EPOXY ENHANCED POLYETHERSULFONE MEMBRANE FOR REMOVAL OF CHROMIUM

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UNIVERSITI SAINS MALAYSIA

2017

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by

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Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science

May 2017

ACKNOWLEDGEMENT

I would like to take this opportunity to thanks a few people as I could not take the full credit to myself for the accomplishment of this study because it would never been possible without the help from many significant individuals. First and foremost, I would like to convey my outmost appreciation to my main supervisor, Dr. Low Siew Chun for her guidance and assistance throughout my study. Her patience, dedication and support had help me through my good and bad times as well as it inspire me to work harder and improve my performance from time to time. I am thankful for her as I would never be able to complete my study without her motivation. I also would like to sincerely thank all the technician and staff from School of Chemical Engineering, USM for their help during my postgraduate study. My heart-felt gratitude also goes to my family who I was blessed to have for their prayers and encouragement that keep me going with strength. Not to mention, my sincere appreciation also goes to all my fellow friends who gave me a lot of support and hands through completing my study. Finally, I wish to thank financial support granted by USM Research Universiti (RU) grant (1001/PJKIMIA/814230).

TABLE OF CONTENTS

CHAPTER TWO: LITERATURE REVIEW

CHAPTER FOUR: RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFM	Atomic-force microscopy
ATR–FTIR	Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy
BSA	Bovine serum albumin
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAE	Cycloaliphatic epoxy resin
DGEBA	Bisphenol A diglycidyl ether
DNA	Deoxyribonucleic acid
ED	Electrodialysis
ELM	Emulsion liquid membrane
EPES	Epoxy functionalized poly (ether-sulfone)
ER	Epoxy resin
FESEM	Field emission scanning electron microscopy
GS	Gas separation
MCL	Maximum Contaminant Level
MF	Microfiltration
MWCO	Molecular weight cut–off
NF	Nanofiltration
NIPS	Non-solvent induced phase separation
NMP	1–methyl 2–pyrrolidone
PA	Polyamide
PAA	Poly(acrylic acid)

PAN	Polyacrylonitrile
PANI	Polyaniline
PEEKWC	Polyetheretherketone
PEG	Polyethylene glycol
PEI	Polyethyleneimene
PES	Polyethersulfone
PI	Polyimide
PMMA	Poly(methyl methacrylate)
PS	Polysulfone
PVC	Polyvinyl chloride
PVDF	Polyvinylene fluoride
PVP	Polyvinyl pyrrolidone
RMSD	Root mean square deviation
RO	Reverse osmosis
SLM	Supported liquid membrane
Sr	Strontium
TIPS	Thermally induced phase inversion
U	Uranium
UF	Ultrafiltration
USEPA	US Environmental Protection Agency
VIPS	Vapor induced phase separation
WHO	World Health Organization

LIST OF SYMBOLS

A	membrane effective area (m^2),
C_o	initial Cr ions concentration in the feed solution
C_p	Cr ions concentration in the permeate
J	flux (l/m^2h)
J_o	initial permeate flux (l/m^2h)
J_t	permeate flux at filtration time t (l/m^2h)
K	fouling constant coefficient
m	mass of permeated water (g)
N	number of data available
n	blocking index
P	porosity
ρ	density (g/cm^3)
R	rejection percentage (%)
t	ultrafiltration operation time (h)
V	accumulated permeate volume (m^3)
V_a	apparent volume (cm^3)
V_e	existence volume (cm^3)
W_1	initial weight of the membrane
W_2	weight of the dried membrane
$x_{i,measured}$	experimental filtration data
$\hat{x}_{i,modelled}$	fouling models predicted data

EPOKSI-TERTINGKAP POLIETERSULFON MEMBRAN UNTUK PENYINGKIRAN KROMIUM

ABSTRAK

Kajian yang dijalankan adalah bertujuan untuk menyingkirkan ion Cr(VI) yang karsinogenik daripada larutan berair melalui proses penurasan ultra menggunakan membran adunan Bisfenol A Diglicidil Eter (DGEBA) dan Polietersulfon (PES), (DGEBA–PES) yang disediakan melalui kaedah penyonsangan fasa kering-basah. Perubahan sifat fizikal telah diukur menggunakan medan pemancaran mikroskopi pengimbas elektron (FESEM), ukuran saiz purata liang dan ukuran keliangan. Hasil kajian telah mengesahkan perubahan bererti pada penyambungan liang antara sublapisan membran adunan apabila parameter sintesis (komposisi PES, komposisi DGEBA dan tempoh penyongsangan fasa kering) diolah. Adunan DGEBA-PES membran juga menunjukkan peningkatan sifat hidrofilik apabila damar DGEBA diperkenalkan ke dalam matriks polimer PES. Aktiviti ion Cr pada pH yang berbeza telah dianalisis terlebih dahulu, di mana jumlah Cr(VI) ditemui tinggi pada larutan alkali (pH > 7). Apabila damar epoksi diolah dalam jumlah komposisi polimer tetap 15 wt.%, adunan membran DGEBA-PES yang mengandungi 10 wt.% DGEBA menunjukkan penolakan ion Cr(VI) dengan nilai 53% tanpa menjejaskan fluks penelapan (12.17 L/m^{2}h). Selain daripada itu, 18 wt.% PES memberi penolakan ion Cr(VI) pada 62% dengan fluks penelapan pada 22.09 L/m^{2}h apabila komposisi polimer PES diolah. Dalam kajian yang dijalankan, adunan membran (18 wt. % polimer PES dan 30 wt.% DGEBA) telah menunjukkan penolakan ion Cr(VI) dengan jayanya pada nilai 90% dengan fluks penelapan 21.06 L/m^{2}h bagi penurasan hujung mati dan penolakan sebanyak 93% dengan fluks penelapan 5.40 L/m^{2}h diperolehi bagi penurasan aliran silang apabila Polietilenaimin (PEI) diperkenalkan di dalam larutan

suapan. Dalam kajian ini, membrane DGEBA-PES yang disintesis melalui kaedah penyonsangan fasa kering selama 1 jam menunjukkan prestasi terbaik bagi penolakan Cr(VI) iaitu pada nilai 88.84% dengan fluks penelapan yang stabil pada nilai 11.27 L/m^2hr bagi proses penurasan aliran silang. Mekanisma kotoran pada proses penurasan hujung mati juga dikaji menggunakan model kotoran Hermia di mana membrane DGEBA-PES didapati kotor disebabkan oleh sekatan liang penuh/dalaman, diikuti dengan mekanisma pembentukan kek di akhir proses penurasan. Daripada keputusan kajian, ia boleh menyimpulkan bahawa membran DGEBA-PES mempunyai potensi yang besar dalam penyingkiran ion Cr(VI) yang karsinogenik daripada aliran sisa yang tercemar. Dengan kajian mekanisma kotoran, membran dengan prestasi pemisahan yang lebih baik boleh direka bentuk.

EPOXY ENHANCED POLYETHERSULFONE MEMBRANE FOR REMOVAL OF CHROMIUM

ABSTRACT

The present work attempted to remove carcinogenic Cr(VI) ions from aqueous solution using Bisphenol A Diglycidyl Ether, (DGEBA) and Polyethersulfone (PES), (DGEBA–PES) blended membrane prepared through dry-wet phase inversion for ultrafiltration process. The changes in physical properties were measured using Field emission scanning electron microscopy (FESEM), mean pore size measurement and porosity measurement. The results confirmed the significant changes of pores connectivity between the sub-layers of the blend membranes as the synthesis parameters (PES composition, DGEBA compositions and duration of dry-phase inversion) were manipulated. The DGEBA–PES blend membranes also demonstrated an enhanced membrane hydrophilicity when DGEBA resin was introduced into the PES polymer matric. The Cr ions activity at different pH was first analyzed, where the amount of Cr(VI) was found to be higher in alkaline solution (pH > 7). When the epoxy resin was manipulated at fixed 15 wt.% polymer compositions, the blended DGEBA-PES membranes with 10 wt.% DGEBA revealed rejection of Cr(VI) ions at 53% without jeopardizing the permeate flux (12.17 L/m^{2}h) . On the other hand, 18 wt.% PES gave the Cr(VI) rejection at 62% with acceptable permeate flux at 22.09 L/m^{2}h when the amount of PES polymer was manipulated. In present work, the blended membrane (18 wt. % PES polymer with 30 wt.% DGEBA) has successfully demonstrated Cr(VI) ion rejection at 90% with permeate flux of 21.06 L/m^{2}h for dead-end filtration and 93% rejection with 5.40 L/m^{2}h permeate flux for cross flow filtration when the polyethylenimine (PEI) was introduced into the feed solution. In this work, DGEBA–PES membrane synthesized through 1 hour of dry phase inversion showed

the best performance of Cr(VI) rejection at 88.84% with steady permeation flux of 11.27 L/m^2hr for cross-flow filtration. Fouling mechanism on dead end filtration membrane was also studied using Hermia's fouling models where the DGEBA-PES membranes were generally fouled by complete/ internal pore blocking, followed by the cake formation mechanism at the end of the process. From the results, it can be conclude that the DGEBA-PES membrane has a great potential in the removal of carcinogenic Cr(VI) ions from the polluted waste stream. With the fouling mechanism study, membrane with better separation performance can be designed.

CHAPTER ONE

INTRODUCTION

1.1 Heavy Metal in Wastewater

With fast development of industries such as metallurgy, electroplating, machinery, manufacturing, mining operations, tanneries and etc (Zhu et al., 2015), the presence of heavy metals in wastewater has been a growing concern in the recent years. Unlike organic pollutants, the majority of heavy metal ions are susceptible to biological degradation and do not degrade into harmless end products (Gupta et al., 2001, Hegazi, 2013). Therefore, the presence of heavy metal ions is a major concern due to their toxicity to many life forms when exposed to the environment. Heavy metal is well known to cause severe damage to aquatic life and human life. Toxic heavy metals of particular concern in treatment of industrial wastewaters include Zn, Cu, Ni, Hg, Cd, Pb and Cr. These toxic and carcinogenic heavy metal ions are non-degradable (Houari et al.) and therefore tends to accumulate in the environment and living organism (Pagana et al., 2011).

Chromium is one of the major heavy metals present in wastewater which has toxic effect and is a strong oxidizing agent capable of being absorbed through living organism. Chromium commonly exists as chromic, Cr(III) and chromate, Cr(VI). Cr(III) is naturally exist in environment while the Cr(VI) form is rarely found in nature and is produced mainly from commercial and industrial processes such as metal extraction, metal fabrication and textile, leather tanning facilities, electroplating, and surface finishing (Pagana et al., 2011). The different types of chromium exhibit different properties, for example, Cr(III) is safe and unharmful to the environment, meanwhile, Cr(VI) is a carcinogenic and mutagenic pollutant which greatly affects the environment. Moreover, Cr(VI) is also known as carcinogenic to human respiratory

system, which caused lung carcinoma. It also could induce mutation in the DNA sequence and destabilize the genome in human body. This would result to diseases like microsatellite instability and defective DNA repair (Hsu et al., 2011).

Therefore, the removal of heavy metals such as chromium ions from industrial effluent has become an important issue globally. The conventional methods of removing heavy metals from wastewater include chemical precipitation, adsorption, ionic exchange, electrochemical deposition and extraction (Tohyama et al., 1973). However, these methods are commonly facing issues of low selectivity, sludge generation that require further treatment and high energy requirement (Nędzarek et al., 2015, Yurekli, 2016). Due to such concern, research on membrane technology has received great attention and gain popularity in the heavy metals separation (Chougui et al., 2014). This was due to the great separation benefits offer by membrane technology such as energy saving, high separation efficiency, space saving (Qdais and Moussa, 2004).

1.2 Removal of heavy metal by ultrafiltration membrane

Membrane techniques have been proven to be one of the effective methods for heavy metal removal because of its simple and economical operating procedure (Vinodhini and Sudha, 2016). There are various types of membrane filtration technique such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) that can be employed for heavy metal removal from wastewater (Kumar et al., 2014), depending on the size of the particle that need to be retained.

Generally, MF membrane rejects particles from about 0.05–0.1 μm to 1.0 μm, and is typically available for the removal of protozoa and bacteria. Due to its bigger

pore channels, the membrane are not compatible to be used for heavy metals separation (Kang and Cao, 2014). On the other hand UF membranes have a pore size range of 0.01–0.1 μm, and are usually characterized by their molecular weight cut–off (MWCO). These membranes are usually used for the removal emulsified oils, metal hydroxides, colloids, proteins, and large molecular weight materials from water. UF processes are often used to remove heavy metal from wastewater due to its medium pore size range that can retain the heavy metal molecule, and also less susceptible to membrane fouling compared to the smaller pore size membranes such as the NF process. NF is the process between UF and RO which can reject particles smaller than 0.001 μm. However, this type of membrane needs details study on the membrane fouling due to its small pore size (Bowen and Welfoot, 2002).

A wide range of polymeric materials have been used to prepare various membrane structural. Polymers including polyethersulfone (PES), polyamide (PA), polyacrylonitrile (PAN), polyimide (PI), polysulfone (PS) and polyvinylidene fluoride (PVDF) have been applied in the development of UF membranes because of their chemical stability and oxidation-resistivity (Xu et al., 2016). However, membrane fouling was found to be an important issues in UF industry where it limits the ability of the membrane to perform in the filtration processes. Membrane fouling is closely related the membrane hydrophobic properties that reduced the separation efficiency of the membrane (Sun et al., 2013). Therefore, the key point that need to be tackle when using the membranes technology is to suppress its hydrophobic properties (Maximous et al., 2009), such as to introduce a hydrophilic agent into the membrane matric.

For several decades, many efforts had been made to modify commercial membrane and to improve their anti-fouling capability using technique such as surface coating, blending and grafting. Grafting of the hydrophilic monomers onto the

membrane surface was found to improve the water flux as well as to enhance the antifouling properties of the membrane (Kumar et al., 2016). However, among these methods, polymer blending was the simplest method to enhance the membrane hydrophilicity. In this method, the commercial polymer was blended with the hydrophilic additives such as polyethyleneglycol (PEG) and polyvinylpyrrolidone (PVP) and epoxy resin (Kumar et al., 2014, Barakat, 2011) during the casting process.

1.3 Interaction between epoxy resin and heavy metal

Epoxy resins are defined as a polymer/macromolecular resin containing high amount of epoxide molecule group and capable to react (cross-linked) with other polymer materials (Gordon et al., 2010). The epoxide group existed in epoxy resin is also sometimes referred as the oxirane group, as shown in Figure 1.1.

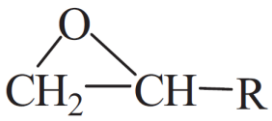

Figure 1.1: Molecular structure of epoxy group.

Epoxy resins are widely used in various applications due to their attractive properties such as excellent chemical and corrosion resistance, good thermal properties, great versatility, low shrinkage, excellent mechanical and electrical properties and ease of handling (Kong et al., 2016, Van de Grampel et al., 2005, Shin et al., 2004). Due to its outstanding properties, epoxy resins are widely used in electronic industries for surface coatings, as the structural adhesives, printed circuit board, insulation materials for electronic devices, and advanced composites matrices (Pan et al., 2007, Shang et al., 2012). Besides, it also used in transportation industries