EFFECTS OF SODIUM BICARBONATE AND CO-AMINE MONOMERS ON PROPERTIES AND PERFORMANCE OF THIN FILM COMPOSITE MEMBRANE FOR WATER AND WASTEWATER TREATMENT

JOHN OGBE ORIGOMISAN

UNIVERSITI TEKNOLOGI MALAYSIA

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JOHN OGBE ORIGOMISAN

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Faculty of Engineering
Universiti Teknologi Malaysia

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ABSTRACT

Polyamide (PA) thin film composite (TFC) nanofiltration (NF) membranes are widely used for the treatment of water and wastewater treatment. However, they still experience lower permeability and rapid flux decline within short period of time particularly in the case where the feed solutions contain high levels of organic pollutants. To solve this problem, a co-amine monomer in the presence of an inorganic additive can be introduced during interfacial polymerization process to alter the PA layer properties of membrane, aiming to improve its water flux and antifouling properties without affecting salt rejection. The main objective of this work is to determine the effects of sodium bicarbonate ($NaHCO_3$) additive loading (0.5, 1.5 and 0.25 wt.%) and piperazine (PIP)/2-(2′aminoethoxy) ethylamine (AEE) co-amine weight ratio (2:0, 1.75:0.25, 1.50:0.50, 1.0:1.0 and 0:2) on the properties and performance of TFC membranes for water and wastewater treatment, respectively. The chemical composition and morphology of the resultant TFC membranes were characterized by field emission scanning electron microscopy (FESEM), surface chemistry through attenuated total reflectance Fourier transform infrared analysis (ATR-FTIR) and hydrophilicity through contact angle measurement. Results showed that polymerization successfully took place forming a thin PA layer on the support membrane pore size within the range of NF. 0.5 wt% $NaHCO_3$ was the best loading to improve membrane water permeability without really affecting Na_2SO_4 rejection. This modified membrane showed 37% higher water permeability than that of membrane without additive. In the presence of 0.5 wt% $NaHCO_3$, it is found that the introduction of AEE into PIP solution at PIP:AEE ratio of 1:1 could more greatly improve the salt rejection of PIP-based membrane from 97.1% to 98.5%, producing a permeate of better quality. The improved separation rate was due to the formation of denser and rougher PA layer upon AEE incorporation. Further characterization on the selected TFC membranes for aerobically treated palm oil mill effluent (AT-POME) treatment indicated that the membrane made of PIP:AEE of 1:1 was able to achieve improved performance, recording 79.15%, 94.26% and 89.3% rejection for conductivity, colour (ADMI) and COD reduction. This work demonstrated the importance roles of additive and co-amine monomer in improving characteristics of TFC membrane for water and wastewater treatment.

ABSTRAK

Membran penuras nano (NF) komposit filem tipis (TFC) poliamida (PA) telah digunakan secara meluas untuk rawatan air dan air sisa. Walau bagaimanapun, ianya masih mengalami kebolehtelapan yang lebih rendah dan penurunan fluks yang mendadak dalam jangka waktu yang pendek terutamanya apabila larutan suapan mengandungi percemar organik pada kopekatan yang tinggi. Untuk menyelesaikan masalah ini, monomer ko-amina dan bahan tambahan bukan organik boleh diperkenalkan semasa proses pempolimeran antara muka (IP) untuk mengubah sifat lapisan membran PA, bertujuan untuk meningkatkan fluks air dan sifat anti-kotoran tanpa mempengaruhi penyingkiran garam. Objektif utarna kajian ini adalah untuk mengkaji kesan muatan bahan tambahan seperti natrium bikarbonat ($NaHCO_3$) (0.5, 1.5 dan 0.25 % berat) dan piperazine (PIP)/2- (2′aminoetoksi) etilamina (AEE) nisbah berat ko-amina (2:0, 1.75:0.25, 1.50:0.50, 1.0:1.0 dan 0:2) pada sifat lapisan membran TFC untuk rawatan air dan air sisa. Komposisi kimia dan morfologi membran TFC yang dihasilkan dicirikan oleh mikroskopi medan pengimbas elektron (FESEM), kimia permukaan melalui spektroskopi inframerah transformasi Fourier pantulan total dilemahkan (ATR-FTIR) dan kehidrofilikan melalui pengukuran sudut sentuh air. Hasil kajian menunjukkan bahawa proses pempolimeran berjaya membentuk lapisan PA yang nipis pada pori membran sokongan dalam ukuran lingkungan NF. 0.5 % berat $NaHCO_3$ adalah muatan terbaik untuk meningkatkan kebolehtelapan air membran tanpa mempengaruhi penyingkiran Na_2SO_4. Membran yang telah diubah suai ini menunjukkan kebolehtelapan air 37% lebih tinggi daripada membran tanpa sebarang bahan tambahan. Dengan adanya 0.5 % berat $NaHCO_3$, ianya didapati bahawa pengenalan AEE ke dalam larutan PIP pada nisbah PIP:AEE 1:1 dapat meningkatkan penyingkiran Na_2SO_4 membran berasaskan PIP dari 97.1% hingga 98.5%, menghasilkan resapan lebih berkualiti. Tahap pemisahan yang lebih baik adalah disebabkan oleh pembentukan lapisan PA yang lebih padat dan kasar semasa penggabungan AEE. Pencirian lebih lanjut pada membran TFC yang dipilih untuk rawatan efluen minyak kelapa sawit yang dirawat secara aerobik (AT-POME) menunjukkan bahawa membran yang diperbuat daripada PIP:AEE 1:1 dapat mencapai prestasi yang terbaik, mencatatkan penolakan 79.15%, 94.26% dan 89.3% untuk kekonduksian, pengurangan warna masing-masing (ADMI) dan COD. Hasil Kajian ini menunjukkan pentingnya peranan bahan tambahan dan monomer ko-amina dalam meningkatkan ciri-ciri membran TFC untuk rawatan air dan air sisa.

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LIST OF ABBREVIATIONS

AEE	-	2-(2′Aminoethoxy) ethylamine
ATR	-	Attenuated total reflectance
BSA	-	Bovine serum albumin
CA	-	Cellulose acetate
COD	-	Chemical oxygen demand
CDA	-	Carboxylated diamine
CNT	-	Carbon nanotube
CSA	-	Camphorsulfonic acid
DEA	-	Diethylamine
DMSO	-	Dimethyl sulfoxide
FESEM	-	Field emission scanning electron microscopy
FRR	-	Flux recovery ratio
FTIR	-	Fourier transform infrared spectroscopy
HCl	-	Hydrochloric acid
IP	-	Interfacial polymerization
IPA	-	Isopropyl alcohol
LiBr	-	Lithium bromide
$MgCl_2$	-	Magnesium chloride
$MgSO_4$	-	Magnesium sulphate
MPD	-	M-phenylenediamine
MF	-	Microfiltration
NF	-	Nanofiltration
$NaHCO_3$	-	Sodium bicarbonate
NaCl	-	Sodium chloride
Na_2SO_4	-	Sodium sulphate
NaOH	-	Sodium hydroxide
NOM	-	Natural organic matter
NPA	-	N-propyl alcohol
NPs	-	Nanoparticles
NTSC	-	Naphthalene-1,3,6-trisulfonylchloride

PA	-	Polyamide
PES	-	Polyethersulfone
PIP	-	Piperazine
PWF	-	Pure water flux
RO	-	Reverse Osmosis
SEM	-	Scanning electron microscope
SDA	-	Sulfonated diamine
SDS	-	Sodium dodecyl sulfate
TEA	-	Triethylamine
TEM	-	Transmission electron microscope
TEPA	-	Tetraethylenepentamine
TFC	-	Thin film composite
TMC	-	Trimesoyl chloride
TU	-	Thiourea
TOC	-	Total organic carbon
UF	-	Ultrafiltration
XPS	-	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

A	-	Effective area of the membrane
T	-	Time taken for filtration
C_f	-	Total feed concentration
C_p	-	Total permeate concentration
C_t	-	Concentration at time, t
C_0	-	Concentration at initial time
J	-	Pure water permeability
Wf	-	Pure water flux
$Wf_{,1}$	-	Initial pure water flux of rinsed membrane
$Wf_{,2}$	-	Final pure water flux of rinsed membrane
θ	-	Contact angle
P	-	trans-membrane pressure difference
R	-	Salt rejection
V	-	Total volume of permeate

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water is indispensable to life and is a major constituent of living tissues. Now, humans and ecosystems are in a distressing situation due to the depletion of freshwater resources. Industrialization and globalization have made the water crisis even more serious in many developing countries. Also, there is gross inaccessibility to portable water in many parts of the world even though water covers about 70% of the earth (Abdikheibari et al., 2020 and Ormanci-Acar et al., 2020). To address this problem, many studies have been conducted on water treatment and several techniques have been successfully employed in the elimination of pollutants from wastewater. They include chemical precipitation, coagulation, adsorption, ion-exchange, electrodialysis and membrane technology. Of all these, the most prominent one is membrane technology for its versatility, efficiency, ease of operation and being low energy intensive (Gohil and Ray., 2017).

The use of membrane-based separation in water treatment has been a technology that is easy to scale up and energy-efficient (Jiang et al., 2019). Amongst different types of membrane structure, thin film composite (TFC) membranes have experienced tremendous development since the concept of interfacial polymerization (IP) was first introduced by Morgan in the 1960s (Cadotte, 1981).

TFC membranes fabricated by IP overwhelmingly dominate the markets for nanofiltration (NF) and reverse osmosis (RO) processes. They are made up of a thin polyamide (PA) layer which is interfacially polymerized onto a microporous substrate (Zhai et al., 2020). Current developments in membrane technology show that the PA film and support layer of TFC membrane can be independently optimized to enhance the membrane performance (Lau et al., 2015). Despite this, it is widely believed the strongest influence on mass transport of the membrane, which generally determines membrane performance, comes from the chemical structure and the surface properties of the PA layer (Jiang et al., 2019).

The primary choice for treatment of water and wastewater remains TFC membranes and some major characteristics of TFC membranes, as pertaining to filtration, is reported to be its good hydrophilicity, surface charge, surface roughness and its enhanced pure water flux, salt rejection and foulant adhesion. Therefore, TFC membrane with advanced PA layer properties for wastewater treatment is worthy of investigation as it is more effective and the process is relatively simple (Misdan et al., 2013).

1.2 Problem Statement

The presence of an active PA separation layer above the support membrane has granted TFC membranes extensive attention in membrane technology (Zhai et al., 2020). The active layer which is typically prepared by IP between two immiscible active monomers in an aqueous phase and an organic phase allows for a promising solute rejection from wastewater (Xiao et al., 2019). PA active layer prepared by the conventional IP process usually possesses an excellent performance for solute rejection including organic pollutants present in AT-POME with the porous substrate providing a stable support. Nevertheless, TFC membranes used for NF usually possess a comparative low water flux and a poor antifouling property after a short period of time, which restrains its practical application. Therefore, fabricating an excellent thin PA layer with improved fouling resistance is a good way to reduce trans-membrane pressure while improving filtration performance. Some of the common strategies used in enhancing PA layer properties are incorporation of inorganic nanoparticles (e.g., graphene oxide, titania nanotubes and carbon nanotubes) into PA matrix, coating via polyelectrolyte self-assembly method, posttreatment optimization (e.g., thermal treatment and rinsing method), introduction of additive/surfactant (e.g., sodium lauryl sulfate and lithium bromide) and utilization of advanced active monomers (Origomisan et al., 2020).

Above all, membranes made with the additive's incorporation have exhibited several shortcomings in treating water and wastewater. In a work done by Shen et al. (2020), NaCl and glycolic acid were used as additives in aqueous solution to tune PA structure of TFC membrane for water treatment. Results showed a very thick PA layer with a poor pure water flux and antifouling performance. Wu et al. (2013) also investigated the performance of dimethyl sulfoxide (DMSO) and glycerol on the properties and performance of TFC membrane. Findings revealed that membrane surface became rougher with a poor salt rejection compared to control membrane. This is as a result of the fluctuating interface reducing the immiscibility between aqueous and organic phases by DMSO hereby causing a poor membrane structure. In another study, Hao et al. (2019) used calcium chloride as an additive to enhance PA layer of TFC membrane. The results demonstrated that the rejection and foulant repulsion of the membrane decreased despite the slight increase in pure water flux. The reason for the decrease of rejection is as a result of calcium ions consuming free carboxyl acid groups, resulting in the decrease of the charge repulsion effect. Most recently, Liu et al. (2020) utilized 1-methylimidazole in preparing PA TFC membrane. It was found that performance with respect to salt rejection decreased as a result of its thin and loosed PA layer with more opened pores caused by the hydrolysis of 1-methylimidazole into TMC during the IP process.

Furthermore, introducing a co-monomer into the PA layer could potentially improve TFC membrane performance and its positive impacts on water flux, rejection, and antifouling properties, however varied depending on the properties of monomers used as well as IP process conditions. Yan-Li et al. (2019) fabricated a TFC membrane fabricated using single amine monomer 3,3' diaminobenzidine (DAB) gave a very poor salt rejection (<15%) although the flux could be retained. Li et al. (2019) also made a PA TFC membrane with a single zwitterionic amine monomer. Resultant membranes experienced a severe absorption of foulants on membrane surface which eventually reduced pure water flux after a short period of time. Guo et al. (2020) also introduced N,Ndiethylethylenediamine (DEEDA) into PIP aqueous solution followed by IP with TMC to develop a cross-linked PA layer. The resultant membrane achieved a drop (~0.2%) in salt rejection which was attributed to the single functionality of DEEDA participating in the IP process and reduced cross-linking structure of PA layer. In another work by Yao et al. (2018), 4,4'-((1,4-phenylenebis(methylene)) bis(azanediyl))dibenzenesulfonic acid, a sulfonated diamine monomer was synthesized and used as a sole aqueous reactant with MPD. Despite the nerve-racking and multiple steps involved in this monomer synthesis, results still gave a poor performance and a lower water permeation of <0.7 L/m^2.h.bar compared to the control membrane.

So far, there has not been enough research effort concentrating on how both a co-monomer and an inorganic salt (additive) influences the morphology and filtration performance of the PA layer of TFC membrane for water treatment. Thus, in this study, IP between the effects of $NaHCO_3$ additive and the presence of secondary amine monomer - 2-(2′Aminoethoxy) ethylamine (AEE) during IP process were studied in order to improve the typical piperazine (PIP)-based NF membrane for water application.

1.3 Research Objectives

In the interest of the growing potential of TFC NF membranes for effective water/wastewater treatment, the aim of this research is to develop a new type of TFC NF membrane with improved properties for effective AT-POME treatment. The specific objectives of this work are:

1. To investigate the impacts of $NaHCO_3$ additive on the PA layer properties of TFC NF membrane and its filtration performance.

2. To assess the effect of co-amine monomers on the PA layer properties of TFC NF membranes by varying PIP: 2,2’-AEE weight ratios in the presence of $NaHCO_3$ additive during IP process for water filtration.

3. To evaluate performance of the TFC NF membranes for AT-POME treatment by examining water flux, solute rejection rate as well as conductivity, colour, and chemical oxygen demand (COD) removal.

1.4 Scope of Work

The scope of this study to achieve the objective stated above are as follows.

a) Studying the impacts of $NaHCO_3$ additive loading (0.5, 1.5, 2.5 and 3.5 wt.%) added to the PIP (2 wt.%) aqueous solution on the PA layer properties of TFC membranes fabricated on a polysulfone (PSf) substrate.
b) Investigating the effect of PIP:AEE co-amine monomer in varying weight ratios (2:0, 1.75:0.25, 1.50:0.50, 1.0:1.0 and 0:2) during IP process in the presence of fixed $NaHCO_3$ concentration on the PA layer properties of TFC membranes.
c) Drying all resultant TFC membranes (after IP process) at 50^{o}C and stored in RO water at room temperature prior to any characterization.
d) Characterizing the fabricated membranes for structural morphology through field emission scanning electron microscopy (FESEM), surface chemistry through attenuated total reflectance Fourier transform infrared analysis (ATR-FTIR) and membrane hydrophilicity through contact angle measurement (CA).
e) Evaluating the filtration performance of all the resultant TFC membranes with respect to water flux and Na_2SO_4 rejection using feed solution containing 1000 ppm at 10 bar.
f) Studying the antifouling properties and flux recovery rate (FRR) of the TFC membranes using feed solution containing 500-ppm bovine serum albumin (BSA).
g) Assessing the performance of resultant TFC membranes with respect to water flux, solute rejection as well as conductivity, colour, and chemical oxygen demand (COD) removal properties during AT-POME treatment.

1.5 Significance of Research

Over the past several years, TFC membranes have always been identified as a promising candidate to tackle the trade-off between selectivity and permeability in pressure-driven membrane processes. Notwithstanding, just few research have been conducted to study the effect of a co-monomer in the presence of an additive in fabricating TFC NF membrane for wastewater treatment. With the tremendous development in TFC NF membranes, this research showed that the presence an additive and a co-monomer in fabricating the PA active layer could improve resultant TFC membrane's filtration properties in treating water and AT-POME wastewater with respect to solute, conductivity, colour, and COD removal. The treated water also possessed a pH value which is near to the neutral conditions (~pH 7) and would not possess a threat upon discharge. Furthermore, both materials - $NaHCO_3$ and AEE which were used in this work to modify PA layer are commercially available and thus researchers do not need to speed time for their synthesis process and can speed up their usage for commercial membrane fabrication and usage.

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LIST OF PUBLICATIONS

1. **Origomisan, J.O**., Lau, W.J., Aziz, F., & Ismail, A.F. (2020). Impacts of secondary mixed monomer on properties of thin film composite (TFC) nanofiltration and reverse osmosis membranes: A review. *Recent Patents on Nanotechnology*, 14(4). https://doi.org/10.2174/1872210514666201014152621. **(Q4, IF: 1.952)**