Mafalda Tomé Pessoa Lopes

Mestre em Engenharia Química e Bioquímica

Wastewater and drinking water treatment by membrane processes: from laboratory to pilot-scale

Dissertação para obtenção do Grau de Doutor em

Engenharia Química e Bioquímica

Orientador: Svetlozar Velizarov, Investigador Auxiliar da Unidade de Investigação LAQV, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa

Co-orientador: João Paulo Goulão Crespo, Professor Catedrático, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa

Júri:

Presidente: José Paulo Barbosa Mota, Professor Catedrático, Faculdade de Ciências e Tecnologia da Universidade NOVA de Lisboa

Arguentes: José Luis Cortina Pallas, Full Professor, Politécnica de Catalunya Barcelona Tech

Rui Manuel Carvalho Viegas, Investigador Auxiliar, Laboratório Nacional de Engenharia Civil (LNEC)

Vogais: Isabel Maria Rôla Coelhoso, Professora Auxiliar, com Agregação da Faculdade de Ciências e Tecnologia da Universidade NOVA de Lisboa,

Vanessa Ranhada Pinto Jorge Pereira, Investigadora do Instituto de Biologia Experimental e Tecnológica (IBET)

Gang Xin, Especialista ao abrigo do nº6 do artº34 do Decreto-Lei nº65/2018, de 16 de agosto, Chief Technology Officer - Wai Environmental Solution-AS Norway

Outubro 2018

Wastewater and drinking water treatment by membrane processes: from laboratory to pilot scale

Copyright © Mafalda Tomé Pessoa Lopes, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

A Faculdade de Ciências e Tecnologia e a Universidade Nova de Lisboa têm o direito, perpétuo e sem limites geográficos, de arquivar e publicar esta dissertação através de exemplares impressos reproduzidos em papel ou de forma digital, ou por qualquer outro meio conhecido ou que venha a ser inventado, e de a divulgar através de repositórios científicos e de admitir a sua cópia e distribuição com objetivos educacionais ou de investigação, não comerciais, desde que seja dado crédito ao autor e editor.

As secções desta dissertação já publicadas por editores para os quais foram transferidos direitos de cópia pelos autores, encontram-se devidamente identificadas ao longo da dissertação e são reproduzidos sob permissão dos editores originais e sujeitos às restrições de cópia impostos pelos mesmos

AGRADECIMENTOS

Chegado ao fim desta etapa tão importante, concluo que foi um longo caminho, com altos e baixos, que depende muito do trabalho e inspiração de quem o executa, mas também da força, ajuda e contribuição de um conjunto de pessoas muito importante.

Em primeiro lugar gostaria de agradecer aos meus orientadores, Professor Doutor João Paulo Crespo e Doutor Svetlozar Velizarov, pela oportunidade de realizar o meu trabalho de doutoramento, por todo o vosso apoio, dedicação, partilha de conhecimento, paciência e entusiasmo transmitidos ao longo destes anos. Obrigada Professor João Paulo por me ter dado oportunidade de trabalhar no seu grupo de investigação, pelas oportunidades que me foram dadas nos projetos nacionais e internacionais e pelo apoio que sempre demonstrou. Ao Zarko pela orientação, exigência, rigor, ambição, total disponibilidade e ainda o interesse demonstrado pelo meu trabalho. Aos dois um Muito Obrigada por terem contribuído para o meu crescimento enquanto aluna de doutoramento e cientista.

Quero também agradecer a todos os meus colegas de trabalho, os que estão e os que estiveram: Mafalda Cadima, Inês, Carmo, Sofia, Rita, Joana, Carla Martins, Usman e Jorge. A todos do BPEG, obrigada pela partilha, entreajuda e simpatia. Aos meus colegas de gabinete: Cláudia Galinha e Sylwin, agradeço muito toda a disponibilidade em ouvirem as minhas dúvidas, por todas as discussões, partilha de conhecimento, boa disposição, motivação e apoio que me prestaram durante o trabalho e principalmente pela amizade e preocupação que sempre demonstraram. Muito Obrigada!

À D. Maria José e à D. Palminha, muito obrigada por toda a simpatia e pelo eficiente trabalho de toda a parte administrativa. Ao Professor Vítor Teodoro agradeço a ajuda na fase final da minha tese.

À minha família, mãe, pai, irmão, avó e bié quero agradecer todo o apoio, incentivo, carinho e motivação que me deram durante estes anos. Muito Obrigada a todos!

Por último, mas não menos importante, muito obrigada ao Dinis por estar sempre do meu lado e pelo apoio incondicional.

Aos meus filhos Francisca e Martim

RESUMO

A preocupação com a qualidade da água em todo o mundo, conduziu à melhoria dos processos de tratamento de águas de consumo humano e águas residuais. Nesta tese foram estudados processos de membranas para água de consumo humano e de um efluente industrial em três casos de estudo diferentes. O objetivo destes estudos foi o de avaliar, otimizar e validar os processos propostos para os respetivos casos de estudo. Os estudos realizados integraram uma fase laboratorial seguida de uma fase à escala piloto.

O primeiro caso de estudo contempla a água residual de uma indústria de borracha a qual apresentava um alto valor de carência química de oxigénio (CQO). Neste estudo, foi avaliado o impacto da adaptação do processo existente para tratamento desses efluentes, através da substituição de um evaporador por um processo integrado compreendendo uma unidade de Nanofiltração. Foram considerados dois modos de operação distintos, em descontínuo e em contínuo, de acordo com o caudal de efluente a tratar diariamente.

O segundo caso de estudo aborda o tratamento de águas superficiais para a produção de água potável com elevada qualidade química e microbiológica. O trabalho de investigação centrou-se na validação de um sistema de multi-barreira incorporando unidades de nanofiltração e de fotólise UV, implementado em três localizações diferentes da linha de produção da água.

O terceiro caso de estudo focou-se no processo de tratamento de águas subterrâneas contaminadas com arsénio com o propósito de desenvolver uma solução aplicável em áreas rurais localizadas longe de infraestruturas centralizadas de abastecimento de água potável. Neste estudo foi proposto um processo com utilização de membranas de permuta iónica, integrando a diálise de Donnan com a precipitação do poluente alvo - arsénio. Este trabalho explora a viabilidade de aplicar um processo de membrana de permuta iônica para a remoção de arsénio de correntes de água contendo sulfato, o qual é transportado preferencialmente através da membrana de permuta iónica. Posteriormente, foi feita uma otimização da remoção de arsénio pelo processo previamente proposto usando a metodologia de superfície de resposta (RSM).

Nesta tese foi realizada uma análise sistemática dos três casos de estudo apresentados, a fim de desenvolver o conhecimento necessário para a resolução de poluição de água em casos semelhantes aos estudados.

Palavras-chave: Tratamento de água, Nanofiltração, Membrana de permuta iónica; Diálise de Donnan, Água de consumo humano, Água residual

ABSTRACT

The concern with water quality problems worldwide has led to the improvement of water/wastewater treatment processes. In this PhD project, industrial water and drinking water treatments using membrane processes were investigated in three different case studies. The main aim of these works was the assessment, optimisation and validation of the process's technologies for the respective case studies. These studies included in a laboratory stage followed by a pilot-scale stage.

The first case study contemplates residual water from a rubber industry presenting high chemical oxygen demand (COD). The impact of retrofitting of the existent wastewater treatment process with the replacement of the previously used evaporator with an integrate system (nanofiltration+ evaporator), was evaluated. Two modes of operation were considered, batch and continuous, depending on the daily flowrate of water to be treated in this industry.

The second case study addresses surface water treatment, for production of drinking water with a high chemical and microbiological quality, required by the current legislation. The research was focused on the validation of a multibarrier system incorporating nanofiltration and UV photolysis performed at three different locations of the surface drinking water production line.

The third case study focuses on a novel treatment process dealing with groundwater contaminated by arsenic (in its inorganic arsenate form) with the purpose to be applied in rural areas located far from centralised drinking water supply infrastructures. It has been a challenge worldwide to treat arsenic contaminated drinking water in order to meet the current strict regulation standard for As. In this research, an ion exchange membrane process, integrating Donnan dialysis with precipitation of this target pollutant was proposed. This work explored the feasibility of arsenic removal from water streams containing sulphate, which strongly competes with arsenate and is preferentially transported through strong-base anion-exchange membranes. Subsequently, the optimisation of arsenic removal from drinking water by the process proposed was performed by using a response surface methodology (RSM).

A systematic analysis of the three case studies was carried out and is presented in this thesis in order to provide a deeper insight into the treatment processes studied (theoretical and practical aspects), which makes the proposed solutions also applicable to other water/wastewater treatment cases, facing similar challenges.

Keywords: Water Treatment, Nanofiltration, Ion-Exchange Membrane, Donnan dialysis, Drinking water, Wastewater

Table of Contents

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

List of Figures

List of Tables

List of Abbreviations

BAT	Best available technology
CIP	Cleaning in place
DOMs	Dissolved organic matters
EC	European commission
EfOM	Effluent organic substances
EPA	Environmental Protection Agency
EPAL	Empresa Portuguesa das Águas Livres
FTIR	Fourier-transform infrared spectroscopy
ICP	Inductively coupled plasma
IEX	Ion exchange
IPPC	Integrated pollution prevention and pollution control
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
OPEX	Operational Expenditure
PLCs	Programmable logic controllers
PP	Polypropylene
ppb	parts per billion (x10^9) (=µg/l or µg/kg)
PPCPs	Pharmaceutical and personal-care products
ppm	parts per million (= mg/l or mg/kg)
RO	Reverse Osmosis
RSM	Response surface methodology
SBA	Strong base anion

SEM	Scanning electron microscopy
UF	Ultrafiltration
UNIFEC	United Nations Children’s Fundation
USEPA	United states environmental protection agency
UV	Ultraviolet
VRF	Volume reduction factor
WHO	World Health Organization

List of Variables

A	Cross-sectional area of the membrane, m^2
C_f	Concentration in feed, mg/L or µg/L or ufc/100ml
C_{fin}	Final concentration, mM
C_{in}	Initial concentration, mM
C_m	Concentration in membrane, mM
COD	Chemical oxygen demand, g/L or mg/L
Cond.	Conductivity, µs/cm
C_p	Concentration in permeate, mg/L or µg/L or ufc/100ml
CQO	Carência química de oxigénio, g/L or mg/L
C_r	Concentration in retentate, mg/L or µg/L or ufc/100ml
L or l	Membrane thickness, m
M_{dry_memb}	Dry mass of the membrane piece, g
O&G	Oil and grease, mg|/L
P	Permeability, m^2s^{-1}
P	Pressure
SF	Separation factor
T	Time, h
TMP	Transmembrane pressure, bar
TOC	Total organic carbon, g/L or mg/L
TS/TSS	Total suspended solids, g/cm^2
V_s	Volume of the test solution, L
VS/VSS	Volatile suspended solids, g/cm^2

Chapter

1

Introduction

1.1 Overview

Water resources are being explored and improved by the growing communities and expanding industries at the same time they add more nutrients and more pollutants to water sources. On the other hand, water supplies are limited in quantity and quality. These facts together with increased public demand for high quality water, at reasonable prices, represent a serious challenge to the water industry, which has a compromise with water regulations and the optimisation of the treatment processes for saving time and money. Therefore, it is extremely important to explore advanced and efficient technologies, understanding the removal of the main pollutants, either organic or inorganic.

This thesis describes how an industrial wastewater, a municipal drinking water and a rural drinking water can meet the required water legislation criteria due to the implementation of specific membrane systems for each case.

There are a number of processes available for water treatment. Process selection depends on the initial water characteristics and required water quality (which solutes or particles are to be removed). Additionally, environmental criteria, such as reduction of chemical addition or alternative operation modes, which minimize energy requirements, lead to the process selection. Finally, the treatment cost determines process selection.

Membrane processes play an important role in the water and wastewater treatment either by recovering materials used in industry before they enter in waste streams, by treating wastewater before discharge to surface water bodies or by treating water for potable use. The potential range of application for membrane processes in water and wastewater treatment is wide.

Membrane separation processes cover a broad particle size range, from suspended solids to small organics and mineral salts. The pressure-driven membrane processes are classified as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), depending on the molecular weight cut-off (MWCO) of the respective membranes.

In this PhD project, a pressure-driven membrane process (Nanofiltration) and an ion-exchange membrane process (Donnan dialysis) were used for the respective case studies.

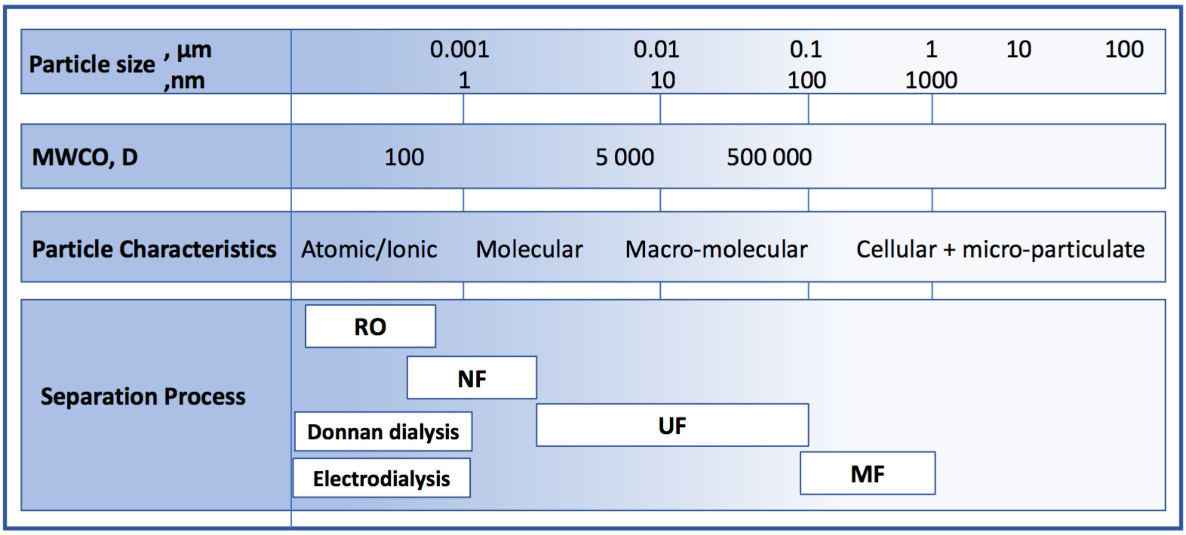

Figure 1-1. Ranges and particle sizes of membrane processes and characteristics of the retained compounds, respectively (adapted from Peter-Varbanets et al.,2009).

Nanofiltration (NF) has been recognized as one of the best technologies in advance wastewater reclamation and in drinking water treatment plants. Its application in water treatment is constantly growing and its popularity stems from its ability to separate divalent salts, high organics and small organic molecules (micro pollutants) to produce high quality water at a more moderate energy consumption when compared with reverse osmosis (RO). In the last decade, NF has been employed combining it with UV photolysis for drinking water treatment for further removal of trace pollutants to satisfy water quality standards (e.g. Molinari et al., 2002, Le-Clech et al., 2006, Patsios et al, 2013).

Donnan dialysis (DD) is a potentially attractive membrane separation process for removing undesirable ionic species from drinking water. The ion exchange membrane used in this process is a selective barrier that carries fixed charge groups, which separates two aqueous phases and allows to exchange counter- ions between them. The process is based on an electrochemical potential difference between the compartments separated by an ion-exchange membrane. This process is of particular interest for drinking water treatment due to its ability to selectively remove target pollutants, while minimizing the risks of secondary pollutions of the treated water. Moreover, it presents the advantages of having low energy requirements and be easy to handle, which make it especially attractive in case of applying it in rural areas. Some potential applications have so far been studied at laboratory scale (Sonoc et al., 2018; Agarwal et al., 2016; Vanoppen et al., 2015; Ricardo et al., 2012; Matos et al., 2006).

1.2 Motivation and Research objectives

In view of the water treatment development, membrane processes have been recognized as the most advanced options and are increasingly implemented in water and wastewater treatment plants (Piadeh et al., 2018; Thomas at al., 2018; Garcia-Vaquero et al., 2014; Hilal et al., 2015). The growing interest in the use of membrane technology started in the mid 80´s, with the production of membranes with enhanced chemical, thermal and mechanical properties or better permeability and selectivity, while the membrane costs decreased. Moreover, membrane technology presents several major advantages: they do not need or require a minimal addition of chemical additives (minimal environmental footprint), are easy to scale up and easy to retrofit to existing facilities, standing alone or combined with other treatment processes.

In the last 30 years, membranes processes have been developed from a laboratory tool to an industrial processes levels with technical and commercial relevance. Laboratory to pilot scale studies are of utmost importance for the successful and reliable implementation of the novel processing schemes.

In these studies, performed in the frame of this PhD project, there was a primary concern on performing laboratory scale studies followed by pilot scale testing, where the concept was first proved, and the system then validated. The three case studies investigated in this PhD work are describe below:

Case study 1 – Rubber industry wastewater treatment

Wastewater treatment in the rubber parts producing industry (tubes for automotive industries, tyres, flasks used as cosmetics containers, etc.) is rather challenging. The production process which implies extrusion and/or injection and post-washing operations generates a huge amount of wastewaters contaminated with demoulding agents (such as Getren R 4510, which is a polyether and non-ionic surfactant, or Struktol VP 6015, which is a water soluble polymer). Therefore, the generated wastewater presents a high chemical oxygen demand (COD >1000 mg/L) and low biodegradability of its main organic constituents.

The problem described is shared by many rubber companies across Europe and the World. Cikautxo is a major rubber parts manufacturer in the Basque Country in Spain, facing this problem. This industry used boilers, as a thermal process, followed by evaporators to treat the wastewater. However, this technology was not meeting the environmental requirements and requires an extremely high energy expenditure.

The factory, where the respective case study was investigated, consumes daily 160 cubic meters of water and produces approximately 70 m^3/d of wastewater from the rubber manufacturing process, including molding, autoclaving and demolding. Moreover, an energy cost of approximately €4.2/m^3 of treated wastewater is nearly prohibitive.

Main objectives

The main objective in this study was to optimise and validate an integrated approach consisting on a nanofiltration and an evaporation process for treatment of the rubber industry wastewater. It was investigated the ability of the membrane process to retain COD and reduce the color and conductivity of the wastewater in order to obtain re-usable water, minimising water disposal volumes and reducing energy consumption and costs. The laboratory studies, followed by a pilot scale study, allowed to develop an integrated process and to evaluate the impact of retrofitting the current wastewater treatment process. Furthermore, two operation modes were evaluated, batch and continuous, depending on the flow rate to be treated daily.

Case Study 2- Drinking water production

The production of drinking water requires (or will required soon) the removal of micro pollutants and control of quality parameters including microbiological characteristics, chemical compounds contents, as well as other indicating parameters (e.g. total organic carbon, turbidity, colour, …). Moreover, several emerging micropollutants in water sources (e.g. pesticides) that are used in several industries, such as agriculture or wood treatment industry, are currently being studied for their potential adverse effects (toxic action), anticipating implementation of more strict water quality regulations.

Conventional water treatment often includes screening, coagulation/flocculation, sedimentation, sand filtration, and final disinfection (chlorination or chloramination). These treating systems may not be sufficient to retain some micro pollutants of concern. Additionally, the use of high quantities of chlorine may induce the formation of disinfection by-products, which are harmful to human health.

Main Objectives

Nanofiltration and UV photolysis are extremely promising technologies to effectively remove a wide range of micro pollutants from water. Therefore, a pilot scale system combining nanofiltration and UV photolysis was proposed for a surface water treatment plant at the major Portuguese water provider EPAL, which supplies water to around 3 million people in 35 districts corresponding to a total supplied area of 7090 km2. The water treatment plant where this study was accomplished is located in Vale da Pedra and treats surface water collected from the Tagus River in Valada Tejo.

This study investigated a multi-barrier system approach with the objective to produce high-quality drinking water in terms of chemical composition and microbial inactivation. The integrated proposed system (NF + UV photolysis) was operated at three different locations of the surface drinking water production line (after screening, after sedimentation and after sand filtration) in order to better evaluate the impact of the new treatment system when retrofitting a water production plant.

Case study 3 – Arsenic contaminated water

Arsenic occurrence in natural water sources poses a serious health risk to millions of people worldwide. Arsenic is one of the most toxic naturally occurring elements present in different locations of the world and its efficient removal from drinking water supplies is still challenging (UNIFEC, 2013; UNIFEC, 2008). The adverse impact of groundwater contaminated with arsenic on human life is widely reported. South East Asian countries are the most affected with arsenic in groundwater, in particular Bangladesh. Therefore, the World Health Organization (WHO), the European Commission (EC) and the United Stated Environmental Protection Agency (USEPA) reduce the maximum contaminant level (MCL) from 50 μg/L to 10 μg/L in January 2006.

Various methods for As removal from water have been reported so far. However, each of them presents inherent limitations (Ungureanu et al., 2015). Therefore, there is a need for the development and validation of an easy to operate process solution, which could be less energy demanding and easy to adopt in rural regions located far from centralised drinking water treatment infrastructures.

Main objectives

This case study evaluates the feasibility of employing an ion exchange membrane process integrating Donnan dialysis with precipitation of the target ionic pollutant As for a decentralised water treatment system.

The first main objective addresses the viability of applying an ion-exchange membrane process for arsenic removal from sulphate containing water streams, due to the strong competition between arsenate and sulphate transport through standard grade strong-base anion-exchange membranes. Afterwards, it was aimed to improve the process proposed, in order to maintain the pH of the treated water within the recommended drinking water range of 6-9, and to develop a tool able to optimise/select the most appropriate operating condition, according with the water characteristics and the desirable arsenic removal

1.3 Technical/Research questions and flow chart

1.3.1 Research questions

The research questions that motivated the investigation of the selected three case studies are the following:

1. **Case study – Rubber industry wastewater treatment**
    - Can an integrated approach system achieve the desirable COD removal in order to meet the environmental requirements?
    - Can a nanofiltration process improve the actual wastewater treatment plant operation with minimal energy input?
    - Is it possible to identify the major contributors to fouling by membrane autopsy?
    - Can the nanofiltration permeated effluent be reused as a boiler feed water to the boiler (see process scheme ahead)?
2. **Case Study- Drinking water production**
    - Is the multi-barrier system approach, including nanofiltration and UV photolysis, able to produce high quality drinking water in terms of chemical composition and microbial inactivation?
    - In which location of the drinking water production line should integrated system be included, in order to improve the treatment performance?
    - How to perform an efficient membrane cleaning for this particular application?
    - What should be the frequency of the clean-in-place (CIP) procedure?
3. **Case study – Arsenic contaminated water**
    - Could the WHO standards for drinking water be achieved using the ion-exchange membrane process proposed?
    - Can the treated water quality in terms of arsenic concentration be predicted if the influent water quality (As concentration) and operating conditions are known?

1.3.2 Flow Chart of the research

The methodology of the three case studies are illustrated in the flow chart, Figure 1-2.

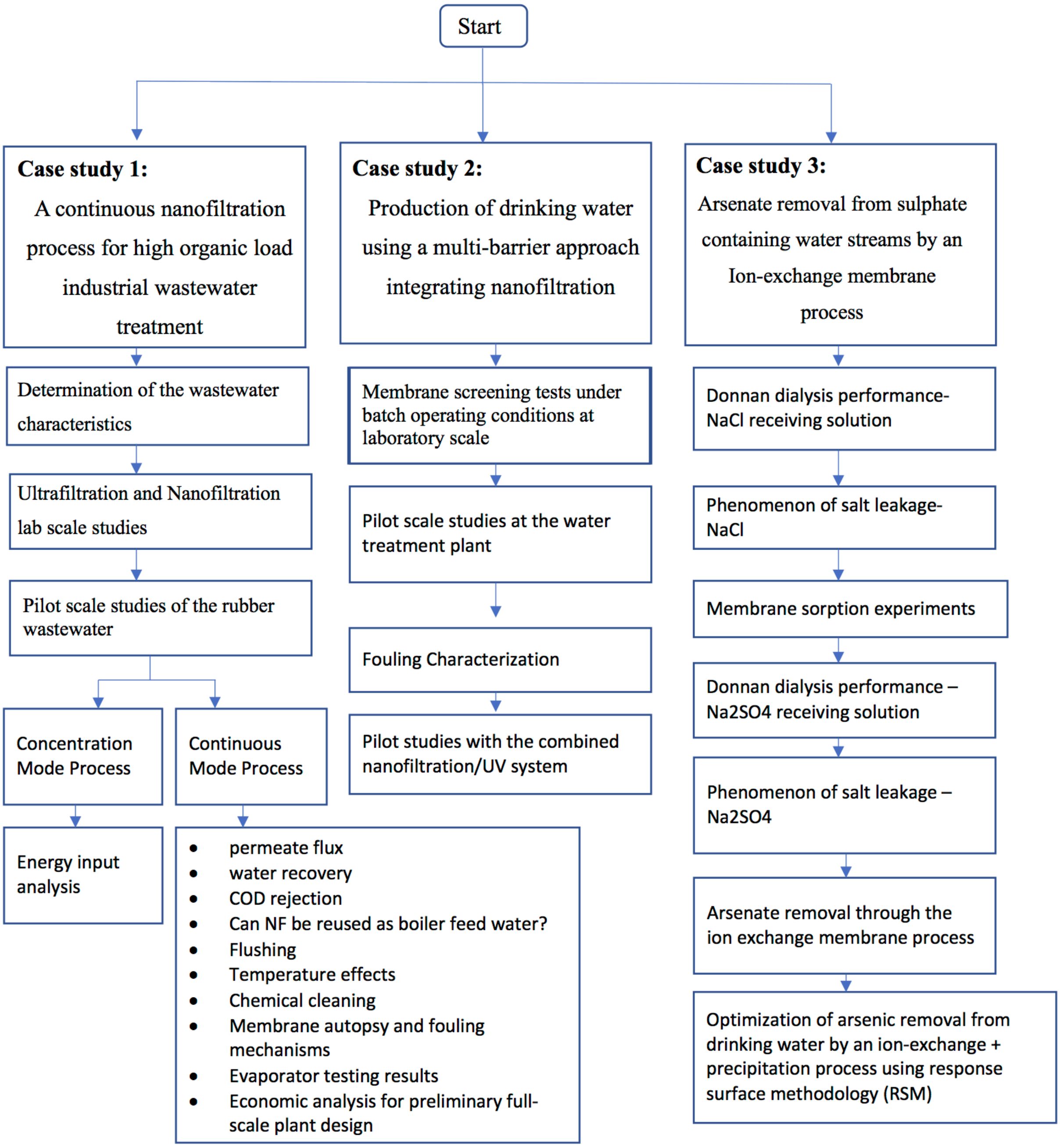

Figure 1-2 Flow chart of research methodology

1.4 Thesis outline

Chapter 1 presents an introduction on the thesis scope and describes the objectives, flow chart, research questions and thesis outline of this PhD research project.

Chapter 2 includes a brief state of the knowledge.

Chapter 3 and 4 present the approach and solution for the rubber plant wastewater treatment (Case study 1).

Chapter 5, 6 and 7 address the treatment of drinking water using membrane systems. In chapter 5 a pilot scale study of a multi-barrier approach with nanofiltration for drinking water production is presented (Case study 2). Chapters, 6 and 7 focus on arsenate removal using a newly proposed integrated ion-exchange membrane process (Case study 3).

Chapter 7 describe a mathematical model for the prediction of arsenic concentration in the treated water using the proposed ion exchange membrane reactor and a mathematical decision tool which simplifies the decision of process operating conditions for the specific characteristics of the income water.

Each chapter (3-7) includes a summary of the work developed, a specific introduction, a description of the materials and methods used, a discussion of the results obtained, and the main conclusions drawn.

Chapter 8 summarizes the main conclusions obtained and suggestions for future reuse.

1.5 References

Garcia-Vaquero, N., Lee, E., Castaneda, R.J., et al., 2014. Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility. Desalination. 347, 94-102.

Hilal, N., Kochkodan, V., Abdulgader, H.A., Mandale, S. et al, 2015. A combined ion-exchange-nanofiltration process for water desalination: II. Pilot scale studies. Desalination. 363, 58-63.

Le-Clech, P., Lee, E.K., Chen, V., 2006. Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters. Water Research., 40, 323-330

Matos, C. T., Fortunato, R., Velizarov, S., Reis, M.A.M., Crespo, J.G., 2006. Simultaneous removal of perchlorate and nitrate from drinking water using the ion Exchange membrane bioreactor concept. Water Research. 40, 231-240.

Molinari, R., Palmisano, L., Drioli E., Schiavello, M., 2002. Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. Journal Membrane Science, 206, 399415.

Patsios, S.I., Sarasidis V.C., Karabelas, A.J.,2013. A hybrid photocatalysis-ultrafiltration continuous process for humic acids degradation. Separation and Purification Technology., 104, 333-341.

Peter-Varbanets, M., Zurbrugg, C., Swartz, C., Pronk, W., 2009. Decentralized systems for potable water and the potential of membrane technology. Water Research. 43, 245-265.

Piadeh, F., Alavi-moghanddam, M. R., Mardan, S., 2018. Assessment of sustainable of a hybrid of advances treatment technologies for recycling industrial wastewater in developing countries: Case study of Iranian industrial parks. Journal of Cleaner Production, 170, 1136-1150.

Ricardo, A.R., Carvalho, G., Velizarov, S., Crespo, J.G., Reis, M.A.M., 2012. Kinetics of nitrate and perchlorate removal and biofilm stratification in na ion Exchange membrane bioreactor. Water Research. 46,4556-4568.

Thomas, M., Zdewbik, D., Bialecka, B., 2018. Using sodium trithiocarbonate to precipitate heavy metals from industrial wastewater- from the laboratory to industrial scale. Polish Journal Environmental Studies, 27, 1753- 1763.

Ungureanu, G., Santos, S., Boaventura R., Botelho C., 2015. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. Journal of Environmental Management, 151, 326-342.

Chapter

2

State of the art

This chapter provides a current state of the knowledge about wastewater, drinking water and arsenic contaminated water treatment: regulation, quality issues and membrane treatments are reviewed for the three case studies considered. A discussion on the effectiveness of the proposed membrane water technologies is also provided for each case study. The concepts and basic principles related with the membrane processes used in this work: - Nanofiltration and Donnan dialysis- are also presented.

2.1 Wastewater Treatment

2.1.1 Wastewater

Water pollution is severely increasing due to release of untreated wastewater into water bodies and land as a consequence of the intensive development of agriculture and the industry. The practice of discharge of large volumes of wastewater from processing factories to soil and watercourses poses high danger to the environment and man (Metcalf & Eddy, 1991; Owamah et al, 2014; Zhao, M. et al, 2016; Thomas, M., et al., 2018).

Industrial activities generate wastewaters that vary significantly in pollution characteristics, and each sector of industry produces its own combination of pollutants. Industrial wastewaters may contain heavy metals, various organic and inorganic compounds, nutrients, colouring matters, pesticides, endocrine disruptive compounds, and some other toxic materials (Samaci et al., 2018). The production processes commonly generate large amounts of wastes with high chemical oxygen demand (COD) and low biodegradability (Metcalf&Eddy, 1991; Lyonnaise des Eaux, 1996). Moreover, untreated wastewater usually contains numerous pathogenic or disease-causing microorganisms and also nutrients that can stimulate the growth of aquatic plants.

Wastewater pollution from rubber processing industries has increased in Africa and Asia as a result of the growing number of rubber producing factories due to the presence of virgin forests with a large number of mature rubber trees. Rubber producing factories are one of the agro-industries that produce large quantities of wastewater. In Nigeria most of the rubber industries discharge their wastes into rivers/water streams because they are rarely equipped with adequate treatment facilities due to the high cost of conventional treatment technologies (Owamah et al, 2014).

In addition, wastewater treatment for reuse in the process is also an important strategy for conserving water resources, especially in areas suffering from water scarcity. Water stress have been reported in 40% of the world population (estimation of 80 countries) and about 30 of these countries are suffering water scarcity in most part or the year (Owamah et al, 2014; Piadeh et al., 2018).

As a result, industrial effluents should be efficiently treated to protect the environment, aquatic life, humans from intoxication and a prevent water shortage. (Samaci et al., 2018). Therefore, it is utmost important an economical wastewater treatment, and appropriate disposal, that allows compliance with legal discharge limits in municipal water bodies and wastewater treatment plants (Wadekar et al., 2017; Rahimpor et al, 2014; Zhao et al., 2016).

2.1.2 Pressure driven membrane process

Successful applications of membrane for the treatment of industrial wastewater can be found in literature (Zheng et al., 2015, Zirehpour et al., 2016). Integrated systems of two, or more, unit operations involving membranes, have been widely used in water treatment to produce the desired water quality (Piadeh et al., 2018; Racar et al., 2017; Ollis, 2003; Liu et al,2016; Sert et al, 2016; Yen et al., 2017). In fact, membrane technologies, and more specifically Nanofiltration, provide an important solution in environmental fields such as pollution reduction and water reuse, and recycling of valuable components from waste streams.

2.1.2.1 Nanofiltration

Nanofiltration (NF) is a pressure driven membrane process which is somewhere between reverse osmosis and ultrafiltration. Some authors refer to NF as charged ultrafiltration (UF), softening, or as low-pressure reverse osmosis (RO). The MWCO of NF membranes is within the 100 to 1000 Da range with solute size < 1 nm ("pore" size < 2 nm in diameter). The range of operating pressures is between RO and UF (Mulder et al., 2003; Afonso et al., 2005; Schafer et al., 2001).

The membrane separation mechanisms are classified into two categories – molecular sieving and solution-diffusion. In physical molecular sieving (steric hindrance) the feed components are separated by pressure-driven flow through small pores, with fixed position and size, and the separation occurs due the differences between their sizes. In nanofiltration this rejection mechanism is dominant for colloids and large molecules. In contrast, in the solution-diffusion mechanism, the chemistry of solute and membrane become increasingly important to permeants that are dissolved in the membrane material and then diffuse through the membrane (Van der Bruggen and Geens, 2008).

Nanofiltration has been pointed out has a good choice for wastewater treatment because of the high reductions of COD, conductivity and color that can be obtained (Samaci et al., 2018; Racar et al, 2017; Wadekar et al, 2017). During membrane treatment of industrial wastewater, two flows are generated: (i) a filtered stream (permeate), which can also be used as a process in industrial processes and (ii) a concentrate stream containing high amounts of COD that must be disposed of.

Nevertheless, untreated wastewaters cannot be used directly for membrane processes because they may have a major influence on the performance of nanofiltration and reverse osmosis processes. Therefore, it is usually necessary to carry out a pre-treatment (i.e. pre-filter) in order to avoid membrane fouling and deterioration.

2.1.2.2 Membrane challenges

There are still some major challenges of the pressure driven membranes that are imperative to overcome which are: the flux decline during the filtration time, selectivity loss and low membrane lifetime (when regular chemical cleaning is performed). These limitations are mainly due to membrane fouling (worsening as a function of time) and polarization of concentration (remaining constant once established) which cause extra resistances and thus slow down solvent transport across the membrane. The reduction can be as severe as 99% of the initial flux value. Therefore, polarization of concentration and fouling are main concerns for membrane processes, which have been widely studied but still remain without a generalized solution. Several reviews can be found in the literature focused on polarization of concentration, fouling and *in-situ* monitoring techniques (Shetty et al., 2003, Chawla et al., 2017, Chon et al., 2016).

Fouling

Fouling refers to the accumulation of retained molecules or particles in the pores of the membrane or at the membrane surface. The retained species can build up a gel or cake layer or can block pores. Fouling potential of the retained species is a complex function of exposure time, temperature, pH, ionic strength and concentration of the various chemical species in solution interacting with the membrane material or among themselves. Fouling leads to a reduced productivity and deterioration of the product water quality, increasing energy demand and maintenance costs, membrane degradation, and reduced membrane lifetime (Mulder, 2003).

Polarization of Concentration

Polarization of concentration occurs when there is a high concentration of the dissolved material rejected by the membrane. Contrasting with the situation of fouling, the material does not deposit on the membrane surface or inside the membrane pores but accumulates in the proximity to the membrane surface (Winston et al., 1992). The consequences of polarization of concentration are difficult to predict. However, they may comprise:

- solute *retention* may be reduced:

Since a higher solute concentration is built up near the membrane surface, an increasing amount of solute may be transported through the membrane either in the form of a diffusive flow. This is generally the case with low molecular weight solutes such as salts.

- solute *retention may become higher*

This behavior may be induced when larger molecules or particles are being retained forming a kind of a “dynamic membrane”, creating an additional resistance for solute transport. This leads to a higher retention of lower molecular weight solutes.

- *flux will be reduced*

If polarization of concentration effects become extensive, solutes at the membrane surface can reach a critical concentration (i.e. solubility limit), beyond which they form a cake/gel layer which fouls the membrane surface (fouling). Under such conditions, fouling increase the resistance to permeate flow throughout the membrane.

To avoid polarization of concentration, improved mass transfer conditions should be implemented in the feed compartment. Relevant parameters are: feed flow velocity (modified through the hydraulic diameter of the feed cell or the pump characteristics), solute diffusion (i.e., changed via the increase of the feed temperature), feed viscosity (idem) and operating conditions with impact on the fluid dynamics (introduction of turbulence promoters, use of pulsating flows to break the boundary layer and increased Reynolds numbers).

2.2 Drinking water Treatment

2.2.1 Drinking water

The production of high quality drinking water requires the removal of micropollutants, including microbiological and chemical compounds, that are currently being studied for their potential adverse effects (Chew et al., 2017; Kukucka et al., 2016; Chon et al., 2013). The risks of microbiological contamination, long-term carcinogenic effects due to disinfection by-products and the so called “new emerging” contaminants are of high concern due to their environmental fate and health impact, which are not well-known (Synder et al, 2003; Taucer-Kapteijn et al., 2016; Papageorgiou et al., 2016). A significant amount of studies have been developed by water providers and researchers, a complex task which is further complicated by the wide diversity of compounds (e.g. pesticides) spread in the environment.

The growth of the world population coupled with urbanization, the increasing exploitation of natural resources, industrial development and pollution resulted in a rapidly increasing demand for high water quality (Ahkola et al., 2017). Furthermore, it has been reported that there is a lack of access to clean and safe drinking water for more than 1.2 billion people in the world (Hilal et al., 2015). According to Owamah et al., 2014 contaminated drinking water and poor sanitation were reported to rank third in the list of the 20 leading health risk factors in developing nations. Problems with access to safe water are expected to grow worse in the coming decades. The UN-Water Global reports that demand for water (in terms of funding) tends to increase about 55% by 2050 since there is a clear evidence that water aquifers are exhausting as a consequence of their over-exploitation (Gando-Ferreira et al., 2017).

Therefore, a great effort has been made in recent years to successfully reduce the presence of persistent organic pollutants (POPs), microbial pathogens, heavy metals occurrence and emerging trace organic contaminants such as pharmaceuticals (Ph´s), personal care products (PCPs), endocrine disrupting chemicals (EDCs) (Chon et al., 2013). These persistent contaminants are driving the scientific community to investigate new solutions to decrease or even eliminate contaminants occurrence in drinking water (Jones et al., 2005; Synder et al, 2003).

Although these compounds usually appear in the aquatic environment at very low concentrations (parts per billion or parts per trillion), they do so consistently due to their frequent use by consumers (Garcia-Vaquero et al., 2014). Consequently, these contaminants are present in water/wastewater treatment plants and they are found to be resilient to most treatment processes (Petrovic et al., 2003).

Natural organic matter or NOM, is one of the most common contaminants present in all water resources with a wide range of molecular weights (MW) and functional groups. Effective removal of NOM has been a challenge for water utilities. Removing NOM, especially humic acids (HA) and fulvic acids (FA) is important because of their contribution to undesirable odor, taste and color (Winter et al., 2017). The presence of elevated concentrations of NOM in drinking water is not harmful to humans, nevertheless it is responsible for bacteria re-growth and it can interact with chlorine-based disinfectants during water disinfection to produce disinfection-by-products (DPBs) such as, carcinogenic trihalomethanes (THMs) (Kukucka et al., 2016; Chang et al, 2009). Long-term adverse health effects of DBPs are widely reported in the literature and have been linked to cancers and adverse reproductive outcomes. However, the amount of these substances in drinking water is strictly regulated. Because of the complex nature of NOM, surrogate parameters such as dissolved organic carbon (DOC), UV254, and specific UV absorbance at 254 nm (SUVA254) are often used as quality parameters.

The widespread use of pesticides has resulted in the presence of their residues in various ecosystems. Traces of these products are commonly detected in surface water and in some cases in groundwater. The detection of pesticides such as atrazine, isoproturon, diuron, alachor and chlorfencinphos in drinking water sources is of great concern due to their negative impact in the environment, given their toxicity, persistence, and potential bioaccumulation. Even at very low concentrations (pg/L to ng/L), pesticide residues have been characterised in toxicological and epidemiological studies with potential health risks, including cancer, genetic malformations, neurodevelopment disorders and damage of the immune system (Plakas et al., 2012). According to the Drinking Water Directive (98/83/EC) (Drinking Water Directive 98/83/EC), the quality of water intended for human consumption has a limit of 0.1 µg/L for a single active ingredient of pesticides, and 0.5 µg/L for the sum of all individual active ingredients detected, regardless of hazard or risk. On the other hand, the residue limits and guideline levels set by the World Health Organization (WHO) or the U.S. Environmental Protection Agency (USEPA) depend on the toxicity of the active substances and are determined using a risk-based assessment.

The most conventional methods for drinking water treatment, still widely employed, comprises coagulation-flocculation, sedimentation, sand filtration and disinfection. However, these common methods may, under specific circumstances, be ineffective for producing potable water.

Coagulation processes mainly remove the NOM associated with suspended particles although the removal efficiency is variable due to the physical and chemical characteristics of the water and the operating conditions. Coagulation processes have a high efficiency for the removal of the hydrophobic fraction of NOM when the molecular weight of NOM is high. However, the major contributions to the formation of disinfection-by-products, are related with the presence of low molecular weight NOM compounds, such as resorcinol, phloroglucinol and p-hydroxybenzoic acid, which are not easily removed by conventional water treatments, such as coagulation (Chang et al, 2009).

There are more advanced final treatment steps, usually involving oxidation by H_2O_2 or O_3 and granular activated carbon (GAC filtration), which are generally considered to be effective, although significant problems still arise, mainly related to saturation of activated carbon, and to toxic chemical by-product, which may develop in the granular activated carbon filters under specific conditions (Chang et al., 2017; Plakas et al., 2012).

2.2.2 Pressure driven membrane process

Several studies have shown that membrane processes are effective to remove contaminants (depending on the membrane) such as bacteria, viruses, particles, dissolved organics and salts by physical and/or chemical retention, when the water is forced with an applied pressure through the membrane. The use of membrane processes is growing fast in the domain of water treatment and this growth is closely related with the progressive decreasing cost of membrane systems and increasingly stringent drinking water quality regulations. Additionally, membrane processes require a small footprint compared to conventional treatments, and a potential for reduction of chemicals usage and very low maintenance requirements. Moreover, since the mid 80´s, developments in membrane technology have resulted in a variety of advancements, which have included enhancement of salt rejection capability, chemical stability, reduction of pressure requirements and, more recently, the ability for the removal of disinfection by-product precursors (Fane et al, 2011; US EPA 2005).

Chang H. et al, 2017 reported that an outbreak of cryptosporidiosis in Milwaukee (Wisconsin, USA) in 1993 and consequent waterborne diseases promoted the rapid development of membrane technology (as an emerging technology) in drinking water treatment plants. Membrane processes demonstrate to effectively remove aquatic substances such as particulate material, pathogens (e.g., Giardia cysts and Cryptosporidium oocysts), and viruses. Taking these advances and improvements in membrane technology, it has been suggested to replace the conventional treatment units, which are less effective for removing trace contaminants and meet the standards of WHO (WHO Guidelines, 2011), by membrane processes.

The type of membrane process and membrane to select are strongly related with the type of pollutants to be removed from the drinking water supply. Important aspects have to be considered when choosing an appropriate membrane: the membrane material (polymer composition) which determines the type of interaction that will be established with the solutes in solution, the surface charge and the degree of ionic species rejection, the molecular weight cut-off (MWCO), indicating the molecular weight of a hypothetical non-charged solute that is 90% rejected (expressed in Dalton), and the membrane porosity.

The significance of each parameter for the removal of micropollutants is directly related to the particular solute properties (molecular weight, molecular size, acid dissociation constant-pKa and hydrophobicity/hydrophilicity- logKow), which determine the strength of the physicochemical interactions between the micropollutants and the membrane.

2.2.2.1 Nanofiltration

Nanofiltration (NF) has been recognized as the best option for the removal of micropollutants for drinking water production (Plakas et al., 2012; Kukucka et al., 2016). The distinct features of nanofiltration membranes are: adequate softening of water (rejection of divalent and multivalent ions) without significant changes in the water salinity (usually relatively low rejection of sodium chloride), the rejection of uncharged dissolved organic compounds, and the possibility to achieve high specific water fluxes at relatively low operating pressures.

Nanofiltration allows for the production of clean and safe-drinking water and is now the second-largest application of membrane processes with approximately 150 plants with a total capacity of 600,000 m^3/day (Lyonnaise des Eux, 1996; Kukucka et al., 2016).

Nanofiltration membranes are capable of achieving high removals of natural organic matter (NOM) and disinfection by-products (DBP) precursors, e.g. pesticides, and several other primary and secondary (e.g. hardness) contaminants from water supplies with a similar efficiency as Reverse Osmosis (RO), with a high recovery and with lower energy consumption and lower costs.

NOM (e.g. polysaccharides and humic acids (HA)) is highly retained by NF/RO membranes mostly due to size exclusion, charge repulsion, and hydrophobic interactions. Furthermore, NOM is the main cause of membrane organic fouling, which reduces the system performance as a consequence of the deposition of suspended and dissolved organic substances onto the membrane surface and within its pores (Imbrogno et al., 2018).

A large number of herbicides, insecticides, fungicides and pesticides have a molecular weight higher than 200 Da and sizes in a range close to 1 nm, that makes RO and NF the most appropriate pressure-driven membrane processes for the removal of pesticides from contaminated water sources (Plakas et al., 2012). Numerous commercially available NF/RO membranes have been used, at laboratory and industrial scale, in the research effort for removing/eliminating pesticides residues from aquatic matrices (Devitt et al., 1998; Boussahel et al., 2000; Agbekodo et al., 1996, Zhang et al., 2004; Plakas et al., 2009; Berg et al., 1997).

The growing interest on hybrid processes is derived by the need for overall process optimization and/or cost reduction. Nanofiltration has been employed combined with conventional activated sludge processes or membrane bioreactors (MBR) for further removal of trace pollutants, aiming to satisfy wastewater reuse standards. Additionally, this advanced treatment technique is being used to reject endocrine disrupting chemicals, pharmaceutical and personal-care products (PPCPs) and disinfection by-product precursors from drinking water. Accordingly, the effluent organic substances (EfOM) from activated sludge processes and dissolved organic matters (DOMs) in drinking water resources are the major contaminants to be removed, and their concentrations, compositions and properties affect nanofiltration membrane flux and biofouling behavior significantly (Shang W. et al., 2018).

Nanofiltration water treatment: full-scale application

The Méry-sur-Oise plant for drinking water production, in the northern part of Paris (France), is an outstanding full-scale application example of nanofiltration water treatment for the removal of pesticides and other naturally occurring organic materials, since 1999 (Plakas et al., 2012, Cyna et al., 2002). Moreover, it presents relatively small operating pressures (with an energy consumption 30-40% lower than the typical RO process) and reduced cost of materials used to construct the treatment plant, thereby reducing the investment costs. Several other high capacity drinking water plants employing nanofiltration are operating in Florida, The Netherlands, Spain, England, and France (Thorsen and Flogstad, 2006).

2.2.2.2 Membrane challenges

Fouling

Fouling presents the major challenge and impediment for full implementation of NF technology in municipal drinking water production due to the decrease of water quality and the effect on operational lifetime of membranes (Imbrogno et al., 2018). The number of scientific publications involving membrane fouling, cleaning and backwash in the water industry has been growing rapidly (Chon et al., 2013; Chang et al., 2017; Imbrogno et al., 2018; Winter et al., 2017; Musbah et al., 2018; Vatankhah et al., 2018).

Major foulants found when treating water sources, comprise microorganisms, natural organic matter and inorganic elements, which interact with the membrane surface and attach to it either reversibly or irreversibly (in other words, material is retained at the membrane surface or inside the membrane pores). Several studies have focused on identifying the causes and mechanisms of colloidal, organic, and biological fouling of membranes (Chon et al., 2016; Winter et al., 2017; Chawla et al., 2017).

NOM is generally considered to be a main contributor to membrane fouling in drinking water treatment applications. The extent of fouling is not necessarily proportional to the total amount of NOM retained but it is rather governed by the retention of specific NOM fractions: they can be hydrophobic or hydrophilic and comprise 40% and 25-40% of the NOM in surface water, respectively. The NOM that has been reported to be mainly relevant to membrane fouling are biopolymers and humic substances, which are mainly of aquatic and terrestrial origin.

However, there are some solutions to cope with fouling such as: appropriate pre-treatment of the feed (adjustment of pH and T, the use of additives, adsorption, pre-filtration); careful selection of the membrane, with low hydrophobicity and the presence of charged or functional groups with specific interactions at the membrane surface; lowering the trans-membrane pressure, in order to better control the balance of forces acting at the membrane surface; and the use of turbulence promotes and backwashing.

Backwashing results in the loosening or detachment of foulants that were deposited on the membrane surface or pores. Backwashing is typically performed every fixed interval, during which the flow direction inside the membrane is reversed for a short period of time. This procedure is used to remove most of the suspended solids layer that has built-up on the feed side of the nanofiltration membrane.

If prevention is insufficient, it should be performed an appropriate chemical cleaning procedure. The concentration used, and the necessary cleaning times are of utmost important for membrane durability. Commonly used chemicals are: acids and bases, enzymes (proteases, amylases, …), detergents, complexing agents (EDTA, polyacrylates, …), disinfectants (H_2O_2, NaOCl, …) and steam sterilization. The procedure of cleaning must take into account the membrane material, as well as the module housings and sealing, which have to be resistant to cleaning agents applied.

2.3 Arsenic contaminated groundwater Treatment

2.3.1 Arsenic

Arsenic is a notorious poison and is recognized to be one of the world´s greatest environmental hazards. The WHO classified this element in Group 1, as a human carcinogen (WHO, 2011). Arsenic is not detected by optical observation and does not affect the taste or smell of the water, unless its concentration is extremely high. Human exposure to this toxic element is mainly through the consumption of drinking water contaminated with arsenic.

Regular exposure to arsenic causes a variety of health problems in humans, including diabetes, hypertension, neurological abnormalities, arteriosclerosis, renal effects, cardiovascular dysfunction and various forms of cancer (e.g. skin, lung and bladder) (Siddiqui et al., 2017; Mondal et al., 2013).

Arsenic (As) is a metalloid element widely distributed throughout the Earth´s crust and ranks 20th among most abundant elements. As has atomic number 33 (Group 15 of the periodic table along with nitrogen, phosphorus, antimony and bismuth), atomic mass 74.92 amu and density 5.72 $g.cm^{-3}$. The distribution of arsenic in the environment is through air, water, soil and sediments. It can be found in inorganic or organic forms; however, arsenic compounds are not usually in the groundwater system (unless for water with a marked impact of industrial pollution) (Henke, 2009).

It has four oxidation states: As(V), As(III), As(0) and As(-III). In groundwater, As commonly exists as an oxyanion of the inorganic form of arsenite [As(III)] and arsenate [As(V)] and their relative distribution is influenced by the pH and redox condition. Both inorganic and organic As(III) forms tend to be more toxic to humans than the As(V) forms. While As(V) is predominant in oxic groundwater environment and the major forms are H_3AsO_4, $H_2AsO_4^{1-}$, $HAsO_4^{2-}$ and AsO_4^{3-}, As(III) is more dominant in anoxic environments with H_3AsO_3 and H_2AsO^{3-} being the common species.

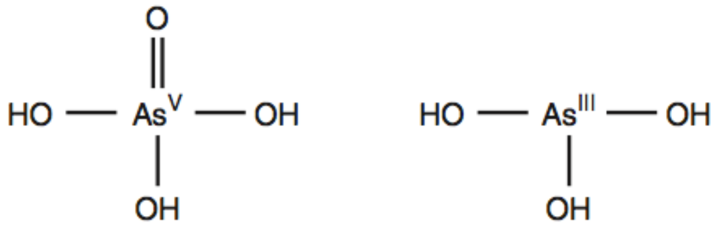

Figure 2-1. Structure of inorganic species – arsenate – As(V) and arsenite – As(III) (Source: Ravenscroft et al., 2009)

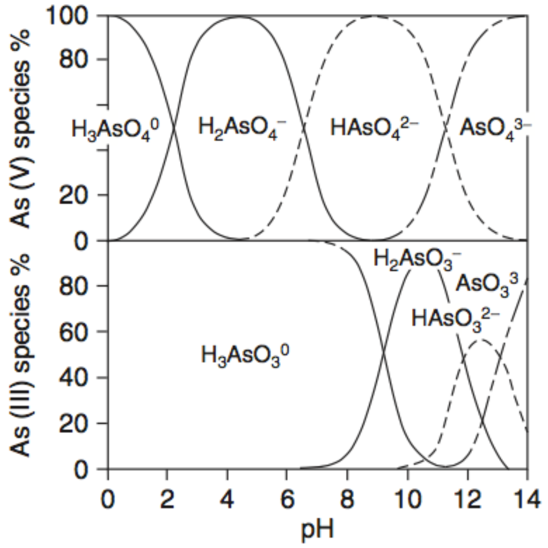

Figure 2-2. Inorganic arsenic species in water. The figure shows the distribution of As(V) and As(III) species as a function of pH at an ionic strength of 0.04 M (Source: Meng et al., 2000).

Under reducing conditions, As (III) is thermodynamically stable and exists as H_3AsO_3 (or $HAsO_2$) at pH below 9.2. In the pH range 4-8 and under an oxidizing environment, arsenic mainly exits in the +5 (As[V]) state in the form of deprotonated oxyanions, namely, $H_2AsO_4^-$ and $HAsO_4{}^{2-}$, which makies arsenate the ubiquitous species in surface waters (Smedley and Kinniburgh, 2002).

2.3.2 Regulation

Removal of arsenic from contaminated water is gaining attention due to the increasingly stringent Maximum Contamination Level (MCL) of arsenic in water, introduced by

(WHO,2011; USEPA,2005), the European Union, and many other countries. An extensive research has been carried out with the specific aim to develop cost-effective arsenic removal techniques (Jadhav et al., 2015).

The objectives of water treatment are determined primarily by national drinking water standards. In recent years, the European Union, the USA and other countries have lowered their arsenic standards from 50 to 10 ppb As, whereas most As affected countries continue to use the value of 50 ppb. The literature should be read with caution because many reports from South Asia report effluent As concentrations of a few tens of ppb as a success, whereas in North America and Europe this is the starting point for arsenic removal.

Some methods described in the literature may effectively reduce As concentrations to <50 ppb but, in many cases, not to <10 ppb As.

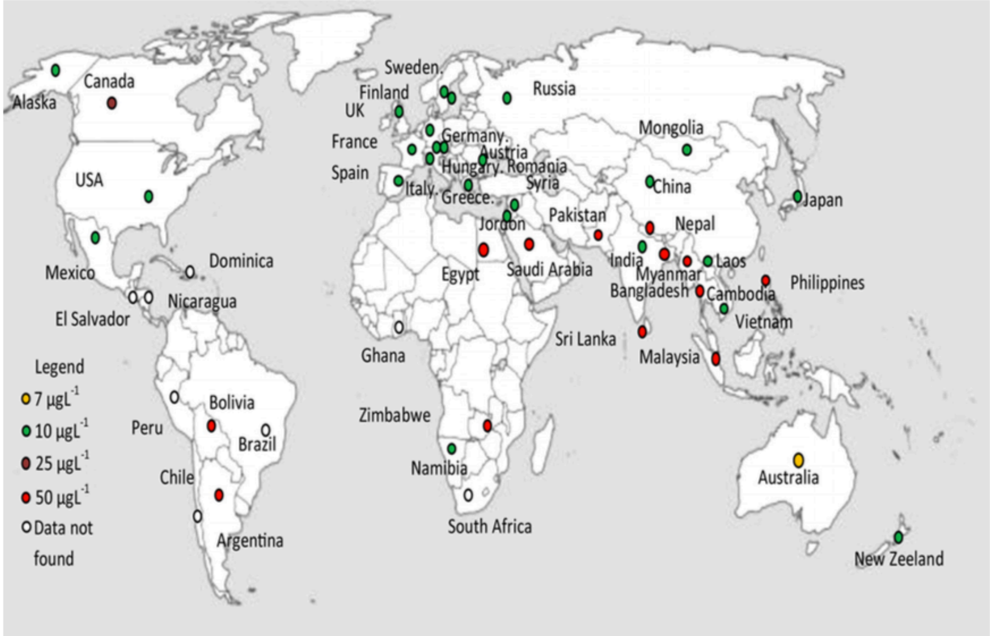

Figure 2-3Affected countries and their respective MCL (source: Mondal et al.,2013

Because of different socio-politico-economical contexts as well as the unavailability of different treatment technologies, the MCL differs in different countries. The most affected countries of the world and theirs respective MCL are shown in Figure 2-3 The affected countries have different characteristics of their contaminated aquifers and therefore, the mechanism of As mobilisation in groundwater is often different. Numerous countries have already adopted guidelines, of 0.01mg/L maximum arsenic limit in drinking water, recommended by the WHO and USEPA (Matschullat, 2000).

2.3.3 Treatment technologies for As removal

The conventional technologies for removing arsenic from groundwater, include: oxidation, coagulation, adsorption, ion exchange and membrane technologies (Wang et al., 2007). The process characteristics and their main advantages and disadvantages are described below:

Oxidation/filtration

Oxidation kinetics rate of As (III) species by dissolved oxygen is very slow in water, which can take weeks to complete. Chemical oxidants are used to increase the oxidation rate of soluble arsenite As (III) to arsenate As(V). Oxidation alone as a technology does not remove arsenic from the solution, thus it has always been added before the main treatment, such as adsorption, coagulation or ion exchange. For instance, oxidation is an important step for anoxic groundwater, since arsenite is the prevalent form of arsenic at neutral pH. There are many chemical oxidants such as, chlorine, ozone, potassium permanganate, manganese oxide and hydrogen peroxide, as well as bacteria that have been used to directly oxidize arsenite in water. Chlorine is considered a good oxidant although it produces unwanted disinfection by-products in the presence of organic matter and is responsible for bad taste and odor. Potassium permanganate produces no harmful compounds but may impart colour.

Coagulation- Flocculation

In the coagulation process, the chemicals used, positively charged coagulants, adsorb and co-precipitate arsenic ions in a particular pH solution, thereby making particles to aggregate and enlarge. Arsenic removal efficiency of different coagulants varies as a function of pH. Commonly used chemicals with this technique are ferric chloride ($FeCl_3$) or aluminum sulphate ($Al_2(SO_4)_3$) (or ammonium sulphate).

Lime treatment is similar to coagulation, but instead of trivalent metal salts, the coagulant used is hydrated lime ($Ca(OH)_2$) or solid form of $Mg(OH)_2$. However, the method of lime treatment cannot serve as a major arsenic removal technique due to its low removal efficiency. Other disadvantage of this process is the daily production of highly toxic sludge.

Flocculation involves the addition of anionic flocculants that causes bridging or charge neutralization between the formed larger particles, leading to the formation of flocs, which undergoes precipitation later (Matsui et al., 2017).

Several researchers reported that, between the two inorganic species, arsenate is more efficiently removed compared to arsenite and, therefore, a pre-oxidation would be beneficial. Moreover, it has also been reported that $FeCl_3$ is a better coagulant than $Al_2(SO_4)_3$ at pH higher than 7.6. Below pH 7.6, $Al_2(SO_4)_3$ and $FeCl_3$ are equally effective in removing arsenic from water. The pH adjustment and proper dosing are very critical to obtain a high process efficiency.

In both processes, the formation of these solids allows the subsequent removal of arsenic through sedimentation and filtration processes. The major disadvantage of these techniques is the production of high amounts of an arsenic-concentrated sludge, which requires a careful management of this sludge to prevent a secondary environmental pollution. Additionally, the treatment of the sludge produced is costly. These limitations make this process less feasible, especially in field conditions (Pallier et al, 2010; Sun et al., 2013).

Adsorption

Adsorption is a process that uses solids as medium for the removal of substances from gaseous or liquid solutions. The substances are separated from one phase and accumulated at the surface of another. This process is driven mainly by Van der Waals forces and electrostatic forces between the adsorbate molecules and the adsorbent surface atoms. Therefore it is important to first characterize the adsorbent surface properties (e.g. surface area, polarity) before being used for adsorption.

Accordingly, to the review published by Giles et al., 2011, the main adsorbents of choice for As removal are Al_2O_3, $Al(OH)_3$, carbon, FeO, Fe_2O_3, modified iron oxides and SiO_2. The iron-based adsorption is a widely used technique for the treatment of arsenic contaminated water due to the high affinity between inorganic species and iron. Iron can remove arsenic from water either by acting as sorbent, co-precipitant or contaminant-immobilizing agent or by behaving as a reductant (LeMire et al., 2010).

As per US Environmental Protection Agency (USEPA) classification, adsorption is amongst the best available technologies for As removal in potable water. Adsorption presents several advantages including relatively high arsenic removal efficiencies, easy operation and handling, cost-effectiveness, and no sludge production.

However, adsorption of arsenic strongly depends on the systems concentration and pH. At low pH, arsenate adsorption is favored, whereas for arsenite, maximum adsorption can be obtained between pH 4 and 9.

One significant disadvantage of the system is the presence of other ions in water such as phosphate and silicate, that compete for the adsorption sites. Furthermore, effectiveness of adsorption in arsenic removal can also be hindered by the type of adsorbent itself. Most conventional adsorbents have irregular pore structures and low specific surface areas, leading to low adsorption capacities. Lack of selectivity, weak interactions with metallic ions, and regeneration difficulties can also limit the ability of these sorbents in lowering arsenic concentrations to levels below MCL (Chatterjee S. et al., 2017).

Ion-exchange

Ion-exchange (IEX) technology for arsenic removal is considered one of the best available technologies (BAT) (EPA, 200a). It is commonly based on the use of strong-base chloride or sulphate forms resins, and the exchange of Cl^- or $SO_4{}^{2-}$ anions for arsenic species and other ions present in the water. The uncharged As(III) cannot be removed by an ion exchange method and a pre-oxidation step is needed if an arsenite solution has to be treated.

The IEX process has two major disadvantage: 1) sorption capacity, because a strong anion competitor such as sulphate (or others, e.g. nitrate) that are commonly present in groundwater thus decreasing the efficiency drastically (resins are highly selective for sulphate ions and there is the risk of arsenic release in the treated water) and; 2) large volumes of hazardous residuals are produced due primarily to frequent regeneration of the exhausted resin. Also an ion exchange method alone is not sufficient to remove arsenic below the maximum contaminant level (MCL) of <10 μg/L (Zhao et al., 2010; Zhao et al., 2012; Dominguez-Ramos et al., 2014; Guell et al., 2011; Jadhav et al., 2015).

Furthermore, it has been proposed the use of metal-loaded polymers (chelating or ion-exchange metal-loaded resins) due to the advantage of these materials to overcome interferences from other accompanying anions and the possibility for removing As(III, V). LeMire et al., 2010 studied the use of iron-impregnated ion exchange beads for As(V) removal and the influence of several factors (particle size, pH, As(V) concentration, competition, adsorbent, temperature and iron content) and concluded that it may be considered as a viable alternative to other iron based adsorbents in terms of durability and efficiency.

Membrane processes

There are two categories of pressure-driven membrane filtration: low pressure membrane such as microfiltratiom (MF) and ultrafiltration (UF), and high-pressure membrane processes such as reverse osmosis (RO) and nanofiltration (NF). According to Shih (2005) these membrane processes are effective to remove arsenic from water, especially high-pressure processes, NF and RO, in order to respect the maximum admissible concentrations. However, source water quality and effluent concentration to be reach are important design parameters (Criscuoli and Figoli, 2018).

As reported by Jekel and Amy, 2006, As(V) rejections observed in NF or RO ranged from 85% to 99% and As(III) rejections between 61 and 87%. Coagulation followed MF for arsenic removal was also shown to be more efficient than conventional filtration. Under optimal conditions, a 100 µg/L of arsenic level was reduced by 97% (Molgora et al., 2013; Pal et al., 2014). An integrated system combining NF + coagulation was proposed for arsenic removal from groundwater. A pre-oxidation step followed by a flat sheet cross-flow nanofiltration attained a 98% of As removal from an initial concentration of 180 µg/L. Arsenite can be rapidly oxidized to arsenate via a pre-oxidation step with, e.g. hypochlorite, permanganate and hydrogen peroxide. However, in this situation, a previous oxidation to convert As(III) to As(V) is not advisable due to the possible damage of the membranes with the chemical (oxidation agents) required to this step.

RO is probably the best practiced technology which can completely purify water and meet the strict water legislations (Holl, 2010; Katsoyiannis and Zouboulis, 2006). Both lab and pilot-scale experiments have shown more than 95% As(V) and 74% As(III) removal efficiencies achieved by RO.

Membrane processes have the main advantage of function without any chemical addition. However, there are some disadvantage such as high initial investment (apparatus, membrane and installation) and operational costs (including energy consumption) involved. Additionally, the presence of Fe and Mn in water prone to fouling due to precipitation of these ions as hydroxide and this type of fouling is irreversible in nature. For removing it, pretreatment of water, monitoring of the operating pressure, and a skilled operator are required. Moreover, in the case of a high arsenic containing water to be treated, the standard value MCL of arsenic is not achieved (Park et al., 2011; Dolores et al., 2017; Fang et al., 2013; Akin et al., 2011; Sen et al., 2010; Xu et al., 2015).

Amongst the conventional technologies presented, coagulation and ion exchange (IEX) are the most used ones due to lower costs, ease of handling and potential reuse of anion-exchangers. In each case, the removal efficiency is influenced by the chemical form of the arsenic present in water, usually as arsenate (As (V)) or arsenite (As (III)). The removal of arsenite is generally less effective by these techniques. However, arsenite can be rapidly oxidized to arsenate via a pre-oxidation step with, e.g. hypochlorite, permanganate and hydrogen peroxide.

The main disadvantages of chemical coagulation followed by settling and/or filtration of the treated water are primarily related to the need for the direct addition of the coagulant to the water, thus leading to residual levels of iron or aluminium, which is undesirable and can give rise to consumer complaints. The EU drinking water directive recommends a limit of 200 ppb for both Fe and Al in drinking water. Moreover, due to the fact that the coagulation process is sensitive to pH, appropriate reagents have to be often added to adjust the pH to the optimal value, additionally increasing the risk of secondary contamination of the treated water by these reagents.

One way to overcome these limitations is by transporting arsenate through anion exchange membranes via an ion exchange membrane (IEM) process - Donnan Dialysis, which is further explained in the following section.

2.3.4 Ion-exchange membrane and processes

Ion exchange membranes (IEMs) have great potential in diverse applications and play prominent roles in addressing energy and environment related issues. Over the past decade, the development of IEMs has attracted much research attention in terms of materials, preparation and applications.

An ion exchange membrane is a selective barrier that carries charge groups that separates two adjacent phases and allows for the exchange of ions between phases. These membranes are made from ionic polymers that are either negatively or positively charged and are bound covalently to the polymer backbone. The ion exchange membranes are classified into two types: anion exchange membranes (AEM) which contain positively charged groups fixed to the polymer matrix; and cation exchange membranes (CEM) which contain negatively charged groups fixed to the polymer matrix. CEMs are selectively permeable to cations and almost impermeable to anions because of their charge, which is the same as that of the fixed charges in the polymer matrix. AEMs have the capability to carry anions (i.e. which are referred as counter-ions) while all cations (co-ions) are almost excluded, since the fixed charges are positive in the polymer matrix (Tas, 2016; Sata, 2004).

2.3.4.1 Ion exchange membrane processes and applications

IEMs are generally used in electrodialysis (Moazeni et al., 2015; Shahmansouri et al., 2015), reverse electrodialysis (Guler et al., 2012; Guler et al., 2013) and diffusion dialysis/Donnan dialysis (Agarwal et al.,2015; Miyoshi et al., 1997). The membrane properties are crucial for determining the performance of these processes. Selective transport of specific ions from multicomponent mixtures is important for e.g. the separation of specific ions in industrial wastewater treatment (Saracco et al., 1993), removing harmful anions (e.g. F^-) from groundwater (Amor et al., 2001), the production of table salt from seawater (Sata, 2004), the electrochemical acidification of milk and water softening to produce drinking milk (Bazinet et al., 2004). So far, Donnan dialysis is not used on a large industrial scale. Most data concerning the performance and process cost data have been generated with laboratory or pilot plant scale equipment in relatively short-term tests. The major applications of Donnan dialysis would be for the production of ultra-pure water or for purification and separation of certain food and pharmaceutical components; or for the treatment of industrial waste streams to recover toxic and valuable materials such as heavy metals or radioactive isotopes (removal of defined heavy metal ions from water).

2.3.4.2 Donnan Dialysis

Donnan dialysis is an ion separation process that uses ion exchange membranes. The process named in honor of F. G. Donnan (1924) who described the equilibrium that resulted when a semipermeable membrane separated two solution of electrolytes, NaA on one side and KA on the other. In this process, a solution of target ionic species is held in a feed compartment separated by an ion exchange membrane from a receiver compartment holding a counter ion stripping solution of high concentration. Migration of counter-ions from the receiver compartment to the feed compartment induces an equivalent counter flow of target ions from the feed to the receiver compartment (Helfferich, 1962).

The concentration difference of e.g. Cl^- ions across the membrane provides a driving force for their diffusion through the membrane. There is no net flow of electric current through the membrane, so any net transfer of Cl^- to the left must be balanced by transfer of an equivalent amount of H_xAsO4^{y-} to the right. These diffusive processes will occur until an equilibrium is established (Figure 2-4).

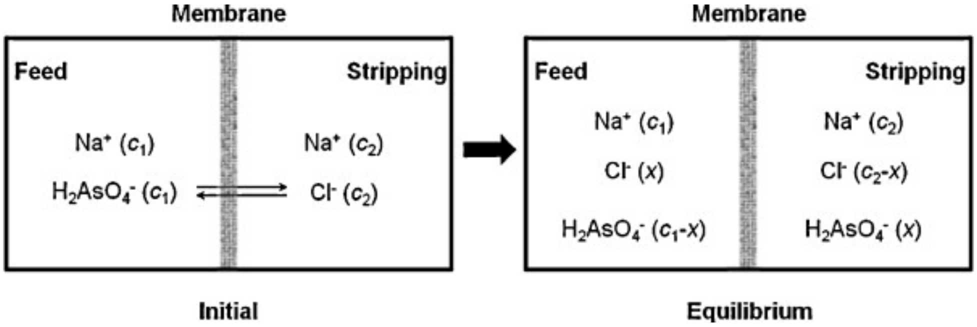

Figure 2-4. Principle of ionic separation by an ion exchange membrane (source: Zhao et al., 2012)

The attractive features of Donnan dialysis lie in operational simplicity, low energy requirement and no chemicals requirement. Donnan dialysis holds a potential for many beneficial water purification processes encompassing hardness removal and elimination of unwanted ions such as borate, nitrate and arsenate (Helfferich, 1962).

2.4 References

Afonso, C.A.M., Crespo, J.G., 2005, Green Separation Processes, WILEY-VCH Verlag GmbH& Co. KGaA, Weinheim.

Agarwal C., Cattrall R.W., Kolev S. D., 2016. Donnan dialysis based separation of gold (III) from electronic waste solutions using an anion exchange pore-filled membrane. Journal of Membrane Science. 514, 210-216.

Agarwal, C.; Mhatre, A.; Goswami, A., 2015. Transport studies of divalent ions through nafion-117 ion exchange membrane in the presence of polyacrylate. Industrial & Engineering Chemistry Research , 54 (13), 3445-3450.

Agbekodo K.M., Legube B., Dard S., 1996. Atrazine and simazine removal mechanisms by nanofiltration: influence of natural organic matter concentration. Water Research, 30, 2535–2542.

Ahkola, H., Tuominen, S., Karlsson, S., et al., 2017. Presence of active pharmaceutical ingredients in the continuum of surface and ground water used in drinking water production. Environmental Science Pollution Research, 24, 26778-26791.

Akin I., Arslan G., Tor A., 2011. Removal of arsenate [As(V)] and arsenite [As(III)] from water by SWHR and BW-30 reverse osmosis. Desalination, 281, 88-92.

Amor, Z., Barious, B., Mameri, N., Taky, M., Nicolas, S. and Elmidaoui A., 2001. Fluoride removal from brackish water by electrodialysis. Desalination, 133, 215-223.

Bazinet L., 2004. Electrodialytic phenomena and their applications in the dairy industry: a review. Critical Reviews in Food Science and Nutrition, 44(7), 525-44.

Berg P., Hagmeyer G., Gimbel R., 1997.Removal of pesticides and other micropollutants by nanofiltration. Desalination, 113, 205–208

Boussahel R., Bouland S., Moussaoui K.M., 2000. A. Montiel, Removal of pesticide residues in water using the nanofiltration process. Desalination, 132, 205–209.

Chang, E., Chen, Y., Lin, Y., Chiang, P., 2009. Reduction of natural organic matter by nanofiltration process. Chemosphere, 76, 1265-1272.

Chang, H., Liang, H., Qu, F., et al., 2017. Hydraulic backwashing for low-pressure membranes in drinking water treatment: A review. Journal Membrane Science, 540, 362-380.

Chatterjee S., De S., 2017. Adsorptive removal of arsenic from groundwater using chemically treated iron ore slime incorporated mixed matrix hollow fiber membrane. Separation and Purification Technology, 179, 357-368.

Chawla, C., Zwijnenburg, A., Kemperman, A.J.B., 2017. Fouling in gravity driven Point-of-use drinking water treatment systems. Chemical Engineering Journal., 319, 89-97.

Chew, C. M., David Ng, K.M., Richard Ooi, H.H., 2017. Polyethersulfone-based ultrafiltration hollow fiber membrane for drinking water treatment systems. Advances Materials for sustainable and growth, AIP conference Proceedings 191.

Chon, K., Cho, J., Shon, H.K., 2013. A pilot-scale hybrid municipal wastewater reclamation system using combined coagulation and disk filtration, ultrafiltration, and reverse osmosis: Removal of nutrients and micropollutants and characterization of membrane Foulants. Bioresource Technology, 141,109-116.

Chon, K., Cho, J.,2016. Fouling behavior of dissolved organic matter in nanofiltration membranes from a pilot-scale drinking water treatment plant: An autopsy study. Chemical Engineering Journal, 295, 268-277.

Criscuoli A., Figoli A., 2018. Pressure-driven and thermally-driven membrane operations for the treatment of arsenic-contaminated waters: a comparison. Journal Hazardous Materials., doi: 10.1016/j.jhazmat.2018.07.047.

Cyna, B., Chagneau, G., Tanghe, N., 2002. Two years of nanofiltration at the Mery-sur-Oise plant, France. Desalination,147, 69-75.

Devitt E.C., Ducellier F., Côté P., Wiesner M.R., 1998. Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure-driven membranes. Water Research, 32, 2563–2568.

Dolores M., Ortega V., Ratnaweera H. C., 2017. Double filtration as an effective system for removal of arsenate and arsenite from drinking wáter through reverse osmosis. Process Safety and Environmental Protection, 111, 339-408.

Dominguez-Ramos A., Chavan K., Garcia V., et al., 2014. Arsenic removal from natural waters by adsorption or ion exchange: an environmental sustainability assessment. Industrial & Engineering. Chemistry Research., 53, 18920-18927.

Drinking Water Directive 98/83/EC.

Fane, A.G., Wang, R., Jia, Y., 2011. Membrane technology: Past, present, and future, in: Wang LK. Chen JP, Hung Y-T, Shammas NK (Eds.), Membrane and desalination technologies. Human Press, New York, USA.

Fang J., Deng B., 2014. Rejection and modeling of arsenate by nanofiltration: contribution of convection, diffusion and electromigration to arsenic transport. Journal of Membrane Science 453, 2014, 42-51.

Garcia-Vaquero, N., Lee, E., Castaneda, R.J., et al., 2014. Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility. Desalination 347, 94-102.

Giles, E. D., Mohapatra, M., Issa, T.B., Anand, S., Singh, P., 2011. Iron and aluminium based adsorption stretegies for removing arsenic from water. Journal of Environmental, 92, 3011-3022.

Grando-Ferreira, L.M., Gaspar, C.S.S., Monteiro, M. et al, 2017. Studies on integration of ion Exchange and nanofiltration for water desalination. Separation Science and Technology. 52, 16, 2600-2610.

Guell R., Fontas C., Anticó E., et al., 2011. Transport and separation of arsenate and arsenite from aqueous media by supported liquid and anion-exchange membranes. Separation And Purification Technology., 80, 428-434.

Guler E., 2014. Anion exchange membrane design for reverse electrodialysis, PhD Thesis, Netherlands.

Guler, E.; Elizen, R.; Vermaas, D. A.; Saakes, M.; Nijmeijer, K., 2013. Performance-determining membrane properties in reverse electrodialysis. Journal of Membrane Science, 446, 266-276. 18.

Guler, E.; Zhang, Y. L.; Saakes, M.; Nijmeijer, K., 2012. Tailor-made anion-exchange membranes for salinity gradient power generation using reverse electrodialysis. ChemSusChem, 5 (11), 2262-2270.

Helfferich F., 1962. Ion exchange. New York: McGraw-Hill.

Henke K. R., 2009. Arsenic – Environmental Chemistry, Health Threats and Waste Treatment. John Wiley & Sons Ltd.

Hilal, N., Kochkodan, V., Abdulgader, H.A., Mandale, S. et al, 2015. A combined ion-exchange-nanofiltration process for water desalination: II. Pilot scale studies, Desalination. 363, 58-63.

Imbrogno A., Tiraferri, A., Abbenente, S., et al., 2018. Organic fouling control through magnetic ion exchange- nanofiltration (MIEX-NF) in water treatment. Journal of Membrane Science., 549, 474-485.

Jadhav S. V., Bringas E., Yadav G. et al., 2015. Arsenic and fluoride contaminated groundwater: a review of current technologies for contaminants removal. Journal of Environmental Management, 162, 306-325.

Jekel, M. and Amy, G.L., 2006.Arsenic removal during drinking water treatment. In Interface Science in Drinking Water Treatment. G. Newcombe and D. Dixon(eds.). Elsevier Ltd. Amesterdam, Chapter 11, pp. 193-206.

Jones, O.A., Lester, J.N., Voulvoulis, N., 2005. Pharmaceuticals: a threat to drinking water?. Trends Biotechnology, 23(4), 449-469.

K.V. Plakas, A.J. Karabelas, 2009. Triazine retention by nanofiltration in the presence of organic matter: the role of humic substance characteristics. Journal of Membrane Science, 336, 86–100.

Kukucka, M., Kukucka, N., Habuda-Stanic, M., 2016. Water reclamation during drinking water treatment using polyamide nanofiltration membranes on a pilot scale. Environmental Science Pollution Research, 23, 17919-17927.

LeMire L.E., Teixeira, M., Reed, B., 2010. Removal of As(V) Using na Iron-Impregnated Ion Exchange Bead. Seoaration Science and Technology, 45(14), 2051-2063.

Liu, C., Liu, J.C., 2016. Coupled precipitation-ultrafiltration for treatment of high fluoride-content wastewater. Journal of the Taiwan Institute of Chemical Engineers., 58, 259-263.

Lyonnaise des Eaux, 1996. American Water Works Association Research Foundation, Water Treatment- Membrane Processes, McGraw-Hill.

Matschullat, J. 2000. Arsenic in the geosphere – a review. Science Total Environment., 249 (1-3): 297-312.

Matsui Y., Shirasaki N., Yamaguchi T., et al., 2017. Characteristics and components of poly-aluminum chloride coagulants that enhance arsenate removal by coagulation: detailed analysis of aluminum species. Water Research, 118, 177-186.

Meng, X., Bang, S., Banerjee, D.M., 2000. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. Water Research., 34, 1255-1261.

Metcalf & EDDY, Inc., Wastewater engineering treatment disposal reuse, McGraw Hill series in water resources and environmental engineering.

Miyoshi, H., 1997. Diffusion coefficients of ions through ion-exchange membranes for Donnan dialysis using ions of the same valence. Chemical Engineering Science, 52 (7), 1087-1096.

Moazeni, M.; Hajipour, H.; Askari, M.; Nusheh, M., 2015. Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents. Materials Research Bulletin, 61, 70-75.

Mohan D., Pittman Jr. C.U., 2007. Arsenic removal from water/wastewater using adsorbents – A critical review. Journal of Hazardous Materials, 142, 1-53.

Molgora, C.C., Dominguez, A.M., Avila, E.M., Drogui, P., Buelna, G., 2013. Removal of arsenic from drinking water: a comparative study between electrocoagulation-microfiltration and coagulation-microfiltration process. Separation and Purification Technology. 188, 645-651.

Mondal P., Bhowmick S., Chatterjee D. et al, 2013. Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions. Chemosphere, 92, 157-170.

Mulder, M.. Basic Principles of Membrane Technology, second edition, reprinted 2003, Kluwer Academic Publishers.

Musbah I., Cicéron D., Saboni A., Alexendrova S., 2018. Removal of pesticides and desethylatrazine (DEA) by nanofiltration: effects of organic and inorganic solutes on solute rejection. Journal of Chemical Technology and Metallurgy, 53, 4, 657-663.

Ollis, D. F., 2003. Advanced Membrane Technology, Edited by Norman N. Li, Enrico Drioli, W.S. Winston Ho, Glenn G. Lipscomb. New York Academic Science, Pag. 65- 84.

Owamah, H.I., Enaboifo, M.A., Izinyon, O.C., 2014. Treatment of wastewater from raw rubber processing industry using water lettuce macrophyte pond and the reuse of its effluents as biofertilizer. Agricultural Water Management 146, 262-269.

Pal, P., Chakrabortty, S., Linnanen, L., 2014. A nanofiltration-coagulation integrated system for separation and stabilization of arsenic from groundwater. Science Total Environment, 476, 601-610.

Pallier V., Feuillade-Cathalifaud G., Serpaud B., et al., 2010. Effect of organic matter on arsenic removal during coagulation/flocculation treatment. Journal of Colloid and Interface Science., 342, 26-32.

Papageorgiou, A., Papadakis, N., 2016. Fate of natural organic matter at a full-scale drinking water treatment plant in Greece. Environmental Science Pollution Research, 23,1841-1851.

Park H., Choi H., 2011. As(III) removal by hybrid reactive membrane process combined with ozonation. Water Research, 45, 1933-1940.

Petrovi,M. Gonzalez, S., Barceló, D., 2003. Analysis and removal of emerging contaminants in wastewater and drinking water. Trends in Analytical Chemistry 22(10), 685-696.

Piadeh, F., Alavi-moghanddam, M. R., Mardan, S., 2018. Assessment of sustainable of a hybrid of advances treatment technologies for recycling industrial wastewater in developing countries: Case study of Iranian industrial parks. Journal of Cleaner Production, 170, 1136-1150.

Plakas, K.V., Karabelas, A.J., 2012. Removal of pesticides from water by NF and RO membranes – A review. Desalination, 287,.255-265.

Racar M., Dolar, D. Spehar A., Kosutic K., 2017. Application of UF/NF/RO membranes for treatment and reuse of rendering plant wastewater. Process Safety and Environmental Protection, 1056, 386-392.

Rahimpour, A., Jahanshahi, M., Peyravi, M., 2014. Development of pilot scale nanofiltration system for yeast industry wastewater treatment. Journal of Environmental Health Science & Engineering,12:55.

Ravenscroft, P., Brammer, H. and Richards, K., 2009. Arsenic Pollution: A Global Synthesis. Wiley-Blackwell, RGS-IBG BOOK SERIES.

Samaci, S.M., Gato-Trinidad, S., Altaee, 2018.A., The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters- a review. Separation and Purification. Techonology,(http://doi.org/10.1016/j.seppur.2018.02.041).

Saracco G., Zanetti, M.C., Onofrio M., 1998, Novel Application of monovalent Ion Permselective Membranes to the Recovery Treatment of an Industrial Wastewater by Electrodialysis. Industrial & Engineering Chemistry Research, 32, 657-662.

Sata T., 2004. Ion exchange membranes – preparation, characterization, modification and application. The Royal Society of Chemistry, Cambridge.

Schafer, A.I., 2001. Natural Organic Removal using Membranes, principles, performance and cost. Technomic publication.

Sen M., Manna A., Pal P., 2010. Removal of arsenic from contaminated groundwater by membrane-integrated hybrid treatment system. Journal of Membrane Science., 354, 108-113.

Sert, G., Bunani, S., Kabay, N., Egemen, O., Arda, M., Pek, T.O., Yuksel, 2016. M., Investigation of mini pilot scale MBR-NF and MBR-RO integrated systrems performance-preliminary field tests. Journal Water Process Engineering., 12, 72-77.

Shahmansouri, A.; Min, J.; Jin, L. Y.; Bellona, C., 2015. Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review. Journal of Cleaner Production, 100, 4-16.

Shang, W., Sun, F., Chen, L., 2018. Nanofiltration fouling propensity caused by wastewater effluent organic matters and surface water dissolved organic matters. Environmental Technology. 15, 1914-1925.

Shetty, G.R., Chellan, S.,2003. Predicting membrane fouling municipal drinking water nanofiltration using artificial neural networks. Journal of Membrane Science., 217, 69-86.

Shih, M.-C., 2005. An overview of arsenic removal by pressure-driven membrane processes. Desalination, 172(1), 85–97.

Siddiqui S. I., Chaudry S.A., 2017. Iron oxide and its modifies forms as an adsorbent for arsenic removal: a comprehensive recent advancement. Process Safety and Environmental Protection, 111, 592.626.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry. 17,517-568.

Snyder S.A., P. Westerhoff, Y., Yoon, D.I., Sedlak, 2003. Pharmaceutical personal care products and endocrine disruptors in water: implications for the water industry. Environmental Engineering Science., 20(5), 449-469.

Sonoc A. C., Jeswiet J., Murayama N., Shibata J., 2018. A study of the application of Donnan dialysis to the recycling of lithium ion batteries. Hydrometallurgy. 175, 133-143.

Sun Y., Xiong X., Zhou G., et al., 2013. Removal of arsenate from water by coagulation with in situ formed versus pre-formed Fe(III). Separation and Purification Technology., 115, 198-204.

Tas S., 2016. Bio-inspierd ion selective crown-ether polymer membranes. PhD Thesis, Turkey (DOI: 10.3990/1.9789036540742).

Taucer-Kapteijn, M., Hoogenboezen, W., Heiliegers, L. et al, 2016. Screening municipal wastewater effluents and surface water used for drinking water production for the presence of ampicillin and vancomycin resistant enterococci. International Journal of Hygiene and Environmental Health, 219, 437-442.

Thomas, M., Zdewbik, D., Bialecka, B., 2018. Using sodium trithiocarbonate to precipitate heavy metals from industrial wastewater- from the laboratory to industrial scale. Polish. Journal of Environmental. Studies, 27, 1753- 1763.

Thorsen, T., Flogstad, H., 2006. Nanofiltration in drinking water treatment – Report elaborated in the scope of the deliverable D 534B of the TECHNEAU project.

US EPA, 2005. Membrane filtration guidance manual (EPA 815-R-06-009). US Environmental Protection Agency, Office of Water, Washington DC.

USEPA – US Environmental Protection Agency, 2005. Treatment Technologies For Arsenic Removal, EPA/600/S-05/006, November.

Van der Bruggen B., Geens J., 2008. Advanced Membrane Technology and Application, Edited by Norman N. Li, Anthony G. Fane, W.S. Winston Ho and T. Matsuura, John Wiley & Sons, Inc., Chapter 11, pag. 271-295.

Vanoppen M., Stoffels G., Demuytere C., Bleyaert W., Verliefde A.R.D., 2015. Increasing RO efficiency by chemical-free ion-exchange and Donnan dialysis: Principles and pratical implications. Water Research. 80, 59-70.

Vatankhah H., Murray, C.C., Brannum, J.W., Vanneste, J., Bellona, C., 2018. Effect of pre-ozonation on nanofiltration membrane fouling during water reuse applications. Separation and purification Technology, 205, 203-211.

Wadekar S., Hayes, T., Lokare, O. et al, 2017. Laboratory and Pilot-scale nanofiltration treatment of abandoned mine drainage for the recovery of products suitable for industrial reuse. Industrial & Engineering Chemistry Research, 56, 7355-7364.

Wang L., Chen A.S.C., Tong N., Coonfare C.T., 2007. Arsenic removal from drinking water by ion exchange U.S.EPA demonstration project at fruitmald, ID six-month evaluation report, EPA, April.

WHO, World Health Organization, 2011. Guidelines for drinking-water quality, Geneva, Switzerland.

Winston Ho W.S. and Sirkar K.K.,1992. Membrane Handbook, Van Nostrand Reinhold, 1992.

Winter, J., Barbeau, B., Berube, P., 2017. Nanofiltration and tight ultrafiltration membranes for natural organic matter removal- contribution of fouling and concentration polarization to filtration resistance. Membranes, 7, 34.

World Health Organization (WHO), 2011. Guidelines for drinking-water quality- 4th ed.

Xu X., Lin L., Papelis C., Myint M., et al., 2015. Use of drinking water treatment solids for arsenate removal from desalination concentrate. Journal of Colloid and Interface Science, 445, 252-261.

Yen, F., You, S., Chang, T., 2017. Performance of electrodialysis reversal and reverse osmosis for reclaiming wastewater from high-tech industrial parks in Taiwan: a pilot-scale study. Journal of Environmental Management, 187, 393-400.

Zhang Y., Van der Bruggen B., Chen G.X., Braeken L., Vandecasteele C., 2004. Removal of pesticides by nanofiltration: effect of the water matrix. Separation and Purification Technology, 38, 163–172.

Zhao B., Zhao H., Dockko S., Ni J., 2012. Arsenate removal from simulated groundwater with Donnan dialyzer. Journal of Hazardous Materials, 215-216, 159-165.

Zhao B., Zhao H., Ni J., 2010. Arsenate removal by Donnan dialysis: Effect of the accompanying components. Separation and Purification Technology., 72, 250-255.

Zhao, M., Xu, Y., Zhang, C., et al, 2016. New trends in removing heavy metals from wastewater. Applied Microbiology and Biotechnology, 100:6509-6518.

Zheng X., Zhang Z., Yu D., Chen X., et al., 2015. Overview of membranes technology applications for industrial wastewater treatment in China to increase water supply. Resource, Conservation and Recycling, 105, 1-10.

Zirehpour A., Rahimpour A., 2016. Nanostructure Polymer Membranes, eds. Visakh P.M. and Olga N., Vol. 2, 159-208 Scrivener Publishing LLC.

Chapter

3

Energy Saving Membrane Treatment of High Organic Load Industrial Effluents: From Lab to Pilot Scale

3.1 Summary

In this study, a nanofiltration unit was implemented at an industrial site, for the treatment of industrial wastewater generated during rubber tubing extrusion. The aim was to reduce the energy input required, while assuring a final effluent quality that meets the requirements of environmental legislation. In a first stage, two membrane process treatments, ultrafiltration and nanofiltration, were evaluated at laboratory scale in order to assess the rejection of pollutants and maximise permeate throughput. Permeate generated from nanofiltration using either a NF90 or NF270 membranes were shown to meet the effluent discharge requirements (<2000 mg COD/l). The less restrictive membrane, NF270, was chosen for study in a pilot plant at the industrial site, due to its higher membrane permeability. The pilot nanofiltration unit was integrated into the treatment plant operation aiming at optimising the process in terms of the efficiency of pollutant removal with minimal energy input. A feasibility study was performed for this case-study and it was concluded that the energy expenditure of the new process represents only 62% of the current energy consumption of the treatment plant. The proposed solution in this work may be retrofitted to full scale wastewater treatment processes, and may be applicable to industries that employ similar manufacturing processes, and face similar difficulties.

Published as: Lopes, M.P., Xin G., Crespo J.G., 2013. Energy saving membrane treatment of high organic load industrial effluents: From lab to pilot scale. Journal of Environmental Management, 131, 161-169.

3.2 Introduction

Wastewater treatment has been a challenge to the rubber parts industry (tubes for automotive industries, tyres, flasks used as cosmetics containers, etc.) (Asia, 2007; Rosman et al.,2003; Vijayaraghavan et al., 2008; Anotai et al., 2007). The production process which implies extrusion and/or injection and post-washing processes generates a huge amount of wastewaters contaminated with demoulding agents (such as Getren R 4510, which is a polyether and non-ionic surfactant, or Struktol VP 6015, which is a water soluble polymer) and, therefore, present a high chemical oxygen demand (COD> 10000 mg/L) and low biodegradability.

The concern to control the environmental impact led to the European Directive 2008/1/EC on integrated pollution prevention and pollution control (IPPC), which sets out measures to prevent or reduce emissions of defined industrial activities, including waste drainage levels of the chemical industry in urban sewage.

The problem described above is shared by many rubber companies across Europe and the World. Cikautxo, a major manufactures of rubber hoses in the Basque Country, in Spain, is a good example of a company that faces this problem and handles it with a thermal treatment process that represents a highly energy intensive solution. The production process of the company leads to a daily consumption of 160 cubic meters of water and the production of approximately 70 m^3/d of wastewater contaminated with a polymeric release agent, Getren, which is the main contributor for high chemical oxygen demand (COD). Currently, the company is employing a thermal process (Figure 3-1a) with the use of a boiler and an evaporator, which leads to an energy cost of €4.2/m^3 of treated wastewater.

The steam boiler was tailored to the concentration of the release agent present in the wastewater, facilitating the treatment of this effluent whilst using this water to generate steam for the factory.

Besides the high energy consumption, there are several other reasons why rubber manufacturers want to stop using boilers for wastewater treatment. Chemicals in the wastewater foul the boiler severely, which leads to frequent and costly maintenance. A significant reduction of boilers' lifetime has also been observed.

Membrane technology is the solution proposed in this study to concentrate the raw wastewater (currently concentrated by the boiler), which is then fed to an evaporator for further volume reduction. This work investigates the development of an integrated approach (Urtiaga et al., 2009; Anglada et al., 2010) (Figure 3-1b) able to treat these high organic loads, in order to reduce pollution to the environment, obtaining re-usable water, reducing waste disposal volumes and reducing energy consumption and costs (Agana et al. 2011).

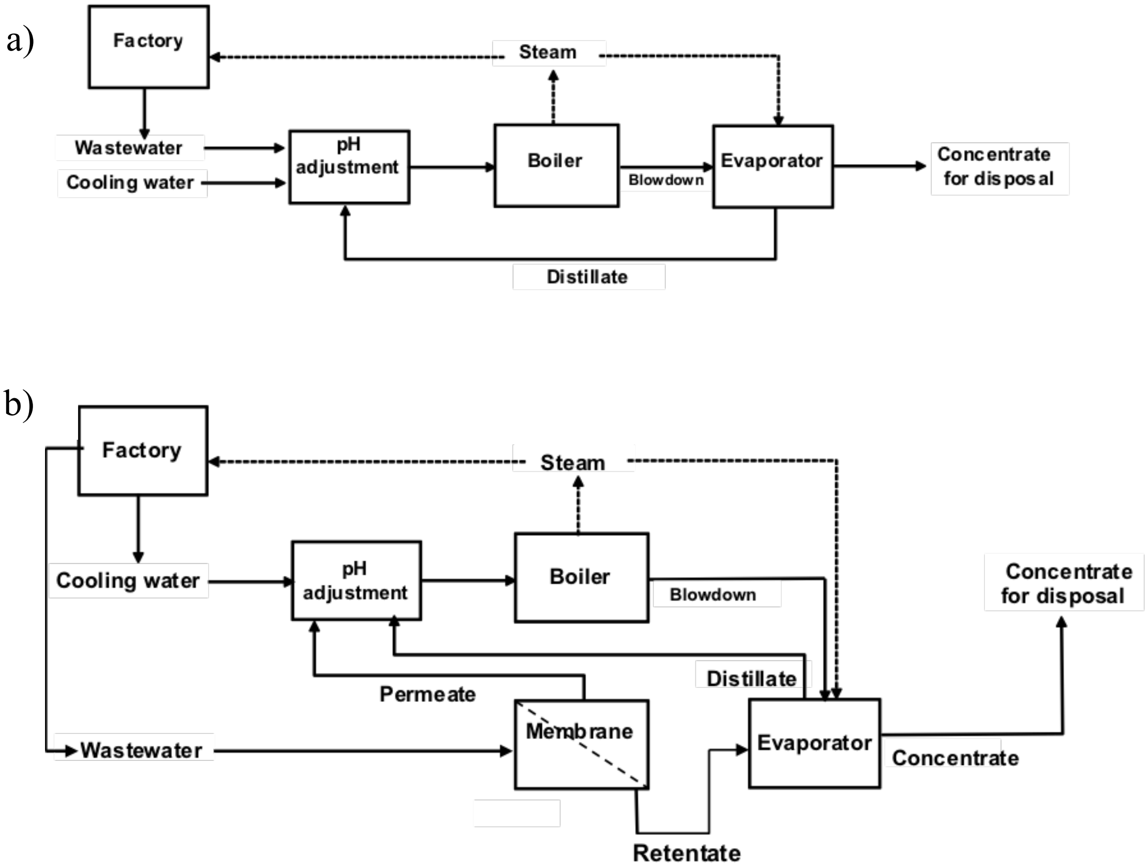

Figure 3-1: Process diagram for the rubber wastewater treatment process at the rubber manufactures, a) current treatment and b) proposed solution.

Both ultrafiltration (UF) and nanofiltration (NF) were tested for treating the rubber wastewater at the laboratory scale (Mänttäri et al. 2002). Ultrafiltration using a selected ceramic ultrafiltration membrane (Barredo-Damas et al. 2010) was firstly evaluated, in order to assure a stable operation in the case that the wastewater was produced in a temperature range above ambient. Additionally, as it was found that the temperature of the effluent is slightly above ambient temperature, it was decided to use polymeric membranes, because their unit cost per filtration area is much lower than ceramic membranes. Nanofiltration membranes were screened in order (Madaeni 2006; Teixeira et al., 2009) to select the best membrane to be used at pilot scale, with the aim to obtain a treated effluent with a target quality.

Based on the laboratory studies performed, a pilot scale study was carried out at an industrial site (Cikautxo, Spain) in order to validate and optimise the outlined process under real operating conditions. Additionally, a membrane fouling analysis was conducted with the membrane module used during the pilot studies, in order to identify the major contributors to fouling (Xu et al., 2010; Darton et al., 2004; Klüpfel 2010; Wei et al., 2010; Lee et al., 2013).

This work evaluates the impact of retrofitting the current wastewater treatment process by replacing evaporator with a nanofiltration unit, which can be operated in a batch or continuous mode, depending on the flowrate to be treated daily. This impact is assessed in terms of the reduction of energy costs, while assuring the required quality of the treated waste stream.

3.3 Materials and Methods

3.3.1 Experimental set-up

The membrane filtration experiments at laboratory scale were carried out in a laboratory test unit shown schematically in Figure 3-2a). For UF experiments, a ceramic tubular membrane from TechSep was used, where the characteristics are presented in Table 3-1: Characteristics of the selected membranes.. A stainless steel cross-flow test cell was used for NF experiments, with a 15 cm^2 effective area for the nanofiltration flat sheet membranes (characteristics also presented in Table 3-1: Characteristics of the selected membranes.) placed between two rectangular cross-section channels (feed and permeate) measuring 150mm x 10 mm x 1mm each.

The feed circulation flow was provided by a high-pressure diaphragm pump (Hydra-cell G-13, Wanner Engineering, USA) with an adjustable pressure to the membrane cell. The system was designed and constructed in order to allow for control of the feed cross-flow velocity and the transmembrane pressure difference.

The diagram of the nanofiltration (NF) pilot plant is shown in Figure 3-2b). The pilot system was equipped with programmable logic controllers (PLCs) for data acquisition.

a)

Não é possível apresentar a imagem ligada. O ficheiro pode ter sido movido, mudado de nome ou eliminado. Verifique se a ligação aponta para o ficheiro e localizações corretos.

b)

Não é possível apresentar a imagem ligada. O ficheiro pode ter sido movido, mudado de nome ou eliminado. Verifique se a ligação aponta para o ficheiro e localizações corretos.

Figure 3-2: Experimental membrane set-up at **a)** laboratory scale and **b)** pilot scale

The main difference between both units (lab and pilot scale) is the size and the fact that the pilot-scale uses membrane modules with a spiral-wound configuration, which lead to fluid dynamic conditions identical to the conditions at full scale. In addition, a pre-filter of 1 μm was placed before the membrane module and the pressure pump. The system was designed and constructed in order to allow for control of the feed cross-flow velocity, the transmembrane pressure difference and the volume reduction factor (VRF – number of times the original feed volume is concentrated in a batch mode).

The experiments were performed in concentration mode where, during membrane filtration, the rejected stream is recirculated to the feed vessel, allowing for concentrating the retentate, while permeating the treated water stream.

In the pilot-scale experiments, the operating pressure was kept constant and the permeate flow was measured over time (decreasing due to membrane fouling). The reject valve was always on, in order to send the reject stream back to the feed tank. The recirculation valve was fully open for internal recirculation of the retentate, to allow for better fluid dynamic conditions.

3.3.2 Membranes and chemicals

One commercial UF membrane and three NF membranes were tested in the present study. The most relevant characteristics of the membranes are described in Table 3-1. For the lab scale studies, a tubular UF membrane was used while flat sheet membranes were used for the lab scale NF experiments. In the pilot scale nanofiltration study, a spiral wound NF270-4040 membrane module (Dow, FILMTEC) was used. All membrane specimens were rinsed with distilled water prior to use, in order to remove preservers, and compacted before experiments, using distilled water at a pressure of 1.5 and 13-15 bar for the UF and NF experiments, respectively. Compaction was carried out until constant flux was achieved (≈3 hours).

The membranes were chemically cleaned *in-situ* after each filtration operation. Two commercial chemical cleaning products were used, Ultrasil 11 and Ultraperm 75 (both from EcoLab). The alkali cleaning with Ultrasil 11 targets mainly the organic foulants on the membrane while the acid cleaning with Ultrasil 75 targets mainly the inorganic foulants.

3.3.3 Membrane performance studies

The UF hydraulic permeability assays were conducted by measuring the permeate flow obtained under different transmembrane pressure differences (0.1 bar; 0.15 bar; 0.2 bar and 0.25 bar), taking into account the membrane area used (11.3 cm^2) and the temperature of the feed stream (22◦C and 50◦C). The ultrafiltration studies with wastewaters were accomplished by performing experiments with the extension of four hours each and with a transmembrane pressure difference of 0.25 bar.

For NF membranes the hydraulic permeability studies were conducted by measuring the permeate flow obtained under different transmembrane pressure differences (4 bar, 6 bar, 8 bar, 10 bar and 12 bar), taking into account the membrane area used (48.6 cm^2) and the operating temperature (22◦C and 45◦C). The nanofiltration experiments took between 3 and 5 hours each, with an applied transmembrane pressure difference of 10 bar.

In the pilot-scale studies (membrane area of 7.6 m^2), the hydraulic permeability measurements were conducted identically to the laboratory scale, at an ambient temperature of 29 ◦C. The NF wastewater treatment studies were performed for 12 hours with an imposed average TMP of 5.1 bar.

The performance of each study was followed by measuring the permeate flux along time and sampling the final concentrate and cumulative permeate for analysis of relevant parameters.

After each experiment, the membranes were chemically cleaned to remove fouling and restore permeability. The membranes were cleaned in-situ with an alkaline cleaning solution (0.5% Ultrasil 11) and with an acid cleaning solution (7.5 g/l of Ultraperm 075).

The membrane permeability was determined at the beginning and end of each experiment and, in selected cases, after applying the chemical cleaning protocol. This procedure allowed us to compare the initial permeability of a fresh membrane (before processing wastewater), with its permeability after processing a given wastewater volume and also with its permeability after chemical cleaning.

Table 3-1: Characteristics of the selected membranes.

Manufacturer	Membrane tested	Material	Membrane type	Cut-off (Da)	Max. Temperature/ Pressure	pH range
TechSep	Carbosep ZrO2	Zirconium oxide selective layer supported in porous carbon	UF	15000	No restriction	No restriction
Nadir	NP010	Polyethersulfone	NF	1000	5-95 °C /40 bar	0-14
Dow	NF270	Polyamide selective layer Polysulfone supporting layer	NF	~400	45 °C /41 bar	2-11
Dow	NF90	Polyamide selective layer Polysulfone supporting layer	NF	~200	45 °C /41 bar	2-11

3.3.4 Fouling analysis

After operation of the pilot unit, the membrane module was opened and the fouled membrane element removed. The membrane element was then unrolled for visual inspection and membrane samples were collected for SEM characterization and foulants identification. The membrane cake layer was analysed in terms of total solids, volatile solids and metal content.

Portions of the cake layer formed on the membrane surface were gently scrubbed off the membrane (from 400 cm^2 of membrane area) using the tip of a laboratory spatula. The foulant material sample was dissolved in 50 ml of Milli-Q water using a vortex mixer, prior to ICP analysis.

Table 3-2: Characterization of Rubber wastewater received for lab scale studies.

Parameter	COD	TOC	Conductivity	pH	Turbidity
Unit	mg/l	mg/l	µS/cm	-	NTU
Value	26700	6293	350	5.35	44

Metal content – analysis by ICP

Na	S	K	Ca	Fe	P	Mg	Al	Ba	Cu
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l
118	75.9	13.6	6.83	4.39	1.81	1.65	0.04	164	24.7

3.3.5 Analytical methods

All samples were analysed in order to quantify the most relevant parameters. Chemical oxygen demand (COD) was determined using analytical kits from Hach Lange LCK (385,386) and total organic carbon (TOC) was measured with a total carbon analyser TOC-VCSH (Shimadzu, Japan). Inductively coupled plasma atomic emission spectroanalysis (ICP) equipped with a radio-frequency (RF) generator of 40.68 MHz, a Czerny-Turner type monochromator with 1.00m (sequential), a AS500 autosampler and data acquisition software was employed to determine the concentration of metals. The pH was determined using an ORION pH meter (Model 720 A). Conductivity measurements were performed with a 120 microprocessor conductivity meter, model Orion (Thermo Spectronic, USA). Turbidity values were determined with a portable turbidity meter from Hanna Instruments. Also, in order to visually characterize the effect of fouling and chemical cleaning of membranes, scanning electron microscope (SEM) images were obtained by Field Emission Scanning Electronic Microscopy (Jeol JSM – 7001F).

3.4 Results and Discussion

3.4.1 Determination of the wastewater characteristics

Table 3-2 presents the main characteristics of the wastewater used in the lab scale study. The wastewater from the rubber industry contains a high level of organic load, caused by the presence of the released agent (Butyl-polyether).

Table 3-3 present the characterisation of the wastewaters used during lab scale and pilot scale study. It can be observed that the wastewater composition varies significantly according with the production activity of the factory (Table 3-2 and Table 3-3).

During the pilot scale study was observed a significant variation of the strength of the effluent from the rubber industrial plant. To better characterise the wastewater under study, several samples were taken, at different periods of time. However, the COD/TOC ratio was found to be relatively constant, indicating no apparent shifting of the main COD contributor during the testing period.

Table 3-3: Characterisation of Rubber wastewater collected during pilot scale studies.

Parameter	COD	TOC	COD/TOC	Conductivity	pH	Turbidity
Unit	mg/l	mg/l	-	µS/cm	-	NTU
Average value	14829	4420	3.6	766	6.4	44
Number of samples	42	17	-	35	34	26
Value before pilot testing	15106	3902	3.8	1175	6.34	60.59

3.4.2 Ultrafiltration and Nanofiltration lab scale studies

Ultrafiltration was the first membrane technique to be studied and evaluated. Even though the wastewater is produced in a temperature range not much above ambient (35-to 45◦C), it was decided to perform these studies with a ceramic ultrafiltration membrane in order to assure highly stable conditions.

The initial hydraulic permeability obtained was 127.4 l/(m^2.h.bar), and after the UF processing of wastewater it decreased to 55.1 l/(m^2.h.bar) Figure 3-3, due to membrane fouling. After chemical cleaning, the membrane permeability was completely restored to values similar to the starting conditions, meaning that the cleaning protocol used was able to eliminate membrane fouling.

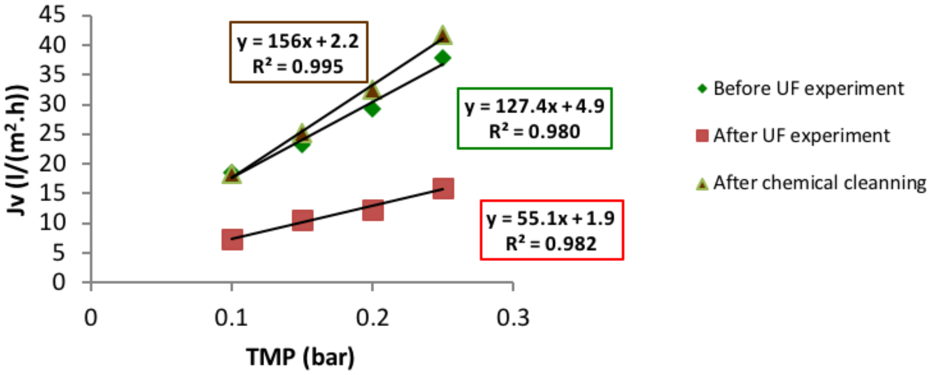

Figure 3-3: Determination of hydraulic permeability using the ultrafiltration membrane.

Table 3-4 presents the permeate characterisation and the efficiency of the ultrafiltration membrane process to reduce COD and TOC in the treated water, with feed values of 26700 mg COD/l and 6293 mg TOC/l. The results obtained with the UF membrane process show a reduction in the range of 45-58%.

Table 3-4. COD and TOC permeate values and rejections obtained during the ultrafiltration experiments performed (COD Feed – 26700 mg/l and TOC Feed – 6293 mg/l).

	COD cumulative permeate (mg/L)	Apparent rejection COD (%)	TOC cumulative permeate (mg/L)	Apparent rejection TOC (%)
UF ≈ 22°C	13300	50.2	3425	45.86
UF ≈ 50°C	11100	58.4	ND	-

ND – not determined.

From these results, the most relevant conclusion that can be drawn is the fact that, although processing of the rubber wastewater by ultrafiltration allows obtaining relatively high permeabilities (and consequently permeating fluxes), the rejection of COD and TOC is clearly insufficient to comply with the legislation requirement for effluent discharge.

Under these circumstances, it was decided to use tighter membranes, with better retentive properties. Processing by nanofiltration (Kurt et al. 2012) is expected to assure higher retention of the carbon compounds present in the effluent under study.

The criteria used for pre-selecting nanofiltration membranes for detailed study were: the nominal molecular weight cut-off (MWCO) of the membranes, which indicates the potential retentive capability of a given membrane (membranes with a MWCO ranging from 1000 Da to 200 Da were tested) and the material of the selective top-layer of the membrane (polyethersulphone and polyamide top-layers were tested).

It was decided to operate at a relatively mild transmembrane pressure (TMP =10 bar), in order to use conditions applicable and economic at industrial scale.

Figure 3-4 shows the hydraulic permeability of the Nadir 10 membrane before and after processing rubber wastewater at ambient temperature (≈ 22 ºC). This figure shows an accentuated decrease of permeability after processing, due to deposition of organic and inorganic components present in the wastewater on the membrane, which causes the membrane fouling.

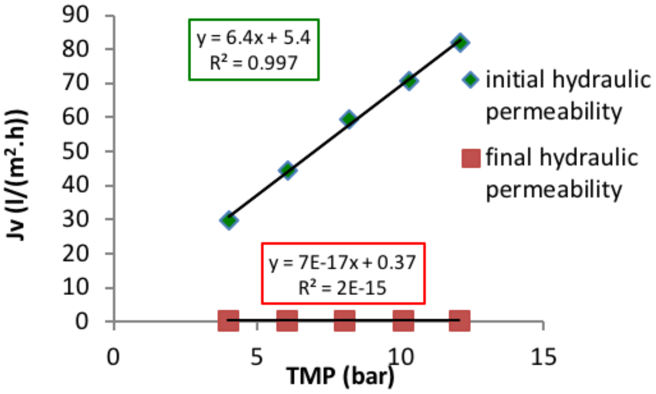

Figure 3-4 Determination of hydraulic permeability for the Nadir 10 membrane at 22 °C.

Table 3-5 shows the Nadir 10 membrane efficiency for the removal of TOC and COD, at the operating temperature studied. The results obtained in this experiment show a high, but insufficient, retention of COD.

Table 3-5. COD and TOC permeate values and rejections of the NF experiments performed (COD Feed – 26700 mg/l and TOC Feed – 6293 mg/l)

	COD cumulative permeate (mg/L)	Apparent rejection COD (%)	TOC cumulative permeate (mg/L)	Apparent rejection TOC (%)
Nadir10 ≈ 22°C	5430	79.7	1346	78.6
NF90 ≈ 22°C	530	98.0	199.3	96.8
NF270 ≈ 22°C	1080	96.0	348.5	94.5
NF270 ≈ 45°C	916	95.6	302.5	95.2

A tighter nanofiltration membrane, NF270, was therefore tested. This membrane was evaluated at ambient temperature and also at its highest temperature limits (45◦C). The initial permeability obtained was 7.7 and 11 l/(m^2.h.bar) for 22◦C and 45◦C, respectively (Figure 3-5). As expected, the permeability observed at 45 ◦C is higher due to the lower viscosity of the permeating water at higher temperature.

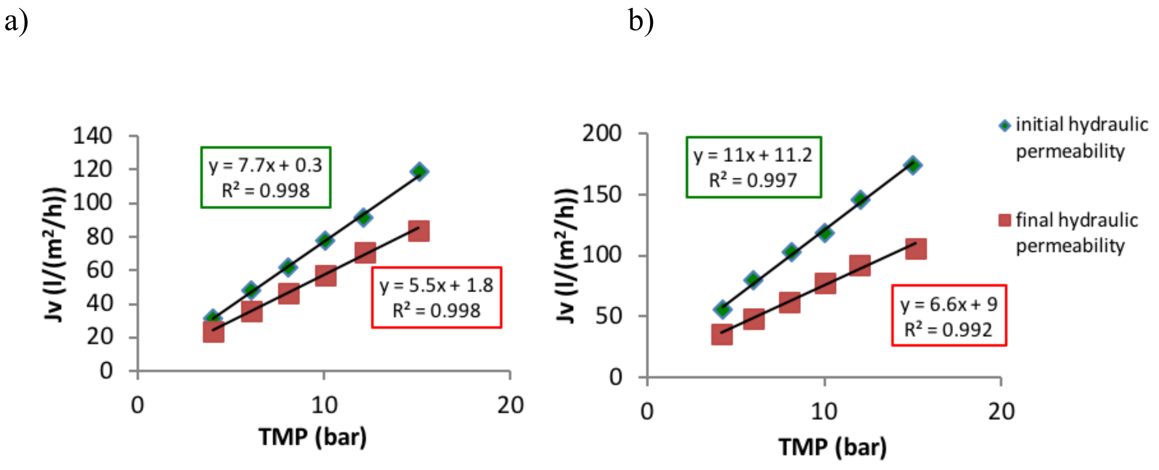

Figure 3-5 Determination of the hydraulic permeability for the NF270 membrane at a) 22°C b) 45°C.

Also, an even tighter membrane, the NF90 membrane, was evaluated and its performance is shown in Figure 6 and Table 4. The hydraulic permeability obtained for the NF90 membrane is lower than for the NF270 membrane, as expected.

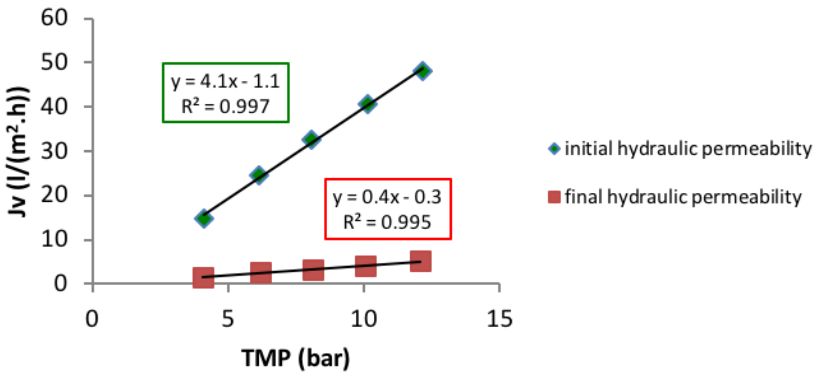

Figure 3-6Determination of hydraulic permeability using the NF90 membrane at 22◦C.

Table 3-5, it can observe that the NF270 membrane presents an excellent rejection of COD and TOC (Mänttäri et al., 2004; Majamaa et al., 2011), ranging from 94-97 %. The results of both experiments, at different temperatures, were similar in terms of the rejection of the polluting compounds. Additionally, and despite its lower permeability, the NF90 shows the highest rejection of TOC and COD, as expected due the lower MWCO of the membrane.

From these results it can be concluded that the NF270 membrane represents the better option for processing the wastewater from the rubber manufacturers. In fact, the ability of this membrane to produce a permeate stream with a sufficiently low level of TOC and COD, assures that the permeating stream can be disposed (it complies with the environmental legislation for industrial disposal) or reused in the productive process.

The retention of metals present in the wastewater streams from the rubber factories was also evaluated. Table 3-7 presents the results obtained when using the NF270 membrane, under different operating temperatures.

Table 3-6.Metal content in the permeate produced by the NF270 membrane, at 22◦C and 45◦C.

Na mg/l	S mg/l	K mg/l	Ca mg/l	Fe mg/l	P mg/l	Mg mg/l	Al mg/l	As mg/l	Si mg/l	Ba µg/l	Cu µg/l
Metal content – NF 270 temperature ≈ 22°C											
5.53	5.62	5.92	0.19	0.06	0.11	0.05	ND	6.57	0	ND	4.83
Metal content – NF 270 temperature ≈ 45°C											
8.77	7.86	10.46	0.38	0.05	0.14	0.10	ND	7.30	0.01	ND	6.04

When comparing these results with the ones shown in Table 3-2, it can be concluded that the NF270 membrane retains a significant fraction of the metals present in the wastewater from the rubber manufacturers. It should be also noticed that metal retention is better at a lower temperature. Operation at lower temperature represents the better option as it is also energetically more favourable.

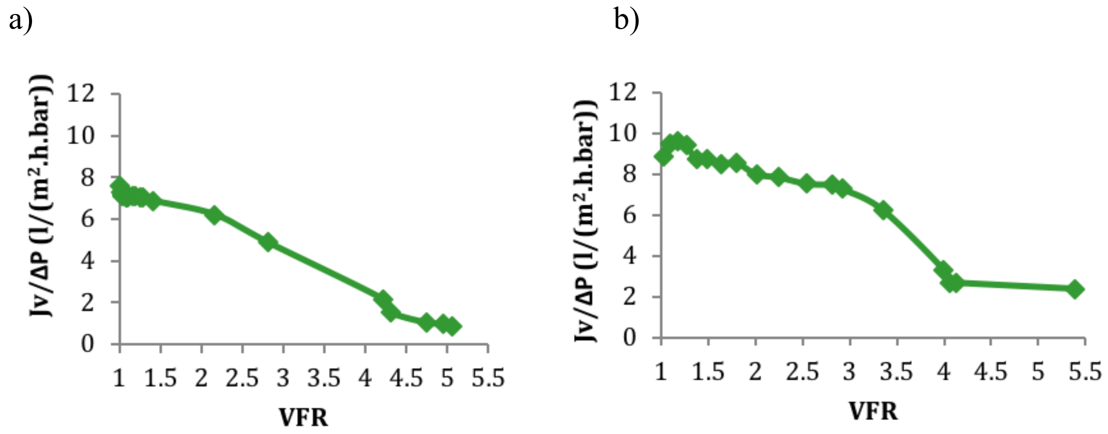

Figure 3-7Evolution of the apparent permeability of the NF270 membrane represented *versus* the volume reduction factor (VRF) **a)** 22 C **b)** 45ºC.

Figure 3-7 shows the evolution of the apparent permeability of the NF270 membrane represented *versus* the volume reduction factor (VRF). This parameter is particularly relevant when operating in batch mode, because it informs directly about the number of times the original feed volume was reduced (at a defined operating time).

A volume reduction factor of 5 to 5.5 may be considered as an excellent result, because it means that only one fifth of the original wastewater volume has to be further concentrated in the evaporator (leading to energy savings, as it will be discussed below), and also that the permeate represents most (80%) of the original volume. This facilitates disposal/reuse, subject to adequate chemical composition of the permeate. Higher volume reduction factors may be achieved if better fluid dynamic conditions are employed. The use of spiral wound modules at pilot scale may offer the opportunity to improve this result, due to the good fluid dynamic conditions assured by this type of module, with a reasonable energy input.

3.4.3 Pilot scale studies of the rubber wastewater using a concentration mode process

A pilot scale study was carried out based on the previous conclusions achieved at the laboratory scale. From the results discussed above, it was concluded that the NF270 membrane represents the better option for processing the rubber wastewaters. The combination of good retentive properties with its high throughput determined its selection for implementation in a pilot unit at an industrial site.

The concentration mode study performed in the pilot unit was carried out for ≈12hour at a low TMP (average TMP ≈5.1 bar) (Figure 3-8). The experiment started with an initial feed volume of 1000 L, which was processed until a final volume of concentrate of 100.51 L, representing a volume reduction factor, VRF, of ≈10.

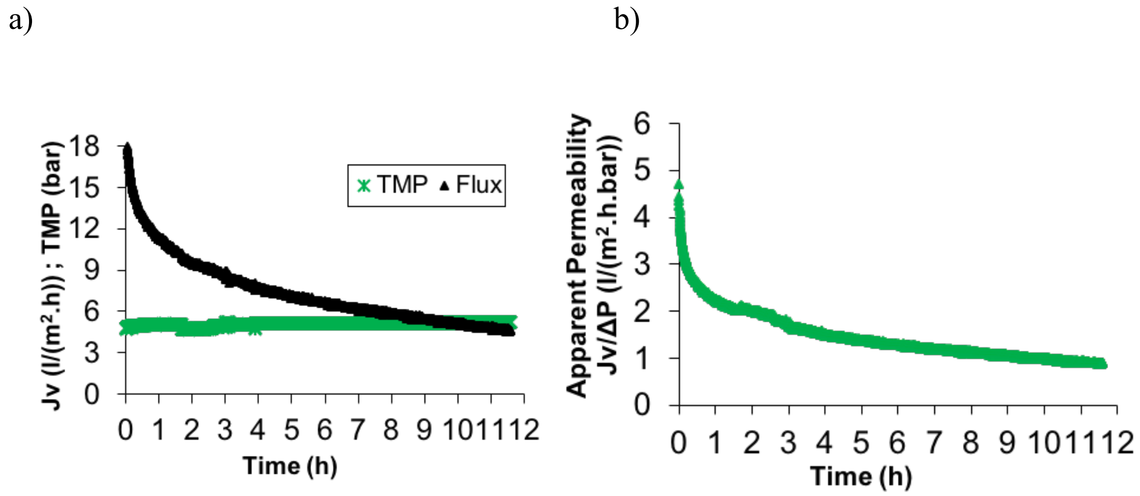

Figure 3-8Permeation results obtained at pilot-scale using a spiral wound NF270 membrane module with a filtration area of 7.6 m2 (average temperature of 26 C. **a)** Flux and TMP plotted along time **b)** Apparent permeability plotted along time.

Table 3-8 summarises the analytical data for the longer experiment performed at pilot scale. The COD in the retentate stream increased along time (due to the high rejection of the polluting compounds) and, as a consequence, the COD levels in the permeate stream also increase along time. Still, the overall cumulative permeate obtained after 11.9 h of operation, led to a volume reduction factor of 10 and presents a quality that complies with the European legislative requirements for water disposal (COD level lower than 2000 mg/l).

Table 3-7. Performance of the pilot-scale NF unit in terms of pollutant removal.

Operating time	Final Concentrate			Cumulative permeate				Rejection	
	COD	TOC	Conductivity	COD	TOC	Conductivity	Turbidity	COD	TOC
h	mg/l	mg/l	µS/cm	mg/l	mg/l	µS/cm	NTU	%	%
11.9	30260	5709	1256	1989	695.5	928	1.38	93.4	87.17

Membrane permeability was evaluated before and after operation at the industrial site and also after chemical cleaning, in order to evaluate the membrane permeability recovery (Figure 3-9). From these results, it was possible to understand the extent of fouling during wastewater processing and how efficient was the chemical cleaning protocol (Van der Bruggen 2001). It can be observed that the membrane chemical cleaning protocol allowed for a complete recovery of the membrane permeability.

After completion of all pilot-scale studies, the fouled membrane was removed from the module and sacrificed for fouling inspection. The membrane element was cut and opened for visual inspection and examined by SEM (images not shown). The cake layer formed on the membrane surface was removed and characterised in terms of total solids, volatile solids and metal content (see Table 3-9).

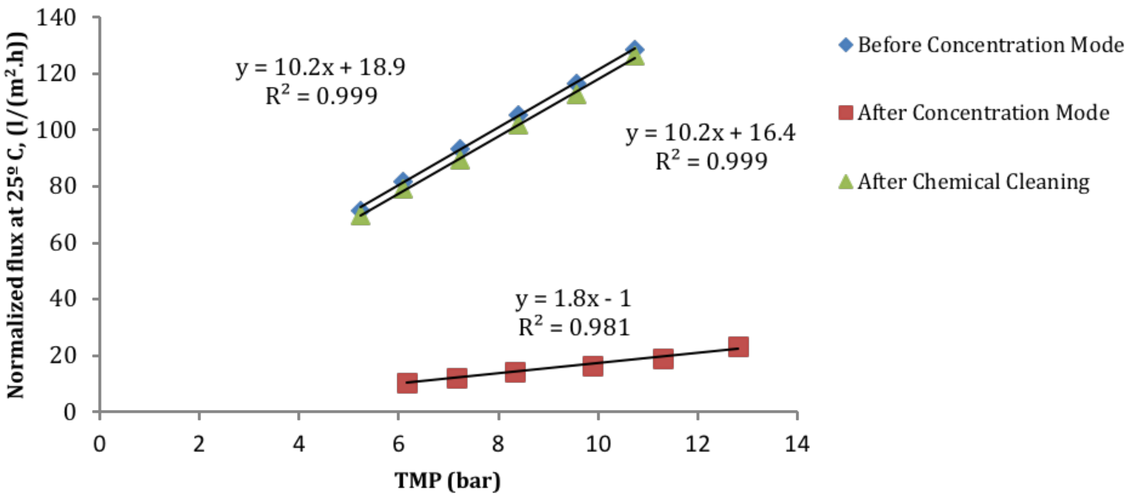

Figure 3-9.Hydraulic permeability in the beginning and end of the pilot scale experiment and after the chemical cleaning.

From visual inspection, it was noted that a dense and homogeneous cake layer was formed, covering all membrane surfaces. A ratio of VS/TS of 82% was obtained, which indicates that organic material has a high contribution for cake layer formation on the membrane surface. Table 3-9 also shows the metal content results, and it can be observed that silica, iron and copper are the major inorganic elements present in the cake layer formed.

Table 3-8.Characterization of the membrane cake layer.

Fouling characterization									
Total solids (g/cm^2)					Volatile solids (g/cm^2)				
2.33					1.9				
Chemical elements (mg/m^2)									
Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Si
0.1	0.8	8	68.2	102	39	6	0.2	0.6	193

It can be noted that organic fouling, especially the cake layer formed by the polymeric demoulding agent, is the main reason for membrane fouling when treating the rubber wastewater. Therefore, alkali cleaning with Ultrasil 11, which is used especially to remove organic fouling agents, was observed to be more effective for the recovery of membrane permeability.

From SEM images (not shown) of the NF270 membranes, it was observed a smooth and clean surface in a new membrane, in contrast with a rough surface of the fouled membrane and then again smooth and without visible deposits after a chemical cleaning membrane

3.4.4 Energy input analysis

The current process of wastewater treatment in rubber industries involves a pre-concentration of the rubber wastewater using a boiler, followed by a final concentration step in a dedicated evaporator. The volume of wastewater produced daily by the rubber manufacturer that collaborated in this study is around 70 m^3, which is reduced to a volume of 7 m^3 in the boiler with the simultaneous production of 63 m^3 of treated water. The 7 m^3 of concentrate are further processed in the evaporator to a final concentrate with a volume of 300 L.

The expenditure of energy in the boiler was determined to be 627.5 kWh per cubic meter of concentrate produced (data provided by the rubber manufacturer), based on daily measurements with the required electrical counters. Considering a cost of 0.0303 Euro/ kWh, from the contract between the company and the energy supplier, the resulting daily energy cost for operating the boiler (reduction of the volume of the wastewater from 70 m^3 to 7 m^3) is 627.5 x 7 x 0.0303 = 133.09 Euros. Additionally, the energy expenditure involved in the evaporator (concentration of 7 m^3 of pre-concentrated wastewater to a final volume of 300 L of final concentrate) was determined to be 23.0 Euros per m^3 of feed, also based on measurements with the required electrical counters. Therefore, the costs related with energy expenditure in the evaporator correspond to a total of 7 x 23.0 = 161.0 Euros.

The overall energy expenditure to convert 70 m^3 of effluent into a concentrate with a volume of 300 L is, therefore, 133.09 + 161.0 = 294.09 Euros. This result corresponds to an energy cost of 4.2 Euros per m^3 of original effluent to be treated. Other operating costs (cleaning and anti-scaling solutions) should be added to this value but, in order to compare with the energy expenditure of the alternative solution discussed in this work this is the value that should be used as a reference.

For the process presented in this work an electrical counter was installed in the cabinet of the nanofiltration pilot unit and operated at the rubber factory facilities, with the objective of measuring accurately the energy expenditure associated with the NF process. All electricity consumption by all components of the pilot, including the feed pump, the pressure pump, electrical valves, sensors, the touch screen, etc., were tracked by the electricity counter. There is no data communication between the electricity counter and the PLC of the pilot, and so manual recording was used during the pilot studies. The energy consumption was registered during the concentration mode study at the rubber factory. Table 3-9 summarizes all the key parameters in this test.

Table 3-9. Summary of the NF pilot results in the study performed with 1 m3 of rubber wastewater.

Operating Time	Average TMP	Permeate produced	Energy consumption	Hourly consumption	Consumption per m3 permeate produced
h	bar	m 3	kWh	kW	kWh
11.9	5.1	0.899	10	0.84	11.1

The NF unit was operated at a relatively constant transmembrane pressure (TMP) and, therefore, the permeate flux decreased over time. The energy consumption rate was 10 kWh for 11.9 working hours and with a volume reduction factor (VRF) of 10 times, which means that with an industrial, NF installation an original volume of 70 m^3 of effluent will be converted to a concentrate effluent with a volume of 7 m^3.

If a full scale NF plant is installed at a rubber manufacturer for treatment of the effluent, the key process parameters, such as the membrane flux and volume reduction factor, can be designed based on the results obtained from the pilot studies. It shall be noticed that the pilot plant, which operated with only one membrane module, may require a higher specific energy consumption than a full scale plant, where the same set of pumps and control system will serve for multiple membrane modules.

As was mentioned above, the overall energy expenditure to convert 70 m^3 of effluent into a concentrate with a volume of 300 L is, using the actual boiler + evaporator process, 133.09 + 161.0 = 294.09 Euros. The first value corresponds to the energy expenditure to concentrate the waste water in the boiler from 70 m^3 to 7 m^3, and the second parcel corresponds to the energy expenditure to concentrate this 7m^3 to a final volume of concentrate with 300 L.

The proposed NF process allows for daily conversion of 70 m^3 of wastewater into a concentrate of 7 m^3, which has to be further processed in the evaporator. The total energy expenditure for processing 70 m^3 by nanofiltration is 70 m^3 × 10 kWh/m^3 × 0.0303 €/kWh = 21.21€. The 7 m^3 obtained after NF processing have to be fed to the evaporator. Therefore, the energy costs of the overall process of NF followed by evaporation are 21.21 + 161 = 182.21 Euros, which represents 62% of the cost associated with the actual boiler + evaporator process under operation at Cikautxo (cost of 294.09 Euros).

3.5 Conclusions

From this study it was concluded that a nanofiltration treatment unit combined with a final effluent concentration using an evaporator leads to significant energy savings. The use of a NF270 nanofiltration membrane represents the best option for processing rubber wastewater. This membrane allows the rejection of over 93% of the COD and the COD levels in the permeate comply with the European legislative requirements for water disposal (COD $\leq$ 2000 mg/l).

During each cycle of membrane nanofiltration, it was observed that the membrane module becomes fouled, mainly by organic compounds present in the wastewater, although also by inorganic compounds such as metals. It was found that the alkali cleaning with Ultrasil 11(particularly efficient for removal of organic fouling agents) was more relevant, considering the character of the foulant compounds, rather than the acid cleaning Ultraperm 75.

An integrated process combining membrane nanofiltration and evaporation was developed in this study and the results obtained allow for clearly concluding that this process leads to a significant reduction of the total energy expenditure required to treat the wastewater. The energy expenditure of the new process represents only 62% of the current energy consumption. Considering the general tendency for increasing energy costs it may be anticipated that the approach and the solution developed in this work will make it possible to achieve even larger reduction in energy costs.

It should be stressed that the proposed integrated process can be easily retrofitted to industrial sites under operation, with a high impact in terms of energy savings.

3.6 References

Agana B. A., Reeve D., Orbell J. D. , 2011. An approach to industrial water conservation – A case study involving two large manufacturing companies based in Australia.

Anglada A., Urtiaga A. M. and Ortiz I. , 2010. Laboratory and pilot plant scale study on the electrochemical oxidation of landfill leachate. Journal Hazardous Materials, 181 (1-3), 729-735.

Anotai J., Tontisirin P. and Churod P. , 2007. Integrated treatment scheme for rubber thread wastewater: sulfide precipitation and biological processes. Journal Hazardous Materials, 141(1), 1-7.

Asia I.O., Akporhonor E.E., 2007. Characterization and physicochemical treatment of wastewater from rubber processing factory. International Journal of Physical Science, 2, 61-67.

Barredo-Damas S., Alcaina-Miranda M. I., Bes-Piá A., Iborra-Clar M. I., Iborra-Clar A. and Mendoza-Roca J. A. (2010) Ceramic membrane behavior in textile wastewater ultrafiltration. Desalination, 250 (2), 623-628.

Darton T., Annunziata U., del Vigo Pisano F. and Gallego S. (2004) Membrane autopsy helps to provide solutions to operational problems. Desalination, 167, 239-245.

Fu F., Wang Q. (2011) Removal of heavy metals from wastewaterions from wastewater: A review. Journal of Environmental Management, 92, 407-418.

Klüpfel A. M. and Frimmel F. H. (2010) Nanofiltration of river water — fouling, cleaning and micropollutant rejection. Desalination, 250 (3), 1005-1007.

Kurt E., Koseoglu-Imer D. Y., Dizge N., Chellam S. and Koyuncu I. ,2012. Pilot-scale evaluation of nanofiltration and reverse osmosis for process reuse of segregated textile dyewash wastewater. Desalination, 302, 24-32.

Lee Y. K., Won Y.-J., Yoo J. H., Ahn K. H. and Lee C.-H. ,2013. Flow analysis and fouling on the patterned membrane surface. Journal of Membrane Science, 427, 320-325.

Madaeni S. S. and Mansourpanah Y. ,2006. Screening membranes for COD removal from dilute wastewater. Desalination ,197 (1-3), 23-32.

Majamaa K., Warczok J., Lehtinen M. ,2011. Recent operational experiences of FILMTEC ™ NF270 membrane in Europe. Water Science Technology, 64 (1), 228-232.

Mänttäri M., Pihlajamäki A. and Nyström M. ,2002. Comparison of nanofiltration and tight ultrafiltration membrane in the filtration of paper mill process water. Desalination, 149, 131-136.

Mänttäri M., Pekuri T. and Nyström M. ,2004. NF270, a new membrane having promising characteristics and being suitable for treatment of dilute effluents from the paper industry. Journal of Membrane Science, 242 (1-2), 107-116.

Qdais H.A., Moussa H.,2004. Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination 164, 105-110.

Rosman N. H., Anuar A.Nor, Othman I., Harun H., Sulong Abdul Razak M. Z., Elias S. H., Mat Hassan M. A., Chelliapan S. and Ujang Z, 2003. Cultivation of aerobic granular sludge for rubber wastewater treatment. Bioresource Technology, 129, 620-623.

Teixeira A. R. S., Santos J. L. C. and Crespo J. G. ,2009. Sustainable membrane-based process for valorisation of cork boiling wastewaters. Separation and Purification Technology, 66 (1), 35-44.

Urtiaga A., Rueda A., Anglada A. and Ortiz I. ,2009. Integrated treatment of landfill leachates including electrooxidation at pilot plant scale. Journal Hazardous Materials, 166(2-3), 1530-1534.

Van der Bruggen B., Vandecasteele C. ,2001. Flux Decline during Nanofiltration of Organic Components in Aqueous Solution. Environmental Science Technology. 35, 3535-3540.

Vijayaraghavan K., Ahmad D. and Yazid A. Y. ,2008. Electrolytic treatment of Standard Malaysian Rubber process wastewater. Journal Hazardous Materials, 150(2), 351-356.

Wei X., Wang Z., Fan F., Wang J. and Wang S. ,2010. Advanced treatment of a complex pharmaceutical wastewater by nanofiltration: Membrane foulant identification and cleaning. Desalination, 251 (1-3), 167-175.

Xu P., Bellona C. and Drewes J. E. ,2010. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: Membrane autopsy results from pilot-scale investigations. Journal of Membrane Science, 353 (1-2), 111-121.

Chapter

4

A Continuous Nanofiltration + Evaporation Process for High Strength Rubber Wastewater Treatment, Water Reuse and Zero Liquid Discharge

4.1 Summary

In the rubber parts industry, the treatment of wastewater from the demolding process utilising polymeric agents, traditionally poses a challenge. This is due to the high strength (COD>10,000 mg/L) and low biodegradability of the main organic content in the wastewater. Typically, a thermal process of boilers followed by evaporators, is commonly employed to treat the wastewater. Besides frequent boiler maintenance due to severe fouling caused by the nature of the wastewater, high energy costs are nearly prohibitive. At Cikautxo, a Spanish rubber part manufacturer, the energy costs are in the region of €4.2/m^3 treated wastewater.

Following an initial lab-scale membrane screening, a pilot study was carried out at Cikautxo in 2012. Nanofiltration with a NF270 membrane was tested and reject stream was collected and used to feed a full size evaporator.

Without pre-treatment, the rate of the nanofiltration process was maintained at a permeate flux of 11 L/m^2.h^{-1} for periods of over 30 h in-between flux recovery cleanings. The use of the NF process gave a significantly improved feed water quality, consequently improving the local capacity of the evaporator when compared with the use of the boiler blow down method. The NF + evaporator solution was shown to effectively reduce energy costs by 55% (from €4.2/m^3 to €1.9/m^3 treated wastewater).

Published as: Xin G., Lopes P.M., Crespo J.G., Rusten B., 2013, A Continuous nanofiltration + evaporation process for high strength rubber wastewater treatment and water reuse, Separation and Purification Technology, 119, 19-27.

4.2 Introduction

The treatment of wastewater from the demolding process in rubber part manufacturing presents a challenge. In particular, when utilising polymeric demolding agents such as Getren^{TM}, (a polyether and non-ionic surfactant). This is due to its high strength (COD>10,000 mg/L) and low biodegradability (Tang et al., 2010) of the main organic content in the wastewater. Membrane filtration was proposed as a preferred treatment technology in two technology screening studies (Fuentes et al., 2000 ; Urkiaga and Fon, 1999).

Cikautxo is a major rubber parts manufacturer in the Basque Country in Spain. The factory produces approximately 70 m^3/d of wastewater from the rubber manufacturing process, including moulding, autoclaving and demolding . A polymeric release agent, Getren^{TM}, is used in the process and ends up in the wastewater. This polymeric release agent contributes to the majority of the chemical oxygen demand (COD) in the wastewater. Currently, a thermal process is employed to treat wastewater at Cikautxo, where boilers followed by evaporators are used for wastewater treatment (Heins et al., 2005). Besides frequent boiler maintenance due to severe fouling caused by the wastewater, an energy cost of approximately €4.2/m^3 treated wastewater is nearly prohibitive.

In an initial lab scale study (Lopes et al., 2013) both ultrafiltration (UF) and nanofiltration (NF) were tested for treating the rubber wastewater from Cikautxo. Although UF allowed relatively high water fluxes, the rejection of contaminants in the wastewater in terms of COD and TOC (total organic carbon) was clearly insufficient to comply with European legislation (the Directive 96/61/EC) for effluent discharges. Permeate generated from nanofiltration using either a NF90 or a NF270 module (Dow, Midland, Michigan, USA) can meet the effluent discharge requirement (<2000 mg COD/l). For the large scale study, the NF270 membrane was chosen due to its higher membrane permeability (Artur et al., 2007; Bellona et al., 2010; Boussu et al., 2006). In order to accomplish maximize reuse of the wastewater, an existing evaporator at Cikautxo was tested for further volume reduction of the membrane reject stream.

Two modes of operation with the use of NF technology are used: continuous mode and concentration mode. Continuous mode operation continuously provides a reject stream is typically used in full scale membrane applications (Ramaswamy et al., 2013). However, in processes where the flow rates are small and discontinuous, the concentration mode is often used (Dow Water & Process Solutions). The reject is sent back to the NF feed tank in the concentration mode operation.

A pilot study was carried out in 2012 at Cikautxo, in which the continuous mode operation was used. The treatment results from the concentration mode study are described in another paper (Lopes et al., 2013). This paper describes the operational and economic challenges of the NF270 process and the integration with the evaporation process. The pilot study had the following objectives:

- Maintaining a competitive permeate flux with a minimal cleaning frequency;
- Meeting the industrial water reuse standards or discharge standards;
- Achieving the desired evaporator performance using a membrane-concentrated feed stream;
- Minimizing energy input to the integrated system;
- Achieving at least 99% of water recovery;
- Minimizing the amount of waste for off-site treatment.

4.3 Materials and Methods

4.3.1 The pilot system

The pilot process involved the integration of nanofiltration and evaporation technologies for rubber wastewater treatment. A NF pilot and a full scale evaporator were used in the study. Figure 1-2 shows the process diagram. The NF pilot and evaporator were equipped with a programmable logic controllers (PLCs) for data acquisition and to facilitate automation and control. From the NF pilot, the following parameters were recorded in the PLC: date, time, pressure after feed pump, pressure after pressure pump, retentate pressure, permeate flow, retentate flow, reject flow, pressure pump frequency and permeate temperature. From the evaporator the following parameters were recorded in the PLC: date, time, pressure in water drum, temperature in water drum, steam flow and steam pressure. An electricity meter was installed in the electricity cabinet of the NF pilot. The electricity consumption by all the components on the pilot, including a feed pump, a pressure pump, electrical valves, sensors, touch screen etc., was logged by the electricity meter.

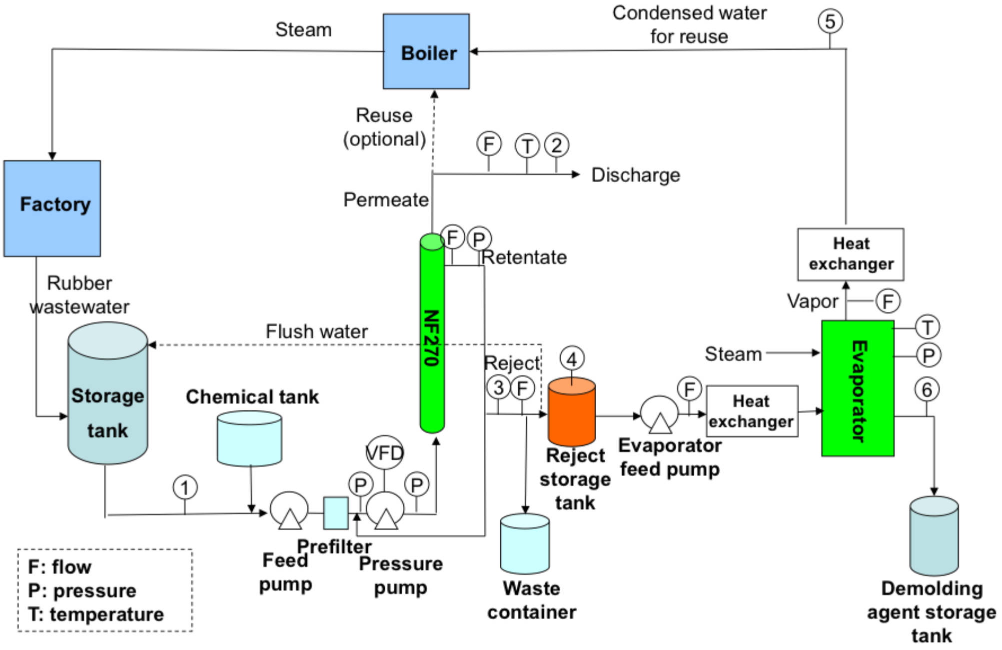

Figure 4-1 Schematic process diagram of the pilot system at Cikautxo. Sensors for flow, pressure and temperature are labelled as F, P and T, respectively. Sampling locations are numbered. VFD: variable frequency drive.

4.3.2 The membrane

Two NF270-4040 modules (active membrane area of 7.6 m^2 per module) were used during the pilot study. Both membrane modules used went through a compaction process with tap water at 12-13 bar for at least 3 hours before treating any wastewater. A magnesium sulphate rejection test was carried out for one of the modules and the test results showed a 98.2% rejection of magnesium sulphate under 4.8 bar pressure and a 27% water recovery, which indicates an adequate membrane performance and module integrity. Polypropylene (PP) cartridge filters with 1 μm pore size were placed before the NF270 module for removing large particles in the wastewater.

4.3.3 NF operation

The NF pilot was operated in a continuous mode, where the permeate flux is an independent variable. This was preset in the PLC by the operators. The TMP (trans-membrane pressure) was a dependent variable, resulting from the preset permeate flux and membrane permeability. Flushing to allow the removal of accumulated material on the membrane surface was employed in the NF operation. During a flushing cycle the pressure pump was turned off for a preset duration with the feed pump on. At the same time, a bypass electrical valve in the reject line was opened by the PLC. Flushing differs from backwashing which typically employs permeate to backwash the membrane from the permeate side. The flushing operation allows to release high pressure in the NF. Consequently, part of the retentate in the system is replaced by feed water and high flow of retentate during the pressure release will create high shear forces that clean the membrane surface periodically.

4.3.4 The evaporator

The evaporator used in the pilot study is a full size drum type evaporator with a design capacity of 5 m^3 per day with the boiler blowdown. The evaporator is always operated in a batch mode. In each batch the evaporator starts with an empty drum. A feed pump is used to feed the drum and the pump is controlled by a level switch that is installed inside the drum. It is believed that the evaporator achieves the best performance in terms of distillate flow rates when the water level in the drum is slightly higher than half way of the drum height and varies within a small range. The evaporator is periodically emptied for discharging residue (from the NF process) to the demolding agent storage tank when a certain amount of wastewater has been processed by the evaporator. Feeding does not commence during drying. The absence of distillate from the evaporator indicates the end of the drying step.

4.3.5 Analytical methods

During the period of operation, feed, membrane permeate and membrane reject were analyzed for total COD, oil and grease, viscosity, total suspended solids (TSS), total volatile solids (VSS), metals, pH, conductivity and turbidity. Hach Lange kits were used for analyses of TOC (LCK385 and 386) and COD (LCK 014, 414 and 514). The amount of oils and grease was measured by a gravity method. The water samples were passed over a solid phase extraction (SPE) column, in which oil and grease was retained by a solid absorbent. This was later eluted with *n*-hexane. The *n*-hexane was allowed to evaporate, and the residue corresponded to concentrations of oil and grease in the original samples (Uriker internal test procedure: PEN/COA-024). Viscosity was measured by using a viscometer (Brookfield, DV-I Prime). TSS and VSS measurements followed the standard methods with 1.2 μm pore size glassfiber filters. Inductively coupled plasma atomic emission spectrophotometres (ICP-AES) equipped with a radio-frequency (RF) generator of 40.68 MHz, a Czerny-Turner type monochromator with 1.00 m (sequential), an AS500 autosampler and data acquisition software was employed to determine the concentration of metals.

4.3.6 Membrane autopsy

Membrane autopsy was conducted with the first NF270 module after it was removed from the pilot unit in April. The membrane module was opened and unrolled for visual inspection. A sample of fouled membrane was removed and a cleaning protocol was performed with a bench scale cross flow filtration unit (GE Infrastructure Water & Process Technologies). Membrane surface and membrane cross-sections were imaged by Field Emission Scanning Electronic Microscopy (Jeol JSM – 7001F).

4.4 Results and Discussion

4.4.1 Wastewater characteristics

The rubber wastewater is a type of high strength wastewater with relatively low conductivity. Temperatures of the wastewater were between 35-45°C at the end of the pipe to the wastewater storage tank. Table 4-1 summarises the main characteristics of the raw wastewater.

The strength of the wastewater varied significantly during the piloting period. It ranged from <5000 mg/L COD to >22000 mg/L COD. But the COD-to-TOC ratio was relatively constant, indicating no shifting of the main COD contributor during the testing period.

Table 4-1. Characteristics of wastewater at Cikautxo.

Parameter	COD	TOC	COD/TOC ratio	TSS	VSS	VSS/ TSS ratio	O&G	pH	Cond.	Turb.
Unit	mg/L	mg/L		mg/L	mg/L		mg/L		µS/cm	NTU
Average	14829	4420	3.6	54	49	0.92	15.1	6.4	766	44
Standard deviation	6269	1520	0.2	17	15	0.05	11.7	0.8	192	15
Number of Samples	42	17	17	20	20	20	2	34	35	26

4.4.2 Results from continuous mode membrane study

Selected test results are shown in Figure 4-2.

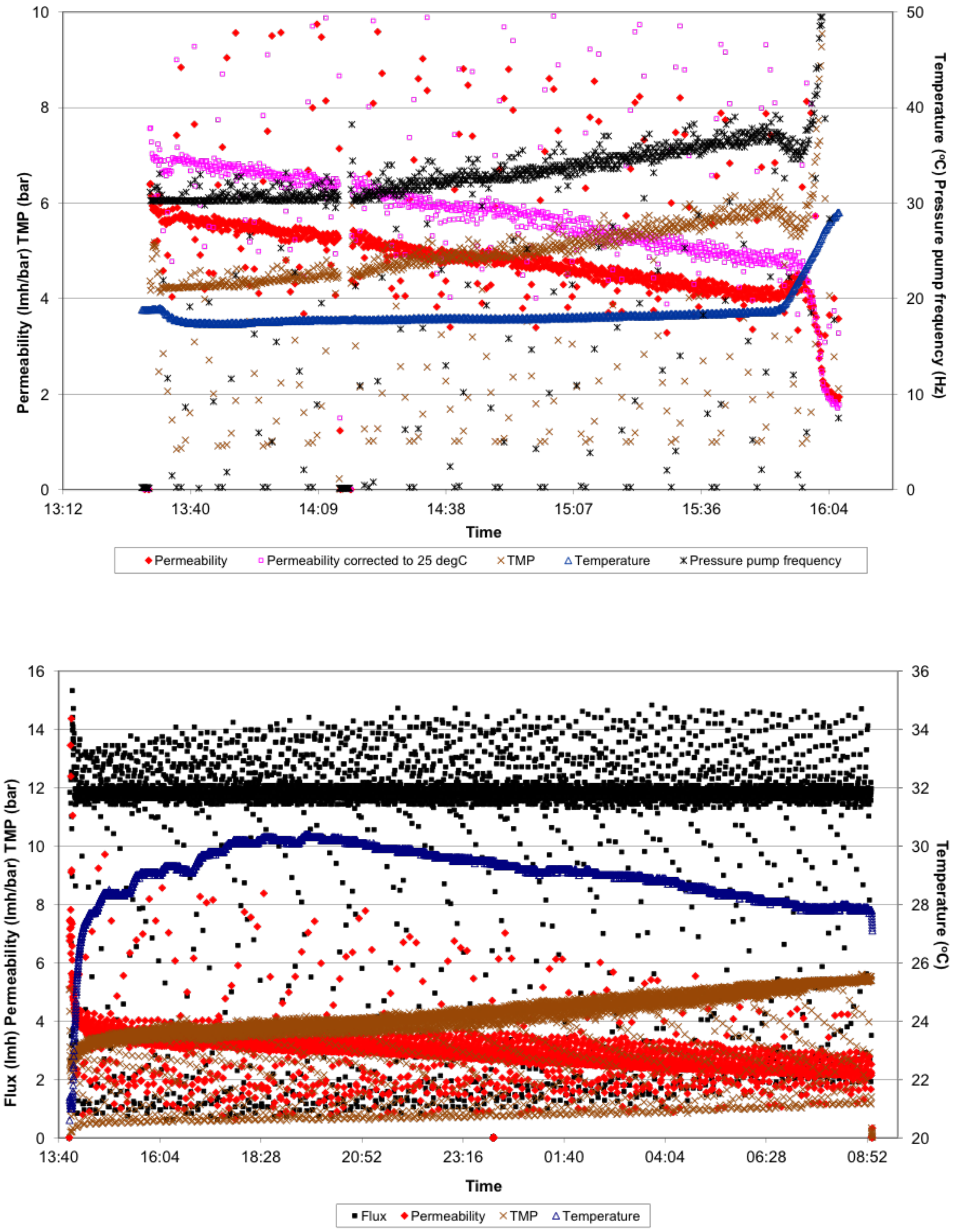

Figure 4-2.Flux, TMP, permeability and temperature for the study performed on the 22nd of March where flux was set at 23.6 L/m^2/h (lmh) (A) and the 27th-28th of April (B).

4.4.2.1 Permeate flux

A wide range of permeate fluxes were tested in this study. At relatively high permeate fluxes TMP rose quickly and the membrane permeability dropped quickly. An example is shown in Figure 4-2A where a permeate flux of 23.6 lmh was maintained. When membrane permeability is below 2 L/m^2.h^{-1}bar^{-1}, recovery cleanings need to be executed for recovering membrane permeability. However, more sustainable membrane performance was observed at lower permeate fluxes imposed (Figure 4-2B). Table 4-2. Summary of the NF pilot results, including calculated energy consumption data, for the tests with rubber wastewater as the feed water. summarizes results from three continuous tests. At an average flux of 11.3 L/m^2.h^{-1}an operation time of 33.3 hours was maintained before the membrane permeability dropped below 2 L/m^2.h^{-1}bar^{-1} during the 20th-22nd of April. Similar performance was also observed on the 23rd and the 27th of April. This can be explained with the "critical flux" phenomenon. At high permeate fluxes strong concentration polarization and high compaction of the deposit layer (cake layer) lead to quick membrane fouling and subsequently fast TMP increases (Schafer et al., 2005). Therefore, it is recommended to maintain a permeate flux below 12 L/m^2.h^{-1} to obtain a sustainable membrane performance when treating the rubber wastewater at Cikautxo.

Table 4-2. Summary of the NF pilot results, including calculated energy consumption data, for the tests with rubber wastewater as the feed water.

Test	Date	Operating hours	Average TMP (bar)	Average flux (L/m^2-h)	Permeate produced (m^3)	Water recovery (%)	Energy consumption (kWh)	Hourly consumption (kW)	Consumption per m^3 permeate produced (kWh)
1	20-22 Apr	33.3	2.4	11.3	2.88	82.4	29	0.85	9.8
2	23-24 Apr	27.2	2.7	11.0	2.28	79.2	22	0.82	9.8
3	27-28 Apr	19.2	3.9	11.1	1.61	>85*	17	0.88	10.5

* Due to the limitation of the flow meter measurement range, no data were recorded when the flow rates of the reject stream were lower than 0.25 L/min.

4.4.2.2 Water recovery

A wide range of water recovery, namely 70 %-93 %, was tested during this study. Due to the limitation of the flow meter measurement range, the reject stream flow rates were recorded as 0 L/min when the actual flow rates were lower than 0.25 L/min. This means that the highest water recovery that can be properly recorded is 85% when the permeate flow is at 1.42 L/min (11.2 $L/m^2.h^{-1}$) or 90 % when permeate flow is at 2.25 L/min (17.8 $L/m^2.h^{-1}$). At the beginning of the study high water recoveries (>85 %) were used when high fluxes were tested. Later, only moderate water recoveries (78-83%) were used due to lower permeate flux imposed. It is found that a low water recovery of 70% did not help much to maintain a stable membrane performance when the permeate flux was high (23.5 $L/m^2.h^{-1}$). In addition a high water recovery (>85%) did not cause a quick membrane fouling when a low flux was imposed (27th of April, Figure 2B).

4.4.2.3 COD rejection

The first NF270 membrane had over 90% COD rejection on the rubber wastewater in the first two weeks (the 7th-22nd of March), but the COD rejection went down to below 80% and the permeate COD went up to over 2000 mg/L after the 11th of April (Figure 4-3A). The reduced COD rejection was probably caused by intensive chemical cleanings employed in this study. Details about the chemical cleaning protocols are discussed in Section 4.4.2.7. The strength of chemical cleaning was reduced for the second membrane. The COD rejection for the second membrane was over 95% during the overall testing period (Figure 4-3B). Therefore, we conclude that high COD rejection can be achieved with the NF 270 membrane, but can be significantly reduced by frequent use of high strength chemical cleanings.

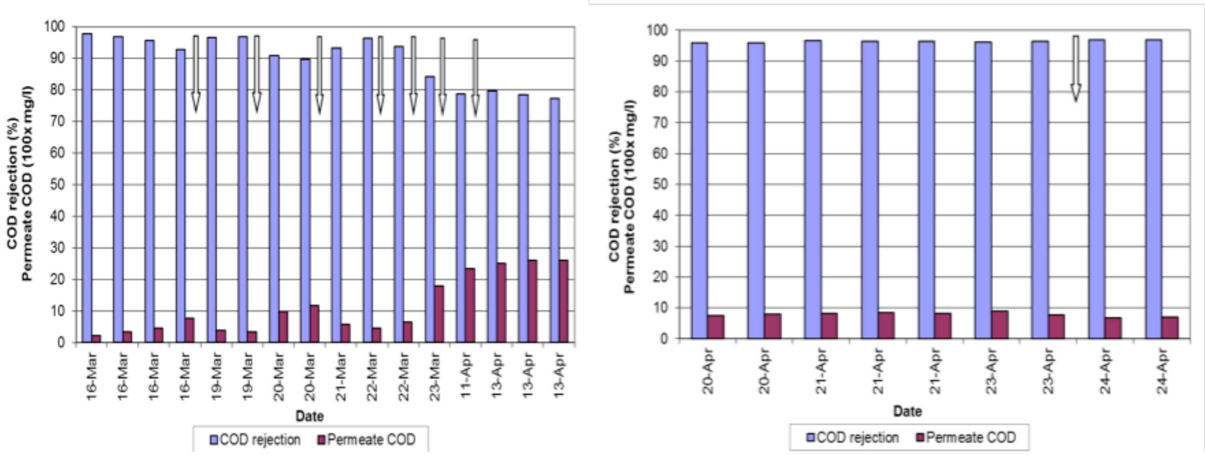

Figure 4-3: COD rejection and permeate COD values for the first membrane (A) and the second membrane (B) with the rubber wastewater as feed water. White arrows indicate when chemical cleanings were carried out.

4.4.2.4 Can NF permeate be reused as boiler feed water?

Table 4-3summarizes the quality of the NF permeate collected in this study with comparison to the boiler feed water requirements. Except for total hardness the characteristics of the NF permeate meet the boiler feed water requirements. Therefore, we conclude that the NF270 permeate can be used as boiler feed water if the total hardness in the permeate is further reduced. Cikautxo is considering using a softener to reduce total hardness in NF permeate and to reuse permeate as process water in future full scale applications.

Table 4-3. Quality of the NF permeate vs. the boiler feed water requirements.

Elements	Unit	Permeate 11 March	Permeate 16 March	Permeate 16 March	Boiler feed water requirements [12]
Conductivity	µs/cm	562	352	375	< 6000
Total hardness	mg/L as $CaCO_3$	24	40	37	< 0.5
Si	mg/L as SiO_2	3.88	4.06	3.93	< 150

4.4.2.5 Flushing

Flushing is an important operation to maintain membrane permeability (Dow Water & Process Solutions). The flushing effects were not significant with long time intervals. With short time intervals it was found that flushing for 5 seconds in every minute (5 s/min) was the optimal setting for maintaining stable membrane permeability without reducing much of the membrane filtration time. The flushing procedure did not lower the water recovery since the flush water was sent back to the feed tank. It is believed that the flushing has 2 major benefits for sustaining the membrane performance: (1) cleaning of the membrane surface at high flush water velocity and (2) relaxing membrane by temporarily lowering TMP.

Subsequently, all tests employed a 5 s/min flushing. Due to the membrane operation down times (shutdown of the pressure pump) introduced by flushing and frequent (every 5-10 s) recording intervals in the PLC, the PLC data for flux and TMP appear scattered, which can be seen in Figure 2.

4.4.2.6 Temperature effects

In surface water treatment and most of wastewater treatment applications, higher temperatures improve membrane permeability due to lower water viscosity (American Water Works Association Research Foundation, 1996) and lower degrees of concentration polarization at the membrane surface associated with higher temperatures (Agashichev, 2009). Similar temperature effects were also observed in this study when feed water temperatures rose from 19°C to 23°C during the test on the 22nd of March as shown in Figure 4-2A. Meantime, it was also clearly observed that membrane permeability quickly dropped once the feed water temperature was 24°C or higher in several tests (one of the test results is shown in Figure 4-2A, where the permeate flux was 23.6 $L/m^2.h^{-1}$). When the water level in the feed tank was low, the level switch opened the feed valve and warm wastewater started flowing into the feed tank at 15:53, which raised the feed water temperature from 19°C to 28°C in 14 minutes. In the first 5 minutes the membrane permeability actually improved due to lower water viscosity and lower degrees of concentration polarization at higher water temperatures, but then the membrane permeability quickly dropped when the feed water temperature kept rising from 24°C to 28°C. This suggests that the feed water temperature, when higher than 24°C, played an important role during the catastrophic drop of the membrane permeability. However, the temperature effect becomes insignificant when the permeate fluxes were set at 11-12 $L/m^2.h^{-1}$ (Figure 4-2B). It is not clear to the authors why high temperatures caused the catastrophic drop of the membrane permeability at high membrane fluxes.

4.4.2.7 Chemical cleaning

Two commercial cleaning chemicals, Ultrasil 11 and Ultrasil 75 (both from EcoLab), were used in this study. The alkali cleaning with Ultrasil 11 mainly targets the organic foulants on the membrane and the acid cleaning with Ultrasil 75 mainly targets the inorganic foulants on the membrane.

The two new membranes had membrane permeability of 5.89 and 6.26 lmh/bar, respectively. With the first membrane 0.5% Ultrasil 11 was used for alkali cleaning. A cleaning duration of 60 min recovered over 90% of membrane permeability, while a cleaning duration of 30 min only recovered approximately 50% of membrane permeability. Occasionally, higher than new membrane permeability was observed for the membrane after a 60 min Ultrasil 11 cleaning, which indicates that the 0.5% Ultrasil solution may be damaging the membrane. The decreasing COD rejection as shown in Figure 4-3A also suggests a damaged membrane. Therefore, 0.2% Ultrasil 11 was used for cleaning the second membrane, which was found to be able to recover approximately 60% of the membrane permeability. Therefore, it is recommended to use 0.2% Ultrasil 11 cleaning on a routine basis and use 0.5% Ultrasil 11 cleaning when an in-depth membrane recovery cleaning is required. Meantime, the cleaning protocol, mainly in terms of chemical composition, needs to be improved to both enhance the membrane permeability recovery and prolong the membrane lifetime.

The acid cleaning with Ultrasil 75 did not show much permeability improvement on the tested membrane, which indicates insignificant inorganic fouling.

4.4.3 Membrane autopsy and fouling mechanism

Membrane autopsy was conducted with the first NF270 module after it was removed from the pilot unit. The module was cut open and samples were taken for making scanning electronic microscopy images. Figure 4-4 shows an inside image of the open NF270 module, where a cake layer made of organics and solids was formed on the surface of the membrane.

Figure 4-5 shows cross-section and surface SEM images of the NF270. A dense cake layer can be seen in both images. Portions of the cake layer were scrubbed off the membrane and used for total solids (TS) and volatile solids (VS) analyses. A ratio of VS/TS of 82% was obtained, which indicates that organic materials make up the majority of the cake layer on the membrane.

The major inorganic elements in the cake layer are silica, iron and copper indicated by the ICP results shown in Table 4-4.

Aggregation and deposition of rejected hydrophilic polymers, a type of colloids, together with rejected salts, oil droplets and fine solids at the membrane surface forms a thin cake layer. On the top of the cake layer there is a polymer polarization layer where concentration polarization occurs. The solute (in this case the polymers) back-diffusion may be hindered in the presence of the cake layer, thus elevating the membrane surface solute concentrations and resulting in higher trans-membrane osmotic pressures (Hoek et al., 2002). Therefore, we believe that double effects of the concentration polarization plus the cake layer, so called cake-enhanced concentration polarization by Hoek and Elimelech, 2003, accelerated fouling of the NF270 membrane during the treatment of the rubber wastewater.

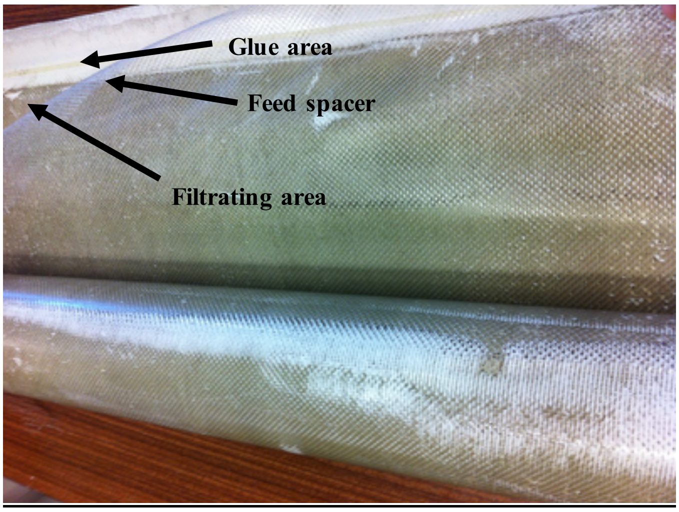

Figure 4-4.Inside image of the 1st NF270 module.

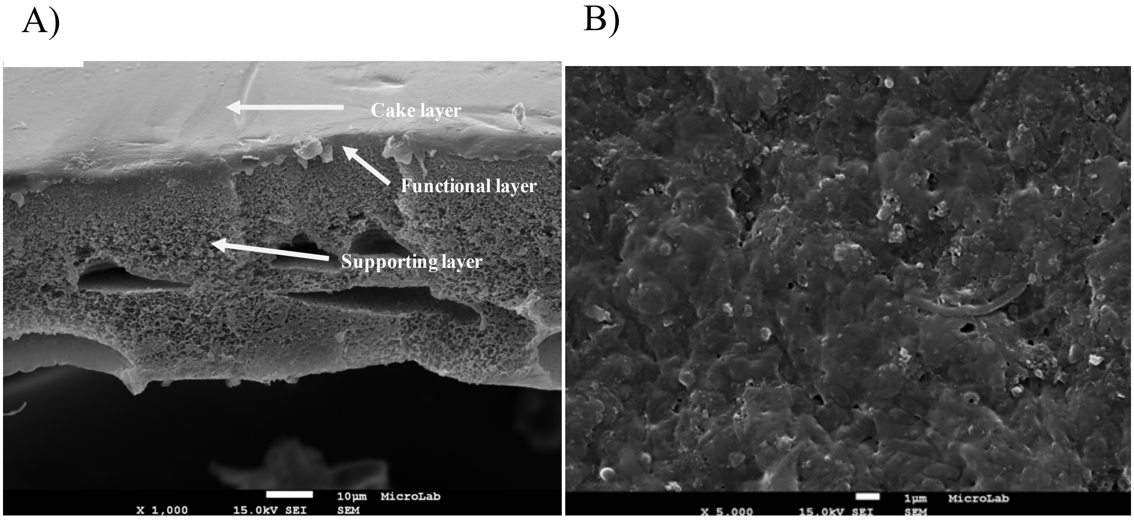

Figure 4-5. SEM image of the 1st NF270. SEM image of cross-section (A) and membrane surface (B).

Table 4-4. ICP analytical results for inorganic contents in the layer scraped off from membrane surface.

Element	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Si
Mass (mg/m^2)	0.1	0.8	8	68.2	102	39	6	0.2	0.6	193

4.4.4 Evaporator testing results

Several tests were carried out in the full-scale evaporator at Cikautxo with the NF270 reject as the feed water. One test with boiler blowdown was also conducted to draw the baseline for evaluating the evaporator performance with the NF270 reject. Results from three evaporator tests are summarized in Table 4-5 and Figure 4-6. The two tests with NF reject showed higher condensed distillate flow rates than for the test with boiler blowdown (Figure 4-6). Distillate conductivity was lower for NF reject than for blower blowdown and the retentate concentration was higher. These results indicate that the evaporator performance was slightly improved with the NF reject. But it should be noticed that the boiler feed water was pH adjusted and contained extra salt from sodium hydroxide which is used for pH adjustment at Cikautxo. The extra salt from sodium hydroxide, which ends up in the boilder blowdown, may have deteriorated the evaporator performance.

Table 4-5. Summary of three evaporator test results.

Test	Date	Feed water	Amount of feed water (L)	Test duration (h)	Amount of retentate (L)	COD of retentate (g/L)
1	26 Apr	NF reject	600	3.4	13	1550
2	27 Apr	Boiler blowdown	600	4.0	40	1126
3	04 May	NF reject	1000	6.3	28	1683

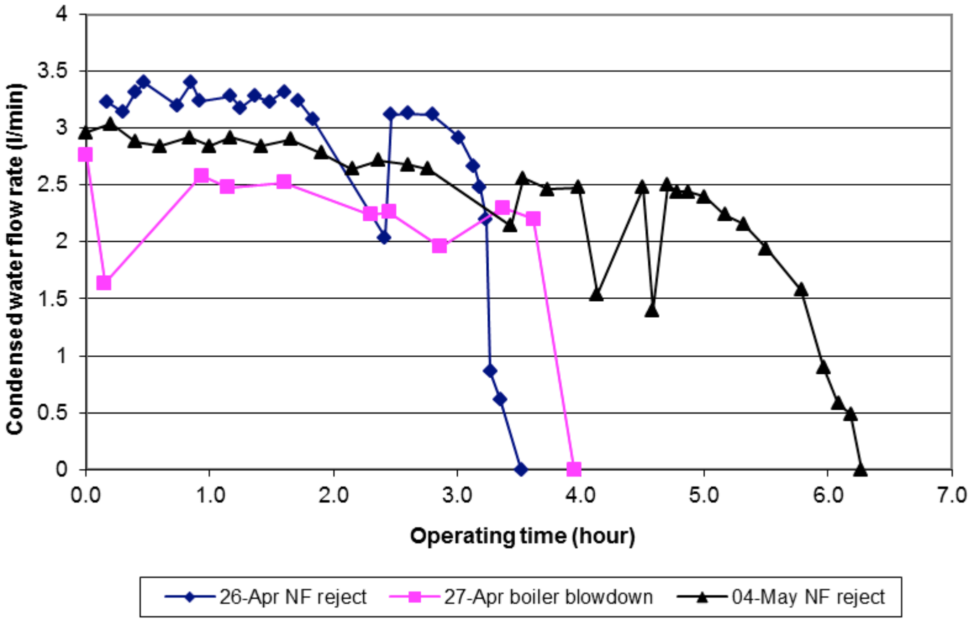

Figure 4-6.Condensed distillate flow rate profiles for the three evaporator tests.

4.4.5 Economic analysis for preliminary full-scale plant design

4.4.5.1 Energy consumption

Table 4-2 summarizes all the key parameters in three tests with controlled permeate flux. The energy consumption rates in the three tests were similar because the NF was operated at similar permeate fluxes and TMPs during the tests.

At Cikautxo the volume of wastewater produced daily is around 70 m^3, which is reduced to a volume of 7 m^3 in the boiler with the simultaneous production of 63 m^3 of treated water. The 7 m^3 of concentrate are further processed in the evaporator to a final concentrate with a volume of 300 L. The expenditure of energy in the boiler has been determined to be 627.5 kWh per m^3 of blowdown produced. Considering a cost of 0.0303 €/kWh at Cikautxo it results in a boiler energy cost of €19/m^3 of blowdown produced. The energy consumption in the evaporator was determined to be €23/m^3 of feed.

Compared to the high evaporator energy consumption, the membrane energy consumption is only a very small fraction (<2%) of the total energy consumption in a NF + evaporator plant. It would further reduce the overall energy costs of the treatment plant if the NF produces less reject water for the evaporator. Therefore, a second stage of NF270 is suggested to be used for treating the reject stream from the first stage of the NF270 membrane. If a permeate flux of 7.5 lmh and a water recovery of 65% for the second stage NF are assumed, the two-stage design, with 23% more membrane area, could further reduce the overall reject flow by 65% compared to the single stage design.

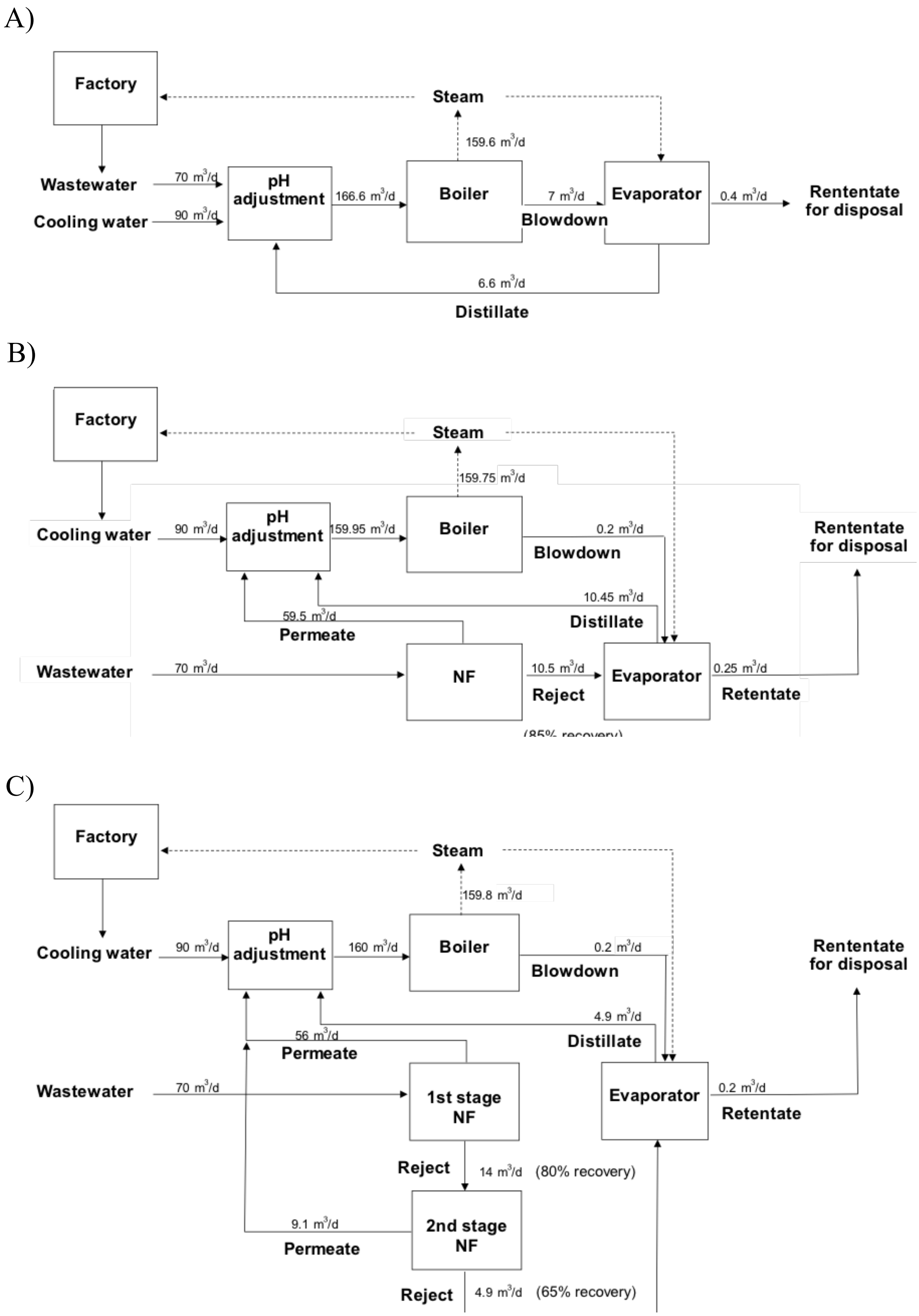

Figure 4-7.Mass balance of the existing process (A), the single stage NF+evaporator (B) and the 2-stage NF+evaporator design (C).

4.4.5.2 Mass balances

Overall water recovery is defined in Equation 4-1: Overall water recovery

$$= \frac{\boldsymbol{cooling\ water\ flow + wastewater\ flow - residue\ flow}}{\boldsymbol{cooling\ water\ flow + wastewater\ flow}} \times \mathbf{100}\%$$

Equation 4-1

Mass balances shown in Figure 4-7 indicate over 99% water recoveries for the existing process, a single stage NF+evaporator design, and a 2-stage NF+evaporator design, with the two-stage NF + evaporator on the top (99.9%).

4.4.5.3 Cost comparisons

In order to compare economics between the existing process, the single-stage and the two-stage designs, a simple model was developed in this study. The existing process and the two alternative processes were compared in terms of capital investment, energy consumption, membrane replacement cost, chemical cost and off-site disposal cost. Total operational expenditure (OPEX) savings were estimated for the two alternatives compared to the existing process, and times for return of investment were also calculated. Results from two sensitivity analyses with varied membrane replacement rates or membrane water recoveries are shown in Figure 4-8, Figure 4-9 and Table 4-6.

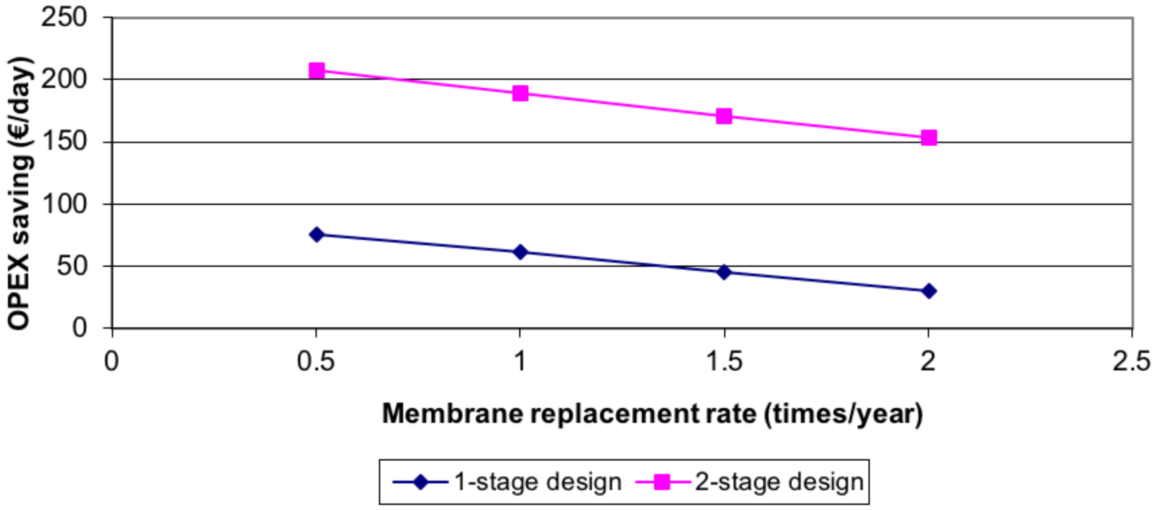

Figure 4-8. OPEX savings at different membrane replacement rates (85% water recovery is assumed for the 1-stage design; 80% and 65% water recoveries are assumed for the 1st and 2nd stages in the 2-stage design).

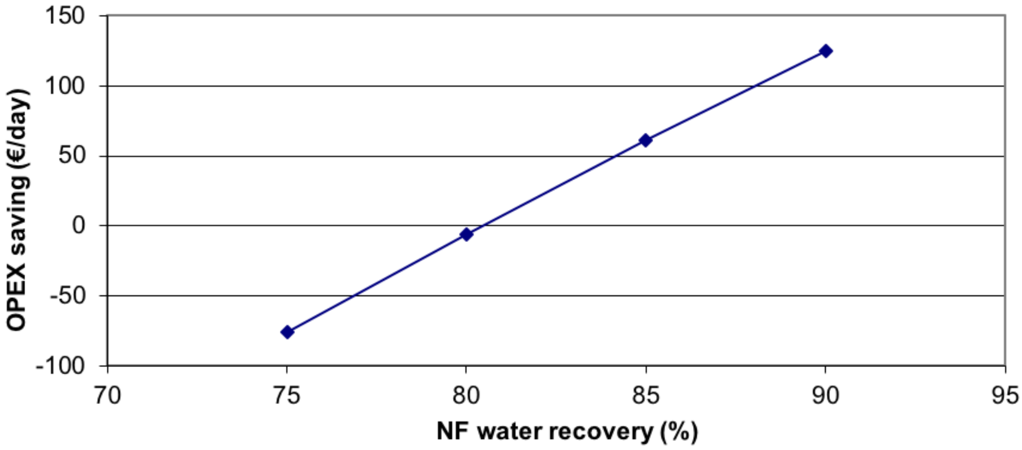

Figure 4-9. OPEX savings at different water recoveries for the 1-stage NF design (the membrane replacement rate is assumed once per year).

The cost model indicates that the two-stage NF design will lead to more operational savings for the integrated solution than the single stage NF design. Periods of return on investment for the single stage NF design and the two-stage NF design are expected to be 1641 days and 648 days, respectively, if a membrane replacement rate of once per year is assumed (considering that the electricity cost of 0.0303 €/kWh at Cikautxo is relatively low and will probably rise in the future, the operational savings will be also enlarged at high electricity prices, meaning shortened periods of return on investment). Therefore, the cost data favor the two-stage NF design in full scale applications.

Table 4-6. OPEX savings at different water recoveries for the 2-stage NF design (the membrane replacement rate is assumed once per year).

First stage water recovery (%)	Second stage water recovery (%)	OPEX saving (€/day)
75	60	161
75	65	170
75	70	173
75	75	165
80	60	188
80	65	189
80	70	183
80	75	162
85	60	212
85	65	205
85	70	187
85	75	151
90	60	233
90	65	217
90	70	185
90	75	130

4.5 Conclusions

A solution combining membrane filtration and evaporation was developed in the PROMETHEUS project aiming to treat high strength, polymer containing rubber part manufacturing wastewater. A pilot study was carried out in early 2012 at a rubber factory in Spain. The following conclusions have been drawn from the pilot study:

- The rubber wastewater is featured with high COD, low conductivity, moderate solids concentration and moderate oil and grease concentration.
- The NF270 membrane can reject over 95% of COD and the NF270 permeate can be either discharged or re-used as boiler feed water, if the total hardness in the permeate is further reduced.
- The membrane can be operated continuously at a controlled permeate flux for over 24 hours if the permeate flux is maintained at no more than 12 $L/m^2.h^{-1}$.
- A water recovery of 80-90% can be achieved by the NF270 as long as the permeate flux is set below 12 $L/m^2.h^{-1}$.

- Frequent flushing, typically flushing for 5 seconds in every minute, can significantly help to sustain membrane performance.
- The concentration polarization enhanced by a cake layer built up with the polymeric demolding agents is believed to be the main mechanism for membrane fouling.
- Alkali cleaning with Ultrasil 11 is more effective than acid cleaning with Ultrasil 75. It is recommended to use 0.2% Ultrasil 11 for daily cleaning and use 0.5% Ultrasil cleaning for in-depth periodical cleaning.
- A slightly higher treating capacity was observed for the evaporator when treating the NF reject compared to treating the boiler blowdown, probably due to lower salt concentrations in the NF reject.
- A two-stage NF design can significantly reduce the overall energy costs of the integrated solution. The two-stage NF design will lead to higher operational savings for the integrated solution than the single stage NF design. The two-stage NF design is recommended for future full scale applications.

4.6 References

A. Urkiaga and J. Font,1999. Estudio de tratabilidad de un efluente industrial de baja biodegradabilidad mediante tecnologías de oxidación avanzadas. Unpublished test report No. X-99-7024 from Geiker (in Spanish).

Agashichev S. P.,2009. Modelling the influence of temperature on gel-enhanced concentration polarization in reverse osmosis. Desalination, 236 , 252-258.

American Water Works Association Research Foundation, Lyonnaise des Eaux and Water Research Commission of South Africa, Water Treatment Membrane Process, McGraw-Hill Publisher, New York, USA, 1996.

Artug G., Roosmasari I., Richau J., Hapke J., 2007. A comprehensive characterisation of commercial nanofiltration membranes. Separation Science Technology, 42, 2947-2986.

Belona C., Marts M., Drewes J., 2010. The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes. Separation and Purification Technology. 74 ,44-54.

Boussu K., Zhang Y., Cocquyt J.,Van der Meeren P., Volodin A., Van Haesendonck C.,. Martens J.A., Van der Bruggen B., 2006. Characterization of polymeric nanofiltration membranes for systematic analysis of membrane performance. Journal of Membrane Science. 278, 418-427.

Dow Water & Process Solutions, FILMTEC ™ Reverse Osmosis Membranes Technical Manual, http://www.dow.com.

Heins W.F., McNeill R., Albion S., 2005.Worlds first SAGD facility using evaporators, drum boilers, and zero discharge crystallizers to treat produced water, in: Proceedings of Canadian International Petroleum Conference, June 7-9, Alberta, Canada.

Hoek E. M. V. and Elimelech M., 2003. Cake-enhanced concentration polarization: a new fouling mechanism for salt-rejecting membranes. Environmental Science & Technology, 37, 5581-5588.

Hoek E. M. V., Kim A. S. and Elimelech M.,2002. Influence of crossflow membrane filter geometry and shear rate on coloidal fouling in reverse osmosis and nanofiltration separations. Environmental Engineering Science, 19 , 357-372.

L. D. L Fuentes, I. Gorostiza, and T. Bargos, 2000. Operación y supervisión in situ con toma y análisis de muestras de un sistema piloto de tratamiento de efluentes mediante separación por membranas, Unpublished test report No. X-6036 from Geiker (in Spanish).

Lopes M. P., Xin G. and Crespo J. G.,2013. Energy saving membrane treatment of high organic load industrial effluents: From lab to pilot scale. Journal of Environmental Management, 131, 161-169.

Ramaswamy S., Huang Hua J., Ramarao B.,2013. Separation and Purification Technologies in Biorefineries, first ed., John Wiley & Sons, West Sussex, UK.

Schäfer A.I., Andritsos N., Karabelas A. J., Hoek E. M. V. , Schneider R. and Nyström M., 2005. Fouling in Nanofiltration, in: Nanofiltration – Principle and Applications. A. I. Schäfer, T. D. Waite, T. D. Dane, A. G. Fane (Eds). Elsevier Advanced Technology, Oxford, UK.

W.W. Tang, X.P. Zeng, Q. Wang, P.Li, 2010. Wet air oxidation of polyether solutions. Chemical Engineering and Processing : Process Intensification. 49, 815-819.

Chapter

5

Production of Drinking Water Using a Multi-Barrier Approach Integrating Nanofiltration: a Pilot Scale Study

5.1 Summary

A multi-barrier system was studied for the production of drinking water with high chemical and microbiological quality. The integration of nanofiltration (NF) and ultraviolet (UV) photolysis was tested at pilot scale in a surface water treatment plant.

The NF membranes tested, Desal DK and NF270, allow for the production of permeates with high quality standards, although the membrane with higher molecular weight cut-off (NF270) revealed to be the best option for surface water treatment due to its higher permeability. The NF270 membrane was also efficient to deliver high quality water, even under high pollutant concentrations, making possible to operate with water recovery rates as high as 98%.

Extensive studies were performed in the water treatment plant where the proposed system was tested at three locations of the drinking water production line. Seeking to achieve the best compromise between high recovery rate, high retention of chemicals and microorganisms as well as preventing operational problems (flux decline and fouling), it was found that the integrated system should be placed after the conventional sand filtration, operating at a 91% recovery rate.

Membrane fouling was also investigated and the major fouling species involved were identified and quantified, enabling optimisation of the membrane cleaning protocol.

Published as: Lopes, M.P., Matos, C.T., Pereira, V.J., Benoliel, M.J., Valério, M.E., Bucha, L.B., Rodrigues A., Penetra, A.I., Ferreira, E., Cardoso, V.V., Reis, M.A.M., Crespo, J.G., 2013, Separation and Purification Technology, 119,112-122.

5.2 Introduction

Drinking water legislation requires a tight control of the water quality for human consumption in order to assure adequate public health conditions (Drinking water directive). Quality parameters include microbiological parameters, chemical parameters, and other indicator parameters (e.g. total organic carbon, turbidity, and colour). There is a growing interest of water providers and researchers to find solutions to increase the chemical and microbiological quality of the drinking water produced, anticipating future regulations that will include new microorganisms and micro pollutants (e.g. pesticides), which are currently being studied for their potential adverse health effects, even when present in the aquatic environment at extremely low concentrations. Pesticides are intentionally used to control pests. However, their toxic action is not specific to the target organisms and they are toxic to many non-target species, including humans (Younes and Galal-Gorchev, 2000).

Conventional surface water treatment often includes screening, coagulation/flocculation, sedimentation, sand filtration, and final disinfection which is often achieved by chlorination. However, such treating systems may not be sufficient to retain the new micro pollutants of concern. Additionally, the use of high quantities of chlorine may induce the formation of disinfection by-products, which are harmful to human health. In this work a multibarrier treatment system is proposed by introducing a combined process with nanofiltration and low pressure UV radiation in a conventional surface water treatment plant. Both treatment processes have shown promising results at independent laboratory scale studies (Pereira et al., 2012; Sanches te al., 2010; Sanches et al., 2012; Sanches et al., 2011).

One of the first nanofiltration plants for treating surface water was constructed in Méry-sur-Oise, France, with a capacity of 140000 m^3/d (Cyna et al., 2002). This plant shows high efficiency for the removal of organic matter still present at the end of conventional treatments. The removal of such organic material is important to prevent the growth of bacteria in the water distribution system and, therefore, decreases the necessity of adding chlorine during water distribution.

Nanofiltration systems are also able to reduce the level of micro pollutant contamination of the drinking water supplies due to retention based on size exclusion (down to ≈200 Da molecular weight) and interactions with the membrane surface. Additionally, nanofiltration is able to eliminate water colour and turbidity, increasing the performance of the UV radiation treatments. The introduction UV photolysis after nanofiltration introduces an additional protective barrier that allows the inactivation of microorganisms (Linden et al., 2002), as well as photo-degradation of resilient contaminants such as pesticides (Koyuncu et al., 2008).

The removal of pesticides from surface waters to levels below µg.L^{-1} has been also a subject of interest in the last years. Several works report the removal of such compounds using membrane technology (Sanches te al., 2012; Koyuncu et al., 2008; Yangali-Quintanilla et al.,2009; Van der Bruggen et al., 2002; McCallum et al., 2008; Schafer et al., 2003) , UV photolysis and advanced oxidation systems (Gozzi et al., 2012; Haque and Muneer, 2003; Wong and Chu, 2003; Wong and Chu, 2003; Zhang et al., 2007; Benitez el al., 2006; Canonica et al., 2008; Huber et al., 2003). However, literature reports the use of such technologies separately and, as demonstrated by previous results, under controlled laboratory conditions, the combination of both nanofiltration and advanced oxidation systems is necessary to achieve an efficient removal of the most resilient micropollutants (Pereira et al., 2012).

Numerous researchers focused their studies on membrane fouling, which remains the main obstacle to an efficient membrane performance (Her et al., 2007; Guo et al., 2012; Kluplel and Fummel, 2010; Xy et al., 2006). Membrane filtration leads to accumulation of material at the membrane surface and intraporous structure, which increases resistance of the membrane to permeation. As a consequence, chemical cleaning has to be applied frequently (which may deteriorate membrane performance and reduce membrane lifetime (Oliveira et al., 2011), leading to higher operational costs. Fouling has been investigated (Peiris et al., 2010; Peldszus et al., 2011; Mi and Elimelech et al., 2009; Mosqueda-Jiminez et al., 2008; Xu et al., 2010) using various types of techniques and different characteristics of feed water, membrane material and operating conditions (e.g. pre-treatments, back flushing, flushing forward, and gas bubbling) (Quaisrani and Samhaber, 2010; Madaeni and Samieirad, 2010; Al-Amoudi and Lovitt, 2007; Spettmann et al., 2007).

The present research work is focused on the validation of a multi-barrier system incorporating both nanofiltration and UV photolysis at pilot scale, in a fully operational surface water treatment plant, in order to guarantee the production of a high quality drinking water in terms of chemical composition and microbial inactivation.

The pilot system (combination of nanofiltration and UV photolysis) was assembled and tested in a surface water treatment plant of the major Portuguese water provider EPAL, which provides water to around 3 million people in 35 districts corresponding to a total area supplied of 7 090 Km^2. The water treatment plant is allocated in Vale da Pedra and treats surface water abstracted from the Tagus River in Valada Tejo.

The validation of the multibarrier system was performed by evaluating the optimal location of the nanofiltration system in the water treatment process, by testing the performance of the nanofiltration operation at three different points of the surface drinking water production line. The UV photolysis was also evaluated on site to determine the benefit of its use and the impact in terms of water quality, with the objective of producing a high quality drinking water.

A complete and careful analysis of the NF membrane fouling agents was performed in this study after continuous operation at the drinking water treatment plant. Different membrane cleaning agents were also tested to determine their efficiency for removal of the detected fouling components.

5.3 Materials and Methods

5.3.1 NF system operation and membrane selection

The nanofiltration system represented in Figure 5-1A was used for membrane selection. This system is composed by a spiral wound membrane module, a valve at the end of the module for pressure control and a diaphragm pump (Hydra-cell G-3, Wanner Engineering, USA), which is able to deliver a constant flow for pressures up to 60 bar. The feed flow rate used in the experiments was 420 l/h. The feed water used in these tests was surface water collected from the Tagus River where EPAL abstracts water. Before being fed to the nanofiltration system, water was firstly filtered through a 0.75 mm filter followed by a 5 µm filter. This system was tested using two spiral-wound membranes – NF270 (Dow Filmtec) and Desal-DK (GE Osmonics) – with different molecular weight cut-off (MWCO), as described in Table 5-1.

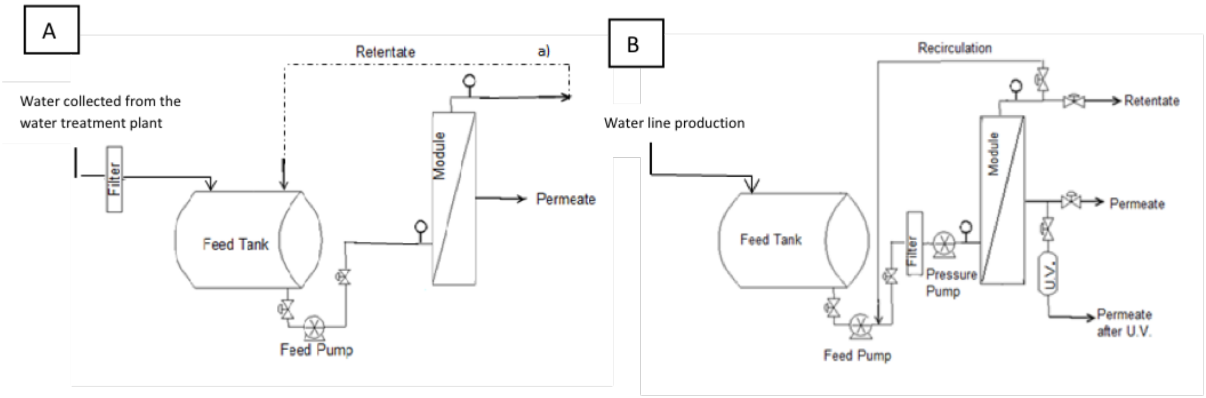

Figure 5-1. Schematic diagram of the pilot systems used: (A) for membrane selection operating in two different modes: single pass and concentration mode (in the later case, the retentate is fully recycled; see line a), B- in the pilot tests at the water treatment plant.

Table 5-1. .Properties of the nanofiltration membranes tested (product information from suppliers: Dow and Osmonics).

Membrane	Manufacturer	Membrane Area (m^2)	Molecular Weight Cut-off (MWCO, Da)	Salt Rejection Na_2SO_4 (%)
NF 270 – 4040	Dow	7,6	~400	97
NF 270 - 2540	Dow	2,6	~400	97
Desal Dk - 2540	Osmonics	1,7	~250	98

This system was used under two different operation procedures: concentration and single pass mode. The membrane module used has the same configuration of the membrane module used in full scale systems and the two different operation procedures allowed to simulate the conditions of a full scale nanofiltration operation.

In the single pass operation, the retentate and permeate were collected continuously in different tanks (TMP= 10 bar). This operation mode can be used to simulate the performance of the first membrane module in a membrane system composed of several membrane modules disposed in series.

In the concentration mode, the retentate was recirculated back to the feed tank (see line a)in Figure 5-1A), while the permeate was recovered in a different tank (TMP =10 bar).This operation method allows to simulate different water recovery rates that could be achieved in different membranes modules, in a system composed by several membrane modules disposed in series.

Periodically, samples were taken from the feed, retentate and permeate and analysed for determination of conductivity, UVA254 nm (detection of aromatic substances), salts, metals, total organic carbon, alkalinity, hardness, and microbiological activity, as detailed below.

The removal degree of different contaminants was calculated according to Equation 5-1:

$$Removal\ (\%) = \frac{(Cf - Cp)}{Cf} \times 100$$

Equation 5-1

Where Cf is the contaminant concentration in the feed water, Cp is the contaminant concentration in the permeate stream.

The apparent rejection of each contaminant by the nanofiltration system was calculated using Equation 5-2:

$$Rejection\ (\%) = \frac{(Cr - Cp)}{Cr} \times 100$$

Equation 5-2

Where Cr is the concentration of contaminant in the retentate stream of the nanofiltration system.

5.3.2 Nanofiltration and UV disinfection tests at the drinking water treatment plant

This study was conducted at the EPAL drinking water treatment plant (in Valada and Vale da Pedra). The water flow was diverted from the treatment system at different locations: after screening, after sedimentation, and after sand filtration treatment (see Figure 5-2). The water flow diverted from the treatment system was fed to a reservoir that ensured the continuous operation of the multi-barrier system (NF + UV).

The pilot-scale unit used in these tests consisted of a nanofiltration system and a low pressure ultraviolet (LP/UV) flow through system that emits monochromatic light at 254nm (Puro-Tap, 2010, Wedeco), represented in Figure 5-1-B. A pump was used to feed the spiral-wound nanofiltration system (placed after a 5 µm pre-filter) at a flow rate of 1179 L/h. The input, output, and recirculation from the membrane were controlled using valves that regulated the flow as well as pressure.

The filtration membrane regime consisted of alternate permeation (60 min) and relaxation with flushing (1 min). During the flushing/relaxation period the pressure pump was turned off and, consequently, the pressure dropped sharply down to 2 bars; the electro valve in the retentate was fully opened and the water circulated along the relaxed membrane, dragging the cake layer to the retentate stream.

Several sampling points allowed the collection and analysis of the pre-filtered water that was fed to the nanofiltration system, as well as the permeate and the retentate water samples, and the samples collected after the LP/UV treatment. The nanofiltration pilot system was operated using the spiral-wound membrane NF270 (Dow-filmtec with a membrane area of 7.6 m2), see Table 5-1, and a transmembrane pressure (TMP) of 8 bar. The nanofiltration studies were performed using a 91% and a 95% permeate water recovery rate (TMP=8 bar).

Several permeability assays were also conducted by measuring the permeate flow obtained using different TMP (15, 12, 10, 8, 6, and 4 bar), taking into account the membrane area used (7.6 m2). The assays were conducted at ambient temperature, which ranged from 17 to 23oC. The membrane permeability was determined in the beginning and at the end of each assay, as well as after each chemical cleaning operation.

The membranes were chemically cleaned in-situ after each filtration operation under a TMP of 2 bar. Two commercial chemical cleaning products were used, Ultrasil 11 and Ultraperm 75 (both from Henkel-EcoLab). The alkali cleaning with Ultrasil 11 targets mainly the organic foulants on the membrane while the acid cleaning with Ultraperm 75 targets mainly the inorganic foulants.

The performance of the UV photolysis was also determined by analysing the quality of the water before and after the UV system, in order to determine the disinfection and pesticide degradation efficiency of the system.

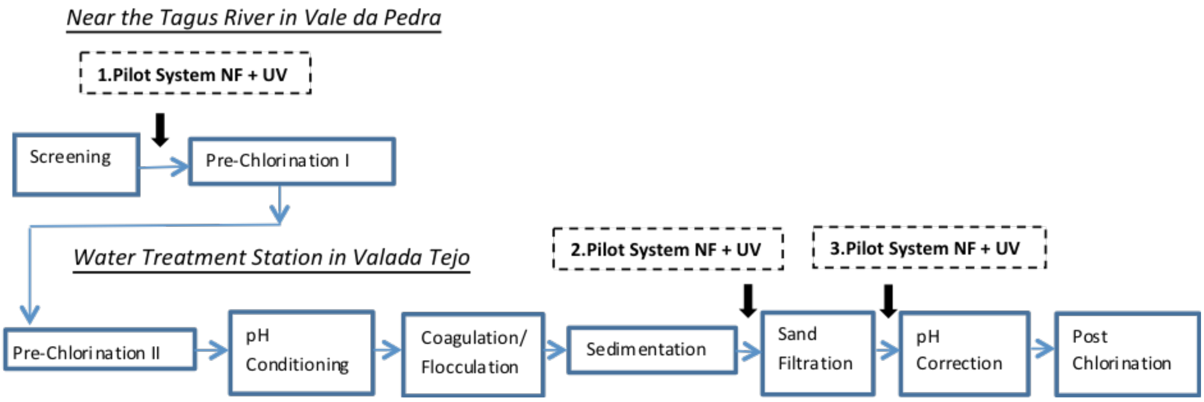

Figure 5-2 Schematic representation of the surface water treatment plant, near the Tagus river. Identification of the three test positions where the pilot system NF+UV was introduced in the drinking water line production: 1. After screening; 2. After sedimentation; 3. After sand filtration.

5.3.3 Fouling analysis procedure

Fouling analysis was conducted in a NF270-4040 module under operation for two months without cleaning. The module was removed from the pilot unit, unrolled for visual inspection and membrane samples were then cut. The deposit present at the surface of each membrane sample was analysed in terms of proteins, polysaccharides, metals, total solids, and total volatile solids as described below. Different membrane samples were also taken for determination of permeability recovery after chemical cleaning. The analyses performed to determine the fouling agents involved and the cleaning protocols tested are described in Figure 5-3.

The permeability and cleaning tests were performed with samples of the fouled membrane under study in a stainless steel cross-flow test cell with 15 cm^2 of effective membrane area, separating two rectangular cross-section channels (feed and permeate) measuring 150mmx10mmx1mm each. The feed circulation flow was provided by a high pressure diaphragm pump (Hydra-cell, Wanner Engineering, USA) with an adjustable pressure control.

5.3.4 Analytical methods

5.3.5 Water analysis

The water used was collected from the Portuguese Tagus River in the abstraction site of Empresa Portuguesa de Águas Livres, S.A. (EPAL). The water matrices and all samples produced were analysed at EPAL´s laboratory installed at the water treatment plant. The feed water, retentate, permeate and U.V. permeate were characterized in terms of their pH (Standard Method 4500-H+), total organic carbon (European Standard EN 1484:1997), turbidity (ISO

7027:1990), alkalinity (Standard Method 2320B), total hardness (Standard Method 2340C), colour (Portuguese Standard NP 627: 1972 – molecular absorption), conductivity (Standards Methods for Examination of Water and Wastewater-SMEWW 2510 B), DOC (European Standard EN 1484), Nitrate and Fluorine (ISO 10304-1:2007), Silica (NP 439:1966), Coliform and E.coli (SMEWW 9223 B) and Faecal Streptococci (ISO 7899-2). Metals were also analysed (internal method, ICP-EOS) (except arsenic, which was analysed by an internal method, AAS). Also selected pesticides were analysed by reverse-phase high performance liquid chromatography (HPLC).

5.3.6 Fouling analysis

The foulant material on the membrane surface was gently scrapped off from a 400 cm^2 of membrane area by using the tip of a laboratory spatula. The foulant material was dissolved in 50 ml of Milli-Q water using a vortex mixer and analysed by the Lowry method for proteins, Lowry corrected method for humic acids, the Dubois method for polysaccharides (Sanches et al., 2013; Lowry et al., 1951) and by ICP analysis for metals.

These methods quantify the level of total protein, humic acids, and polysaccharides in solution by means of a colorimetric technique using a spectrophotometer, where the total concentration is exhibited by colour change of the sample solution in proportion to concentration. The metals content was determined employing inductively coupled plasma emission spetroanalysis (ICP) equipped with radio-frequency (RF) generator of 40.68MHz a Czenrny-Turner type monochromatic with 1.00m (sequential), AS500 autosampler, and data acquisition software. Also, scanning electron microscope (SEM) images were performed by Field Emission Scanning Electronic Microscopy (Jeol JSM – 7001F).

The determination of total and volatile solids of the cake layer was performed by drying in an oven at 105ºC and then heated to dryness at 510ºC, respectively.

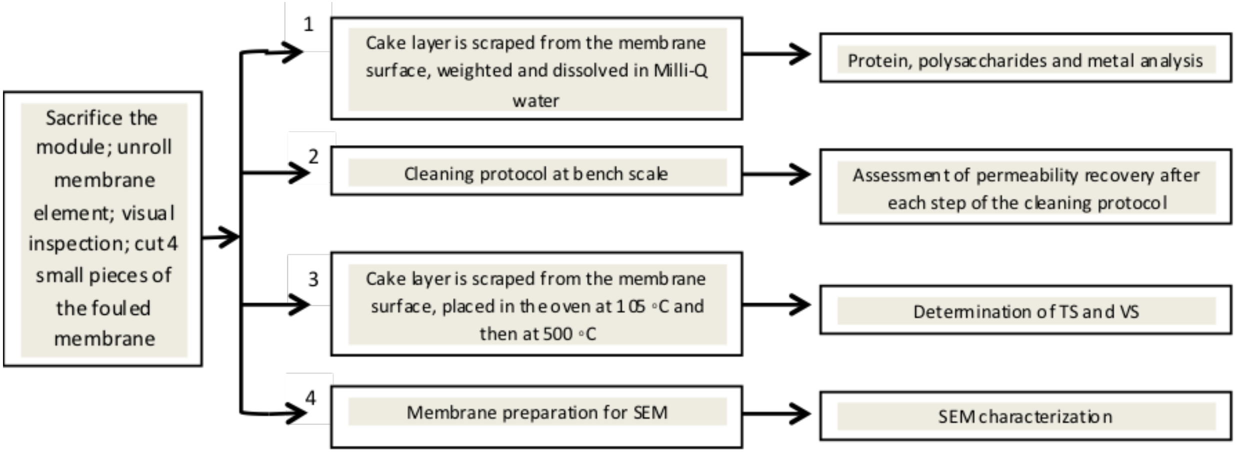

Figure 5-3. Autopsy experimental design for fouling characterization of fouled membrane.

5.4 Results and Discussion

In this work a combined system using both nanofiltration and UV photolysis was evaluated, in order to increase the chemical and microbial quality of the drinking water produced. This study was performed under real water treatment conditions.

5.4.1 Membrane selection

The optimisation of this process requires in first place the selection of an adequate membrane. Membrane screening tests were performed using the system described in 5.3.1 under batch operation conditions, using water collected from the Tagus River with a relatively constant composition during all experiments. This system allowed to test a membrane module with the same geometry (spiral wound) of the modules used at the water treatment plant. Therefore, membrane selection was performed under similar conditions as those present in the real water treatment plant. The membrane used for drinking water treatment should present a high water permeability, low flux decrease due to fouling and should satisfy the compromise between high retention of chemical and microbiological contaminants and preservation of the water alkalinity and hardness at the required levels. Two spiral wound membranes were tested and their characteristics are presented in Table 5-1.

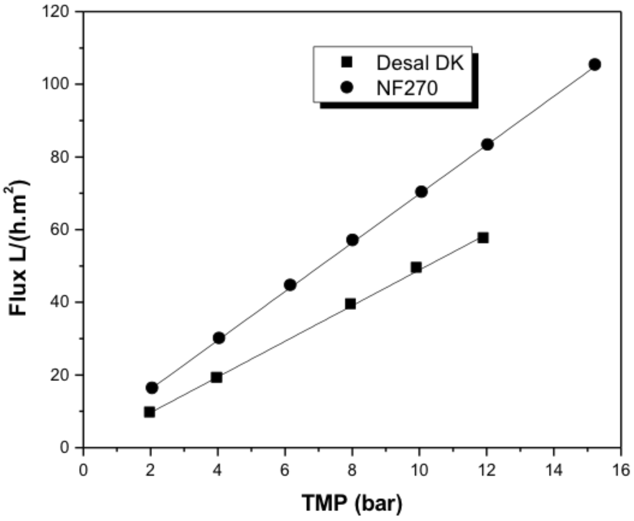

Figure 5-4. Permeabilities of NF270 and Desal DK membranes when processing surface water collected from the Tagus River.

Figure 5-4 depicts the results for the permeability achieved with the two tested membranes - Desal DK and NF270 - for the surface water under study. The results show that the NF270 membrane presents a higher permeability when compared with the Desal DK membrane.

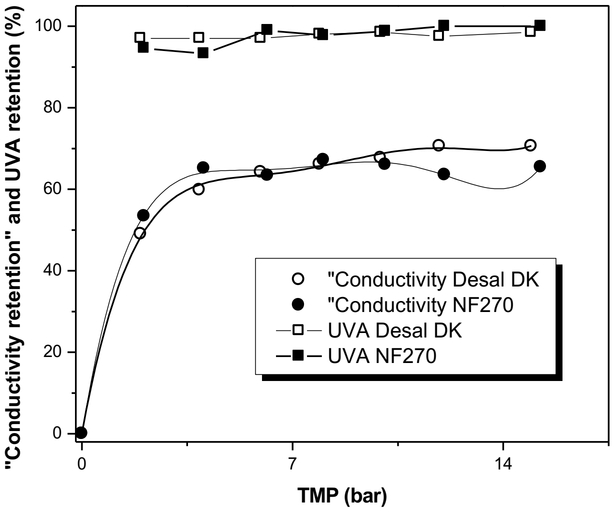

Figure 5-5. Rejection of UVA254 nm and conductivity using the NF270 and Desal Dk membranes, in the treatment of surface water at different applied pressures.

The results presented in Figure 5-5 show that the membranes tested present extremely high and similar rejection of aromatic substances, which was measured by UVA 254 nm in the samples.

Figure 5-5 clearly demonstrates that the rejection of UVA 254nm does not depend from the applied pressure, for the pressure range studied. However, the retentate conductivity increased with the increase of applied pressure (up to 4 bar). These results suggest that the membranes tested exhibit a good retention of the aromatic species present in the polluted water and that salt retention can be optimised according with the target objective, by adjusting the transmembrane pressure.

The membranes were tested under two different operation modes in order to determine their retention to the various compounds present in the water stream (as described in section 5.3.1).

The results of different water quality parameters achieved in the single pass experiment are presented in Table 5-2. These results show that these membranes lead to similar removal degrees. It can be observed that both membranes were able to remove all pathogens from the surface water, as well as high removal of colour, turbidity, TOC, phosphorous, calcium, magnesium, aluminium and iron. Under the experimental conditions used, the water produced by Desal Dk is highly soft, since the membranes strongly rejected calcium and magnesium from water. The retention of these cations can be optimised by using a membrane with a higher molecular weight cut-off or by applying a lower transmembrane pressure (TMP).

When operating in a concentration mode, the water in the feed tank is concentrated since only the retentate is recirculated back. Table 5-3 presents the water quality parameters achieved in concentration studies with Desal Dk and NF270 membranes. The permeate composition was characterised for permeate samples collected after an operation that allowed to concentrate the initial feed water 2x and 6.2x. These concentration factors simulate continuous operations with recovery rates of 50 and 84%, respectively.

Table 5-2. Water quality parameters, in the feed and the permeate streams, and removal degree obtained for the NF270 and the Desalt DK membranes, during single pass studies.

Parameters	NF270 Single Pass test			Desal DK Single Pass test		
	Feed	Permeate	Removal (%)	Feed	Permeate	Removal (%)
Colour (mg/l Pt-Co)	8.7	<1	>88.5	7.21	<1	>86.1
Turbidity (NTU)	3.9	<0.2	>94.9	3.7	<0.2	>94.6
Alkalinity	n.a.	n.a.	n.a.	56	14.5	74.1
Nitrate (mg/l)	2.37	2.72	0.0	4.3	3.58	16.7
Chloride	40.6	24.2	40.4	30	16.8	44.0
Phosphorus	112	<50	>55.4	314	<50	>84.1
Fluorine (µg/l)	84	<70	>16.7	200	134	33.0
Calcium (mg/l)	29.5	<5	>83.1	24.1	<5	>79.3
Magnesium (mg/l)	9.4	1.02	89.1	7.03	<1	85.8
Sodium (mg/l)	35.6	17.1	52.0	24.8	12.6	49.2
Potassium (mg/l)	3.18	1.4	56.0	2.74	1.24	54.7
Aluminium (µg/l)	202	<40	>80.2	299	<40	>86.6
Iron (µg/l)	174	<20	>88.5	306	<20	>93.5
TOC (mg/l)	3.5	<1	>71.4	3.61	<1	>72.3
Coliform Bacteria (ufc/100ml)	320	0	100	670	0	100
E. coli (ufc/100ml)	320	0	100	670	0	100
Faecal streptococci (ufc/100ml)	18	0	100	230	0	100

n.a. not analysed

Table 5-3. Water quality parameters in the feed and the permeate streams, obtained with the NF270 and the Desalt DK membranes, during concentration studies (2x and 6.2x)

Parameters	NF270 Concentration tests			Desal DK concentration tests		
	Feed	Permeate (conc. 2x)	Permeate (conc. 6.2x)	Feed	Permeate (conc. 2x)	Permeate (conc. 6.9x)
Colour (mg/l Pt-Co)	8.7	<1	<1	10.4	<1	<1
Turbidity (NTU)	2.9	<0.2	<0.2	10.4	<0.2	<0.2
Alkalinity	112	20	43	86	<20	32
Nitrate (mg/l)	2.37	2.93	3.08	4.44	4.41	5.36
Chloride	40.6	30.3	48	30.4	25.1	37.4
Phosphorus	112	<50	<50	265	<50	<50
Fluorine (µg/l)	84	<70	<70	125	119	118
Calcium (mg/l)	29.5	5.96	13.1	22.5	<5	10.6
Magnesium (mg/l)	9.4	1.34	2.5	7.25	<1	1.39
Sodium (mg/l)	35.6	21	35.9	25.9	19.1	35.1
Potassium (mg/l)	3.18	1.77	3.25	2.85	1.86	3.75
Aluminium (µg/l)	202	<40	<40	720	<40	<40
Iron (µg/l)	174	<20	<20	565	<20	<20
TOC (mg/l)	3.5	<1	<1	4.31	<1	<1
Coliform Bacteria (ufc/100ml)	320	0	0	1267	0	0
E. coli (ufc/100ml)	320	0	0	498	0	0
Faecal streptococci (ufc/100ml)	18	0	0	198	0	0

The results in Table 5-3 show that, even at high concentration pathogens, colour, turbidity, TOC, iron, aluminium and phosphorous, the rejection degree achieved by these membranes is adequate. Also, the water softening effect was lower, due to the increased concentration of calcium and magnesium in the concentrated feed tank.

By comparing the results achieved for both membranes it is clear that the NF270 membrane allows for the production of water at a higher flow rate without compromising the water quality. Therefore, this membrane was chosen for the pilot tests in the water treatment plant. Other studies reported in the literature for surface water treatment selected the membrane NF270 or

NF200, which has similar characteristics (Cyna et al., 2002; Dubois et al., 1956; Marconnet et al., 2009).

In order to determine the ability of this membrane to deliver high quality water, even under higher pollutant concentrations and at higher water recovery rates, an experiment was performed in the concentration mode (see Figure 5-1- B), concentrating the feed water 50 times, in order to simulate a water recovery rate of 98%.

Table 5-4. Water quality parameters in the feed, retentate and permeate streams, obtained with the NF270 membrane during concentration studies (50x)

Parameters	Feed Water	NF retentate (Conc. 50x)	Permeate	Rejection (%)
Colour (mg/L Pt-Co)	8.7	506.1	<2	99.6
Turbidity (NTU)	2.8	50.2	<0.2	99.6
Coliform Bacteria (ufc/100 ml)	800	1000	0	100
E.coli (ufc/100ml)	300	1000	0	100
Faecal streptococci (ufc/100ml)	39	345	0	100
Clostridium perfringens (ufc/100ml)	155	75	0	100
Hardness (mg/l CaCO3)	112	5701.6	195.8	96.5
TOC (mg/l)	3.2	184.3	<0.4	99.8
DOC (mg/l)	3.03	162.8	<1	99.4
Total Pesticides (µg/l)	N.D.	184.3	N.D.	100
Nitrate (mg/L)	2.37	3.2	2.74	14.4
Nitrite (mg/L)	0.005	0.0283	0.0289	-
Silica (mg/L)	<4.3	9.1	6.2	32
Fluorine (µg/L)	84	1620	630	61
Boron (µg/L)	<55.5	96	28.2	70.6
Calcium (mg/L)	2.95	1368	60.1	95.6
Magnesium (mg/L)	9.4	554.9	11.1	98
Sodium (mg/L)	35.6	430	121	72
Potassium (mg/L)	3.18	47.5	12.4	74
Aluminium (µg/L)	202	2688	<40	98.5
Iron (µg/L)	174	1644	<20	98.8
Manganese	19	297	<5	98.3
Barium (µg/L)	15.8	557	18.2	96.7
Copper (µg/L)	<11.1	144	<10	93
Arsenic (µg/L)	2.63	144.7	0.68	99.5

N.D. – below the detection limit

Table 5-4 shows that even under these conditions the NF270 membrane was able to produce a permeate water with high quality standards. The permeate produced was totally free of microorganisms and the levels of colour, turbidity, total pesticides, TOC, DOC, aluminium, iron, manganese, and copper were below the detection limits of the analytical methods. TOC and DOC were almost completely removed from water, which is important to prevent growth of bacteria in the water distribution systems, diminishing the necessity of adding chlorine in the distribution network.

The data from Table 5-4 show that the feed water concentration allowed detecting pesticides and arsenic in the retentate. However, both parameters were retained below the reference limits for drinking water.

5.4.2 Pilot-scale studies at the water treatment plant

The NF pilot system was firstly tested for filtering of untreated surface water. During these studies at the Tagus river abstraction site, the system was not able to work for a long period of time (< 3 hours) due to complete blocking of the pre-filter, even when using low recovery rates (53% and 61%). As already reported by other authors (Dubois et al., 1956), efficient pre-treatment of raw surface water is essential to prevent membrane fouling. Therefore, the nanofiltration system should be introduced after preliminary water treatment steps, such as coagulation, flocculation, sedimentation and sand filtration.

When experiments with different water recovery rates were performed with the pilot system positioned after sedimentation and after sand filtration (see Figure 5-2), the system was under operation over 4 months. These experiments allowed to evaluate the impact of the nanofiltration and UV system in the quality of the drinking water produced. Table 5-5 and Table 5-6 depict the results of the permeate quality of the water treated, for the recovery rates of 91% and 95%, when the pilot scale system was placed after sedimentation and after sand filtration, respectively.

Table 5-5. Water quality parameters in the feed and permeate streams, during continuous operation with a 91% and a 95% recovery rate (Nanofiltration operation performed after sedimentation)

Parameter	Recovery Rate 91% - After Sedimentation			Recovery Rate 95% - After Sedimentation			Legal limit (DL n.º 306/200)
	Feed	Permeate	Removal (%)	Feed	Permeate	Removal (%)	
Colour (mg/L Pt-Co)	5.37	<1.00	>81.37	2.95	<1.00	>66.10	20
Turbidity (NTU)	1.10	<0.20	>81.82	0.95	<0.20	>78.95	4
pH (E.Sorensen)	6.84	6.89	-	7.19	7.27	-	≥6,5 e ≤9
Conductivity (µS/cm a 20)	286.67	162.33	43.37	307.00	206.50	32.74	2500
Nitrate (mg/L NO3)	3.93	4.27	-	5.15	4.70	8.74	50
Silica (mg/L SiO2)	6.23	6.17	1.07	6.45	6.20	3.88	-
Hardness (mg/L CaCO3)	89.70	37.70	57.97	97.50	48.80	49.95	500
Total Organic Carbon (mg/L C)	3.64	<1.00	>72.55	3.23	<1.00	>69.04	-
Chemical Oxygene Demand (mg/L C)	3.35	<1.00	>70.12	3.15	<1.00	>68.25	-
Metals							
Calcium (mg/L Ca)	22.80	<11.10	51.32	25.35	12.35	51.28	100
Magnesium (mg/L Mg)	7.89	3.08	60.92	8.35	4.39	47.43	50
Sodium (mg/L Na)	25.07	23.30	7.05	27.25	24.55	9.91	200
Potassium (mg/L K)	2.35	1.85	21.31	2.63	2.23	15.21	-
Aluminium (µg/L Al)	350.33	<55.50	>84.16	316.00	<55.50	>82.44	200
Barium (µg/L Ba)	14.77	<11.10	>24.83	15.45	<11.10	>28.16	-

Table 5-6. Water quality parameters in the feed and permeate streams, during continuous operation with a 91% and a 95% recovery rate (Nanofiltration operation performed after sand filtration.

Parameter	Recovery Rate 91% - after sand filtration			Recovery Rate 95% - after sand filtration			Legal limit (DL n.º 306/200)
	Feed	Permeate	Removal (%)	Feed	Permeate	Removal (%)	
Colour (mg/L Pt-Co)	2.46	<0.74	>69.77	2.10	<1.00	>52.38	20
Turbidity (NTU)	0.36	<0.20	>44.00	0.23	<0.20	>11.11	4
pH (E.Sorensen)	7.01	6.98	0.47	7.01	6.97	0.46	≥6,5 e ≤9
Conductivity (µS/cm a 20)	278.71	153.57	44.90	316.00	166.50	47.31	2500
Nitrate (mg/L NO3)	4.19	4.20	-	4.63	4.65	-	50
Silica (mg/L SiO2)	6.61	6.34	4.10	6.70	6.65	-	-
Hardness (mg/L CaCO3)	109.77	49.16	55.22	103.25	39.50	61.74	500
Total Organic Carbon (mg/L C)	3.08	1.26	59.23	2.66	<1.00	>62.37	-
Chemical Oxygene Demand (mg/L C)	3.01	1.23	59.16	2.76	<1.00	>63.70	-
Metals							
Calcium (mg/L Ca)	30.63	14.40	52.99	26.48	11.18	57.79	100
Magnesium (mg/L Mg)	8.10	3.15	61.07	9.03	3.24	64.07	50
Sodium (mg/L Na)	24.16	16.94	29.86	28.38	21.60	23.88	200
Potassium (mg/L K)	2.76	1.90	31.14	2.64	1.91	27.49	-
Aluminium (µg/L Al)	60.51	63.14	-	62.85	<55.50	>11.69	200
Barium (µg/L Ba)	17.26	11.74	31.95	17.80	<11.10	>37.64	-

Table 5-5 shows that the use of the NF system allows removing aluminium below the legal limits even with the higher recovery rate of 95%. Other critical parameters (such as colour, turbidity, TOC) were also removed below the detection limits or to very low levels, highly increasing water quality. The results achieved clearly show that the system produces higher quality water then the conventional sand filter. However, the results obtained in terms of permeability evolvement show that a recovery rate of 91%, using water after the sand filtration unit, leads to lower fouling making possible to operate for a longer period assuring higher membrane permeability.

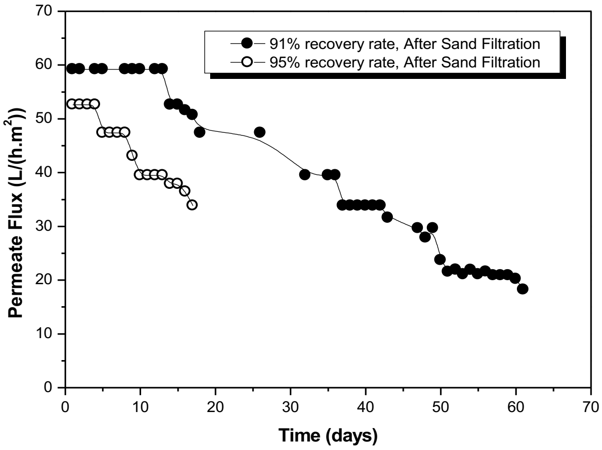

Figure 5-6. Membrane performance in terms of permeates flux evolvement for studies performed after sand filtration, using different recovery rates.

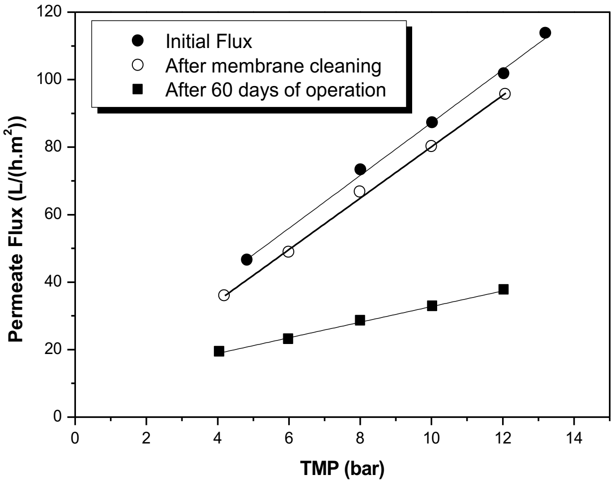

Figure 5-7. Hydraulic permeabilities, obtained in the pilot plant, for the membrane at the beginning and at the end of experiment and after chemical cleaning.

The membrane flux performance after filtration with different recovery rates is presented in Figure 5-6. This figure clearly shows that the system is able to work without cleaning for at least 15 days with no flux decline. Therefore, a cleaning-in-place protocol may be applied every

15 days to avoid a decrease of membrane performance. Membrane cleaning cycles performed after 60 working days and using water and cleaning agents for about one hour each, with a transmembranar pressure of 2 bar, showed to be effective in restoring the initial membrane permeability (see Figure 5-7).

The literature reports similar results in terms of TOC removal and water softening (Cyna et al., 2202). Cyna et al., 2002, reported the consumer's satisfaction with the improvement of the water taste quality after the introduction of a NF operation in the water treatment plant, due to the decrease in chlorine and hardness.

Several pilot and full scale studies reported in the literature were performed at lower water recovery rates (< 85%) [7, 38]. In this study higher recovery rates were used in order to diminish water losses and also to evaluate fouling effects under higher foulant concentrations.

The system was allowed to operate after sand filtration for sixty days without any stops for cleaning at a recovery rate of 91%. The nanofiltration process, using a recovery rate of 91%, reduced several parameters significantly making possible for drinking water utilities to cope with future, more stringent, regulations and possible drinking water outbreaks.

5.4.3 Fouling characterization

The NF270 fouled membrane was autopsied after 60 working days without cleaning, in the pilot unit system installed at the drinking water treatment plant.

The purpose of this membrane autopsy was to identify the nature and amount of the major feed water foulants and their contribution to membrane fouling. The identification of foulants is extremely important to better understand the dominant fouling mechanisms (Guo et al., 2012), decide the cleaning agents to use and decide about the most adequate cleaning procedure.

Figure 5-8. Images of the module membrane sacrificed for autopsy and characterisation of fouling.

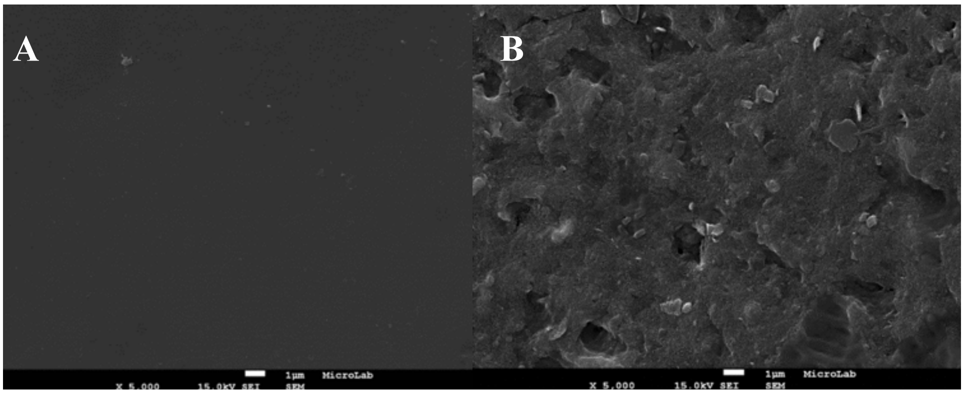

Figure 5-9. SEM images of the NF270 membrane surface (x5000): A- new membrane and B- fouled membrane.

A dense cake layer was observed on the surface of the membrane, as can be seen in both images of Figure 5-8. Portions of cake layer were scrubbed off the membrane and used to identify the nature of the compounds deposited. It is observed in Figure 5-9-A that the surface of a fresh membrane is smooth and without irregularities, which contrasts with Figure 5-9- B where a rough fouled surface clearly demonstrates the presence of deposits.

It is believed that the major contribution to reversible fouling in drinking water treatment plants is natural organic matter (NOM) and colloidal/particulate matter (Klupfel and Frimmel, 2010). The results in Table 5-7 show volatile solids (VS) and total solids (TS) values; the ratio VS/TS obtained is 72%, which indicates that organic material has a higher contribution to the cake layer on the membrane surface. As shown in Table 5-7 the NOM present in the analysed membrane is mainly composed of three foulant classes, which are: proteins, polysaccharides (colloidal/particulate matter) and humic substances (humic acid and fulvic acids).

Table 5-7. Membrane fouling characterization.

Fouling characterization		Metals (µg/cm2)		
Total mass of cake (mg/cm2)	2.753		Al	7
Total Solids (mg/cm2)	0.65		As	≈ 0
Volatile Solids (mg/cm2)	0.47		Ba	≈ 0
Proteins (mg/cm2)	0.016		Ca	1
Polysaccharides (mg/cm2)	0.031		Cu	1
Humic Acids (mg/cm2)	0.004		Fe	≈ 0
			K	10
		Metals (µg/cm2)	Mg	2
			Mn	≈ 0
			Na	61
			Si	1

In order to determine the effectiveness of different cleaning protocols the permeability of different pieces of fouled membrane were measured after each cleaning protocol studied. The permeability results are shown in Figure 5-10. The alkali cleaning with Ultrasil 11, used especially to remove organic fouling agents revealed to be more effective (see Figure 5-10) than the acid cleaning with Ultraperm 75, which is used for removal of inorganic fouling agents. These chemical compounds are commonly used in membrane cleaning, however they must be used in the right quantity in order to prevent membrane damage.

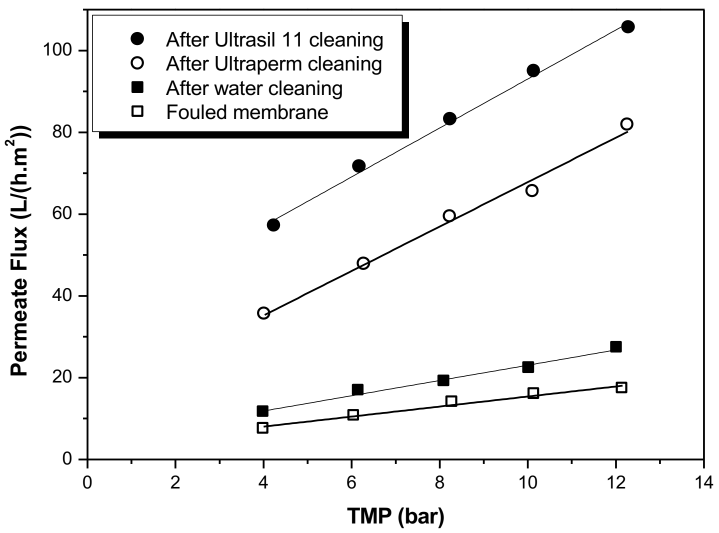

Figure 5-10. Hydraulic permeability of the membrane sample recovered for autopsy, after each step of the cleaning protocol.

5.4.4 Pilot studies with the combined nanofiltration/UV system

The main objectives of these studies were: to evaluate the integration of the proposed system at different stages of the treatment plant (see Figure 5-2); to optimize the nanofiltration treatment process by satisfying the compromise between high recovery rates and high retention of chemicals and microorganisms; and to test the integration of nanofiltration and LP/UV disinfection to produce safe water in terms of microbial and chemical pollutants.

The combined treatment of NF and UV photolysis was analysed after sedimentation and after sand filtration at a recovery rate of 91%. The treatment efficiency was analysed for the removal of low concentration levels of pesticides found to occur in the water.

Figure 5-10 and Figure 5-12 show the results achieved for the removal of the pesticides detected at different days of operation. The levels of pesticides measured in the water were below the European regulations for drinking water that set a maximum concentration of 0.1µg/L for individual pesticides and 0.5µg/L for total pesticides present in a sample (98/83/EC) (Drinking water directive). Nevertheless, the results show that the combined system is highly efficient for the removal of these pollutants and could be used to achieve high quality water even if a sudden increase in these compounds occurs in the water source.

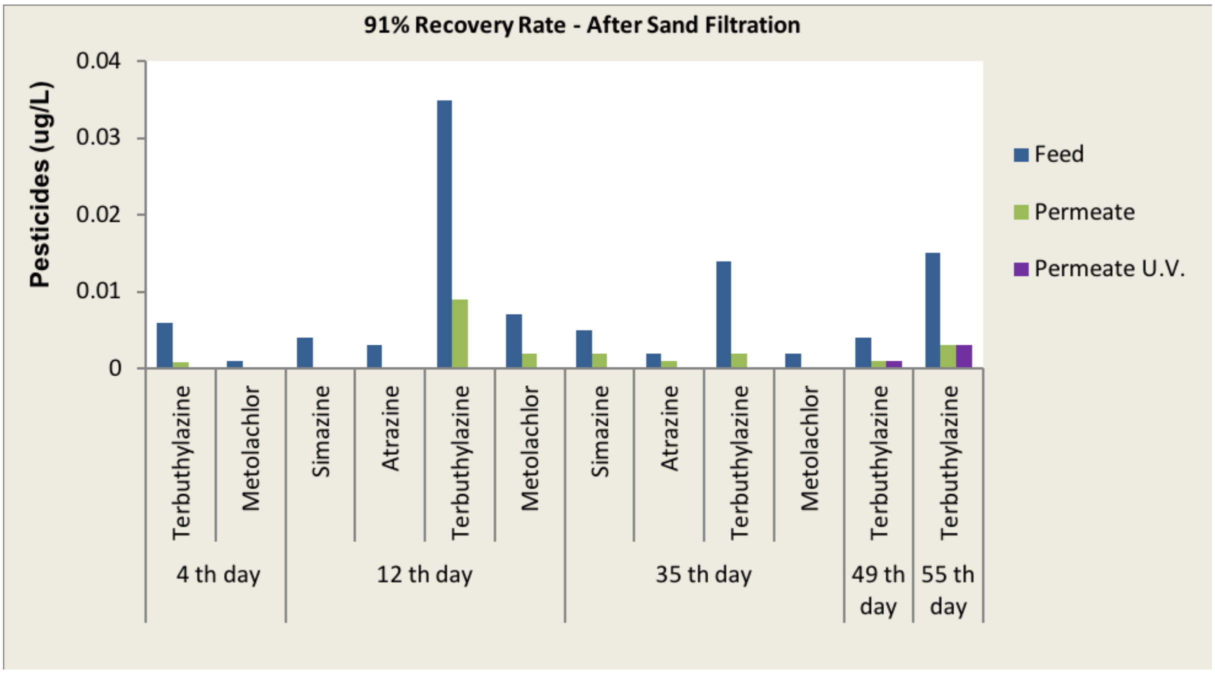

Figure 5-11. Pesticides' analysis for the study performed after sand filtration, 91% recovery rate. Pesticides' concentrations detected after sand filtration, in the nanofiltration permeate and after nanofiltration + UV photolysis.

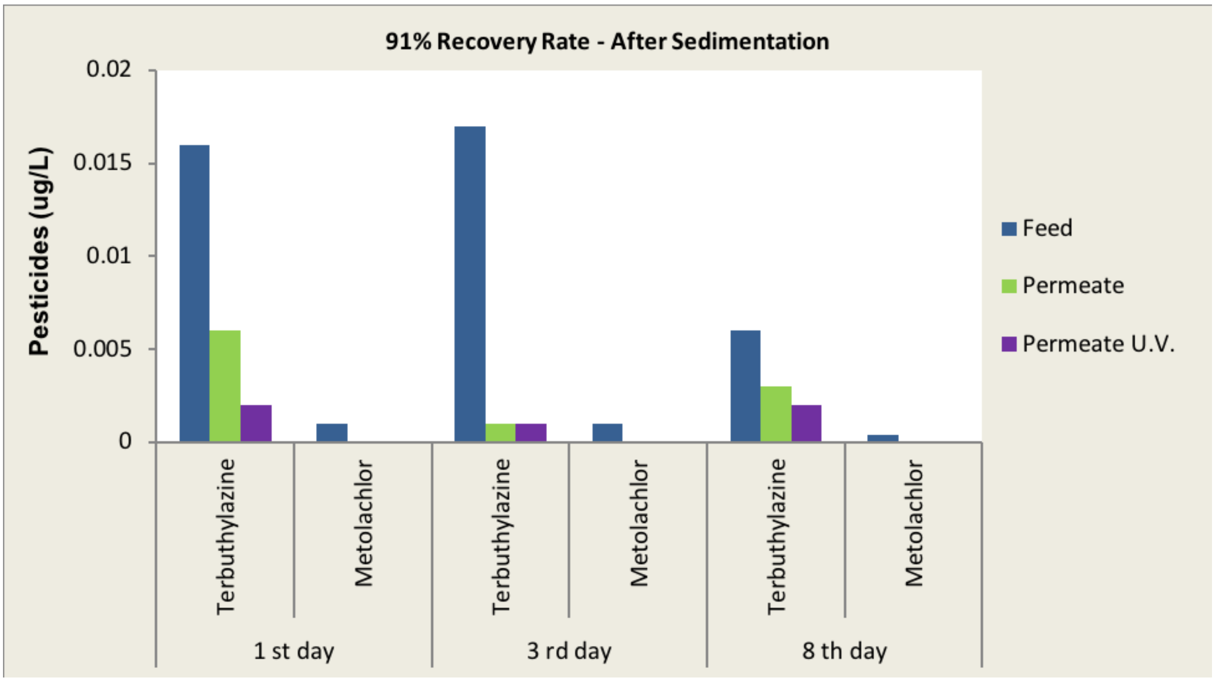

Figure 5-12. Pesticides' analysis for the study performed after sedimentation, 91% recovery rate. Pesticides' concentrations detected after sedimentation, in the nanofiltration permeate and after nanofiltration + UV photolysis.

The combined nanofiltration and LP/UV system proved to be efficient for the removal of the two main pesticides that were found to be present in the surface water collected after sedimentation (terbuthylazine and metolachlor) at different sampling days. Metalachlor, a chloroacetanilide herbicide and terbuthylazine (CBET) are among the pesticides most commonly used throughout the world both for agricultural and non-crop applications. Nevertheless, the toxicological properties of these compounds and their main metabolites cause concern. Metalachlor has been classified as human carcinogenic by WHO (1993) and some metabolites such as 2-ethyl-6-methylaniline (EMA) show significant toxicological properties (Wu et al., 2007; Wols and Hofman-Caris, 2012).

The results obtained show that high removal rates are obtained when comparing the nanofiltration permeate and the feed samples. Even when using a low UV fluence of approximately 400 mJ/cm2, the integration of nanofiltration and UV photolysis allowed for improving the removal of terbuthylazine.

The importance of using UV photolysis, after NF, to remove resilient compounds such as pesticides and hormones was also demonstrated in previous published results, performed at laboratory controlled conditions (Pereira et al., 2012; Sanches et al., 2010; Sanches et al., 2012). The results of the present study clearly show the high efficiency of the combined system under real full plant conditions.

5.5 Conclusions

This research work shows that both nanofiltration and UV disinfection are important solutions for treatment of surface water for the production of drinking water. The integration of both systems increases the performance of water treatment making possible the production of highly pure water, assuring the removal of pesticides below the detection limits, while allowing for lowering the level of chlorine dosage.

The results obtained in a full scale surface water treatment plant using an integrated pilot scale system (nanofiltration and UV) show that, due to the high turbidity and natural organic matter content of surface water, the nanofiltration process should be placed after conventional sand filtration in order to improve nanofiltration performance, avoiding flux decline and minimizing fouling problems. The analysis of the fouling agents shows that organic material is the major contributor for fouling and that alkaline cleaning of the membrane is efficient to restore the initial membrane permeability. According with the operation results, an alkaline cleaning-in-place protocol should be performed every 15 days of nanofiltration operation with a recovery rate of 91%, in order to restore membrane performance.

5.6 References

Al-Amoudi A., Lovitt R.W., 2007. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. Journal of Membrane Science, 303, 4-28.

Benitez F.J., Real F.J., Acero J.L., Garcia C., 2006. Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters. Journal Hazardous Materials. 138, 278–287.

Canonica S., Meunier L., von Gunten U., 2008. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. Water Research 42, 121–128.

Cyna B., Chagneaub G., Bablon G., Tanghe N., 2002. Two years of nanofiltration at the M&y-sur-Oise plant, France. Desalination 147, 69-75.

Drinking Water Directive 98/83/EC.

Dubois M., Gilles K.A., Hamilton J.K., Rebers P.A., Smith F., 1956. Colorimetric Method for Determination of Sugars and Related Substances. Analytical Chemistry, 28, 350-356.

Gozzi F., Machulek Jr. A., Ferreira V.S., Osugi M.E., Santos A.P.F., Nogueira J.A., Dantas R.F., Esplugas S., de Oliveira S.C., 2012. Investigation of chlorimuron-ethyl degradation by Fenton, photo-Fenton and ozonation processes. Chemical Engineering. Journal., 210, 444-450.

Guo W., Ngo H.H., Li J., 2012. A mini-review on membrane fouling. Bioresource Technology 122, 27-34.

Haque M.M., Muneer M., 2003. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. Journal of Environmental Management, 69 (2), 169–176.

Her N., Amy G., Plottu-Pecheux A. and Yoon Y.,2007. Identification of nanofiltration membrane foulants. Water Research, 41(17),3936-3947.

Huber M.M., Canonica S., Park G.Y., Von Gunten U., 2003. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environmental Science & Technology, 37, 1016–1024.

Klüpfel, A.M., Frimmel F.H., 2010. Nanofiltration of river water — fouling, cleaning and micropollutant rejection. Desalination 250, 1005–1007.

Kluplel, A.M. , Fummel F.H., 2010. Nanofiltration of river water- fouling, cleaning and micropollutants rejection. Desalination 250, 1005-1007.

Koyuncu I., Arikan O.A., Wiesner M.R., Rice C., 2008. Removal of hormones and antibiotics by nanofiltration membranes. Journal of Membrane Science. 309, 94–101.

Linden K., Shin, G., Faubert G., Caims, W. and Sobsey, M., 2002. UV disinfection of Giardia lamblia cysts in water. Environmental Science & Technology, 36 (11), 2519 – 2522.

Lowry O.H., Rosebrough N.J., Farr A.L., Randall R.J., 1951. Protein Measurements with the Folin Phenol Reagent. Journal of Biological Chemistry, 193, 265-275.

Madaeni S.S., Samieirad S., 2010. Chemical cleaning of reverse osmosis membrane fouled by wastewater. Desalination, 257, 80-86.

Marconnet C., Houari A., Galas L., Vaudry H., Heim V., Di Martino P., 2009. Biodegradable dissolved organic carbon concentration of feed water and NF membrane biofouling: a pilot train study. Desalination, 242, 228–235.

McCallum E.A., Hyung H., Do T.A., Huang C.H., Kim J.H.,2008. Adsorption, desorption, and steady-state removal of 17β-estradiol by nanofiltration membranes. Journal of Membrane Science, 319, 38–43.

Mi B., Elimelech M.,2009. Organic fouling of forward osmosis membrane: Fouling reversibility and cleaning without chemical reagents. J. Memb. Sci. 348,337-345.

Mosqueda-Jiminez D.B., Huck P.M., Basu O.D., 2008. Fouling characteristics of an ultrafiltration membrane used in drinking water treatment. Desalination, 230, 79-91.

Oliveira F.R.P., Matos C. T., Moura J. J.G., Portugal C. A. M., Crespo J. G., 2011. Study of membrane ageing and grafting mechanisms using electron paramagnetic resonance. Desalination and Water Treatment, 27, 150-158.

Peiris, R. H., Budman H., Moresoli C. and Legge R. L., 2010. Understanding fouling behaviour of ultrafiltration membrane processes and natural water using principal component analysis of fluorescence excitation-emission matrices. Journal of Membrane Science 357(1-2), 62-72.

Peldszus S., Halle C., Peiris R.H., Hamouda M., Jin X., Legge R.L., Budman H., Moresoli C. and Huck P.M., 2011. Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. Water Research, 45(16), 5161-5170.

Pereira V.J., Galinha J., Barreto Crespo M.T., Matos C.T. and Crespo J.G., 2012. Integration of nanofiltration, UV photolysis, and advanced oxidation processes for the removal of hormones from surface water sources. Separation and Purification Technology, 95, 89-96.

Qaisrani T.M., Samhaber W.M., 2010. Impact of gas bubbling and backflushing on fouling control and membrane cleaning. Desalination, 266,154-161.

Sanches S., Barreto Crespo M.T. and Pereira V.J., 2012. Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. Water Research, 44(6),1809-1818.

Sanches S., Leitao C., Penetra A., Cardoso V.V., Ferreira E., Benoliel M.J., Crespo M.T. and Pereira V.J., 2011. Direct photolysis of polycyclic aromatic hydrocarbons in drinking water sources. Journal Hazardous Materials, 192(3), 1458-1465.

Sanches S., Penetra A., Rodrigues A., Cardoso V.V., Ferreira E., Benoliel M.J., Barreto Crespo M.T., Crespo J.G., Pereira V.J., 2013. Removal of pesticides from water combining low pressure UV photolysis with nanofiltration. Separation and Purification Technology, 115,73-82.

Sanches S., Penetra A., Rodrigues A., Ferreira E., Cardoso V.V., Benoliel M.J., Barreto Crespo M.T., Pereira V.J. and Crespo J.G., 2012. Nanofiltration of hormones and pesticides in different real drinking water sources. Separation and Purification Technology. 94, 44-53.

Schäfer A., Nghiem L., Waite T., 2003. Removal of the Nature Hormone Estrone from Aqueous Solutions Using Nanofiltration and Reverse Osmosis. Environmental Science & Technology, 37, 182–188.

Spettmann D., Eppmann S., Flemming H., Wingender J., 2007. Visualization of membrane cleaning using confocal laser scanning microscopy. Desalination, 224, 195-200.

Van der Bruggen B., Braeken L., Vandecasteele C., 2002. Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds. Desalination 147, 281–288.

Wols B.A., Hofman-Caris C.H.M., 2012. Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water. Water Research, 46, 2815-2827.

Wong C., Chu W., 2003. a.The hydrogen peroxide-assisted photocatalytic degradation of alachlor in TiO2 suspensions. Environmental Science & Technology, 37 (10), 2310–2316.

Wong C., Chu W., 2003. b.The direct photolysis and photocatalytic degradation of alachlor at different TiO2 and UV sources. Chemosphere, 50 (8), 981–987.

Wu C., Shemer H., Linden K.G., 2007. Photodegradation of metalochlor applying UV and UV/H2O2. Journal of Agricultural and Food Chemistry, 55, 4059-4065.

Xu P., Bellona C., Drewes J.E., 2010. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: Membrane autopsy results from pilot-scale investigations. Journal of Membrane Science, 353, 111-121.

Xu P., Drewes J.E., Kim T., Bellon C., Amy G., 2006. Effect of membrane fouling on transport of organic contaminant in NF/RO membrane applications. Journal of Membrane Science, 279, 165-175.

Yangali-Quintanilla V., Sadmani A., McConville M., Kennedy M., Amy G., 2009. Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. Water Research, 43, 2349–2362.

Younes and Galal- Gorchev, 2000. Pesticides in drinking water – A case study. Food and Chemical Toxicology ,Volume 38, Supplement 1, 1 April 2000 Pag. 587-590.

Zhang Y., Zhou J.L., Ning B., 2007. Photodegradation of estrone and 17β- estradiol in water. Water Research, 41, 19–26.

Zularisam A.W., Ismail A.F., Salim R., 2006. Behaviors of natural organic matter in membrane filtration for surface water treatment – a review. Desalination, 194, 211-231.

Chapter

6

Arsenate Removal From Sulphate-Containing Water Streams by an Ion-Exchange Membrane Process

6.1 Summary

A possible limitation of applying Donnan dialysis for arsenate removal from drinking water supplies is when sulphate is present as an accompanying anion in the water to be treated, due to strong competition between arsenate and sulphate transport through standard grade anion-exchange membranes. This work aims at evaluating the feasibility of employing an ion-exchange membrane Donnan dialysis based process with a new strategy of using sulphate as the driving counter-ion for arsenate counter-transport and removal from sulphate-containing drinking water streams. The process performance with different arsenate receiving solutions (containing chloride or sulphate as driving counter-ions and with or without arsenic precipitation) was investigated and compared. Experiments were carried out to separate arsenate from contaminated water comparing the performance of three anion-exchange membranes: one with mono-valent anion permselective properties and two standard grade membranes. As selection criteria, the transport rate of arsenate and its membrane retention were investigated. The effects of pH variation and co-ion (cation) leakage on the Donnan dialysis process efficiency were also studied. Efficient arsenic removal was achieved through integrating Donnan dialytic transport of arsenate with its simultaneous precipitation in the receiving compartment with $FeSO_4$. The process proposed is environmentally friendly and with minimal maintenance requirements, which makes it especially attractive to be applied in rural areas located far from centralized drinking water supply infrastructures.

Published as: Pessoa-Lopes, m., Crespo, J.G., Velizarov, S., 2016, Arsenate removal from sulphate-containing water streams by an ion-exchange membrane process, Separation and Purification Technology, 166, 125-134.

6.2 Introduction

Arsenic (As) incidence has been the focus of increasing attention since a number of countries are facing the challenge of treating their drinking water supplies in order to meet the current regulation standards for As. Due to its toxicty, mutagenicity and carcinogenicity, the World Health Organization (WHO), the European Commission (EC) and the United States Environmental Protection Agency (USEPA) reduced the maximum contaminant level (MCL) from 50 µg/L to 10 µg/L in January 2006 (Malik et al., 2009; Mondal et al., 2013). This stiffening of regulations reflects the need of developing highly efficient technologies for selective arsenic removal from water since recent estimations indicate that over 130 million people worldwide are potentially exposed to harmful levels of arsenic in drinking water (Fontàs et al., 2014).

Arsenic occurrence in natural water sources is a consequence of leaching from natural deposits (rocks/minerals) in the earth crust, and, to a lesser degree, due to anthropogenic causes, such as agriculture practices and mining industry pollution. Moreover, arsenic in its inorganic form is more toxic than in its organic form (Akin et al., 2011).

Several treatment options have been applied so far for As removal from water streams, including nanofiltration (Figole et al., 2010), reverse osmosis (Akin et al., 2011) , chemical precipitation and coagulation (Hering et al., 1997; Lacasa et al., 2011), adsorption (Shipley et al., 2011; Baskan and Pala, 2011; Swarnkar and Tomar, 2012; Zhang et al., 2007) and ion exchange (IEX) (Urbano et al., 2012; Issa et al., 2011; Donia et al., 2011). Among them, adsorption and anion exchange processes are the most extensively studied ones, because they generally provide relatively lower costs, ease of handling and potential reuse/recycling of the adsorbents/anion-exchangers.

Different adsorbents and IEX media have been applied such as biological materials, mineral oxides, activated carbons and polymeric resins (Urbano et al., 2012; Issa et al., 2011; Donia et al., 2011; An et al., 2011). The US Environmental Protection Agency (US EPA) has identified IEX as the best available technology (BAT) although the arsenate removal can suffer from interferences due to the presence of accompanying anions that are normally present in drinking water sources in much higher concentrations than that of the arsenic-containing species. The following selectivity order has been reported for strong base anion (SBA) exchangers (United States Enviromental Protection Agency, 2000): $SO_4^{2-} > HAsO_4^{2-} > Cl^- > H_2AsO_4^- > HCO_3^- > OH^-$.

On the other hand, sulphate can be present in groundwater, at levels that sometimes can exceed 1000 mg/L [http://www.health.state.mn.us/divs/]eh/wells/waterquality/sulfate.htm], while arsenic-containing species are most commonly present within the µg/L concentration range. Therefore it is extremely difficult to reduce the As concentration in such sulphate-containing waters below the MCL of 10 µg/L of As using conventional strong anion-exchange resins. Their high affinity for sulphate leads to the need of a frequent regeneration before reuse, thus producing large volumes of brines (An et al., 2010|; Saha and Sarkar, 2012; Awual et al., 2012).

An ion-exchange membrane process, integrating Donnan dialysis with precipitation of target ionic pollutant(s), can offer the possibility of their selective removal, while minimizing the risks of secondary pollution of the treated water, which can occur in conventional IEX treatment after the resin saturation (once the target pollutant breakthrough has occurred). Although the ion-exchange membrane process has relatively slow kinetics when compared to electrodialyisis, it presents several possible advantages, especially in the case of rural applications in developing countries, for being energy saving and an easy to handle process (Oehmen et al., 2011).

In a prior study, performed with model single arsenate solutions, it has been demonstrated that the Donnan dialysis process performance depends strongly on the type of anion-exchange membrane used especially under batch operating conditions (Velizarov, 2013). The removal of ions by Donnan dialysis is, however, affected by several other factors, such as the nature and concentration of accompanying ions, composition and concentration of the receiving solution and pH, amongst others (Hichour et al., 1999).

Therefore this work explores the feasibility of applying an ion-exchange membrane process for arsenic removal from sulphate-containing water streams. The aims of the study are: (1) Examine the transport behavior of arsenate and sulphate and compare their sorption on a mono-valent anion permselective and on two standard grade anion-exchange membranes; (2) Identify optimal process conditions (membrane type and composition of the receiving solution, with and without addition of a precipitant) for arsenate removal and; (3) Investigate the effect of co-ion (sodium) leakage on the process performance.

In this study, a set of Donnan dialysis experiments using NaCl as a receiving solution was first performed. It was investigated if a mono-anion permselective membrane would favor the transport of monovalent arsenate in the presence of divalent sulphate. Subsequently, the performance of two membranes with no claimed mono-anion permselectivity was tested. The affinity of the membranes towards arsenate and sulphate was also studied through dedicated sorption experiments.

A new strategy of using Na_2SO_4 in the receiving solution in order to minimize the interference of the competing sulphate was then studied. Finally, an ion exchange membrane process, Donnan dialysis for membrane transport of arsenate with its simultaneous precipitation by iron using $FeSO_4$ in the receiving solution was evaluated.

6.3 Materials and methods

6.3.1 Reagents and solutions

All reagents ($Na_2HAsO_4.7H_2O$, Na_2SO_4, NaCl and $FeSO_4$) used were of analytical grade. The solutions were freshly prepared with deionized water (conductivity ≤ 1 µS/cm). Feed solutions were spiked with sodium arsenate and sodium sulphate to the desired concentrations, whereas receiving solutions were prepared either with sodium chloride, sodium sulphate or ferric sulphate depending on the aim of the experiment.

6.3.2 Membranes

Three commercial anion-exchange membranes (AEM) were tested: Neosepta ACS (Tokuyama Soda , Japan) which is a mono-valent anion permselective membrane, characterized by a compact surface structure, which causes the rate of transport and efficiency of large anions transport to decrease noticeably; a low-crosslinked PC 200D membrane purchased from PCA-Polymerchemie Altmeier GmbH (Germany), which is a membrane suitable for transport of anions with a molecular mass of up to about 200 Da [http://www.pca-gmbh.com/membrane/membrane.htm]; and an alkali resistant Neosepta AXE 01 membrane from Tokuyama Soda, Japan, suitable for transport of anions with a molecular mass of up to about 300 Da (Tahaikt et al., 2006). All membranes are homogeneous and contain quaternary ammonium as fixed charged groups. Their main properties are listed in Table 6-1.

Table 6-1.Properties of the studied anion-exchange membranes

Manufacturer	Reference	Matrix	Electrical resistance* (Ω cm^2)	Water content* (%)	Ion exchange capacity* (meq g^{-1}dry membrane)	Thickness (mm)**
Tokuyama Soda	Neosepta ACS	Cross-linked polystyrene in a poly(vinly chloride) reinforcing net	2.0 – 2.5	25	1.4 - 2	0.12±0.01
PCA GmbH	PC 200D	Ethyl oxide / polyepichlorohydrin copolimer	2	45	1.3	0.09±0.01
Tokuyama Soda	Neosepta AXE 01	Cross-linked polystyrene in a poly(vinly chloride) reinforcing net	1.5	26.5	1.6-2	0.15±0.01

* Manufacturer data ** Determined in this work

The membrane thickness (in their wet chloride form) was determined (average of five measurements) using a picometer after wiping the membranes with a filter paper for moisture removal.

6.3.3 Dry Weight

The dry weight of membrane circle samples (with an area of 11.3 cm^2 each) was measured after drying in an oven to a constant weight at 60ºC for 9 hours. Immediately after drying, the membrane samples, were put in a desiccator until cooling down to the room temperature before being weighed. This procedure was also applied for longer periods of drying (24 and 72 hours) and the results were found to be consistent with those obtained for 9 hours of drying.

Table 6-2. Dry weight and total fixed charge of the membrane samples used

Membrane	Dry weight (g)	Total fixed charge (meq)*
Neosepta ACS	0.1820 ± 0.0022	0.31
PC 200D	0.2843 ± 0.0014	0.37
Neosepta AXE 01	0.2208 ± 0.0015	0.40

Calculated based on the ion-exchange capacity(IEC) data obtained from the manufacturers. IEC X Dry weight = Total fixed charge (meq)

6.3.4 FTIR measurements

Infrared analyses were performed on a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15xobjective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode (4 cm-1, 128 scans), using a Thermo diamond anvil compression cell in the range 4000-650 cm-1. Periodically the system was purged with nitrogen prior to data acquisition. For all infrared spectra the CO2 adsorption at circa 2400-2300 cm-1 was removed.

6.3.5 Donnan dialysis experiments

These experiments were carried out in a dialysis cell made of plexiglass Figure 6-1, in which two compartments (136 ml each) are in contact through a circular window, where the studied membrane sample (with an area of 11.3 cm^2) was placed. Each compartment was equipped with a stirrer (with a stirring rate set to 700 rpm, to avoid/minimize concentration polarization effects). All experiments were performed in batch operation mode in an air-thermostated room at 24ºC. At pre-defined time intervals, samples (2 ml each) were taken from the feed and receiving solutions compartments for inductively coupled plasma (ICP) analyses.

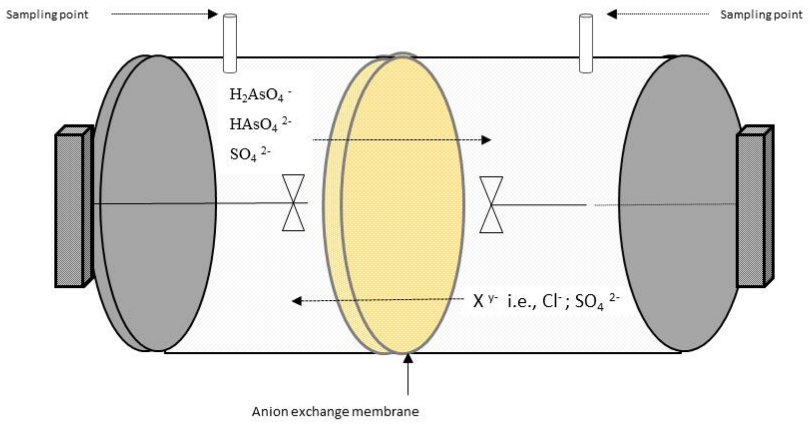

Figure 6-1. A schematic representation of the dialysis cell used.

In the feed (polluted water) compartment, As (in the forms of HAsO42- and H2AsO4-) and SO42- , competing for the transport through the anion-exchange membrane are shown. In the receiver, X y- represents the driving counter-ion used (i.e. chloride or sulphate).

The data obtained were compared in terms of arsenic removal (%) from the feed water as follows:

$$\eta(Removal)(As) = \left(1 - \frac{[As], feed(t)}{[As], feed(0)}\right) \times 100\%$$

Equation 6-1

where $[As]_{feed(0)}$ and $[As]_{feed(t)}$ denote , respectively the arsenic concentrations at the time 0 and at an elapsed time, t, in the feed water compartment.

Two sets of experiments were performed. The first one with feed solutions that contained $Na_2HAsO_4.7H_2O$ and Na_2SO_4, and a NaCl aqueous solution as the receiver. The experimental conditions are presented in Table 6-3, and the results obtained in section 6.4.1. The second set of experiments was performed with feed water solutions containing $Na_2HAsO_4.7H_2O$ and Na_2SO_4, and a receiver solution containing Na_2SO_4 (Table 6-3, Section 6.4.3). Finally, Table 6-3 (Section 6.4.4) presents the experimental conditions used with $Na_2HAsO_4.7H_2O$ and Na_2SO_4 in the feed water and a $FeSO_4$ solution used as the receiver. In all experiments, the concentration of sulphate in the feed was set to be equal or higher than that of arsenate.

Table 6-3. Experimental conditions. - *Section 3.1; 3.3 and 3.4*

Experimental Conditions		Receiving	Feed	
			Arsenate (mM)	Sulphate (mM)
Section 3.1	Neosepta ACS	NaCl (mM) ≈500	0.06	0.04 – 0.2
	PC 200 D		0.04	
	Neosepta AXE 01		0.04	
Section 3.3	Neosepta ACS	Na_2SO_4 (mM) ≈26	0.5	0.5
	PC 200 D		0.5	0.5
	Neosepta AXE 01		0.5	0.5
Section 3.4	Neosepta AXE 01	$FeSO_4$ (mM) 26	0.05	0.3

The schematic representation of the experiments performed is presented in Figure 6-2.

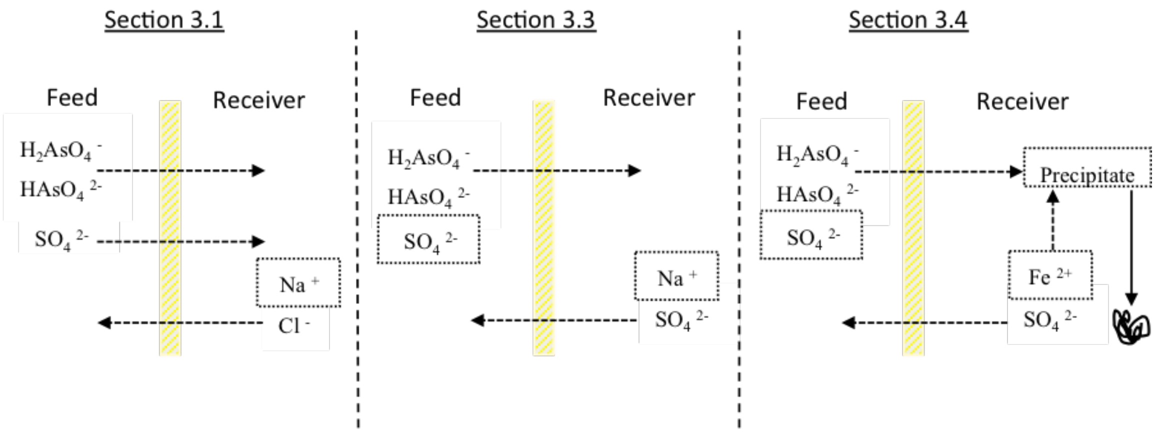

Figure 6-2. Schematic representation of the Donnan dialysis experiments performed.

A binary separation factor was used to compare the efficiency of separation of the two competing ions, (arsenate and sulphate), during the course of the experiments performed with the anion-exchange membranes under study. Similarly to the approach followed in (Clifford, 1999; Logette et al., 1998; Berdous and Akretche, 2002), the arsenate/sulphate separation factor (SF) was defined as:

$$SF = \frac{\left(\frac{[H_xAsO_4^{y-}]}{[SO_4^{2-}]}\right)receiver}{\left(\frac{[H_xAsO_4^{y-}]}{[SO_4^{2-}]}\right)initial\ feed} \text{ E}$$

Equation 6-2

in which $[H_xAsO_4{}^{y-}]$ and $[SO_4{}^{2-}]$ are the molar concentrations of arsenate and sulphate, respectively.

6.3.6 Sorption experiments

Sorption experiments were carried out for the three membranes in order to compare their affinities for arsenate and sulphate, when present in a mixed solution (Section 6.4.2). The tests were performed in conical flasks filled with 50 ml of each test solution after immersing a 9 cm2 piece of the membrane under study. The initial solutions contained equimolar amounts of arsenate and sulphate in the range 0.1 – 1mmol/L, and were placed in a rotary shaker at 200 rpm at room temperature (≈24 ºC) for 6 days. The arsenate and sulphate concentrations in the membranes studied were calculated through Equation 6-3.

$$\mathrm{Cm} = \frac{(\mathrm{C_{in}} - \mathrm{C_{fin}})}{\mathrm{m_{dry\_memb}}} \times \mathrm{V_S}$$

Equation 6-3

where C_{in} and C_{fin} are respectively the initial and final concentration (in mM) of arsenate (or sulphate) in the test solution, Vs is the volume of the test solution (L) and mdry_memb is the dry mass of the membrane piece added (g).

6.3.7 Analytical

The concentrations of arsenate, sulphate and sodium ions, from the samples withdrawn were estimated based on the determined contents of As, S and Na elements, measured by inductively coupled plasma- atomic emission spectrometry (ICP-AES) (Ultima model, Horiba Jobin-Yvon France) equipped with a radio frequency (RF) generator of 40.68 MHz a Czerny-Tner type monochromator with 1.00m (sequential) and with a Hydride Generator with concomitant metals analyzer (CMA) (detection limit for As of 0.5 ppb) , AS500 auto sampler and data acquisition software. The pH was measured with an ORION pH meter (Model 720 A) and the conductivity was followed with an ORION conductivity meter (Model 120).

6.4 Results and discussion

6.4.1 Donnan dialysis performance – NaCl receiving solution

The purpose of these experiments was to evaluate and compare the performance of the membranes selected to transport arsenate in the presence of sulphate, under Donnan dialysis operating conditions using chloride as the driving counter-ion. Figure 6-3 presents the data obtained in the course of the experiments performed with sodium chloride as the receiving solution. The time evolvement of the arsenate and sulphate concentrations (Figure 6-3 A,B,C and D) and of the separation factor (SF) (Figure 6-3E), defined by Equation 6-2, were followed. The measured pH profiles in the feed and receiver solutions are also shown in Figure 6-3 -A and B. Considering that As (V) exists in both its monovalent ($H_2AsO_4^{-}$) and divalent ($HAsO_4^{2-}$) forms (which at the initial feed pH of 6.7 were present in fractions of 62% and 38%, correspondingly), it was firstly investigated whether a mono-anion permselective membrane (ACS) would favor the monovalent $H_2AsO_4^{-}$ transport, compared with the two other membranes, PC 200D and AXE 01, which do not have a claimed mono-anion permselectivity and possess more "open" polymeric structures (Table 6-1).

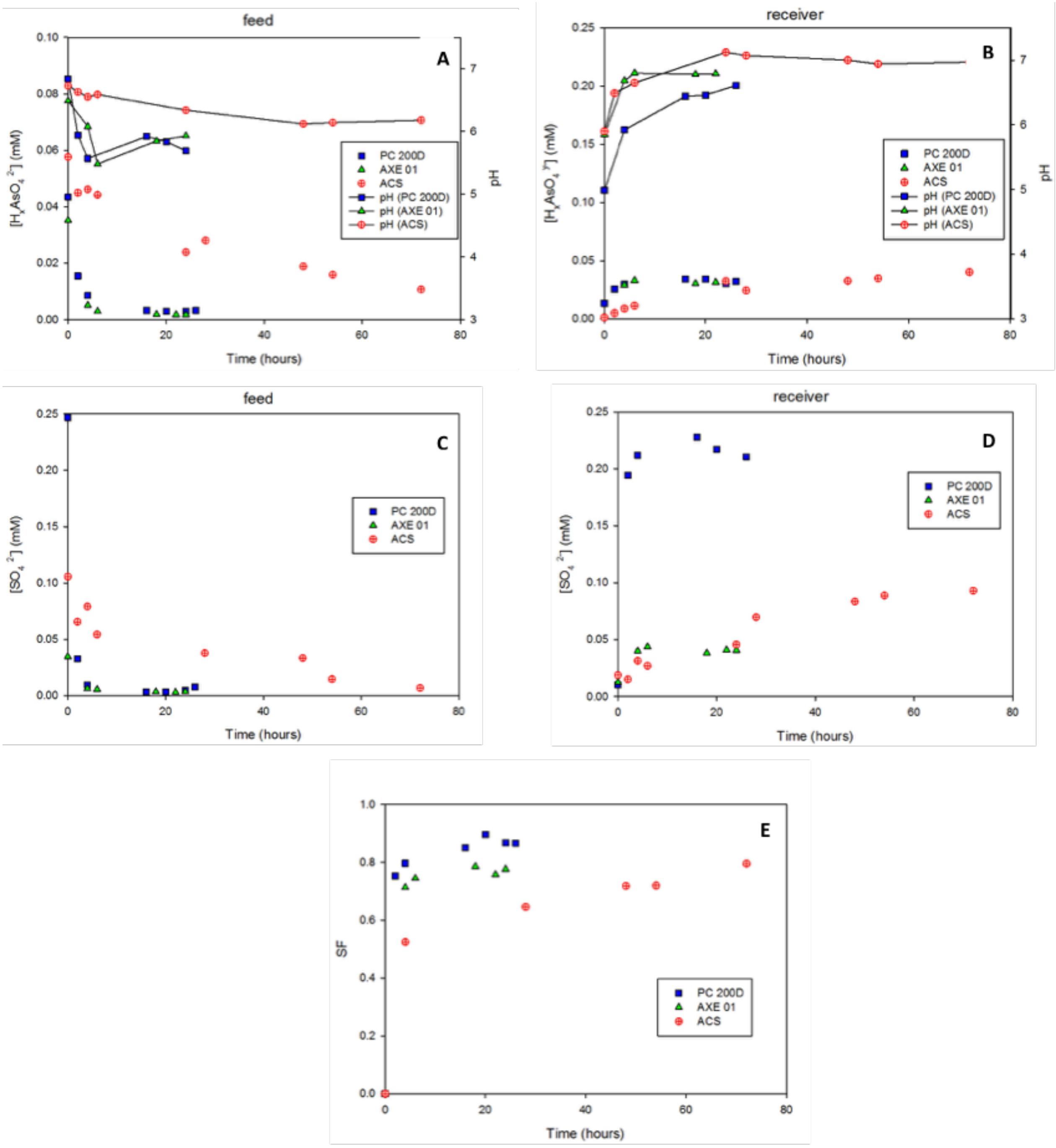

Figure 6-3. Experimental data obtained with the three anion-exchange membranes studied using NaCl solution as a receiver: A- arsenate concentration and pH variation in the feed B- arsenate concentration and pH variation in the

receiver C- sulphate concentration in the feed D- sulphate concentration in the receiver E-Arsenate/sulphate separation factor.

In spite of the presence of a thin highly cross-linked layer on both ACS membrane surfaces (Saracco, 1997), which is supposed to render monovalent-anion-permselective properties to this membrane, no evidence of a preferential (H_2AsO^{4-}) transport was detected. On contrary, with this membranes a significant decrease in divalent sulphate concentration of the feed was observed (Figure 6-3C).

As it can be also observed in Figure 6-3A, the ACS membrane showed the slowest arsenate transport although, after 72h, the degree of arsenate removal (calculated by Equation 6-1) with this membrane reached a value of 81.5%, which was close to those obtained with the other two membranes for a shorter time.

The slowest arsenate and sulphate transport rates , observed with the ACS membrane is due to the fact that this membrane hampers permeation of relatively big divalent anions because of its denser polymeric structure, as demonstrated and discussed in detail by Saracco (Saracco, 1997).

Recently, Fox et al.,2014 also reported a slow perchlorate transport kinetic across the ACS membrane in a study devoted to its removal from contaminated groundwater, which could be attributed to the strong affinity of the membrane to this more hydrophobic anion. Thus, an additional reason for the data obtained with the investigated arsenate/sulphate mixtures could be a stronger sorption/retention of sulphate compared to that of arsenate in this membrane. This hypothesis was experimentally tested and the results obtained are presented in Section 6.4.2.

The pH values in the feed and receiver solutions were followed (Figure 6-3A and B) in order to gain more insight into the time variation of the arsenate speciation, which is pH-dependent. It can be observed that during the first 6 hours of operation, the pH decrease faster with AXE 01 and PC 200D than with the ACS membrane.

This is an indirect indication of the lower arsenate flux across the ACS membrane because, according to Horng and Clifford (Horng and Clifford, 1997), the intra-membrane (when it is in the chloride form) conversion of monovalent to divalent and of divalent to trivalent arsenate would be expected to occur with a HCl formation as follows:

$$2R_4N^+Cl^- + H_2AsO_4^-, \leftrightarrow (R_4N^+)_2HAsO_4^{2-} + Cl^- + H^+Cl^-$$

$$3R_4N^+Cl^- + HAsO_4^{2-}, \leftrightarrow (R_4N^+)_3AsO_4^{3-} + 2Cl^- + H^+Cl^-$$

in which R4N+ represents a fixed anion-exchange site on a strong-base quaternary amine resin.

In Figure 6-3E, it is possible to observed that the AXE 01 membrane has a similar (slightly lower) arsenate/sulphate separation factor compared to that of the PC 200D membrane. Moreover, with the AXE 01 membrane a 95% removal of arsenic from the feed (as calculated by Equation 6-1) was achieved. The higher thickness of this membrane, a characteristic that usually leads to a higher resistance to mass transport, is most probably counterbalanced with its higher anion-exchange capacity and a more "open" polymeric matrix structure (Table 6-1), which facilitate the intra-membrane arsenate transport.

The latter is experimentally evidenced by the data (expressed in two different manners) obtained with this membrane (Figure 6-4). For the data presented in Figure 6-3B, it was assumed that only divalent arsenate anions exist inside the anion exchange membrane since the intramembrane pH value is higher than in the bulk solution due to the Donnan co-ion (H^+) exclusion (Guell et al., 2011).

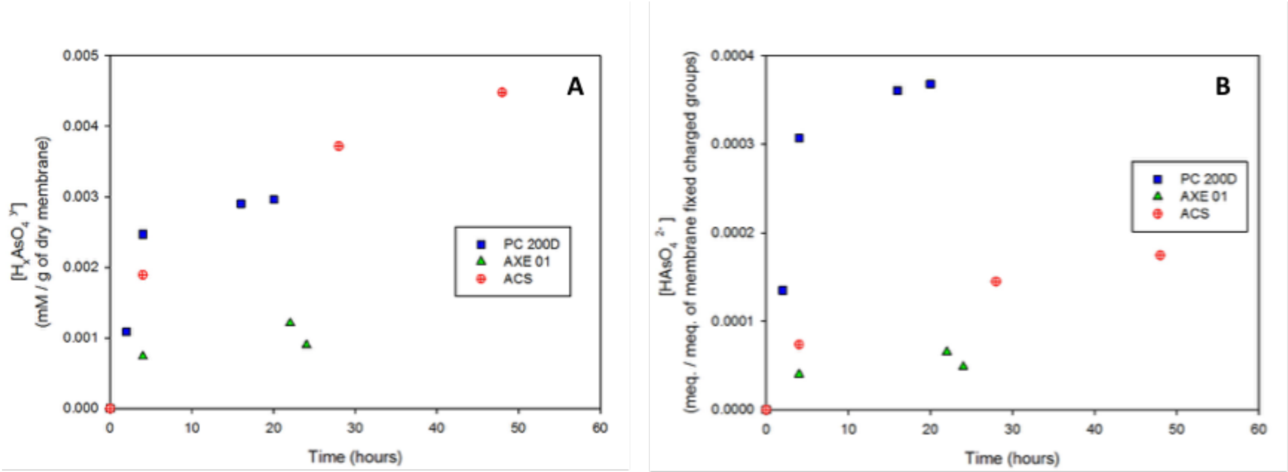

Figure 6-4. Membrane retention of arsenate for the experiments using chloride as a driving counter-ion, for the three membranes under study. A)- mM of arsenate

per g of dry membrane and B) – meq. Arsenate (assumed as divalent) per meq. of membrane fixed charged groups.

As it can be seen, the PC 200D membrane presents the highest sulphate transport rate to the receiver (Figure 6-3D). With this membrane also the higher (92.6%) removal of arsenate from the feed was obtained. It is important to observe the notoriously higher arsenate retained, on the basis of avalaible fixed charged groups in the PC 200D membrane (Figure 6-4B), although this membrane posseses a total amount of fixed charged groups (Table 6-2), that is comparable to that of the AXE 01 membrane sample.

This behaviour of the PC 200D membrane could be attributed to several structure and functionality related reasons. A more open and flexible structure facilitates an easier re-orientation of neighboring fixed charges towards divalent arsenate. Furthermore, according to the manufacturer (http://www.pca-gmbh.com/membrane/datasht2.htm), this membrane contains not only strong (quaternary amine), but also some weak (tertiary amine) fixed charges, with an expectedly high affinity to arsenate.

Indeed, while dedicated FTIR measurements demonstrated practically identical infrared spectra for the Neosepta ACS and Neosepta AXE 01 membranes, significant differences were observed for the PC 200D membrane (see Figures. SM1, SM2 and SM3, in Supplementary material). Besides its different chemical composition, another important difference is that for reinforcement of the polymeric structure, polyester is used, instead of polyvynil chloride for the Neosepta membranes family as revealed by the FTIR measurements.

Overall, as it can be observed in Figure 6-3E, all studied membranes show preferential transport of sulphate over arsenate (SF < 1). A similar retardation of arsenic transport due to the presence of sulphate as an accompanying anion has been reported for other anion-exchange membranes, e.g., for an JAM homogenous membrane (Huanyld, China) (Zhao et al., 2010). The arsenate / sulphate SF values increased along the experimental time, when the arsenate remaining in the feed could apparently not undergo competition from the accompanying sulphate anions already transported to the receiver compartment.

6.4.1.1 Phenomenon of salt leakage - NaCl

It is known that Fickian diffusion of an electrolyte across an ion-exchange membrane can occur due to its concentration gradient between the receiving and the feed solution thus diminishing the membrane counter-ion permselectivity to values that are lower than those expected based on an ideal Donnan co-ion(s) exclusion. In pratical terms, electrolyte “leakage” to the feed solution is an undesirable phenomenon in drinking water treatment, since it may increase the mineralization of the treated water above acceptable levels (Hichour et al., 2000).

In order to investigate the relevance of the phenomenon of co-ion leakage in the experiments performed with the three investigated membranes, the initial and final values of conductivity and sodium ion concentrations in the feed solutions were measured and compared (Figure 6-5).

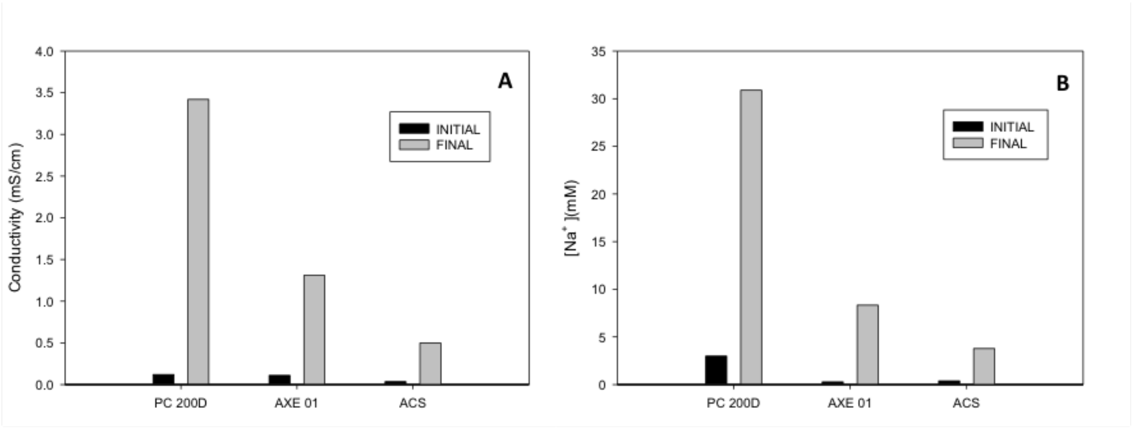

Figure 6-5. Conductivity (A) and sodium ion concentration (B) in the feed solution (in the experiments performed with 500 mM of sodium chloride (initial conductivity of 46.5 mS/cm) in the receiver solution.

As it can be observed in Figure 6-5A, a NaCl leakage occurred from the receiver to the feed compartment, thus increasing the final conductivity of the feed solutions in the order PC 200D>AXE 01>ACS membrane.

The efficiency of the Donnan exclusion of the co-ions (sodium ions in the case studied) by the anion-exchange membranes is presented in Figure 6-4B. Since the water content of ACS and AXE 01 membranes is much lower than that of PC 200D (Table 6-1), it can be anticipated that salt diffusion would be reduced across these membranes (Hichour et al., 1999; Garmes et al., 2002).

Moreover, the PC 200D is composed of low-crosslinked polymeric chains consisting of aliphatic polyethers. Therefore it is not suprising that the Na$^+$ exclusion is much less efficient than that oferred by the PS-DVB based polymeric structures, characteristic for the membranes of the Neosepta family [http://www.pca-gmbh.com/public/forum.htm]. If the PC 200D membrane is to be applied, a possible solution to the electrolyte leakage problem could be to use multivalent co-ions(*e.g.,* Mg^{2+}, Fe^{3+}, etc.) instead of monovalent Na^+ co-ions in the receiving compartment in order to enhance their Donnan exclusion from the membrane.

6.4.2 Membrane Sorption Experiments

Dedicated sorption experiments were performed in order to better understand the possible reasons for the differences detected in the performance of the three membranes.

The sorption preference of the membranes towards arsenate and sulphate were compared for model solutions containing arsenate and sulphate anions present at equal concentrations of 0.1, 0.5 and 1 mM (Figure 6-6).

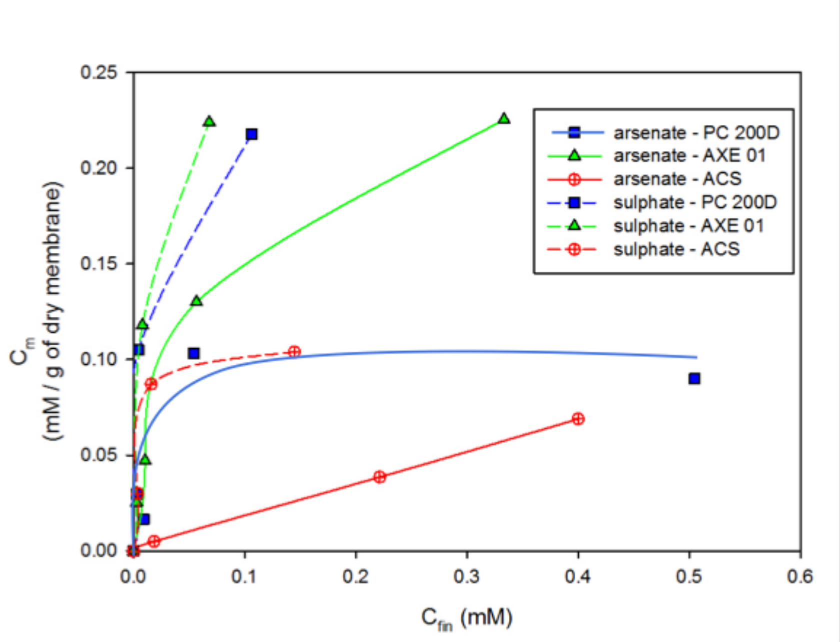

Figure 6-6. Arsenate and sulphate concentrations in the studied membranes (C_m) for final concentrations (C_{fin}) in the external solutions.

The data presented in Figure 6-6 verified that all membranes have higher sorption for sulphate compared to that for arsenate. The most distinctive behaviour can be observed for the ACS membrane, which offers the lowest arsenate sorption within the studied concentration range. The arsenate profile with the ACS membrane did not reach a plateau (Figure 6-6), which may indicate that the equilibrium distribution between the membrane and the liquid phase is dominated mainly by steric hindrance and to a lesser degree to charge repulsion effects as already discussed in section 6.4.1.

6.4.3 Donnan dialysis performance – Na2SO4 receiving solution

In order to minimize the interference of sulphate as a competing anion and to increase the arsenate removal efficiency, the use of the sulphate as a driving counter ion, instead of the commonly used chloride was investigated. The working hypothesis was that arsenate in the feed solution will be replaced by sulphate, which, in turn, would not compete with the arsenate transport across the membrane (see Figure 6-2). Furthermore, since the arsenic levels in contaminated drinking water supplies rarely exceed a few mg/L, their necessarily equal (in equivalent terms) replacement by sulphate (with a MCL in drinking water of 250 mg/L (Background document for development of WHO guidelines for drinking water quality; EC, 1998) is not expected to be problematic from a drinking water quality viewpoint.

Figure 6-7 presents the arsenate and sulphate concentration profiles in the feed and receiver compartments and the corresponding pH of the two solutions (in Figure 6-7 A and B) during the experiments with the three membranes under study.

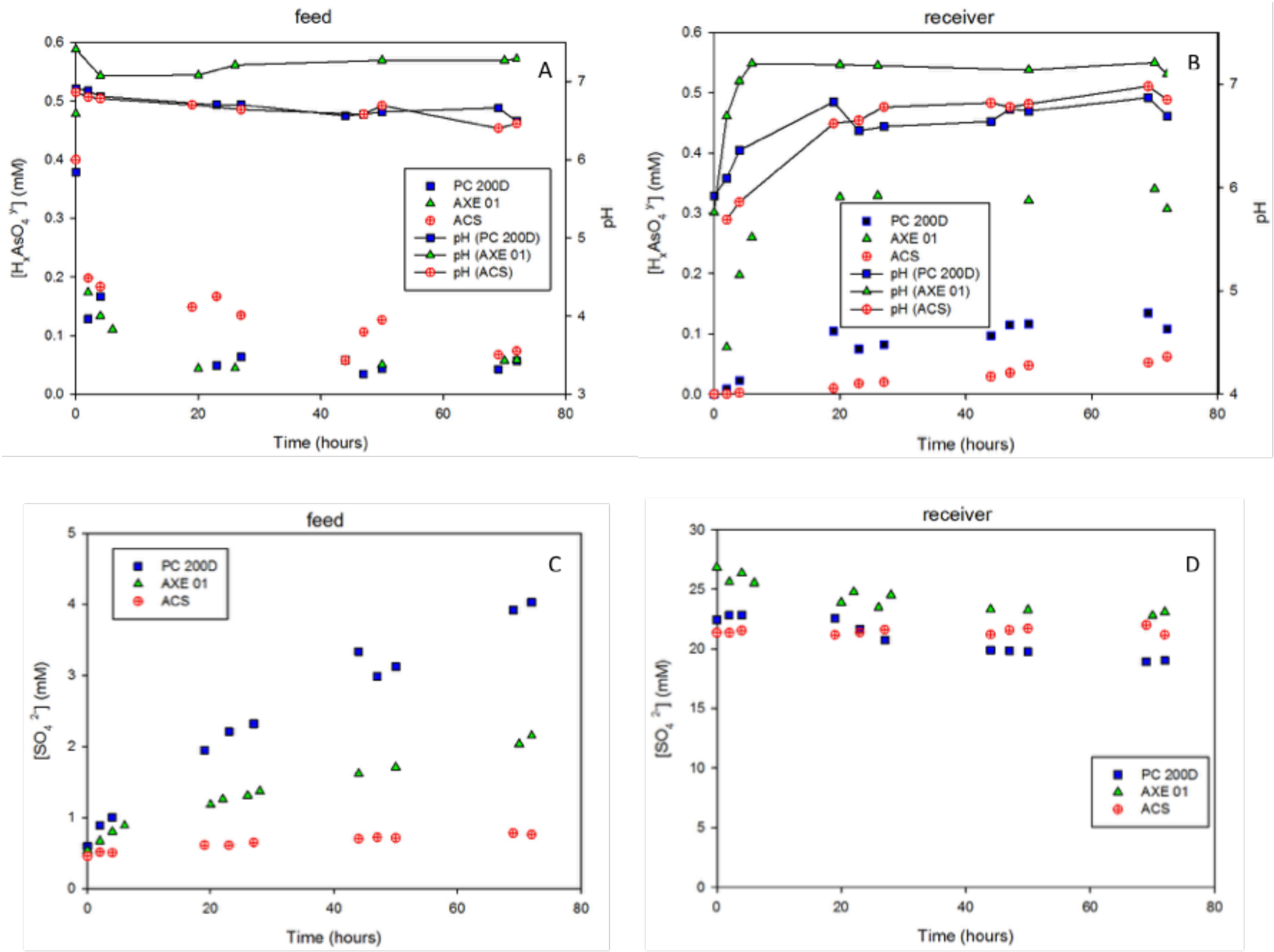

Figure 6-7. Arsenate (A and B) and sulphate (C and D) concentrations in feed and receiver compartments, respectively, using sulphate as a driving counter-ion. A)- arsenate in feed ; B)- arsenate in receiver; C) – sulphate in feed and D) – sulphate in receiver.

From the results presented in Figure 6-7 A, it can be inferred that with the three membranes provide a similar decrease in the arsenate concentration over time in the feed compartment occurs, while in the receiver, the AXE 01 membrane provides the faster increase of the arsenate concentration (Figure 6-7B).

Comparing the pH evolution trends observed with Na_2SO_4 as the receiver solution (Figure 6-7A and B) with the case of using NaCl as the receiver solution (Figure 6-3A and B), it is noticeable that, with all tested membranes, the feed pH decrease was less abrupt when using SO_4^{2-} instead of Cl^- driving counter-ions. This behaviour could probably be attributed to a lesser H^+ formation when using SO_4^{2-} as driving counter-ions, due to an equivalent divalent arsenate – divalent sulphate exchange without H^+ liberation.

As expected, the lowest sulphate transport to the feed compartment was documented for the ACS membrane (Figure 6-7C). The PC 200D membrane demonstrated a sulphate decrease of 3.5mM in the receiver, which corresponded well to the sulphate increase in the feed of 3.4 mM. The data for the AXE 01 membrane showed that 2.17 mM of the sulphate anions remained retained inside the membrane, corresponding to an increase in the sulphate concentration in the feed of 1.57 mM.

Figure 6-8 presents the arsenate retention in the membranes, assessed through the respective mass balances applied for the feed and receiver compartments.

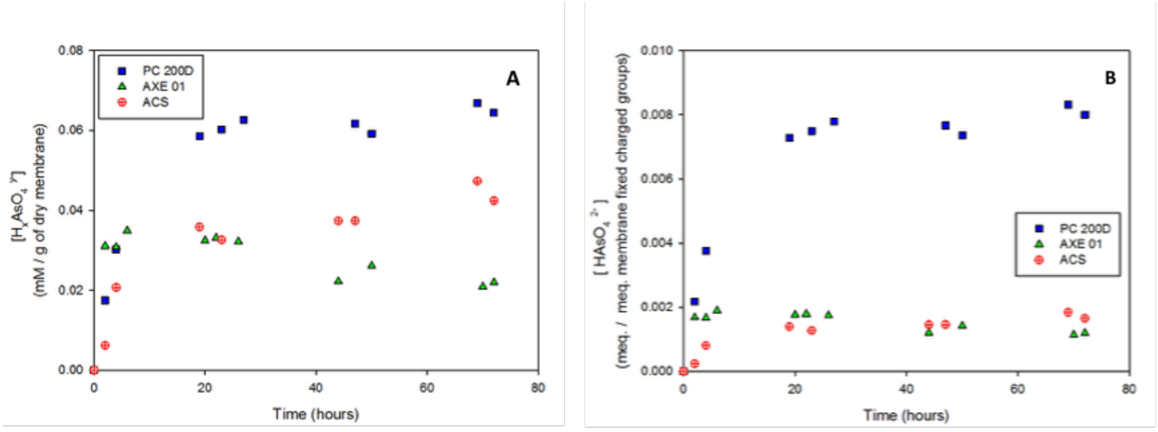

Figure 6-8. Arsenate membrane retention when using sulphate as a driving counter-ion. A)- mM of arsenate per g of dry membrane and B)- meq. of divalent arsenate per meq. of membrane fixed groups.

Similar initial rates of arsenate retention can be observed for the three studied membranes, however the PC 200D membrane demonstrated the highest final arsenate retention, which is consistent with the data obtained when using chloride as the driving counter-ion (see Figure 6-4). This behaviour could be probably related to its distinct chemical polymeric structure and to the presence of a polyester support confirmed by FTIR (see supplementary material) which may render more flexible and hydrophilic properties to this membrane.

The faster initial arsenate saturation kinetics of the AXE 01 membrane may be explained by its more open polymeric structure, providing a better mobility of arsenate and its easier release to the receiver solution.

6.4.4 Phenomenon of salt leakage – Na2SO4

The importance of the phenomenon of salt leakage in the experiments performed with sulphate as the driving counter-ion was investigated (Figure 6-9) and compared to the case of using chloride as the driving counter-ion (Figure 6-5).

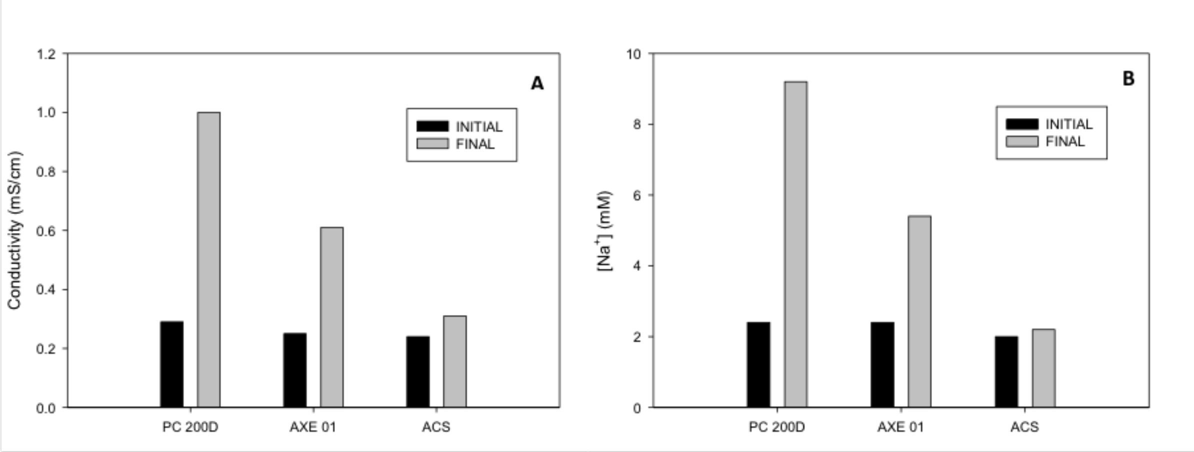

Figure 6-9. Conductivity (A) and sodium ion concentration (B) in the feed solution (in the experiments performed with 26 mM of sodium sulphate (initial conductivity of 5 mS/cm) and in the receiver solution.

The data presented in Figure 6-9 reveal the same general trend for salt leakage across the membranes as presented in Figure 6-5, namely PC 200D > AXE 01 > ACS membrane. However, as it was anticipated, the salt leakage phenomenon is less important with sulphate as driving counter-ion, due to its larger size and divalent charge, which leads to lower Na_2SO_4 diffusion rates from the receiver to the feed. This effect is especially notorious for the case of Neosepta ACS membrane, which is achieved at the cost of a significantly lower arsenate mass transport rate from the feed to the receiver compartment. However, if a very selective removal of arsenate is desired, or the water to be treated contains high sulphate levels that are close to its MCL value, the use of the Neosepta ACS membrane may prove to be a good choice.

6.4.5 Arsenate removal through the Ion Exchange Membrane Process

The feasibility of integrating Donnan dialysis for the transport of arsenate through an anion exchange membrane with its simultaneous precipitation by iron, using $FeSO_4$ in the receiving solution, was studied in this experiment. The Neosepta AXE 01 membrane was selected since it provides an efficient arsenate transport with a relatively low arsenate membrane retention and acceptable electrolyte leakage.

The arsenate and sulphate concentration profiles obtained in the feed and the receiver compartments for a feed water containing initially 0.05 mM (7.5 mg/L) of arsenate and 0.3 mM (≈25 mg/L) of sulphate are presented in Figure 6-10.

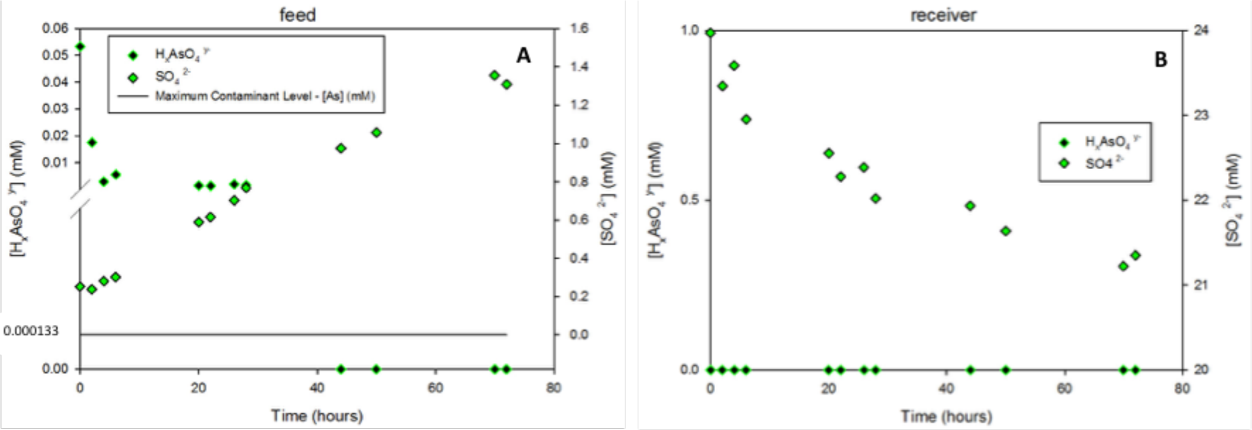

Figure 6-10. Arsenate and sulphate concentration profiles in the feed (Arsenate $_{initial}$ – 0.05 mM ; $SO_4{}^{2-}{}_{initial}$ - 0.3 mM) and receiver solutions when using 26 mM of $FeSO_4$ as a receiver solution. The membrane used was Neosepta AXE 01. The straight line at 0.000133 mM of arsenate in Figure A represents the MCL level of 10 ppb of As.

The results show that within less than two days the arsenate content in the feed water dropped to below the arsenic detection limit (0.5 µg/L of As), thus guaranteeing arsenic removal far below its MCL of 10 µg/L. Moreover, the presence of $FeSO_4$ in the receiver compartment allowed to maintain the arsenate mass transport driving force across the membrane at its maximal possible value due to the efficient arsenate precipitation in the receiver compartment.

At the same time, the amount of sulphate permeating to the water compartment remained under its drinking water MCL of 250 mg/L during the entire duration (72 hours) of the experiment.

6.5 Conclusions

The results obtained in the present study demonstrate that the ion-exchange membrane process concept used can be successfully applied for arsenate removal from sulphate-containing water streams. The major outcomes of the study can be defined as:

The use of mono-anion permselective membranes such as Neosepta ACS membrane for separation of arsenate from sulphate with chloride as the driving counter-ion is not recommendable since sulphate transport was favoured, despite the mono-anion permselective properties of the membrane.

Applying a new concept of using sulphate as a driving counter-ion for arsenate counter-transport across anion-exchange membranes with distinct properties, demonstrates that efficient and, if necessary, highly selective arsenate removal from sulphate containing water streams can be achieved.

The Neosepta AXE 01 membrane seems to be an appropriate candidate for the arsenate separation / purification by providing a good compromise between performance (high arsenate membrane transport with relatively low arsenate membrane retention) and an acceptable salt leakage from the receiver to the treated water compartment.

The undesirable phenomenon of salt ($NaCl$ or $NaSO_4$) leakage from the receiver to the feed compartment was found to be significant in the experiments with the PC 200D membrane. A possible way to its minimization could be the use of multivalent co-ions (e.g., Mg^{2+}, Fe^{2+}, etc.) instead of Na^+ due to their expectedly more efficient Donnan exclusion from the positively charged membrane fixed charges.

The use of $FeSO_4$ in the receiving solution causes arsenic precipitation and maintains the arsenate concentration difference between the receiver and the feed solutions at its maximum possible value. The latter ensures high arsenate transport driving force across the membrane.

Further work consists in validating the concept proposed with groundwater (from the region of Ponte de Sôr, Portugal), which is naturally contaminated with arsenic.

6.6 References

Akin I., Arslan G., Tor A., Cengeloglu Y., Ersoz M., 2011. Removal of arsenate [As(V)] and arsenite [AS(III)] from water by SWHR and BW-30 reverse osmosis. Desalination 281, 88-92.

An B., Fu Z., Xiong Z., Zhao D., SenGupta A.K., 2010. Synthesis and characterization of a new class of polymeric ligand exchangers for selective removal of arsenate from drinking water. Reactive Functional Polymers. 70, 497-507.

Awual Md R. , Shenashen M.A. , Yaita T., Shiwaku H., Jyo A., 2012. Efficient arsenic (V) removal from water by ligand exchange fibrous adsorbent. Water Reserach. 46,5541-5550.

Background document for development of WHO Guidelines for Driniking-water Quality, Sulfate in Drinking-water, WHO/SDE/WSH/03.04/114.

Baskan M.B. , 2011. A. Pala, Removal of arsenic from drinking water using modified natural zeolite. Desalination, 281, 396-403.

Berdous D., Akretche D.E., 2002. Recovery of metals by Donnan dialysis with ion exchange textiles. Desalination, 144, 213-218.

Clifford D.A.. Ion Exchange and Inorganic Adsorption in Water Quality and Treatment, A Handbook of Community Water Supplies, American Water Works Association, 9.1-9.91.McGraw-Hill, New York, NY.

Donia A., Atia A., Mabrouk D., 2011. Fast kinetic and efficient removal of As(V) from aqueous solution using anion Exchange resins. Journal Hazardous Materials, 191, 1-7.

EC, Council Directive 98/83/EC/3-11-1998/ on the quality of water intended for human consumption, Official Journal of the European Communities L330 (1998) 42.

Figoli A., Cassano A., Criscuoli A., Mozumder M.S.I., Uddin M.T., Islam M. A., Drioli E., 2010. Influence of operating parameters on the arsenic removal by nanofiltration. Water Research, 44, 97-104.

Fontàs C., Vera R., Batalla A., 2014. A novel low-cost detection method for screening of arsenic in groundwater. Environmental Science Pollution Research,. 21, 11682-11688.

Fox S., Oren Y., Ronen Z., Gilron J., 2014. Ion exchange membrane bioreactor for treating groundwater contaminated with high perchlorate concentrations. Journal Hazardous Materials, 264, 552-559.

G. Saracco, 1997. Transport properties of monovalent-ion-permselective membranes, Chemical Engineering Science., 52, 3019-3031.

G.J. Hering, P. Chen, J.A. Wilkie, M. Elimelech, 1997. Arsenic removal from drinking water during coagulation, Journal Environmental Engineering, 123 No 8, 800-807.

Garmes H., Persin F., Sandeaux J., Pourcelly G., Mountadar M., 2002. Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis. Desalination, 145, 287-291.

Guell R., Fontàs C., Anticó E., Salvadó V., Crespo J.G., Velizarov S., 2011. Transport and separation of arsenate and arsenite from aqueous media by supported liquid and anion-exchange membranes. Separation and Purification Technology, 80, 428-434.

Hichour M., Persin F., Molénat J., Sandeaux J., Gavach C.,1999. Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. Desalination 122, 53-62.

Hichour M., Persin F., Sandeaux J., Gavach C., 2000. Fluoride removal from waters by Donnan dialysis. Separation and Purification Technology, 18, 1-11.

Horng L.L., Clifford D.,1997. The behavior of polyprotic anions in ion-exchange resins. Reactive and Functional Polymers, 35, 41-54.

Issa N.B., Rajakovic-Ognjanovic V. N. , Marinkovic A. D., 2011. Separation and determination of arsenic species in water by selective Exchange and hybrid resins. Analitica Chimica Acta, 706,191-198.

Lacasa E., Canizares P., Sáez C., Fernández F.J., Rodrigo M.A., 2011. Removal of arsenic by iron and aluminium electrochemically assisted coagulation. Separation and Purification Technology, 79, 15-19.

Logette S., Eysseric C., Pourcelly G., Lindheimer A., Gavach C., 1998. Selective permeability of a perfluorosulphonic membrane to different valency cations. Ion-exchange isotherms and kinetics aspects. Journal of Membrane Science, 144, 259-274.

Malik A. H., Khan Z.M., Mahmood Q., Nasreen S., Bhatti Z.A., 2009. Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries – Review. Journal Hazardous Materials, 168 1-12.

Mondal P., Bhowmick S., Chatterjee D., Figoli A., Bruggen B., 2013. Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions-Review. Chemosphere, 92(2),157-170.

Oehmen A., Valerio R., Llanos J., Fradinho J., Serra S., Reis M.A.M., Crespo J.G., Velizarov S., 2011. Arsenic removal from drinking water through a hybrid ion Exchange membrane – Coagulation process. Separation and Purification Technology, 83, 137-143.

Saha S., Sarkar P., 2012. Arsenic remediation from drinking water by synthesized nano-alumina dispersed in chitosan-grafted polyacrylamide. Journal Hazardous Materials, 227-228, 68-78.

Shipley J. H., Engates K.E., Guettner A.M., 2011. Study of iron oxide nanoparticles in soil for remediation of arsenic. Jouranl of Nanoparticles Research, 13, 2387-2397.

Tahaikt M., Achary I., Sahli M.A.M., Amor Z., Taky M., Alami A., Boughriba A., Hafsi M., Elmidaoui A., 2006. Defluoridation of Moroccan groundwater by electrodialyisis continuous operation. Desalination, 189, 215-220.

United States Environmental Protection Agency, 2000. Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants, EPA/600/R-00/088,

Cincinnati, OH., Swarnkar V., Tomar R., 2012. Use of surfactant-modified zeolites for arsenate removal from pollutant water. Journal Dispersion Science technology, 33,913-918.

Urbano B.F., Rivas B. L., Martinez F., Alexandratos S.D., 2012. Water-insoluble polymer-clay nanocomposite ion Exchange resin based on N-Methyl-D-glucamine ligand groups for arsenic removal. Reactive and Functional Polymers, 72,642-649.

Velizarov S., 2013. Transport of arsenate through anion-exchange membranes in Donnan dialysis. Journal of Membrane Science, 425-426,.243-250.

Zhang Q.I., Lin Y.C., Chen X., Gao N.Y., 2007. A method for preparing ferric activated carbon composites adsorbents to remove arsenic from drinking water. Journal Hazardous. Materials, 148, 671-673.

Zhao B., Zhao H., Ni J., 2010. Arsenate removal by Donnan dialysis: Effect of the accompanying components. Separation and Purification Technology, 72, 250-255.

6.7 Supplementary data

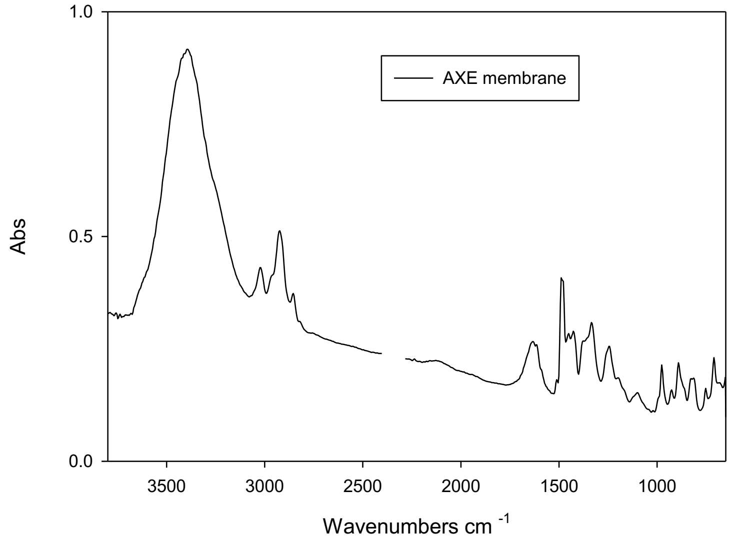

Figure SM1. An infrared spectra of a Neosepta AXE 01 membrane.

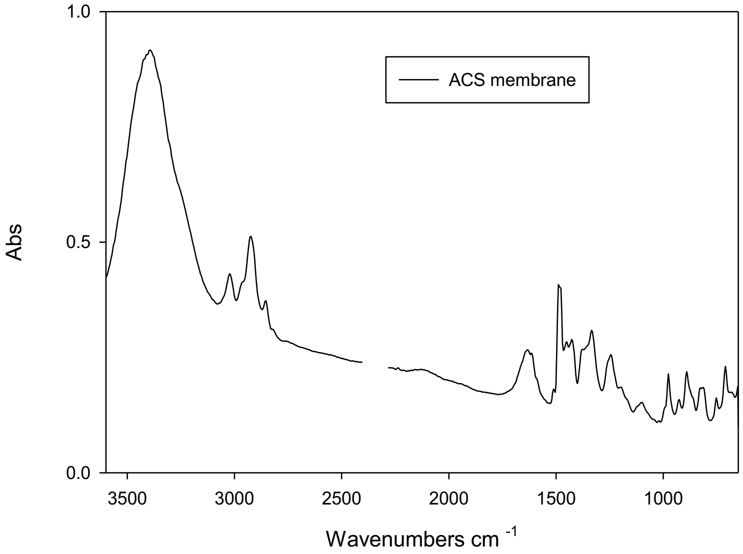

Figure SM2. An Infrared spectra of a Neosepta ACS membrane.

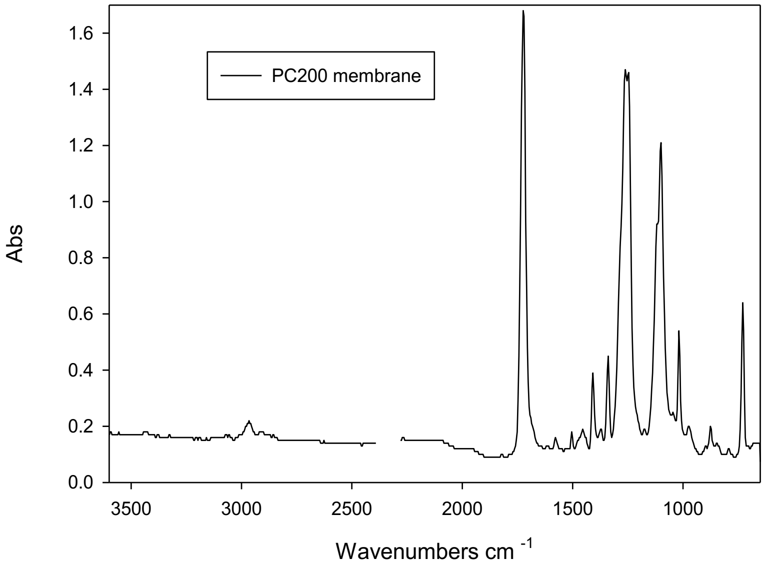

Figure SM3. An infrared spectra of a PC 200D membrane.

Chapter

7

Optimization of arsenic removal from drinking water by an integrated ion-exchange membrane

7.1 Summary

Arsenic contamination of drinking water affects more than 140 million people worldwide, and despite the various methods proposed for arsenic removal, there is still a need for development and validation of an easy to operate process solution, with less energy demand that can be easily adaptable in rural regions located far from centralised drinking water treatment infrastructures. Therefore, the present work investigates the performance of an ion exchange membrane process for arsenic removal, consisting in integrating Donnan dialytic transport of arsenic with its simultaneous precipitation in a separate receiver compartment. The process performance was improved by adding a bicarbonate-carbonate buffer in the receiver solution, where iron (III) chloride was used to precipitate the arsenic. This system allowed to maintain the treated water pH within the acceptable drinking water range of 6-9. Response surface methodology (RSM) was used to infer about the effect of the water characteristics and operating conditions on the degree of arsenic removal. Through mathematical modelling it was found that besides the initial arsenic concentration in water, the water pH and the mass ratio of iron to arsenic, the initial pH of the receiver solution was also a required input to predict accurately the arsenic concentration in the treated water. The model developed using interaction and quadratic terms, with a fitting R2 value of 0.99 and a prediction error of 6.6 μg/L of As, proved to be an adequate tool to predict the optimal conditions for arsenic removal from drinking water (during predefined operation period of time). Moreover, the methodology presented in this work permits to develop a simple decision tool (either through the use of equations or contour plots) to determine the effective amount of iron to be used in the treatment of As contaminated water.

Submitted to Water Research as: Pessoa Lopes, M., Galinha, C.F. Crespo, J.G., Velizarov, S., 2018, Optimisation of arsenic removal from drinking water by an integrated ion-exchange membrane process. (Under Revision).

7.2 Introduction

The removal of arsenic (As) from drinking water has been an extremely important research topic during the last few decades (Mohanty, 2017; Mondal et al., 2013). Arsenic is one of the most toxic naturally occurring elements present in different locations of the world and its efficient removal from drinking water supplies is still challenging (UNIFEC, 2013; UNIFEC, 2008). Elevated concentrations of arsenic have been discovered in groundwater and surface water resources in a number of different locations. Ravenscroft et al. (2009) reports at least 70 countries worldwide with contaminated waters, affecting more than 140 million people. Countries, such as Bangladesh and India (West Bengal), are the most affected regions. Numerous authors (Nidheesh and Singh, 2017; Vieira et al., 2017; WHO, 2011) reported that in Bangladesh groundwater sources are contaminated with As in concentrations ranging between 100-5000 μg/L.

The World Health Organization (WHO) and the US Environmental Protection Agency recommend As concentration of 10 μg/L (0.01 mg/L) as the permissible limit in drinking water (WHO, 2011). This limit is applied in the European Union, Japan, Taiwan, USA, Canada. Some countries apply even more restricted limits, such as Australia (7 μg/L), Denmark and US (New Jersey) (5 μg/L) (Nidheesh and Singh, 2017), while other countries like China, Bangladesh, Pakistan, Thailand, Vietnam, Nepal, Ghana and most South American countries apply a maximal arsenic permissible limit of 50 μg/L (Bhatti et al., 2018).

The chemistry and composition of arsenic-contaminated water are major factors affecting the removal of arsenic. In aqueous solution, arsenic speciation is mostly controlled by the redox potential (Eh) and pH. Arsenic Eh-pH diagrams are well documented and easily found in literature (Smedley and Kinniburgh, 2002). Under oxidizing conditions, in the pH range 4-8, typically found in natural environments, $H_2AsO_4^-$ and $HaSO_4^{2-}$, are expected to be dominant in aqueous solution (Fontàs et al. 2014).

Various methods for As removal from water have been reported so far, however, each of them presents inherent limitations (Ungureanu et al., 2015). For example, precipitation and coagulation/flocculation (Wickramasinghe et al., 2004; Matsui et al., 2017; Choong et al., 2007;

Han et al., 2002) require pre-oxidation of the primary water stream. Electrocoagulation processes exhibit low efficiency as reported by Laksmanan et al. (2010), Nidheesh and Singh (2017) and Lacasa et al. (2013). Adsorption by iron oxides and activated alumina (Lakshmanan et al., 2008; Park, 2016) is highly pH sensitive and the adsorbents require frequent regeneration. Ion exchange processes (Mohan and Pittman, 2007; Litter et al., 2010) are strongly dependent from the presence of competing ions and there is a need of frequent regeneration of the exhausted resin. Pressure-driven membrane processes (Chatterjee and De, 2017 ; Dolore et al., 2017; Geucke et al., 2009) such as nanofiltration and reverse osmosis are an attractive alternative, however, they are energy intensive and prone to fouling problems. Therefore, there is a need for the development and validation of an easy to operate process solution, which could be less energy demanding and easy to adopt in rural regions located far from centralized drinking water treatment infrastructures.

Despite its relatively slow kinetics, when compared to electrodialysis, Donnan dialysis process (Velizarov, 2013; Wiśniewski and Kabsch-Korbutowicz, 2010) has less energy requirements and is easy to operate. In a recent study (Pessoa-Lopes et al., 2016), it was demonstrated that an ion-exchange membrane process, integrating Donnan dialytic transport of arsenate with its simultaneous precipitation in a receiving compartment, can be successfully applied for arsenic removal from sulphate-containing water streams. However, it was observed that when a high concentration of iron (required to precipitate As removed from the water) is added to the receiver compartment, the water is acidified due to protons' leakage to the treated water compartment.

It has been suggested in the literature (USEPA, 2005) that for an efficient arsenic removal by iron-containing precipitants the [Fe]/[As] mass ratio in the water to be treated should be higher than 20/1 (which assumes that 1 mg of Fe removes 50 μg of As). However, the optimal [Fe]/[As] ratio for the ion-exchange membrane process is not necessarily the same due to the use of different operating conditions (membrane transport and subsequent precipitation, rather than a single precipitation step of As by Fe addition directly to the treated water). Therefore, it is necessary to optimise the process performance in terms of precipitant (Fe) quantity, treated water pH and elimination (minimisation) of possible iron leakage (transport from the receiver to the treated water compartment).

Response surface methodology (RSM) is a multivariate regression tool, based on statistical analysis, that allows to find correlations between factors (explanatory variables) and response variables through regression models, optimised for each response studied (Kikhavani et al., 2013). To define the experiments required for the development of such regression models, a design of experiments (DoE) is required. The DoE introduces the variation in the independent factors that directly affect the variation of responses. At the same time DoE is used aiming at reducing the number of experiments required to develop a model. Such statistical methods can be applied to reveal the relationships between the factors (e.g. operation parameters of the process) and responses (e.g. performance variables), within specific operating ranges, and thus, allowing process optimisation.

The ion-exchange process in study involves different ions, their transportation kinetics through an ion-exchange membrane, precipitation of different species in the receiver compartment and several chemical equilibria between different species in the water and in the receiver compartment. Therefore, with the objectives of achieving a simple tool able to infer about the optimal conditions required to treat drinking water contaminated with As, a statistical approach, such as RSM, can be used to correlate operating conditions and process performance. In contrast with a mechanistic approach, where the complete characterisation of the species present in both compartments is required, this tool can be applied using less analytical data and/or using different types of analysis (e.g. pH, conductivity, alkalinity, hardness).

In the present study, ferric chloride was added as a precipitant to a bicarbonate – carbonate buffer solution separated from As contaminated water by an anion-exchange membrane. Under these conditions, the As removal process performance was investigated in order to optimise the ratio of [Fe]/[As] required for reducing the As content in the contaminated water below the imposed maximum contaminant level (MCL). The initial As concentration in the contaminated water, the employed [Fe]/[As] ratio, and the pH of the feed (contaminated) water stream were used as DoE factors, while the response assessed was the final concentration of As in the treated water.

7.3 Materials and methods

7.3.1 Reagents and solutions

All reagents ($Na_2HAsO_4.7H_2O$, $FeCl_3.6H_2O$, Na_2CO_3, $NaHCO_3$, NaOH and HCl) used were of analytical grade. The solutions were freshly prepared with deionized water (conductivity ≤1 μS/cm). Feed solutions were prepared with deionised water and sodium arsenate ($Na_2HAsO_4.7H_2O$) to the desired concentrations. The receiving solutions were prepared with a sodium bicarbonate-carbonate buffer ($NaHCO_3 + Na_2CO_3$) and ferric chloride ($FeCl_3.6H_2O$).

The buffer was prepared for an ambient temperature of 20°C according to the supplier (Sigma – Aldrich, biological buffers) instructions for a pH ~9.2.

7.3.2 Membranes

The commercial anion-exchange membrane (AEM) Neosepta AXE 01 membrane from Tokuyama Soda, Japan, selected in a previous work (Pessoa-Lopes et al., 2016), was used.

Table 7-1.Properties of the used anion-exchange membrane.

Manufacturer	Reference	Matrix	Electrical resistance* (Ω cm^2)	Water content* (%)	Ion exchange capacity* (meq g^{-1}dry membrane)	Thickness (mm)**
Tokuyama Soda	Neosepta AXE 01	Cross-linked polystyrene in a poly(vinly chloride) reinforcing net	1.5	26.5	1.6-2	0.15±0.01

* Manufacturer data ** Determined in this work

7.3.3 Experimental

The dialysis cell used in the experiments consists in two compartments (136 ml each), which are in contact through a circular window, where the anion-exchange membrane (with an area of 11.3 cm^2) was placed. Each compartment was equipped with a stirrer (stirring rate set to 700 rpm), in order to minimise possible concentration polarization effects. All experiments were performed in a batch operation mode in an air-thermostated room at 24ºC. Samples of 2 ml each were taken periodically (pre-defined time intervals ≈ 2 hours) from the contaminated water and receiving solution compartments for measurement of pH, conductivity and subsequent analyses.

A schematic layout of the experimental cell used is presented in Figure 7-1. In the water compartment, As (in the form of arsenate) is the target pollutant to be transported through the anion-exchange membrane. In the receiver compartment, X^- represents the "driving" counter-ions used (i.e., Cl^- and HCO_3^-/CO_3^{2-}) while Fe^{3+} is used to precipitate As, thus maintaining the arsenate concentration difference between the receiver and the water solutions at its maximum possible value, to ensure the highest driving force for arsenate transport across the membrane.

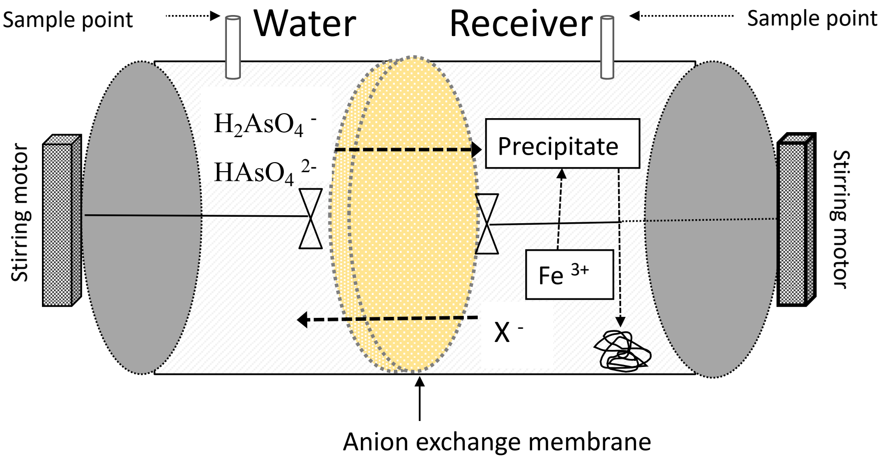

Figure 7-1.Schematic representation of the Donnan dialysis experiments performed.

7.3.4 Analytical techniques

The concentrations, of arsenate, ferric and sodium ions, in the samples withdrawn were determined based on the analysis of As, Fe and Na elements, measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Ultima model, Horiba Jobin-Yvon, France) equipped with a radio frequency (RF) generator of 40.68 MHz, a Czerny-Tner type monochromator with 1.00 m (sequential) and a Hydride Generator with concomitant metals analyser (CMA) (the detection limit for As was 0.5 µg/L), AS500 auto sampler and data acquisition software. The pH was measured with an ORION pH meter (Model 720 A) and the conductivity was followed with an ORION conductivity meter (Model 120).

7.3.5 Response surface methodology

For the experimental design, three independent factors were considered: the Fe/As ratio (in mass units) to be used, the initial concentration of arsenic in the water and the pH of the water (respectively, [Fe]/[As] ratio, $[As]_{water(i)}$ and $pH_{water(i)}$). A DoE methodology was applied using a central composite face centred (CCF) design with three replicas of the central point. This experimental design allowed to infer about the correlation of the 3 factors, at 3 levels with 17 experiments. The three levels were minimums, maximums and middle values of the 3 factors selected, accordingly with Table 7-2. The [Fe]/[As] ratio, pH and As concentrations to be used in each of the 17 experiments are shown in Supplementary data, Table S1.

Table 7-2. Range of factors studied.

	Minimum	**Medium**	**Maximum**
$[As]_{water(i)}$ (mg/L)	0.5	2.75	5
$pH_{water}(i)$	6	7	9
[Fe]/[As] ratio	100	275	400

For the response surface methodology (RSM), a multi-linear regression (MLR) model, integrating quadratic and interaction factors, was chosen. The DoE and data analysis were performed using MODDE 12 software. The statistical parameters (R^2, Q2, Model validity and Reproducibility) associated to model quality were calculated by the software, as described in User Guide to MODDE (2017).

7.4 Results and discussion

7.4.1 Optimisation of the As removal process

In order to maintain the drinking water pH within an acceptable range (between 6 and 9) (Mohanty, 2017) during the treatment process, a pH control is required. Although this could be done through the use of precise pH reagents dosing pumps and pH control systems, it increases the complexity of the process, which would hamper its implementation in remote areas. Therefore, an initial experiment was performed using a bicarbonate-carbonate buffer in the receiver compartment (Figure 7-2). In this experiment, an initial arsenic concentration of 4 mg/L (4000 µg/L) and a [Fe]/[As] mass ratio of 200 were applied. The results showed that, after 7 hours, the arsenic content in the feed water dropped to 36 µg/L, and after 26 hours of operation the concentration decreased further to 20 µg/L of As. This As concentration is acceptable for many countries, in which, the MCL is set at 50 µg/L. Moreover, it is perceptible that arsenic precipitation occurred in the receiver compartment, remaining only 87 µg/L of soluble As in the receiver solution (Figure 7-2A). These results proved a working process concept; however, there is a need of using a higher [Fe]/[As] ratio, to reach As concentration levels in the treated water below the MCL of 10 µg/L.

In Figure 7-2B it is also noticeable that the use of the buffer maintained the water pH within acceptable values for drinking water. It is also noticeable that the water pH tends to approach the pH of the receiver (the pH of the feed water after 26 hours of operation was 8.09). Therefore, if a higher iron (III) chloride concentration is used, the buffer capacity might not be sufficient. Consequently, all the subsequent experiments performed for optimisation of the [Fe]/[As] ratio were performed with a 0.2 M bicarbonate – carbonate buffer, independently of the amount of l.

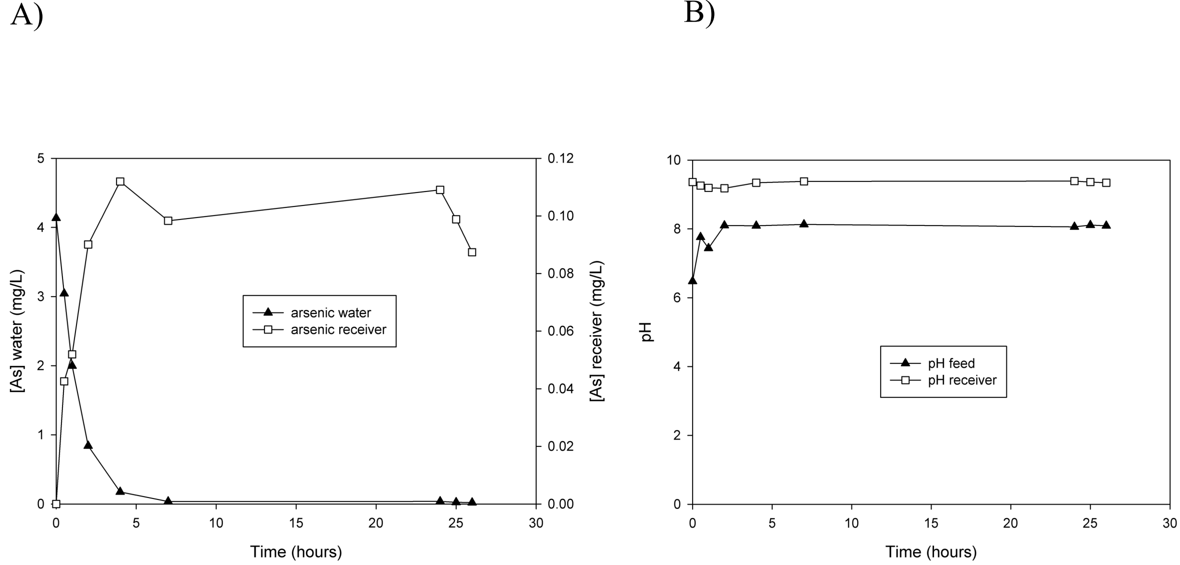

Figure 7-2.Experimental data obtained: A) Arsenic concentration profiles in the water and receiver solutions and B) pH in the water and receiver solutions, when using the initial conditions [As]= 4 mg/L; pH= 6.48; ratio Fe/As= 200 and 0.1M of bicarbonate - carbonate buffer).

To further optimise the removal process (in terms of the $FeCl_3$ content required for As removal) and study the effect of As concentration and water pH in the process performance, a Response Surface Methodology (RSM) methodology was used. The study was performed for [Fe]/[As] ratios between 100 and 400, and assuming As contamination levels between 0.5 and 5 mg/L, in water with pH varying between 6 and 9.

The response studied was the concentration of As in the treated water (the variable to be predicted/minimised). However, since the performance of this process may evolve along time, the As concentration in the treated water was assessed at 4, 6, 8 and 22 hours of operation. Considering the reasonable time that can be spent for treatment of a batch volume of water under real conditions (possibly overnight, for practicality and process simplicity), a scenario of 8 hours of operation was selected as the time of treatment, for modelling purposes.

The 17 experiments resulting from the DoE (supplementary data, Table S1) were applied in practice with slightly different values, mainly due to differences between the amount of As added to water and measured analytically (the analytical values were used), and taking into account the amount of $FeCl_3$ added in the receiver compartment. The [Fe]/[As] ratio was calculated from the amount of Fe added and As measured (as it would be done by an operator of the system in the field). The conditions actually used in the 17 experiments as well as the As concentration in the water compartment after the 8 hours of treatment, $[As]_{water(8h)}$, (the response) are displayed in Table 7-3.

Table 7-3.Design of experiments (DoE) results – Central composite Face (CCF) design matrix along with dependent terms: pH in the receiver and the experimental values of arsenic in the treated water after 8h of working process.

Design of Experiments				**Dependent factor**	**Response**
Exp. Name	$[As]_{water(i)}$ (mg/L)	$pH_{water(i)}$	[Fe]/[As] ratio	$pH_{receiver(i)}$	$[As]_{water(8h)}$ (mg/L)
N1	0.54	6.00	92.6	8.63	0.007
N2	6.00	6.00	83.3	7.92	0.122
N3	0.60	9.00	83.3	9.01	0.262
N4	6.23	9.10	80.2	8.30	0.063
N5	0.53	6.00	377.3	8.53	0.006
N6	6.12	6.00	326.8	7.24	0.224
N7	0.58	9.05	344.8	8.37	0.007
N8	6.04	9.00	331.1	6.66	0.000
N9	0.46	7.25	271.7	8.70	0.005
N10	5.36	7.25	233.2	7.38	0.061
N11	3.08	6.00	223.2	7.86	0.094
N12	2.58	8.10	266.5	8.05	0.003
N13	3.02	7.25	91.0	8.94	0.000
N14	2.95	7.50	372.9	7.30	0.000
N15	3.13	7.25	219.9	8.07	0.000
N16	2.97	7.25	231.5	8.25	0.000

N17	3.24	7.25	212.2	8.04	0.000

The RSM was applied to this experimental data in order to find a mathematical model able to correlate the factors selected with the performance response after 8h of working process. However, the first model obtained using the three selected factors ($[As]_{water(i)}$; $pH_{water(i)}$ and [Fe]/[As] ratio) fitted poorly the experimental values, even after model optimisation by input selection and by addition of quadratic and interactions terms (best model achieved with a R^2 of 0.6). Therefore, the inclusion of other variables assessed during the experiments (pH, water conductivity and iron concentration, in both compartments) was also tested. This approach aimed at adding more information about the process to the model and, thus, achieving better fitting of the experimental data. It was found that, besides the three independent factors initially considered ($[As]_{water(i)}$; $pH_{water(i)}$ and [Fe]/[As] ratio), the initial pH in the receiver, (shown in Table 7-3 – $pH_{receiver(i)}$), shows a strong effect on the process performance and should be also included as a model input. In fact, despite the bicarbonate-carbonate buffer present in the receiver compartment, which was the same in all experiments, when iron is added in high concentrations causes a significant pH change in the receiver solution. Therefore, this variable has to be considered a dependent variable, depending from the Fe concentration, and cannot be considered independently of the composition of the receiver solution.

The best model obtained, after optimisation, included as inputs the three independent factors and the initial pH in the receiver. The prediction of the response ($[As]_{water(8h)}$) was obtained by considering quadratic and interaction terms, as shown in Equation 7-1:

$$\mathbf{[As]_{water(8h)}} = +3.41938 + 0.104225\times[As]_{water(i)} - 0.220328\times pH_{water(i)} + 0.00267933\times[Fe]/[As] - 0.638289\times pH_{receiver(i)} + 0.00311434\times[As]_{water(i)}^2 + 0.0236131\times pH_{water(i)}^2 - 8.90E\text{-}07\times([Fe]/[As])^2 - 0.0340887\times pH_{receiver(i)}^2 - 0.0187849\times[As]_{water(i)}\times pH_{water(i)} - 0.0003761\times pH_{water(i)}\times[Fe]/[As]$$

Equation 7-1

The arsenic concentration in the water after 8 hours of process operation can be predicted using the mathematical model defined in Equation 7-1 and compared with the experimental values obtained and presented in Table 7-3, $[As]_{water(8h)}$. The plot of the observed *versus* predicted values for $[As]_{water(8h)}$ (Figure 7-3) shows the agreement between the predicted values and the values measured experimentally.

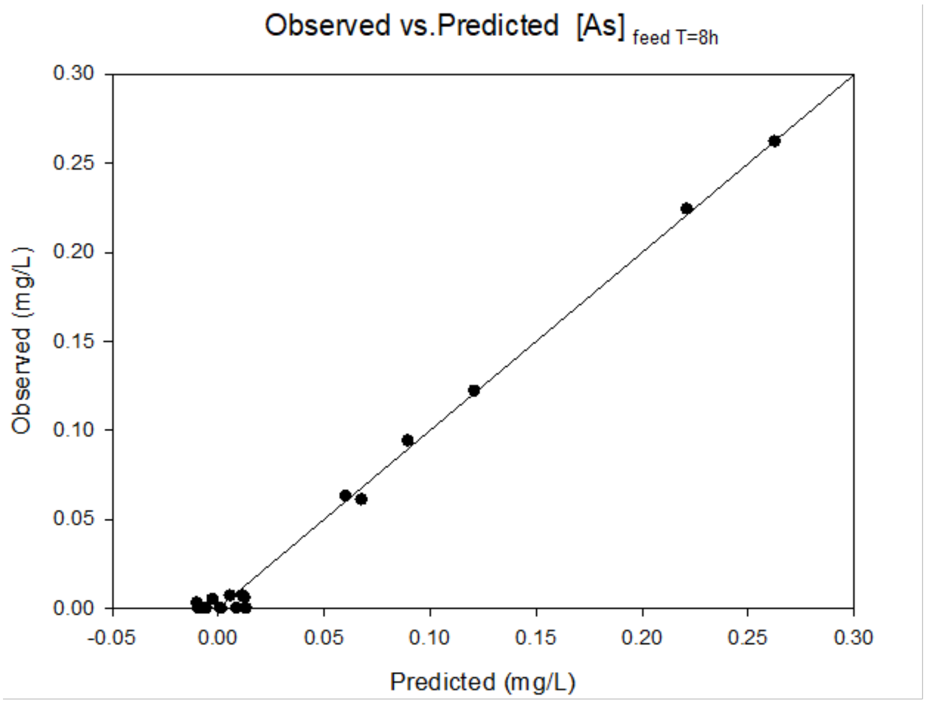

Figure 7-3. Observed (measured) versus Predicted values of As concentration in water after 8 hours of treatment

As it can be seen in Figure 7-3, the predicted and observed values of As in the treated water (after 8h) are extremely close, indicating an excellent model fitting and agreement between experimental and predicted values (with a regression coefficient R^2 of 0.993). Additional model statistics (Q2, Model validity and Reproducibility), provided by the software used, confirmed model fitting and validity. By definition (User Guide to MODDE, 2017), Q2 estimates the future prediction precision and should be greater than 0.1 for a significant model and greater than 0.5 for a good model. The value of Q2 obtained for the present model was 0.926, assuring that a good model prediction was obtained. Regarding model validity, which was 0.62 for the present model, it should be higher than 0.25, to exclude statistically significant problems, such as the presence of outliers, an incorrect model or a transformation problem (User Guide to MODDE, 2017). Furthermore, when the replicates are almost identical, or in models with Q2>0.9, the model validity can be low even though the model is good. For the present model, despite the high value of Q2, the model validity is considerably higher than 0.25, meaning that the model is statistically valid. Reproducibility, defined as the variation of the replicated compared to overall variability should be greater than 0.5 (User Guide to MODDE, 2017), which was confirmed by its value of 0.998.

Nevertheless, in Figure 7-3, some dispersion can be seen at values below 10 µg/L, which is the range where the experimental error and detection limit most impact the accuracy of the values (measured and predicted). Indeed, the error of the model (calculated as root mean square error, RMSE) is 6.6 μg/L, which is in the range of the detection limit of As by ICP (5 μg/L). However, since the target values of As concentration in the treated water are near zero, an error similar to the detection limit is acceptable. Furthermore, the model was developed based on experimental data (arsenic concentration in the initial and treated water, pH measurements in water and receiver compartments and amount of iron added to the receiver), which have associated experimental and analytical errors. Actually, arsenic measurements had an average error of 10% calculated for the entire range of As used in this work, resulting both from ICP instrument error and sampling collection. Models' accuracy is, in the best case, as good as the accuracy of the experimental data used, meaning that the best prediction error that can be achieved will be always equal or higher than 10%.

The effect of input parameters on the final As concentration in the treated water can be seen in Figure 7-4, where the normalised coefficients are displayed (to allow comparison between input weights). The coefficient bars (relative to each input variable) indicate that $[As]_{water(8h)}$ is significantly affected by the pH in the receiver and the [Fe]/[As] ratio. Moreover, although it is not possible to infer about positive or negative impact of all variables (due to the quadratic and interaction terms involved), the negative effect of the [Fe]/[As] ratio on the concentration of As in the treated water is noticeable (as expected). Among the interactive terms, the interaction of pH_{water} x $[As]_{water(i)}$ and pH_{water} x [Fe]/[As] are the most significant ones meaning that variations of these parameters have a high impact on the As concentration in the treated water.

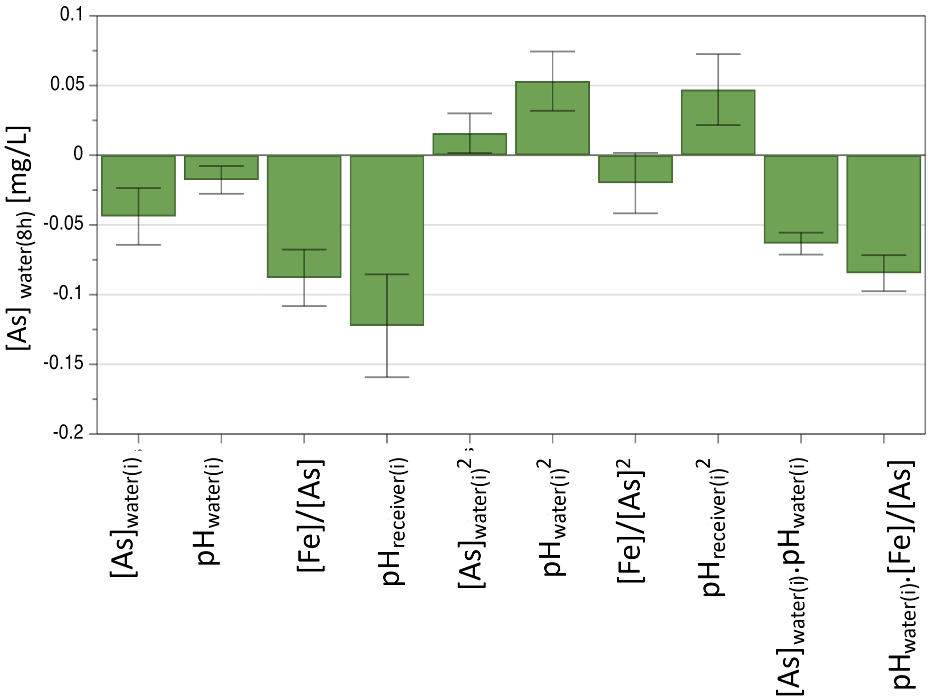

Figure 7-4.Coefficients (scaled and centered) of the model for $[As]_{water(8h)}$.

7.4.2 Model Validation

Aiming at validating the model developed and ensure that its predictions are accurate, two case studies where performed: one at high arsenic contamination (5 mg/L, 500x more than the MCL), and the other at medium/low arsenic contamination (1 mg/L, 100x more than the MCL).

After preparing the synthetic contaminated water samples, through addition of Na_2HAsO_4 and pH adjustment, they were analysed in terms of arsenic content by ICP. The arsenic concentration and pH of the two samples are shown in Figure 7-4. To treat these samples, 1312 mg/l and 258 mg/L of Fe were used, respectively for each case study, aiming at similar [Fe]/[As] ratio in both experiments. However, despite the similar [Fe]/[As] ratio used in both the receiver solutions, the amount of iron is different, resulting in different receiver pH values.

Table 7-4.Conditions of the experiments and model predictions of [As] after 8h of operation.

		Case study 1	**Case study 2**
inputs	[As]water(i) (mg/L)	4.8	1.0
	pHwater(i)	8.1	7.1
	[Fe]/[As] (w/w) (Fe (mg/L))	273 (1312)	258 (258)
	$pH_{receiver}$(i)	7.10	8.54
model prediction	$[As]_{water(8h)}$	0.046	below 0

Figure 7-4 shows, for each case study, the conditions of the validation experiments and the model prediction of the final arsenic concentration in treated water after 8h of operation (using Equation 7-1). According with the model, in case study 1, the As is partially removed, while in case study 2 the Fe concentration used is optimal for complete removal of As.

The experimental results obtained for case study 1 are shown in Figure 7-5.

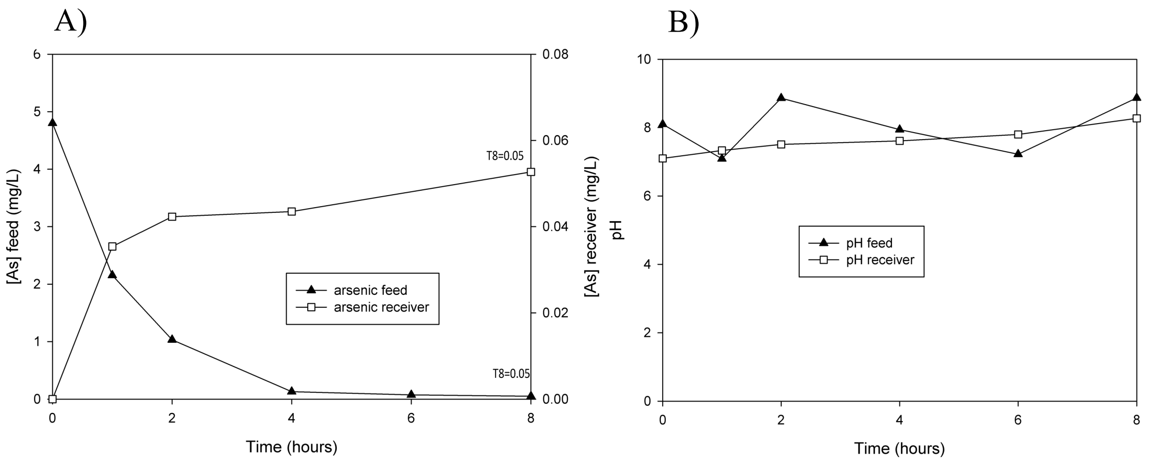

Figure 7-5. Experimental data obtained during 8 hours of water treatment for case study 1: A) arsenic concentration in water and receiver compartments; B) pH variation in water and receiver compartments.

As it can be seen in Figure 7-5A, the As concentration in the treated water was 0.050 mg/L after 8 hours of operation, which is in excellent agreement with the model prediction of 0.046 mg/L (within the ±6.6 μg/L error), with an error below 10%.

The experiment presented a slight iron leakage to the water compartment, <0.021 mg/L, although it remained well below its drinking water MCL of 0.5 mg/L during the 8 hours duration of the experiment. The water pH (Figure 7-5B) was maintained within the acceptable drinking water pH range (between 6-9).

The results obtained through the operation time for the second validation experiment are shown in Figure 7-6.

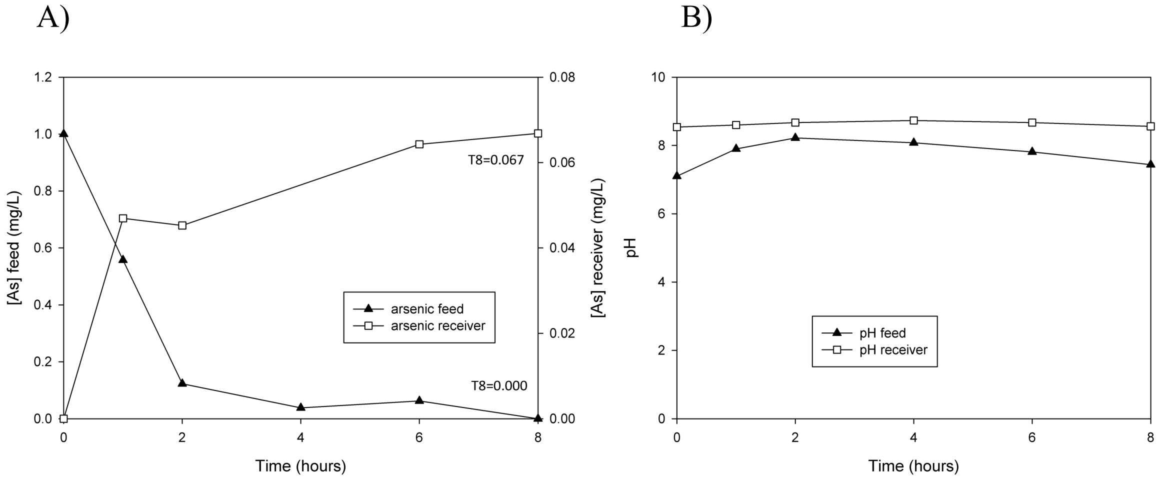

Figure 7-6Experimental data obtained during 8 hours of water treatment for case study 2: A) arsenic concentration in water and receiver compartments; B) pH variation in water and receiver compartments.

As it can be seen in Figure 7-6A, the As concentration data after 4 hours was already below the MCL of 50 µg/L. Furthermore, the actual experimental value was 0 µg/L of As after 8 hours. Moreover, the iron leakage observed during the 8 hours of experiment was minimal (below 0.010 mg/L) and the water pH (Figure 7-6B) was maintained within the acceptable drinking water pH range.

Overall, the results obtained prove the accuracy of the model and suggest that the approach followed in this work can be successfully used to develop a practical mathematical tool able to be used in the decision of the amount of iron required to treat an As contaminated drinking water. For practical uses, a special care must be taken when selecting the conditions for the development of the mathematical models (in order to be in agreement with the real conditions), such as the characteristics of the feed water. The experiments required to develop (calibrate) the model should be done with a water with similar physicochemical properties and ionic composition.

7.4.3 Mathematical decision tool

To estimate the concentration of iron, in the receiver compartment, required to treat a specific feed water (characterised by pH and As concentration) Equation 7-1 can be used (e.g., by assuming $[As]_{water(8h)}$=0). However, the pH of the receiver is not known before preparing the receiver solution (it depends on the composition of the receiver solution). Thus, a correlation between the pH and iron present in the receiver was considered. Figure 7-7 presents the plot of initial receiver pH versus iron concentration, obtained for the 17 experiments performed. This plot shows a significant correlation, with a R^2 of 0.86.

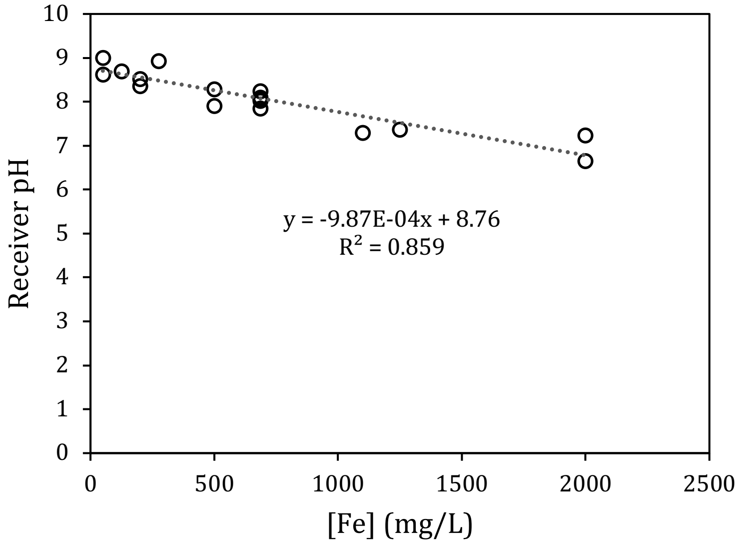

Figure 7-7. Correlation between iron concentration and pH in the receiver.

Therefore, for prediction purposes, the correlation between initial pH of the receiver and the initial iron concentration was used by inclusion of the following equation:

$$pH_{receiver(i)} = -0.0010[Fe] + 8.7555$$

Equation 7-2

in which the *[Fe]* is the initial iron concentration in the receiver (calculated from [As] water(i) x ratio [Fe]/[As]) and the $pH_{receiver(i)}$ is the initial pH in the receiver.

A useful equation (for decision purposes) is then achieved through the replacement of the $pH_{receiver(i)}$ by this equation (Equation 7-2) in the initial model (Equation 7-1):

$$\mathbf{[As]_{water(8h)}} = +3.41938 + 0.104225\times[\mathrm{As}]_{\mathrm{water(i)}} - 0.220328\times\mathrm{pH}_{\mathrm{water(i)}} + 0.00267933\times[\mathrm{Fe}]/[\mathrm{As}] - 0.638289\times(-0.001\,[Fe] + 8.7555) + 0.00311434\times[\mathrm{As}]_{\mathrm{water(i)}}^{2} + 0.0236131\times\mathrm{pH}_{\mathrm{water(i)}}^{2} - 8.90\mathrm{E}\text{-}07\times([\mathrm{Fe}]/[\mathrm{As}])^{2} - 0.0340887\times(-0.001\,[Fe] + 8.7555)^{2} - 0.0187849\times[\mathrm{As}]_{\mathrm{water(i)}}\times\mathrm{pH}_{\mathrm{water(i)}} - 0.0003761\times\mathrm{pH}_{\mathrm{water(i)}}\times[\mathrm{Fe}]/[\mathrm{As}]$$

Equation 7-3

Using Equation 7-3 it is possible to estimate the Fe concentration required in the receiver (e.g. using the Solver Function in Excel) in order to reach a defined concentration of As in the treated water ($[\mathrm{As}]_{\mathrm{water(8h)}}$). This mathematic decision tool is valid in the range of concentrations tested with the design of experiments.

Equation 7-3 can be also used to assess visually the effect of feed water pH and As concentration, and [Fe]/[As] ratio in the As removal. In Figure 7-8, Equation 7-3 is plotted as contour plots for different initial As concentrations in contaminated water. The shapes of the contour plots show the extent of the interactions between factors and arsenic removal.

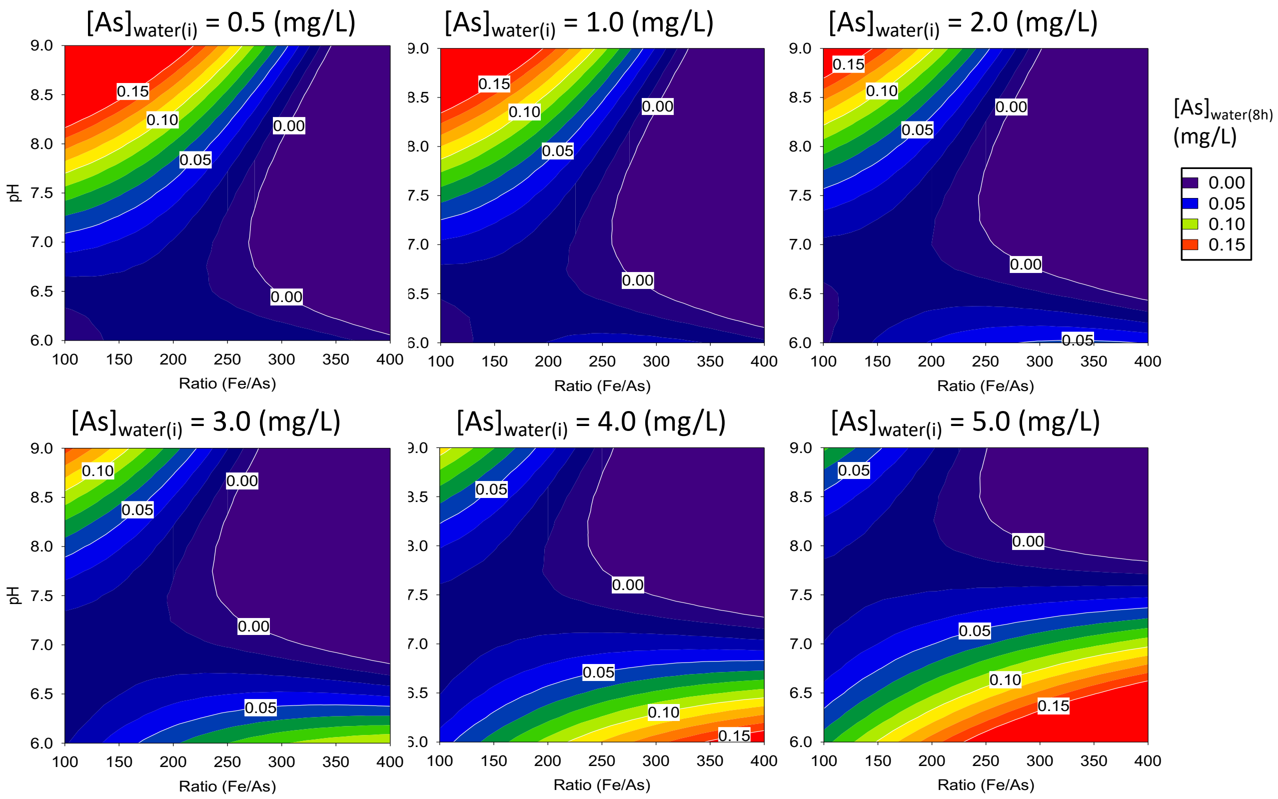

Figure 7-8. Response contour plots of the Model for different As water contamination levels (in the range 0.5 to 5 mg/L).

The contour plots show the efficiency of As removal, when varying the pH in the water and the [Fe]/[As] ratio, accordingly with the arsenic concentration in the contaminated water to be treated. In case of a relatively low As contamination (0.5 mg/L), it can be noted that, according to the model, a [Fe]/[As] ratio between approx. 350 and 400 can be used successfully used for water treatment, independently of the water initial pH (for the entire pH range in study 6-9). However, to minimise the use of iron (and thus avoid iron leakage to the water), a smaller ratio (<300) can be used, when the water pH is between 6.5 and 7.5.

For high As contamination (5 mg/L) in drinking water, it can be observed that, for acidic water, it is not possible to reach values below the MCL of 10 µg/L, under the operating conditions used. However, it is interesting to note that better results are obtained at the lowest ratio of 100. Furthermore, when analyzing the experiment N6 (Table 7-3) (Supplementary data, Figure S1), where the water used had 6.12 mg/L of As and pH of 6, although the removal of As was not complete after 8 hours of operation, after 22 hours, the concentration of As in the water was 0 mg/L (bellow the ICP detection limit). This result indicates that the removal of As in these conditions may be slower, but achievable, meaning that the degree of As removal achieved after 8 hours of operation could be increased with the extension of operating time.

Based on the model developed, it can be concluded that for As concentrations between 0.5- 2 mg/L, it is always possible to have an almost complete removal (to ~0 µg/L) of As. This result is important because reducing the arsenic concentration to values below 10 µg/L has been reported to be highly challenging by using other arsenic removal techniques (Mohanty, 2017; Mondal et al., 2013).

According with the model obtained, a possible option for an efficient removal of As (within 8 hours of operation), when its initial concentration is very high, can be the addition of an alkali to the water to increase its pH. Although addition of chemicals to drinking water may sometimes not be feasible and/or desirable, a simple correction of pH proves to be a possible way to ensure efficient As removal. Furthermore, from a practical and process engineering perspective, this tool (Equation 7-3) can be used when the operator first knows the actual amount of arsenic of the water to be treated.

Figure 7-9 shows the overlapping of the contour plots in Figure 7-8 (made through the sum of [As]water(8h) for each pH/Ratio pair).

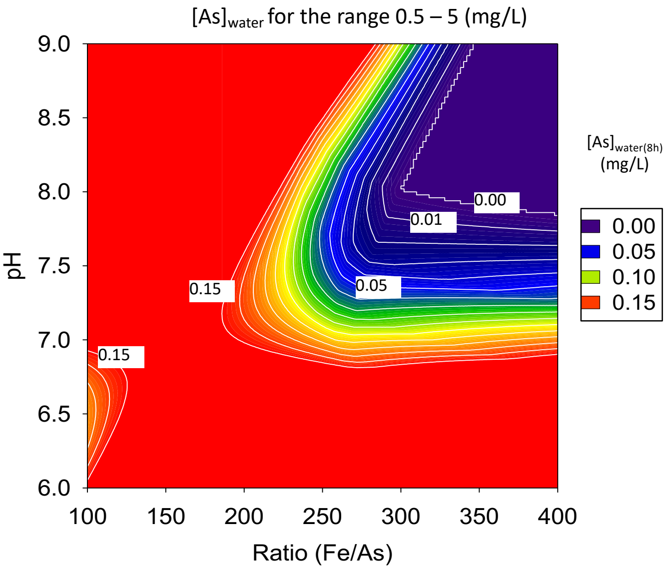

Figure 7-9.Overlapping (through the sum) of the 6 response contour plots from Figure 7-8.

In this Figure, the area where the As concentration is zero corresponds to complete As removal for all the ranges studied (pH, [Fe]/[As] ratio and initial As water content). From the overlapping of the contour plots, it can be concluded that for [Fe]/[As] ratios above 300 and initial water pH in the range 8-9, the treatment process will always reduce the arsenic contamination to levels below 5 µg/L (detection limit of ICP) independently of the initial arsenic concentration (within the As range studied - 0.5 to 5 mg/L).

Despite the increased difficulty in treat acidic water with high As concentration, revealed by the model obtained, it is important to note that the study was limited to a [Fe]/[As] ratio between 100 and 400, and only 8 hours of operation, meaning that other performances may be achieved by changing ratio and operation time. However, due to its empirical nature, it is not possible to use the model obtained to extrapolate beyond the calibration range.

7.5 Conclusions

In the present work an optimised ion exchange membrane process was achieved for the removal of arsenic in drinking water. It was demonstrated how the process can be operated and optimised through the use of $FeCl_3$ and a bicarbonate-carbonate buffer in the receiver solution. The system studied allowed to maintain the treated water pH within the recommended drinking water range of 6-9. Furthermore, it was shown that a [Fe]/[As] mass ratio range between 100 and 400 can be used to optimise the arsenic removal process, allowing arsenic removal without significant iron leakage to the treated water.

A mathematical model for the prediction of arsenic concentration in the treated water was developed using quadratic and interaction terms with a fitting R^2 value of 0.99 and a prediction error of 6.6 µg/L of As. Furthermore, with the integration of the correlation between the iron concentration and pH in the receiver, the model permits to optimise (minimise) the amount of iron used in the treatment of As contaminated water and, therefore, to reduce the iron leakage to the treated water (to values far below its allowed drinking water limit). The analysis of the mathematical correlation between the factors studied and the As concentration in the treated water, through contour plots, allows also to define the optimal process performance conditions in a simple visual way.

Due to the advantages of the ion exchange membrane process, integrating Donnan dialysis with precipitation of the target pollutant: i) selective removal; ii) no contact between treated water and receiver solution; iii) low energy requirements (only for stirring) and iv) easy to handle operation (enhanced by the use of the buffer, which avoid the need of pH control during the treatment process), the arsenic removal system studied has a high potential for application in decentralised water treatment. Additionally, the use of a mathematical decision tool, properly calibrated for the local contaminated water, simplifies the decision about the optimal process operating conditions for the specific characteristics of the income water, thus enhancing the applicability of the process (even in the absence of specialised operators).

7.6 References

Bhatti, Z.A., Qureshi K., Khuhawar M. Y. et al., 2018. Low cost indigenous technologies for removal of arsenic from drinking water: case study of Pakistan. IJRRAS, 34(3), 66-76.

Chatterjee S., De S., 2017. Adsorptive removal of arsenic from groundwater using chemically treated iron ore slime incorporated mixed matrix hollow fiber membranes. Separation and Purification Techology, 179, 357-368.

Choong, T.S.Y., Chuah, T.g., Robiah Y., et al., 2007. Arsenic Toxicity, health hazards and removal techniques from water: an overview. Desalination, 217, 139-166.

Dolores, M., Ortega, V., Ratnaweera, H. C., 2017. Double filtration as an effective system for removal of arsenate and arsenite from drinking water through reverse osmosis. Process Safety and Environmental Protection, 111, 399-408.

Fontàs, C., Vera, R., Batalla, A., Kolev, S. D., Anticó E., 2014. A novel low-cost detection method for screening of arsenic in groundwater. Environ Sci Pollut Res, 21:11682–11688.

Geucke, T., Deowan, S.A., Hoinkis, J., Patzold, Ch., 2009. Performance of a small-scale RO desalinator for arsenic removal. Desalination, 239, 198-206.

Han, B., Runnells, T., Zimbron, J., Wickramasinghe, R., 2002. Arsenic removal from drinking water flocculation and microfiltration. Desalination, 145, 293-298.

Kikhavani,T., Ashrafizadeh S.N., Bruggen B.V., 2013. Identification of Optimum Synthesis Conditions for a Novel Anion Exchange membrane by Response Surface Methodology. Applied Polymer Science., 131, 39888.

Lacasa, E., Saez, C., Canizares, P., et al., 2013. Arsenic removal from high-arsenic water sources by coagulation and electrocoagulation. Separation Science Technology, 48 (3), 508-514.

Lakshmanan, D., Clifford, D., Samanta, G., 2008. Arsenic removal by coagulation- with aluminium, iron, titanium and zirconium. Journal- American Water Works Association, 100 (2), 76-88.

Lakshmanan, D., Clifford, D., Samanta, G., 2010. Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation. Water Research., 44(19), 5641-5652.

Litter, M.I., Morgada, M.E., Bundschuh, J., 2010. Possible treatments for arsenic removal in Latin American waters for human consumption. Environmental Pollution, 158, 1105-1118.

Matsui, Y., Shirasaki, N., Yamaguchi, T., et al., 2017. Characteristics and components of poly-aluminum chloride coagulants that enhance arsenate removal by coagulation: Detailed analysis of aluminium species. Water Research, 118, 177-186.

Mohan, D., Pittman, Jr. C.U., 2007. Arsenic removal from water/wastewater using adsorbents – a critical review. Journal Hazardous Materials, 142, 1-53.

Mohanty D., 2017. Conventional as well as Emerging Arsenic Removal Technologies – a Critical Review. Water Air Soil Pollution, 228-381.

Mondal P., Bhowmick S., Chatterjee D., Figoli A., Bruggen B., 2013. Remediation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technologies solution – review. Chemosphere, 92 (2), 157 – 170.

Nidheesh, P.V., Singh T.S.A., 2017. Arsenic removal by electrocoagulation process; Recent trends and removal mechanism. Chemosphere, 181, 418-432.

Park, J.H., Han, Y., Ahn, J.S., 2016. Comparison of arsenic co-precipitation and adsorption by iron minerals and the mechanism of arsenic natural attenuation in mine stream. Water Research, 106, 295-303.

Pessoa-Lopes M., Crespo J.G. and Velizarov S., 2016. Arsenate removal from sulphate-containing water streams by an ion-exchange membrane process. Separation Purification Technology, 166, 125-13.

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic Pollution: a Global Synthesis. Wiley-Blackwell, Oxford, p.580.

Sigma- Aldrich, biological buffers, website: http/www.sigmaaldrich.com/life-science/core-bioreagents/biological-buffers/learning-center/buffer-reference-center.printerview.pdf.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry.17 (5), 517-568.

Ungureanu, G., Santos, S., Boaventura R., Botelho C., 2015. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. Journal of Environmental Management, 151, 326-342.

UNIFEC, 2008. Arsenic Primer. United Nations Child Fund (UNIFEC), New York.

UNIFEC, 2013. Arsenic contamination in Groundwater.

USEPA – US Environmental Protection Agency, 2005, Treatment Technologies For Arsenic Removal, EPA/600/S-05/006, November (https://www.epa.gov/nscep).

User Guide to MODDE, 2017. Sartorius Data Analytics, version 12.

Velizarov, S., 2013. Transport of arsenate through anion-exchange membranes in donnan dialysis. Journal of Membrane Science, 425-426, 243-250.

Vieira, B.R.C., Pintor, A.M.A., Boaventura, R.A.R., et al., 2017. Arsenic removal from water using iron-coated seaweeds. Journal of Environmental Management, 192, 221-233.

WHO, 2011, Arsenic in Drinking water, Background Document for Development of WHO Guidelines for Drinking-water Quality.

Wickramasinghe, S.R., Han, B., Zimbron, J., Shen, Z., Karim, M.N., 2004. Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. Desalination, 169(3), 231-244.

Wiśniewski, J.A., Kabsch-Korbutowicz, M., 2010. Bromate removal in the ion-exchange process. Desalination, 261, 197–201.

7.7 Supplementary Data

Table S1: Design of experiments (DoE) – Central composite Face (CCF) design matrix.

Exp Name	$[As]_{water(i)}$ (mg/L)	$pH_{water(i)}$	Fe/As ratio
N1	0.50	6.00	100
N2	5.00	6.00	100
N3	0.50	8.50	100
N4	5.00	8.50	100
N5	0.50	6.00	400
N6	5.00	6.00	400
N7	0.50	8.50	400
N8	5.00	8.50	400
N9	0.50	7.25	250
N10	5.00	7.25	250
N11	2.75	6.00	250
N12	2.75	8.50	250
N13	2.75	7.25	100
N14	2.75	7.25	400
N15	2.75	7.25	250
N16	2.75	7.25	250
N17	2.75	7.25	250

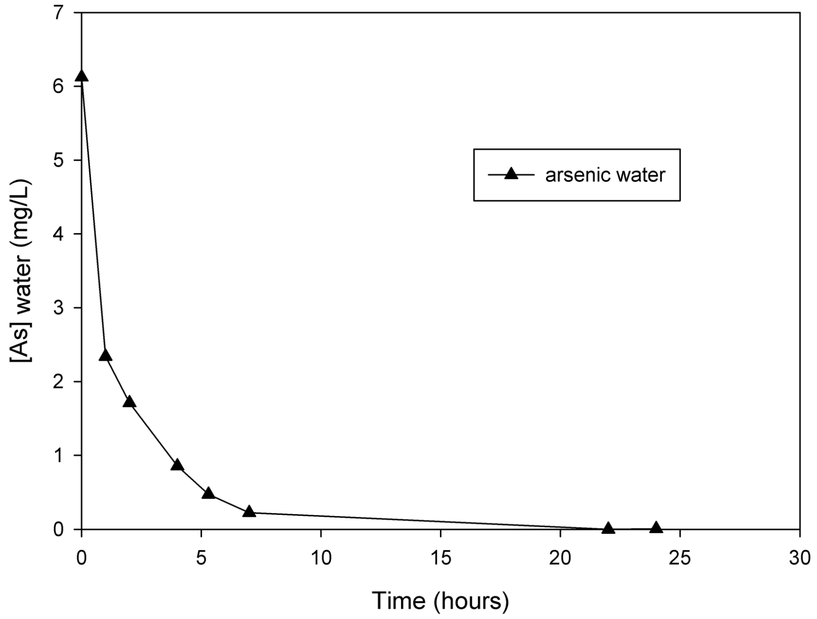

Figure S1: Arsenic concentration profile in the treated water of experiment N6 from the Design of Experiments (with the initial conditions: [As]water(i)=6.12 mg/L; pHwater(i)=6.00 and [Fe]/[As] ratio= 326.8).

Chapter

8

Conclusions and future work

8.1 Conclusions and future work

This PhD thesis contributes to the better understanding of different water/wastewater problems and their potential solutions: - treatment of an industrial effluent with high organic load; production of a high quality drinking water in terms of chemical composition and microbial inactivation; and arsenic removal from contaminated water bodies, aiming its application for rural areas located far from centralized drinking water supply infrastructures. The main conclusions of this research project are highlighted in this section, with a particular emphasis on future work recommendations for the proposed technologies for water/wastewater treatments.

8.1.1 Industrial wastewater Treatment

The integrated NF + Evaporator processes allowed to reach the following objectives:- reduce the COD levels to comply with European legislation requirements for water disposal (COD< 2000 mg/l), and significantly reduced of the total energy expenditures required to treat the wastewater under study.

It was concluded that the NF270 nanofiltration membrane is the best option for processing the rubber wastewater produced, thus allowing the rejection of over 93% of the COD. The NF270 permeate can be either discharged or re-used as boiler feed water, if the total hardness in the permeate is further reduced.

The membrane can be operated continuously at a controlled permeate flux for over 24 hours if the permeate flux is maintained at no more than 12 L/m^2. h. A water recovery of 80-90% can be achieved by using a nanofiltration process with a NF270 membrane as long as the permeate flux is set below 12 L/m^2. h.

After the economic analyses for a full-scale plant design, another concluding remark was drawn regarding a 2-stage NF design that can significantly reduce the overall energy costs of the integrated solution. The 2-stage NF design will lead to higher operational savings for the integrated solution than the single stage NF design.

The proposed treatment was successfully applied (by retrofitting) in the existent wastewater treatment plant and is currently under operation. The solution developed and tested may considered for similar wastewater contamination problems and high energy spending situations.

The proposal wastewater membrane treatment scheme should be performed for at least one year to include seasonal variations, such as oscillations of COD concentrations and temperature. Higher temperatures should improve membrane permeability due to lower viscosity and lower degrees of concentration polarization at the membrane surface, however, it was observed that when temperature reached 24°C or higher the membrane permeability dropped in several tests. Thus, as future work, it should be further understood the effect of higher temperatures on the process performance. The possibility of using a ceramic membrane should be also evaluated, since they can stand operation at higher temperatures. Moreover, a pre-treatment of the feedwater could also be considered, in order to reduce membrane fouling and consequently the membrane cleaning periodicity and lifetime.

8.1.2 Drinking water Treatment

The integrated system combining nanofiltration + UV photolysis increases the performance of water treatment making possible the production of highly pure water, assuring the removal of pesticides below the detection limits, while allowing for lowering the level of chlorine dosage.

It was concluded that the integrated pilot scale system (nanofiltration and UV) should be placed after conventional sand filtration of the surface water treatment plant of EPAL in order to improve nanofiltration performance, avoiding flux decline and minimizing fouling problems.

The fouling agents were identified to be mainly organic material. Therefore the alkaline cleaning of the membrane is more efficient to restore the initial membrane permeability. According with the operation results, an alkaline cleaning-in-place protocol should be performed every 15 days of nanofiltration operation with a transmembrane pressure of 8 bar and a recovery rate of 91% in order to restore the membrane performance.

It is suggested as future work, studies with operation under milder transmembrane pressure conditions in order to minimize excessive convective transport towards the membrane surface and reduce fouling conditions. Finally, an economic analysis should be performed in order to compared a new plant design with the existent process and calculate the payback periods.

8.1.3 Arsenic contaminated drinking water Treatment

It was proved that applying a new concept of using sulphate as a driving counter-ion, in order to promote arsenate counter-transport across anion-exchange membranes, is efficient and that a highly selective arsenate removal from sulphate containing water streams can be achieved.

The Neosepta AXE 01 membrane was the best membrane option for the arsenate separation / purification by providing a good compromise between performance (high arsenate membrane transport with relatively low arsenate membrane retention) and an acceptable salt leakage from the receiver to the treated water compartment.

The use of $FeSO_4$ in the receiving solution causes arsenic precipitation and maintains the arsenate concentration difference between the receiver and the feed solutions at its maximum possible value. The latter ensures high arsenate transport driving force across the membrane.

An optimised ion exchange membrane process was achieved through the use of $FeCl_3$ and a bicarbonate-carbonate buffer in the receiver solution. The system studied allowed to maintain the treated water pH within the recommended drinking water range of 6-9. It was concluded that a [Fe]/[As] mass ratio range between 100 and 400 can be used to optimise the arsenic removal process, allowing arsenic removal without significant iron leakage to the treated water.

A mathematical model was developed for the prediction of arsenic concentration in the treated water, optimising (minimising) the amount of iron used for precipitation of As and, therefore, allowing to reduce the iron leakage to the treated water (to values far below the drinking water limit). The analysis of the mathematical correlation between the factors studied and the As concentration in the treated water, through contour plots, allows also to define the optimal process performance conditions in a simple visual way.

Due to the advantages of the ion exchange membrane process, integrating Donnan dialysis with precipitation of the target pollutant:

i) selective removal

ii) no contact between treated water and receiver solution

iii) low energy requirements (only for stirring)

iv) easy to handle operation (enhanced by the use of the buffer, which avoid the need of pH control during the treatment process),

the arsenic removal system studied seems to have a high potential for application in decentralised water treatment systems.

As further investigation, it is suggested the use of a mathematical decision tool, properly calibrated for the real contaminated water and evaluated in terms of the arsenic concentration prediction in real conditions. It is also important to validate the proposed methodology for more complex waters streams taking into account other possible parameters that may influence As removal, such as the presence of the competing ions like sulphate, bicarbonate and hydroxide (SO_4^{2-}, HCO_3^-, OH^-, …).

Validation of the solution studied and proposed should be conducted for an extended period of time under real conditions, operated by non-skilled personnel. The purpose is an evaluation of this solution for rural areas, where access to a dedicated operator is not realistic.