ZEOLITE-A DEPOSITED ON GLASS/YTTRIA STABILIZED ZIRCONIA FORWARD OSMOSIS MEMBRANE FOR DESALINATION APPLICATION

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Dedicated to my mother,

(Hamiah Binti Tasripan)

my beloved siblings,

(Muhammad Khairul Anwar and Siti Nur Nabilah)

my sister in law,

(Wan Noraswa)

my beloved nephews,

(Muhammad Asyraf and Muhammad Haniff)

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May this thesis be an inspiration and guidance in the future.

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ABSTRACT

The global water scarcity is now a major concern, which made recovering fresh water from seawater is the best alternative. Membrane-based technologies have been widely adopted in desalination, performed using reverse osmosis (RO) and forward osmosis (FO). Zeolite membrane showed great potentials for desalination due to the chemical and thermal stabilities. Zeolite membrane is generally developed by depositing zeolite onto a support material. However, there is a great tendency for delamination to occur. Unsupported zeolite membrane was developed as an alternative to overcome the cracking problem, but the unsupported zeolite membrane transforms into a glass membrane during sintering process. The glass membrane produced have a dense structure, which increased the water resistance pathway in the membrane, and resulted in low flux. Hence, in this study yttria-stabilized zirconia (YSZ) particles were added to increase the flux. Zeolite membrane was developed by depositing zeolite onto glass/YSZ hollow fibre, using the hydrothermal method, to improve the performance of the membrane. Thus, this study aims to i) fabricate glass hollow fibre using zeolite as a starting material, ii) investigate the effects of YSZ particles addition on the membrane performances and iii) evaluate zeolite deposition parameters on the glass/YSZ hollow fibre performances. The glass membrane was fabricated using a phase inversion and sintering technique, by a transformation of zeolite to glass during the sintering process. The YSZ was added into the glass hollow fibre through the same method of the aforementioned glass hollow fibre. The zeolite was deposited onto the glass/YSZ hollow fibre through a hydrothermal method, in an autogenous condition at 120 °C for various synthesis time. Zeolite transformed into glass due to the changed in the arrangement of the molecular structure. Zeolite, a crystalline phase changed to glass, an amorphous phase, when exposed to high temperature. The addition of the YSZ particles improved the permeation by reducing the pathway resistance through the void formed during the sintering process but gave low rejection. To improve the rejection, zeolite was deposited onto the membrane at different concentration and synthesized time. It was found that the suitable conditions were at 0.66 M concentration, and synthesis for 18 hours. The zeolite deposited on glass/YSZ membrane was able to perform sodium chloride (NaCl) rejection thus gave 62.25 L m^{-2} hr^{-1} and 0.11 kg m^{-2} hr^{-1} for solute flux and reverse solute flux, using FO water filtration system. It can be concluded that the zeolite membrane on glass hollow fibre was capable for desalination application with high flux and low reverse solute flux. A further investigation on the zeolite membrane deposited on glass hollow fibre i.e., to control the zeolite layer and a study to reduce the risk of delamination of the zeolite layer should be conducted.

ABSTRAK

Perolehan air tawar daripada air laut telah menjadi alternatif yang terbaik bagi masalah kekurangan air yang dihadapi dunia pada masa kini. Teknologi berasaskan membran mengunakan osmosis balikan (RO) dan osmosis depan (FO) telah digunakan secara meluas dalam aplikasi penyahgaraman. Membran zeolit telah menunjukkan potensi yang sangat besar dalam aplikasi penyahgaraman disebabkan oleh kestabilan kimia dan haba. Membran zeolit, secara amnya dibangunkan dengan menghasilkan mendakan zeolit diatas sesuatu bahan sebagai sokongan, namun lapisan zeolit tersebut berpontesi untuk terkupil. Justeru, membran zeolit tanpa bahan sokongan dibangunkan sebagai alternatif kepada masalah ini, tetapi membran zeolit tersebut bertukar menjadi membran kaca semasa proses pensinteran. Membran kaca yang dihasilkan ini mempunyai struktur yang padat, dimana struktur tersebut telah meningkatkan rintangan laluan air di dalam membran tersebut dan akhirnya menghasilkan fluk yang sedikit. Oleh itu, dalam penyelidikan ini zarah-zarah yttria-zirkonia stabil (YSZ) telah di tambah ke dalam membran kaca tersebut untuk meningkatkan penghasilan fluks. Membran zeolit telah dibangunkan melalui mendakan secara hidroterma diatas gentian berongga kaca/YSZ sebagai sokongan, untuk meningkatkan prestasi membran. Oleh itu, kajian ini bertujuan untuk: i) menghasilkan serat berongga kaca menggunakan zeolit sebagai bahan permulaan, ii) menyiasat kesan zarah-zarah YSZ pada prestasi membran dan iii) mengkaji parameter pemendapan zeolit terhadap prestasi serat berongga kaca/YSZ. Membran kaca dihasilkan dengan menggunakan fasa penyongsangan dan teknik pensinteran, dengan penjelmaan zeolit kepada kaca semasa proses pensinteran. YSZ telah ditambahkan ke dalam serat berongga kaca melalui kaedah yang sama seperti serat berongga kaca yang telah disebut sebelum ini. Zeolit telah dimendakkan ke atas serat berongga kaca/YSZ melalui kaedah hidroterma iaitu dengan menjana secara sendiri pada 120°C untuk pelbagai masa sintesis. Zeolit berubah menjadi kaca kerana terdapat perubahan pada susunan struktur molekul zeolit tersebut. Zeolit adalah fasa kristal berubah menjadi kaca iaitu fasa amorfus apabila terdedah kepada suhu tinggi. Penambahan zarah YSZ meningkatkan kebolehtelapan air dengan mengurangkan rintangan pada laluan air tersebut melalui ruang-ruang yang terbentuk semasa proses pensiteran, tetapi ia juga menghasilkan penolakan yang rendah. Untuk meningkatkan kadar penolakan, zeolit telah dimendakkan ke membran pada kepekatan dan masa sintesis yang berbeza. Didapati bahawa keadaan yang sesuai ialah pada kepekatan 0.66 M, selama 18 jam. Zeolit yang telah dimendakkan pada membran kaca/YSZ telah menghasilkan fluks zat terlarut pada 62.25 L m^{-2} hr^{-1} dan kebolehtelapan fluks songsang pada 0.11 kg m^{-2} hr^{-1} untuk penyingkiran natrium klorida (NaCl) menggunakan sistem penapisan air (FO). Dapat disimpulkan bahawa membran zeolit yang dimendakkan pada serat berongga kaca/YSZ sesuai untuk digunakan bagi aplikasi penyahgaraman, serta menghasilkan fluks yang tinggi dan kebolehtelapan fluks songsang yang rendah. Kajian mengenai membran zeolit yang dimendakkan pada serat berongga kaca seperti untuk mengawal lapisan zeolit dan kajian untuk mengurangkan risiko penyingkiran lapisan zeolit boleh dilakukan pada masa hadapan.

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LIST OF ABBREVIATIONS

Al_2O_3	-	Aluminum Oxides
Al^{3-}	-	Aluminum
BET	-	Brunauer-Emmett-Teller
BSA	-	Bovine Serum Albumin
CPG	-	Controlled Pore Glasses
DMAc	-	Dimethylacetamide
DMSO	-	Dimethylsulfoxide
DS	-	Draw Solutions
DTA	-	Differential Thermal Analysis
FESEM	-	Field Emission Scanning Electronic Microscope
FO	-	Forward Osmosis
FS	-	Feed Solutions
FTIR	-	Fourier Transform Infrared Spectroscopy
HDA	-	High Density Amorphous
HPLC	-	High Performance Liquid Chromatography
JMA	-	Johnson-Mehl-Avrami
LDA	-	Low Density Amorphous
MD	-	Membrane Distillation
MF	-	Microfiltration
MWCO	-	Molecular Weight Cut-Off
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
O^{2-}	-	Oxygen
PESf	-	Polyethersulfone

PG	-	Porous Glass
PSf	-	Poly Sulfone
PVDF	-	Polyvinylidenefluoride
RO	-	Reverse Osmosis
RTI	-	Rayleigh-Taylor Instability
SBU	-	Secondary Building Unit
SEM	-	Scanning Electronic Microscope
Si^{4+}	-	Silicon
SLRO	-	Sweeping Liquid Reverse Osmosis
SPG	-	Shirasu Porous Glass
TG	-	Thermal Gravimetric
TGA	-	Thermogravimetric
TiO_2	-	Titanium Dioxide
TMC	-	Trimethylene Carbonate
TOC	-	Total Organic Carbon
UF	-	Ultrafiltration
UV	-	Ultraviolet
VG	-	Vycor Glass
XRD	-	X-Ray Diffractometer
YSZ	-	Yttria Stabilized Zirconia
ZrO_2	-	Zirconium Oxides

LIST OF SYMBOLS

Å	-	Armstrong
C	-	Celcius
Da	-	Dalton
g	-	Gram
hr	-	Hour/hours
J_w	-	Water flux/fluxes
K	-	Kilo (10^3)
L	-	Liter
m	-	Meter
min	-	Minutes
mL	-	Mili Liter
MPa	-	Mega Pascal
Nm	-	Nano Meter
ppm	-	Part per million
wt.%	-	Weight Percentage

CHAPTER 1

INTRODUCTION

1.1 Research Background

Recovery of fresh water from various sources is a major concern nowadays due to the water scarcity experienced by most countries. Seawater is the best alternative water source covering approximately 97% of water source in the world [1]. Various technologies have been used to recover fresh water from this source; electrodialysis, distillations and membrane-based techniques [1,2]. Compared to available technologies, desalination membrane-based technologies have been widely adopted in desalination. Desalination using membrane that mostly performed using reverse osmosis has become a current practice in seawater desalination with water recovery reported ranging from 30 % to 35 % [3]. The membrane technology uses lower specific energy consumption (kWh/M^3) which makes it more preferable [4]. In 2016, the desalination water recovery is estimated to surpass 38 billion m^3 per year compared to 2008 worldwide [5].

Inorganic membranes is an attractive alternative in desalination technologies where the conventional polymeric membranes are inefficient due to the severe fouling and instability of the materials [6]. Among inorganic materials, zeolite has been regarded as a promising material for seawater desalination. Zeolite membranes have been proved to have an excellence performance for ion removal from aqueous solutions by reverse osmosis (RO) processes [7–9]. Zeolite membranes also have excellent selectivity over water (up to 10,000) when used for purification of organic pollutant [10]. Apart from performance in purification, zeolite membranes have great potentials for desalination due to chemical and thermal stabilities [8]. The zeolite membranes were generally fabricated by coating the zeolite onto the support membrane. Glass membrane can be a good support for zeolite coating due to chemical bonds formed during the synthetization process.

Thus, the synthesis of zeolite has been regarded as one of the most important factors in research and development of zeolite for the past decade [11]. Zeolite is commonly prepared using hydrothermal crystallization, in-situ hydrothermal synthesis, vapor phase transport, sol gel method, chemical growth, galvanic metal deposition, leakage-blocked method, seeding method (embedding zeolite microcrystal into a support) and microwave synthesis [7,12–14]. Typically, hydrothermal synthesis has been used to prepare zeolite membranes supported on a porous support. This approach produces a thin dense layer of zeolite membrane suitable for seawater desalination [7]. However, if the synthesis process is not properly controlled, thick and loose zeolite layers will be produced.

1.2 Problem Statement

Porous glass membrane has gained a lot of interest due to its advantages such as high thermal stability with high mechanical strength [15]. Despite those advantages, glass membranes were not a priority if compared to ceramic membrane due to the cost. Porous glass membrane required higher cost than ceramic membrane. The higher cost of glass membrane is mainly caused by the starting materials (glass powder) and membrane fabrication process (molding, heating and acid leaching). In addition, many research have been done to improve porous glass membrane such as pore size uniform controlled of the glass membrane as been done by Kukizaki et al. [15]. The author proposed using gas flow to control the glass membrane pore size. None of the research includes microstructures of porous glass membrane. To reduce the cost of porous glass membrane, ceramic-zeolite powder was found as an alternative for starting materials of porous glass membrane with simpler fabrication technique which is phase inversion-sintering technique. Compared to glass powder (RM 2559.00/100g, Sigma-Aldrich), zeolite (RM356.50/500g, Sigma-Aldrich) is much cheaper. In terms of fabrication, zeolite powder is also easier to handle and easier to fabricated by using phase inversion-sintering. The limitation of this method was that the glass membrane has limited porosity and dense structure to allow the diffusion of water. To improve its porosity, another ceramic material, namely yttria stabilized zirconia (YSZ), was added into ceramic suspension prior to the extrusion process. YSZ co-existed with glass physically after sintering process.

Although the composite membrane consisted of glass and YSZ particles have enhanced permeability, this characteristic caused low salt rejection for desalination. To improve separation properties of the glass membrane, additional deposition of zeolite membrane onto the glass membrane were proposed. Zeolite, which has been known to possess a unique framework, was used as separation layer for desalination. The existence of the unique framework enabled water to pass through the membrane while rejecting salt without using high pressurized water system, which made the desalination using zeolite are desirable. Nevertheless, zeolite deposition on the glass hollow fiber using hydrothermal process remained a challenge. Therefore, a number of the in-situ synthesis parameters of zeolite were investigated.

1.3 Objectives and Scopes

Based on the problem statement that has been mentioned before, the objectives of this study are:

1. To evaluate the feasibility of zeolite membranes transformation to glass membranes on the chemical properties, physical properties and separation performance of the glass hollow fibers.

2. To determine the effects of YSZ addition into ceramic suspensions on phase transformation, chemical properties, physical properties and water permeability of glass hollow fibers
3. To exploit the effect of in-situ synthesis parameter such as zeolite concentration and synthesis time on the deposition of zeolite onto glass hollow fiber on the membrane's morphology and performances on the desalination application using forward osmosis water system.

Five main scopes have been identified to achieve the objectives mentioned above, which are:

1. The glass hollow fiber membrane was developed from zeolite ceramic suspension for a spinning process. The parameters involved in the spinning process were ceramic loading (from 46 wt.% to 52 wt.%) and bore fluid rate (from 7 ml/min to 10 ml/min) while constant the air gap and suspension extrusion rate at 15 cm and 10 ml/min, respectively. The latter is then undergone calcination and sintering process at temperature ranging from 600 °C to 1400 °C. The transformation of zeolite to glass was analyzed using thermogravimetry (TGA), x-ray diffraction (XRD) and Fourier transform infra-red (FTIR). The glass membranes then were tested by 3-point bending for the mechanical strength and observed the morphology by scanning electron microscopy (SEM). The performance of the membranes was tested using reverse osmosis water system for pure water and synthetic contaminant. The synthetic contaminant used was bovine serum albumin with the size of 67 kDa weight molecular cut-off (MWCO) prepared at 1 g/L. The concentration of the contaminants after the filtration was determined using total organic carbon (TOC) analyzer to calculate the rejection percentage of the BSA.

2. YSZ ranged from 5 wt.% to 20 wt.% was added into the zeolite ceramic suspension for a spinning process. The spinning parameters were ceramic

loading of zeolite/YSZ (30/20 wt.% to 50/0 wt.%) at constant bore fluid, air gap and suspension extrusion rate at 9 ml/min, 15 cm and 10 ml/min, respectively. The latter is then undergone sintering process at temperature 1000 °C. The transformation of zeolite/YSZ to glass/YSZ was analyzed using thermogravimetry (TGA), x-ray diffraction (XRD) and Fourier transform infra-red (FTIR). The glass/YSZ membranes then were tested by 3-point bending for the mechanical strength and observed the morphology by field emission scanning electron microscopy (FESEM). The performance of the membranes was tested using reverse osmosis and sweeping liquid assisted reverse osmosis water system for pure water.

3. The zeolite was deposited on the glass/YSZ hollow fiber membrane using in-situ hydrothermal method. Synthesized time for zeolite was varied at 3, 6, 12, 18 and 24 hours while maintaining the zeolite concentration. Zeolite concentration was varied from 0.13 M to 0.66 M. To study the effect of zeolite concentration, the dilution of zeolite using water was done while maintaining the Si/Al ratio for 24 hours reaction time. The membrane then was dried in an oven for 24hours at temperature 60 °C. The membrane morphology was characterized using field emission scanning electron microscopy (FESEM) and tested using forward osmosis water system for desalination application.

1.4 Significance of the Research

This study contributed on the knowledge of developing porous glass membrane using simpler steps. The fabrication of glass membrane using phase inversion and sintering techniques enabled glass membrane to have various morphology based on desired application. This contribution can be used as a stepping-stone in producing transparent glass membranes for various applications, i.e. photocatalytic membrane and UV assisted cleaning membrane. This study reported, first time ever, the glass membranes were used as support for zeolite membranes for desalination. In addition, this study contributed on the desalination system that focused on hollow fiber configuration. To date, there is no study of desalination system that utilized composite membrane that consisted glass and ceramic material.

5.2 Recommendations

Based on the present study, some recommendations can be made for future work.

i. Some alternative zeolite materials such as zeolite X, Y, Sil-1, and ZSM-5 could be replaced as glass starting materials. The materials suggested contains higher silica content which may enhance the chemical stability and mechanical properties of the glass membranes, which may be used in a harsh environment.

ii. The zeolite membranes could be deposited with perfluoro polymers to preserve the zeolite layer deposited on the glass hollow fiber. This is to avoid the delamination of the layer occurred. The polymers served as a shielding coating of the membrane without affecting the membranes' performances.

iii. It is suggested that by reducing zeolite in-situ hydrothermal deposition temperature from 120°C to 100°C would reduce the zeolite's particles size. Working at different temperatures would help to understand the growing process and the deposition process of zeolite on the glass hollow fiber membranes, as particles size affects the thickness of zeolite layer and the membranes' performances. Further study on the developed zeolite membranes in this work should be carried to have a better knowledge on the zeolite mechanism of the membranes formation and to be able to control/predict the zeolitization process.

iv. In this study, a new FO water filtration for ceramic hollow fiber membranes was proposed. Therefore, further study on this filtration system is needed. A modelling on the membranes' performances; pure water, solute fluxes and reverse solute flux, should be done to study the conditions which would affect the performances. This FO then could be coupled with RO water filtration as a whole water system to form a new complete water purification system.

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