BAHAGIAN PENYELIDIKAN & PEMBANGUNAN CANSELORI

UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

1) **Nama Penyelidik**: **Professor Madya Dr. Ghasem Najafpour**

Nama Penyelidik-Penyelidik: **Professor Madya Dr.Latif Ahmad**

Lain (*Jika berkaitan*)

2) **Pusat Pengajian/Pusat/Unit**: **School of Chemical Engineering**

3) Tajuk Projek: **DEVELOPMENT OF INORGANIC MEMBRANE TO REMOVE OIL EMULSIFIER FROM DOMESTIC WASTEWATER.**

4) (a) **Penemuan Projek/Abstrak**

*(Perlu disediankan makluman di antara 100 - 200 perkataan di dalam **Bahasa Malaysia** dan **Bahasa Inggeris**. Ini kemudiannya akan dimuatkan di dalam Laporan Tahunan Bahagian Penyelidikan & Pembangunan sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti)*

The rapid development of membranes in wastewater treatment was a great encouragement to participate and fabricate inorganic membrane. The results yielded to an expansion of knowledge and producing various types of ceramic membrane. The ceramic membrane has a great potential and market, ceramic membrane represents a distinct class of inorganic membranes, especially the metallic coated has many industrial application. The porous ceramic was prepared for to fabricate the supported membrane. A thin film of Aluminum and Zirconium were formed. Unsupported membrane was also prepared.

The sol-gel is one of the most useful techniques for preparation of inorganic membrane with fine pores in the nanometer range (1-5 nm). The sol is a stable suspension of colloidal solid particles within soft uniform solution. The gel was obtained based of hydrolysis process with open reflux in 24 hours at 85-90^{0}C. The detail and process preparation of inorganic membrane are discussed in the attached final report with exact material and method.

The advantage of sol-gel technology is the ability to produce highly pure γ-alumina and zirconia membrane at medium temperature about 700^{0}C with uniform pore size distribution in a thin film. However, there disadvantages as sensitive to heat treatment resulted crack on the film layer. There were successful crack free product, but needed special care and time for suitable heat curing only γ-alumina membrane has the disadvantage of a poor chemical and thermal stability. There was not any opportunity to carry heat treatment at very high temperature above 700^{0}C, where at 900 ^{0}C, where it was expected the transformation of γ-alumina from $\gamma \rightarrow \theta \rightarrow \alpha$- alumina may take place. The successful coated on supported membrane product was obtained using ZrO_2.

In this research project, zirconia-coated-γ-alumina membrane coated on ceramic support was developed with implementation of sol-gel technique. The technique will obtain the crack free unsupported membrane, which was expected to have pore size of 1-2nm. The developed crack free membrane in the above section will not have the same strength without the support. The next stage of this work was to carry characterization. In this stage there was limitation of human resources, fund and time to reach a level for industrial use and other application.

(b) **Senarai Kata Kunci yang digunakan di dalam abstrak:**

Bahasa Malaysia	**Bahasa Inggeris**
Membrane inoganik	Inorganic membrane
Membrane "Zirconia-coated" diatas γ-alumina	Zirconia-coated on γ-alumina membrane
Teknologi Sol-gel	Sol-gel technology
Membrane γ-alumina	γ-alumina membrane
Penyokong seramik	Ceramic support

5) **Output Dan Faedah Projek**

(a) Penerbitan (*termasuk laporan/kertas seminar)*
(Sila nyatakan jenis, tajuk, pengarang, tahun terbitan dan di mana telah diterbit/dibentangkan)

The paper in process of preparation will be submitted for publication in near future

Achievements

i. Development of new inorganic ceramic membrane coated with zirconium and alumina.

ii. Developed of a thin film of alumina and zirconia unsupported membrane.

iii. Method developed with sol-gel technique.

(b) **Faedah-Faedah Lain Seperti Perkembangan Produk, Prospek Komersialisasi Dan Pendaftaran Paten.**
(Jika ada dan jika perlu, sila gunakan kertas berasingan)

The suitable supported and unsupported zirconia alumina membranes were developed and fabricated, sol-gel technique was used. More than 50 samples of successful and unsuccessful membrane for demo were fabricated. The successful results are discussed and presented in the attached final report. In this project, the porous ceramic supports were fabricated in our research lab.

(c) **Latihan Gunatenaga Manusia**

i) *Pelajar Siswazah:*

Trained and transferred research knowledge to a number of students

List of students have been involved :

1. Jul Syarmi Zawati Othman, Msc student 2002.

ii) *Pelajar Prasiswazah*:

2. Asmida Bt. Idris, graduated 2002. Final year project: Manufacture of Ceramic Membrane
3. Lim Jit Kang, BSc. 2002, research assistant.
4. Lai Huey Keat, undergraduate student 2003, research assistant.

iii) *Lain-lain*:

6) **Peralatan Yang Telah Dibeli**: None, Just Chemicals

UNTUK KEGUNAAN JAWATANKUASA PENYELIDIKAN UNIVERSITI

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TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
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Final Report on Short Term IRPA

Project tilte:

DEVELOPMENT OF INORGANIC MEMBRANE TO REMOVE OIL EMULSIFIER FROM DOMESTIC WASTEWATER.

Project Leader: ***Professor Madya Dr. Ghasem Najafpour***

School of Chemical Engineering

Engineering Campus

Universiti Sains Malaysia

Seri Ampangan

14300 Nibong Tebal, Penang

27 October 2003

Introduction

In this research project zirconia- alumina membrane with and without support has been developed using sol-gel technique. The unsupported membrane was not strong; it was very fragile and not useful to be used directly. The supported membrane on highly porous ceramic was very strong, but the coating was covered did not show a solid surface, the shape of coating was exactly in the same trend as the porous cramic was prepared. The ceramic support was very strong after the treat treatment. Beside ceramic support, a very fine power of MgO with PVA binder was prepared, a smooth membrane ziconia-alumina coating was developed, but its strength was not the same as ceramic. The uniform coating and crack free membrane were examined with SEM monograms.

The overall process involved is shown in the Figure 1. The main activities of the research were:

- Preparation and development of inorganic membrane with and without support (zirconia-coated on γ-alumina).
- Characterization of the membrane surface by electronic scanning.
- Testing the strength of the fabricated membrane.

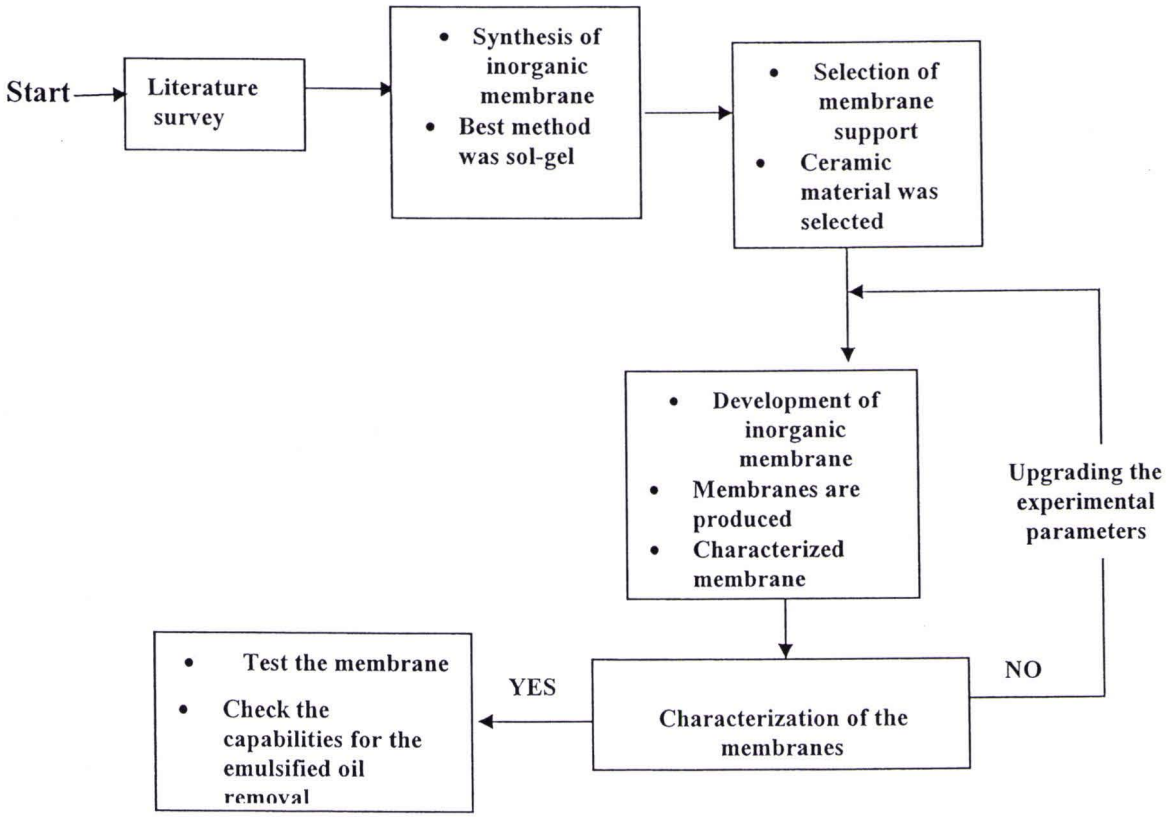

Figure 1. Overall scheme and stages invovolved for fabrication of inorganic mambrane

In preparation of the membrane, a clear sol was obtained using aluminum sec-butoxide. Aluminum monohydroxides formed by the hydrolysis of aluminum alkoxides, which are peptizable to a clear sol. Peptization was required by addition of nitric acid and heat treatment was\carried out for a sufficient time. The resulting sols are poured into the petridishes and dried out in an oven at controlled drying rate, to obtain gel layer. The mole ratio of zirconia salt to alumina was a controlling variablr to obtain the crack free zirconia-coated-γ-alumina membrane. Finally, the dried gel is sintered and treated with heating at 500^0C.

Support materials were prepared by blending the fine power as statted in the later part of this report. The PVA was used as the binder. The organic macromolecule was used to create sufficient pores in the material when burned out after solid strong support was formed. Drying was provided by application of heat from under-neath, high temperature furnace was used. The shape of the support and the thickness of the support was based on the mass of the material and the way it was moulded.

Once the membrane was been successfully produced, it was checked and send for characterization and scanning. Some important parameters of characterization were:

- Pore size
- Particle size
- Mechanical and thermal strength

Analysis and Major Equipment

Finally, analytical equipments were used for characterization such as XRD, SEM, TEM and light Scattering, avail in school of mineral and material engineering.

Unfortunately the last part of the work for testing the produced membrane to remove emulsifier oil from domestic wastewater, have been accomplished based on limitation of budget and postgraduate sudent. The experimental rig and membrane module is required and budget was needed for fabrication and also the need of experimental data for application of the supported membrane may show the reall success of this project.

Preparation of PVA Solution

PVA was used as a temporary binder due to its water solubility, excellent binding strength and clean burning characteristic. To prepare the PVA solution, 4g of polyvinyl alcohol were added into a 100ml of distillated water. The mixture was heated and stirred vigorously until all the PVA were dissolved in the water. This step took around half an hour. The peptization was carried out by addition of 5ml of 1M HNO_3 into the solution. Finally the solution was refluxed for 4 hours. The PVA solution was used in the preparation of Sol Gel. The preparation of PVA solution is summarized as following:

i.) 4g of PVA were added into a 250ml beaker

ii.) 100ml of double distillated water was stirred vigorously until all the PVA were dissolved.

iii.) Boil the solution until all the PVA was dissolved. This step took at least 0.5-1 hour.

iv.) 5ml of 1M HNO_3 was added into the solution.

v.) Reflux the solution for 4 hours.

Preparation of Zirconia Coated Alumina Membrane

The supported and unsupported membranes were produced by a sols gel dipping technique. The sol gel was made of Aluminium tri-sec-butoxide and Zirconium (IV) Oxide. If compare with the pure Alumina membrane, the Zirconia Coated Alumina membrane had high chemical resistances that allowed steam sterilization and cleaning procedures in the pH range of 0-14, possessed good pure heating permeability and high membrane flux in separation and filtrations and it has a high thermal stability, which was an attractive for catalytic membrane reactor may be used at high temperature. The molar ratio were Al^{3+}: H^{+}: Zr: H_2O = 1:0.07:0.15:100. While the volumetric ratio at the basis of 100ml of H_2O is Al^{3+}: H^{+}: Zr: H_2O = 1: 3.88ml: 1.0275g: 100ml. the 100ml of double distilled water is heated on a hot plate at temperature between 80-85°C to ensure the formation of γ-AlOOH. A 14.25ml of Aluminium tri-sec-butoxide was added into the double distillated water. The solution was vigorously stirred with magnetic stirrer until a homogenous mixture was obtained. A 3.88ml of HNO_3 (1M) was added to the sol for peptization, and the mixture was again stirred for additional 15 minutes. After that 1.0275 g of ZrO_3 was added into the mixture. The sol was kept at boiling condition in the open flask for 1 hour. The PVA solution was added to the mixture according to the ratio of PVA: sol = 1: 20, stirred the mixture continuously. The product was refluxed under continuous stirring at temperature 90°C for 16 – 20 hours to ensure complete mixing and hydrolysis. The sol was cooled down slowly and left a side for a few hours. Repeat the above steps with different amount of ZrO_3. The sol was dried under the ambient condition until gelatin and viscous gel was

obtained. Transfer the sol to the support by dip coating method to prepare a thin layer of gel on the support. The membrane thickness firstly increased linearly with the dipping time, then the thickness may reached a limit. It was noted that a thicker and non-uniform gel layer was more liable to crack than a thinner, uniform gel layer during heating and calcinations. After that dip coating the sol on the surface of the support, the membrane was heat treated in the furnace. The furnace temperature started at 30°C and raised the temperature to 300°C with 0.5°C/min keep the furnace temperature at 300°C for 0.5 hour for relaxation of the gel to avoid the stress exceeds the elastic strength of the gel. The temperature from 300°C was raised to 700°C with the rate of 0.5°C/min. The sintering of inorganic membrane was carried out at furnace temperature of 700°C for 5 hours. The cooling for decreasing temperature was conducted at the temperature rate of 1°C/min, to ambient temperature about 30°C. The preparation of porous ceramic support is summarized as following:

1. Raw material
   - ii) Feldspar potash
   - iii) Ball clay
   - iv) Kaolin
   - v) Silica Power
   - vi) Sodium Hexametaphosphate flake
   - vii) Distilled water

2. Preparation of PVA Solution
   - i) 7.5 g of PVA was gradually added to 250ml to deionize water at ambient temperature.
   - ii) Stir the solution until all the PVA distributed equally.
   - iii) Boil the solution until all PVA are dissolved and stir the solution carefully. The step should be taken at least 40 minutes.
   - iv) 10 ml of 1M HNO_3 added into the solution.
   - v) Reflux the solution for 4 hours.

3. Sieve all the feldspar potash, ball clay, kaolin and silica powder by mesh size, 90μm.

4. All the powders were mixed according to mass ratio given below:
   - i) 25% Feldspar potash
   - ii) 25% Ball clay

iii) 25% Kaolin

iv) 25% Silica powder

5. Mixing 20g of mixed powder and 25ml PVA solution were formed the concentrated slurry support. Different composition of mixed powder and PVA solution was used.

6. Dip the sponge in the mixture. After that put the sponge inside the furnace with the starting temperature at 30°C, raise the temperature with 1°C/min up to 1200°C. Maintain the temperature for 2 hours. After the heating duration the furnace temperature was decreased by 1°C/min back to 30°C.

Preparation of Sol Gel

1. Chemicals needed
   - i.) Aluminium Sec-Butoxide [$Al(OC_4H_9)_3$]
   - ii.) Zirconium (IV) Oxide
   - iii.) Nitric Acid 1M
   - iv.) Double distillated water
   - v.) Polyvinyl alcohol solution (PVA)
   - vi.) Sodium Bicarbonate

2. Preparation of Zirconia Coated Alumina Sol

- i.) Molar ratio of Al^{3+}: H^+: Zr: H_2O = 1:0.07:0.15:100
- ii.) The volume ratio at the basic of 100ml of H_2O is Al^{3+}: H^+: Zr: H_2O = 1:3.88ml:1.0275g:100ml
- iii.) A 100ml of double distillated water was heated on a hot plate at temperature about 80-85°C.
- iv.) A 14.25ml of Aluminium tri-sec-Butoxide was added into the double distillated water. Stir the solution vigorously with magnetic stirrer until homogenous mixture was obtained.
- v.) A 3.88ml of HNO_3 (1M) was added to the sol, and the mixture was stirred for 15 minutes.
- vi.) A 1.0275g of ZrO_3 was added into the mixture.
- vii.) The sol was kept boiling in the open flask for 1 hour.

viii.) PVA was added to the mixture according to the ratio of PVA: Sol = 1:20, stirred the mixture continuously.

ix.) The product was refluxed under continuous stirring at temperature 90°C for 16-20 hours.

x.) The sol was cooled down slowly and left a side for at least for a few hours.

xi.) Repeat the above steps with different amount of ZrO_3.

3. The sol was dried under ambient condition until gelatin and viscous gel was obtained.

4. Apply the sol on the support by dip coating method. After that the sol with support heat treated in the furnace.

5. The furnace temperature started at 30°C then raised the temperature to 300°C with a ramp of 0.5 °C/min. The furnace temperature was kept at 300°C for 0.5 hour for relaxation of the gel. The temperature from 300°C was raised to 500°C with the rate1°C/min. The furnace temperature was kept at 500°C for 3-4 hours for sintering purposes. After that decreased the temperature with the rate of 1°C/min to cool down to 30°C.

Porous Ceramic Support

1. Raw material:
   - i) Feldspar potash
   - ii) Ball Clay
   - iii) Kaolin
   - iv) Silica powder
   - v) Sodium Hexa-meta-phosphate flake (calgen)
   - vi) PVA 3%
   - vii) Distilled Water

2. Preparation of PVA Solution
   - i) A 7.5g of PVA 72000 is gradually been added to 250ml of deionized water at ambient temperature.
   - ii) Stir the solution until all of the PVA distributed equally.
   - iii) Boil the solution until all PVA were dissolved and stir the solution carefully (bubbling might occur for vigorous stirring). This step should be taken for at least 40 minutes.
   - iv) After that 10ml of 1M HNO_3 was added into the solution.
   - v) Reflux the solution for 4 hours.

3. Sieve all the feldspar, ball-clay, kaolin and silica powders by mesh size 1mm, 710μm, 500μm, 425μm, and 106μm.

4. All the powders were mixed according to mass ratio as follow:
   25% Feldspar potash
   25% Ball-clay
   25% Kaolin
   25% Silicon powder

5. Preparation of dispersion solution:
   i) 250ml of PVA solution
   ii) 400ml of Distilled Water
   iii) (The volume ration of PVA to Distilled water is 5:8)
   iv) 3.9 g of Calgen was added into the mixed solution to get 0.6% of concentration.

6. The concentrated slurry support was formed by
   i) 20g of mixed powder(4) : 20ml dispersion solution(5)
   ii) 20g of mixed powder(4) : 17.5ml dispersion solution(5)
   iii) 20g of mixed powder(4) : 15ml dispersion solution(5)

7. Some experiences are needed in order to carry out step 6 efficiently. From our previous work, the strength of ceramic support will increase with decrease the amount of dispersion solution.

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