	Hydrophilic	0.2

Table 2.

Membrane	Emulsifier	Emulsifier (% w/w)	Droplet size average at third premix cycle (μm)	Span at third premix cycle	Flux at third premix cycle ($kg/m^2 \cdot s$)
Nylon	Tween 20	2	1.502	0.914	25.17
	Whey Protein Isolate	1	3.237	0.739	3.92
		10	1.719	0.843	2.89
	NaCAS	1	1.945	0.788	3.01
	Arabic gum	10	4.160	0.782	1.99
Nitrocellulose ester	Tween 20	2	1.874	0.923	21.73
	Whey Protein Isolate	1	3.237	0.624	3.02
		10	2.482	0.913	2.11
	NaCAS	10	1.751	0.956	2.98
Glass	Tween 20	2	1.993	1.004	N/A

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Acknowledgements

The authors acknowledge funding from the Spanish Ministry of Economy and Competitiveness for supporting this research work (Project funding CTQ2011-22793) and Dallant S.A for providing the essential oil and technical support. Jaume Carmona thanks Universitat Rovira i Virgili for his scholarship.

FORMULACIÓN Y EXTRACCIÓN DE ÁCIDO LÁCTICO CON NIOSOMAS DE SPAN 80 MODIFICADOS CON SDS MEDIANTE MICROFILTRACIÓN

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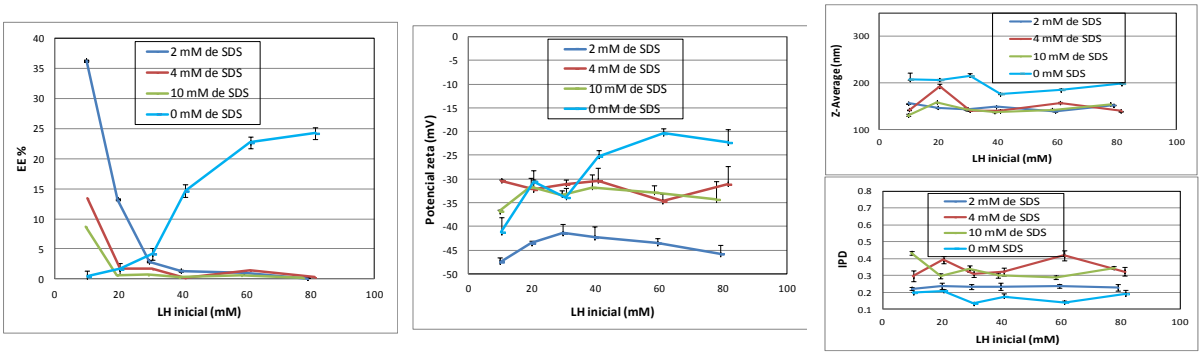
El objetivo de este trabajo es evaluar el potencial que presenta el uso de niosomas como agentes selectivos de extracción de solutos en soluciones acuosas diluidas. Los niosomas son estructuras vesiculares formadas por una o varias membranas bipolares de tensioagentes no iónicos, que contienen en su interior una cavidad acuosa interna. Por lo general, son termodinámicamente inestables y requieren el aporte de energía para su formación. Debido a su configuración, los niosomas son capaces de encapsular tanto sustancias hidrosolubles como liposolubles, por lo que son ampliamente utilizados en la industria farmacéutica, cosmética y, en menor medida, en la alimentaria. Las sustancias hidrófilas serán atrapadas en las zonas acuosas, y las lipófilas quedarán unidas a la parte hidrofóbica de la bicapa [1]. La eficacia en la encapsulación depende de diversos factores, tales como el tipo de vesícula formada (multilamelar, unilamelar o multivesicular), la longitud del grupo hidrofóbico del tensioagente que forma la bicapa, la naturaleza de la cabeza hidrófila y su tamaño, el pH y la composición del medio de formulación, y la naturaleza del soluto (hidrofobicidad, polaridad, peso molecular y solubilidad). Los métodos de formación de niosomas son muy variados y dependen fundamentalmente del soluto a encapsular [2, 3]. Los más utilizados son la hidratación de una película lipídica seca, la inversión de fases y la sonicación, que es el método utilizado en el presente trabajo.

En una primera etapa, se investigó la formulación más adecuada para la encapsulación de ácido láctico en niosomas. En este trabajo se presentan los resultados obtenidos con Span 80 (monooleato de sorbitán) como tensioagente encapsulante, SDS (dodecil sulfato sódico) como modificador de la membrana, y ácido láctico.

La aplicación de ultrasonidos se realizó utilizando un procesador ultrasónico de alta intensidad (Vibra-Cell VCX 500, Sonics & Materials Inc., USA) provisto de una sonda bicilíndrica de aleación de titanio de 3 mm de diámetro. Las condiciones de aplicación fueron 500 W, 30% de amplitud, y tiempos efectivos de 5 minutos en pulsos de 5 segundos (5 s *on* y 5 s *off*) sobre 10 mL de muestra contenida en un matraz de poliestireno de base redonda de 115 mm de altura y 29 mm de diámetro (Labbox, España). Estos tubos llevan un faldón de 1 cm sobre su base que sirvió de referencia para situar la posición de la sonda de forma homogénea en todas las experiencias. Durante la aplicación de ultrasonidos, las muestras fueron sumergidas en un baño de hielo para evitar el sobrecalentamiento. Posteriormente se centrifugaron (centrífuga Eppendorf 5804) a 9000 r.p.m. durante 45 min para eliminar las partículas sólidas desprendidas de la sonda, y el sobrenadante fue sometido a ultrafiltración centrífuga con membranas de celulosa regenerada de 10 kDa (Millipore Amicon Ultra-15), para la separación de los componentes no encapsulados.

La caracterización de los sistemas niosomales se realizó mediante medida del tamaño medio de partícula y distribución de tamaños por difracción dinámica de luz láser (DLS), y medida del potencial zeta, como principales propiedades. Para ello se utilizó un equipo Zetasizer Nano ZS (Malvern Instruments Ltd., UK). El análisis de componentes se realizó por valoración ácido-base o HPLC (Beckman System Gold) para el ácido láctico, y por el método espectrofotométrico de violeta de etilo [4] para el SDS.

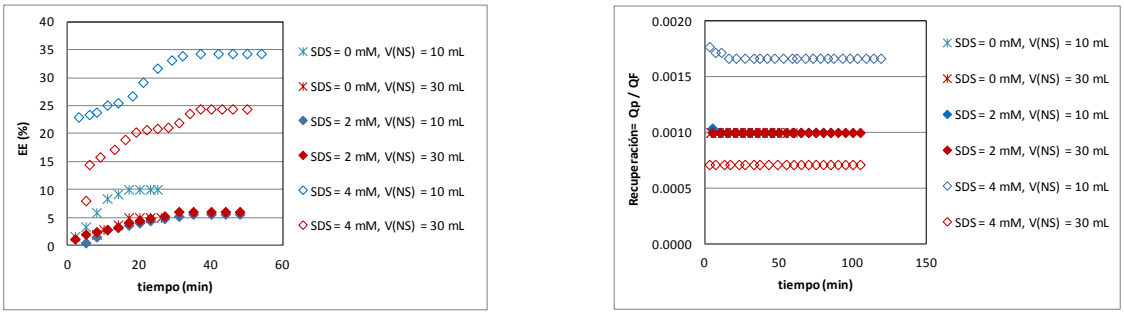
La Fig. 1 muestra que, a baja concentración de ácido láctico, las mayores eficiencias se obtuvieron con niosomas modificados con 2 mM de SDS, mientras que a concentraciones de ácido láctico superiores a 20 mM, las mayores eficiencias se obtuvieron con niosomas sin SDS. Además, el SDS aumenta la carga negativa de las partículas, principalmente en los sistemas con 2 mM de SDS, y reduce el tamaño de los niosomas por debajo de 150 nm.



a) b) c)

Figura 1. Resultados de las dispersiones niosomales en formulaciones de Span 80 (20 mM) + SDS (0, 2, 4 y 10 mM) y ácido láctico (10–80 mM): a) Eficiencia de encapsulación de ácido láctico, b) Potencial zeta y c) Tamaño medio de partícula e índice de polidispersión (IPD).

En una segunda etapa se estudió la cinética y la capacidad de extracción de ácido láctico que presentan los niosomas vacíos. Se utilizó un sistema Tami de microfiltración con membranas cerámicas planas de ZrO_2 de 0.2 μm. Inicialmente se trabajó a concentración constante, con recirculación del permeado y del retenido, al objeto de medir la cinética de extracción. Posteriormente se trabajó en modo de concentración, es decir con retirada del permeado, al objeto de analizar el flujo y la composición tras la concentración.



a) b)

Figura 2. Microfiltración extractiva de ácido láctico con niosomas de Span 80 (20 mM) y SDS (2 y 4 mM): a) Grado de encapsulación y b) Recuperación. Solución acuosa inicial: 400 mL de disolución acuosa de ácido láctico 10 mM. Volumen añadido de suspensión de niosomas: 10 mL y 30 mL. Presión transmembranal = 0.3 bar.

La Fig. 2 muestra que la cinética de encapsulación es más rápida y la capacidad de encapsulación es mayor cuando se utilizan niosomas con 4 mM de SDS. Con esta formulación los flujos de permeado fueron menores que los obtenidos con niosomas con 2 mM de SDS, como consecuencia de la mayor polarización por concentración, aunque en todos los casos el flujo permaneció constante durante la etapa de concentración.

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Agradecimientos: Este trabajo ha sido subvencionado por el Ministerio de Economía y Competitividad de España mediante el proyecto CTQ2011-25239.

Membranes for Energy Generation and CO_2 Capture

- **Oral session 14**

INTEGRATION OF MEMBRANE NEW TECHNOLOGIES FOR CO_2 REMOVAL FROM NATURAL GAS IN OFFSHORE PLATFORMS

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The use of natural gas has grown as an alternative energy source and chemical raw material due to its excellent combination of properties, price and worldwide supplies. Nevertheless, impurities such as carbon dioxide (CO_2) must be removed because they affect the heating power of natural gas. Carbon dioxide emissions have also been frequently pointed out as a major factor in the global warming. In 1991, the Norwegian government began one of the first initiatives to control CO_2 emissions by imposing fines. In the first decade, the amount paid only by the Norwegian oil companies for CO_2 emissions was equivalent to $53 per ton of CO_2 generated, motivating strong efforts for exploring new technologies for CO_2 capture [1].
Liquid absorption in packed columns is the actual conventional technology for CO_2 removal from a gas mixture. It uses liquid absorbents that preferentially remove this contaminant from the gas phase. However, problems of flooding and foaming are common, since the gas mixture is dispersed into the liquid phase to increase the contact area [2, 3]. On the other hand, membrane contactors allow the gas-liquid contact only at the membrane interface without phase dispersion, [4, 5]. In this case, the two phases flow on opposite sides of the membrane, being operated almost independently. In addition to advantages in operating conditions, the compact nature of membranes requires less physical space, reaching reductions up to 70% and 66% in size and weight, respectively, compared to conventional absorption columns [6]. The highest packing density can be obtained with membranes in hollow fibers geometry.
In this study we further examined the use of hollow fiber membranes contactors with microporous polypropylene (PP) composite polytetrafluorethylene/polyetersulphone (PTFE/PES) for CO_2 capture from a gas mixture in a lab scale system (Fig. 1 (a)).

(a) (b)

Fig. 1: Membrane contactors system (a) lab scale (b) pilot plant

The composite membranes exhibited higher efficiency than microporous membranes, as shown in Fig. 2, which was attributed to the prevention of pore wetting due to the PTFE present in the top layer of the membrane. The influence of liquid flow rate, temperature and absorbent on the CO_2 removal was investigated. A better performance of CO_2 transfer to the liquid phase was observed when a reacting absorbent (sodium hydroxide) is present, and when the feed flow rate is increased and the temperature decreased.
To further evaluate the use of the membrane contactors system in offshore platforms, a pilot plant (Fig. 1 (b)) was designed and assembled in our laboratory. Current work is focused on experiments run at conditions similar to field operating pressure, high temperature and high flow. The pilot plant also allow the recycling of the absorbent using amines with an additional membrane contactor performing a CO_2 stripping of the liquid.

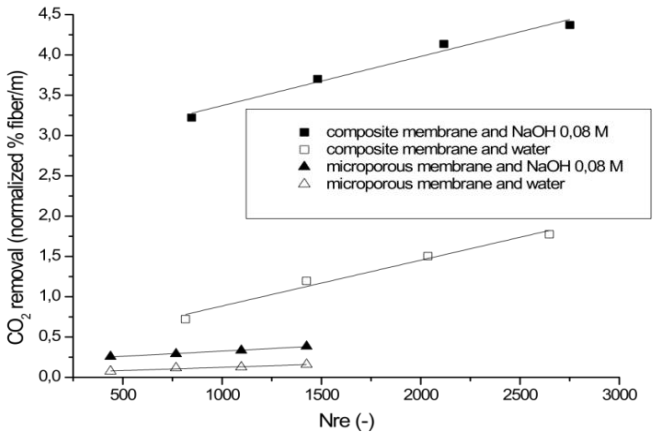

Fig. 2: Comparing the efficiency of CO_2 removal from microporous and composite membranes. Feed: 20 % v/v CO_2 and 80 % v/v N_2; Liquid pressure: 1.5 bar; gas pressure: 1 bar; gas flow: 100 mL/min; absorbent temperature: 20ºC.

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Acknowledgements

The authors would like to dedicate this paper to Professor Alberto Luiz Coimbra, in the 50th anniversary of COPPE (1963-2013), The Graduate School of Engineering of the Federal University of Rio de Janeiro.

PLAYING WITH IONIC LIQUID MIXTURES TO DESIGN MEMBRANES WITH IMPROVED CO_2 SEPARATION PERFORMANCE

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Due to environmental concerns and consequent legislative constrains, great effort has been put on the development of energy efficient processes and high selective materials to capture and separate carbon dioxide from light gases. Membrane-based technologies, in particular, supported ionic liquid membranes (SILMs) have recently attracted considerable attention not only due to the low volatility of ionic liquids (ILs) but also to their highly tunable nature, which makes them absolutely unique when compared to other conventional solvents.

In the past few years, several studies on the permeation properties of gases through SILM systems have explored the effect of the IL structure on the CO_2 separation performance of these membranes [1]. Although SILMs have shown good CO_2 separation performances, the permeability and selectivity of SILMs is not high enough for highly efficient industrial applications. In order to increase flexibility in tailoring the permeability and selectivity of SILMs for flue gas separation (CO_2/N_2), we have recently proposed the use of IL mixtures [2]. The obtained results showed that a proper balance combining both the most CO_2 selectivity and the less viscous anions is crucial to achieve improved CO_2 separation performances. These aspects motivated us to further explore the use of binary IL mixtures with specifically tailored properties as a mean to design liquid phases for preparing membranes with fine-tuned gas permeation properties and consequently enhanced CO_2 separation performances.

Several mixtures based on a common cation (1-ethyl-3-methylimidazolium) and different anions with carboxylate, sulfate, cyano, fluorinated and amine-containing groups were prepared and their CO_2 and N_2 permeation properties through SILMs were investigated. Since both the IL viscosity and molar volume impact the gas permeation properties of SILMs, the thermophysical properties of the pure ILs and their mixtures, namely viscosity and density, were also determined so that trends between the two types of properties could be evaluated. In this communication, the aim is not only to provide results for the understanding of the effect of different anion species on the CO_2 separation performance of SILMs but also show that IL mixtures is a powerful strategy to design advanced engineered liquid phases for CO_2 separation membranes.

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Acknowledgements

Liliana C. Tomé is grateful to FCT (Fundação para a Ciência e Tecnologia) for her PhD grant (SFRH/BD/72830/2010). Isabel M. Marrucho and Carmen S.R. Freire acknowledge FCT/MCTES (Portugal) for contracts under *Investigador FCT 2012*. This work was supported by FCT through the projects PTDC/QUI-QUI/121520/2010 and PTDC/EQU-FTT/1686/2012.

ZIF-BASED MIXED MATRIX MEMBRANES FOR CO_2 CAPTURE

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Membrane technologies for gas separation and purification are promise as energy efficient alternative to energy intensive distillation processes. One of the major applications includes pre- and post-combustion CO_2 capture. In pre-combustion high flux H_2 selective membranes (H_2/CO_2 mixture) are required yielding directly compressed CO_2 ready for transportation or storage.

Even though low permeable pure polymer membranes rule the commercial scene due to their easy processing and mechanical strength, there appears to be some limitations in their gas separation performance to boost the Robeson upper-bound [1]. During the last decades, several solutions have been proposed, such as the synthesis of new polymers with improved performance, the modification of the properties of existing polymers, or the fabrication of the so called mixed matrix membranes (MMMs). A MMM comprises homogeneous dispersion of filler particles in a polymeric matrix therefore combining the advents of both phases. Among the most sophisticated nanostructured fillers studied in the form of MMM are the Metal-Organic Frameworks (MOFs) [2], and in particular zeolite imidazolate frameworks (ZIFs) since they have high porosity and surface area, transition metal centers and tailored linkers combined with high thermal and chemical stabilities, and framework diversity [3]. Among them, ZIF-8 (with SOD-type zeolitic topology that contains small apertures of 3.4 Å and large pores of 11.6 Å) and ZIF-11 (with RHO-type zeolitic topology and large pores of 14.6 Å connected through pore apertures of 3 Å) would allow shape and size selective separation for H_2 (kinetic diameter of 2.9 Å) over other large molecules.

Several polymers are proposed in this work as continuous phase to prepare MMMs for pre-combustion CO_2 capture application: the commercial polyimide Matrimid® and polybenzimidadol, PBI [4] and the synthesized improved performance polymer PIM-1 (polyimides of intrinsic microporosity) [5], being excellent candidates for high temperature H_2/CO_2 separation. Those expected H_2 selective membranes will be characterized by several techniques (SEM, XRD, TGA/DSC, FTIR, etc.) and applied at moderate pressures and middle temperatures in the separation process. The latter approach induces two main advantages: i) the mixture of H_2 and CO_2 that follows typical shift reactors is already at high pressure, and ii) the selective H_2 permeable membranes can deliver CO_2 at high pressure thus reducing compression costs. Concerning temperature it is likely that the H_2/CO_2 selectivity demonstrated at 25 ºC [5] will be enhanced at the required elevated temperatures (ca. 150 ºC) due to a large reduction in CO_2 solubility that facilitates CO_2 transport at lower temperatures [6].

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Acknowledgements
The research leading to these results has received funding from the European Union Seventh Framework Programme (*FP7/2007-2013*) under *grant agreement* n° 608490, project M^4CO_2.

PREPARATION AND CHARACTERIZATION OF IONIC LIQUID-POLYMER HYBRID MEMBRANES FOR CO_2/N_2 SEPARATION

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The ability to efficiently separate CO_2 from other light gases has received a great deal attention aiming at reducing greenhouse gas emissions. Membrane technology is seen as a green efficient alternative to energy-intensive conventional CO_2 capture processes. Although polymeric membranes are already commercially available for this application, their permselectivity is still low to compete advantageously with amine scrubbing. Supported ionic liquid membranes (SILMs) using acetate-based ionic liquids as green solvents, have been studied in our laboratory, in the range 298-333 K [1], with high permeability and selectivity, but their liquid state may lack of stability in the long term. Chitosan (CS) is the second most abundant polysaccharide in nature, containing amine and hydroxyl groups in the solid polymer structure, which makes it attractive for CO_2/N_2 separation [2] but the mechanical strength is still a challenge, because the high viscosity of chitosan solutions obliges using low polymer concentration upon membrane preparation.

In this work, a new hybrid solid membrane material is prepared from pure chitosan 1.5 wt.% solution loaded with 5 wt.% 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) ionic liquid (IL). Gas permeability and solubility are evaluated in the temperature range 298-323 K, whereas diffusivity is calculated by using the solution-diffusion mechanism. The results are shown in Figure 1 in comparison with Robeson's upperbound [3]. In order to have insight on the competitiveness of the novel materials in real operation conditions, thermal and mechanical stability are evaluated. Thermal properties are investigated by TGA-DTA in a TA 60H Shimadzu thermobalance. The properties that evaluate the mechanical strength are tensile stress and strain or elongation at break, which are measured by Zwick/Roel UTM in 5 mm wide membrane strips.

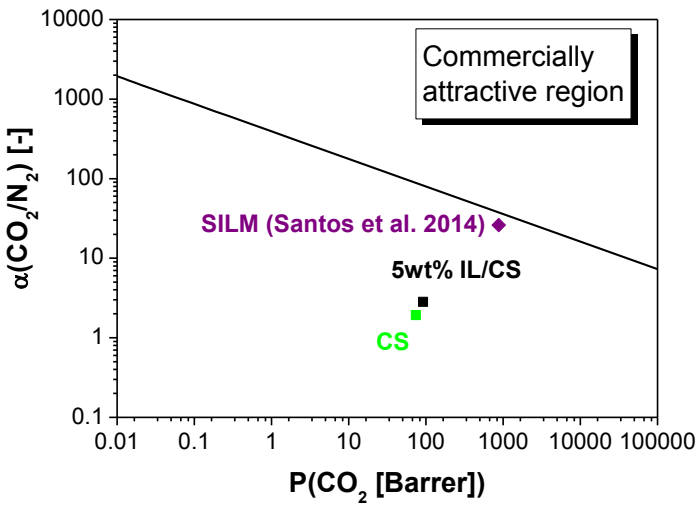

Figure 1. Robeson plot of CO_2/N_2 permselectivity through CS and IL/CS hybrid membranes.

The temperature influence in the gas permeability, solubility and diffusivity is well adjusted by Arrhenius-van't Hoff exponential relationships. Activation energies are calculated (listed on Table 2) and compared with those obtained for SILMs [1].These results show that the influence of temperature is enhanced by the presence of the ionic liquid in the membrane.

Table 2. Arrhenius parameters for CO_2 and N_2 in CS and IL/CS membranes.

Membranes	E_p (KJ/mol)		ΔHs (KJ/mol)		E_D (KJ/mol)	
	CO_2	N_2	CO_2	N_2	CO_2	N_2
CS	26.43	30.01	-31.17	-14.45	7.88	11.03
IL [1]	19.37	25.32	-8.29	-	7.91	-
IL/CS	21.37	22.45	-30.68	-18.54	5.81	9.51

An improvement in the thermal stability is observed due to the introduction of the ionic liquid in the chitosan matrix to make a hybrid IL/CS membrane. The thermal degradation is shifted to higher temperatures for the membranes as compared to the pure components as shown in Figure 2(a). The mechanical strentgh and elongation at break of the CS and IL/CS hybrid membranes are represented in Figure 2(b), revealing the higher flexibility of the hybrid membrane material due to the introduction of the IL in the hybrid membrane. The tensile stress of pure CS membranes agrees with literature [4,5].

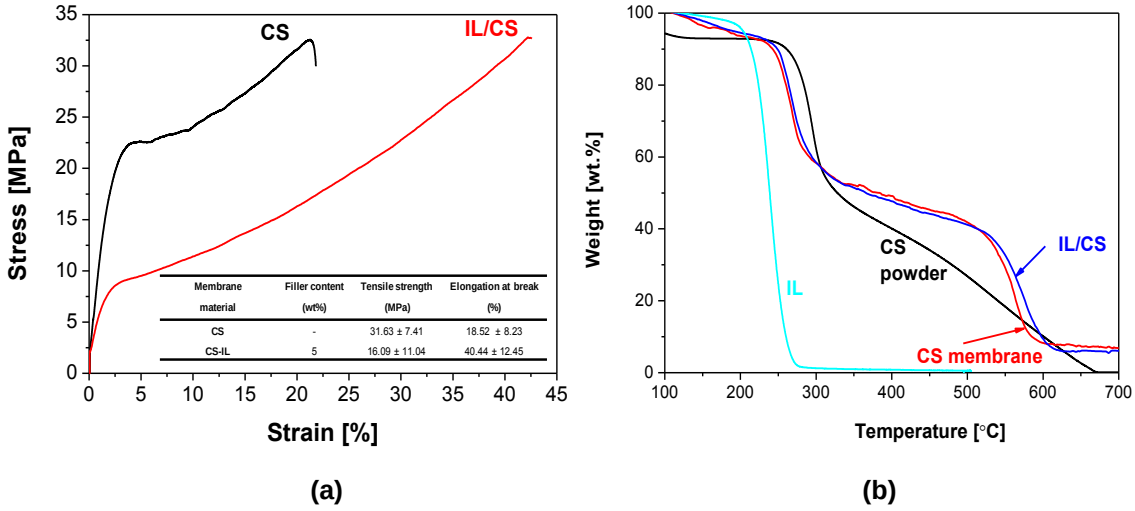

Figure 2. Mechanical (a) and thermal (b) properties of CS based membranes.

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Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) under projects ENE 2010-14828 and CTQ2012-31229, as well as Ramón y Cajal program (RYC-2011-08550) at the Universidad de Cantabria, is gratefully acknowledged.

HYDROGEN PERMEATION THROUGH $La_{5.5}WO_{11.25-\delta}$-$La_{0.87}Sr_{0.13}CrO_3$ COMPOSITES

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The lanthanum tungstate, $La_{5.5}WO_{11.25-\delta}$ (LWO), presents an important mixed electronic-proton conduction [1,2] at high temperatures in hydrogen-containing atmospheres and enough stability under atmospheres containing CO_2, H_2O and H_2S environments [3,4]. These two properties are needed in order to apply this kind of compounds in membranes for the separation of hydrogen at high temperature in processes as integrated gasification combined cycle (IGCC) and catalytic membrane reactors [5]. However, the fluxes recently obtained for this material [6] are not high enough to apply them in the abovementioned industrial processes due to the lack of electronic transport presented by LWO below 800ºC.
On the other hand, $La_{0.87}Sr_{0.13}CrO_3$ (LSC) shows high mixed ionic (protonic)-electronic conductivity in reducing atmospheres and sufficient stability in both oxidizing and reducing conditions [8,9], but its sinterability is very bad, and it is difficult to get dense membranes of this material.
This work presents the preparation, primary characterization, hydrogen permeation and stability study of $La_{5.5}WO_{11.25-\delta}$/$La_{0.87}Sr_{0.13}CrO_3$ (LWO/LSC) composites. The mixture of LWO and LSC phases in different composites allows to improve the LSC sintering behavior and to obtain compounds with high total conductivity, higher than that of LWO and LSC single phases and with sufficient protonic and electronic conductivity at low temperatures to permit both protonic and electronic percolation.
Dense membranes of LWO/LSC composites were prepared and the influence in the hydrogen permeation of composite composition, temperature, hydrogen concentration, humidification degree of the membrane, membrane thickness and catalytic layer were deeply studied.
The hydrogen permeation of the studied composites showed higher fluxes than LWO membrane and 50%-LWO/LSC composite was the best tested membrane. In Figure 1 it is plotted the hydrogen flows obtained as a function of the temperature for 50%-LWO/LSC membranes with a thickness of 370 µm and 500 µm feeding 50% H_2 with both sides of the membrane hydrated.

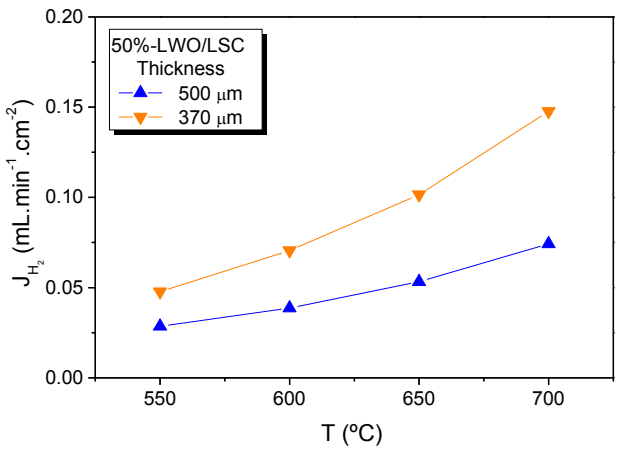

Figure 1: Hydrogen flow as function of temperature for 50%-LWO/LSC membranes with a thickness of 370 µm and 500 µm feeding 50% H_2 with both sides of the membrane hydrated.

Furthermore, hydrogen permeation measurements were performed at 850ºC using 15% CO_2 in Ar as sweep gas and 50% H_2 in helium as feed gas and humidifying both sides of the membrane. Hydrogen flow obtained under CO_2 containing atmosphere remained unchanged at least for 23 hours. This fact demonstrates the stability of the compound in these conditions.
Finally, it is remarkable that the hydrogen flows of a 370 µm thick 50%-LWO/LSC membrane (0.15 $mL \cdot min^{-1} \cdot cm^{-2}$ at 700 ºC) are the highest values reported nowadays for bulk mixed protonic electronic membranes.
For these two properties, high hydrogen permeation and CO_2 stability, LWO/LSC composites are presented as a promising candidates for hydrogen separation at high temperatures.

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Acknowledgements

Financial support by the Spanish Ministry for Science and Innovation (Grants JAE-Pre 08-0058, ENE2011-24761, CSD-2009-0050 and SEV-2012-0267) is kindly acknowledged.

PREPARACIÓN DE NUEVAS CO-POLI(BENZOXAZOL-IMIDA)S MEDIANTE TRANSPOSICIÓN TÉRMICA Y EVALUACIÓN DE SUS CAPACIDADES EN PROCESOS DE PERMEACIÓN DE GASES

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La separación de gases mediante membranas poliméricas es en la actualidad una alternativa real a los métodos de separación tradicionales como son la separación mediante absorbentes específicos o la destilación criogénica. Dentro del extenso número de familias poliméricas, las poliimidas aromáticas (PIs) presentan excepcionales capacidades para su aplicación debido fundamentalmente a sus elevadas temperaturas de transición, a sus excelentes propiedades mecánicas y a su alta productividad en procesos de permeación de gases. En particular, las PIs que contienen grupos hexafluoroisopropilideno o grupos laterales voluminosos han dado lugar a membranas con excelente balance entre selectividad y permeabilidad para diferentes parejas de gases[1].

Recientemente, la obtención de nuevos polímeros heterocíclicos mediante transposición térmica (polímeros TR) ha significado, junto con el descubrimiento de los polímeros de microporosidad intrínseca (PIMs)[2], un salto cualitativo en la separación de gases condensables como CO_2 y CH_4. Se ha comprobado que las poliimidas *orto*-hidroxiladas son capaces de transformarse en polibenzoxazoles (TR-PBOs) mediante tratamientos térmicos a alta temperatura en estado sólido [3]. En forma de filmes densos, estos nuevos polímeros son extraordinariamente eficientes en la separación de CO_2 de otros gases siendo comparables con las zeolitas y los tamices moleculares de carbón, CMS, con la ventaja de ofrecer mejores propiedades mecánicas.

En este contexto, esta investigación se ha dirigido a la preparación de nuevos polímeros TR capaces de separar gases con gran eficiencia. En particular, en este trabajo se han preparado membranas de poliimidas *orto*-hidroxiladas obtenidas a partir de la diamina 2,4-diaminofenol (2,4-DAP) y el dianhidrido 2,2-bis-hexafluoroisopropiliden-diftálico (6FDA). Esta poliimida se puede transformar en estado sólido, a temperaturas cercanas a los 450 ^{o}C, en un copolímero de poli(imida-benzoxazol) (PI-TR-DAP), *Fig. 1*, que combina las excelentes propiedades de las PIs y de los TR-PBOs para la separación de gases.

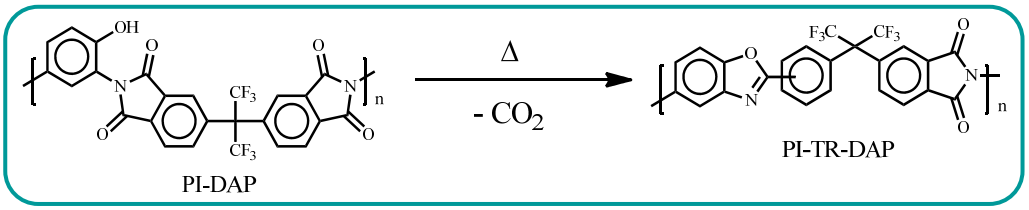

Figura 1. Conversión térmica de PI-DAP a PI-TR-DAP

La poliimida PI-DAP se preparó mediante la vía general de síntesis de poliimidas, en disolución a baja temperatura y ciclación azeotrópica, obteniéndose con alto rendimiento y elevado peso molecular. Debido a la presencia de grupos 6F y grupos hidroxilo, este polímero amida-imida aromático es soluble y se pudo procesar mediante deposición y eliminación controlada de disolvente (NMP), obteniéndose filmes de varias decenas de micras de espesor

con excelente resistencia a la tracción. Estos filmes se sometieron a un tratamiento térmico a distintas temperaturas (350-450 ^{o}C) en un horno tubular bajo atmósfera de nitrógeno (0.3 L min^{-1}) con el objeto de conseguir su conversión a PI-TR-DAP. Para cada una de las películas obtenidas, previamente caracterizadas por TGA, DSC y por ATR-FTIR, se calculó su densidad y la fracción de volumen libre (FFV) y se determinaron sus propiedades de permeación frente a diferentes gases.

Mediante *Espectroscopía de Infrarrojo ATR-FTIR* se pudieron seguir convenientemente los cambios experimentados en la composición química al calentar hasta 450 °C, *Fig. 2*. A esta temperatura las bandas características de poliimida a 1720 y 1780 cm^{-1} disminuyen de intensidad y pueden observarse nuevas bandas de absorción a 1474 cm^{-1} y 1059 cm^{-1}, que son características de polibenzoxazol.

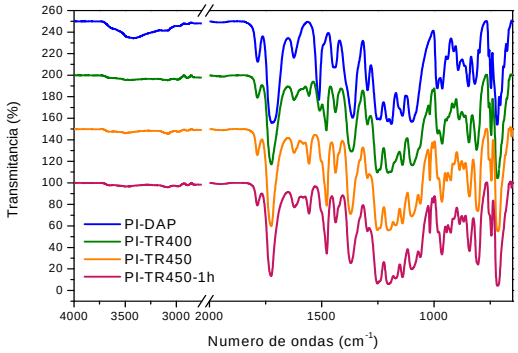

Figura 2. Espectro de Infrarrojo de PI-DAP y PI-TR-DAP.

	Permeabilidad (Barrer)					Selectividad	
	He	N_2	O_2	CH_4	CO_2	O_2/N_2	CO_2/CH_4
PI-DAP	60	0,38	2,7	0,11	10	7,2	91
PI-TR400	100	1,4	8,3	0,56	33	5,9	60
PI-TR450	170	4,8	24	2,4	100	5.0	43
PI-TR450-1h	560	28	120	17	530	4.1	31

Tabla 1. Propiedades de Separación de Gases de PI-DAP y PI-TR-DAP

Las medidas de permeación de las películas densas de PI-DAP y PI-TR-DAP, *Tabla 1*, se determinaron en un permeador barométrico de volumen constante diseñado en nuestro laboratorio a 30 °C, a una presión de alimentación de 3 bares.

En la conversión de PI a TR-PBO hay un reordenamiento para pasar de imida a benzoxazol, con pérdida de una molécula de CO_2, que produce cambios importantes en la estructura final y el ordenamiento espacial del material dando lugar a la generación de nuevos elementos de volumen libre y, consecuentemente, a un aumento de la permeabilidad de gases de la membrana de PI-TR-DAP respecto de la membrana de PI-DAP. Las membranas de PI-TR-DAP obtenidas después del tratamiento térmico más extremo (450°C) presentaron unas propiedades de separación de gases, en particular para la pareja de gases CO_2/CH_4, muy superiores a las de muchos materiales polímeros descritos en la literatura especializada, y con valores comparables a los materiales TR más recientemente obtenidos. Este hecho es importante, ya que la diamina empleada en este trabajo es mucho más barata y fácil de obtener que el monómero 2,2-bis-(3,3-diamino-4,4′-hidroxifenil) hexafluropropano, que es el monómero más utilizado hasta ahora para la obtención de TR-PBOs.

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Aknowledgements

The finantial support provided by the MICINN (MAT2010-20668/MA/2011-25513) and the CCS R&D Center funded by the Ministry of Education, Science and Technology of Korea is greatly acknowledged. Bibiana Comesaña-Gándara is endepted to the MICINN by a PhD grant associated to the project MAT2010-20668/MAT.

Membranes for Energy Generation and CO_2 Capture

- **Poster session 2**

ZEOLITE A / POLY(1-TRIMETHYLSILYL-1-PROPYNE MIXED MATRIX MEMBRANES FOR CO_2/N_2 SEPARATION

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The atmospheric concentration of greenhouse gases (GHGs) has increased significantly over the last century. Additionally, CO_2 recovery from flue gas (primarily in mixtures with N_2) is becoming more important due to global warming, and there are initiatives that might eventually require CO_2 removal from flue gas [1].

Membrane technology can offer several advantages over current techniques, such as lower energy consumption, mechanical simplicity, ease to scale up and smaller footprints for CO_2 separation from light gases [2].

There is a well-known trade-off between permeability and selectivity of polymer membranes [3]. Poly (1-trimethylsilyl-1-propyne) (PTMSP) has the highest known permeability of any polymer to gases. However, the high permeability is coupled with low ideal selectivity and its gas permeability decreases rather dramatically with time. Many attempts have been made to overcome this problem [4].Mixed-matrix membranes (MMMs) exhibit the molecular sieving effect and catalytic properties of inorganic fillers and combine desirable mechanical properties with the economical processing capacity of polymers [5]. Zeolites, crystalline alumina-silicates composed of AlO_4 and SiO_2 tetrahedra, which build up a network of channel and cavities, were the first molecular sieves used as fillers in MMMs. With extremely glassy polymers such as PTMSP, the key challenge is the adhesion between the zeolite particles and the polymer matrix. Numerous attempts have been reported to incorporate zeolite particles into polymer matrices for gas separation because of their crystalline character with well-defined pore structures and shape selectivity properties [6].

In this work, mixed matrix membranes have been prepared from PTMSP and commercial Zeolite 4A (Si/Al = 1) at different loadings of the zeolite and their performance in CO_2 / N_2 separation has been evaluated at different temperatures and using Maxwell based models to investigate the interphase between zeolite particles and the glassy polymer and take the additional transport through the MMM into account.

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Acknowledgements
Financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) under project CTQ2012-31229 and Ramón y Cajal programme (RYC-2011-08550) at the University of Cantabria is gratefully acknowledged.

Direct Osmosis Process for Power Generation using Salinity Gradient: FO/PRO Prototype Investigation using Hollow Fiber Modules

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With the exponentially growing population and the depletion of fossil fuels, water and energy have become two of the most important global resources. Both water shortages and energy crises have plagued many communities around the world. Less polluting renewable energy sources allow to reduce harmful gases emissions into the environment, promoting greater sustainability. Therefore, the development of renewable energy sources like solar energy, biodiesel, ethanol and wind power becomes a global priority. Meanwhile, attractive and innovative membrane-based technologies options such as forward osmosis (FO) and pressure retarded osmosis (PRO) processes have shown great promise in both water supply and energy production. In these processes, a net water movement occurs through a semi-permeable membrane under osmotic pressure gradient. This stream can be partially used for electric power generation.

Although this concept is quite old, the process is still facing some difficulties to be widely operationalized by lack of adequate membranes that shall make the process economically competitive

Currently, one of the few initiatives in the pilot and plant scale development of electric power generation process by direct osmosis is done by Norwegian company STATKRAFT. In Brazil, the laboratory of membranes separation processes of COPPE/UFRJ has been involved in membranes synthesis and processes researches for nearly three decades, being a national and international reference in the field. The area of phase inversion techniques for the preparation of anisotropic membranes has been one of the keys to their success.

This work consists in the production of self-supported polymeric hollow fibers membranes made of a porous support body and a top dense thin layer skin which can maximize the water flux across the membranes, maintaining a high salt rejection. These fibers must be packed in permeation modules within the flow of solutions with different salinity on both sides of the membrane generates an osmotic pressure difference which can be turned into electric power. The design and configuration of these modules is also an object of study and innovation, mainly in order to reduce hydraulic losses and to control the mass transfer. Therefore the building and testing of a FO/PRO prototype is part of this work's purpose.

Acknowledgements
We would like to thank TRACTEBEL ENERGIA for financial support.

Efficient Oxygen Production by means of Advanced Ceramic Membranes based on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

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Several mass-production processes in industrial applications use pure oxygen, with an oxygen demand of 100 million tons per year. Main industries demanding pure O_2 are steel industry (40.7%) and chemical industry (22.4%), as well as power generation plants (29.4%). There is a growing interest in the use of pure oxygen, mainly due to the benefits in the process efficiency improvement and the waste emissions minimization. Nowadays, oxygen is produced from cryogenic air distillation and swing absorption processes, the use of oxygen produced by means of these techniques is not economically viable in the most of target applications, due to huge and large energy demanding installations are needed. Oxygen separation by means of Oxygen Transport Membranes (OTM) is a relatively novel technology and it is in a good position for replacing conventional techniques, since it is possible to obtain oxygen with a high purity (near 100%) with a simple and lower energy consumption process. Moreover, it is possible to integrate OTM modules as O_2 suppliers in small and medium scale industrial processes avoiding dramatic changes in the plant configuration, particularly if good thermal integration in high-temperature industrial process is realized.

OTM are materials consisting in metallic oxides presenting Mixed Ionic-Electronic Conducting (MIEC) properties, what makes them able to be used as oxygen permeation membranes at high temperatures in the range 1000-600ºC (since oxygen can permeate through the ceramic lattice in the ionic form O^{2-}). MIEC membranes yielding higher permeation rates are those with perovskite structure.

Amongst MIEC materials, perovskite type materials such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) have become of great interest due to their high oxygen permeation fluxes and excellent stabilities when exposed to CO_2 and reducing environments, being these features very interesting for applying this material in oxycombustion and for conducting chemical reactions (e.g. partial oxidation of methane, coupling of light alkanes,…). Thus, a 30 μm supported LSCF membrane with the formula $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ has been tested determining its behavior at different pO_2, varying CO_2 content in sweep stream (0-100%) at 1000-900 ºC, and when performing catalytic activation via surface modification. All the experiments have proved the good performance and stability of LSCF membranes. High permeation fluxes were achieved, e.g., 11.87 $ml \cdot min^{-1} \cdot cm^{-2}$ at 1000 ºC and 300 $ml \cdot min^{-1}$ argon sweep when using pure oxygen as feed (Figure 1). The application of the catalytic layer improved oxygen fluxes, especially at low temperatures (below 800ºC). enhancing oxygen permeation up to ca. 300% with respect to the bare membrane at 600 ºC (Figure 2). Additional permeation tests using CO_2-rich sweep gas demonstrated the good stability and performance of these LSCF asymmetric membranes at 900 and 1000ºC (Figure 3).

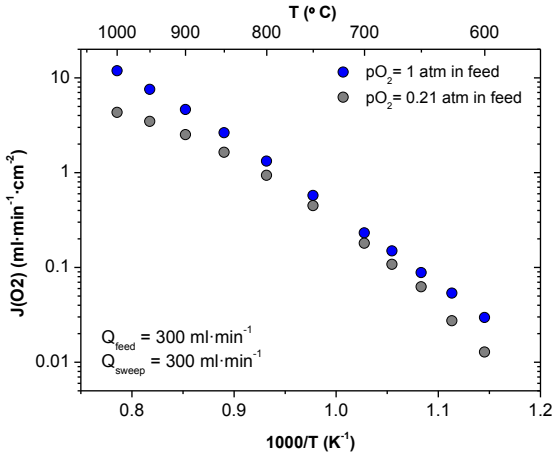

Figure 1: Temperature dependence of oxygen permeation at different pO_2 in the feed.

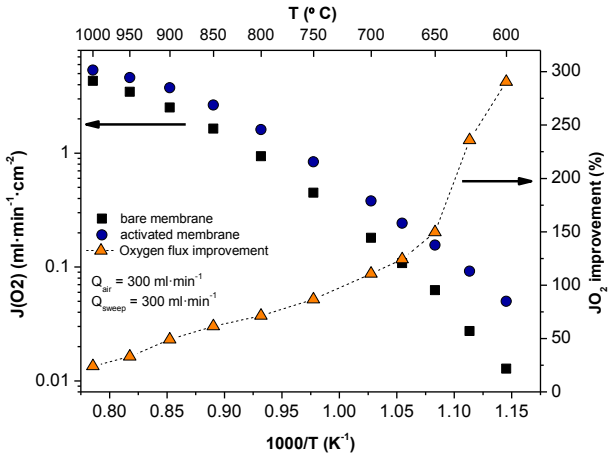

Figure 2: Evolution of oxygen permeation in dependence of temperature and catalytic activation. Oxygen flux improvement of the activated membrane with respect to the bare membrane.

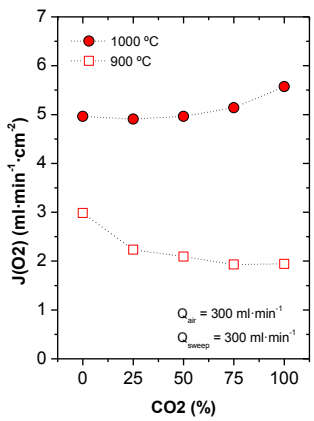

Figure 3: Oxygen permeation in dependence of CO_2 content in sweep stream at 900 and 1000ºC.

Acknowledgements
Financial support by the Spanish Government (ENE2011-24761 and SEV-2012-0267 grants) and the Helmholtz Association of German Research Centres through the Helmholtz Portfolio MEM-BRAIN is kindly acknowledged.

OPTIMIZATION OF THE ELECTROCHEMICAL PROPERTIES OF $Ln_{5.5}WO_{11.25-\delta}$ MIXED PROTON-ELECTRONIC CONDUCTING MATERIALS

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Mixed proton-electronic conductors (MPEC) based membranes enable hydrogen separation at high temperatures. MPEC materials transport protons through the crystal lattice while are charge compensated by a flux of electrons and the hydrogen separation is uniquely driven by the chemical potential gradient across the membrane.
Among the different proton conducting oxides, the tungstates ($Ln_{6-x}WO_{12-y}$) present sufficient mixed conductivity (protonic and electronic) [1,2] and they are stable in CO_2-rich and sulphur-containing environments [3,4]. These two properties present the tungstates as one of the most promising materials for hydrogen permeable membranes at high temperature.
This contribution presents a comprehensive study of the transport properties of $La_{5.5}WO_{11.25-\delta}$ and $Nd_{5.5}WO_{11.25-\delta}$ compounds and the improvement of their electrochemical properties by doping using different lanthanides and transition metals [5,6,7,8].
The evolution of the crystalline structure was followed as a function of the sintering temperature and it was observed a different evolution of the structure depending on the lanthanide and the transition metal.
The influence of the partial substitution was studied by total DC conductivity measurements at different environments, e.g., wet and dry argon, hydrogen and oxygen. Furthermore, for the understanding of the proton transport and the study of the isotopic effect, conductivity measurements were carried out in H_2/D_2 saturated with H_2O/D_2O at 25 ºC for selected sample compositions. The improvement of the total conductivity of $Nd_{5.5}WO_{11.25-\delta}$ with the increase of Mo content in the sample can be observed in Figure 1 where total conductivity for $Nd_{5.5}W_{1-x}Mo_xO_{11.25-\delta}$ compounds is plotted as a function of Mo content at 600 and 800 ºC under wet reducing atmospheres.

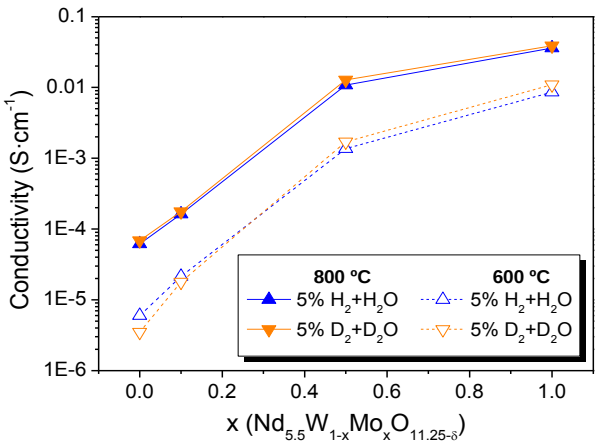

Figure 1: Total conductivity for the $Nd_{5.5}W_{1-x}Mo_xO_{11.25-\delta}$ compounds as a function of the Mo concentration at 600 and 800 ºC under wet reducing atmospheres (H_2 and D_2, both diluted in 95 % He and saturated at room temperature with H_2O and D_2O, respectively).

Thermogravimetric H_2O/D_2O uptake measurements were done on these compounds previously treated with H_2 saturated with H_2O and D_2 saturated with D_2O at 20 ºC. The uptake treatments were done at different temperature and the H_2O/D_2O incorporation in the compounds structure was studied by XRD.
In addition, the kinetics of $La_{5.5}WO_{11.25-\delta}$ and $Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$ proton conductors was studied by conductivity relaxation. Exchange and diffusion coefficients have been obtained from (1) oxidation-reduction experiments in both dry and wet oxygen; and (2) hydration-dehydration experiments in both H_2O saturated and D_2O saturated oxygen [9].
Finally, different chemical stability tests were carried out under CO_2, H_2S, CO, HCN, COS and H_2 containing atmospheres and all the studied compounds were stable and did not suffer any degradation during the treatments as it was checked by XR-diffraction.

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Acknowledgements

Financial support by the Spanish Ministry for Science and Innovation (Grants JAE-Pre 08-0058, ENE2011-24761, CSD-2009-0050 and SEV-2012-0267) and the Helmholtz Association of German Research Centres through the Helmholtz Alliance MEM-BRAIN (Initiative and Networking Fund) is kindly acknowledged.

Ultra and Microfiltration

- **Oral session 15**

EVALUATION OF DRINKING WATER QUALITY PRODUCED BY ULTRAFILTRATION MEMBRANES IN DISTRIBUTION SYSTEMS

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Membrane technology is being increasingly applied in water treatment as an alternative to conventional techniques [1]. Specifically, ultrafiltration membranes are among the most used in drinking water production because it possible to obtain a high-quality water [2] without significant clogging problems [3]. However, the quality of water obtained with this technology may decrease along the distribution system due to various factors such as the generation of disinfection by-products (DBP) [4], the development of biofilm on pipeline [5] or deposits of organic material [6].

The present study aims to evaluate the most important parameters that define the quality of water produced by ultrafiltration (UF) membranes, with or without pretreatment, in a drinking water distribution system (DWDS).

The work was carried out in a pilot scale plant capable of treating up to 1 m^3/h of low-quality surface water through a submerged spiral-wound UF membrane (TriSep corporation) with 0.03 µm pore size and 20.9 m^2 filtration area. Furthermore, the facility has a coagulation-hydraulic flocculation pretreatment (C-F) that can be coupled to the UF membrane. So, two different configurations were tested,UF membrane (without pretreatment) and coagulation-hydraulic flocculation prior to UF membrane.

The permeated water by UF membrane was passed through a DWDS, which was simulated with a 300 meters pipeline through which water flows at a minimum speed of 1 m/s by a impeller pump. This network was equipped with a post-chlorination system to maintain adequate residual chlorine dose.

Samples water from DWDS were taken and analyzed daily, as well as fragments of pipe which were taken monthly for further analysis with scanning electronic microscopy (SEM) for biofilm development analysis.

The results of the study showed that drinking water treated by UF membranes favors deposits of organic matter on the surface of the pipeline, given the high concentration of dissolved organic matter (DOM) in the circulating water. Despite this high DOM content, trihalomethanes (THM) generation was insignificant.

Regarding microbiological parameters, the water of the DWDS became practically zero values in the case of total aerobic bacterial count at 22°C and total absence of *Escherichia coli* regardless of pretreatment used, showing the effectiveness of UF membranes in bacteria retention.

The water temperature had a significant influence on the development of biofilm on the inner walls of pipeline throughout the study period, showing an exponential behavior in the bacterial count present in the biofilm.

On the other hand, C-F pretreatment was an improvement in most of the analyzed parameters in the water of DWDS regarding the first stage as the turbidity (12.6%), removal of total organic carbon (TOC) and dissolved organic carbon (DOC) (17.07% and 19.88%,

respectively) and SUVA index (18.5%). The decrease of SUVA meant a decreased risk of generation of DBP, as reflected in the decline of THM (31.27%) in this period. Also a slight decrease in pH was observed due to the effect of the coagulant ($FeCl_3$).

Water quality in DWDS treated with UF membranes meets the quality standards established by legislation even without pretreatment, although it improves the quality of this water.

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This study was supported by the Spanish Department of Science and Innovation (CTM2010-18899-TECNO). It was conducted at the Institute of Water Research (University of Granada) and Parque de las Ciencias of Granada (Spain) with the collaboration of CADAGUA S.A.

EFFECT OF DIFFERENT ADDITIVES ON THE FABRICATION OF HYDROPHILIC POLYSULFONE ULTRAFILTRATION MEMBRANES

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Abstract

In the present work the effect of the concentration of different additives (PVP and LiCl) as well as polymer concentration, on the final characteristics of the different polysulfone flat ultrafiltration membranes were evaluated. Different ultrafiltration membranes were prepared by phase inversion process using N-methyl-2-pyrrolidone as solvent (Figure 1). Fabricated membranes were characterized by water permeability, atomic force microscopy (AFM) (Figure 2) and molecular weight cut-off (MWCO). Molecular weight cut-off of the membranes was determined using dextrans of average molecular weight of 15-20, 70 and 148 kDa were used. Obtained results are shown in Table 1. The thickness of the membranes was also measured.

In an organic composite membrane manufacture process via phase inversion, the characteristics of the membranes depend on the used components [1, 2]. These compounds are classified in three groups: polymer, additives and solvent. In this work, polysulfone was used as polymer. This polymer is commonly used for membrane casting due to its thermal and chemical stability and mechanical strength [3], However, these membranes have the disadvantage of being hydrophobic in nature, as it is proved that hydrophobic membranes are more prone to foul than hydrophilic ones [4]. Nevertheless, this problem can be reduced by adding some hydrophilic functional polymers in order to increase the hydrophilicity of this kind of membranes [5, 6]. Moreover, it is necessary to add other additives to minimize macrovoid formation and increase mechanical stability of the membrane [7, 8]. Therefore, the aim of the additives is to improve membrane properties. In this case, polyvinylpyrrolidone and lithium chloride were used to hydrophilize the hydrophobic membrane and maintain a narrow pore size distribution on the membrane, respectively.

M1.1	M1.2	M1.3
18% PS	18% PS	18% PS
4% PVP	2% PVP	0% PVP
0% LiCl	2% LiCl	4% LiCl
78% NMP	78% NMP	78% NMP
M2.1	**M2.2**	**M2.3**
20% PS	20% PS	20% PS
4% PVP	2% PVP	0% PVP
0% LiCl	2% LiCl	4% LiCl
76% NMP	76% NMP	76% NMP

M2.1	M2.3
20% PS	20% PS
4% PVP	0% PVP
0% LiCl	4% LiCl
76% NMP	76% NMP
M2.4	**M2.5**
20% PS	20% PS
4% PVP	2% PVP
2% LiCl	4% LiCl
74% NMP	74% NMP

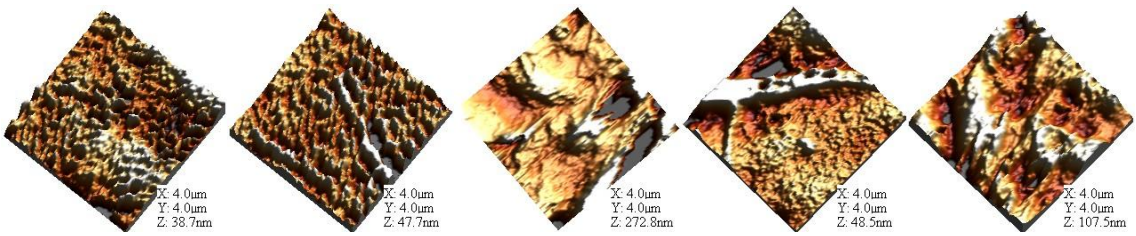
M3.1	M3.2
14% PS	22% PS
4% PVP	0% PVP
4% LiCl	0% LiCl
78% NMP	78% NMP

Figure 1. Casting solution composition of the different prepared experimental matrixes (varying polymer and additives concentration).

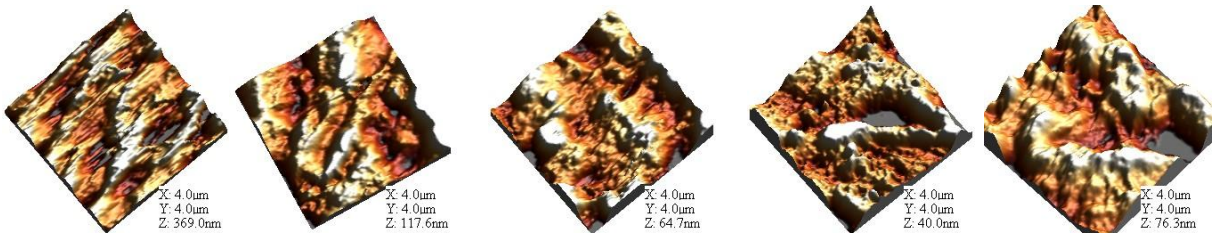
Table 1. Intrinsic permeability and molecular weight cut-off of the different fabricated membranes

Membrane	Membrane composition	Permeability, L/hm²bar	Molecular weight cut-off, MWCO, kDa
M1.1	18% PS/NMP, 4% PVP, 0% LiCl	1.976*TMP + 0.038	MWCO > 148
M1.2	18% PS/NMP, 2% PVP, 2% LiCl	1.575*TMP + 0.149	MWCO > 148
M1.3	18% PS/NMP, 0% PVP, 4% LiCl	0.319*TMP + 0.041	MWCO > 148
M2.1	20% PS/NMP, 4% PVP, 0% LiCl	0.788*TMP + 0.056	70 < MWCO < 148
M2.2	20% PS/NMP, 2% PVP, 2% LiCl	0.219*TMP + 0.327	MWCO < 15-20
M2.3	20% PS/NMP, 0% PVP, 4% LiCl	-*	-
M2.4	20% PS/NMP, 4% PVP, 2% LiCl	0.772*TMP + 0.116	MWCO > 148
M2.5	20% PS/NMP, 2% PVP, 4% LiCl	-*	70 < MWCO < 148
M3.1	14% PS/NMP, 4% PVP, 4% LiCl	1.705*TMP + 0.493	MWCO > 148
M3.2	22% PS/NMP, 0% PVP, 0% LiCl	0.027*TMP + 0.007	15-20 < MWCO < 70

* The permeate flux was negligible at pressure of 2 bar.



M1.1: 18% PS/NMP 4% PVP 0% LiCl. **M1.2:** 18% PS/NMP 2% PVP 2% LiCl **M1.3:** 18% PS/NMP 0% PVP 4% LiCl **M2.1:** 20% PS/NMP 4% PVP 0% LiCl. **M2.2:** 20% PS/NMP 2% PVP 2% LiCl



M2.3: 20% PS/NMP 0% PVP 4% LiCl | **M2.4:** 20% PS/NMP 4% PVP 2% LiCl. | **M2.5:** 20% PS/NMP 2% PVP 4% LiCl | **M3.1:** 14% PS/NMP 4% PVP 4% LiCl. | **M3.2:** 22% PS/NMP 0% PVP 0% LiCl

Figure 2. AFM images of the obtained polymeric membranes

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Acknowledgements

We would like to express our appreciation to Lati Ibérica, S.L. and Ahlstrom MT for the disinterested supply of samples.

EVALUATION OF THE MEMBRANE FOULING IN THE SEPARATION OF BOVINE SERUM ALBUMIN AND LACTOFERRIN MIXTURES BY ULTRAFILTRATION

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Abstract

Separation processes using filtration membranes are increasingly important in a number of industrial applications, such as water treatment, biotechnology, food and dairy and pharmaceutical processes. The nature of separation processes and the presence of suspended particles in contact with the membrane surface produce undesirable fouling [1]. Fouling translates into pore blockage, a decline in flux, and modifications to the membrane surface properties [2]. This results in an increase of maintenance and operational cost, being the major obstacle to the wide application of membrane separation process.

Generally in filtration processes two types of fouling are distinguished [3]. The first one, the static fouling or adhesive fouling, is due to the macromolecule absorption that occurs even in the absence of filtration. It refers to the specific intermolecular interactions between the particles and the membrane and is often irreversible. Some of the mechanisms of this adhesive fouling are hydrogen bonding, hydrophobic interactions, van der Waals interaction and extracellular macromolecular interactions [4].The second type is the dynamic fouling, known as filtration-induced macrosolute or particle deposition and is usually reversible, nonadhesive fouling where the accumulation of rejected particles on the top of the surface membrane is prominent (cake formation) [5].

Over the last few years a big effort has been made to control or eliminate membrane fouling, including fabrication of antifouling membranes the use of shear-enhanced process and pretreatment of the feed solutions. In this work we analyse experimentally the membrane fouling in the separation of a protein mixture constituted of Bovine serum albumin, BSA, and Lactoferrin, LF [6] through the determination of protein adsorption on the membrane and the zeta potential of the membranes before and after use. The dynamic fouling experimental results were compared with theoretical predictions in which the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory was used to calculate the foulant–membrane physicochemical interaction forces. Both proteins were adsorbed onto the membrane surface and the main fouling mechanism was identified as adsorptive; additionally it was assessed that for the positively charged membrane and at a working pH of 5.0 up to 70% of the fouling could be reversed whereas fouling could be almost completely reversed for the negatively charged membrane at pH 9.0 .

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Acknowledgements

This work has been financially supported by projects CTQ2011-25262, CTM2011-23912 and CTQ2012-31639 (co-financed by ERDF Funds).

CONCENTRATION OF VINASSE BY MICROFILTRATION: BENCH AND PILOT SCALE

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Introduction

The vinasse is an effluent of the distillation of fermented juice or molasses from sugarcane in ethanol production, which is characterized by high concentration of organic matter, low pH and high levels of suspended solids and nutrients [1]. It is estimated that 15 liters of this residue is generated per liter of alcohol produced. In Brazil, the disposal of this effluent is done by fertigation; however, when this technique is not performed correctly it results in several environmental problems [2]. An alternative is vinasse concentration previous to its reuse as a fertilizer, which brings advantages as greater product stability and reduced volume. Membrane separation processes present high potential for this aplication since, in addition to nutrients concentration in retentate, it can also generate a permeate suitable for reuse after other biological post-treatment for organic load reduction. Thus, the aim of this study was to evaluate the use microfiltration for vinasse concentration. Tests were done in both bench and pilot scale.

Methods

Vinasse used throughout this study was collected in the alcohol distillery Irmãos Malosso located in Itápolis, Brazil. Submerged hollow fiber microfiltration modules (polyetherimide, average pore size of 0.40µm, 0.02 m² in bench scale and 3.50 m² in pilot scale), supplied by Pam Membranas Seletivas Ltda (Rio de Janeiro, Brazil), were used for vinasse concentration. In bench scale tests, the profile of permeate flux over time was evaluated for three different pairs of operational conditions (MF of raw vinasse and of vinasse after pH adjustment, with and without backwash, and with aeration by aerators positioned beneath the module and by small roles among membranes fibers). The ideal recovery rate was also evaluated. These experiments were performance using pressure of 0.2 bar. Pilot scale tests were performed using pressure of 0.1 bar. The trials consisted in monitoring permeate flux over time for three different aeration flows: 0, 15 and 30 m^3_{air}/h, which corresponded to approximately 0.0, 1.1 and 2.1 $m^3_{air}/h.m^2_{membrane}$.Feed, permeate and retentate chemical oxidation demand (COD) were determined for bench and pilot MF.

Results

Bench scale

It was evaluated the performance of the MF of the raw vinasse (pH 4.7) and of the effluent after pH adjustment (pH 7) (Figure 1-a). It may be noted that fouling at pH 7.0 was superior due to lower permeate flux. From Figure 1-b it can be observed that the use of the backwash (15 seconds of backwash after each 15 minutes of filtration) increased average permeate flux from 20 to 24 L/h.m². The production of permeate during operation without backwash was 480 L/d and with backwash it was 560 L/d, indicating an increase in productivity.

Normally, submerged membrane aeration is accomplished through the placement of aerators beneath the modules. In this study, a membrane module, which has small holes in its base for aeration among the membrane fibers, was tested and the performances of the two types

of aeration (beneath the module and among the fibers) were compared. One can see that the permeate flux is higher when aeration among the fibers is applied.

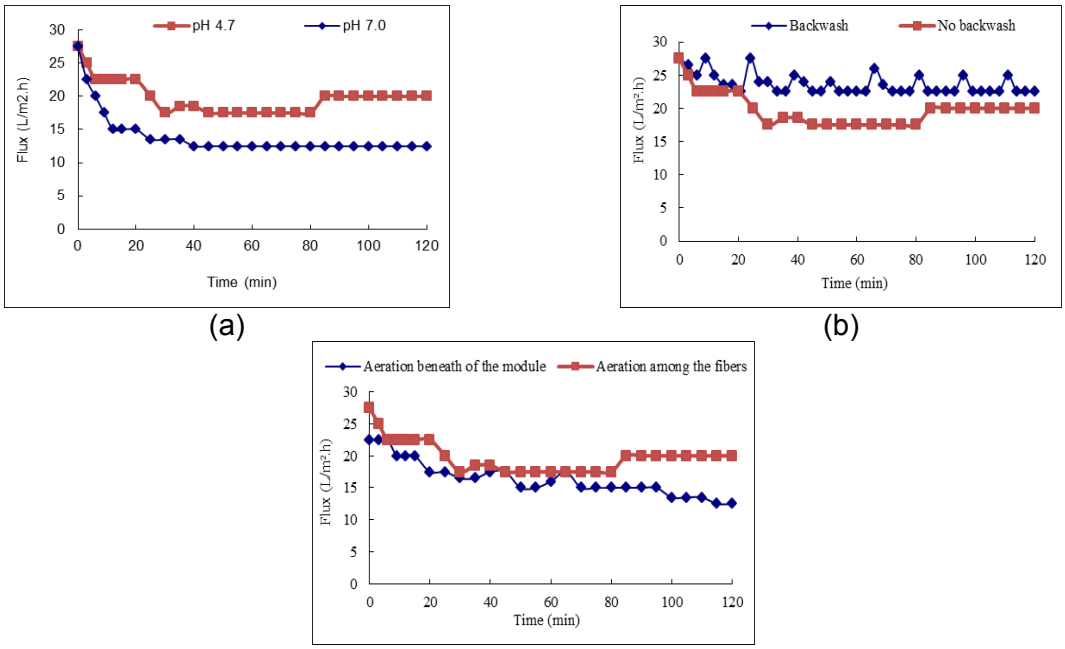

Figure 1. Permeate flux versus time (bench scale)

For assessment of recovery rate, the system was operated in fed-batch until obtaining a final retentate volume of 2L from an effluent initial volume of 26 L, thereby presenting a recovery rate of 93%. The permeate flux decreased 53% during the first 4 hours of operation. After this decay, the flow stabilized at values around 7 L/h.m² corresponding to a permeability of 20 L/h.m².bar.

Pilot scale

In pilot scale trials, three aeration flow rates were evaluated. The best result was obtained for the largest aeration flow rate, which allowed higher permeabilities and lower rate of permeate flux decay. For aeration flow of 30 m³/h, it was possible to operate the system for more than 300 hours without any chemical cleaning.

Bench scale MF showed 60% retention efficiency for COD, while in pilot scale it was only 33% (Table 1). These differences may be related to changes in vinasse characteristics and changes inherent in the scale up of bench scale process to pilot scale, such as alterations in hydrodynamic conditions, temperature, etc.

Table 1. COD concentrations in feed, permeate and retentate of MF.

	Bench scale			Pilot scale		
	Feed	Permeate	Retentate	Feed	Permeate	Retentate
COD (mg/L)	19,921	8,063	24,032	34,594	23,031	37,313

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SEPARATION OF CYCLODEXTRINS BY COMPLEXATION ULTRAFILTRATION

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α-, β- and γ-Cyclodextrins (CDs) are cyclic oligosaccharides composed respectively of 6, 7 and 8 glucose units. They are produced in mixture by enzymatic degradation of starch by an enzyme called CycloglucanoTransferase (CGTase). CDs have an hydrophobic inner cavity which allow them to form inclusion complexes with many hydrophobic compounds. Thanks to their complexing properties, they are very used in different industries [1].

Actually, CDs are separated from the reactionnel mixture by selective precipitation which requires the use of organic solvent. Our work aims at designing a new process enabling purifying α- and β-CD mixtures by membrane process which is an environmental friendly process. As α- and β-CD have similar sizes, the strategy has been to conduct a selective complexation of β-CD using Igepal Co 890 as complexing agent [2] to increase artificially the size of the β-CDs and then continue the operation by UltraFiltration of the mixture. The effects of experimental conditions (as UF MWCO, pressure, Igepal/β-CD molar ratio or α-CD/β-CD mass proportion) on the selective separation of α and β-CD were studied. The results indicate that the studied parameters have an influence on the separation efficiency and in particular conditions the separation factor between the two CDs can increase from 1.5 to 68.

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Ultra and Microfiltration

- **Poster session 2**

HIFH FLUX MICROFILTRATION MEMBRANES WITH SILVER NANOPARTICLES FOR WATER DISINFECTION

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Microfiltration (MF) processes show a growing market for water disinfection, being estimated in 1.6 billions of dollars in 2013, and expected to grow up to 1.8 billions of dollars in 2015 [1]. However, this process is limited by fouling and biofouling of the membrane, which reduces the permeate flux. New membranes with higher resistance to flux decline are a growing area of research and investment. Nanotechnology is one of the main approaches to develop membranes with unique surface properties. For instance, the use of silver nanoparticles (AgNps) can reduce microorganism growth and, consequently, the membrane biofouling. Furthermore, presence of AgNps in MF membranes improves disinfection of the permeate, allowing the use of membranes with high porosity and permeabilities.

In the most accept mechanism for water disinfection, silver ions interact with thiol groups in proteins, resulting in inactivation of enzymes and leading to the production of reactive oxygen species. It was also shown that AgNps prevent DNA replication and affect the structure and permeability of the cell membrane [2]. In the other hand, no evidence has been found on toxicity of AgNps for human [3].

This work synthesized silver nanoparticles by chemical reduction of silver nitrate ($AgNO_3$) in aqueous solution using polyvinylpirrolidone (PVP) as reduction and stabilizer agent. The MF membranes were prepared by inversion phase technique using PVP, polyethersulfone (PES) and dimethylacetamide (DMAc). The AgNps were incorporated in the microfiltration membranes and the resulting membrane was used for water disinfection. The MF-AgNps membranes were characterized by scanning electron microscopy with X-Ray microanalysis.

Membranes with different pore size and porosity were selected and the presence of silver in the transversal section was confirmed. The antibacterial properties were analyzed against *Pseudomonas fluorenscens* by the inhibition zone method after 24 and 96 hours of incubation and the bacterial count method.

It was observed an inhibition ring of 20-30% of the sample diameter only around the membranes containing AgNps, indicating the suppression of microorganism activity nearby the membrane.

The permeate was analyzed using Coliert methodology to count the total coliforms. The coliform retention was 99,9% and 99,999% for membranes without and with AgNps,

respectively. These results confirm the bactericide properties of the MF-AgNps membranes and the great potential to application for water treatment.

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SALINE CLEANING OF TWO POLYMERIC ULTRAFILTRATION MEMBRANES FOULED WITH WHEY MODEL SOLUTIONS

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In the dairy industries, ultrafiltration (UF) is one of the most used membrane processes. Cleaning of these membranes is a key step in the production process to remove fouling deposits from the membrane surface or inside its pores and to recover the permeability and selectivity of the membrane. These cleaning procedures need to be carried out up to once a day [1]. For that reason, research is mostly focused on selecting the best cleaning agent to avoid membrane damage and the optimal operating conditions to reduce costs [2]. On the other hand, some authors reported the capability of several anions and cations to increase protein solubility (salting-in effects) [3].

The aim of this work is to analyze the effectiveness of NaCl solutions to clean two polymeric UF membranes. The effect of experimental cleaning conditions (temperature, NaCl concentration and crossflow velocity) on the hydraulic cleaning efficiency (HCE) was investigated.

Experiments were performed in an UF pilot plant using two flat-sheet polymeric membranes (Microdyn Nadir, Germany) of polyethersulfone (PES) and permanently hydrophilic polyethersulfone (PESH) with molecular weight cut-offs (MWCOs) of 5 and 30 kDa, respectively. Two different whey model solutions that contained BSA (1 % w/w) and BSA (1 % w/w) and $CaCl_2$ (0.06 % w/w in calcium) were used as feed solutions during the fouling step, which was performed at 2 bar, 2 m/s and 25 ºC. After the fouling and rinsing steps, a cleaning step was carried out at a transmembrane pressure of 1 bar and different experimental conditions of temperature, NaCl concentration and crossflow velocity. When the initial permeation conditions of the membranes were not achieved after the cleaning process, chemical cleaning with NaOH at a pH of 11 was performed.

Figs. 1-3 show the influence of NaCl concentration, temperature and crossflow velocity, respectively, on the HCE. As it can be observed, HCE increased as NaCl concentration increased up to an optimal value. However, a further increase in NaCl concentration did not result in an increase in HCE. Low salt concentrations favor the salting-in effects because the surface tension is lower [3]. In addition, when salt concentration increases up to the optimal value, accumulation of salt molecules on the membrane surface and inside its pores may occur and thus, fouling and cleaning mechanisms may become competitive [2]. Calcium is one of the most salting-out cations and it acts as crosslinking agent between proteins. Thus, cleaning of membranes fouled with BSA and $CaCl_2$ solutions is more difficult and higher NaCl concentration is needed, as it can be noticed from Fig. 1. From Figs. 2 and 3 it can be observed that HCE increased as temperature and crossflow velocity increased. An increase in temperature results in a decrease in the surface tension of the cleaning solution and in an increase in protein solubility [3]. An increase in crossflow velocity favors the removal of fouling deposits from the membrane surface due to the higher shear stress caused [4]. NaCl solutions were able to clean the polymeric membranes tested when BSA and BSA and $CaCl_2$ solutions were used as feed solutions.

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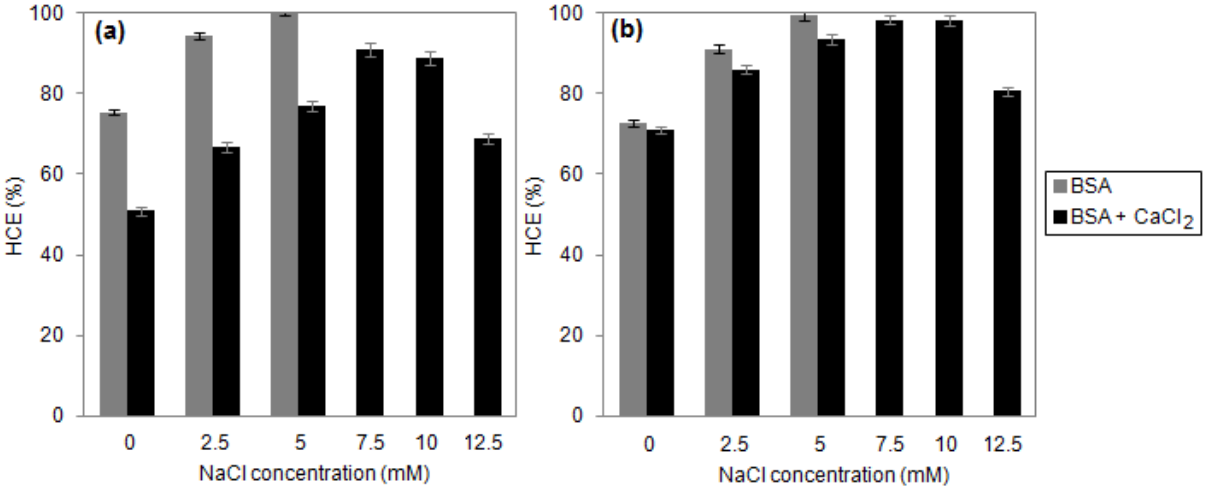

Fig. 1. Effect of NaCl concentration on the HCE for (a) 5 kDa membrane and (b) 30 kDa membrane when the cleaning solution temperature was 50 ºC and crossflow velocity was 2.18 m/s.

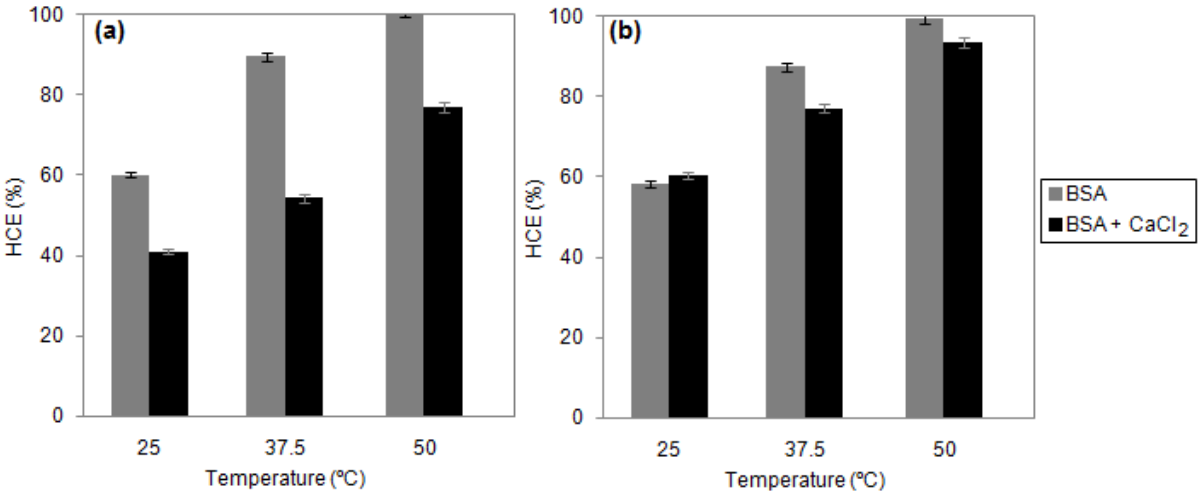

Fig. 2. Effect of temperature on the HCE for (a) 5 kDa membrane and (b) 30 kDa membrane when NaCl concentration was 5 mM and crossflow velocity was 2.18 m/s.

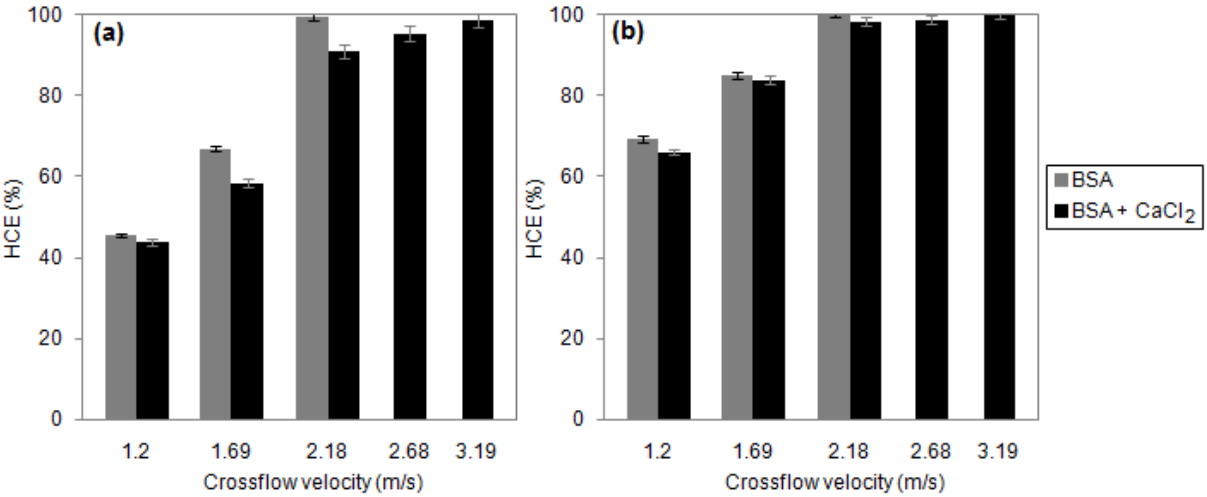

Fig. 3. Effect of crossflow velocity on the HCE for (a) 5 kDa membrane and (b) 30 kDa membrane (temperatures and NaCl concentrations were 5 mM and 50 ºC for BSA and 7.5 mM and 50 ºC for BSA and $CaCl_2$ solutions).

Acknowledgements
The authors of this work wish to gratefully acknowledge the financial support from the Spanish Ministry of Science and Innovation through the project CTM2010-20186.

CLEANING OF ULTRAFILTRATION MEMBRANES FOULED WITH WHEY PROTEINS WITH TENSIOACTIVE AND ULTRASOUNDS

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Introduction

Membrane processes are considered an excellent technology for many industrial applications. Within the dairy industry, ultrafiltration (UF) is widely used for purifying and concentrating macromolecular (10^3 - 10^6 Da) solutions, especially protein solutions.

However, the major disadvantage of their application is that permeate flux declines as a consequence of membrane fouling. In the dairy industry, the main components which cause membrane fouling are proteins and ions, mainly calcium and phosphorous [1]. Proteins are adsorbed onto the membrane surface and they cause internal pore blockage [2]. Thus, the cleaning of the membrane is a key factor on the overall process efficiency.

This work is focused on comparing the membrane cleaning with a tensioactive with and without ultrasounds (US) application. In addition, the influence of the operating conditions of the chemical cleaning process on membrane performance was studied.

Methods

A UF Minipilot plant (Orelis, France) was used in this study. The membrane module employed was a Rayflow flat sheet module from ORELIS (France) with capacity for two membranes of 100 cm^2 for each, working by cross-flow filtration mode and operating in series.

The membranes tested in this study were two organic membranes from Microdyn Nadir. One of them was a hydrophilic polyethersulfone (PESH) membrane with a molecular weight cut-off of 30 kDa (membrane UH030) and the other one was a polyethersulfone (PES) membrane with a molecular weight cut-off of 5 kDa (membrane UP005).

A whey protein concentrate solution was chosen for the fouling. The whey powder (Reny Picot, Spain) was employed with a concentration of 1% w/w in proteins.

The membrane fouling tests were carried out at 25 ºC and transmembrane pressure of 2 bar. After the fouling test, the cleaning procedure included: a rinsing step with distilled water, a chemical cleaning step (with P3 Ultrasil 115 solution, at 1 bar and for 30 min), and a final rinsing step. Chemical cleaning conditions were varied between 0.5% v/v and 0.9% v/v and between 25ºC and 45ºC for concentration and temperature of the P3 Ultrasil 115 respectively. The properties of the US waves were a frequency of 20.5 kHz and a nominal power of 300 W.

Permeability recovery higher than 95% after each test was required before beginning the following experiment.

Results

Results showed that for almost every test using US slightly higher cleaning efficiency values than those achieved without ultrasounds application at the same cleaning conditions were obtained. For tests carried out with US, the highest cleaning efficiency value (100% and 99.61% for membranes UH030 and UP005, respectively) for both membranes was achieved at temperature of 45ºC and concentration of P3 Ultrasil 115 of 0.9% v/v. On the other hand, for tests carried out without US, the highest cleaning efficiency value (96.64% and 96.44% for membranes UH030 and UP005 respectively) was achieved at 45ºC and 35ºC for membranes UH030 and UP005 respectively and at concentration of 0.7% v/v for both membranes.

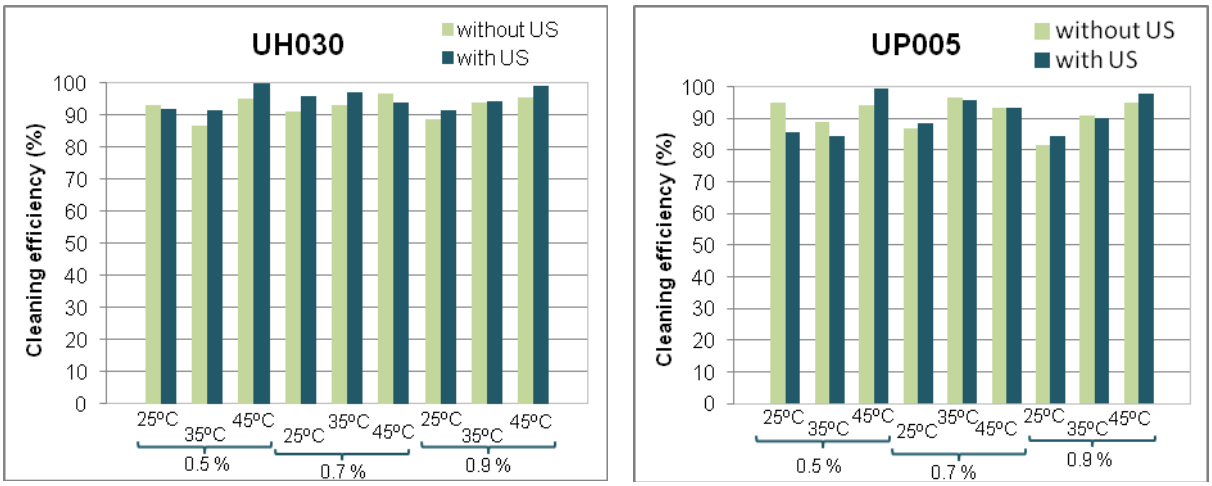

Figure 1: Cleaning efficiency for membrane UH030 and UP005.

Conclusion

Experimental results from this work showed slight improvements of the cleaning efficiency using US in the cleaning process. However, no more significant differences were obtained with and without US because cleaning efficiency with Ultrasil in general is very high for both membranes. It can be concluded that US is a promising technique when the chemical cleaning is not good enough for membrane permeability recovery.

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This research was supported by the Spanish Ministry of Science and Innovation (CTM 2010-20.186).

ULTRAFILTRATION FOULING TREND SIMULATION OF A MUNICIPAL WASTEWATER TREATMENT PLANT EFFLUENT WITH MODEL WASTEWATER

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In some applications, such as agriculture, the quality of the secondary treatment effluent (STE) from a Municipal Wastewater Treatment Plant (MWTP) is not good enough and it is necessary to perform a tertiary treatment. Among tertiary treatment technologies, ultrafiltration (UF) has been proven to be a reliable reclamation process.

UF processes have an important disadvantage: membrane fouling. Fouling causes a decline in permeate flux with time and increases the operational costs. Fouling mechanisms knowledge is a key step to achieve fouling minimization. As STEs from MWTPs contain a large amount of different compounds, the use of a simplified model wastewater consisting of only few compounds may help to understand the fouling mechanisms occurring during UF. It will also provide the scenario to study individual contribution of each type of fouling agent to membrane flux decline. The aim of this work is to prepare a model wastewater that could mimic the fouling trend of MWTP.

The main components responsible for UF membrane fouling with a STE of a MWTP are extracellular polymeric substances (EPS). EPS are mainly composed of proteins and polysaccharides [1], thus these components are commonly used to prepare model wastewaters.

The proteins used were whey protein concentrate (WPC) 45% and bovine serum albumin (BSA). The carbohydrates used were dextran and xanthan. BSA and dextran mixtures were used by Zator [2] and Xiaou [3]. Also xanthan was used as a model foulant by Nataraj [1] and WPC was studied by Omprakash [4].

The membrane used in the UF tests was UFCM5 Norit X-flow® hollow fiber. This membrane has hydrophilic properties. It is made of a blend of PES/PVP, and it has 200 KDa of MWCO and 1.5 mm of diameter. Its configuration is inside-out.

Different concentrations and combinations of proteins and carbohydrates were used to prepare simulated wastewater. In order to select the most appropriate model wastewater, three parameters were determined. These parameters were protein and carbohydrates concentration and chemical oxygen demand (COD). The composition of wastewater to be mimicked was 16.48 mg/l of proteins, 7.32 mg/l of carbohydrates. Its COD was 39 mg/l.

The variation of the permeate flux with the time was studied for both the simulated solutions and the secondary effluent. Thus, their fouling trends were compared in Figure 1. Figure 1 shows that the initial flux decay was sharper when increasing WPC concentration, whereas the steady state permeate flux remained almost constant. However, dextrans seemed to exert more influence on long term membrane fouling than the WPC did at the concentrations tested. The combination of WPC with dextran almost reproduced STE fouling trend. The model wastewater that represented the best the fouling trend of the STE had a composition of 15 mg/l of BSA and 5.5 mg/l of dextran. For this model solution the DQO was determined and its value was 27 mg/l.

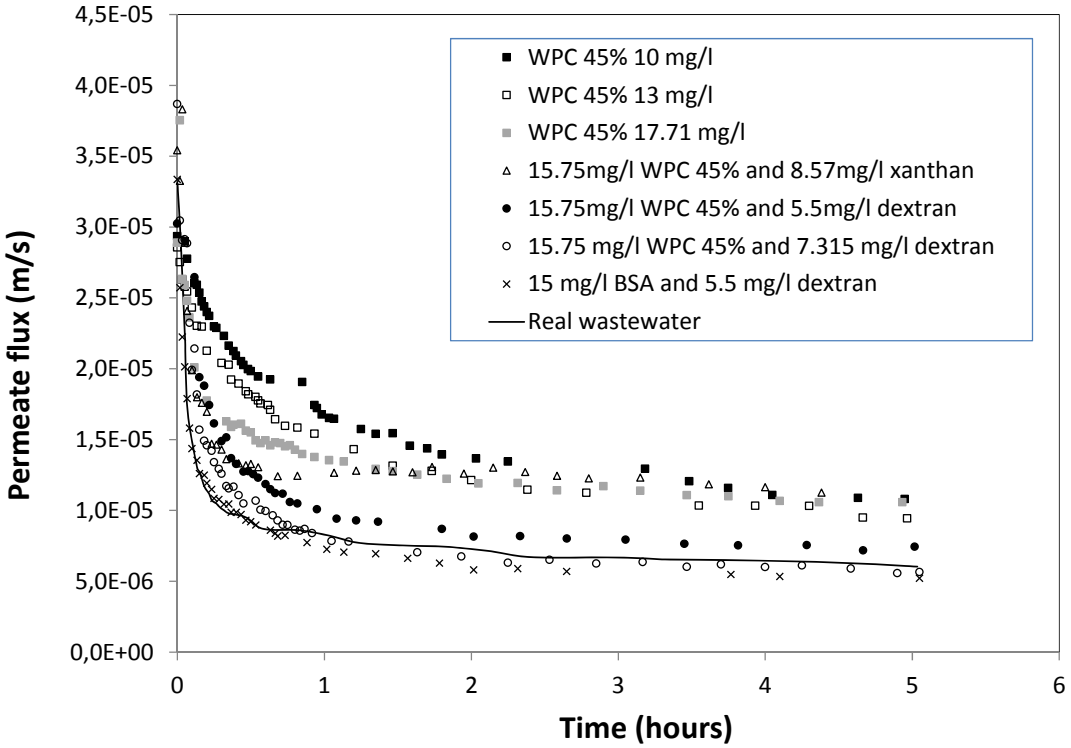

Figure 1. Ultrafiltration fouling trend for different simulated wastewaters and a secondary wastewater effluent from Municipal Wastewater Treatment Plant (Transmembrane pressure = 0.7 MPa and Crossflow velocity = 1 m/s)

Other authors [5] that tested similar model wastewaters concluded that dextrans were appropiate to simulate membrane fouling trend of STEs. Zator [2] studied a mixture of BSA and dextrans and they found that this blend accurately represented STEs UF performance.This is in accordance with the results presented in this work.

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Acknowledgements

The authors of this work wish to gratefully acknowledge the financial support from the Generalitat Valenciana through the program “Ayudas para la realización de proyectos I+D para grupos de investigación emergentes GV/2013”.

DECOLORACIÓN DE MELAZAS AZUCARERAS MEDIANTE UN PROCESO COMBINADO DE ULTRAFILTRACIÓN CON CARBÓN ACTIVO

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La melaza de remolacha es un subproducto de la industria azucarera que presenta un elevado contenido en sacarosa (45–50% en peso) y en bioactivos (betaína, ácidos carboxílicos y vitaminas del grupo B), aunque es de difícil manejo por su textura densa y viscosa, y por presentar un elevado contenido en compuestos coloreados que le otorgan un color tostado negruzco. Estos compuestos coloreados son sustancias, generalmente poliméricas, de alto peso molecular, que confieren a la melaza una elevada capacidad antioxidante, pero que promueven numerosas reacciones complejas que modifican sustancialmente su composición durante el tiempo de almacenamiento, además de interferir en los procesos posteriores a los que pueda someterse, como su fermentación para la formación de bioetanol y/o la recuperación de sus bioactivos mayoritarios [1-3]. En este trabajo se presentan los resultados experimentales alcanzados en el estudio de viabilidad y optimización de un proceso combinado de adsorción y ultrafiltración aplicado a la decoloración de melazas azucareras.

En una primera etapa, se seleccionó el tipo de carbón activo, su concentración y el pH. Para ello se realizaron las isotermas de adsorción a 25 ºC y se seleccionaron las mejores condiciones para obtener el mayor grado de decoloración y la menor pérdida de los bioactivos (ácido láctico, ácido cítrico y betaína) presentes en la melaza, por su interés alimentario y farmacéutico. Los mejores resultados de decoloración se obtuvieron utilizando como agente adsorbente carbón activo Norit en polvo (Sigma-Aldrich), con concentraciones comprendidas entre 3–5 g/dm^3 y a pH = 3. Con este carbón activo, la adsorción en el equilibrio de ácido láctico y cítrico fue inferior al 20%, sin adsorción de betaína y sacarosa.

El equipo utilizado en el proceso combinado de adsorción y ultrafiltración a 25 ºC está formado por un tanque agitado Pobel de vidrio en el que se añade 1 dm^3 de melaza alimentación (50 g melaza/dm^3) a pH = 1, 3 y 7, y la cantidad correspondiente de carbón activo (3–5 g/dm^3) seleccionada como óptima en la etapa anterior. La alimentación se bombea desde el tanque al módulo de membrana a través de tubos L/S 15 de silicona, utilizando una bomba peristáltica (Masterflex HV-77201-62). El uso de la bomba peristáltica impide que el adsorbente se ponga en contacto con partes internas de la misma, facilitando la limpieza del sistema. Durante la operación, la membrana presenta una doble función: actúa como soporte físico del lecho poroso de carbón activo y es también el medio de separación de las fases (carbón activo y melaza decolorada). Así, la elección del tipo, material, corte molecular y geometría de la membrana es fundamental para asegurar el éxito del proceso. En este trabajo se seleccionó una membrana monocanal de TiO_2 (Filtanium, Tami Industries) con geometría tubular, de 100 kDa y 47 cm^2 de área efectiva, que proporcionó la retención total del carbón activo. La presión transmembrana (PTM) se ajustó al valor deseado utilizando una válvula de regulación situada en la línea de retorno del retenido al tanque de alimentación. El equipo tiene además dos manómetros Bourdon para medir la presión a la entrada y a la salida del módulo de membrana, que puede considerarse lineal a lo largo del mismo. La PTM se calculó como el valor medio de las dos lecturas experimentales de presión. La temperatura se controló durante todo el experimento con un termómetro de mercurio introducido en el tanque de alimentación. Los experimentos se realizaron en modo concentración, con recirculación completa del retenido al tanque de alimentación y salida continua del permeado.

Se analizó la influencia de la PTM, del caudal de alimentación, del pH y de la concentración de carbón activo sobre la decoloración de la melaza, la pérdida de sacarosa y bioactivos y el ensuciamiento de la membrana. No hubo una pérdida significativa de sacarosa y bioactivos durante la decoloración de la melaza bajo ninguna de las condiciones de operación utilizadas. Se aplicó el modelo de resistencias en serie para el cálculo de la resistencia hidráulica de la membrana (R_m = 3.67×10^{12} ± 0.05×10^{12} m^{-1}) y de las resistencias secundarias debidas al ensuciamiento. Los resultados han demostrado que la adición del carbón activo a la melaza alimentación provoca una disminución considerable del ensuciamiento de la membrana. La eliminación del color (Fig. 1) de la melaza fue elevada, con valores superiores al 97%, en tiempos inferiores a 3 h de proceso y trabajando bajo las condiciones de operación óptimas: 1 bar de presión transmembrana, 4.24 dm^3/h de caudal de alimentación, pH = 3 y concentración de carbón activo de 5 g/dm^3.

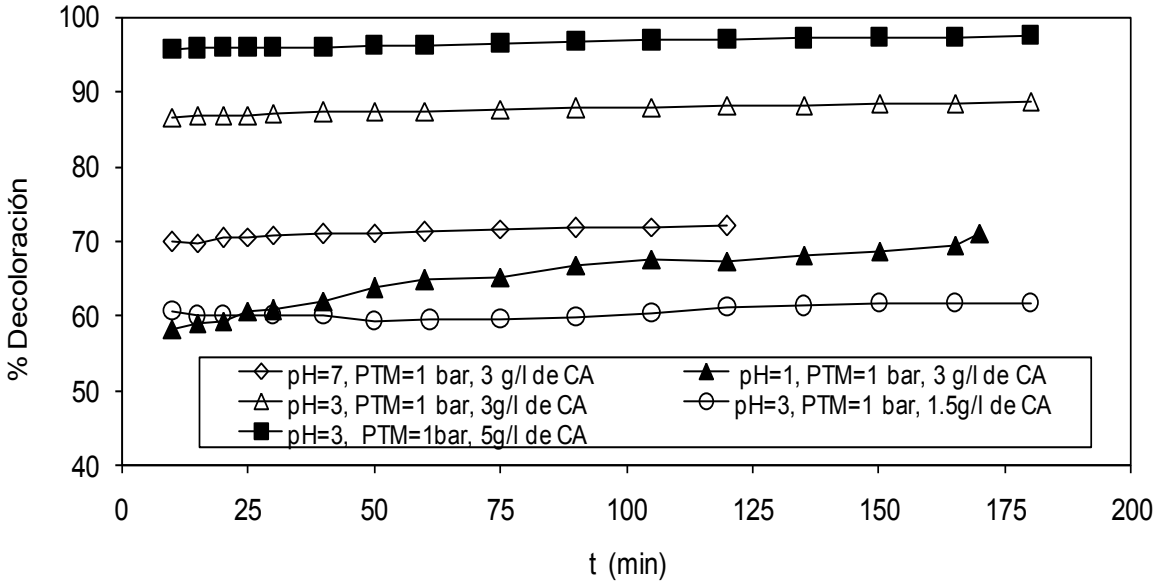

Figura 1. Efecto del pH y de la concentración de carbón activo sobre el grado de decoloración de la melaza en función del tiempo, para los experimentos de ultrafiltración con carbón activo Norit (CA) a 25 ºC en modo concentración, durante tiempos de operación de 120–180 min y con una PTM de 1 bar.

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Biomedical Membrane Applications

- **Oral session 16**

CONTROLLED RELEASE OF GEMFIBROZIL FROM NOVEL POTENTIAL DEVICES

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In recent years, pharmaceutical research was focused on the development of formulations suitable for application in controlled drug delivery, owing to their advantages over the conventional pharmaceutical forms [1]. They include the maintenance of the plasma concentration of a drug in the therapeutic range and the reduction of the administration frequency thus allowing to reduce the incidence of the side effects [2]. New materials were exploited with the aim to develop transdermal patches. These systems are based on the use of synthetic membranes to control the passage of the drug through the skin and to bypass the gastrointestinal tract. In this way, it is possible to increase the drug bioavailability and to reduce the irritation effect [3]. Recently, Algieri *et. al*. [4] and Donato *et al*. [5] investigated the possibility to employ mixed matrix membranes (MMMs) zeolite-loaded for the controlled release of Ibuprofen and tramadol, respectively. Authors demonstrated as the presence of hydrophilic zeolite crystals allowed to modulate the release kinetics of both drugs with respect to the pure polymer membrane.

The present work was focused on the development of MMMs for the transdermal delivery of Gemfibrozil (2,2-Dimethyl-5-(2,5-dimethylphenoxy) pentanoic acid). This drug is a lipid-lowering agent used in dyslipidemias characterized by an increase of triglycerides and a decrease of high density lipoprotein (HDL). Its short biological half life (~1.5 h) requires multiple daily dosage, therefore, a controlled release system may be convenient to reduce the frequency of administration, to avoid toxicity and to improve patient compliance [6]. In particular, a transdermal delivery of the gemfibrozil permits to reduce the side effects which generally occur at gastrointestinal tract. The polymer used for the preparation of the membranes was the polydimethylsiloxane (PDMS) which is a rubbery biocompatible material. The elastomeric property of PDMS permits the preparation of defect-free membranes due to the high mobility of the polymeric chains [7].

The effect of zeolite and drug content on the release kinetics was investigated. Initially, morphological characterizations as well as swelling ratio, erosion and moisture uptake were performed. Subsequently, in vitro and *ex-vivo* release studies were carried out to identify the best promising system as delivery device. The experimental results were fitted with different mathematical models (zero order, first order, Higuchi, Bhaskar, and Korsemeyer-Peppas) to interpret the drug release mechanism from the different MMMs.

Interestingly, *ex-vivo* experiment results showed a constant release of gemfibrozil in the time. These data reflect one of the main features of a controlled release system namely the development of zero order release devices. Our study evidences the potential application of the prepared membranes as transdermal devices for the controlled release of the gemfibrozil.

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DEVELOPMENT OF FUNCIONALIZED POLY(ETHERIMIDE) MEMBRANES FOR APPLICATION IN HEMODIÁLYSIS

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Hemodialysis is a treatment that aims the elimination of toxic metabolites and excess of water, in the artificial kidney equipment. This is accomplished through the transport of solutes and water across a permeable membrane, which allows metabolic waste products such as urea, creatinine, uric acid, and inorganic phosphate to be depleted from the bloodstream of patients to the dialysate stream. Some key blood proteins such as albumin and immunoglobulin must be preserved [1]. Despite being one of the most widely method of treatment used for chronic kidney diseases, hemodialysis still requires improvements in order to decrease the mortality and increase the quality of life of patients.

Commercial membranes generally used in hemodialysis consist of polymers such as polysulfone, polyethersulfone, polycarbonate, polyamide or cellulose acetate [2]. These membranes are imported in Brazil and represent a very high cost for the SUS (the Brazilian Unified Health System), setting a limit for the number of patients in hemodialysis centers. The development of new membranes can lead to improvements to the hemodialysis treatment, in terms of biocompatibility and selective removal of solutes. In this context, poly(etherimide) – PEI – could be a good material candidate due to its excellent properties such as mechanical strength, thermal stability, chemical resistance, good processability and low price [3]. The present study aims at synthesizing membranes of polyetherimide (PEI) for hemodialysis with chemical immobilization of heparin on its surface in order to increase their biocompatibility.

Membrane fabrication explored the phase inversion method, using water as non solvent and n-methyl-2-pyrrolidone (NMP) as solvent. Polyvinylpyrrolidone (PVP) was added in different concentrations to the casting solution to promote pores formation. The synthetized membranes were characterized by morphological analysis, hydraulic permeability and rejection to urea (MW 60 Da), creatinine (113 Da), phosphate (MW 134 Da), vitamin B12 (MW 1.4 kDa), lysozyme (MW 14.3 kDa) and albumin (MW 66 kDa).

The surface of synthesized membranes was covalently heparinized. Funcionalized membranes were characterized by attenuated total reflection (ATR) Fourier transform infrared (FT-IR), adsorption of protein (albumin), contact angle, activated partial thromboplastin time (aPTT), platelet adhesion and hemolysis test.

The synthesized membranes have high permeability to low molecular weight solutes and rejections for medium and higher molar mass solutes comparable to the low flux commercial dialyzers. The immobilization of heparin on the surface of these membranes improved their surface properties, leading to increased hydrophilicity, reduction of protein adsorption and platelet adhesion. Moreover, in contact with blood, the membranes did not cause hemolysis, and the presence of heparin on the surface increased the aPTT, resulting in anti-thrombogenic characteristics, highly required in hemodialysis.

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Nutrients permeability through poly(ε-caprolactone) membranes applied for neural tissue engineering

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One of the major chanllenges that tissue engineering and regenerative medicine are facing nowadays is to successfully produce large size *in vitro* central nervous system (CNS) tissues regenerated from issolated neural cell lineages. CNS tissue is very sensitive to the sourronding conditions and therefore, research efforts are currently focused on finding the most favourable conditions to promote axonal regrowth [1]. Among the different regenerative strategies studied, the employment of artificial substrates or scaffolds to bridge the two extremes of a damaged nerve may provide support for the surrounding brain tissue and for the cell growth and axon regeneration [2]. The ideal artificial scaffold would be easily processed, with high and interconnected porosity and adequate resorbability which maintains mechanical stability and avoids immune responses. Moreover, the limitations of nutrients supply towards the cells in *in vitro* bioreactors is a major problem that hampers the growth and proliferation of the cells and the size that tissues can achieve.

The objective of the present work is to develop a flat polymeric membrane with high nutrients permeability that procures an adequate substrate for cells to be employed as scaffold to hold 3D neural tissue proliferation in *in vitro* bioreactors.

Polymers can be easily processed by, for instance, phase separation to form membranes. By tailoring the process variables, highly porous membranes with high nutrients permeability can be fabricated [3]. Synthetic biodegradable polymers can be resorbed and their properties (mechanical stability or degradability) can be tailored. Poly(ε-caprolactone) (PCL) is a polyester widely investigated for biomedical applications, and thus, highly biocompatible. PCL is a long term degradation polymer (1-2 years) that ensures mechanical stability and low concentration of the degradation products that may cause the immune response of the regenerating cells.

In previous works, PCL flat membranes were fabricated by phase inversion to be applied as scaffolds for CNS regeneration. Two coagulation baths were employed (ethanol, PCL1 and isopropanol, PCL2). The physical structure, morphology and topography were characterized using Scanning Electron Microscopy (SEM). PCL1 and PCL2 presented homogeneous structure (Figure 1) with a well interconnected and high porosity (> 85%) that contributed to the high water permeabilities observed (~350-590 mL m^{-1} bar^{-1} h^{-1}). *In vitro* culture tests of human glioblastoma cells after 48 hours under static conditions showed good attachment and penetration in the scaffolds indicating promising properties as scaffolds for neural tissue regeneration.

For long term cell culture under dynamic *in vitro* culture conditions, the mass transport of nutrients must be as high as possible. Therefore, in this work, further nutrients permeability through the PCL membranes has been evaluated using proteins mass transfer, e.g. bovine serum albumin (BSA), to evaluate the applicability of PCL1 and PCL2 in *in vitro* bioreactors for neural cell tissue engineering. The experiments have been conducted in dead-end and cross flow to evaluate as well the effect of the culture medium flow configurations in dynamic bioreactors on the rejection and flux of nutrients through the membranes. Moreover, fouling effects and protein adsorption on the membrane surface have been assessed.

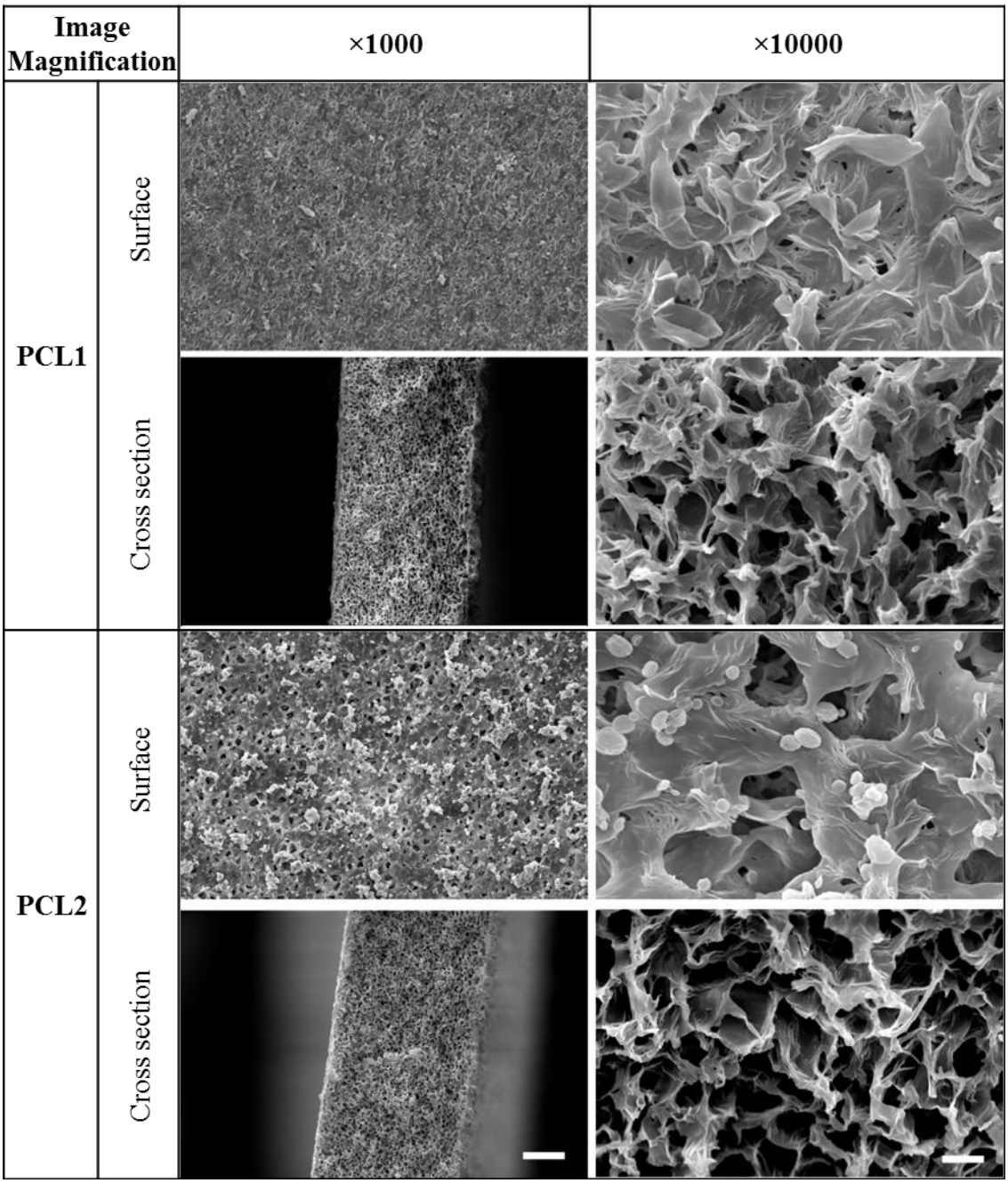

Figure 1. SEM images of surface and cross section of PCL flat scaffolds at different magnifications (Scale bars represent 30 μm and 3 μm at ×1000 and ×10000 magnifications, respectively).

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REMOVING ENDOTOXINS FROM SOLUTIONS BY MEMBRANE ADSORBER WITH L-HISTIDINE

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The endotoxins are substances present in the outer cell wall of Gram-negative bacterias. They are also known as lipopolysaccharides (LPS). The LPS are formed by three regions: lipid A, core polysaccharide and long chain polysaccharide. The lipid A corresponds to the toxic part of the endotoxins, participating of the pathogenicity mechanisms of the bacterial cell [1]. Endotoxins in contact with the bloodstream of human beings can cause fever, vasodilatation, diarhea, blood coagulation, damage in the liver functions and in the endocrine system, chills, headache, malaise, yawns and even death. Because of these effects, it is extremely important ensuring endotoxin removal from hemodialysis water and injectable solutions, such as: antivenin, erythropoietin and immunoglobulin G. Therefore the objective of this research was to investigate the use of the membrane adsorber technology to remove endotoxins, without denaturation and loss of products, as alternative to conventional processes, as chromatography process.

Based on the state of art reviewed [2-9], it was chosen to achieve the objectives a nylon membrane covered with polyvinyl alcohol (PVA) containing L-histidine as ligand for endotoxins. All glassware, plastics, membrane system and membranes were depyrogenated as described in [3]. The adsorption experiments were done in static mode, the endotoxin concentration determined by limulus amoebocyte lysate (LAL) assay or Purpald method and the ligand density was determinated using a spectrophotometric method with EDTA-copper complex solution [6, 10].

It was found ligand densities of 7.38 mg/g and 6.30 mg/g for dry membrane adsorbers. After recirculation of the 0.05 M copper sulphate solution through the system, it was possible to notice that the membrane surfaces became slightly blue, confirming the presence of L-histidine bound with copper. Using the LAL method it was verified the eficciency of the depyrogenation procedures used, which showed values of endotoxin lower than 0.25 EU/ml (value accepted to injection water) after depyrogenation.

The endotoxins removal by membrane adsorbers was up to 65% of the feed solution in the static mode. This result is superior to those reportedby Acconci [6] in similar conditions. The diference between the researches can be attributed to the high L-histidine density obtained with the nylon support used in this work.

During the research the stability of the membrane adsorber was evaluated through ~~the~~ measurement of its ligand density. For 2.5 years the ligand density remained 7.38 mg/g, decreasing to 0.75 mg/g after that. The membrane adsorber lifetime was estimated as 30 months. Finally, it was not verified endotoxins adsorption onto unmodified membranes, proving that the removal of endotoxins is exclusively due to the specificity of the membrane adsorber to endotoxins.

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Acknowledgements
The authors thank Capes for research funding (Projeto Rede NABNIOTEC), National Institute of Quality Control in Health of the Oswaldo Cruz Foundation (INCQS/FIOCRUZ), Membrane Separation Processes, Biotechnological Processes, Engineering of Cell Cultures and Interfacial Phenomena Laboratories of the Chemical Engineering Program of Alberto Luiz Coimbra Institute for Graduate Studies and Research in Engineering of the Universidade Federal do Rio de Janeiro.

Biomedical Membrane Applications

- **Poster session 2**

SYNTHESIS OF POLYSULFONE MEMBRANES FOR HEMODIALYSIS

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The kidney is a vital organ which functions include removing waste metabolites form blood, regulating water level in body and regulating acid–base equilibrium. Statistics about irreversible kidney failure indicates that prevalence of kidney diseases in global population is about 1/10,000 [1]. Since the development of artificial kidneys, based on membrane dialyzers, hemodialysis is the most common treatment strategy, along with peritoneal dialysis and kidney transplantation. In hemodialysis, removal of small solutes through hemodialysis is based on diffusion. Medium and high molecular weight solutes, as well as water, are removed by convective flux.

Main polymers used for manufacturing hemodialyzers inlcude polysulfone, polyethersulfone, polycarbonate, polyamide or cellulose acetate [2]. Brazil imports the totality of dialyzers, making the treatment very expensive and limiting the access to the treatment.

The objective of this work is to develop hollow-fiber type polysulfone membranes for use in hemodialysis. The developed membranes were characterized regarding the morphology and transport property and their results compared with those obtained for the same commercial membranes.

The scanning electron microscopy made it possible to study the morphology of the membranes. Two membranes were selected to be compared. The result is found in Figure I. There is great similarity between the surfaces of the membranes, which are very porous. Characterization of rejection to polyethylene glycol (MW 20, 10 and 2kDa) show that developed membranes have a smaller average pore size.

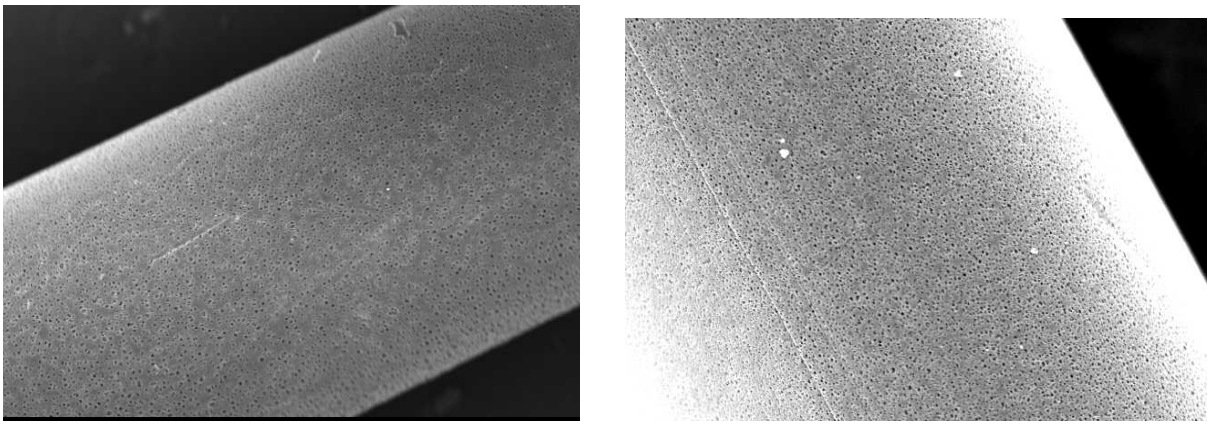

Figure I: Photography membrane obtained by scanning electron microscopy (a) developed in this work (PAM1) (b) commercial high flux polyethersulfone membrane

The transport properties were studied in bench scale. The results are shown in Table I. It is seen that the membranes developed in this work, as a high flux commercial membrane,

satisfactorily remove uremic solutes of low molecular weight. In fact, PAM-3 membrane presents a lower and, thus, more convenient, rejection of creatinine, urea and B12 vitamin.

The next step of the work consists of making similar commercial modules and characterize in a hemodialysis machine simulating a real process.

Table I: Caracterization of commercial membranes and membranes developed in this work.

Membrane	Composition	Hydraulic Permeability (L/h.m²bar)	Rejection of Uremic Solutes (%)			
			B12	Creatinine	Phosphate	Urea
Commercial 1	Polysulfone	9.0	10.26	30.28	26.07	38.82
Commercial 2	Cellulose Acetate	2.5	30.5	30.64	27.93	39.25
Commercial 3	Polyethersulfone	79.6	9.99	17.42	14.58	18.92
PAM-1a	Polysulfone	89.1	5.07	6.35	19.26	16.75
PAM-1b	Polysulfone	21.3	10.92	3.58	16.45	11.06
PAM-2	Polysulfone	39.7	12.67	19.21	21.01	10.98
PAM-3	Polysulfone	104.3	8.66	1.9	15.85	4.1
PAM-4	Polysulfone	78.1	6.05	22.13	20.29	11.41
PAM-5	Polysulfone	81.9	25.24	18.46	19.2	2.96
PAM-6	Polysulfone	47.4	16.94	15.98	15.5	10.29

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Membrane integration in biomedical microdevices

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The objective of the project is to develop an artificial blood oxygenator in the form of microdevice with highly oxygen permeable membrane.

In the last 60 years the development of Extracorporeal Membrane Oxygenators (ECMO) increased significantly. ECMO are composed of hollow fibers or porous propylene membranes and even if they are able to deliver high amount of oxygen compared to dense membranes, plasma could leak through the pores and these membranes are considered only for short term use, several hours [1]. Microchannel technologies in the artificial lung are developing since 10 years with different microchannels architecture, microdevice sizes and membrane materials, achieving various oxygen transfer, flow rates and priming volumes of the blood [2-16]. An oxygen transfer rate of 1.9 ml O_2/min with a blood flow of 30 ml/min, which is one of the best achievement nowadays, would increase the oxygen saturation of a neonate from 70% to 100% [17]. These values indicate that the room for improvement still exists.

The target of the artificial lung fabrication is to achieve the lowest priming volume, portability, high value of blood oxygenation and carbon dioxide removal in neonates. Another application is the removal of ammonia in the newborn which is responsible for hyperammonemia. In order to achieve that we designed the microdevice which is composed of liquid chamber for blood, gas chamber for pure oxygen and thin, oxygen permeable membrane in between. The material we chose is polydimethyl siloxane (PDMS) thanks to its outstanding permeability to oxygen and biocompatibility. What is more the oxygen delivery increases linearly with the blood flow which indicates that mass transfer limitations occur in the blood side. For this reason the design of the liquid chamber microchannels was fabricated in order to mimic the natural lung vasculars and to obtain the lowest possible pressure drop inside the device.

The experimental set-up consisted of mass and pressure flow controllers connected to the device and to the UV-VIS spectrometer was designed. The oxygen concentration in the blood was calculated from the absorbance measurements.

Variety of different membrane morphologies, sizes, materials and surface modifications will be prepared and tested in order to optimize the device. The device will be composed of different chambers and membrane layers in order to obtain the highest variability in terms of different applications.

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Composite Membranes

- **Oral session 17**

NANOCOMPOSITE: NEW MATERIALS FOR CATALYTIC MEMBRANES DEVELOPMENT

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The development of Catalytic Membranes (CMs) is a topic of great importance due to their wide range of applications in various fields such as petrochemical processes and water treatment [1-3]. In general terms, a CM consists of a membrane that controls the transfer of chemical compounds together with a catalyst providing the conversion of reactants to products [3]. The immobilization of a heterogeneous catalyst in a CM allows for the easy separation of the catalyst of the reaction medium and the possibility to reuse the catalytic species without any loss in the catalytic efficiency [4].
Recently, polymeric membranes have attracted more and more attention for the development of CMs but their application is usually restricted to mild conditions (close to ambient temperatures and/or pressures and in a media without corrosive products) to avoid degradation [5,6]. As a consequence, very efficient catalysts have to be designed to work with. With the raise of Nanotechnology, this drawback has found a great solution: the use of transition Metal Nanoparticles (MNPs) as effective and selective catalysts giving rise to nanocomposites membranes [7-9].
Anyhow, the inclusion of MNPs in polymeric matrices for CMs development is a great challenge since it is imperative to choose an appropriate polymeric matrix suitable for synthesis or adsorption of MNPs without a lost of efficiency due to immobilization. In this sense, Intermatrix Synthesis (IMS) [10], a technique based on the immobilization of MNPs precursors (metal ions or complexes) into polymeric matrices followed by their chemical or electrochemical reduction, provides the production of the desired nanocomposite materials, which exhibit both catalytic and/or bactericidal properties [11,12], useful for water treatment procedures. However, for a successful IMS, the polymers must contain ionogenic or coordination groups, so as to allow the immobilization of MNPs precursors. Regarding this request, two options have been considered up to now: i) the use of existing functionalized polymers (i.e. Nafion®) [11] or ii) the modification of non-functionalized polymers either by direct sulfonation [13], layer-by-layer deposition [14,15] or photochemical grafting [16].
In this work we provide a general overview of the use of nanocomposites for CMs development and report and compare two types of nanocomposite CMs obtained by two of the three-abovementioned modification routes: a) polyethersulfone (PES) hollow fibers membranes modified by photografting of sodium p-polystyrene sulfonate; and b) flat sheet membranes made of sulfonated PES (Cardo type). The sulfonation procedure was achieved by a simple and unexpensive direct sulfonation with concentrated sulfuric acid.
Membrane characterization was carried out by several techniques, such as Transmission Electron Microscopy (TEM). Obtained results for all of the matrices proved that small non-aggregated palladium MNPs were obtained by IMS but their distribution was highly dependent on the modification route.
The catalytic activity of the nanocomposite CMs was studied by monitoring a model catalytic reaction in flow conditions: the reduction of p-nitrophenol to p-aminophenol in aqueous media, which does not take place in absence of catalyst. Although an induction time was sometimes necessary to start the reactions, all the nanocomposites exhibited good catalytic activities and, therefore, in our opinion, some of the developed materials are suitable to operate at larger scale with promising results.

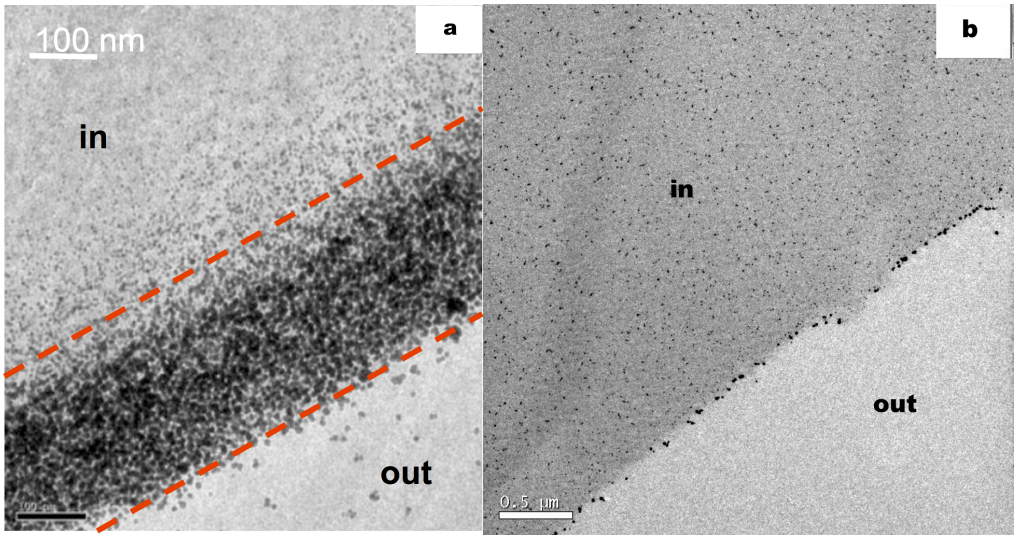

Figure 1. Nanocomposite membranes containing PdMNPs: a) TEM image of a PES membrane modified by photografting, and c) TEM image of a sulfonated PES-C membrane.

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HOLLOW FIBER POLYURETHANE MEMBRANES TO REMOVE SULFUR COMPOUNDS FROM NAPHTHA BY PERVAPORATION PROCESS

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The removal of sulfur in fuels has been an important issue in the refining industry. In Brazil, about 70% of the gasoline pool is comprised of naphtha derived from the fluid catalytic cracking process (FCC, Fluid Catalytic Cracking) without any additional treatment. In general, this current can be found a high sulfur content (average 1.000 mg / kg), which directly contributes to SO_2 emission and corrosion of equipment and pipelines. Separation processes with membranes (SPM), in particular the process of pervaporation has been studied in a growing number of articles and patents for the desulfurization of liquid hydrocarbon streams. The advantages of this process are usually common characteristics of SPM, i.e., selectivity, low cost and simplicity of operation, modular and compact equipment and easy to scale up. When compared to the conventional hydrodesulfurization of FCC naphthas, the pervaporation enables to removing organosulfur compounds without hydrogen consumption (lower operating costs and without loss of octane) operate at relatively low temperature and pressure, and dispense the use of catalysts . The efficiency of the pervaporation to desulfurization is related to the use of membranes with affinity to sulfur compounds such as polydimethylsiloxane (PDMS), polyimide, polyethylene glicol and polyurea/urethane. However the main problem in these membranes is the high swelling degree, which may reduce the membrane selectivity and accelerate the chemical degradation at high temperature and pressures. The main objective of this research is the development of membranes with high affinity to sulfur compounds present in naphtha. The polyurethane was selected as membrane material due to its excellent properties of chemical, mechanical and heat resistance, besides having an affinity for sulfur compounds. The potential of polyurethane membranes have already been exploited for the removal of aromatic compounds, showing the feasibility of using for separating organic streams [1].
In this study, membranes were prepared in flat sheet and hollow fibers geometry. As feed charge, was chosen initially a binary mixture containing 1,500 parts per million of 2-methyl thiophene (sulfur compound more difficult to be removed in the traditional process) in iso-octane (the main component of naphtha). Experiments were performed at 3 different temperatures in the feed side. Binary mixture was fed into the upstream side under ambient pressure using a gear pump drive and on the downstream side was kept <1mmHg by a vacuum pump. Permeate was collected in a liquid nitrogen cold trap and weighed and the compositions were determined by gas chromatography (Perkin Elmer, model Clarus 500) using a capillary column and a flame ionization detector (FID). The results os pervaporation showed high selectivity for sulfur compound with a relatively low permeate flux for the binary mixture. Currently, the work is focused on the preparation of asymmetric membranes in order to increase the permeate flux, keeping the selectivity obtained.

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Acknowledgements

The authors would like to dedicate this paper to Professor Alberto Luiz Coimbra, in the 50th anniversary of COPPE (1963-2013), The Graduate School of Engineering of the Federal University of Rio de Janeiro.

Preparation, characterization and performance of PES membranes modified by binary metal oxides $Ti_{(x)}Zr_{(1-x)}O_2$ for wastewater filtration

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Introduction

Membrane fouling is considered one of the main drawbacks in the performance of ultrafiltration membranes, often related to hydrophobicity [1]. One of the methods proposed in the recent literature to avoid membrane fouling is the use of hydrophilic particles as additives to the membrane compositions. Due to the hydrophilic nature of additives immersed in the membrane structure, the undesired hydrophobic interactions that take place between organic foulants and membrane surface can be reduced considerably. The main focus is on the use of transition metal oxides to manufacture ultrafiltration membranes with a more hydrophilic character [2]. The objective of this work is the preparation and characterization of a new class of composite membranes applied to wastewater treatment, for which binary oxide metals have been synthesized in different stoichiometric combinations of TiO_2 and ZrO_2 in order to produce membranes with different permeation characteristics. In this work the influence of physico-chemical properties of the particles and its spatial distribution inside the membrane structure on the morphology and performance of new binary metal oxides doped membranes have been explored.

Materials and Methods

Composite TiO_2-ZrO_2 nanoparticles were prepared by the sol-gel process. The crystal structure of the samples was studied by XRD measurements. Structural characterization was carried out by transmission electron microscopy (TEM). The TiO_2 and ZrO_2 molar concentrations of the samples were determined by inductively coupled plasma spectroscopy (ICP). The percentage of UV–vis reflectance of powder samples was also measured.
Neat and modified PES membranes were synthesized by immersion precipitation. Hydrophilicity, morphology and particle pattern distribution of doped membranes were some of the studied membrane properties. Pure water flux, fouling performance and solute rejection studies were accomplished using a cross-flow filtration set-up.

Results and Discussion

The metal oxides TiO_2 and ZrO_2 form aggregates in micronsizes with an average particle size around 3 µm. In particular, the prepared ZrO_2 oxides are monodisperse aggregates, exhibiting a narrow particle size distribution, with a peak at 3 µm; the average particle size is smaller than the one observed for TiO_2 particles (Figure 1).

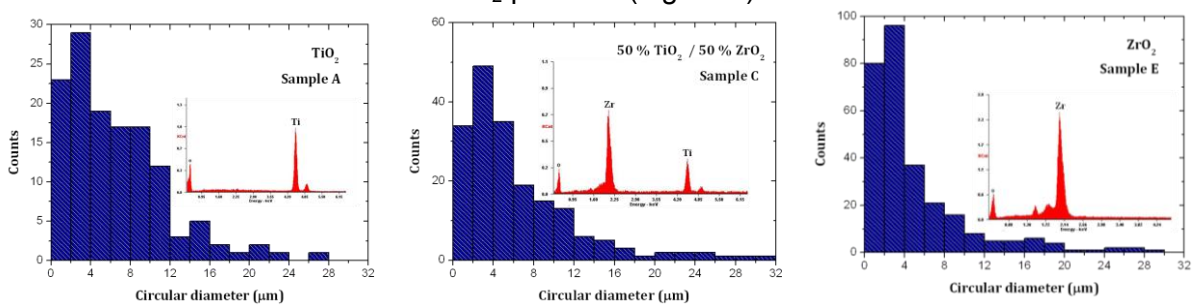

Fig 1.Particle size distribution of synthesized metal oxides.

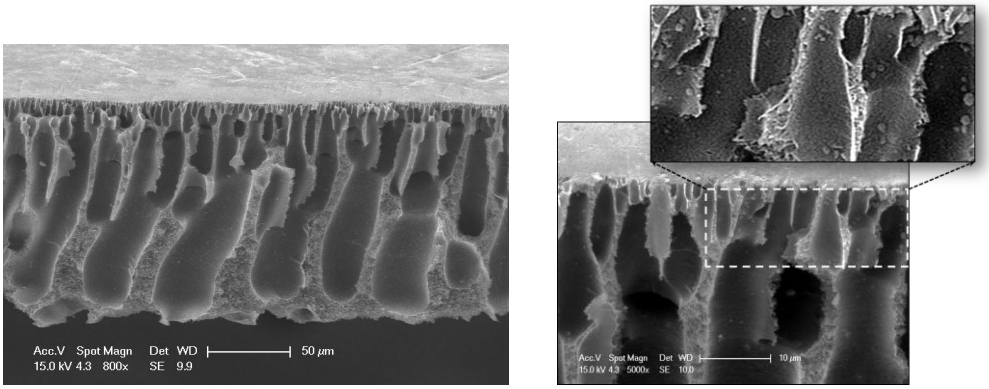

Fig 2. SEM cross-section images of synthesized membranes

The spatial distribution of particles in the membrane cross-section was explored by EDS collecting the detected signal of chemical elements dispersed inside the membrane structure by X-ray maps (Figure 3). As shown, pure TiO_2 is evenly distributed through the membrane cross section, in contrast to the pure ZrO_2 pattern distribution that reveals that particle density is poor near the skin membrane layer.

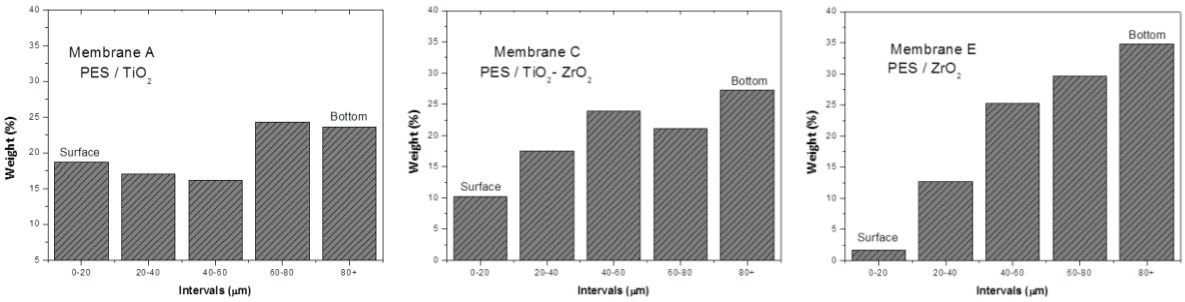

Fig 3. Metal oxide particle depth distribution from top to bottom in doped membranes

The incorporation of metal oxide particles into the polymer matrix caused a significant increase of the membrane flux. The PES-binary oxide doped membrane, PES/ TiO_2 membrane, had a 48% higher flux compared to the control PES membrane. In order to explore the effect of fouling on the BSA rejection, the observed rejections for each membrane were also explored. The rejection of the doped membranes is hardly affected by the incorporation of metal oxides fillers. The impact of membrane modification on the membrane fouling performance was quantitatively studied using the resistance-in-series model [3].

In general, the fouling performance is dominated by the hydrophilic nature of membrane. The control PES membrane has the highest total and irreversible resistance due to its lower hydrophilicity. However, the addition of metal oxides does not have a larger impact on the reversible fouling of membranes. This similar performance in the reversible fouling can be caused by the low number of particles distributed at the membrane and pore surfaces, which is a disadvantage for the improvement of the membrane performance. The main difference in fouling resistance of the membranes was observed to be irreversible fouling. However, the irreversible resistance tracks closely with intrinsic resistance, suggesting that the main observed improvement is rather associated to the flux increment.

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Clay nanoparticles effects on performance and morphology of PVDF membrane

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Introduction: In order to incorporate hydrophilic proprieties in the conventional hydrophobic poly(vinylidene fluoride) (PVDF) membranes for performance improvement, additions of inorganic nanoparticles in dope solutions has become an attractive and simple method for membranes casting, through the phase inversion process ([1] and [2]). Some authors, MIERZWA *et al.* (2013) and MA *et al.* (2012), had already evaluated the addiction of clay nanoparticles (nanoclay) in polyethersulfone (PES) and polysulfone (PSf) membrane. Their results showed that composite membrane has higher water permeate flux and higher rejection capacity. Furthermore, the results demonstrated that nanoclay addition induces changes in membrane morphology and mechanical characteristics. Considering the promising results obtained in the cited studies, the main objective of this research was to evaluate the effect of inorganic clay nanoparticles (hydrophilic montmorillonite) on the morphology and performance of three different types of PVDF (polymer and copolymer) membranes. Membranes were cast by the phase inversion process. Results from filtration tests were used for comparing composite and neat membranes performance.

Key words: poly(vinylidene fluoride) membrane, clay nanoparticles; membrane modification.

Material and Methods: Polymeric solutions were prepared with poly(vinylidene fluorine) at a fixed concentration (18%wt) dissolved in N-methyl-2-pyrrolidone solvent and specific amounts of nanoclay (0%wt, 2%wt, 4%wt and 8%wt) were direct added and dispersed in the solution. Two different types of PVDF were used: Kynar®761, Kynar Flex®2821 (copolymer of poly(vinylidene fluorine) and hexafluoropropylene). All the chemicals were used as they were received. The solution was stirred using a mechanical stirrer for 24 hours at 50ºC until a homogenous polymeric solution and complete clay nanoparticles dispersion were obtained. Membranes were produced by the phase inversion process. Each solution was spread onto a glass plate to produce a flat sheet membrane (casting temperature: 25ºC; casting knife: 130µm or 100µm; casting speed: 0.04 m/s). The polymeric film was immediately immersed into the coagulation bath with a non-solvent. From the coagulation bath, cast membranes were transferred to another bath (demineralized water at ambient temperature), for at least 24 hours to remove any residual solvent. For performance evaluation, demineralized water flow tests were conducted using a laboratory-scale cross flow test cell. At least three different rectangular membrane samples (0,13 m x 0,09 m, with a net filtration area of 0,0077 m^2) from different membranes were tested. Based on the series resistance model, the permeate flux (J; [$m^3/m^2.h$]) and the clean membrane hydraulic resistance (R_M [m^{-1}]) were calculated. The porosity was determined by the difference between dry and wet membrane weight. The membranes thickness was measured by a micrometer. Membranes cross section images were obtained using the Scanning Electron Microscopy (SEM).

Results and Conclusions: Table 1 summarize the results obtained for membrane performance. It can be noticed that, nanoclay addition improved membrane permeability, for both polymers, comparing to the neat membrane. However, Kynar®761 polymer and Kynar Flex®2821 copolymer did not presented the same behavior. For the Kynar Flex®2821 copolymer, permeability increased with increasing nanoclay concentrations (2%wt clay: 483% improvement; 4%wt clay: 501% improvement; 8%wt clay: 1837% improvement). On the other hand, for the Kynar®761 polymer, permeability increased until 4%wt nanoclay addition (2%wt clay: 14% improvement; 4%wt clay: 1684% improvement) and after that decreased (8%wt clay - 1153% improvement). Moreover, Kynar Flex®2821 copolymer presents a higher permeability variance compared to the Kynar®761 polymer, indicating that Kynar Flex®2821 membranes are less uniform than Kynar®761 membranes. These results

suggest that Kynar Flex®2821 membrane are more influenced by phase inversion process parameters. The Kynar Flex®2821 copolymer presented better results than the Kynar®761 polymer. But these results can be affect by casting knife gap and consequently by the final thickness. However, Kynar Flex®2821 copolymer presented a higher reduction compared to Kynar®761 polymer. In both cases, membranes with nanoclay showed the highest thickness reduction. For the Kynar®761 polymer, nanoclay addition didn´t improve the porosity comparing to the neat membrane. Differently, for the Kynar Flex®2821 copolymer, it can be noticed that the addition of nanoclay improved the membrane porosity. SEM cross section images analysis (Figure 1) showed that PVDF membranes internal morphology changed with the addition of clay nanoparticles. In the case of the Kynar®761 membranes, a significant change on the finger-like pores extension and bottom layer structure, with reduced sponge-like pores thickness. In the case of Kynar Flex®2821 membranes the main change on morphology is related to an apparently reduction on the sponge-like density at the membrane bottom layer, and the production of more extended finger-like pores at the membrane top. It can be observed that the best permeability results are associated with morphology defined by extended finger-like pores and less dense sponge-like structure.

Table 1 Effect of additives on PVDF membrane performance and morphology evaluation

Membrane type	Average permeate flux ($L.h^{-1}.m^{-2}.bar^{-1}$)	Median hydraulic resistance ($E^{+13}m^{-1}$)	Porosity (%)	Thickness (µm)	% reduction in thickness
Kynar® 761 (Neat)	0,9		44	93	28
Kynar® 761 + 2% clay	1,0	65	43	75	42
Kynar® 761 + 4% clay	15,9	1,6	40	77	41
Kynar® 761 + 8% clay	11,2	4,1	42	71	45
Kynar Flex® 2821 (Neat)	2,8		32	57	43
Kynar Flex® 2821 + 2% clay	9,5	3,2	55	24	76
Kynar Flex® 2821+ 4% clay	17,0	1,9	46	47	53
Kynar Flex® 2821+ 8% clay	54,7	0,9	70	27	73

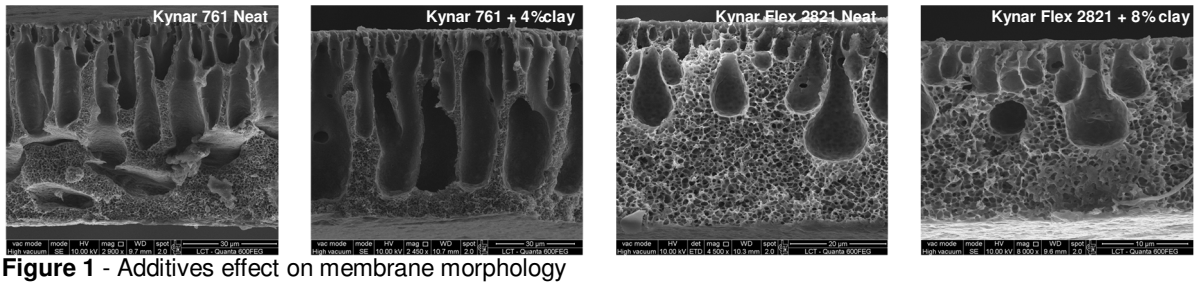

Figure 1 - Additives effect on membrane morphology

In this study, the influence of nanoclay on the performance of two types of PVDF membranes has been evaluated. Addition of clay nanoparticles can improve pure water permeate flux compared with neat membrane for both cases. Kynar Flex®2821 copolymer presents best permeate flux than Kynar®761 polymer. However, Kynar®761 polymer presents a lower permeability variance compared to Kynar Flex®2821 copolymer. The nanoclay addition didn´t improve the porosity for Kynar®761, but it improved the porosity for Kynar Flex®2821 copolymer. The effect of clay nanoparticles addition on membrane performance seems to be associated to changing on membrane morphology. The results obtained suggest that the interaction with nanoclay and Kynar®761 polymers and with nanoclay and Kynar Flex®2821 copolymer occurs differently. The effect of clay nanoparticles addition on membrane performance seems to be associated to the changes in membrane morphology, increasing finger-like pores extension and decrease dense sponge-like structure.

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Composite Membranes

- **Poster session 1**

SÍNTESE DA MEMBRANA (Al-SBA-15/ZSM-5/α-ALUMINA)

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Introdução

Membranas e técnicas de separação por membranas têm atraído interesse por pesquisadores devido a eficiente separação de componentes quando comparada com outras tecnologias de separação [1]. Os materiais compósitos, que é a combinação de materiais microporosos com mesoporosos, apresentam propriedades e aplicações derivadas das características das fases individuais [2]. Devido a excelente propriedade existente no compósito, este trabalho relata a síntese da membrana compósita (Al-SBA-15/ZSM-5/α-alumina) utilizando o método de mistura mecânica.

Experimental

Síntese do material:

Síntese da peneira molecular Al-SBA-15: Com base no procedimento experimental adaptado do trabalho de Zhao [3] foi realizada a preparação da peneira molecular SBA-15, acrescentando pseudobohemita (Oxidróxido de alumínio AlOOH), razão 0,75, como fonte de alumínio na síntese, gerando a peneira molecular Al-SBA-15. A calcinação foi realizada a 550 ºC (10°C/min) durante 24 horas, gerando Al-SBA-15 calcinada.

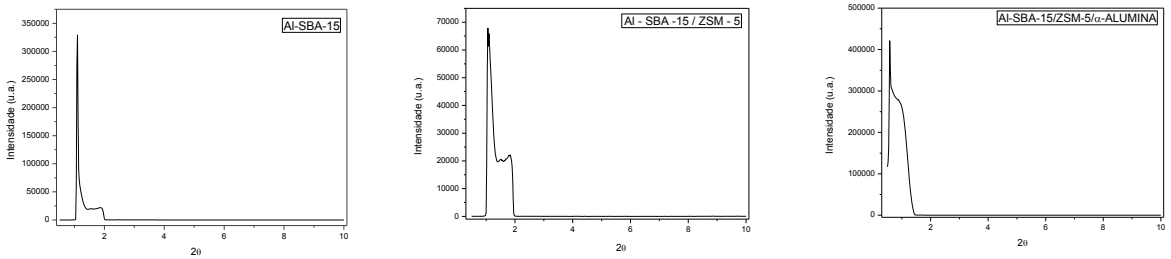
Síntese do compósito Al-SBA-15/ZSM-5: Foi utilizada a impregnação de uma solução de TPABr na Al-SBA-15 obtida conforme descrita acima. 5 g de Al-SBA-15 foi posta em contato com um volume da solução de TPABr, com agitação contínua a T=25ºC por 1 hora. O material obtido foi submetido a secagem em estufa, a 60 ºC por 24 h. Após este período, foram adicionados 100 mL de água destilada no sólido e ajustado a pH 10 (NaOH a 0,1 mol/L). A mistura foi agitada por 24 horas a T=25ºC. A mistura reacional foi transferida para uma autoclave onde a cristalização do material foi realizada em estufa a 150 ºC e período de 3 dias. O material foi retirado da autoclave, lavado com água destilada, centrifugado, seco por 2 horas a 100 ºC e calcinado a 550 ºC durante 5 horas.

Síntese do suporte cerâmico: A alumina foi fornecida pela ALMATIS em forma de pó. Prepararam-se 200 ml de dispersão com a seguinte composição: 40 % de alumina; 0,2 % de PABA (dissolvido em álcool); 0,5 % de ácido oléico e 59,3% de álcool etílico. A mistura foi moída em um moinho de bolas durante 1 hora e então, foi colocada na estufa por 24 horas a 60 ºC; umidificou-se com 7 % de água, deixou-se repousar por 24 horas. Pesou-se 1 g do material que foi compactado e prensado. A prensagem foi realizada com 4 toneladas por 3 minutos e o material prensado foi submetido à sinterização a 1400 ºC a uma taxa de 5ºC/min, permanecendo por mais 4 h após atingir a temperatura. O suporte cerâmico (α-alumina) foi obtido na forma de disco, onde o mesmo possuía a seguinte configuração: 1mm de espessura e 20mm de diâmetro.

Síntese da membrana Al-SBA-15/ZSM-5/α-alumina: A síntese da membrana zeolítica consistiu na mistura mecânica do compósito (Al-SBA-15/ZSM-5) e do suporte cerâmico (α-alumina) na mesma proporção. A mistura foi desaglomerada num almofariz e posteriormente submetidas à prensagem mecânica e em seguida a membrana foi levada à mufla a 550 ºC durante 20 horas e posteriormente submetida a caracterização.

Resultados

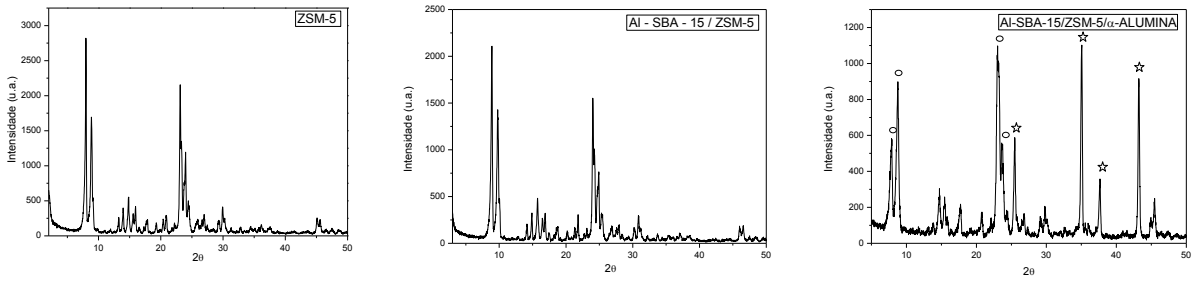
Nas Figuras 1 (a, b, c) são apresentados os difratogramas de raios X amostras, em baixo ângulo (0,5-10º).



(a) (b) (c)

Figura 1. Difratrogramas das amostras: Al-SBA-15 (a), Al-SBA-15/ZSM-5 (b) e Al-SBA-15/ZSM-5/α-ALUMINA (c).

Nas Figuras 2 (a, b, c) são apresentados os difratogramas de raios X do material microporoso ZSM-5, com varredura de 5 a 50º.



(a) (b) (c)

Figura 2. Difratogramas do microporo: (a) ZSM-5, (b) Al-SBA-15/ZSM-5, (c) Al-SBA-15/ZSM-5(o)/α-ALUMINA(*)(c).

A propriedade estrutural da peneira molecular Al-SBA-15 foi caracterizada tendo como padrão um difratograma de DRX que apresenta três picos (Figura 1a). O primeiro pico apresenta uma elevada intensidade, atribuída a linha de reflexão do plano (100) e os outros dois com menores intensidades, que são correspondentes às reflexões dos planos (110) e (200) caracterizando assim a estrutura hexagonal mesoporosa conforme descrito por [3]. Os compósitos foram comparados por meio dos DRX's, em baixo ângulo (0,5-10º) (Figuras 1 a, b e c) e em alto ângulo (5-50º) (Figuras 2 a, b e c) com os padrões da Al-SBA-15, ZSM-5 e α-alumina. Observa-se a fase referente à peneira molecular Al-SBA-15, o material microporoso ZSM - 5 presente no compósito e a fase correspondente ao suporte α-alumina, confirmando a formação das estruturas e suas fases.

Conclusões

De acordo com o difratograma de raios X da membrana obtida através da mistura mecânica conclui-se que ocorreu à formação de cristais do material meso e microporoso (Al SBA – 15/ ZSM – 5), sendo observados picos característicos do suporte (α-alumina), evidenciando o sucesso da síntese da membrana zeolítica.

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Agradecimentos

Os autores agradecem a Capes pelo apoio financeiro dado a esta pesquisa e a Petrobras.

PREPARAÇÃO DA MEMBRANA ZEOLÍTICA COMPÓSITA (ZSM-5/MCM-41/α-Al_2O_3) UTILIZANDO O MÉTODO DE MISTURA MECÂNICA

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Introdução

As membranas zeolíticas tem sido objeto de intensa pesquisa nos últimos anos devido às suas potenciais aplicações nos domínios da separação de gases, nanofiltração [1]. Materias que apresentem características das zeólitas e das peneiras moleculares mesoestruturadas podem ser alternativa para aproveitar as vantagens de ambos os materiais. Membranas zeolíticas podem ser preparadas sob a forma de uma camada individual de zeólita, cristais de zeólita na matriz, ou uma camada de zeólita sobre um suporte [2]. O método de preparação da membrana zeolítica por mistura mecânica [3] tem como objetivo a mistura física da zeólita com o suporte e posterior prensagem e sinterização para formação da membrana.O presente trabalho visa a preparação e sinterização da membrana zeolítica (ZSM-5/MCM-41/α-Al_2O_3) via método de mistura mecânica e caracterização por Difração de raios X (DRX) para investigar as modificações ocorridas na estrutura da membrana zeolítica.

Experimental

Preparação do suporte cerâmico (α-alumina): a alumina foi fornecida pela ALMATIS em forma de pó. Prepararam-se 200 ml de dispersão com a seguinte composição: 40 % de alumina; 0,2 % de ácido para-amino benzóico (dissolvido em álcool); 0,5 % de ácido oléico e 59,3% de álcool etílico. A mistura foi moída em um moinho de bolas durante 1 hora e então, foi colocada na estufa por 24 horas a 60 ºC; umidificou-se com 7 % de água, deixou-se repousar por 24 horas. Pesou-se 1 g do material que foi compactado e prensado. A prensagem foi realizada com 4 toneladas por 3 minutos e o material prensado foi submetido à sinterização a 1400 ºC a uma taxa de 5ºC/min, permanecendo por mais 4 h após atingir a temperatura. O suporte cerâmico (α-alumina) foi obtido na forma de disco, onde o mesmo possuía a seguinte configuração: 3,6 mm de espessura e 26,6 mm de diâmetro. **Síntese do compósito (ZSM-5/MCM-41/α-Al_2O_3):** Para a preparação do compósito ZSM-5/MCM-41 de composição molar: 1:0SiO_2:0,07Al_2O_3:0,4TPAOH:0,25CTABr:40H_2O [4] a mistura reacional de síntese da ZSM-5 foi preparado de acordo com um procedimento reportado [5]. A mistura reacional foi envelhecida durante 40 horas à temperatura ambiente e cristalizado a 90°C, sob pressão autógena, durante 6 dias a fim de promover a geração de sementes de zeólitas. Depois disso, a formação da mesoestrutura foi conseguida através da adição do surfactante (CTABr) e água à solução de sementes. **Síntese da Membrana Zeolítica (ZSM-5/MCM-41/α-Al_2O_3):** Para a preparação da membrana zeolítica ZSM-5/MCM-41/α-Al_2O_3, foi realizada uma mistura mecânica (física) dos dois sólidos: Compósito ZSM-5/MCM-41 e o suporte cerâmico (α- Al_2O_3). Após esta etapa foi realizada uma prensagem mecânica com 4 toneladas por 2 minutos e em seguida a membrana foi levada à mufla a 550ºC com taxa de aquecimento de 5°C/min durante 4 horas. **Caracterização: DRX:** As análises por difração de raios-X (DRX) foram realizadas num equipamento Shimadzu XRD-6000 com a radiação Kα Cu (40 kV, 30 mA), em 2θ °de 2,0- 50,0° e de 2,0 a 80,0°.

Resultados

Nas Figuras 1 (a, b, c, d) são apresentados os difratogramas de raios X do suporte α-Al_2O_3, compósito ZSM-5/MCM-41 em baixo ângulo e alto ângulo, e da Membrana zeolítica. ZSM-5/MCM-41/α-Al_2O_3.

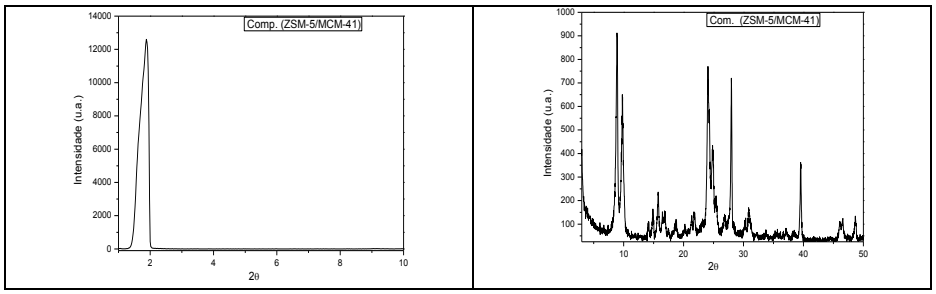

Figura 1. Difratogramas do compósito ZSM-5/MCM-41: a) baixo ângulo e b) alto ângulo.

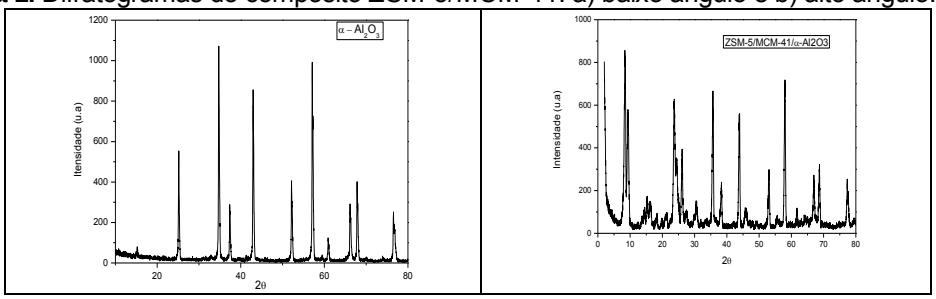

Figura 2. Difratogramas das amostras: (a) suporte cerâmico poroso α-Al_2O_3, (b) Membrana zeolítica. ZSM-5/MCM-41/α-Al_2O_3.

Os difratogramas do compósito ZSM-5/MCM-41 evidenciam: - (Figura 1(a) baixo ângulo) a fase mesoporosa MCM-41, onde as reflexões são correspondentes ao plano de Miller (100) [6]. - (Figura 1(b) alto ânguo) apresentou a fase microporosa ZSM-5, com picos característicos da estrutura do grupo MFI, nos intervalos de 2θ = 7 - 9º e 23 - 25º, esses picos confirmam a formação da estrutura ZSM-5 da zeólita [7]. A amostra inerente do compósito explicitou contaminação por quartzo (picos localizados em 2θ = 28° e 39°), isso ocorreu devido a um longo processo de cristalização das sementes zeolíticas da zeólita. Observa-se (Figura 2(a)), a formação dos picos característicos do óxido de alumínio na região correspondente a 2θ = 25 - 45°, comprovando que a amostra possui somente a estrutura cristalina da α- Al_2O_3 [8]. Observa-se na Figura 1(d), a presença das fases cristalinas do compósito ZSM-5/MCM-41 e suporte cerâmico (α- Al_2O_3), evidenciando a formação da membrana zeolítica ZSM-5/MCM-41/α-Al_2O_3.

Conclusões

O compósito preparado foi obtido com sucesso de acordo com os resultados de DRX. Foi evidenciado neste trabalho a formação da membrana zeolítica ZSM-5/MCM-41/α-Al_2O_3 utilizando o método de mistura mecânica. O padrão de difração de raios X apresentou picos característicos da estrutura ZSM-5/MCM-41, evidenciando que após a mistura mecânica e calcinação a estrutura do compósito foi preservada.

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Agradecimentos

Os autores agradecem a CAPES pela bolsa concedida e a Petrobras pelo apoio financeiro dado a esta pesquisa.

Synthesis and characterization of films of silver nanoparticles dispersed in poly(urethane urea) for the separation of petrochemical gases

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The use of new materials applied to processes of membrane separation has been the target of constant academic and technological researches. In permeation of petrochemical gases, the modification of polymeric structure and the application of facilitated transport membranes are worthy available options [1,2,3,4]. The goal of this work was to chemically, structurally and thermally evaluate the influence of the addition of silver nanoparticles (AgNps) in poly(urethane-urea) (PUU) films. Also, the objective was to study the permeability of petrochemical gases (C_2H_4, C_2H_6, CO_2 e N_2) in order to evaluate the influence of AgNps in gas transport through the PUU film. In this work, the PUU was synthesizes by reacting poly (propylene glycol) (PPG), block copolymer based on poly(ethylene glycol) (EG-b-PG) and PPG, dimethylolpropionic acid (DMAP) and isophorone diisocyanate (IPDI). The ratio between the equivalent-number of NCO groups and the equivalent-number of OH groups was 1,5 in NCO-terminated prepolymer. The proportion of polyols was 25% of PPG and 75% of EG-b-PG. The carboxylic groups of DMPA were neutralized by reacting triethylamine (TEA). The prepolymer was dispersed in deionized water, and then submitted to the chain extension reaction with ethylenediamine (EDA) [5,6]. Waterbone PUU (WPUU) with a solid content of about 30% was obtained, and after it was diluted to 6% of solid content. The AgNps powder was dispersed into WPUU by sonification for 2h, using a high intensity ultrasonic processor [7]. Three PUU/AgNps nanocomposite films were prepared by evaporating the water from the dispersion: < 0.2 %wt, 0.2 %wt, and 1%wt of AgNps to PUU in the final film. X-ray photoelectron spectroscopy (XPS) showed 0.02% of silver in film with less than 0.2%wt of AgNps. Infrared spectrometry (FTIR) spectra of this films exhibited changes in the C-O-C and C=O stretching bands profile (from urethane and urea groups) and X-ray diffractometry (XRD) analyses exhibited shifts in AgNps peaks. These results suggest the AgNps interacted with the ether oxygen of PUU (**Fig. 1**) [5,8,9].

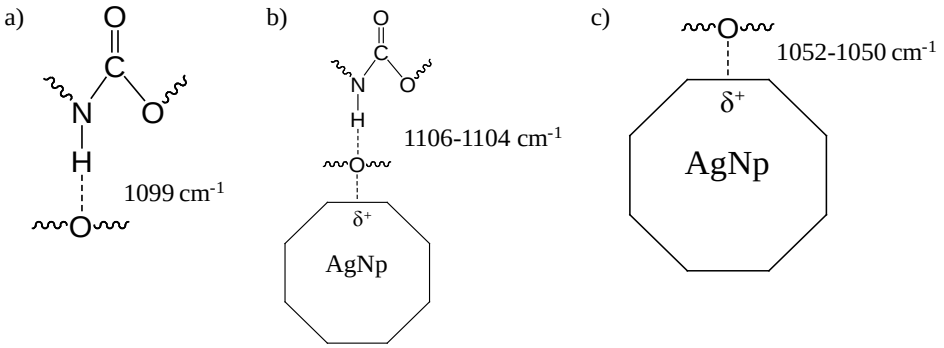

Fig. 1. FTIR stretching bands of ether linkage in three different chemical neighborhoods: (a) interacting with urethane group; (b) interacting with urethane group and AgNps simultaneously; and (c) interation with AgNps

The thermal properties of the films were evaluated by thermogravimetry (TG). The interaction with AgNps reduced the thermal stability of polymer soft segments, where the ether linkages are located. Transmission electron microscopy (TEM) images showed a lower dispersion of Np in the polymer matrix. The interaction between AgNps and ether groups also decreased the permeability of all gases (**Table 1**). Reduction of CO_2 and C_2H_4 permeability were clear, demonstrating the hindrance promoted by the AgNps in the sorption of both gases in the polymer matrix.

Table 1
Pure gas permeability in PUU/AgNps films at 25°C and a feed pressure of 0,2 MPa (2 bar)

AgNps content	Permeability (Barrer*)				$\alpha^{id\#}$ (C_2H_4/C_2H_6)
	CO_2	C_2H_4	C_2H_6	N_2	
none	180	61.8	45.4	3.80	1.36
<0.2 %wt	134	47.0	26.9	3.56	1.74
0.2 %wt	83.8	30.5	25.4	1.70	1.20
1 %wt	72.5	27.8	27.5	1.59	1.01

Note: *barrer = 10^{-10} cm^3(CNTP) $\cdot cm \cdot cm^{-2} \cdot s^{-1} cmHg^{-1}$; # α^{id} = pure gas permeability ratio

The ether linkage can interact with the CO_2 and C_2H_4 preferably [10,11]. The interaction between the AgNps and ether oxygen decrease the availability of ether oxygen to interact with both gases, thus changing their sorption coefficient in the polymer. The olefin facilitated transport through the polymeric films was not verified. This is partially caused by the lower dispersion of AgNps in the polymer matrix. Although an interaction between the AgNps and ether oxygen was observed, it was not possible to confirm if the Nps surface was really activated to facilitate transport. However, considering the results obtained it was possible to propose the interaction mechanism between AgNps and PUU; and also to indicate how the presence of Nps can change the interaction between the polymeric matrix and the petrochemical gases.

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SYNTHESIS OF A NEW MOF FOR COMPOSITE MEMBRANES

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Introduction

Metal Organic Frameworks (MOFs) are a relatively new class of hybrid materials built from metal ions as connectors and organic bridging ligands as linkers. By carefully selecting the metal and organic linkers, it is possible to produce a variety of topologies and structures [1]. In this work it is presented different ways of synthesis for the same Nickel (II) MOF. Changes in solvothermal synthesis conditions such as time and temperature allowed forming Ni-MOF with different crystal structures. Depending on size and shape of MOF crystals as well as metal centre features it is posible to build up new composite materials [2]. Variety of polymers and MOFs can render materials with electrical, optical, catalitic and barrier properties. XRD and SEM images of Ni-MOFs are shown as well as preliminary results of gas barrier properties.

Materials and Methods

Nickel (II) sulphate hexahydrate was provided by ANEDRA (Arg. Ind.) and 1, 3, 5-benzenetricarbonyl trychloride (>98 %, Sigma-Aldrich) were used as received. N, N-dimethylformamide (DMF, Fluka) was dehydratated by using a rotary evaporator. Polyetherimide (PEI, ULTEM 1000) was provided by General Electric, Pittsfield, MA. Chloroform (ClF, Fluka) and Dichloromethane (DClM, Fluka) were used without purification. Gas permeation assays were performed with H_2, CH_4 and CO_2 (99,95 %) provided by Air Liquid (Arg.).

Synthesis of Ni-MOFs

Ni-MOF was synthesized following different time and temperature procedures. However, in all cases 0.97 g of $NiSO_4.6H_2O$ were dissolved in 50 mL DMF at room temperature. Then, 0.097 g of organic linker were added to Ni-DMF solution under constant agitation. Inmediately after, 0.2 mL Pyridine were incorpored in order to catalize the reaction. The system was let to react at room temperature about 1 h, then time-temperature programmes were applied and they are shown in Table 1.

Table 1. Time and temperature programmes

MOF	First Step	Second Step	Final Procedure
1	50°C-1h a 80°C-1h	90°C-24h	AT°-SEx
2	AT°-24h a 110°C-1h	120°C-72h	AT°-SEx
3	50°C-1h a 110°C-1h	120°C-72h	AT°-SEx

AT° = ambient temperature; SEx = solvent exchange.

Activation process (solvent exchange process) was performed during 72 h using chlorofom as the solvent of exchanging. The solution was renewed every 24 h.

Results and discussion

XRD of MOF 1, 2 and 3 are shown in Figure 1. It can be observed MOF 1 and 3 showed narrower peaks in 2θ range of 5-50 °. It means they have well-defined crystalline structures. On the other hand, MOF 2 showed a less crystalline diffraction pattern. However, narrow peaks in MOF 2 diffractogram are placed on the same 2θ angle than MOF 3. This means both MOFs presented similar molecular arrangement, but MOF 2 possess lower crystal size than MOF 3. Besides, it could also be infered that an inclomplete both synthesis and activation process could occurre in MOF 2 synthesis.

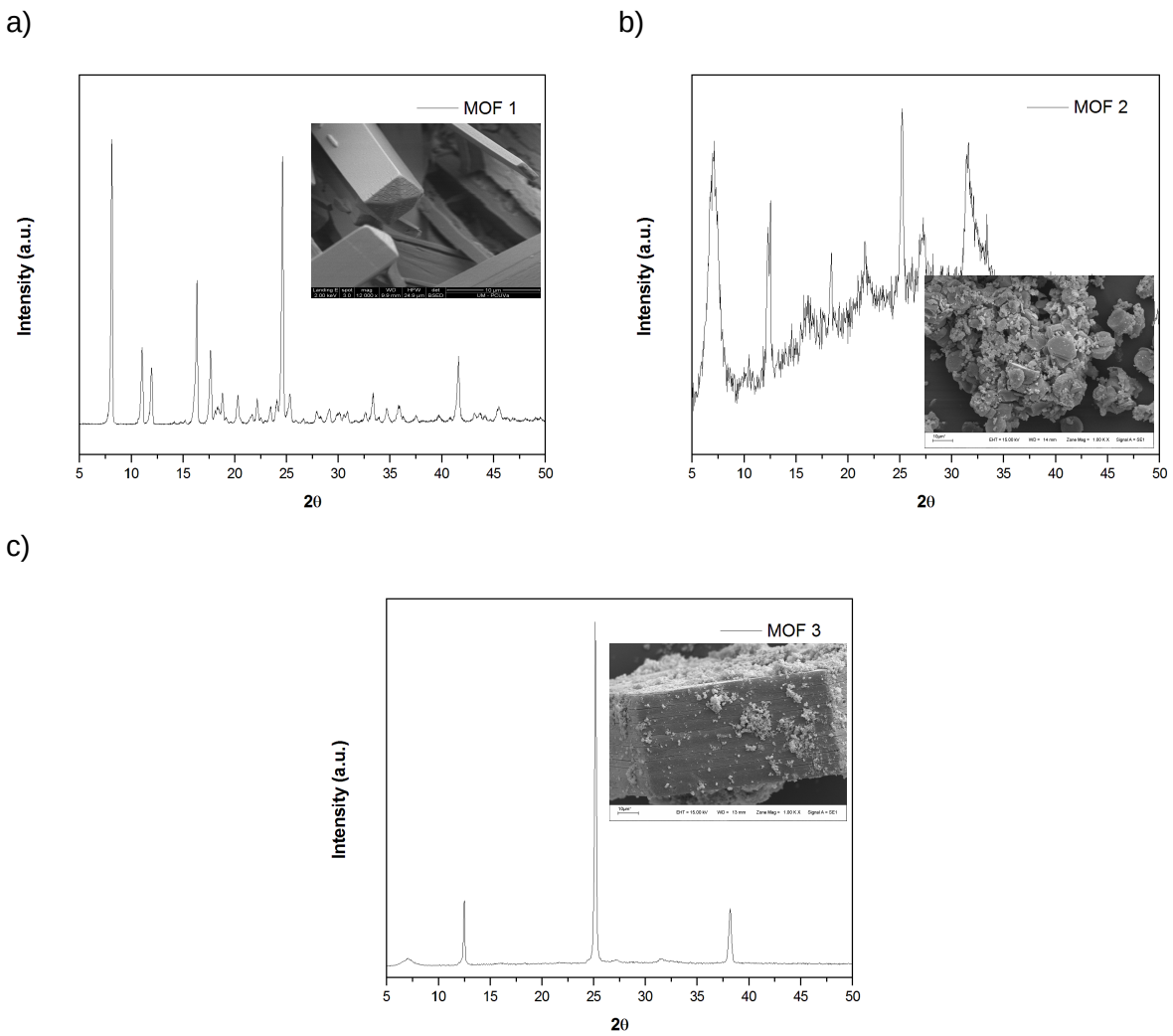

Fig. 1- XRD diffractograms of a) MOF 1, b) MOF 2, c) MOF 3.

MOF 1 and 2 were used to prepare PEI-MOF composites. MOFs were added at 5 wt.% respect to PEI. Gas permeation properties were measured through a time lag equipment. Results are shown in Table 2.

Table 2. Gas Permeation coefficients (T = 35 °C; p = 3 atm)

MMM	P_{H2} (B)	P_{CH4} (B)	P_{CO2} (B)	$\alpha_{H2/CH4}$	$\alpha_{H2/CO2}$	$\alpha_{CO2/CH4}$
PEI	6.904	0.029	1.561	238.07	4.42	53.83
PEI/MOF1	9.690	0.040	1.712	242.25	5.66	42.80
PEI/MOF2	9.161	0.514	1.370	17.82	6.69	2.66

P = 1 Barrer (B) = 10^{-10} (cm^3(STP)cm/cm^2 cmHg s).

Conclusion

Changes in MOF synthesis render filler materials with different size and shape crystals. Preliminary gas permeation assays showed rod-like MOF 1 has H_2/CH_4 selectivity while sheet-like MOF 2 presents H_2/CO_2 selectivity. Taking into account size and shape of crystals probably sheet-like MOFs are more promising fillers for composite materials.

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BIOMIMETIC AQUAPORIN MEMBRANES IN FORWARD OSMOSIS APPLICATIONS

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With diminishing freshwater supplies and the increasing demand for potable water and water for industrial use, new membrane technologies such as forward osmosis (FO) are increasingly attracting interest. However, despite recent advances in FO research, FO technology is not yet generally implemented as a large-scale water treatment for several reasons. First, a new type of membrane is needed, which has to be very thin in order to minimize internal concentration polarization. Second, a new system solution is needed: an FO membrane cannot simply replace an RO membrane in a conventional module design due to issues with interfacial polarization effectively diminishing the osmotic driving force. Finally the question of draw solution selection and potential recovery must be addressed. Not only the recovery process itself needs to be considered – also, for any type of draw solution potentially unfavorable interactions with known (conventional) membrane materials may occur. However biomimetics may hold important clues as how to design effective water processing systems. Most biomimetic membrane strategies are based on a bottom-up approach where few elements e.g. proteins and lipids are combined to create a membrane system with desired properties [1]. Here we present how water-selective aquaporin proteins together with suitable amphiphiles can be used to create a semi-permeable membrane with application potential [2, 3]. We characterize the membranes with respect to flux and surface properties and we present results of forward osmosis biomimetic aquaporin membrane performance for various applications including fertilizer drawn forward osmosis, waste water volume, reduction and peptide up-concentration.

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Acknowledgements

This work was suppported by a grant from the Danish National Advanced Technology Foundation for the project *IBISS: Industrial Biomimetic Sensing and Separation.*

COMPOSITE MEMBRANE BY DEPOSITION OF ACRYLIC ACID PLASMA POLYMER

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Plasma is a gas state of matter which includes a variety of neutral and ionized species such as molecules, atoms, electrons, ions, free radicals, and photons, which can be used to modify and functionalize the materials surface. Plasmas modify surface physical–chemical properties (hydrophilicity, adherence, chemical composition) keeping however bulk properties unaltered. Treatments with radio frequency plasma at low pressure were successful in generating functional groups and thin organic layer deposition.

The phase inversion technique has been widely used to synthesize anisotropic porous membranes over which plasma treatments have been applied. Polyethersulfone (PES) was selected as the starting bulk polymer due to its excellent properties. The obtained asymmetric membranes were then treated with non-polymerizable CO_2 plasma to clean and activate the surface.

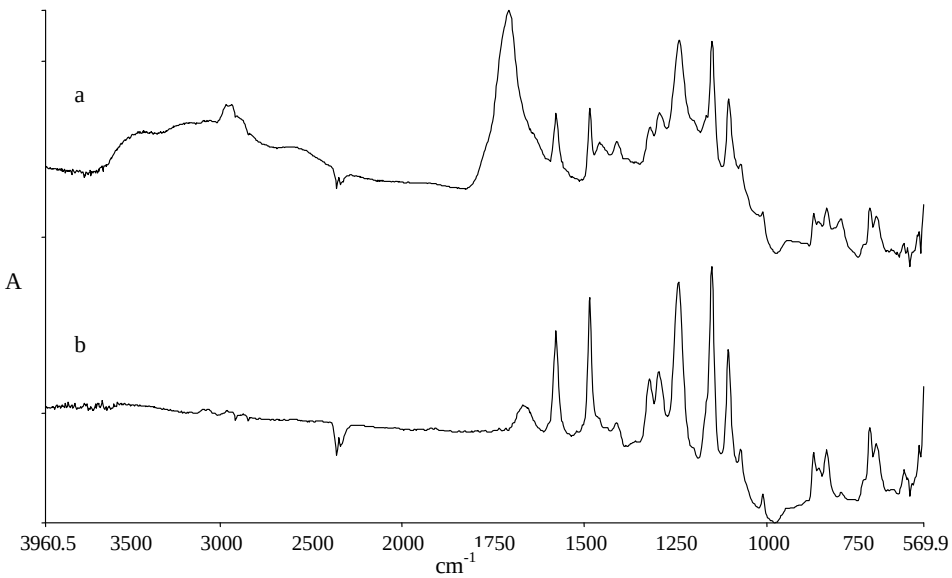

Fig. 1. FT-IR/HATR spectra of (a) AA plasma/PES composite membranes (PESM40) and (b) PES support membranes.

In a second stage, an acrylic acid (AA) layer produced by controlled plasma polymerization in situ was deposited over the previous activated surface. Surface chemical nature was studied using FTIR-HATR. Surface physicochemical properties were analyzed through measurements of contact angle (θ),

estimation of surface free energy and adhesion work. Cross-section and surface morphologies were investigated by SEM. Finally, pure gas permeation experiments (N_2 and CO_2) were performed to determine components' permeability and ideal selectivity.

A truly composite membrane has been obtained with a non-porous skin deposited onto the PES porous membrane (which surface was previously activated by a CO_2 plasma). The θ value of 64° observed with the PES support membranes. Plasma CO_2 treatment (7.2 W, 160 Pa, 5 min) cleans and activates the substrate membrane surface, removing weakly bound surface material and creating active sites. It leads to an important decrease of θ value to 33°. Then the plasma treatment with AA vapor (5 W, 8 Pa, 40 min) produces a stable top layer with a 27° θ value. Observation of the composite PESM40 membrane spectrum is shown to detect the presence of chemical groups (Fig. 1). It is inferred that the deposited film retains a high grade of AA monomer functionalities (1760 cm^{-1}) and AA dimer (1710 cm^{-1}), revealing that AA monomer structure was preserved under power and pressure reaction conditions (Fig. 1). The plasma polymer deposition on the PES-activated surface increases total mass transfer resistance up to 650 times for the exposure time of 40 min and N_2 permeation.

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Nanofiltration and Reverse Osmosis

- **Oral session 18**

PURIFICATION OF POLYPHENOLS AND SUGARS IN BERGAMOT JUICE BY NANOFILTRATION MEMBRANES

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Citrus bergamia Risso (bergamot) is a small tree belonging to the family Rutaceae. 90% of bergamot worldwide production occurs in the Southern coasts of Calabria region (Italy), where the microclimatic characteristics are particularly suitable for its cultivation. Bergamot fruit is used mostly for the extraction of its essential oil from the peel, a basic component of fragrances.

Bergamot juice, which is obtained from the endocarp after essential oils extraction, is considered just as a secondary and discarded product with related disposal costs. Over the past few years, bergamot juice attracted large attention as a result of its remarkable content of polyphenols and particularly flavonoids, known for their anticancer, antioxidant and anticholesterolemic activities [1-2].

The pharmacological properties of flavonoids (polyphenols) and their health benefits have intensified research efforts to discover and utilize methods for the extraction, separation and purification of these compounds from natural sources.

Extraction methodologies are mainly focused on the application of environmentally friendly solvents while novel separation technologies, including membrane separation techniques, have been developed and studied [3].

Ultrafiltration (UF) and nanofiltration (NF) technologies are interesting approaches for the recovery of bioactive compounds from vegetable sources and by-products of their industrial transformation [4-5].

The aim of this work was to compare the efficiency and performance of different NF membranes in the treatment of clarified bergamot juice finalized to the separation and concentration of phenolic compounds (mainly flavonoids) from sugar compounds. For this purpose, the clarified bergamot juice, coming from a preliminary ultrafiltration (UF) treatment, was processed with three different NF spiral-wound membranes (NP010 and NP030 from Mycrodin Nadir and NF 270 from Filmtec-Dow) characterized by different molecular weight cut-off (MWCO) (from 200 to 1000) and different polymeric material (polyethersulphone (PES) and polyamide (PA)).

The performance of selected membranes was evaluated in terms of productivity and selectivity towards compounds of interest (sugars, flavonoids, total phenolic compounds) and total antioxidant activity (TAA) in different operating conditions.

An analysis of fouling index together with the evaluation of hydraulic resistances of selected membranes was also carried out.

According to their MWCO PES membranes exhibited higher permeate fluxes in comparison with the PA membrane in selected operating conditions. On the basis of measured rejections these membranes produced also a better separation of sugars from phenolic compounds (Figure 1).

Retentate fractions exhibited high TAA and represented formulations of interest for nutraceutical applications (i.e. functionalized fruit juices) due to the presence of bioactive compounds (mainly flavonoids) recognized for their capacity to interfere with cholesterol metabolism.

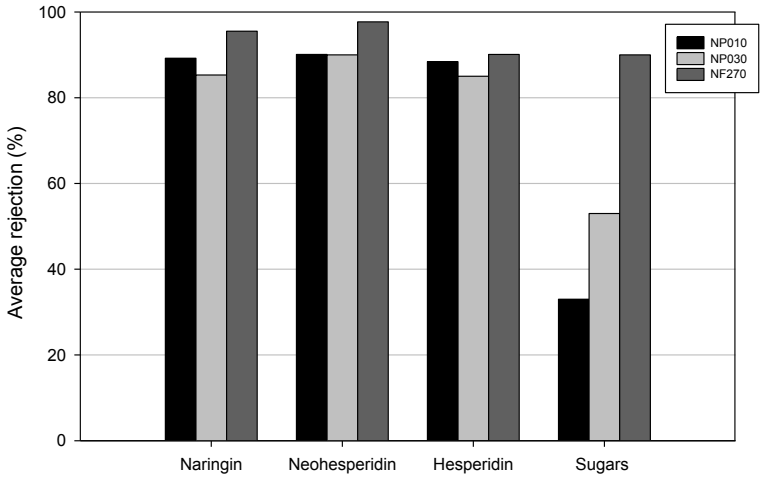

Figure 1 - Average rejection of NF membranes towards flavonoids and total soluble solids

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UP-SCALING OF NANOFILTRATION HOLLOW FIBER MEMBRANES FOR SULFATE REMOVAL

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The increasingly strict environmental regulations and the economic advantages of using membranes, such as the reduced waste disposal, led to advances in nanofiltration (NF). Many commercial NF composites are based on the interfacial polymerization (IP) of an aqueous piperazine film on an ultrafiltration support by hydrophobic aromatic crosslinkers. An important application is the removal of the sulfate for oil field seawater injection operations. It is a clean technology that allows the separation of components without phase change, low energy consumption and high productivity. However, there are still many limitations to overcome with the development of better membranes. The major restrictions are the increase in productivity of treated water (permeability) while maintaining membranes selectivity, the production of membranes more resistant to fouling and the production of membranes that can be operated in a wide range of pH, high temperature and/or in the presence of oxidative reagents [1,2].

The challenges of this work were three: 1) develop self-supporting hollow fiber membranes that are sulfate ion-selective 2) design and construct a NF prototype module and 3) test the module using a membrane filtration pilot plant. We have investigated the synthesis of NF hollow fiber membranes by using polyetherimide (PEI) as a porous support. This polymer presents good chemical and thermal stabilities and asymmetric morphology generated by the Loeb-Sourirajan phase inversion technique [3].

The hollow fiber membranes were made from a polymer solution composed of PEI, poly(vinyl pyrrolidone) and N-methyl-2-pyrrolidone (NMP). The bore liquid was composed of NMP and water. The solutions were placed into a spinning set-up (Figure 1) and subjected to a coagulation bath in water. The temperature of polymer solution and the air gap between the spinneret and the coagulation bath, were varied in order to evaluate their effect on the morphology and performance of the fibers. The thin dense layer was made by interfacial polymerization of hydrazine, piperazine and trimesoyl chloride (TMC) on the outer surface of the PEI support. The scanning electron microscopy images (SEM) indicated the existence of pores (size range 100-400 nm) on the support, while no visible pores could be observed on the selective layer (Figure 2).

Laboratory modules contain an effective area of 0.0036 m^2 and the transport properties were determined using a crossflow permeation setup. The hollow fiber NF membranes showed a salt rejection range of 85 to 92% and permeability of 1.1 to 2.0 $l/h.m^2.bar$ for a feed aqueous solution containing 2,000 mg/l $MgSO_4$ operated at 10 bar (Table 1).

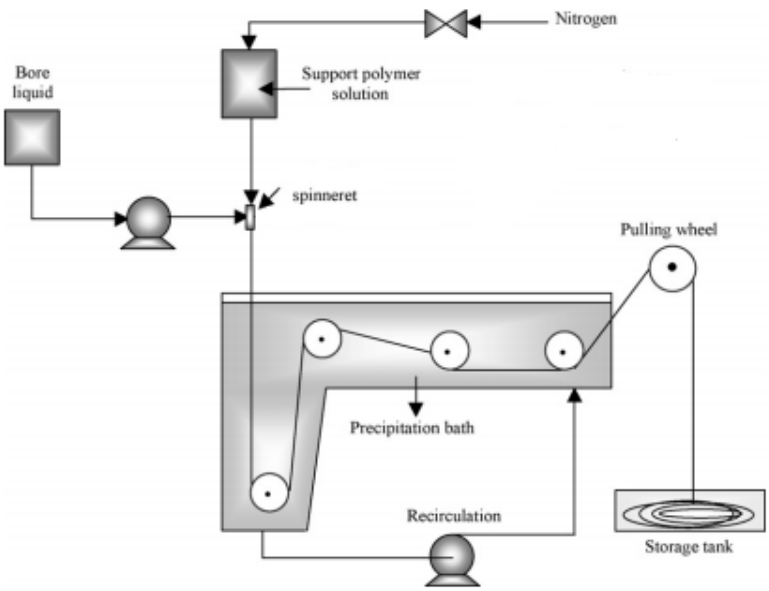

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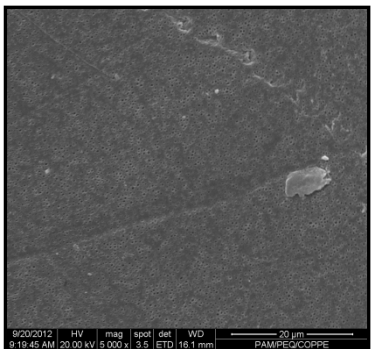
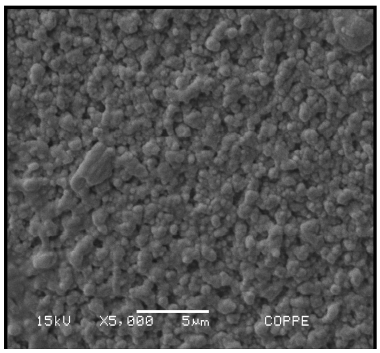
Figure 1. Schematic of Spinning Set-up



Support



IP dense selective layer

Figure 2. Morphologies at the outer surface of the membrane by SEM

Table 1. Retention and Permeability Measurements

Batch	Saline Rejection	Permeability (L/h.m².bar)
1	85%	1.1
2	92%	1.8
3	87%	2.0

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Acknowledgements
We would like to thank PETROBRAS for the financial support.

PHOSPHATE RECOVERY FROM TERTIARY TREATMENT EFFLUENTS USING NANOFILTRATION MEMBRANES

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Phosphate recovery will become more important within the next decades due to depletion of mineral phosphorus resources [1]. Waste water has been identified as a secondary resource of this substance and nanofiltration (NF) is an attractive membrane process for selective phosphate recovery, since high rejections of NaCl are not required. This technique has similar performance as reverse osmosis (RO). However, NF membranes allow higher salt passage than RO membranes, which decreases osmotic pressure. Furthermore, the high permeability of NF membranes also reduces the pressure needed for phosphate recovery making NF a more cost effective process. Experimental studies evaluated the recovery of phosphate, however scare data on the description of the rejections could be found. Although those studies have obtained interesting results under several conditions, they do not explain the rejections of the phosphate under the extent of a rigorous transport model [2,3]. In this work the Solution-Diffusion-Film Model (SDFM) was used, to describe the phosphate transport through a planar NF membrane in the separation process of tertiary treatment effluents (TTEs) [4]. Experimental data was obtained with synthetic aqueous solutions of different major salts, present in TTEs, with phosphate as ion trace. The experiments were carried out with a polyamide thin-film composite NF membrane NF270 (Dow Chemical Company, Midland (USA)). A cross-flow set-up equipped with a test cell (GE SEPA™ CF II) with a spacer-filled feed channel and the possibility of independent variation of trans-membrane pressure and cross-flow velocity was used. A flat sheet membrane with an effective filtration surface of 0.014 m^2 was used (See Figure 1). The SDFM performed a good prediction of the behavior of species in solution, and rejection streams, with small deviations between mesured and predicted values. Then, it can be considered as a suitable model for design and calculations. According to Figure 2, high performance in the separation of phosphate in solution was observed (above 90%), demonstraiting that NF is an appropriate membrane process for phosphate recovery. In turn, the phosphate rejection is not considerably affected by the different major salt used in the solution.

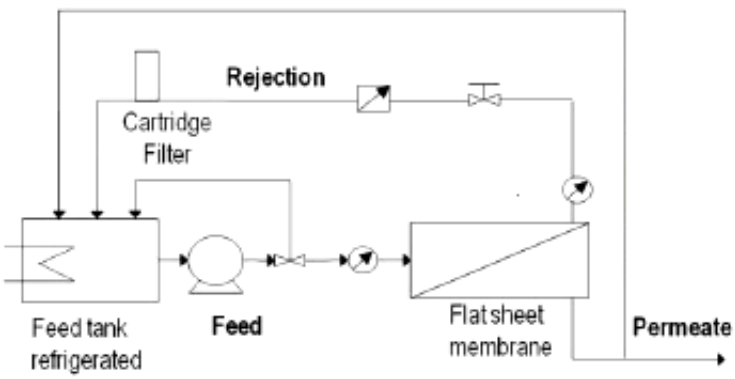

Figure 1. Experimental setup.

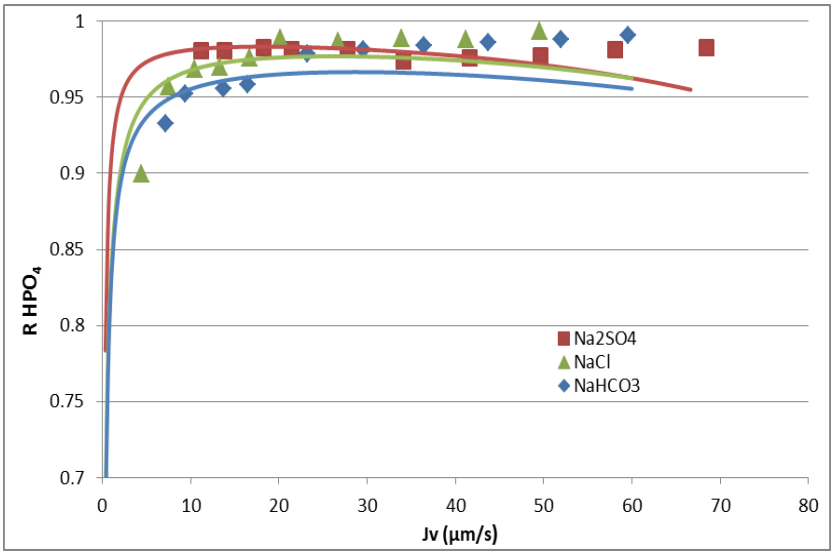

Figure 2. Phosphate rejection with different major salts in the solution in terms of trans-membrane flow (Jv).

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Acknowledgements

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DETECTION OF DAMAGES ON REVERSE OSMOSIS MEMBRANES

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Abstract

Water treatment by reverse osmosis technology has as main aim to reject the maximum percentage of ions from raw water, giving as much treated water flow as possible. When there is a loss in these two parameters performance, it is essential to find the source of the failure, in order to use the necessary tools for its recovery. At this point, membrane autopsies are a very valuable source of information in order to understand the mechanisms that may have produced membrane capabilities loss.
Genesys Membrane Products (GMP) laboratory has developed during last decade more than 500 autopsies of membranes from all over the world. Therefore all the data obtained from these autopsies are a very valuable source of information about membrane failures. These membranes studies have shown that in almost the 60% of the cases, fouling is the main cause of membrane failures and this is one of the reasons because there is a broad research developed in fouling mechanisms understanding. The data obtained from these autopsies, have demonstrated also that the worst and main impact of fouling on membranes performance is the damage of polyamide layer and on rejection capabilities (1).

During the performance of reverse osmosis membranes in plants, there are many different processes that can damage the membrane surface: increases in differential pressure, backpressure phenomena, abrasion processes from fouling, massive or micro damages from scaling, oxidation processes or even degradation with time or cleanings. These damages, are commonly related to an increase in flow rate permeate and in a salt rejection decrease.
A well knowledge of membrane damage is very important considering that in more than the 30% of the membranes autopsied in GMP this phenomenon was found severe. These phenomena study is important also because, in many cases, damage is hidden by fouling and autopsies are the only way to detect a first step damage that could be prevented in plant if appropriated remedies are applied. GMP autopsies results demonstrate that almost the 80% of the studied membranes show slight signals of damage on the membrane surface, which were probably not detected in plant considering only performance failures.

In this study, statistical analysis from autopsies data will be used to check membrane damages, considering plants performance, membrane position, kind of fouling, feed water type, etc.

When membrane damage is studied, it is very important to distinguish between chemical and physical damage. During the study of the autopsies developed in GMP laboratories the percentage of membranes with a severe physical damage was very similar to the membranes with a relevant degree of chemical damage. When this damage is severe, it is quite easy to detect and even to distinguish its source, but it is much more common that the detected damages are mild or slight, and in these cases it is more difficult to determinate the main cause of the damage.
On the other side, when the damage has been produced by oxidation, it is easy to demonstrate it when a relevant presence of chlorine is detected but, in some cases, there are clear signals of oxidation with no presence of halogens on the membrane surface.

The study of a membrane surface during an autopsy, involves different analytical techniques that will provide the needed information for a final diagnostic. For membrane damage determination, some traditional analyses and parameters to consider are:
- *Flow rate and salt rejection* compared with manufacturer reference values: Performance parameters are the main signals of membrane failures, but values changes may be hidden by the presence of fouling.
- *Fujiwara test*: It will determine if membrane has been in contact with halogens, but presence must be relevant enough for its detection. This test won't detect presence of oxidant agents different than halogens.
- *Methylene blue test*: This test will detect polyamide damages by using a high molecular weight compound that should not be detected on the permeate side of the membrane, if there were not damages on it. Traditionally, a positive answer on this test has been related to physical damage if Fujiwara test was negative and to chemical damage if Fujiwara test resulted positive.
- *Scanning Electronic Microscopy with X-ray dispersive energy detection (SEM-EDX)*: Microscopy techniques are a good tool for distinguishing abrasion marks, but mainly when they are small. There are other physical damages on membrane surface as polyamide bubbles, which cannot be easily detected by this technique (SEM). The detector used in this kind of microscopy for elementary analyses (EDX) allows to get very useful information about the composition of the surface/particles/deposits from images but it is not sensitive enough for the detection of elements that can be bound to the membrane surface.
- *Electron spectroscopy for chemical analysis (ESCA, also known as XPS)*: This technique is used for the detection of compounds different than membrane components, in order to detect possible sources of oxidation. This technique allows to distinguish different oxidation states of the detected elements.
- *Infrared Spectroscopy by Attenuated Total Reflectance (FTIR-ATR)*: Reverse osmosis membranes show a characteristic polyamide-polysulphone spectrum that can be used as reference, in order to detect structural changes on polyamide layer. When these changes are not very relevant, it is very difficult to determinate if slight decreases on polyamide bands could be due to an oxidation process.

Besides, there are some other techniques as *confocal microscopy*, *atomic force microscopy, z-potential* and other useful parameters that are not commonly used during autopsied, but that could give complementary information about membrane surface and its damages.

From the results obtained using some of these techniques on the autopsies carried out on GMP laboratory, the author intends to do also a review of the different analytical tools available for membrane damages detection and to check their advantages and disadvantages.

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Nanofiltration and Reverse Osmosis

- **Poster session 2**

EVALUATION OF INHIBITION PROPERTY OF SCALE REMOVER IN OFFSHORE NANOFILTRATION SYSTEM

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The Sulfate Removal Units (SRU) are situated in offshore plataforms. It removes the sulfate ions of the seawater by nanofiltration. So, the risk of scale formation is decreased during oil recovery by seawater injection.[1-2]

The nanofiltration system of SRU are made by permeation modules with nanometric pores and sulfate ions selective membranes. In this system, the sulfate and calcium ions are retained in membrane surface and there is high risk of gypsite formation in this localization (polarization region). This fact can decrease the process efficiency and increase the costs.

To minimize this problem, some chemical products as biocides and scale inhibitors are dosed in SRU and they avoid the gypsite and biofilm formation in surface membrane. [3-4]

Additionally, it is recommended periodic chemical cleanings in permeation modules. The chemical cleaning with quelant agents as Na_4EDTA are very recommended for nanofiltration and reverse osmosis systems. In this kind of cleaning are removed organic and inorganic composites and biofilms. [5]

In the current study was evaluated the inhibition property of Na_4EDTA aqueous solutions. So, it would avoid the dosage of different chemicals in SRU and therefore reducing the incompatibility risk among chemicals and costs.

Assays were made in lab considering the situation of high risk for gypsite formation in the nanofiltration membranes of the SRU (membrane surface). The ionic composition of the aqueous fluid considered in these assays was estimated by ionic composition of the feed and permeated and concentration polarization and transport mechanism in nanofiltration.[4,6]

The assays temperature was 25°C (the same temperature that SRU operate) and 1 bar (pressure more severe than pressure that SRU operate, considering the gypsite formation).

Dissolution and inhibition static efficiency assays were made in lab for evaluate the both porpeties of the Na_4EDTA aqueous solutions. In the dissolution assays, 5,0g of $CaSO_4$ remained immersed in 40mL of Na_4EDTA aqueous solutions (2, 5 e 10% (v/v), all with pH 10,8), to 25°C for until 10 hours. Each 2 hours one aliquot was colected to define the calcium concentration in solution by ICPOES (inductively coupled plasma optical emission spectroscopy). The Table 1 shows the dissolution results.

Table 1: Dissolution of the $CaSO_4$ in Na_4EDTA solutions, to 2, 5 e 10% (v/v), until 10 hours and 25°C.

Time, hours	g of $CaSO_4$ dissolved / L Na_4EDTA aqueous solutions		
	Solution to 2% (v/v)	Solution to 5% (v/v)	Solution to 10% (v/v)
2	0,0164	0,0330	0,0619
4	0,0161	0,0344	0,0619
6	0,0167	0,0337	0,0619
8	0,0157	0,0306	0,0550
10	0,0160	0,0330	0,0584

Inhibition static efficiency assays were made to 25°C, with the aqueous fluid simulated for nanofiltration membrane surface of SRU and the Table 2 shows the ionic composition of this fluid.

Table 2: Ionic composition (mg/L) of aqueous fluid simulated for nanofiltration membrane surface.

$[Na^+]$	$[K^+]$	$[Ca^{+2}]$	$[Mg^{+2}]$	$[Sr^{+2}]$	$[Cl^-]$	$[Br^-]$	$[SO_4^{-2}]$	$[HCO_3^-]$	pH 25°C	[NaCl]
1100	486	4266	23261	95	1876	59	28474	1000	8,00	30964

The Na_4EDTA aqueous solutions were prepared in the concentrations of 20 and 30% (v/v), because, in general, the commercial inhibitor solutions for offshore nanofiltration system are prepared in these same concentrations.
In the aqueous fluid the Na_4EDTA aqueous solutions were dosaded in the concentrations of 5 mg/L (recommended dosage by makers of the scale inhibitor for offshore nanofiltration system) and 15 mg/L (superdosage for comparation). Write assays were made in the same time to enable the calculation of the static efficiency to $CaSO_4$, through comparative analysis of the calcium concentrations almog the original aqueous fluid, white assays and real assays (with dosages of the Na_4EDTA aqueous solutions). The Equation 1 shows the the calculation of the static efficiency.

$$([Ca^{+2}]_{assay} - [Ca^{2+}]_{write})/([Ca^{2+}]_{orig}-[Ca^{2+}]_{write})*100 \qquad \text{Equation 1}$$

where:

$[Ca^{+2}]_{assay}$ is the calcium concentration in the assays with inhibitor of Na_4EDTA;
$[Ca^{2+}]_{write}$ is the calcium concentration in the assays without inhibitor of Na_4EDTA;
$[Ca^{2+}]_{orig}$ is the calcium concentration in the aqueous fluid estimaded for membrane surface.

The Table 3 shows the inhibition static efficiency results for Na_4EDTA aqueous solutions (20 and 30% (v/v)), dosaded in concentrations of the 5 and 15 mg/L, in aqueous fluid estimaded for membrane surface of SRU, to 25°C for until 1 hour.

Table 3: Inhibition static efficiency results for Na_4EDTA solutions (20 and 30% (v/v)), dosaded in 5 and 15 mg/L, until 1 hour and 25°C, in aqueous fluid estimaded for membrane surface of SRU.

Products	Assays	Inhibition static efficiency results, %			
		10 minutes	20 minutes	40 minutes	1 hour
Product with 20% Na_4EDTA pH10,8	5 mg/L	100	100	100	28
	15 mg/L	100	100	100	17
Product with 20% Na_4EDTA pH 10,8	5 mg/L	100	100	100	100
	15mg/L	100	93	89	84

The results of dissolution and inhibition static efficiency of the $CaSO_4$ can concluded that Na_4EDTA aqueous solutions (concentrations equal or above 2%) can be considered good to removal of $CaSO_4$ at 25 ° C for the nanofiltration membrane surface conditions of the URS. In additional it is possible conclude that the same chelate agent (Na_4EDTA) can be used to inhibit gypsite formation in SRU conditions (concentration equal to or greater than 30% and considering a good dosage of the 5 mg/L in SRU' seawater. Further studies are recommended in the same research involving lab units of continuous flow with nanofiltration membrane and aqueous solutions Na_4EDTA as inhibitory solutions of gypsita.

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Acknowledgments

To Laboratório de Tecnologia de Incrustação (CENPES – Petrobras Research Center) and the work time this lab.

Nanotechnological Application in WAter DESalination (NAWADES)

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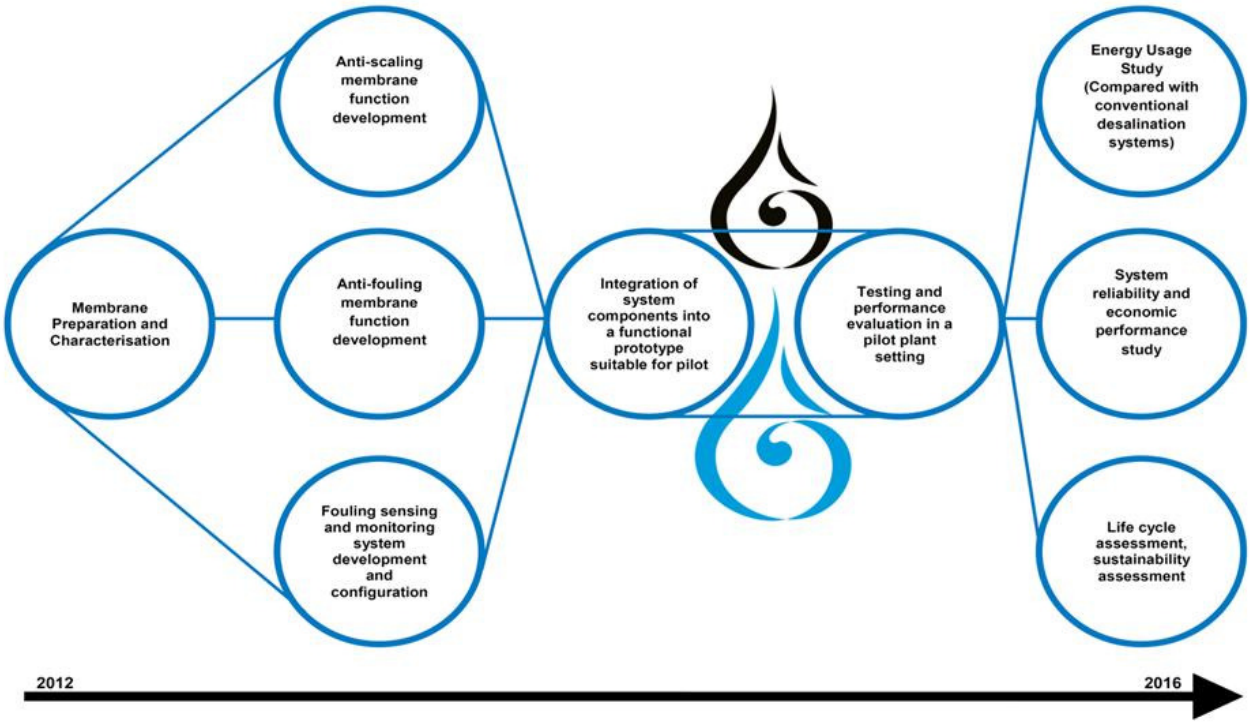
Pollution, over-exploitation of natural resources, damage to aquatic ecosystems, climate change and security aspects are challenging the sustainability of European water systems. Given global economic and population growth, the 2030 Water Resource Group reports that the worldwide water supply-to-demand gap is likely to reach approximately 40% by 2030 unless significant efficiency gains can be made. The Intergovernmental Panel on Climate Change (IPCC) predicts that by the year 2050, around 60% of the world's population could experience severe water shortages, with 33% already thought to be under stress.

There is an urgent need to protect diminishing clean water resources and to upgrade/develop alternative water sources, promoting investments in water treatment and desalination. Membrane technologies for RO applications are very well suited for use in commercial desalination plants. However desalination using RO membranes is a process that presents a number of environmental challenges generating waste streams of brine and chemical agents, and consuming considerable quantities of energy.

The objective of the NAWADES project is to develop a new innovative and cost-efficient water desalination system design, comprising micro and ultra-filtration as a pre-cleaning step within one membrane or within separate membrane process steps.
There are two main topics addressed in the NAWADES project, namely concentration polarization and organic fouling. Our research aims to overcome these limitations and develop a sustainable RO process, by reduction of concentration polarization and organic fouling, providing a longer membrane life, higher efficiency, less energy consumption (lower pressure), and less maintenance (lower cost).



The new filter technology will provide long-life and non-fouling filters to be used in Sustainable Reverse Osmosis Water Desalination processes with pure and chemical-free salt harvesting, low energy consumption due to lower pressure loss, and low maintenance due to the automated anti-fouling and anti-scaling effects that will result in lower overall costs. The filters will not need flushing with aggressive and environmentally harmful chemical agents.

The qualitative and quantitative targeted results in NAWADES will be:

- Development of a sustainable RO process reaching permeate quality of 500 mg/l of total dissolved salts (TDS) from seawater feed (at 35,000 mg/l TDS)
- Increasing the operational life of the membrane filter by a factor of 3 to a minimum of 8 years
- Quantitative harvesting a clean salt fraction and thereby solve brine disposal issues
- Development of a filter system with minimal maintenance requirements (set-and-forget filter system)
- Reducing estimated overall cost of desalinized water by approximately 20% to below €0.30/m^3

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Acknowledgements

- The authors are grateful to the funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement nº 308439)

Partners

EVALUATION OF ELECTROLYTE MIXTURES REJECTION BEHAVIOR USING NANOFILTRATION MEMBRANES USING SPIRAL WOUND AND FLAT SHEET CONFIGURATIONS

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Nanofiltration (NF) is a growing separation technology for water treatment processes at different industrials lands. It can be used in different membrane configurations, such as flat sheet (FS) or spiral wound (SW). Usually, FS configuration is used at lab-scale test membrane. On the other hand, SW membrane configuration is used at industrial scale, due to the need for more active membrane area and the space optimization. For this reason, the aim of this study is to determine the reliability of the data obtained in a FS lab-scale set up when they are implemented at industrial scale level using SW configuration.

Two different pilot plants were used to evaluate the ion rejection of mixed feed salt solutions, based on a dominant and a trace salt. The membrane used in both pilot plants was the NF270 membrane, supplied by Dow Chemical, with an active membrane area of 0.014m^2 and 2.6m^2 for the FS and SW configuration, respectively. The membrane used has a negative superficial charge. Experimental conditions in both membrane configurations were the same: different synthetic salt mixture feed solutions were used working at constant temperature while the trans-membrane pressure (TMP) varied from the osmotic pressure to 20 bars with increments of approximately 2 bars. For each sample taken at different pressures, a trans-membrane flux was obtained. The concentrate and the permeate streams were recirculated in both cases to maintain constant the feed solution concentration during the experiment. Different parameters such as, pH, conductivity, temperature, TMP and flow rate were measured and monitored along the experiment. Synthetic solutions were prepared representing brackish waters of Catalonian rivers, such as Llobregat and Ebre. For this reason, NaCl, $MgSO_4$ and $MgCl_2$ were used as dominant salts, and Br^-, NH_4^+, K^+ and I^- were used as ion traces. This experimental design was used to study the effect of different electrolyte mixtures to a trace ion rejection. Trace salt concentration was set from 0.5 to 2% of the dominant one.

The results of each experiment were modelled using the Solution-diffusion-film model (SDFM) [1] and compared taking into account the membrane configuration. By means of the SDFM the ion permeability of each ion can be calculated. This value depends on the capacity of the ion to cross the membrane.

Figure 1 shows the measured and predicted ion rejection data as a function of trans-membrane flux for each feed salt solution using both membrane configurations. Results showed that the most rejected ions were divalent ones in both configurations, in which SO_4^{2-} was the most rejected one followed by Mg^{2+}. NaCl is rejected moderately and K^+ has shown a negative rejection. This phenomena was previously explained by Pages et al. [2]

Comparing both membranes configurations, it is observed that fairly similar results are been obtained. However, for the same operation conditions, more trans-membrane flux was obtained working with FS configuration. Besides, the ion permeability order for each experiment was the same in both membrane configurations.

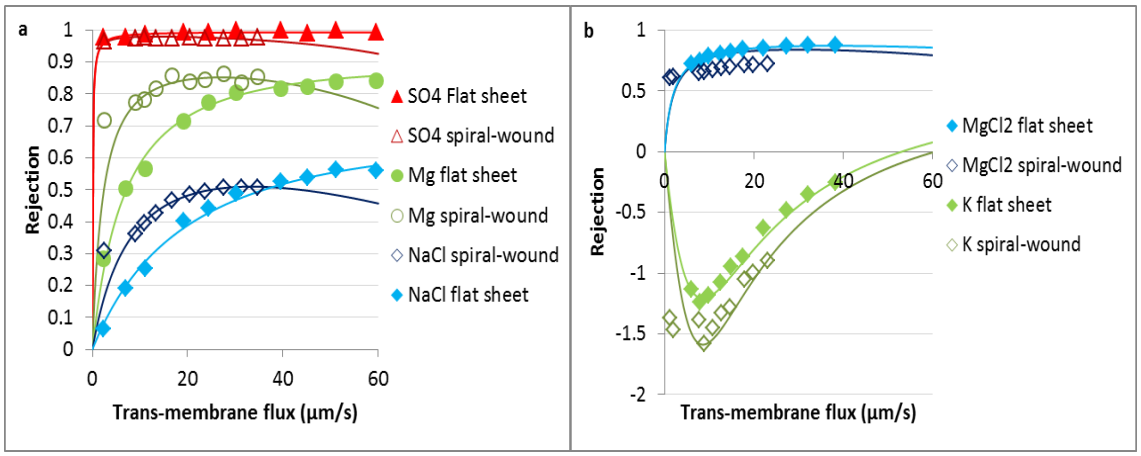

Figure 1. Dominant salt and trace ions rejections depending on the trans-membrane flux for both FS and SW configurations membrane with different salt feed mixtures: a) NaCl as dominant salt and $MgSO_4$ as trace; b) $MgCl_2$ as dominant salt and KCl as trace. Solid lines correspond to SDFM fits.

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Acknowledgements

This research was supported by the ZERO-DISCHARGE project (CTQ2011-26799) financed by “Ministerio de Economía y Competitividad” and the Catalan Government (Project Ref. 2009SGR905), Spain. The work of Mònica Reig was supported by the Spanish Ministery within the scope of the grant BES-2012-051914

SEPARACIÓN Y RECUPERACIÓN DE COMPUESTOS DE INTERÉS PRESENTES EN DISOLUCIONES DILUIDAS Y MEZCLAS COMPLEJAS MEDIANTE NANOFILTRACIÓN

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La nanofiltración (NF) es un proceso de separación con membranas que ha experimentado un gran desarrollo en los últimos años. Las membranas utilizadas en esta tecnología tienen un corte molecular comprendido entre 100 y 1000 Da y además poseen una ligera carga superficial, siendo capaces de retener partículas de tamaño superior a 1 nm y de poder separar sales monovalentes de sales multivalentes, así como iones y sales multivalentes del resto de solutos presentes en la disolución utilizada como alimentación al proceso. Por ello, la tecnología de NF se aplica extensamente en el tratamiento de agua potable y también en la industria alimentaria, por ejemplo en la concentración de zumos, en la desmineralización de disoluciones azucaradas y en la purificación de ácidos orgánicos [1, 2].

Los mecanismos de transporte que intervienen en la permeación de componentes en el proceso de NF pueden ser de muy diferente naturaleza. Así, la separación de solutos no cargados puede obedecer tanto a un mecanismo de separación basado en la diferencia de tamaños, propio de la ultrafiltración, como a un mecanismo de disolución-difusión, propio de la ósmosis inversa. En ocasiones es el efecto combinado de varios mecanismos de transporte el que explica la separación de componentes de una mezcla [3]. En el caso de sales y moléculas cargadas, pueden alcanzarse mayores grados de retención que el esperado por su tamaño molecular. Las membranas de NF suelen presentar carga en la superficie de los poros, con mayor o menor densidad de carga en función del pH y la fuerza iónica del medio. Como consecuencia, se produce la retención de co-iones (iones de igual carga que la membrana) y la permeación de iones puede estar controlada por el principio de exclusión de Donnan [4]. Otros efectos que pueden afectar la retención de solutos por la membrana son el efecto electroviscoso (fricción) en los poros, el hinchamiento de la membrana en presencia de sales, o la modificación del radio de Stokes de los solutos no cargados en presencia de sales.

La complejidad de las interacciones entre los solutos y la membrana justifica la necesidad de seleccionar la membrana de NF que sea más apropiada para cada situación particular y, por tanto, la necesidad de realizar una adecuada caracterización de las mismas.

El objetivo principal del presente trabajo ha consistido en la caracterización de membranas espirales poliméricas de nanofiltración de diferente corte molecular y en la posterior evaluación de su capacidad para la separación, a escala piloto, de compuestos de interés presentes en disoluciones acuosas diluidas.

Los experimentos se realizaron en una planta piloto de nanofiltración, equipada con bombas de alta presión y sistemas de control de presión y temperatura, trabajando con lotes de 10–20 litros de alimentación durante períodos de tiempo de 3–6 horas. Se utilizaron dos membranas espirales poliméricas de diferente corte molecular (200 Da y 500 Da), con un área de membrana de 1.7 m^2. Las experiencias se realizaron con recirculación total de retenido y permeado al tanque de alimentación para trabajar a concentración constante, con un caudal de alimentación de 1050 L/h, una temperatura de operación de 27ºC, y variando la presión entre 10 y 17 bar.

En primer lugar, se caracterizaron las dos membranas mediante la determinación de su permeabilidad hidráulica y el rechazo a una variedad de solutos de diferente tamaño y carga iónica en disoluciones acuosas simples de un único componente. Los solutos seleccionados fueron los siguientes: betaína, sacarosa, ácido láctico, ácido cítrico, cloruro sódico, cloruro potásico y sulfato de magnesio, que son los componentes principales de las melazas de remolacha azucarera. Se determinó la concentración de dichos solutos, tanto en la alimentación inicial como en los permeados y retenidos obtenidos para las diferentes presiones de operación. Para determinar la concentración de las sales (NaCl, KCl y $MgSO_4$) se utilizó un conductivímetro Crison GLP31, mientras que la concentración de sacarosa se determinó por polarimetría (polarímetro MCP500 Sucromat, Anton Paar) y la de betaína, ácido láctico y ácido cítrico por cromatografía líquida (HPLC-10 AD, Shimadzu).

Posteriormente, se utilizaron diferentes modelos matemáticos para describir los mecanismos de transporte y retención de los solutos a través de las membranas de NF, obteniendo los mejores resultados al aplicar el modelo de Spiegler-Kedem-Katchalsky (SKK). Este modelo [1, 5, 6], basado en la termodinámica de no-equilibrio, considera que el transporte a través de la membrana es consecuencia de la combinación entre un flujo convectivo, debido a la aplicación de un gradiente de presión, y otro difusivo, debido a la diferencia de concentración a ambos lados de la membrana, proponiendo una relación entre la densidad de flujo de disolvente (J_v) y de soluto (J_s) a través de la membrana. En estos sistemas de un componente en disolución acuosa se ha observado un buen ajuste del modelo de SKK para el rechazo de los solutos no cargados y de las sales. En el caso de solutos cargados, como son el ácido láctico y el ácido cítrico, existen desviaciones del modelo de SKK que indican interacciones entre la membrana cargada positivamente al pH de la disolución, que es menor que el punto isoeléctrico de las membranas, y los iones presentes en la disolución se transportan siguiendo un mecanismo de exclusión Donnan.

Por último, se estudió la separación de solutos en mezclas complejas, en ausencia y en presencia de sales, simulando una melaza de remolacha azucarera diluida, observándose interacciones entre componentes que afectan a la selectividad de la operación, como se observa en la Tabla 1.

Tabla 1. Rechazos experimentales (%) de los solutos en disolución simple y en mezclas complejas, sin sales (Sintética I) y con sales (Sintética II).

	Membrana 200 Da			**Membrana 500 Da**		
	Simple	**Sintética I**	**Sintética II**	**Simple**	**Sintética I**	**Sintética II**
Sacarosa	99.66–99.75	96.19–96.83	96.48–99.08	93.10–93.59	91.73–93.62	94.05–94.34
Betaína	95.41–96.75	86.90–90.51	80.80–89.88	69.08–70.03	80.48–82.30	63.22–70.37
Ác. Cítrico	89.96–92.12	70.10–70.80	89.62–93.57	27.85–27.97	27.34–35.58	28.79–39.25
Ác. Láctico	24.66–32.75	23.85–20.78	25.67–31.98	8.93–10.16	0.26–5.30	3.32–5.08

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DISEÑO DE UN PROCESO COMBINADO ULTRAFILTRACIÓN/NANOFILTRACIÓN PARA LA DECOLORACIÓN DE VINAZAS INDUSTRIALES

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La melaza, obtenida en el proceso de producción del azúcar a partir de caña o de remolacha, es el principal subproducto valorizable de la industria azucarera. Su elevada producción (aproximadamente 4 kg melaza/100 kg remolacha tratada) y su contenido en azúcares (55% en peso, mayoritariamente sacarosa), hacen que se emplee principalmente como sustrato en fermentaciones para la producción de etanol y bioetanol [1] y de ácidos orgánicos [2, 3]. El residuo generado por estas industrias basadas en la fermentación de melazas azucareras son las vinazas. Dichos efluentes residuales presentan gran cantidad de sustancias coloreadas, que son las responsables del color marrón característico de las vinazas, así como de su elevada carga orgánica. La mayor parte de la carga orgánica de las vinazas puede ser eliminada tras un tratamiento biológico adecuado. Sin embargo, el color no desaparece y puede incluso aumentar debido a la repolimerización de los compuestos coloreados.

Los compuestos coloreados más abundantes en las vinazas son las melanoidinas, que son polímeros de elevado peso molecular. La formación de melanoidinas comprende una secuencia de reacciones químicas simultáneas que tienen lugar entre compuestos orgánicos nitrogenados y carbohidratos, que se conoce como reacción de Maillard. Mediante un tratamiento convencional anaerobio-aerobio de las vinazas se consigue degradar únicamente un 6–7% de melanoidinas. Por tanto, es necesario estudiar tratamientos adicionales para eliminar el color de estos efluentes industriales y cumplir así con la normativa vigente [4, 5], con el fin de evitar problemas medioambientales derivados de su vertido a cauces fluviales, como pueden ser la reducción de la actividad fotosintética y la disminución de la concentración de oxígeno disuelto.

La eliminación de melanoidinas mediante tratamientos físico-químicos requiere el uso de elevadas dosis de agentes químicos que generan un problema medioambiental y económico añadido. Por ello, en este estudio se pretende explorar la viabilidad de la separación con membranas para la decoloración de vinazas por ser una tecnología limpia con grandes expectativas de aplicación. La evolución del color a lo largo del tiempo se midió a través de la absorbancia de las muestras a una longitud de onda de 475 nm (UA_{475}) donde presenta máxima absorción el color marrón, propio de la vinaza objeto de estudio, utilizando un espectrofotómetro Hitachi U-2000. También se midió la absorbancia a 420 nm (UA_{420}), longitud de onda a la que presenta máxima absorción el color amarillo, y a 270 nm (UA_{270}), que es la longitud de onda a la que tienen máxima absorción las melanoidinas. El grado de decoloración en los permeados se calculó como el rechazo de la membrana a los compuestos coloreados.

El objetivo principal ha consistido en diseñar un proceso combinado ultrafiltración (UF)/nanofiltración (NF) a escala piloto para la decoloración de vinaza suministrada por una empresa de tratamiento de aguas residuales (vinaza bruta), con las siguientes características: 4118.4 mg/L SST, 13380 mg/L DQO, 4990 mg/L DBO, 200 mg/L betaína, 175.9 mg/L amonio, 548.8 mg/L nitrógeno Kjeldahl, 231.7 mg/L calcio, 1443.3 mg/L dureza, 205 mg/L fósforo total, 2137.8 mg/L sulfatos, 4972 mg/L carbono total, 915.8 mg/L nitrógeno total y 22.89 mg/L carbono inorgánico, con una conductividad de 11648 μS/cm.

El elevado contenido en sólidos en suspensión (SST) y materia coloidal hace necesario que la vinaza bruta se someta a un pretratamiento antes de la etapa de nanofiltración. El proceso propuesto consta de tres etapas: a) Pretratamiento de la vinaza bruta, previa dilución al 50% en volumen con agua desionizada, mediante ultrafiltración (UF) utilizando una membrana cerámica tubular de 100 kDa, a 25ºC y 1 bar de presión; b) Decoloración del permeado obtenido en la etapa anterior mediante nanofiltración con una membrana polimérica espiral de 500 Da, a 27ºC y 3 bar; c) Decoloración del permeado obtenido en la etapa de NF anterior, mediante una nueva NF utilizando una membrana polimérica espiral de 200 Da, a 30ºC y 10 bar. El resultado final del tratamiento propuesto fue la decoloración total de la vinaza, como se observa en la Tabla 1.

Tabla 1. Decoloración de la vinaza bruta tratada mediante el proceso combinado UF/NF propuesto.

Soluciones	UA_{475}	UA_{420}	UA_{270}	Decoloración a 475 nm relativa a la vinaza bruta	Decoloración a 420 nm relativa a la alimentación de cada etapa	Reducción de UA_{270} relativa a la vinaza bruta
Vinaza bruta	2.857	---	2.083			
Vinaza diluida (50% v/v)	1.823	---	1.936	36.19%		7.06%
Permeado UF 100 kDa	0.752	1.470	2.083	73.68%		0.00%
Retenido NF 500 Da	0.327	0.712	2.083	88.55%	51.56%	0.00%
Permeado NF 500 Da	0.013	0.028	0.421	99.54%	98.10%	79.79%
Retenido NF 200 Da	0.008	0.028	0.214	99.72%	0.00%	89.73%
Permeado NF 200 Da	0.000	0.000	0.022	100.00%	100.00%	98.94%

Finalmente, se realizó el tratamiento de los retenidos generados en las etapas de UF y NF anteriores. Para ello, se ha propuesto un proceso híbrido de ultrafiltración con carbón activado (UF-CA), utilizando la misma membrana cerámica tubular de UF de 100 kDa y seleccionando un carbón activado de origen vegetal (madera) en polvo (Norit 97876, Sigma-Aldrich). Las membranas de UF, que no tienen capacidad de retener los compuestos coloreados debido a su elevado tamaño relativo de poro, pueden funcionar con dicha finalidad en presencia de CA. Un proceso híbrido UF-CA reúne las ventajas de elevadas densidades de flujo de permeado obtenidos en los procesos convencionales de ultrafiltración y una elevada eficiencia en la decoloración mediante adsorción con CA. Además, la adición de CA reduce el ensuciamiento de la membrana y alarga su vida útil.

La tecnología híbrida de ultrafiltración con carbón activado se ha demostrado eficaz en el tratamiento de decoloración de efluentes, con mayor eficiencia en el tratamiento de los efluentes exentos de material biológico. Por ejemplo, el grado de decoloración alcanzado en el retenido de NF 500 Da, tras el proceso híbrido UF-CA, utilizando 5 g/L de CA, fue superior al 90% y el retenido residual, tras la separación del CA mediante filtración o centrifugación, posee también un grado de decoloración superior al 62%, que puede ser vertido directamente al cauce receptor o enviado a una estación depuradora de aguas residuales.

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MEMBRANE CHARACTERIZATION BY AFM AND INFLUENCE OF OPERATING CONDITIONS ON THE REJECTION OF Cr(VI) FROM SINGLE AQUEOUS SOLUTIONS BY NANOFILTRATION (NF)

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1 Introduction

Nanofiltration membranes have properties that combine size and electrical effects, as those present in ultrafiltration membranes, and they have solution diffusion mechanisms as those typically ruling transport in non-porous reverse osmosis membranes. The size and electrical effects that transport through nanofiltration membranes merge are total charge density, dielectric exclusion, etc, with solution diffusion mechanisms. The pores are typically near 1 nm in diameter and have fixed charges developed by dissociation of groups as sulphonated or carboxyl acids. Due to these characteristics, nanofiltration membranes retain multivalent complex ions and transmit small uncharged solutes and low charged ions [1] Heavy metals are potentially hazardous to human health even in minimal quantities. Industrial wastewater often contains toxic transition and heavy metals and other leachates that endanger the environment and public health [2]. Chromium is a typical heavy metal which is used extensively in industries such as electroplating, tanning, textile and is widely present in the effluents of these industries [3].

Traditionally, conventional treatment techniques, such as chemical precipitation, coagulation−flocculation, flotation, adsorption, and ion exchange, have been employed to remove heavy metals from industrial wastewater and/or drinking source water. However, these methods for removal of heavy metals have their limitations and may contribute to other problems [4]. Nevertheless, membrane filtration using reverse osmosis (RO) and nanofiltration (NF) plays an important role in the removal of chromate, arsenate, and/or perchlorate and has also been a promising technology for water treatment [5,6,7].

Here the Rejection of Cr(VI) has been measured under different conditions (varying concentration, temperature, pressure and feed cross flow velocity) in a pilot plant, through an AFC40 membrane from PCI. The membrane was characterized in detail using Atomic Force Microscopy (AFM), retention test of different neutral solutes and liquid.liquid displacement porosity [8].

2. Experimental

2.1 Pilot plant, membrane system and chemicals. Pilot Plant experiments were performed in the industrial pilot plant, designed and patented by the IPFM Research Group at the University of Cantabria [9]. The performance of aromatic polyamide thin-film composite (TFC) commercial membrane (AFC40 ^{PCI}) (NF) have been experimentally investigated. The technical specifications for NF B1 series flow module are: 18 tubes in series; 1.2m tube length; 0.0125 m tube diameter and 0.864 m sq membrane area. According to the manufacturers, the recommended working temperature is below 60 ◦C, the maximum applied pressure is 6.0MPa and pH must be in the 1.5–9.5 range. The Apparent Retention Character is 60% for $CaCl_2$. An aqueous solution of Cr (VI) (PA-E. Merck, Darmstadt, Germany) were

used. All solutions were prepared from ion-exchange demineralised and reverse osmosis treated water.

2.2 Filtration experiments. Total recirculation was used, with both permeate and concentrate returning of the feed tank to stationary conditions. The following parameters were measured: pressure (10-50 bar); temperature (25 – 40 ºC); feed cross flow (Qf) in the range of 400-1600 L/h and a concentration of feed solutions of Cr (VI) of of 5.10^{-5} M – 5.10^{-3} M. The composition of permeate and retentate was determinated at each pressure level.

2.3 Analytical Methods. The concentration of the electrolytes in the feed and product (permeate flux) solutions, were determined by conductivity measurement at 25 ±0.1 º C, using precision Crison conductimeter, model 2202. Analyses were validated using the ICP (Inductively Coupled Plasma) method.

2.4 Microscopy. AFM (Atomic Force Microscope) was performed by using a MultiMode Scanning Probe Microscope Nanoscope IIIA from Digital Instruments with an AS-10 E scanner.

3. Results

3.1. Water permeability, permeate flux and rejection. The water flow versus pressure is shown in Fig. 1, along with the corresponding permeate flux (Jp) for several concentrations of Cr(VI) solutions. Figure 2 presents the results of rejection Cr (VI).

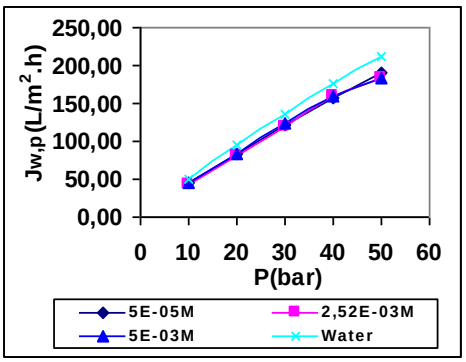

Fig.1. Water permeability and permeate flux (Jp) of the AFC40 membrane. Qf= 1000 L/h.T=30ºC.

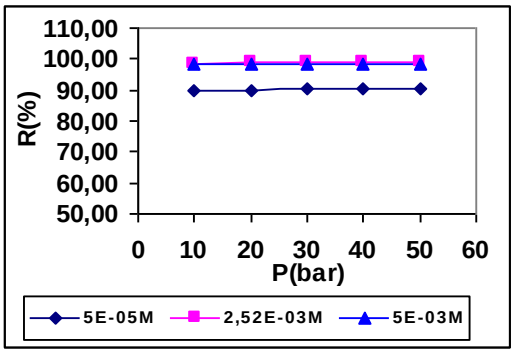

Fig.2. Rejection of Cr(VI) vs. pressure, as a function of the feed concentration c for a AFC40 membrane. Qf= 1000 L/h. T=30ºC.

3.2. Pore Size. The pore size distribution correspond to a value of r_P = 0,44±0.07 nm and agrees within the error ranges for: AFM, retention test of different neutral solutes and liquid-liquid displacement porometry.

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ANALISIS OF LEAD (II) RETENTION FROM SINGLE AQUEOUS SOLUTIONS BY TFC AROMATIC POLYAMIDE NANOFILTRATION (NF) MEMBRANE AND CHARACTERIZATION BY XPS

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1 Introduction

Transport through nanofiltration (NF) membranes combines size and electrical effects, such as total charge density, dielectric exclusion, etc., with solution diffusion mechanisms. Actually it joins factors typically relevant in reverse osmosis with those usually controlling ultrafiltration. The pore size of nanofiltration membranes is typically near and frequently below 1 nm in diameter. They have fixed charges developed by dissociation of appropriate groups present in the membrane materials [1]. The environmental challenges related to industrial wastewaters are especially important when heavy metals are included as contaminants due to their dangerous and accumulatively toxic and carcinogenic effects [2].The coupling of the membrane techniques such as the nanofiltration with traditional methods of physicochemical treatment seems the promising solution to the problem posed. Lead is a common pollutant that can be found in various industrial effluents. Consequently, and concerning water pollution, the removal of lead cations from both industrial and municipal water is a matter of major importance [3]. In this paper, experiments with single salt solutions will be described which were carried out with commercially available ($AFC40^{PCI}$) aromatic polyamide TFC nanofiltration (NF) membrane.
The X-ray photoelectron spectroscopy (XPS) has allowed to accurately determining the electronic state of polymeric materials which are composed of NF membranes [4].

2. Experimental

2.1. Pilot Plant experiments were performed in the industrial pilot plant, designed and patented by the IPFM Research Group at the University of Cantabria [5].
2.2. Membrane system and chemicals. The performance of aromatic polyamide thin-film composite (TFC) commercial ($AFC40^{PCI}$) NF membrane have been experimentally investigated. The technical specification for NF B1 series flow module are: 18 tubes in series; 1.2 m tube length; 0.0125 m tube diameter and 0.864 m^2 membrane area. According to the manufacturers, the recommended working temperature is below 60 °C, the maximum applied pressure is 6.0MPa and pH must be in the 1,5–9,5 range. The Apparent Retention Character is 60% for $CaCl_2$. The aqueous isotonic saline solutions (0.01M) for the characterization of the membranes were prepared from NaCl, $CaCl_2$, Na_2SO_4 (PA, Panreac, Spain), and working solutions for Pb (II) ($PbCl_2$: PA-E. Merck, Darmstadt, Germany) was used. All solutions were prepared from ion-exchange demineralised and reverse osmosis treated water. The pH value of the water varied between 5.9 and 6.8.
2.3. Filtration experiments. Total recirculation was used, with both permeate and concentrate returning of the feed tank to stationary conditions. The following parameters were measured: pressure (10-50 bar); temperature (25 – 40 ºC); feed cross flow (Qf) in the range of 400-1600

L/h and the concentration of feed solutions of $PbCl_2$ between 5.10^{-5} M – 5.10^{-3} M. The composition of permeate and retentate was determinated at each pressure level.

2.4. Analytical Methods. The concentration of the electrolytes in the feed and product (permeate flux) solutions, were determined by conductivity measurement at 25 0.1 º C, using precision Crison conductimeter, model 2202. Analyses were validated using the ICP (Inductively Coupled Plasma) method.

2.5. X-ray Photoelectron Spectroscopy. XPS spectra were recorded with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyzer and an unmonochromatized Mg Kα, X-ray source at 150W and a pass energy of 20 eV.

3. Results

3.1. Rejections measurements. Salt retention measurements with NaCl, $CaCl_2$ and Na_2SO_4 in the range of pressures (1-5MPa) were carried out with AFC40 ^{PCI} membrane (Fig.1). Rejections for solutions of Pb (II) are shown in Figure 2. The retention sequence is: R (Na_2SO_4) > R ($CaCl_2$) ≈ R(NaCl). The AFC40 membrane has about the same retention for $CaCl_2$ than NaCl, whereas Na_2SO_4 retention is much higher. These results are similar to those found by Peeters et al. [6] for NF70^{FilmTec} polyamide membrane.

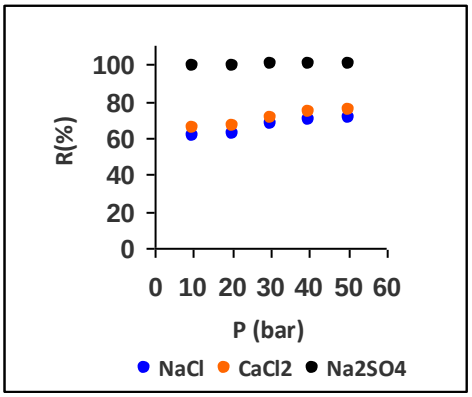

Fig.1. Retention R (%), of different salts for AFC40 membrane. Qf = 1000 L/h. T= 30ºC.

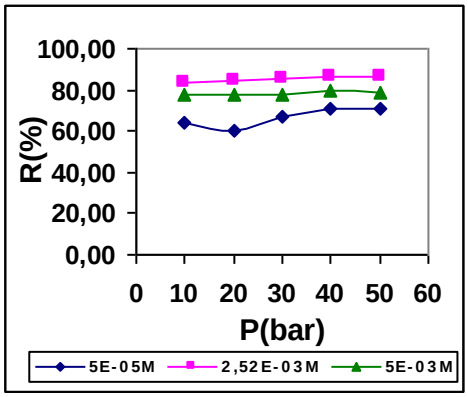

Fig.2. Rejection of the Pb(II) vs. pressure, as a function of the feed concentration c for a AFC40 membrane. Qf = 1000 L/h. T= 30ºC.

3.2. X-ray Photoelectron Spectroscopy. The chemical composition of the NF membrane surface was investigated by XPS (Table 1).

Table 1. XPS results of the membranes surface

	%at C	%at O	%at N	O/C	N/C	N/O
AFC40	69.11	23.70	7.19	0.343	0.104	0.304

The observed atomic concentration of C, O, and N are typical of aromatic polyamide film [7,8] .The differences observed in relation to the atomic concentration of C, O and N, can help us to explain the behaviour of the AFC40 membrane in the separation process.

4. References

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MEMBRANE BASED PROCESS FOR HCl AND NaOH PRODUCTION FROM REVERSE OSMOSIS BRINES

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Desalination is an emerging and promising alternative for obtaining drinking water and water for urban, agricultural and industrial use with a worldwide projected capacity of 98 million m^3/day by 2015. An increasing number of desalination plants use membrane technologies (reverse osmosis (RO), electrodialysis (ED)) that result in the generation of a waste brine; around 55% of the feed water ends as brine in seawater RO desalination plants. Those brines are characterized by their high salts concentration, mainly sodium chloride (NaCl). In coastal desalination plants, brines are directly discharged to the sea, posing adverse environmental effects on the receiving marine environment [1]. In inland desalination plants, brine management is an even worst issue with not many feasible alternatives: evaporation ponds, which require huge land extensions, and deep-well injection, which can lead to salinization of groundwater and soils, are the management options currently applied [2].

The treatment options applied to RO brines should be focused on achieving the highest global recovery of freshwater combined with the recovery of the valuable compounds contained in the brines [3]. The purpose of this work is to develop an advanced treatment for reverse osmosis brines that allow not only to decrease the environmental problem associated to these effluents but also to recover valuable compounds. In this line of investigation, an integrated process based on bipolar membrane electrodialysis (BMED) with the aim of recovering hydrochloric acid and sodium hydroxide has been developed. BMED was proved to be a technically feasible option for the production of 1.0 M acid and base solutions working with model seawater concentrates in a laboratory bench-scale set-up [4]. The achievement of the quality requirements of commercial hydrochloric acid and sodium hydroxide implies an intermediate pretreatment step, because other impurities (cations and anions) need to be removed from the brine before the application of BMED. Also potential precipitation and scaling on the BMED membrane surface needs to be avoided. Therefore,brine has to be pre-treated to remove calcium and magnesium.

In the present study, brine purification has been addressed by two complementary technologies, nanofiltration and ion exchange, that have been experimentally assessed to the pretreatment of real RO brines generated in seawater and inland brackish water desalination plants. A tandem system of cation and anion exchange columns was focused on the brine softening;the selective removal of calcium and magnesium was succesfully achieved. However sulfate removal was found particularly troublesome for the available ion exchange materials. Furthermore, sulfate removal was studied using commercial nanofiltration membranes, showing promising results.

An overview of the overall process composed of the brine purification steps by ion exchange and nanofiltration, and the recovery of products, hydrochloric acid (HCl) and sodium hydroxide (NaOH), by bipolar membrane electrodialysis will be presented, together with the preliminary assessment of the efficiencies achieved in each step.

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Acknowledgements

This work has been financially supported by projects CTQ2008-0690, ENE2010-15585 and CTM2011-23912 (co-financed by ERDF Funds). The authors would like to acknowledge SADYT, S.A. for providing real brines for this work and the Spanish delegation of LANXESS Chemicals, S.L. who kindly provided resins samples.

STUDY OF THE DIRECT FITTING OF A NANOFILTRATION MODEL USING MODEL SOLUTIONS OF DIFFERENT IONIC COMPLEXITY

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Nanofiltration (NF) is an effective technique for desalination of brackish waters. To further develop NF processes, a deeper knowledge of the mechanisms that are involved in the separation is needed, being models based on the use of the Nernst-Planck equation of great help in this purpose. One of these models is the Donnan steric-partitioning pore model with dielectric exclusion (DSPM-DE) [1]. The determination of the model parameters is a critical step. Although there is special interest in obtaining NF models with parameters based on measurable properties of the membrane and independent from feed and operating conditions, many times, from a practical point of view, NF parameters can be directly fitted from experimental data [2,3]. Therefore, deciding how many and what type of experiments are needed to obtain this information seems to be an appropriate new approach.

This works is focused on the study of the effect of the ionic complexity of the model solutions used for fitting the DSPM-DE model on the prediction of NF performance. For this purpose, the experimental behavior of a validation case was compared with the one predicted by the model fitted using experimental results with different sets of salt solutions of different ionic composition complexity. Fittings and predictions with different number of salts and levels of applied pressure and total concentration were performed in order to know if more information yields to a better prediction of the validation case even mantaining a low number of experiments.

These experiments, with feeds of increasing complexity and different operating conditions are collected in Table 1. The permeate flux and total rejection data obtained for each experiment, were used to fit the characteristics parameters of the DSPM-DE model: pore size (r_p),ratio of the membrane thickness to the effective porosity ($\Delta x/A_k$), membrane charge density (χ_d) and dielectric constant of the membrane (ε). With the obtained parameters, for each experimental set, the model was used to simulate the NF of the validation case, previously experimentally tested. The feed of the validation case was a 50 mN solution with the following equivalent percentages: 20% of NaCl, 30% of $NaNO_3$ and 50% of $MgSO_4$. Five leves of applied pressure were studied: 5, 7, 9.5, 12 and 13 bar.

Table 1. Present salts, composition, total concentration (C_T) and applied pressure (P) for the experimental tests.

Experiences	Single salt	Ternary mixtures (common cation)	Ternary mixtures (common anion)	Quaternary mixtures (common cation)
Salts	NaCl $NaNO_3$ Na_2SO_4 $MgCl_2$ $Mg(NO_3)_2$ $MgSO_4$ $CaCl_2$ $Ca(NO_3)_2$	NaCl-$NaNO_3$ NaCl-Na_2SO_4 $NaNO_3$-Na_2SO_4 $MgCl_2$-$Mg(NO_3)_2$ $MgCl_2$-$MgSO_4$ $Mg(NO_3)_2$-$MgSO_4$	NaCl-$MgCl_2$ $NaNO_3$-$Mg(NO_3)_2$ Na_2SO_4-$MgSO_4$	NaCl-$NaNO_3$-Na_2SO_4 $MgCl_2$-$Mg(NO_3)_2$-$MgSO_4$
Composition		50%-50%	50%-50%	33%-33%-33%
C_T (mN)	10 25 40 55 70	40 70	40 70	40 70
P (bar)	5 10	5 10	5 10	5 10

The experiments were carried out in a pilot plant equipped with a module to test flat membrane sheets and the membrane used was the ESNA1-LF2 commercialized by Hydranautics. Both permeate and retentate streams were recirculated into the feed tank in

order to keep constant feed concentration. Applied pressure was fixed with two different valves and controlled with three manometers upstream, downstream and on the membrane module. The effect of concentration polarization was reduced with a turbulence promoter in the feed side of the membrane and by setting a flux velocity of 2 m/s. Feed solutions were prepared with deionized water and pure grade salts, fixing its temperature at 25 ºC and the pH at a value of 6. The ion concentration of the feed and permeate solutions was measured by ion chromatography.

For the single salt experiences, the difference between the total rejection for the validation case obtained with simulations and experimentally can be observed in Fig. 1. From these results, it can be concluded that there are solutions that seem to better predict the behavior of the membrane: Na_2SO_4, $MgCl_2$ and NaCl solutions. This result agrees with the analog study for the permeate flux that is shown in Fig. 2 although a smaller difference between the prediction of the different salts is observed.

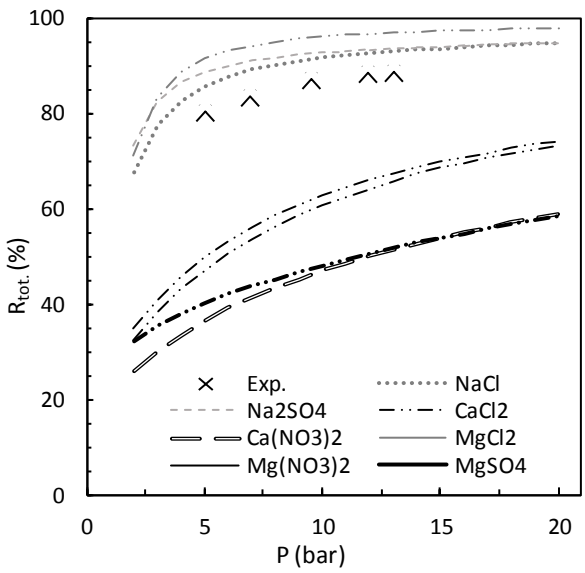

Fig. 1. Total rejection (R_{tot}) for the validation case obtained experimentally and simulated with the obtained parameters for the single salt experimental sets.

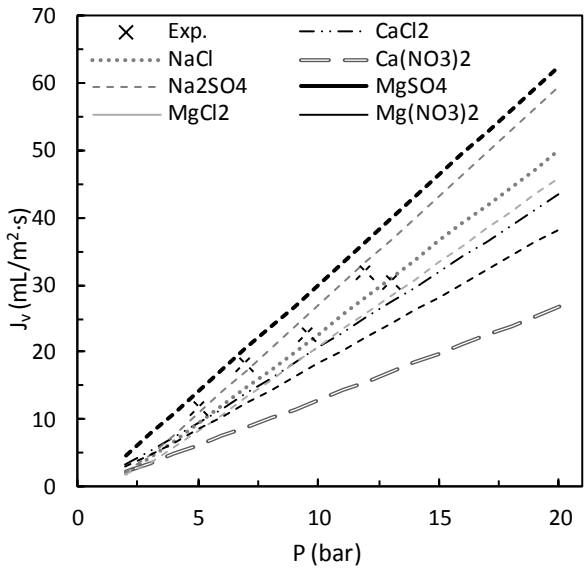

Fig. 2. Permeate flux (J_v) for the validation case obtained experimentally and simulated with the obtained parameters for the single salt experimental sets.

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Acknowledgments

The Spanish Ministry of Economy and Competitiveness (Project OPTIMEM CTM2010-20248) is kindly acknowledged.

REMOVAL OF SULPHATE FROM WASTEWATERS BY NANOFILTRATION

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Introduction

Sulphur can exist in nature in different chemical forms but in waters oxidized form sulphate (SO_4^{2-}) is the most common specie. [1] Sulphate is not regarded as toxic compound as itself and therefore, legislation does not give explicit limits of sulphate charge in waters. However, sulphate can cause significant problems in aquatic environment. For example, it can increase the salinity of natural water. In addition, it can disturb water equilibrium by changing the solubility of iron in natural waters and facilitating the release of phosphorous which can cause eutrophication of natural waters [2]. Also sulphate reduced species can volatilize from waters to athmosphere where it can form acidic rain causing e.g. acidification of soils [3, 4]. In mining industry, high concentration of sulpate in wastewaters is common due to oxidation of sulphide mineral when it is in contact with oxygen and water. [5] In mining high concentration of sulphate in water can cause scaling e.g. in pipings and process equipments. If sulphate is associated with protons, it can cause also corrosion of process equipments. [6]

Precipitation and biological treatment are commonly used techniques for the treatment of sulphate rich wastewaters in mining industry. [5] Also membrane techniques have been researched in laboratory and pilot scale in mine water treatment. One of the main challenges in membrane technology is membrane fouling and scaling due to to high concentration of sulphate in mine waters. [6] To make membrane processes more effective for mine water purification, new methods for sulphate reduction has to be developed.

The efficiency of membrane processes can be improved by combining them with other techniques. For example catalytic materials can facilitate the separation of compounds on the membrane surface. In this study, catalysis is combined into membrane process by coating nanofiltration membrane with ZnO catalyst. Catalyst attached on the surface can reduce membrane fouling due to changes in membrane surface charge and in other membrane properties. [7] The objective of this study was therefore, to evaluate removal of sulphate from synthetic wastewaters by catalytically active nanofiltration membranes. Also the effect of pH on sulphate rejection and fouling in nanofiltration process was studied.

Materials and Methods

The effect of pH on the sulphate removal efficiency and membrane fouling was studied using Sepa CF cross-flow membrane cell. For this purpose two unmodified membranes were used, NF90 and NF270 membranes by Dow Filmtec. Membrane surface coating was conducted by adding ZnO layer (thickness 20 nm) by ALD (atomic layer deposition) technique. The membranes coated were NF90 and NF270 nanofiltration flat sheets. During all the experiments the waters used were synthetic waters which contained sulphate 1 g/L.

Results

It was observed that ZnO coated membranes had lower permeate flux compared to unmodified NF90 ad NF270 membranes probably due to the catalytic layer which gave extra resistance for filtration. However, in the experiments high rejection of sulphate was obtained. Unexpectedly, coated NF270 membrane rejection increased from 69 to 92% during the experiment. That might be due to unfavourable properties of the coating layer on sulphate removal. It was noticed that the ZnO layer suffered from mechanical wearing in some extent during the filtration process that affects on the separation properties. Also moderate

membrane fouling was observed. Although sulphate can be severe membrane foulant, extensive fouling did not occur due to its relatively simple characteristics and low concentration of sulphate of synthetic water.
On the other part of the research the sulphate removal was better at pH 8 (97% with NF270 and 99% with NF90 membrane) compared to pH 3 (90% and 98%, respectively) as was expected based on the solubility of sulphate.

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Acknowledgements

This study was part of the SULKA-project financed by European Regional Development Fund. Also HYMEPRO-project funded by Tekes (the Finnish Funding Agency for Innovation) is acknowledged for providing material. Marja-Leena Kääriäinen and Tarja Seppänen from University of Eastern Finland are acknowledged for coating of the membranes.

REMOVAL OF PERFLUORINATED COMPOUNDS FROM CONTAMINATED WATERS BY NANOFILTRATION AND REVERSE OSMOSIS

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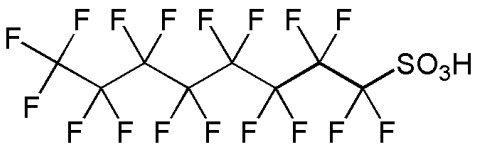
Perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are perfluorinated compounds that have been widely used several industrial sectors such as metal plating, material surface coating, textile, etc. (Figure 1). Due to this widely usage and because of the degradation of other perfluoroalkyl substances, PFOS and PFOA are emitted to the environment and are found in several environmental compartments [1]. Currently, PFOS and PFOA are intensively researched due to their persistence, potential to bioaccumulation, possibility of biomagnification in the food chain and toxicological concern. Contaminated water is identified as one route of human exposure to PFOS and PFOA [2]. Several studies have shown the existence of PFOS and PFOA in drinking water sources and/or tap water worldwide at ng/L level [3, 4]. This presence is due to the inefficiency of the conventional water treatment processes and to the biodegradation of precursors possibly during the activated sludge treatment [5].

a)



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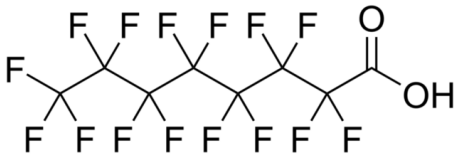

Figure 1. Chemical structures of a) PFOS and b) PFOA

The scientific community is facing the challenge of developing clean technologies for the treatment at source of the emissions of PFASs and for the abatement of the existing water polluted sites. Application of technologies such as oxidation, sonochemical and sorption are not technically and economically viable for treating large volumes of diluted effluents. Membrane processes such as nanofiltration (NF) and reverse osmosis (RO) are promising technologies for the removal of PFOA and PFOS from aqueous systems [6,7]. However, few research has been conducted on this topic.

Our research regards the removal of PFOS and PFOA from aqueous systems using NF and RO membranes. The main aim is the evaluation of operational parameters such as

membrane type, feed concentration and transmembrane pressure on the flux through the membrane and on the rejection of the membranes towards the perfluorinated compounds.

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Acknowledgements

Juan de la Cierva Programme of the Spanish Ministry of Economy and Competitiveness is acknowledge for finantial aid.

APPLICABILITY OF COMBINED FENTON OXIDATION AND NANOFILTRATION TO THE PROCESS WASTEWATER OF PHARMACEUTICAL INDUSTRY

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Pharmaceuticals and cosmetics, supplements and other personal care products are used in large amounts throughout the world. Early identification and research of pollutants resulting from the pharmaceutical industry is extremely important because of potential damage to the environment and human health [1]. Biological treatment is the cheapest available technology to remove contaminants but in the case of pharmaceutical wastewater, completely treatment of pharmaceutical active substances (PhACs) or ensure of discharge standards could not be possible. Most of PhACs have toxic effects on the biological treatment process. In addition, concentrations of some compounds have been found to increase during the treatment process, probably as a consequence of the transformation of conjugates back to the parent compounds [2]. Consequently, after passing through wastewater treatment, PhACs, amongst other compounds, are released directly into the environment [3,4]. In this context, pre-treatment using advanced oxidation methods are required to ensure the discharge standards and PhACs removal. Only a few studies reported in literature deal by combined treatments involving chemical oxidation plus membrane filtration [5]. Also, PhACs removal from real wastewater was not studied. The main objective of this study is to investigate the applicability of combined Fenton oxidation and membrane filtration for the treatment of a real process wastewater resulting from the production of a PhAC (etodolac). The wastewater sample was obtained from the cleaning of the tanks after production of etodolac -a nonsteroidal anti-inflammatory pharmaceutical- and prior to production of another PhAC.

The effects of H_2O_2 and Fe^{2+} dosages on treatment efficiency of Fenton oxidation were investigated at pH 3 and 25±1°C. H_2O_2 and Fe^{2+} dosages were ranged between 0.025 and 5 M and 0.001 and 0.1 M, repectively. The Fe^{2+} dosage was kept constant at 0.05 M while studying the effect of H_2O_2 dosage, and H_2O_2 concentration was kept constant at 2 M in the experiments for Fe^{2+} dosage. The membrane stage was conducted in a cross-flow operation mode using a lab-scale membrane system equipped with a flat-sheet membrane 80 cm^2 in size that was purchased from Osmo, Germany. A commercial flat-sheet NF membrane, FM NP010 provided by Microdyn-Nadir, GmbH, Germany with a molecular weight cut-off (MWCO) of 1000 Da, was used for the experiments. The transmembrane pressure was kept constant at 12 bar throughout filtration experiments. In the experiments, a constant cross-flow rate of 3 L min^{-1} and a constant temperature of 25±1°C were maintained. The nanofiltration experiments were performed both with real process wastewater and wastewater pre-treated by Fenton oxidation. The influence of the operating conditions on the UV_{254}, COD and etodolac removal efficiencies was studied. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Precisely Spectrum One, USA) was used to investigate changes in chemical bonds on membrane surfaces. All FTIR measurements were conducted on both clean and fouled membranes.

In Fenton (Fe^{2+}/H_2O_2) study, the best removal efficiency of 84% COD removal was obtained with Fe^{2+}:H_2O_2 = 1:40 ratio. Although COD could not be reduced to discharge standards, etodolac is fixed close to 100%. Figure 1 shows the flux declines as a function of time for (a) real process wastewater and (b) wastewater pre-treated by Fenton oxidation. Flux obtained from the nanofiltration of real process wastewater was decreased from 65 to 22 L/m^2.h, whereas a decrease from 135 to 50 L/m^2.h was determined for the nanofiltration of

wastewater that pretreated with Fenton oxidation. The UV_{254} and COD rejections were approximately 93% and 6%, while the etodolac rejection was 99.5% for real process wastewater. 100% etodolac, 96% COD and 88% UV_{254} rejections were found for the combined Fenton oxidation and membrane filtration. From the FTIR spectrum for the membrane of fouled with pharmaceutical wastewater, it can be seen that new intense band at 1087 cm^{-1} appeared. This band is in the wave number range of 1040–1100 cm^{-1}, which is characteristic of SO_4^{2-} and/or CO_3^{2-} ions [6]. The calcium salts could be the main foulants on the membrane surface [7]. As a result, effective removals of etodolac (>99.5) were obtained for combined and single systems. However, single stage membrane treatment was insufficient by removal of organic matter. Also, Fenton oxidation is recommended as pre-treatment to ensure discharge standards for organic matter (COD).

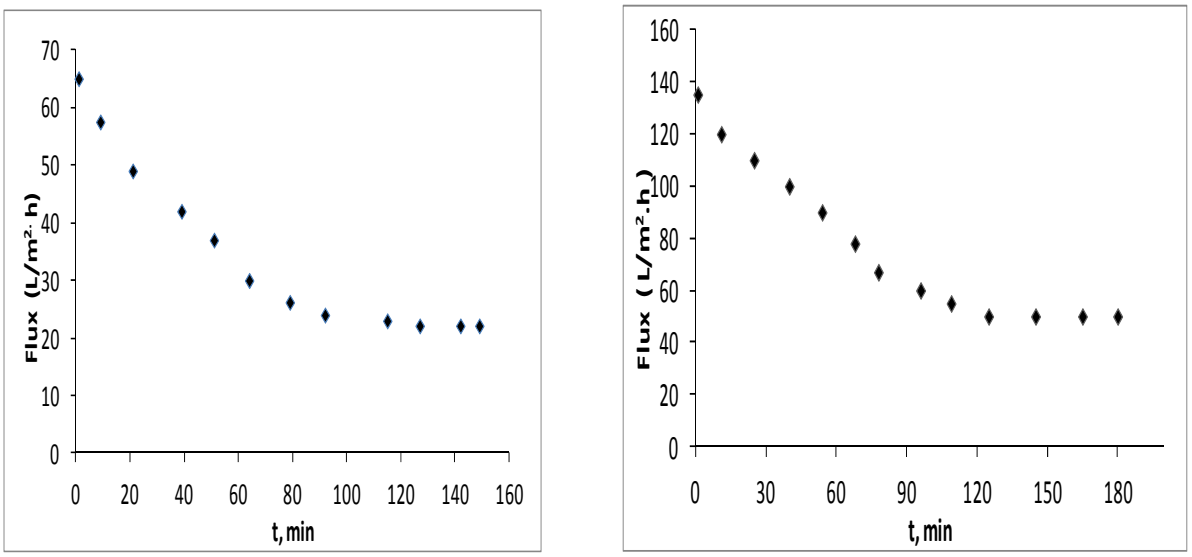

Figure 1: Flux declines as a function of time for (a) real process wastewater and (b) wastewater pre-treated by Fenton oxidation.

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Acknowledgements

This work was supported by the Research Fund of the Istanbul University (Project number: 20408).

Membrane Characterization

- **Oral session 19**

PREPARATION AND CHARACTERIZATION OF CHITOSAN BASED ANION-EXCHANGE MEMBRANES FOR ALKALINE MEDIA AS ALTERNATIVE TO NAFION

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Alternative to Nafion membranes for the use in fuel cells is nowadays an encouraging issue due to the higher cost of proton exchange membrane (PEM) as well as the slow electrode kinetic, CO poisoning of generally Pt electrocatalysts, crossover and carbonate formation. For that reason, commercial anion-exchange membranes or hydroxide exchange membranes (HEM), i.e. those from Fumatech company among others, are a proper option in alkaline conditions and somewhat overcomes the problems found in based fuel cells using nafion exchange membranes [1]; however, HEM still show low thermal stability and high crossover limitations. In this regard, chitosan is a low-cost biopolymer and weak alkaline polyelectrolyte, obtained from natural resources. In the dry state, a crosslinked unmodified-chitosan membrane is very fragile, and non-conductive. Nonetheless, upon water swelling, the chitosan membrane has been reported remarkable ionic conductivity and therefore improved its specific conductivity.

Motivated by the improvement of the mechanical and thermal stability as well as the amellioration in the specific conductivity, mixed matrix membranes (MMM) have become our main interest. MMM consist of a continuous polymer matrix with a small amount of dispersed fillers, usually zeolites or inorganic particles, as a means of obtaining an heterogeneous membrane with synergistic properties of the fillers (conductivity, flexibility, or molecular sieving) with the low cost and processability of the polymer. Moreover, inorganic fillers also provide mechanical strength to the pristine polymer.

In this work, we propose that the biopolymer chitosan (low cost and from natural resources, with polyelectrolyte nature) can be tuned to exchange cations or anions depending on the treatment and that novel materials (layered nanoporous materials with enhanced barrier properties, room temperature ionic liquids, and metallic nanoparticles) can be added into the chitosan biopolymer. Thus, the aim of the paper targets the development of new membranes with high mechanical, chemical and electrochemical stability in extreme alkaline solutions, for a longer durability and successful performances in organic electrosynthesis, electroanalysis and fuel cell technology.

Herein, we present a very well detailed synthesis procedure of chitosan mixed matrix membranes. Chitosan membranes were prepared according to well established procedure in the literature. On the other hand, MMMs were prepared by adding a certain volume of a 2 wt% dispersion of the inorganic fillers in pure water to the chitosan solution, then stirred until an homogeneous mixture was observed, then the mixture was degassed and casted on a plate. The fillers used were: ETS-10 [2], AM-4 [3], UZAR-S3, a layered stannosilicate [4], ionic liquid [emim][Ac] and metallic Sn powder. Results and discusion will be provided in terms of the physicochemical characterization of the different chitosan based membranes by scanning electron microscopy, FT-IR, X-ray diffraction, thermogravimetric analysis, water

uptake, ion-exchange capacity, electrochemical characterization by cyclic voltammetry and electrochemical impedance spectroscopy and alkaline stability.

Table 1 summarizes some of the most important parameters from the physic-chemical and characterization.

Table 1. Summary of some physicochemical characteristic of the membranes tested in this work. Percentage refers to material incorporated into the polymeric matrix to polymer weight ratio. Commercial hydroxide exchange membranes FAA and AHA were chosen for comparison.

Membrane composition	Thickness (10^3 cm)	Specific Conductivity (mS / cm)	IEC (mmol/g)	Termal stability, T_{onset} (ºC)
Chitosan, CS	4.1 ± 0.5	0.041	0.83	272 ±2.8
LI:CS (5% wt.)	8.78	0.065	1.37	228±24.7
AM-4:CS (20% wt.)	8.2 ± 0.4	0.046		271±9.24
UZAR-S3:CS(20% wt.)	13.9 ± 0.6	0.060	0.83	284±1.3
Sn:CS (20% wt.)	7.0 ± 0.7	0.084	1.68	273
*FAA	14	4.30	1.43	-
*AHA	22	3.46	1.8	
Crosslinked quaternary chitosan	110-113	9	0.53-0.83	194-222

* Commercial membranes.

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Acknowledgements

This work has been funded by the Spanish MINECO through grants CTQ2010-20347, at the University of Alicante, and CTQ2012-31229 and RYC2011-08550, at the University of Cantabria.

ELECTROCHEMICAL CHARACTERIZATION OF A MEMBRANE MANUFACTURED BY A BACTERIAL EXOPOLYSACCHARIDE

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Polysaccharides are high molecular weight (10^4 – 10^7) polymeric biomaterials with a large structural diversity, being composed of one or more monosaccharides joined by glycosidic bonds, often forming repeating units and presenting different degrees of branching [1]. Moreover, the capacity to form biodegradable films shown by some polysaccharides (e.g. starch, alginate or cellulose derivatives) enables their use in packaging, pharmaceuticals and other industrial applications, while their biocompatibility also enables their use as scaffolds or matrices for tissue engineering, wound dressing and drug delivery [2]. The mechanical and barrier properties of a polysaccharide based membrane depend on the structure, relative humidity, film composition, plasticizer additives, cross-linking agents, and the preparation procedure [3]. Bacterial polysaccharides can replace plant, algae and animal polysaccharides, either in their traditional or in new applications. The main constraint to their wider use is production cost, which is still higher than that of other natural and synthetic polymers [4]. Recently, it has been reported an expolysaccharide (EPS) produced with a low cost, abundant carbon source, the glycerol by-product of the biodiesel industry. It is a high molecular weight, negatively charged heteropolysacchride, composed by sugars (galactose, glucose, fucose, mannose and rhamnose) and acyl groups (pyruvil, succynil and acetyl) [5].
In this work, the electrochemical behaviour of this EPS membrane (swelling degree S_w = 103 %) was determined from membrane potential and salt diffusion measurements performed with NaCl solutions at different concentrations [6]. For comparison, values obtained for a membrane also from a natural hydrophilic polymer such as regenerated cellulose (average swelling degree $\langle S_w^{RC} \rangle$ = (115 ± 12)%) under similar external conditions are also indicated [7].
Fig. 1 (a) shows membrane potential values for EPS and RC membranes as well as theoretical values for an ideal cation-exchanger (solid line) and NaCl solution diffusion potential (dashed line), while the results from diffusive experiments for EPS and RC membranes are shown in Fig. 1 (b).

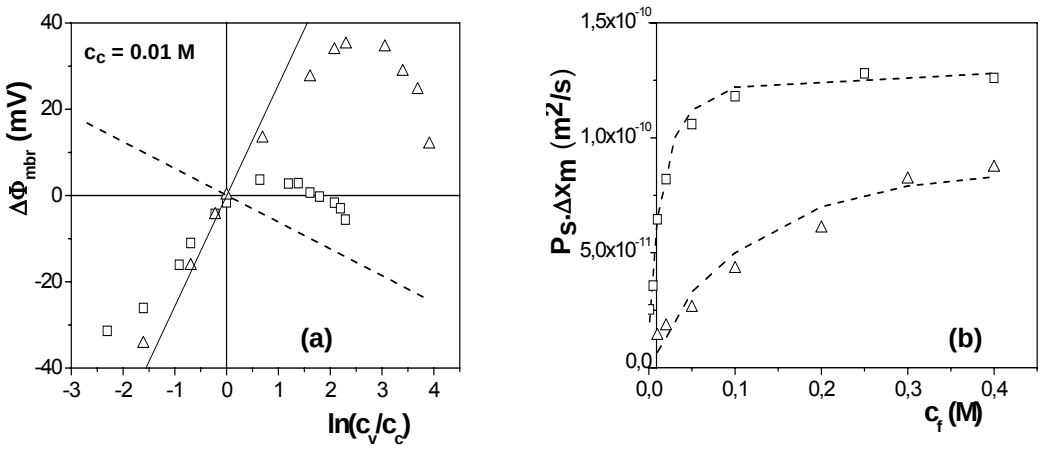

Fig. 1: (a) Membrane potential versus solutions concentration ration; (b) Membrane diffusivity as a function of feed solution values. (△) membrane EPS, (□) membrane RC.

These results show significant differences between both membranes, although they show similar concentration dependence. Differences could be partially associated to the higher swelling degree of the RC membrane but also to the effective fixed of each membranes, since EPS membrane exhibit higher electronegative behaviour and lower diffusivity that regenerated cellulose RC one.

According to the results shown in Fig. 1(a), membrane potential values for the EPS sample hardly differ from those expected for a cation-exchange for concentration interval between 10^{-3} M and 0.1 M, but differences are more significant when variable concentration ranges between 0.1 M and 0.5 M. The analysis of these results by using the TMS model [8] has permitted us to estimate the following values for the membrane effective fixed charge (X_{ef} = -0.15 M) and Na^+ average transport number (t_{Na}+ = (0.84 ± 0.05)), while the estimated salt diffusion coefficient (between $8x10^{-11}$ m^2/s and 10^{-10} m^2/s) is also in the range of cation-exchage membranes. Fig. 1(b) shows salt diffusion results, where a comparison between experimental (points) and calculated values (dashed lines), these latter estimated with the expression proposed by Filipov et al [9] and using the parameters determined from membrane potential measurements.

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Acknowledgements

To CICYT, Spain, for financial support (Project CQT2011-27770, FEDER funds).

CHARACTERISATION OF DENSE FILMS: MODELLING TRANSIENT PERMEATION FROM TIME-DEPENDENT DIFFUSIVITIES

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Transport through dense membranes (used for pervaporation processes, but also for vapor permeation, gas separation or organic solvent nanofiltration OSN processes [1]) is based on solute-membrane interactions, typically described by the solution-diffusion model. The interactions between a membrane material and permeating species with affinity to that membrane may rearrange the membrane material [2]. These changes in the membrane material occur in the transient period of the permeating process, which are directly linked to the diffusion of the permeating species through the membrane. Acquisition of data during the transient period allows for studying mutual interactions between membrane, solvent and solute. Therefore, the study of the transient period greatly enhances the fundamental understanding of transport through dense membranes.

Transient studies are only possible to perform with on-line, real-time monitoring techniques, such as the on-line and real-time mass spectrometry (MS) analytical tool, with few data-point acquisition each few seconds (depending on the number of compounds to be monitored). The feasibility of using mass spectrometry (MS) for on-line, quantitative monitoring of pervaporation processes performed under variable operating conditions was reported in literature [3, 4]. The MS monitoring also allows for defining a steady-state period, from which time-lag is determined, and then an average value of the diffusion coefficient of the transient period, using time-lag approach, as extensively reported in pervaporation [5], vapour permeation and gas separation processes [6]. In this work, transient mass transport phenomena were characterised through mass spectrometry monitoring, namely for calculating on-line permeate partial pressures and fluxes, as in previous works [3, 4]. Time-dependent solute diffusion coefficients in the whole transient were also calculated, evaluating rearrangements that the membrane material might have in the transient period.

Additionally, a mathematical model was developed for characterising the transient mass transport of a solute through a dense membrane material. Usually the output of this type of models is a constant diffusion coefficient of the transient regime. The model proposed in this work uses time-dependent diffusion coefficient in the whole transient regime and its ouput is the estimation of the concentration profile of permeating species along the membrane and over time.

The systems under study were two typical examples of a hydrophilic and an organophilic pervaporation systems, respectively the dehydration of an alcohol (isopropanol) and the aroma recovery (recovery of ethyl acetate at trace concentration from water). The membranes used, typical in each application, have different characteristics, namely in terms of structure and rigidity. An organic-inorganic membrane (ceramic, hybrid silica-based, HybSi®) was used for isopropanol dehydration and a modified silicon–rubber composite polymeric membrane (polyoctylmethylsiloxane, POMS) was used for aroma recovery. This methodology may be applied to other pervaporation, solvent resistant nanofiltration, vapour permeation and gas separation systems.

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Acknowledgements

The authors acknowledge the finantial support of the FP7-SME-2010-1 European project entitled SOLVER, Solvent Purification and Recycling in the Process Industry using Innovative Membrane Technology. The authors acknowledge grant numbers SFRH/BD/81814/2011 and SFRH/BPD/79533/2011 from Fundação para a Ciência e a Tecnologia, Portugal. The authors also acknowledge GKSS and Pervatech for the kind donation of respectively POMS-PEI and HybSi® membranes.

CARACTERIZACIÓN DE UNA CELDA ELECTRODIALITICA. AUTOMATIZACION Y CONTROL DEL PROCESO

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Resumen

Las membranas intercambiadoras se emplean en electrodiálisis (ED) para desalar disoluciones acuosas El procedimiento de caracterización se basa en la aplicación de sucesivas diferencias de potencial para la determinación de intensidades de corriente asociadas, resultando las curvas corriente-voltaje y a partir de cuyo trazado siguen las intensidades de corriente límite para las presiones de alimentación de la pila. Se pretende el establecimiento de una relación entre las densidades de corriente límite y el caudal de producto en una celda unitaria, para su posterior extrapolación a la planta piloto EDR.

Introducción

En este trabajo se establece una metodología aplicable a una sola celda ED, constituida por una membrana aniónica, un espaciador de corriente desmineralizada, una membrana catiónica y un espaciador de corriente concentrada, estando situado todo el sistema entre dos placas metálicas que contienen sendos electrodos. Todos los elementos del conjunto son comerciales y provienen de una planta piloto EDR Aquamite I de Ionics. El rendimiento del proceso está limitado por los efectos de concentración-polarización en las interfases membranas-disoluciones, en las que la corriente eléctrica crece inicialmente de forma lineal con la diferencia de potencial eléctrico aplicada, moderando después su crecimiento hasta alcanzar una zona de "*plateau*" caracterizada por una corriente límite [1,2]

La correcta caracterización corriente-voltaje de una planta EDR es importante, resultando de gran interés la determinación de las corrientes límites para el sistema de membrana completo (membrana+capas límite de difusión). En trabajos anteriores hemos determinado las condiciones experimentales más favorables para la desalación, mediante barridos de voltaje a diferentes presiones [3,4]. Ahora se trata de determinar densidades de corriente límite para 1 celda EDR (Fig.1), a partir de las curvas I-V y a diferentes valores de la presión de alimentación (y por tanto del caudal de suministro), mediante trazado de tangentes en la zona de "*plateau*" de las mismas, para cortar con la prolongación del primer tramo ascendente de éstas. Los resultados permiten la caracterización del régimen hidrodinámico del sistema, en los rangos de caudal y salinidad considerados.

Resultados y discusión

La densidad de corriente eléctrica en una celda ED se relaciona con la velocidad media del fluido en sus canales (v), mediante la ecuación [5,6,7] $i_{lim}=\alpha C v^{\beta}$, donde C es la concentración electrolítica en la entrada, α y β son constantes, la primera dependiente de la geometría del canal y de la naturaleza de las membranas, y la segunda del régimen hidrodinámico. El estudio de la representación $ln(i_{lim}/C)$ *vs* $ln(v)$, (Fig.2) pone en evidencia un comportamiento lineal, extrapolable a cada una de las etapas eléctricas de una planta EDR.

En este trabajo se han obtenido las densidades de corriente límite para una celda electrodialítica (membranas *Ionics*: aniónica AR204SZRA; catiónica CR64LMR), en un rango de salinidad bajo, para disoluciones de cloruro sódico. La caracterización se llevó a cabo, aplicando la misma presión (*P*), y efectuando para cada valor, un barrido de tensión eléctrica entre *0,5* y *5,0 V*, en pasos de *0,1 V*. La presión varió entre *0,3* y *0,5 atm*, determinándose el valor medio de la intensidad de corriente en la celda, para cada tensión y presión aplicadas.

Todo el proceso de control y toma de datos se automatiza con un PLC (Omron, CPM1 20CDR-A) y una tarjeta AD (National Instruments NI USB-6210), para los que se ha diseñado una aplicación SCADA en entorno LabVIEW (v.9.0), que proporciona una interfaz

gráfica para control del autómata y su comunicación con la tarjeta AD, a la vez que lee y archiva los datos recogidos por la misma. El autómata gobierna la planta, controlando las bombas de alimentación y recirculación, válvulas de entrada y salida (3 vías) y establece la diferencia de potencial en las etapas eléctricas y en su caso, provocaría el cambio de polaridad. Los datos recopilados son presión de entrada a la planta, voltaje e intensidades de la etapa eléctrica y conductividades del agua de alimentación y producto. Con estos datos se obtienen las curvas I-V a cada presión, de donde sigue las densidades de corriente límite (i_{lim}) y su dependencia con la velocidad v en el canal de producto, resultando $i_{lim}=\alpha C v^{\beta}$ con $\beta \cong 0,27$ y $\alpha \cong 581,73$ para el rango de salinidades considerado.

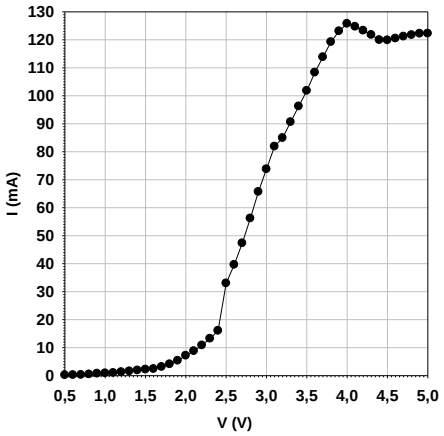

Figura 1

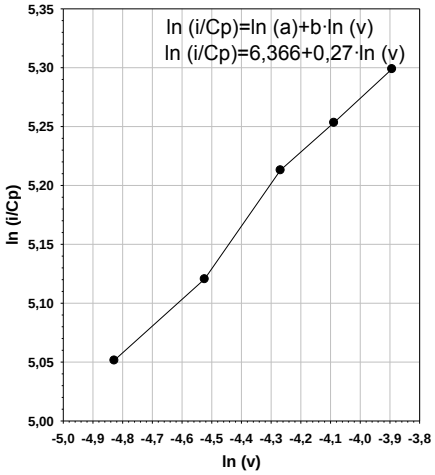

Figura 2

Conclusiones

1. Las densidades de corriente en una pila EDR muestran valores críticos para los que los efectos de capa límite empiezan a ser importantes. En orden a establecer las densidades de corriente máximas que pueden emplearse sin fenómenos de polarización, se obtuvo para cada valor de *P*, las curvas I-V.
2. Las curvas I-V muestran inicialmente un comportamiento lineal. A medida que la tensión aumenta la densidad de corriente se dispara, alcanzándose un valor límite para la misma.
3. Las densidades de corriente se correlacionaron con las velocidades *v*.
4. La automatización del proceso permite controlar y caracterizar en tiempo real, lo que posibilita la inmediata reconfiguración del mismo, si fuese necesario.

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Membrane Characterization

- **Poster session 2**

Chemical treatments of an electrodialysis membrane: Effect on ion transport numbers and conductivity

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Electrodialysis is a well established membrane separation process which uses electrical potential difference as driving force able to separate positive from negative ions and from neutral solutes [1]. Charged membranes with high conductivity are used to control the transport of ions: cation-exchange membranes allow the passage of cations and positively charged species, excluding practically the transport of negatively charged particles, while anion-exchange membranes allow the passage of anions and negatively charged species and they exclude or significantly reduce the transport of cations. Some traditional electrodialysis applications are separation of amino acids, production of chlorine and caustic soda via the "chlor-alkali" process or even the production sulfuric acid and caustic soda using bi-polar membranes, that is, the union of a cation-exchange membrane and an anion-exchange membrane with and intermediate layer [1].

In order to determine possible effects of acidic/basic solutions on membrane behaviour, pieces of a positively charged commercial membrane (AR204-SZRA-412 by Ionics) were maintained in 0.1 M solution of H_2SO_4 or NaOH two different periods of time (1 weak and 1 month). These membranes will hereafter named as Ionics(+)/1wH_2SO_4, Ionics(+)/1wNaOH, Ionics(+)/1mH_2SO_4 and Ionics(+)/1mNaOH. Membrane electrical characterization was performed by measuring cell potential (ΔE) and electrical resistance (R_e) with NaCl solutions at different concentrations, and the results compared with that obtained for an untreated membrane (sample Ionics(+)/UNT). Membrane potential measurements were performed keeping constant the concentration of the solution at one side of the membrane (c_c = 0.01 M) and gradually changing the concentration of the solution at the other side ($10^{-3} \leq c_v$ (M) $\leq$ 0.1), while membrane electrical resistance was determined with wet membranes, after immersion for at least 24 h in a 0.01 M solution, by using an AC bridge for frequency ranging between 100 kHz and 500 KHz [2]. From these measurements cation transport number (t_+) and membrane conductivity (σ_m) can be determined by [3]:

$$t_+ = \Delta E/2\Delta E_{max} \qquad (1)$$

$$\sigma_m = \Delta x_m/S.R_e \qquad (2)$$

where ΔE_{max} represents the maximum electrical potential difference for a given pair of solutions concentrations, while Δx_m and S are the membrane thickness and area, respectively.

Fig. 1(a) shows the variation of anion transport number with average concentration ($c_{avg} = (c_c + c_v)/2$) for the studied membranes, while average value of anion transport number for each membrane is indicated in Table 1. According to these results, H_2SO_4 solutions slightly decrease the anion transport number in the membrane (~ 6-8 %) but immersion in 0.1M NaOH solution for 1 month seems to affect more notably that parameter (~ 15 %).

Fig. 1(b) shows a diagram representing the values of the electrical resistance for each membrane. As can be observed, R_e values for samples maintained one weak in 0.1 M H_2SO_4 or NaOH solutions slightly differ from original Ionics(+)/UNT membrane value, but R_e value significantly increase after immersion of the samples for 1 month in both solutions. This result agrees with the reduction in counter ion transport number and it might also be an indication of other kind of changes in the membrane structure caused by chemical treatment, which could modify the chemical and hydrophilic character of the original membrane. These measurements are under study.

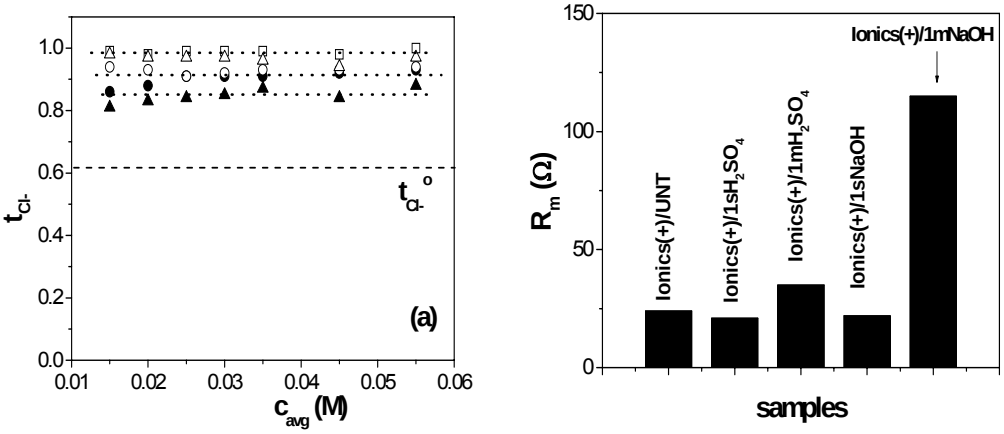

Fig. 1: (a) Variation of anion transport number, tCl-, with average NaCl solutions concentration, Ionics(+)UNT (□), Ionics(+).1s.H_2SO_4 (o), Ionics(+)1m.H_2SO_4 (●), Ionics(+)1s.NaOH (Δ), Ionics(+)1m.NaOH (▲). (b) Electrical resistance of the studied membranes after 24 h equilibration in 0.01 M NaCl solution.

Table 1: Average value of anion transport number for the studied membranes.

membrane	<t>
Ionics(+)/UNT	0.986 ± 0.029
Ionics(+)/1sH_2SO_4	0.924 ± 0.011
Ionics(+)/1mH_2SO_4	0.912 ± 0.023
Ionics(+)/1sNaOH	0.964 ± 0.008
Ionics(+)/1mNaOH	0.842 ± 0.022

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Acknowledgements

To CICYT, Spain, for financial support (Project CQT2011-27770, FEDER funds).

EVALUATION OF THE CHEMICAL RESISTANCE NANOFILTRATION MEMBRANES APPLIED IN LIQUID RADIOACTIVE WASTE

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The application of membrane separation processes (MSP) in the area of treatment of radioactive waste in Brazil is not yet adopted by not being known for your potential and the high initial cost [1,2]. However, the process of separation by nanofiltration has been studied worldwide for the treatment of nuclear waste with great prospects [3,4]. Nanofiltration membrane has as main characteristic the high rejection of multivalent ions, which becomes very attractive for the treatment of nuclear waste, such as radioactive waste originated from uranium mining and those generated in the nuclear fuel cycle. The goal of treatment this type of waste is to reduce the uranium content in the permeate and recovery of uranium, which can return to the productive process of UO_2 pellets [5].
The application of MSP for this purpose requires a number of previous experiments prior to installation in a nuclear plant. The membrane should be suitable for treating of waste, as the membrane shall be exposed to the radioactive liquid. In this study polymeric membranes have been used, depending on the waste may show changes in the structure, resulting in transport properties loss [6]. In this study, a waste called "carbonated water" generated in the conversion of gas uranium hexafluoride (UF_6) was used. This type of waste may contain about 50 mg L^{-1} of uranium in solution. Two nanofiltration membranes with selective polyamide layer were studied and were identified as NF and SW, Dow/Brazil. The chemical composition and properties of the waste transport (permeate flux and rejection of chloride and sulfate ions, 1000 mg L^{-1} solutions at pH 7) of the membranes are shown in Tables 1 and 2 respectively.

Table 1: Concentration of uranium and chemical species (mg L^{-1}) in the waste (pH 9.4)

U (uranium)	**F^-** (fluoride ion)	**CO_3^{2-}** (carbonate ion)	**NH_4^+** (ammonium ion)
8.0×10^0	5.2×10^2	9.8×10^4	7.0×10^4

Table 2: Transport properties of membranes before immersion in the waste (P = 0.5 MPa)

Membrane	**Permeate flux ($L\ m^{-2}\ h^{-1}$)**	**Rejection (%)**	
		Cl^-	**SO_4^{-2}**
NF0	26.4 ± 2.6	18.3 ± 6,5	98.3 ± 1.0
SW0	29.6 ± 4.0	12.3 ± 5.0	99.2 ± 0.5

The molecular weight cutoff (MWCO) membranes were estimated using polyethylene glycol (PEG) of the 600 Da, having rejections greater than 99% [1].
Then the membranes were immersed in the waste by 24, 48, 72h and 5000h to evaluate the chemical resistance of the membranes. After the set time, the membranes were evaluated

again with PEG 600 Da. The table 3 presents the values for the rejection of the PEG membranes after periods of immersion time.

Table 3: PEG 600 rejections and permeated flux of NF and SW membranes after immersion in the waste for several periods (P = 0.5 MPa)

Membranes	Rejection (%)	Initial permeate flux ($L\ m^{-2}\ h^{-1}$)	Final permeate flux ($L\ m^{-2}\ h^{-1}$)
NF24-72h	99.7 ± 0.2	29.1 ± 0.8	29.1 ± 0.8
NF5000h	72.4 ± 0.2	23.0 ± 1.2	23.0 ± 1.2
SW24-72h	98.0 ± 0.2	30.5 ± 0.5	30.5 ± 0.5
SW5000h	66.0 ± 0.2	28.7 ± 1.1	28.7 ± 1.1

Table 3 clearly shows that the rejection of PEG 600 was immersed until 72 h in the waste membranes was not altered, presenting rejections above 98%, however, the membranes immersed for 5000 h showed low rejections, 72 and 66%, this fact is explained by the release of a layer onto the surface of both membranes, identified by infrared (FTIR) as a protective layer of crosslinked polyvinyl alcohol (PVA), very common in some membranes in order to improve the transport properties of the membrane [5].

Table 4: Results of permeation of the waste with membranes SW0 and SW5000h

Membranes	Permeate flux* ($L\ m^{-2}\ h^{-1}$)	Uranium rejection (%)	Permeate flux** ($L\ m^{-2}\ h^{-1}$)
SW0	28.0 ± 0.1	94.0 ± 0.1	2.3 ± 0.1
SW5000h	28.7 ± 1.1	73.0 ± 0.1	43.0 ± 0.1

* Permeate flux with destilate water and P = 0.5 MPa

** Permeate flux with waste

After losing the layer SW membrane, permeation of waste was carried, the results are shown in Table 4. We could observe that membrane showed SW5000h rejection of uranium 20% lower than the SW0 membrane. This result suggests that the loosening of the surface protective layer has left of most vulnerable membrane to waste. We can also observe that the SW5000h membrane presented the highest permeate flux, is in agreement with the confirmation of an additional layer of PVA. This result also agrees with the PEG rejection tests (Table3).

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Acknowledgments

We acknowledgments Dow/Brazil for kindly provided the membranes used in the work.

SURFACE AND STRUCTURAL CHARACTERISTICS AND PERMEATION PROPERTIES OF POROUS POLYVINYLIDENE FLUORIDE MEMBRANES PREPARED BY PHASE INVERSION

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Introduction

Because of its good thermal stability, chemical resistance and excellent film forming ability, polyvinylidenefluoride (PVDF) represents a very interesting polymer in the field of porous membrane manufacturing, [1]. PVDF membranes are easy to prepare through a simple phase inversion process, [2], based on the immersion of a polymeric solution into a polymer non-solvent bath (usually water). By varying properly the characteristics of the polymeric solution (type of solvent, additives or doping agents) as well as casting and immersion conditions, membranes with different properties can be obtained for large variety of applications ranging from traditional (MF and UF) and emerging (membrane/osmotic distillation, membrane contactors) processes to innovative technologies (gas diffusion layers in PEM fuel cells, barriers in lithium ion batteries), [1].
This presentation deals with the preparation of porous PVDF membrane starting from casting solution prepared by dissolving the fluorinated polymer in N-methyl-2 pyrrolidone (NMP) e triethylphosphate (TEP). The effect of the variation of casting solvent on the surface and structural characteristics and air permeability of the resulting membrane is reported.

Experimental

Polymer solutions (C_{PVDF} = 10 wt %) were first cast onto the surface of a non-woven support (PP/PE, FO 2461, Viledon, Freudenberg Vliesstoffe KG) to form a thin film (350 mm thick), then exposed to room temperature air for 30s, and finally immersed in a water bath (15°C) to precipitate the polymer and form the membrane. Surface and structural properties of the membrane were investigate through porosimetric and microscopic techniques. A commercial (Coulter II, from Beckman Coulter Inc.) gas/liquid displacement porometer (GLDP) and a liquid/liquid displacement porosimeter (LLDP) developed in our labs [3,4] were used to evaluate pore size distribution of the membrane. Coulter porometer was used to determine air permeability. Surface images were taken with a scanning electron microscope (SEM, Stereoscan 440, Leo) as well as with an atomic force microscope (AFM, Nanoscope IIIa, Digital Instrument).

Results

Inspection of SEM micrographs (Figs. 1a and 1b) reveals profound differences between characteristics of the PVDF membrane deposited on the non-woven support. The surface of membrane cast from NMP solution (Fig.1a) appears highly irregular with a great number of large and tapered cavities (1-2 μm) along with numerous pores of noticeable lower size. On the contrary the use of TEP as casting solvent leads to a membrane with more homogeneous surface, lower porosity and apparently narrow pore size distribution.
The differences on the surface characteristics between the two membranes can be better appreciated from the AFM images shown in Figure 2. The values of the average roughness evaluated by AFM analysis are reported in the second column of Table 2.

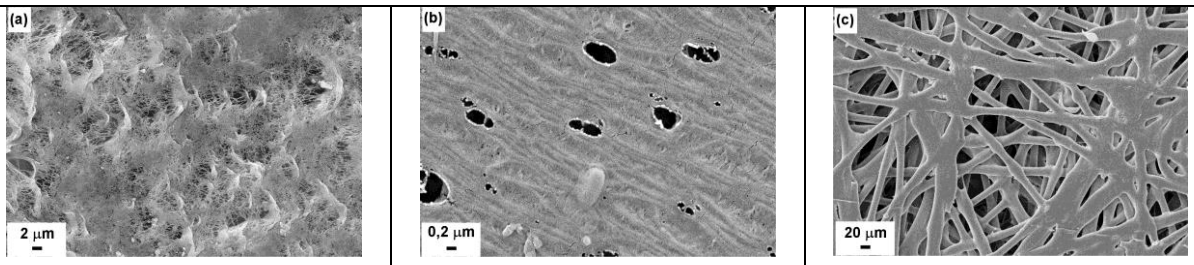

Figure 1 – SEM micrographs of the surface of PVDF membranes prepared from NMP (a) and TEP (b) solutions cast onto the non-woven support (c)

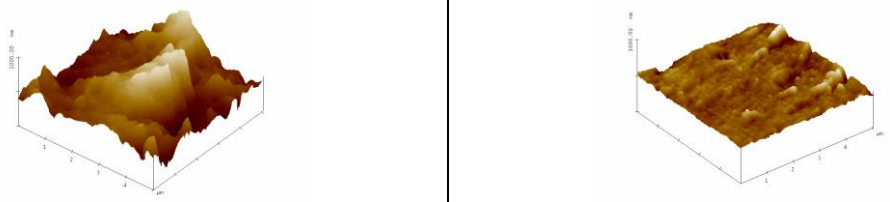

Figure 2 – AFM images of the surface of PVDF membranes prepared from NMP (a) and TEP (b) solutions

Results of porosimetric measurements (LLDP or GLDP, depending on membrane pore size) are also reported in Table 1 along with air permeability values evaluated by Coulter II.

Table 1 – Effect of casting solvent on the ain characteristics of the membrane

Casting solvent	Av. surface roughness (nm)	GLDP pore radius (μm)			LLDP pore radius (μm)			Air permeability (L / m^2 h bar)
		min	max	mean	min	max	mean	
NMP	12591	1,5	4,5	2,5				$6 \cdot 10^6$
TEP	9703				0,01	0,09	0,04	$5 \cdot 10^5$

Minimum GLDP pore radius does not correspond to the size of smallest pores of NMP membrane (see Fig.1) as too high pressures are needed to displace wetting liquid (Fluorinert®, 3M) from these pores due to a high surface tension (γ = 16 mN/m) of the fluids interface. For the same reason, air permeability of the MNP membrane should be underestimated since the air cannot flow through the wet smaller pores.

Conclusion

PVDF membranes with quite different properties to be applied in different separations (filtration for NMP membranes and microfiltration, membrane distillation, membrane contactor for those from TEP) were prepared and characterized by a variety of techniques. Work is running to investigate the influence of the casting parameters (type of support and exposure time of the cast solution before water immersion) on membrane characteristics.

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Characterization of different type of fibers with PVDF for CO_2 absorption

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Among the available membranes, dense polymer composite hollow-fiber membranes are promising for gas permeation applications coupled with the use of gas/liquid contactors [1]. Carbon dioxide capture is one of the main challenges regarding the technical options for climate change control. Post-combustion technology constitutes a strategy for reducing greenhouse gas impacts from fossil fuels in industrial processes [2]. Gas/liquid direct contact can be avoided by the use of membrane devices, as they enable mass transfer without dispersion of one phase into the other. The non-dispersive absorption process offers several technical advantages such as high surface area per unit volume, especially when hollow fibre membrane modules are used. However, the membrane constitutes an additional mass transfer resistance itself, depending on the membrane material and selected solvent [3].

The aim of this work is the characterization of four types of hollow-fiber based on PVDF and different additives. In order to compare the fibers under study, the thickness of the composite fiber was examined by scanning electron microscopy. In a typical procedure, fibers were first immersed in ethanol, cryofractured in liquid nitrogen, and then cut. The thickness was measured from the SEM image of a cross section. The mechanical properties were also evaluated. The deformation to traction and the elasticity were calculated using the Bluehill program . The gas permeation of composite hollow fibers was measured using pure CO_2. Self-fabricated stainless steel modules were used for the tests. One to three fibers around 30 cm long were assembled in each module. The gas was fed into the shell side and the gas permeation flux was measured at the outlet of the lumen side. The pressure was increased gradually from 0.3 bar to 15 bar. Each measurement was recorded after 100s of flux stabilization. Finally the bubble point was measured. All the above tests were performed with the fibers in both wet and dry conditions.

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Acknowledgements

This research has been funded by the Spanish Ministry Economy and Competitiveness (Project ENE2010-14828).

PREPARATION AND ELECTROCHEMICAL CHARACTERIZATION OF POLYMER INCLUSION MEMBRANES BASED ON ALIQUAT 336

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The presence of heavy metals in natural waters or industrial and domestic wastewaters is a major problem in different areas of the world due to their high toxicity, which encourages the development of separation systems for the treatment of polluted waters as those using polymer inclusion membranes (PIMs) [1]. A typical PIM consists of a polymer to get the gel-like network needed to entrap the carrier and to provide mechanical strength, a plasticizer/modifier to give elasticity and increase the solubility of the chemical species in the membrane phase, and a carrier or extractant to facilitate the selective transport [1].
In this work we compare the effect of the content of the extractant Aliquat 336, an ionic liquid at room temperature with is also used as plastizicer, and cellulosetriacetate (CTA) as base polymer in the electrochemical behaviour of the PIMs, in order to determine differences in the equivalent fixed charge and ion transport numbers or ionic diffusion coefficients.
The PIMs studied were prepared by dissolving CTA and Aliquat 336 in chloroform as it was extensively explained in [2]. Membranes are identified according to their Aliquat 336 percentage: CTA/26% Aliquat 336, CTA/48% Aliquat 336, CTA/60% Aliquat 336 and CTA/70% Aliquat 336. Chemical characterization of membranes was performed by IR spectroscopy taken in an Alpha Brucker FT-IR spectrometer using a single reflection ATR system. Changes in the hydrophilic character of the membranes were determined from contact angle measurements performed with a Teclis T2010 instrument equipped with a video system [3]. Membrane potential ($\Delta\Phi_{mbr}$), or equilibrium electrical potential difference between two solutions with different concentrations at each membrane side, was measured in a dead-end test cell [4] with the solution stirred at 540 rpm. Measurements were performed using two reversible Ag/AgCl electrodes for determination of the cell potential (ΔE), by changing the concentrations of the NaCl solutions at both membrane sides but keeping constant the concentration ratio $c_1/c_2 = 2$, from c_2 ranging between 0.01 M and 0.1 M. $\Delta\Phi_{mbr}$ values were obtained by subtracting the electrode potential ($\Delta\Phi_{elect}$) to the measured cell potential: $\Delta\Phi_{mbr} = \Delta E - \Delta\Phi_{elect}$.
Effective fixed charge, X_{ef}, and ion transport number, t_i, or fraction of the total current transported for one ion ($t_i = I_i/I_T$) are two significant parameters which can be determined from membrane potential values ($\Delta\Phi_{mbr}$). According to the Teorell-Meyer-Sievers or TMS theory [5-6], membrane potential can be considered as the sum of two Donnan potentials (one at each membrane-solution interface), associated to the exclusion of the co-ions (or ions of the same sign as the membrane charge), plus a diffusion potential in the membrane due to the different mobility of the ions inside the membrane, that is: $\Delta\Phi_{mbr} = \Delta ø_{Don(I)} + \Delta ø_{dif} + \Delta ø_{Don(II)}$. Membrane potential can be expressed as [7]:

$$\Delta\Phi_{mbr} = -\frac{RT}{wzF}\left[U \ln \frac{\sqrt{4y_v^2+1}+wU}{\sqrt{4y_f^2+1}+wU} - \ln \frac{c_f}{c_v}\frac{\sqrt{4y_v^2+1}+w}{\sqrt{4y_f^2+1}+w}\right]$$

where U is a parameter related to the ions transport numbers ($U = ((D_+ - D_-)/(D_+ + D_-) = t_+ - t_- = 2t_+ - 1$), $y_j = K_j.c_j/|X_{ef}|$ and K_j is the partition coefficient or membrane/solution concentration ratio.

Fig. 1(a) shows membrane potential values for the studied membranes as a function of the external NaCl solution concentration, where differences in $\Delta\Phi_{mbr}$ values for the membrane with lower Aliquat 336 concentration can be observed, but values hardly depends on Aliquat 336 content for concentration higher than ~ 45 %, in agreement with previous results obtained with dry samples [8]. The fit of these experimental values allows us the estimation of X_{ef}, t_i and D_i values.

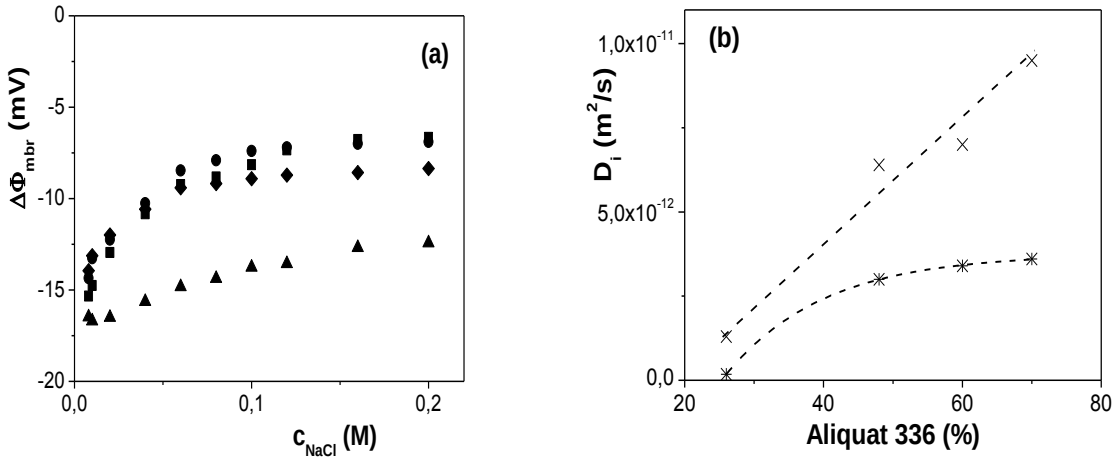

Fig. 1: (a) Membrane potential vs NaCl concentration for CTA/26% Aliquat 336 (▲), CTA/48% Aliquat 336 (●), CTA/60% Aliquat 336 (▼) and CTA/70% Aliquat 336 (♦). (b) Increase of ions diffusion coefficients, D_{Na+} (*) and D_{Cl-} (x), in the membranes with the increase of Aliquat 336 content.

Fig. 1(b) shows the dependence of D_{Na+} and D_{Cl-} values with the increase of Aliquat 336 content in the membrane. As can be observed in the figure, the increase of Aliquat 336 content in the membrane slightly increase the cation diffusion coefficient, which might be associated to the augment of the hydrophilic character according to contact angle results [3], but it significantly amplify the anion diffusion. The reliability of these values has also been established by impedance spectroscopy measurements performed with wet samples (after 24 h immersed in a 0.01 M NaCl solution).

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Acknowledgements
To CICYT, Spain, for financial support (Project CQT2011-27770, FEDER funds).

X-RAY FLUORESCENCE SPECTROMETRY, A SIMPLE AND NON-DESTRUCTIVE TECHNIQUE FOR MEMBRANE HOMOGENEITY TESTING

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Membrane characterization is of paramount importance when designing or manufacturing new membranes in order to ensure the quality of its final application. Obviously, the nature of the membrane demands the different parameters to be considered for its characterization, and thus, the techniques to be used.

Among the different type of membranes, homogeneous, non-porous organic membranes are not easy to characterize. This is the case of polymer inclusion membranes (PIMs). PIMs are thin and flexible films that are easily prepared by casting an organic solution containing a base-polymer, such as poly(vinyl chloride) (PVC) or cellulose triacetate (CTA), an extractant as carrier, an often a plasticizer or modifier. Separation by PIMs is achieved as in supported liquid membranes (SLMs). The separation effectiveness of both types of membranes depends significantly on the use of an appropriate carrier. It is notorious that PIMs exhibit better mechanical properties and chemical resistance since the carrier is immobilized onto a polymer matrix. For that, PIMs have good stability because the rate of loss of the membrane liquid phase to the aqueous phase that the membrane is in contact with is small compared to other types of membranes, such as SLMs. Even though PIMs have successfully been designed for the separation of different species such as metal ions, small molecules and inorganic anions [1], there is no any industrial processes using this kind of membranes yet. Thus, it is of paramount importance to deeply study this kind of membranes in terms of manufacturing and stability to show their potential and to facilitate its integration in separation processes at industrial, water treatment or engineering scale.

One of the issues to consider when characterizing PIMs is their homogeneity. In this work, we have prepared different PIMs consisting of the polymer CTA, and the ionic liquid, Aliquat 336 as carrier. Aliquat 336 is a mixture of long alkyl chain quaternary ammonium chlorides, and is one of the most useful extractant for anionic species in PIMs. For that, 200 mg of CTA were dissolved in 20 mL chloroform for 5 hours, and after this time of mixing, the appropriate volume of a 0.5M Aliquat 336 solution also in chloroform was added. After 2 more hours mixing, the resulting solution was poured into a 9 cm diameter flat bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporated for 24 h at room temperature, and the resulting film was then carefully peeled off from the bottom of the Petri dish and was ready to characterize or to use for transport experiments.

Typical techniques to evaluate the amount of carrier per area of membrane can be, for example, thermogravimetric analysis (TGA) or elemental analysis, which are destructive techniques. Also, XPS is often used, but this technique only allows the determination of the atomic concentration percentages of the elements present on the membranes surfaces.

In this work, we have investigated the areal distribution of the carrier in different PIMs prepared with CTA and Aliquat 336 ranging form 20 to 50% content (weight) by the determination of chlorine (present in Aliquat 336) K alpha intensity by milli-energy dispersive X-ray fluorescence (EDXRF) instrumentation (Helmut Fisher XDV-SD). A mapping program was used to measure 25x25 (625 points) for each membrane and 25 seconds counting time for each point. Distribution of chlorine along the membrane ($\mu g \cdot cm^2$) was calculated according the fundamental parameters approach using the WinFTM software as described in the work of Roessiger and Nensel [2].

In Fig. 1 it is shown the mapping of the chlorine content in the PIM consisting of 70% CTA and 30% Aliquat 336. As it can be observed, there is a variation of the Cl content (µg Cl cm^{-2} membrane) from about 40 in the central part to near 70 in the periphery. Similar results were obtained with the other membranes investigated containing 20, 40 and 50% of Aliquat 336. It is believed that this difference in Aliquat 336 distribution can be due to thickness variation of the membrane.

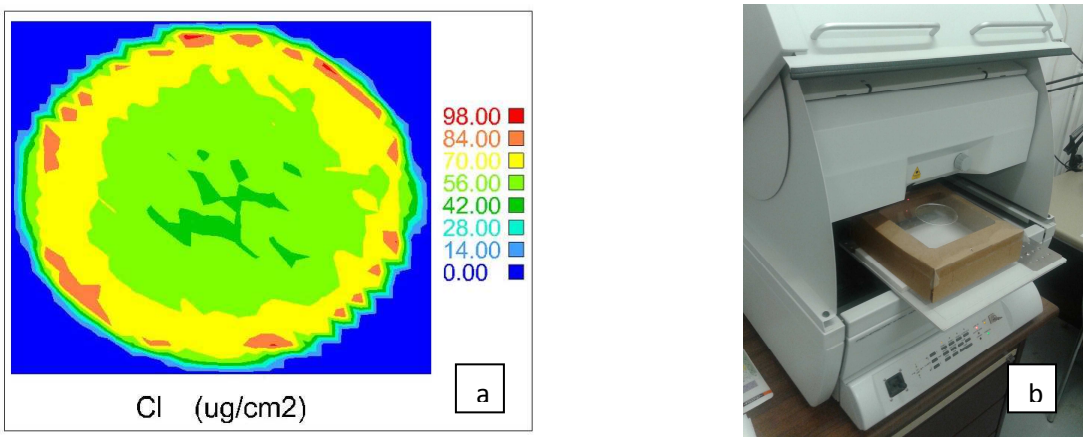

Fig.1. a) Mapping of chlorine content of a 70%CTA+30%Aliquat 336 PIM, b) Benchtop EDXRF instrument used for areal analysis of membranes

Moreover, the same technique allows the investigation of the possible loss of carrier when the PIM is in contact with aqueous solutions. This can be easily done by comparing the Cl mapping of the same membrane, since it is a non-destructive technique.

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Acknowledgements

This work has been carried out with the financial support of the Spanish National Funding for R&D projects (project ref. CGL2010-22168-C03-01)

TRAGACANTH MODIFIED DENSE MEMBRANES

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A variety of renewable biopolymers such as polysaccharides derived from plants have been investigated for the development of edible/biodegradable, non-petrochemical-based packaging materials and edible coatings. Tragacanth gum is an interesting alternative to synthetic water-barrier polymers in packaging applications. Films have low water permeability under dry conditions due to their high content of hydrogen bonds. Films were prepared from aqueous solution of tragacanth (exudate tree called Astragalus Gossipinus). Then they were crosslinked with glutaraldehyde (Sigma Grade II) at different ratios (5, 7 and 10% vol.) and contact times from 0.2 to 120 hours, in 100 ml of acetone-HCl 1% vol (Biopack) solution.

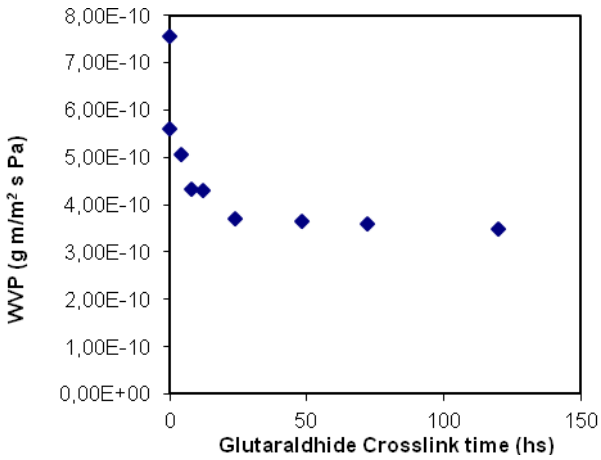

Figure 1: Tragacanth films crosslinked with glutaraldehyde at different ratios.

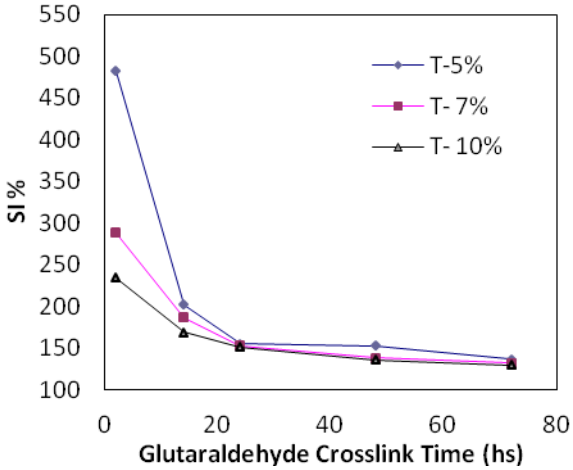

Figure 2: Swelling index.

Table 1: Theta Angles (θ) and dspacing values of tragacanth membranes crosslinked and uncrosslinked.

Samples	2 θ	$d_{spacing}$ (Å)
Trag	21.65	4.09
Trag-24-5	14.43	6.13
Trag-24-7	14.84	5.96
Trag-24-10	15.45	5.72

Table 2: Theta Angles (θ) and dspacing values of tragacanth membranes uncrosslinked and crosslinked 5% glutaraldehyde at different times.

Samples	2 θ	$d_{spacing}$ (Å)
Trag	21.65	4.10
Trag-24-5	14.43	6.13
Trag-72-5	14.24	6.21

The increase in water resistant of crosslinked tragacanth films is mainly due to their higher hydrophobicity and consequent insolubility reached at higher crosslinking times. A more interconnected network within polar groups present in polysaccharide was achieved. Crosslinking times from 0.2 to 120 h provided water vapor permeation values in the range

from 7.56 to 3.50 x 10^{-10} g m/m^2 s Pa (figure 1), swelling indexes from 480 to 130% (figure 2) and water uptake values of 185 to 125 g/g.

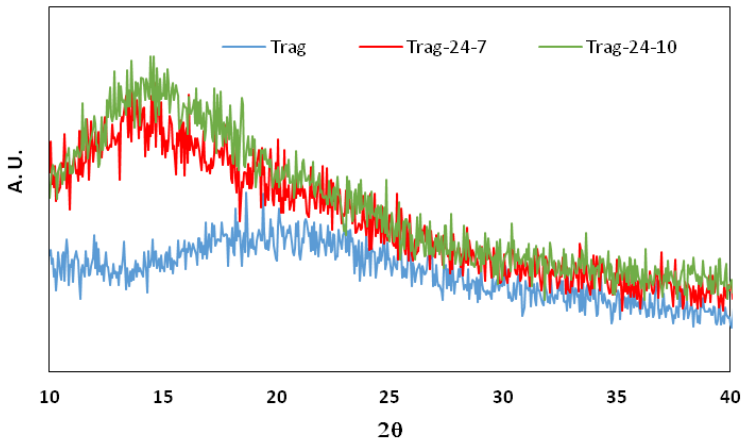

Figure 3: X-ray diffraction.

X-ray diffraction patterns (figure 3) showed a shift to lower 2θ as glutaraldehyde concentration increases. These changes can be attributed to the loss of water molecules when polymeric matrix is conditioned for XRD measurements (dryed at 60ºC). This effect is intensified when the membrane has not been crosslinked, showing a higher interchain spacing reduction or higher packing. These results explain the increase in "d spacing" when the membrane is crosslinked (Table 1). Swelling index and water vapor permeation properties stabilize in approximately 24 h (Fig. 1, 2). These membranes exhibit excellent water resistance and adsorption properties, which make them useful for eco-friendly applications.

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ESTUDIO DEL POTENCIAL ZETA Y CORRIENTE DE FLUJO EN MEMBRANAS DE ULTRAFILTRACION EN CONTACTO CON UN TENSOACTIVO ANIÓNICO

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Introducción

El uso de las membranas de ultrafiltración (UF) en el tratamiento de aguas es una técnica muy utilizada debido a la calidad de agua obtenida y a su bajo costo. Dentro de los principales contaminantes de aguas grises se encuentran los tensoactivos, los cuales pueden ser adsorbidos en las membranas afectando su rendimiento. El estudio de las propiedades electrocinéticas nos ayuda a entender las interacciones tensoactivo-membrana, por lo que es un análisis primordial dentro del área de membranas. En éste trabajo nos hemos enfocado en el estudio del potencial zeta (PZ) y corriente de flujo, en membranas de UF adsorbidas con un tensoactivo aniónico a diferentes concentraciones, lo anterior con el fin de entender las interacciones tensoactivo-membrana.

Materiales y métodos

Se utilizaron membranas de UF de polietersulfona (PES), marca KOCH, con una línea de corte de 5 KDa. El tensoactivo aniónico utilizado fue el Dodecil Sulfato de Sodio (SDS) de la marca Sigma-Aldrich con un grado de pureza ≥ 99.0%.

La determinación del PZ se realizó a través del SurPASS electrokinetic analyzer (Anton Paar GmbH). Los experimentos fueron llevados a cabo a temperatura ambiente con KCl ($1x10^{-3}$ M). Ésta determinación se hizo tanto para las membranas limpias de diferentes hojas como para membranas previamente adsorbidas con SDS a diferentes concentraciones (4, 8, 16, 30 y 40 mM). La adsorción se llevó a cabo a través de un sistema de flujo tangencial, y la cantidad de SDS adsorbido por unidad de área se calculó a través de un balance de materia. También se estudió la variación del PZ de las membranas limpias al ponerlas en contacto con SDS a diferentes concentraciones. Se llevó a cabo la medición de la corriente de flujo para diferentes concentraciones de SDS en función del tiempo.

Resultados y discusión

En la Figura 1 se presenta la variación del PZ y la masa de SDS adsorbida en la membrana en función de la concentración de SDS al equilibrio. Para la isoterma de adsorción podemos observar dos regímenes diferentes, en la primera parte la cantidad de SDS adsorbido aumenta con respecto a la concentración. En la segunda etapa se llega a un máximo el cual se mantiene (concentración de tensoactivo > 8mM). Este comportamiento se puede explicar si se considera que a concentraciones por debajo de la CMC (8 mM) los monómeros se absorben en la membrana, por encima de este valor, los monómeros se agregan en forma de micelas las cuales no son capaces de adsorberse, sin embargo en esas condiciones existe una concentración de monómeros que puede ser constante, lo que explica la segunda parte de la curva. En el caso del PZ se observa primeramente una disminución (valores más negativos) con respecto al valor observado para membranas limpias, seguido de un aumento en el PZ, donde los valores son similares al de la membrana limpia y finalmente una disminución. Tomando en cuenta que las membranas de PES están cargadas negativamente[1], se puede suponer que la adsorción de los monómero de SDS se lleva a cabo a través de la cola lipofílica dejando la cabeza cargada negativamente hacia la solución, por lo que el PZ se hace más negativo.

La Figura 2 nos muestra el estudio de la variaicón del PZ en la membrana al ponerla en contacto con SDS a diferentes concentraciones, en función de la concentración de SDS. En ésta figura se puede observar que inicialmente el PZ disminuye con respecto a la membrana

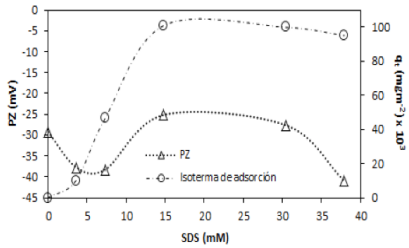

Figura 1. Potencial zeta y cantidad de SDS adsorbido por unidad de área en función de la concentración de SDS.

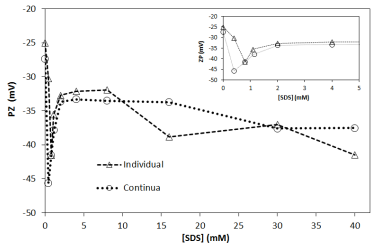

Figura 2. Potencial zeta de las membranas adsorbidas (individual y continuo) con SDS a diferentes concentraciones.

limpia observándose luego un incremento hasta llegar a un valor que se mantiene practicamente constante a partir de una concentración de SDS 2 mM. Estos resultados nos sugieren que la cantidad de SDS adsorbido en la superficie de la membrana se mantiene prácticamente constante a partir de una concentración de 2 mM. Se puede observar la disminución de PZ a 40 mM para ambas series de experimentos, lo cual podría deberse a los agregados micelares formados) a esa concentración. Después de la adsorción se realizaron lavados consecutivos para analizar el grado de desorción, encontrándose valores similares para todas las concentraciones (-23.40 mV). El valor de PZ de las membranas desorbidas es muy cercano al de las membranas limpias (-26.21 mV), indicándonos que la adsorción del SDS por esta metodología no es permanente y que este se desorbe casi en su totalidad.

Finalmente se realizaron cinéticas de primer contacto. En la Figura 3-a se puede observar que para concentraciones por debajo de la CMC, el comportamiento de las curvas es similar durante los primeros segundos la corriente de flujo. Estos resultados nos permiten suponer que la adsorción se da de manera muy rapida sobre la membrana, llegando al equilibrio a los 5 segundos, la cantidad de SDS adsorbida se incrementa con la concentración. Para el resto de las concentraciones se puede observar en la Figura 3-b que durante los primeros 5 segundos la corriente de flujo incrementa, después de este tiempo hay un decaimiento que es mayor en función de la concentración seguida de un incremento de la corriente de flujo que finalmente se mantiene estable. Estos resultados nos permiten suponer que al principio se adsorbe una gran cantidad de SDS la cual al verse afectada por el flujo se desorbe llegando finalmente a una etapa de estabilización. Comportamientos similares a lo descrito ya han sido propuestos para otros sistemas[2][3].

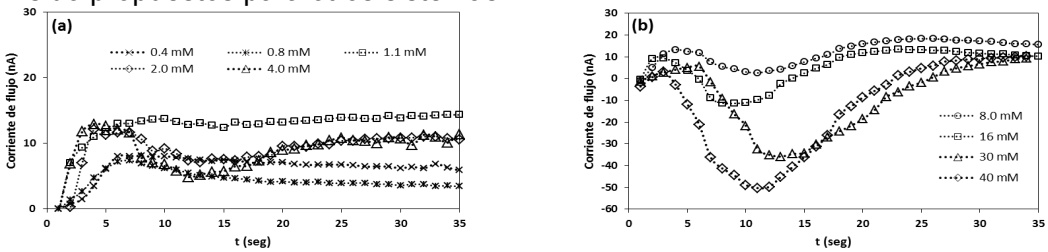

Figura 3. Variación de la corriente de flujo en función del tiempo, para bajas (a) y altas (b) concentraciones de SDS en membranas de UF de PES.

Conclusiones

A través del estudio de las propiedades electrocinéticas se pudieron analizar las cargas superficiales de las membranas adsorbidas con SDS. Los resultados muestran que la adsorción de tensoactivo modifica el PZ de las membranas de PES, y que la adsorción podría darse a través de la parte lipofílica del tensoactivo.

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Acknowledgements.

A DAIP por el apoyo otorgao para la realización de este proyecto a través de la Convocatoria Institucional 2013.

DISTRIBUTION OF HEAVY METALS PB (II), CD (II) AND CR (II) IN CHITOSAN/PVA GEL BEADS BY SEM-EDX.

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With dwindling freshwater supplies , the increasing demand for drinking water and water for industrial use new technologies are needed for wastewater treatment that are efficient and economical. In this work chitosan/polyvinyl acetate (PVA) gel beads were used for the adsorption of heavy metals in mine water. However to perform this study a semi-synthetic effluent was prepared from mine water, ie the concentration of the metals of interest Pb (II), Cd (II) and Cr (II) was increased . The gel beads of chitosan/PVA have a content 3.8 % weight of chitosan/PVA with a ratio 1:6. It was determined that the optimum pH is pH 5, being chosen as working condition for the experiments related to the kinetics [1]. It was performed two Kinetic experiments, one with 3 g with another 15 g of chitosan/PVA gel beads, in a volume of 500 ml of semisynthetic effluent. A sample of 10 beads to 48h kinetics performed with 3 g of beads were taken , while the experiment with 15 g of chitosan/PVA gel beads was sampled 10 beads at time 10 min, 30 min, 2h, 3h, 5h, and 24h . These beads were then cut transversely tested in a SEM-EDX microscope in order to know how metals are distributed within the bead, this was made possible by mapping each sample. From the data obtained from the analysis it can be seen that the metals Pb, Cd and Cr are distributed across the width of the bead being able to say that the bead has active sites throughout its volume in a uniform manner, and also can say that the intraparticle diffusion is not a brake for the adsorption of these metals.

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DEVELOPING NEW POLYMERIC INCLUSION MEMBRANES WITH INCREASED STABILITY IN AQUEOUS SOLUTIONS

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The use of ionic liquids (ILs) as components of polymer-based membranes in various morphologies and configurations have taken a privileged position in the membrane science and technology, and has become one of the most important topics of research in the world today [1]. This is due to the numerous advantages that can be obtained by mixing the relatively inert polymeric supports with these new environmentally benign solvents that are replacing the conventional organic solvents, toxic and no biodegradable. Indeed, the well-known properties of the ionic liquids relative to their near-zero vapor pressure, good chemical, thermal stability and tailoring manufacture, make them widely applicable in a number of extraction and separation processes, for example, in the selective simultaneous separation of the substrates and products of a transesterification reaction, that can be accomplished by using the supported ionic liquid membranes (SILMs), a type of membrane which has proved to be very useful for selective separation purposes [2].

Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray (EDX) analysis was used to evaluate the operational stability of SILMs based on ionic liquids [3]. Our research group found that the SILM stability increased with the polarity of the solvent used as receiving phase after immersion of the SILM in different feed/receiving phases decreased and with the hydrophilic character of the ILs used as liquid phase increased. Despite the good results obtained combining different hydrophilic ionic liquids with nonpolar organic solvents (n-hexane, dimethyl sulfoxide, tert-butyl methyl ether), the SILM technique is not fully utilized commercially at high scale, primarily due to its progressive performance decay with time. In particular, the biggest losses of ionic liquid were obtained when the water was used as the contact phase [4]. The instability of the organic liquid in the pores of the inert membrane as support reduces the period of utilization which has prevented its widespread use. These long term difficulties can be partly overcome by using polymer inclusion membranes (PIMs). This type of membranes exhibit great stability and versatility, and they have been recently applied for the selective extraction, separation and recovery of metals and other ions [5].

For these reasons and in order to obtain membranes stable in an universal and polar solvent, as water, and thereby extend the industrial applications to processes that mainly occurs in aqueous media, casting methods were used to prepare polymeric inclusion membranes (PIM) by using a PVC matrix and the ionic liquids $[MTOA^+][Cl^-]$, $[omim^+][NTf_2^-]$, $[omim^+][PF_6^-]$, $[bmim^+][NTf_2^-]$, $[bmim^+][PF_6^-]$, $[omimm^+][BF_4^-]$, $[THTDP^+][Cl^-]$ in several ratios IL/PVC. The aim of this work was to optimize the composition of the PIMs made of the aforementioned ionic liquids, using the casting method, and testing the stability of the membranes after being immersed in water for a period of time by using Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray (EDX) analysis.

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Acknowledgements

This work was partially supported by the MICINN ENE2011-25188 and SENECA Foundation 15260/PI/10 grants.

Mixed matrix membranes and carbon membranes

- **Poster session 1**

CARBON MOLECULAR SIEVE MEMBRANES FOR GAS SEPARATION

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Carbon molecular sieve membranes (CMSM) have been studied as promising and energy-efficient membranes for gas separation. Compared to polymeric membranes, CMSM show very attractive characteristics such as superior thermal resistance, chemical stability in corrosive environments, high permeabilities as well as excellent selectivities [1,2]. In this work, we report the preparation and characterization of supported carbon molecular sieve membranes from resorcinol-formaldehyde precursor in one dipping-drying-carbonization step.

Composite carbon molecular sieve membranes (c-CMSM) were prepared on alpha-alumina supports by carbonization of a resorcinol-formaldehyde resin loaded with boehmite nanoparticles. Two series of c-CMSM produced at 500 ºC and 550 ºC carbonization end temperatures were prepared. The morphology and qualitative elemental composition of c-CMSM were determined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). SEM microphotographs of cross-section of a supported c-CMSM carbonized at 550 ºC are showed in Figure 1. A carbon matrix with well-dispersed Al_2O_3 nanowires was formed on the top of the alpha-alumina supports resulting from the decomposition of the resorcinol-formaldehyde resin and dehydroxylation of boehmite.

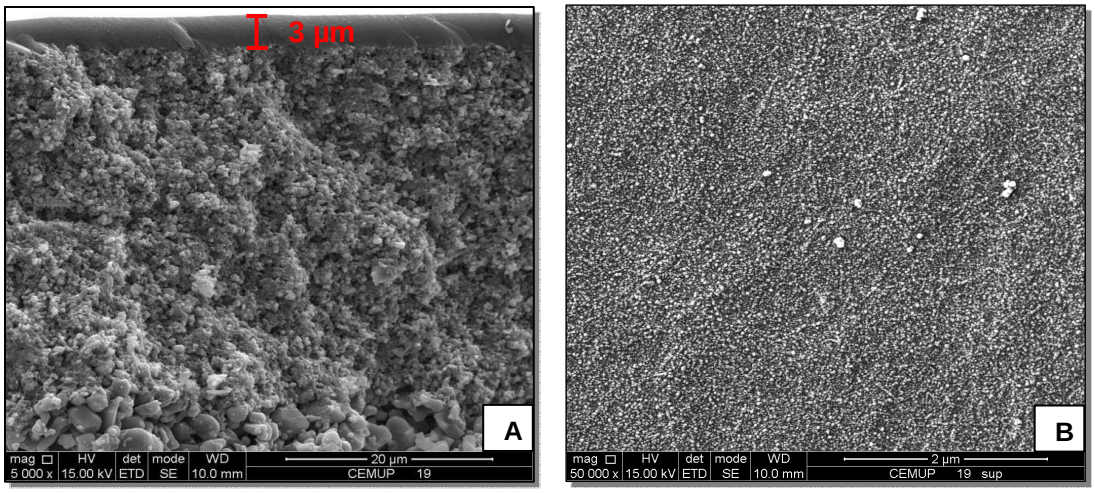

Figure 1. SEM micrographs of a supported c-CMSM carbonized at 550 ºC: (A) cross section; (B) surface view.

The pore size distribution for the produced c-CMSM was determined using the method proposed by Do *et al* [3,4]. Figure 2 presents the pore size distribution for c-CMSM carbonized at 500 ºC and 550 ºC. Comparing the two carbon membranes carbonized at different temperatures, it can be observed that c-CMSM carbonized at 500 ºC have a large number of micropores with larger dimensions and c-CMSM carbonized at 550 ºC have a large number of micropores with narrower pore size distributions. The permeance of CMSM obtained at 500 ºC and 550 ºC was assessed for N_2, O_2, He, H_2 and CO_2 at temperatures from 25 ºC to 120 ºC.

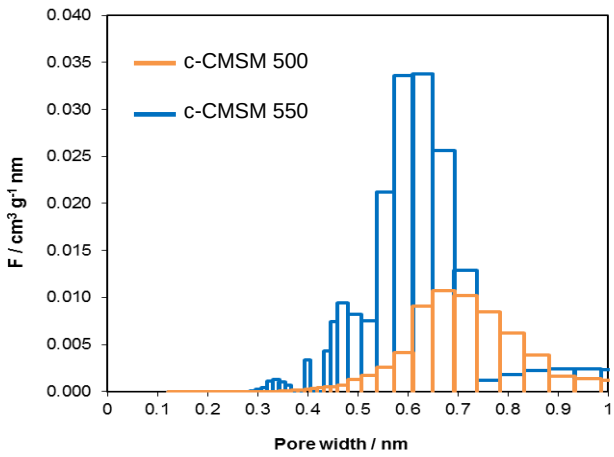

Figure 2. Pore size distributions of c-CMSM carbonized at 500 ºC and 550 ºC.

Table 1 shows the permeances as function of feed pressure for c-CMSM 500 and c-CMSM 550. Ideal selectivities obtained for both CMSM sets are shown in Table 2.

Table 1. Gases permeances as function of feed pressure for c-CMSM 500 (A) and c-CMSM 550 (B). Membranes were activated at 140 ℃ for 2h under N_2 atmosphere before experiments being performed.

Feed Pressure (kPa)	Permeance [10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}]									
	N_2		O_2		He		H_2		CO_2	
	A	B	A	B	A	B	A	B	A	B
500	0.025	< 0.0085	0.15	0.11	3.95	4.61	5.48	5.03	0.48	0.20
300	*	*	0.16	0.11	4.02	4.65	5.57	4.78	0.43	0.18
100	*	*	0.14	0.08	4.19	4.76	5.93	5.31	0.16	< 0.085

*Below detection limit

Table 2. Ideal selectivities for c-CMSM 500 and c-CMSM 550. Membranes were activated at 140 ℃ for 2h under N_2 atmosphere before experiments being performed.

	Ideal Selectivity			
	O_2/N_2	He/N_2	H_2/N_2	CO_2/N_2
c-CMSM 500	5.9	221	158	15.4
c-CMSM 550	>11.5	>544.0	>586.0	>23.3

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Acknowledgements (10 pt)
The authors would like to acknowledge the funding provided by the Portuguese Foundation for Science and Technology (FCT) through the projects PTDC/EQU-EQU/114944/2009, PTDC/EQU-EQU/104217/2008 and EXPL/QEQ-PRS/0342/2013. The authors are also grateful to the European Union´s Seventh Framework Programme (FP7/2007) for Fuell Cells and Hydrogen Joint Technology for funding under grant agreement number 303476.The authors are thankful to CEMUP for the SEM/EDS analysis.

DESIGN AND CHARACTERIZATION OF MIXED MATRIX MEMBRANES WITH IONIC LIQUIDS FOR CO_2 CAPTURE

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Separation of carbon dioxide (CO_2) from emission sources generated by power plants has been attracting much attention due to the enhanced greenhouse effect. Therefore, the research and development of efficient gas separation technologies is mandatory to minimize the CO_2 release from post-combustion streams. Currently, amine-based solvent systems are used for scrubbing CO_2; however these conventional absorption technologies are rather energy intensive and present technical problems, such as corrosion and degradation of the absorbing amines. The separation and capture of CO_2 with minimum energy used is essential, and thus membrane-based processes show clear advantages when compared with other absorptive methods. Polymeric membrane-based separation processes have proved to be an energy-saving and cost-effective alternative to absorption or pressure swing adsorption processes for CO_2 separation. The efficiency of this technology depends mainly on the selection of the membrane materials, their properties, and the permeation mechanism. Even though membranes are already used for CO_2 capture, their performance is still compromised by the relation between membrane selectivity and permeability.

In the last years, significant research work has been performed in the preparation and use of porous metal organic frameworks (MOFs) for application in selective adsorption of distinct gases, particularly for H_2, CH_4 and CO_2, demonstrating their great potential in the separation and purification of different gas mixtures. MOFs are build-up by metal or metallic cluster centers linked by organic molecules into extended ^{1}D, ^{2}D or ^{3}D ordered networks. In some MOFs the pores are large enough to accommodate several types of gases yet still exhibit adsorption selectivity arising from thermodynamic equilibrium or the kinetic effect [1]. Despite the potential of using MOFs for gas separation processes, the use of these materials in membrane technology studies is still scarce.

The approach proposed in this project is to prepare new membranes, designed as mixed matrix membranes (MMMs), which result from the combination of a polymeric membrane with hybrid materials, such as MOFs. These new membranes combine the superior CO_2 permeability and selectivity of MOFs with the flexibility and ease of preparation of polymeric membranes. Additionally, MMMs will also be prepared by incorporation of ionic liquids with a high affinity towards CO_2 to further increase its permeability and selectivity. Ionic liquids are compounds consisting entirely of ionic species, with an organic cation and an inorganic or organic anion. In membrane processes, ionic liquids are being used in the design and modification of advanced materials that enable performance levels not typical of conventional materials for application in gas separation processes [2].

In this work, the mixed matrix membranes (MMMs) were prepared by dispersing different MOFs in concentrations (between 5 and 90% w/w) in an organic solution of Matrimid® (polymeric material). The MOFs studied were MOF-5, MOF-199, ZIF-8, MIL-53 and Cu-BTC. The solutions were sonicated in order to have a good dispersion, spread in a flat support and let to dry to form a film. Mixed Matrix Membranes with ionic liquids (MMM-ILs) membranes were also prepared by dispersing the ionic liquids $[C_4MIM][Tf_2N]$ and $[C_4MIM][PF_6]$ in different concentrations in the MMMs. The prepared membranes were then characterized by scanning electron microscopy (SEM), thermogravimetry, differential scanning calorimetry (DSC) and

contact angles. The mechanical properties of the membranes were obtained by tensile tests. Finally, single gas permeation experiments were carried out for CO_2 and N_2 at 30ºC.

SEM images reveal a dense membrane and a good interaction between Matrimid® and the MOF, for MOF concentrations up to 30% (w/w). However, when the ionic liquid was incorporated inside the MMMs, from the cross-sectional images it was possible to distinguish a thin dense film on the surface and a porous structure. Thermogravimetric analysis showed that all the membranes prepared are stable at temperatures up to 300 ºC. The mechanical properties of the prepared membranes showed that both the tension and the elongation at break decrease with increasing MOF concentration, as well as, with the increase of ionic liquid concentration, which is an indication that the membranes become more rigid and fragile when compared with Matrimid®. The experimental results of the pure gas permeability showed that the permeability depends on the MOF concentration. It has been observed an increase in permeability for concentration values up to 20%, and a decrease for higher MOF concentrations. For all the MOFs concentrations tested, the mixed matrix membranes prepared are selective towards CO_2 when compared with N_2. Regarding the effect of the presence of ionic liquids in the MMMs, it has been observed an increase in CO_2 permeability, and depending on the MOF tested it was possible to observe an increase in CO_2/N_2 ideal selectivity. These results show the high potential of using mixed matrix membranes with ionic liquids for gas mixtures separations.

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Study of the inclusion of carbon nanoparticles in polyurethane membranes for separation process.

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Introduction: Several studies have recently been proposed in order to increase the transport properties of the membranes by the inclusion of inorganic particles into polymer matrix (mixed matrix membranes MMM). MMM consist of a dispersed phase of inorganic particles like zeolite, carbon nanoparticle or carbon nanotubes, embebed in a continuous phase of polymer matrix. In this work, novel nanocomposite dense membranes containing carbon nanoparticles inside polyurethane polymer matrix have been developed and characterized in pervaporation and gas separation.

Experimental:
Membrane Fabrication: Fullerene and activated carbon were chosen as carbon nanoparticles. Commercial polyether-based polyurethane (PU) was used as polymer matrix. Tetra Hydro Furan (THF) was used as a solvent in the polymer solution. For all membranes the total content of solids in the solution was adjusted in 10%. The carbon nanoparticles content was 1% (referred to the polymer). Polymer was previously dried at 60°C for 24 hours before the use. The polymer was dissolved in part of THF during 2 hours until total dissolution of polymer. The carbon nanoparticles were then suspended in the other part of the THF and subsequently sonicated during 30 minutes. After that, the nanoparticles with THF were added into the polymer solution and stirred overnight, leading to a homogeneous suspension. Membranes were cast onto a Teflon (reg.mrk) plate and covered with a glass sheet allowing slow evaporation of solvent for 24h at 25°C. Then, films (thickness of 100 μm) were pealed off the plate and dried at 25°C for another 24h before the tests. Membranes of pure polymer were made for comparison of the results.
Characterization: Morphology of the membranes was obtained using Scanning Electron Microscopy (SEM, Quanta 250). Swelling was determined by cutting 1cm^2 of samples and soaking them in a solution (Methanol/MTBE 15/85 w) at 30°C during 24h. Single gas permeation tests were performed at 25°C with purified CO_2, O_2 and N_2 using a constant volume [1] varying pressure apparatus at 25°C and pressure of 2 bar. Pervaporation experiments were carried out using the same standard apparatus system reported by Cunha *et al* [2]. The feed solution was a binary mixture of Methanol (MeOH) with methyl-t-butyl ether (MTBE) (15%w Methanol) at 30°C. Compositions of feed and permeate were determined by gas chromatography.

Results and discussion:
Figure 1 shows all that membranes exhibit a dense morphology. The presence of carbon nanoparticles at 1%, apparently do not modify the morphology of the pure PU membrane. Gas permeation results (Table 1) exhibit that membranes containing carbon nanoparticles increase the CO_2 and O_2 permeability of PU membrane, suggesting nanoparticles interaction with O_2 molecules, facilitating the transport though the membrane. In the case of CO_2, membranes with carbon nanoparticles presented a great increase in permeability and ideal selectivity compared with the pure PU membranes. Table 2 shows that the three membranes presented swelling in the range of 12-20%. This is may be the cause of the high pervaporation flux, much higher than the reported by Weibel et al. [3]. Selectivity of membrane presented an increase only for the one with the inclusion of activated carbon nanoparticles.

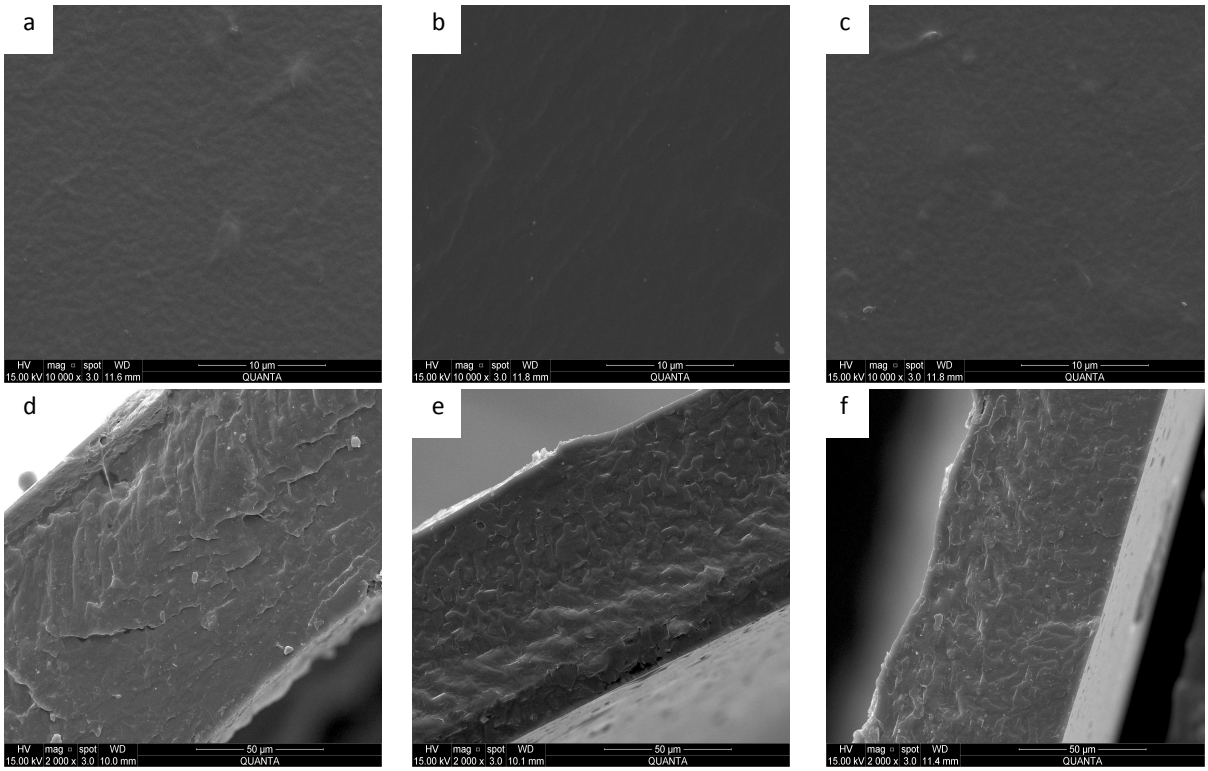

Figure 1. Micrographs of surface and cross section of polyurethane membranes: Pure PU (a,d), PU+Fullerene (b,e), PU+ Activated carbon (c,f).

Table 1. Gas permeation results.

Membrane	Gas Permeability (Barrer)			Ideal Selectivity	
	N_2	O_2	CO_2	CO_2/N_2	O_2/N_2
Pure PU	0,73	3,83	50,78	69,56	5,25
PU + Activated Carbon	0,76	7,10	96,08	126,43	9,34
PU + Fulerene	1,05	5,13	102,57	97,68	4,88

Table 2. Swelling and pervaporation results for the mixture of 15%w MeOH in MTBE.

Membrane	Swelling (%)	Pervaporation Flux ($gm^{-2}h^{-1}$)	Selectivity
Pure PU	17,4	812,77	3,27
PU + Fulerene	12,8	850,33	3,28
PU + Activated Carbon	19,2	800,58	3,75

Conclusions

This work shows preliminary indications that the presence of carbon nanoparticles can modify the transport properties of polyurethane membranes, and may have promising applications in the O_2/N_2, CO_2 removal and the MeOH/MTBE separation.

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Acknowledgements: The authors would like to thank CAPES for a fellowship grant.