SILVER ION EXCHANGE FILLERS INCORPORATED WITH MIXED MATRIX MEMBRANE FOR ANTIBACTERIAL APPLICATION

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TO MY BELOVED FAMILY,

MY LOVELY FATHER AND MOTHER

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ABSTRACT

The objective of this work is to investigate silver ion exchanged fillers in the mixed matrix membrane for antibacterial application. Flat sheet Polyethersulfone (PES) mixed matrix membrane (MMM) was fabricated and characterized. MMM was fabricated using a dry/wet phase inversion technique. The work was performed to investigate the effect of incorporating Ag^{+}-ion exchanged halloysite nano tubes (HNT) clay as large pore size filler in MMMs for bacterial removal. The chemical modification of HNTs involved silylation and Ag^{+}-ion exchanged treatment. The silylated HNTs was prepared by treating them with N-β)) (aminoethyl)-γ-aminopropyltrimethoxy silane agent. It is interlude to show that Ag^{+}-ion exchanged fillers can control the Ag^{+} leaching to very low amount which was 14 ppb during fabrication and 11 ppb during filtration. Membrane characterization were performed using Fourier Transforms Infrared (FTIR), Field Emission Scanning Electron Microscopy (FESEM), energy dispersive X-rays (EDX), atomic absorption spectroscopy (AAS). The differential coliform agar (DCA) was used as antibacterial test. *Escherichia coli* (*E-coli*) were considered as a typical bacteria in this study. A fabricated PES asymmetric MMM flat sheet membrane successfully removed bacteria from the treated water, whereby, almost all bacteria have been inhibited.

ABSTRAK

Objektif kajian ini adalah untuk menyiasat kesan penukaran ion perak terhadap pengisi di dalam membran matrik campuran untuk penyingkiran bakteria. Membran matrik campuran (MMMs) Poliethersulfona (PES) kepingan rata telah dihasilkan dan dicirikan. Membran matrik campuran dihasilkan melalui teknik fasa balikan kering/basah. Kajian ini dijalankan untuk mengkaji kesan campuran tiub nano halloysite (HNTs) yang telah melalui penukaran ion Ag^{+} sebagai pengisi berliang besar dalam MMM untuk penyingkiran bakteria. Pengubahsuaian kimia ke atas HNTs telah melibatkan rawatan sililasi dan penukaran ion Ag^{+}. HNTs telah melalui rawatan sililasi dengan menggunakan N-β-(aminoetill)-γ-aminopropiltrimetoxi silan. Pengisi yang telah melalui penukaran ion menunjukkan yang ia dapat mengawal kehilangan Ag+ semasa oleh jumlah sangat rendah yang mana 14 ppb semasa rekaan dan 11 ppb semasa penurasan untuk permohonan antibakteria penambahan ion perak ke dalam dop. Pencirian membran telah dibuat menggunakan spektroskopi inframerah transformasis fourier (FTIR), mikroskopi imbasan elektron pemancaran medan (FESEM), penyerakan tenaga sinar X (EDX), spektroskopi penjerapan atom (AAS), pembezaan koliform agar (DCA) digunakan sebagai penguji anti-bakteria. *Escherichia coli (E-coli)* digunakan sebagai bakteria tipikal untuk kajian ini. Membran matrik campuran tuk simetri PES dijangka daput menyingkir bakteria daripuda air yang dirawat. Ini menunjukan bahawa hampir semua bakteria telah dapat diskat.

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LIST OF ABBREVIATIONS

MMMs	-	Mixed matrix membranes
MF	-	Microfiltration
DBPs	-	Disinfection by-products
DOM	-	Dissolved organic matter
UF	-	Ultrafiltration
LRV	-	Log-reduction value
UV	-	Ultra-violet
E.coli	-	*Escherichia coli*
DNA	-	Deoxyribonucleic acid
BE	-	Binding energy
HNT	-	Halloysite Nano tubes
EDX	-	Energy dispersive X-ray
CFU	-	Colony forming unit
NOM	-	Natural organic matter
DOC	-	Dissolved organic carbon
pH	-	$-\log[H^+]$
WHO	-	World of Health Organization
FTIR	-	Fourier transform infra-red spectroscopy
FESEM	-	Field emission scanning electron microscope
ppb	-	Part per billion
ppm	-	Part per million
PWP	-	Pure water permeation
TOC	-	Total organic carbon
MW	-	Molecular weight
NA	-	Nutrient agar
rpm	-	Revolution per minute
v/v	-	Volume per volume
Fig.	-	Figure
Wt.	-	Weight
Eq.	-	Equation
SD	-	Standard deviation
DMFC	-	Direct methanol fuel cell

LIST OF SYMBOLS

%	-	Percent
˚C	-	Degree Celcius
h	-	Hour
°	-	degree
g	-	gram
θ	-	Theta
µM	-	Micro molar
wt. %	-	Weight percent
d	-	diameter
J_v	-	Pure water permeation (Flux)
r_m	-	Mean pore diameter
ε	-	Porosity
Q	-	Volume of permeate
A	-	Membrane surface area
ΔT	-	Permeation time
µm	-	Micrometer
nm	-	Nanometer
C_p	-	Concentration of permeate
C_f	-	Concentration of feed
mg/L	-	Miligrams per litre
mm/min	-	Milimeter per minute

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Membrane separation process has been proven to be effective for desalination of sea water and brackish water, reclamation of wastewater and agricultural drainage water, drinking water supply containing toxic substances and production of high quality pure water for industrial process such as in semiconductor manufacturing. Microfiltration, ultrafiltration, nanofiltration and reverse osmosis filtration have been widely used and successfully applied in drinking water treatment for the removal of colloidal particles, turbidity, dissolved organic matter (DOM) and microorganisms (Yuan and Zydney, 1999; Mohammad *et al.,* 2004; Ismail *et al.,* 2006; Mohammad *et al.,* 2007; Schafer, 1999). This advanced technology is capable of producing superior water quality far beyond the current regulatory requirements and therefore can be adopted to serve as an alternative to conventional clarification and filtration water treatment process.

The membrane filtration such as UF/MF procedure has been used for drinking water bacteriological testing for many decades and showed a great advantage in testing large numbers of water samples. In this way some pollutants such as *Escherichia coli* (*E.coli)* can remove trough the membrane process. Recently many studies have been done to decrease the membranes problem due to the uncontrolled accumulation of micro-species. For this reason some of the area such as membrane modification, low flux operation and chemical cleaning are focused more (Chang *et al.,* 2002).

On the other hand, weakness in membrane performance has encouraged to development of membrane with new materials and structures that exhibit both higher selectivity and permeability. Mixed matrix membranes (MMMs) are the latest emerging polymer based organic-inorganic composite membrane materials which may potentially surpass this upper bound. The successful implementation of this new membrane technology is greatly dependent on the appropriate selection of the polymer matrix and inorganic filter and most importantly the elimination of interface defects. Development of new membrane materials with higher selectivity requires a proper material selection for both polymer matrix and molecular sieves. Polymer matrix selection determines the minimum performance of mixed matrix material to be fabricated. The addition of molecular sieving materials can only enhance the selectivity of the membrane in the absence of defects (Mahajan and Koros, 2002). Properties of the pure polymer matrix are the first aspect to be considered. A polymer matrix candidate must not only attractive from the economic point of view, but also provide industrial acceptable performance. Hence, bacteria removal and seawater desalination by Mixed matrix membranes (MMMs) has good result because of high selectivity (Dipak *et al.,* 2010; Hoek *et al.,* 2003).

1.2 Problem Statement

Membrane technology has been effectively applied for water treatment purpose. Therefore ultrafiltration (UF) membrane has been utilized for bacteria removal. To enhance the separation effectively silver ion was utilized recently as an antibacterial agent (Basri *et al.,* 2010). Also, thin film composition membranes have been utilized for bacteria removal using different silver salts as additive (Dipak *et al.,* 2010). They could strongly remove more than 90% of the bacteria, however, Ag^+ ion leached heavily during membrane fabrication. Then fabrication of high performance UF membrane for bacteria removal along with preserving Ag^+ ion during the membrane fabrication of high fabrication step in one of the challenges that must be taken into consideration.

1.3 Objective of the Study

Based on the problem statement the objectives of this study are as follows:

1. To reduce silver leaches by functionalization and characterization of Halloysite nano-tubes (HNTs) clay using coupling agent.
2. To develop an antibacterial membrane by incorporating silver (Ag) as an antibacterial agent
3. To perform Ag^+ ion exchange treatment on Halloysite nano-tubes (HNTs) clay to prepare and characterize mixed matrix membrane (MMM).

1.4 Scope of the Study

To achieve the objectives of the study, the following scopes of the study have been identified:

1. Fabricating of flat sheet mixed matrix membranes using Polyethersulfone (PES) and functionalized halloysite nano tubes clay.
2. Conducting Ag^{+} ion exchange treatment of halloysite nano-tubes to improve the selectivity, hence the final MMMs permeability.
3. Functionalization of halloysite nano-tubes clay using N-β-(aminoethyl)-γ-aminopropyltrimethooxy silane (AEAPTMS) as coupling agent.
4. Membrane characterization was Field Emission Electron Microscopy (FESEM), Fourier Transform Infra Red Spectroscopy (FTIR), Energy Dispersive X-rays (EDX), atomic adsorption spectroscopy (AAS), antibacterial test, and constant pressure permeation test.
5. Performance evaluates of each mixed matrix membrane for bacteria removal.

1.5 Research Significance

This study is of significance to the research of water treatment which involves disinfection steps. The mixed matrix antibacterial membranes extend the multi-steps options for water treatment to a stand-alone removal and disinfection of bacteria. The results obtained in the study also provide the information in bacteria-removal and which lead to the most effective options in treating polluted water. Furthermore, the information on fillers incorporating obtained in this study would be beneficial to the other related fields such as in medicine and electrical field where silver loss is optimized in wound dressings and conducting material.

1.6 Organization of the Thesis

The thesis is divided into five chapters. The first chapter presents research background, problem statement, objectives, scopes and significance are also highlighted in the first chapter. Second Chapter provides the literature review on membrane separation, ultrafiltration membrane, bacteria removal, antibacterial agent, mixed matrix membranes and ion exchange method. Chapter three is dedicated to the detailed description of the research methodology. The material selected for dope preparation, membrane fabrication and performance testing conducted in this work are explained in this chapter. In chapter four, the effect Ag^{+} -ion exchanged fillers in the mixed matrix membrane for bacteria removal properties and performance of fabricated membranes are explored and discussed. Finally in Chapter five, the conclusion of the research is drawn and the potential future works are proposed.

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