THIN FILM COMPOSITE MEMBRANE BASED FORWARD OSMOSIS WITH COMPLEX INORGANIC DRAW SOLUTION FOR COPPER REMOVAL

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ABSTRACT

In order to efficiently remove heavy metal ions from wastewater using forward osmosis (FO), selection of preferable membrane and draw solution (DS) is essential. Thus, the purpose of this study is to investigate the synergistic effect of thin-film composite membranes (TFCs) with complex $MgCl_2$ draw solution for the removal of copper (II) from its aqueous solution using FO. A total of five TFCs with different concentration ratio of polyethyleneimine (PEI) over piperazine (PIP) annotated as 1.0-PIP, 0.3-PEI, 0.5-PEI, 0.7-PEI and 1.0-PEI were fabricated and the physicochemical properties of these membranes were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy, zeta potential and contact angle analysis. Preliminary performance study was done using nanofiltration system on their water fluxes and Cu (II) rejection. The used TFCs were then autopsied under energy dispersive X-ray (EDX) to examine copper attachments on it. Meanwhile, $MgCl_2$ undergoes complexation with complexing agent poly(sodium 4-styrenesulfonate) (PSS). The affinity of $MgCl_2$ with PSS with fixed loading was first studied at different pH (3.0, 5.0, 7.0 and 9.0) using dead-end filtration system. Study of PSS loadings (0.0, 0.1, 0.5, 1.0, 2.5 and 5.0 w/w%) was done later using FO system at 1.0 M $MgCl_2$ DS and reverse solute flux (RSF) was determined. From all of the aforementioned experiments, removal of Cu (II) using FO was carried out at different feed concentrations (1000, 2000 and 5000 ppm) and the performances in term of water flux and rejection were discussed. Physicochemical analysis confirmed the formation of polyamide layer for all TFC membranes. Zeta potential revealed that the positivity of the TFCs' surface charge increased in an order of 1.0-PIP < 0.3-PEI < 0.5-PEI < 0.7-PEI < 1.0-PEI. Consequently, 1.0-PEI exhibited higher flux compared to 1.0-PIP owing to its higher hydrophilicity. Interestingly, excellent selectivity of 1.0-PEI resulted in Cu (II) ion rejection of more than 95% and 99% in NF and FO operation respectively outperforming the other produced TFCs. EDX result further explained that the copper rejection was also facilitated by the electrostatic interaction with the surface charge of the TFCs. Based on the performance evaluation, 1.0-PIP was selected for complexation study since it portrayed good capability of Cu (II) retention and better FO water flux. Complexation of $MgCl_2$ with PSS was able to lower the effect of RSF up to 60% reduction while maintaining satisfactory water fluxes compared to the control $MgCl_2$ DS. Final Cu (II) rejection by FO using 1.0-PIP and the 1.0 w/w% PSS-$MgCl_2$ complex DS revealed that the water flux slightly decreased with average Cu (II) retention of 95% with increasing Cu (II) feed concentration. This study promotes FO as a promising option for heavy metals removal application using innovative DS with lowered RSF.

ABSTRAK

Untuk menyingkirkan ion logam berat secara berkesan daripada air sisa dengan menggunakan osmosis hadapan (FO), pemilihan membran yang lebih baik dan larutan penarik (DS) adalah penting. Oleh itu, tujuan kajian ini adalah untuk mengkaji kesan sinergistik membran komposit filem nipis (TFCs) dengan larutan penarik $MgCl_2$ kompleks bagi penyingkiran kuprum (II) daripada larutan akueusnya menggunakan FO. Sebanyak lima TFCs dengan nisbah komposisi polietilenaimina (PEI) atas piperazina (PIP) yang berbeza iaitu 1.0-PIP, 0.3-PEI, 0.5-PEI, 0.7-PEI dan 1.0-PEI disediakan dan sifat fizikokimia membran dicirikan menggunakan spektroskopi inframerah jelmaan Fourier, mikroskopi imbasan elektron, mikroskopi daya atomik, potensi zeta dan analisis sudut hubungan. Kajian prestasi awal dilakukan menggunakan sistem penapisan nano ke atas fluks air dan penyingkiran Cu (II). TFCs yang telah digunakan kemudiannya dianalisa dengan penyebaran tenaga sinar-X (EDX) untuk memeriksa lekatan kuprum di atasnya. Sementara itu, $MgCl_2$ menjalani proses kompleksasi dengan agen kompleksasi poli(natrium 4-stirenasulfonat) (PSS). Keserasian $MgCl_2$ dengan PSS pada pemuatan tetap dikaji terlebih dahulu pada pH yang berbeza (3.0, 5.0, 7.0 dan 9.0) menggunakan sistem penapisan buntu. Kajian muatan PSS berbeza (0.0, 0.1, 0.5, 1.0, 2.5 dan 5.0 w/w%) seterusnya dilakukan menggunakan sistem FO pada 1.0 M $MgCl_2$ DS dan fluks zat terlarut berbalik (RSF) ditentukan. Berdasarkan daripada semua eksperimen yang telah dinyatakan, penyingkiran Cu (II) pada kepekatan permulaan berbeza (1000, 2000, dan 5000 ppm) menggunakan FO kemudian dijalankan dan prestasinya dari segi fluks air dan penyingkiran logam dibincangkan. Analisis fizikokimia mengesahkan pembentukan lapisan poliamida untuk semua membran TFCs. Potensi zeta mendedahkan kenaikan cas positif permukaan TFCs ialah dalam urutan 1.0-PIP <0.3-PEI <0.5-PEI <0.7-PEI <1.0-PEI. Oleh itu, 1.0-PEI memperlihatkan fluks yang lebih tinggi berbanding 1.0-PIP disebabkan oleh sifat hidrofilik yang lebih tinggi. Menariknya, 1.0-PEI menunjukkan penyingkiran ion Cu (II) masing-masing lebih daripada 95% dan 99% dalam operasi NF dan FO, mengatasi TFCs lain. Hasil EDX menjelaskan bahawa penyingkiran kuprum juga dibantu sedikit oleh interaksi elektrostatik dengan permukaan TFCs yang bercas. Berdasarkan penilaian prestasi, 1.0-PIP dipilih untuk kajian kompleks kerana ia menggambarkan keupayaan penyingkiran Cu (II) yang baik dan fluks air FO yang lebih baik. Kompleksasi $MgCl_2$ dengan PSS berjaya merendahkan kesan RSF sehingga 60% pengurangan sambil mengekalkan fluks air yang memuaskan berbanding dengan larutan penarik $MgCl_2$ kawalan. Akhirnya, penyingkiran Cu (II) oleh FO menggunakan 1.0-PIP dan 1.0 w/w% PSS-$MgCl_2$ kompleks DS mendedahkan bahawa fluks air sedikit menurun dengan purata penyingkiran Cu (II) pada 95% apabila kepekatan permulaan Cu (II) dinaikkan. Kajian ini mempromosikan FO sebagai alternatif yang berguna untuk digunakan dalam penyingkiran logam berat menggunakan DS inovatif dengan kesan RSF yang rendah.

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LIST OF ABBREVIATIONS

AL-FS	-	Active Layer Facing Feed Solution
AFM	-	Atomic Force Microscopy
Ag	-	Silver
As	-	Arsenic
ATR-FTIR	-	Attenuated Total Reflectance – Fourier Transform Infrared
Ca	-	Calcium
Cd	-	Cadmium
CMC	-	Carboxymethyl Cellulose
CPCB	-	Central Pollution Control Board of India
Cr	-	Chromium
Cu	-	Copper
Cu (II)	-	Copper (II) Ion
$CuSO_4$	-	Copper (II) Sulphate
DS	-	Draw Solution
EDX	-	Energy Dispersive X-ray
Fe	-	Iron
FESEM	-	Field-Emission Scanning Electron Microscopy
FO	-	Forward Osmosis
H^+	-	Hydrogen Ion
Hg	-	Mercury
IP	-	Interfacial Polymerization
MD	-	Membrane Distillation
Mg	-	Magnesium
Mg (II)	-	Magnesium (II) Ion
$MgCl_2$	-	Magnesium Chloride
$MgSO_4$	-	Magnesium Sulphate
MWCO	-	Molecular Weight Cut-off
Na^+	-	Sodium Ion
$Na_2(SO)_4$	-	Sodium Sulphate
NaCl	-	Sodium Chloride

NF	-	Nanofiltration
Ni	-	Nickel
PA	-	Polyamide
Pb	-	Lead
PEI	-	Polyethyleneimine
PEUF	-	Polymer Enhanced Ultrafiltration
PES	-	Polyethersulfone
PIP	-	Piperazine
PSf	-	Polysulfone
PSS	-	Poly (Sodium 4-Styrenesulfonate)
PSS-$MgCl_2$	-	Poly (Sodium 4-Styrenesulfonate) – Magnesium Chloride complex
RO	-	Reverse Osmosis
RSF	-	Reverse Solute Flux
SEM	-	Scanning Electron Microscopy
TFC	-	Thin Film Composite
TFI	-	Thin-film Inorganic
TMC	-	Trimesoyl Chloride
UF	-	Ultrafiltration
USEPA	-	United States Environmental Protection Agency
WHO	-	World Health Organization
Zn	-	Zinc

LIST OF SYMBOLS

mg	-	Milligram
g	-	Gram
μL	-	Microlitre
mL	-	Millilitre
L	-	Litre
cm^2	-	Centimetre square
m^2	-	Meter square
M	-	Molarity
min	-	Minute
ppm	-	Part per million
R,%	-	Percent rejection
w/v%	-	Weight over volume percent
w/w%	-	Weight over weight percent
F_w	-	Pure water flux
J_V	-	Water flux
J_S	-	Solute flux
LMH	-	Litre per meter squared per hour
LPM	-	Litre per minute
GMH	-	Gram per meter squared per hour

CHAPTER 1

INTRODUCTION

1.1 Research Background

It is known to all that water is the most precious natural resource and serves as a vital need for every living thing on this planet. It has even been mentioned in the Holy Book of Quran more than 1400 years ago that all living things are mostly made up of water as per said in an excerpt which means:

“Allah has created every [living] creature from water. And of them are those that move on their bellies, and of them are those that walk on two legs, and of them are those that walk on four. Allah creates what He wills. Indeed, Allah is over all things competent.”

The above excerpt from chapter 24 of the Quran, Surah An-Nur (The Light) verse 45, solely explains the importance of water to every living thing especially to human as water keeps us hydrated so that biological processes inside our body can be well-functioned (‘4 Biology of water’, 1993).

Unfortunately, human activities and industrial management malpractices have mistreated the environment (Shannon *et al.*, 2008). One of the common heavy metals ion abundantly found in the industrial wastewater stream is copper (Cu) for it has wide usage and vast application for instance electroplating, etching, metal finishing, pigment and alloy manufacturing (Bradl, 2005a; Al-saydeh *et al.*, 2017). Even though the bio-importance of copper in iron metabolism and many other roles in human biochemistry has been made known by all, it is only at a trace presence, approximately 100 mg Cu needed in human body (Bost *et al.*, 2016). In fact, it is an open secret for any intake in excess will cause only harm to the system. According to Kurniawan *et al*. (2006), excessive accumulation of Cu in human can lead to liver damage, Wilson disease and insomnia. In addition, the European Union had included copper into what was called “The Grey List” back in 1976 which was an old list of hazardous materials that became a main concern for their content in the disposal to be reduced (Crini *et al.*, 2017). Due to these reasons, the tolerable amount of this metal in drinking water has been put down to lower acceptable concentration level, for instance 1.3 ppm by USA Environmental Protection Agency and <2.0 ppm by World Health Organisation (WHO) (Puri and Kumar, 2012; Al-Saydeh *et al.*, 2017). Moreover, stringent government policy in accord with the matter of the effluent discharge from the manufacturing of the electronic products also may elevate the concern for a proper treatment of its wastewater containing that aforementioned heavy metal.

A lot of techniques have been specialised into treatment of wastewater containing heavy metals. There goes many conventional methods have been used upon decontamination of heavy metal, such as chemical precipitation, coagulation and flocculation, ion exchange and flotation (Kurniawan *et al.*, 2006). Nevertheless, inconsistency and incomplete elimination often becomes the major barrier of these techniques. In addition, some of the methods could also generate secondary pollutants. Therefore, it is necessary to find other methods that could serve as another alternative treatment of water laden with heavy metals. Among of those techniques, membrane filtration is presented as an advantageous candidate for removal of heavy metals.

Membrane technology in various separation applications is growing rapidly as if it is enhancing every day. Due to massive research on the membrane technology, a lot of new improvement and discoveries have been found. Technically, the membrane separation technology evolves from the traditional pressure-driven membrane separation system such as microfiltration (MF), nanofiltration (NF), ultrafiltration (UF) and reverse osmosis (RO) to the thermally driven membrane distillation (MD) and concentration driven processes for example forward osmosis (FO). These traditionally pressure-driven membrane separation systems are often known to suffer from severe fouling and low rejection capability due the high pressure applied to the system. Nevertheless, forward osmosis (FO) has recently emerged as the outstanding candidate to cater these sorts of problems.

“Forward osmosis (FO),” despite being old of it concept, this application seems to successfully acquires great attention for research purposes in the last two decades (Dutta and Nath, 2018). Being natural, clean, eco-friendly process, FO is seen interestingly potent to substitute or complement various other application in separation process including food and beverages processing, pharmaceutical industry, desalination, power generation, waste water treatment, irrigation system and heavy metal removal (Cath *et al.*, 2006; Zhao *et al.*, 2012; Lutchmiah *et al.*, 2014; Chekli *et al.*, 2016). Instead of being a pressure driven which consume electricity, the transmembrane transportation of an FO system on the other hand is catalysed by the concentration gradient. Difference in concentration of the feed solution and draw solution creates the gradient in osmotic pressure that technically becomes the driving force for the system to be functional. Some desirable features include high salt rejection, require less operating hydraulic pressure and more importantly, less susceptible to fouling. Owing to these features, FO is paving possibilities in treating hypersaline, high fouling propensity or otherwise challenging feed waters in a more efficient way (Altaee and Hilal, 2014; Chekli *et al.*, 2016; Wang *et al.*, 2018).

Nonetheless, there are some inherent disadvantages of FO, such as lower permeate water flux compared to pressure driven membrane processes, internal concentration polarisation (ICP) and high energy consumption of draw solution recovery. As Zhao *et al.* claimed, FO is known to suffer from severe internal concentration polarization, greatly reducing its water flux. Moreover, the need for a powerful draw solution that meets its favourable criteria is overwhelming. This is due to the requirement to drive the osmosis process across the membrane efficiently without giving the membrane significant drawbacks and at the same time easier for the draw solution to be recovered. Moreover the product is not a pure water, hence necessitates additional purification using either RO, NF, UF, MD or any other system (hybrid system) which then obliges extra energy input (Zhao *et al.*, 2012). Above all the shortcomings from the application of FO, Ansari *et al*., nevertheless saw it no differently instead they claimed that FO has the potential for simultaneous treatment and resource recovery from municipal wastewater (Ansari *et al.*, 2017).

Up to this day, research of FO extensively focuses on desalination for water reclamation (Wang *et al.*, 2018), but less on other fields. There have been studies reported on beverage concentration (Kim *et al.*, 2019), protein yield enhancement (Yang *et al.*, 2009), desert restoration (Duan *et al.*, 2014), fertilizer-drawn FO (Chekli *et al.*, 2017), limited literatures on heavy metals removal (HMR) (Liu *et al.*, 2017) and several others. While the available studies of FO in heavy metal removal are then concentrating on either membrane modification or draw solution formulization parts. In conjunction, this research will focus on both in the membrane part and the improvisation of existing draw solution.

1.2 Problem Statement

It has been ascertained that FO possessed a huge potential in various application including removal of heavy metals from wastewater. However, in order for an FO to be operationally excellent, there are two key components that play the most important role. The two components are the membrane itself and the draw solution (DS). A favourable membrane for heavy metal removal application should have a high rejection of heavy metal and high-water flux. According to previous research, fabrication of thin-film composite (TFC) membrane via interfacial polymerization (IP) not only will introduce a highly selective layer of polyamide (PA) on top but also carries electrical charge along with it. The selective barrier practically will only permit water molecules to pass through while limit the passage of most other undesired constituents across the membrane. The electrical charge embedded on the membrane surface then facilitate with the retention of charged particles. (Almutairi *et al.*, 2012).

Previously, extensive studies have been done on the fabrication of TFC membranes (TFCs) using different amine monomers and different acid chloride (Saha and Joshi, 2009; Wu *et al.*, 2015). Besides, there has been a study on fabrication TFCs using different substrate (Misdan *et al.*, 2014). But because of the PA layer that carries significant role in permselectivity of the membrane, therefore extra attention was given onto the study with different reactants' monomers for PA layer formation. Previously, Wu *et al*. had a study on TFC based nanofiltration (TFC-NF) membranes fabrication using different concentration ratio of polyethyleneimine (PEI) and piperazine (PIP) monomers to be hydrolysed with trimesoyl chloride (TMC) to form PA layer. The findings showed promising results of NF water fluxes for mixed amine TFCs and excellent rejection of $MgCl_2$ which was 95% averagely while varied percent rejection of other salts ($MgSO_4$, $Na_2(SO_4)$ and NaCl) depending on the ratio concentration of the PIP/PEI content of the TFC membranes produced (Wu *et al.*, 2015). However, the study is limited to NF process and common salts rejection experiment even though the TFCs produced seems to be potential for heavy metals removal application. Therefore, in order to fill in the research gap, we study the effect of different PEI/PIP loadings ratio toward the performance of the produced TFCs for copper (II) removal from its aqueous solution under FO operation.

In which draw solution (DS) holds another key to an effective FO, Zhao *et al.* did outline some characteristics for a good draw solution should have. Among those mentioned are of a good osmotic pressure generator, exhibits low reverse solute diffusion, demote internal concentration polarization, low cost and toxicity and finally easy to be recovered economically (Zhao *et al.*, 2012). However, it is impossible to obtain a perfect draw solution that is one-size-fits-all criteria of a good draw solution since every draw solution must have their own advantages and shortcomings. Taking aqueous magnesium chloride ($MgCl_2$) as the draw solution, it has been known to have the ability to generate preferably high osmotic pressure, low cost and non-toxic. However, looking at the bad side of this inorganic salt, $MgCl_2$ is bounded by high reverse solute flux (RSF) that takes into account the loss of the draw solute representing a gradual reduction in osmotic pressure. Typically, RSF of 1.0 M $MgCl_2$ can vary from as low as 0.004 mol/m^2hr to 0.66 mol/m^2hr (Saren *et al.*, 2011).

Thus, improving this type of draw solution by reducing the RSF to a negligible amount by adopting the concept of polymer enhanced ultrafiltration (PEUF) seems to be an innovative option since there is no similar study available up to this point. By definition, the said PEUF carry a method called complexation of the targeted metal ion with macro ligand, a water-soluble polymer which acts as the complexing agent simply by the addition of complexing agent into the solution containing the metal ion – in this context $MgCl_2$ DS. For this study, complexing agent poly (sodium 4-styrenesulfonate)

(PSS) will be used for complexation of $MgCl_2$ salt ions to increase its molecular weight hence it is expected to reduce the RSF. Additionally, since the complexation of metal ions is heavily dependent on pH of the solution and the loading of the complexing agent (Rivas *et al.*, 2011; Crini *et al.*, 2017), thus both of these parameter are also studied.

1.3 Objectives of the Study

Main goal of this study is to explore the technique of Cu (II) removal by mean of FO using inorganic DS with lowered RSF. Therefore, the objectives of this study are divided into three which are:

a) To synthesis, characterize and evaluate the performances of thin-film composite membranes (TFCs) fabricated by using different loading ratio of piperazine (PIP) and polyethyleneimine (PEI) with trimesoyl chloride (TMC) via interfacial polymerization (IP) reaction.

b) To evaluate the effect of pH variation and the complexing agent poly (sodium 4-styrenesulfonate) (PSS) loadings on the complexation affinity with $MgCl_2$ draw solution.

c) To evaluate the performance of the complex DS with the selected TFC towards copper (II) removal at different concentration using forward osmosis.

1.4 Scopes of Study

a) Preparation of Polyamide (PA) layer monomer solutions containing different PEI/PIP ratio of 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 to be interfacially polymerized onto substrates of polysulfone (PSf) with molecular weight cut-off (MWCO) of 20,000 Da.

b) Characterization of the synthesized TFCs membranes for their physicochemical properties using SEM, FESEM, FTIR, zeta potential, AFM, and contact angle goniometer.

c) Evaluate the preliminary performances of TFCs under NF process for its pure water flux and Cu (II) rejection using initial feed of 200 ppm Cu^{2+} ion concentration. Membrane autopsy was done after the preliminary Cu (II) rejection study using EDX analysis.

d) The best two TFCs membranes that exhibit high Cu rejection from previous experiment were to be used in FO experiment under active layer facing feed solution (AL-FS) configuration for the water flux and reverse solute flux with DI water was used as feed and $MgCl_2$ as draw solution at different concentration of 0.5 M, 1.0 M and 2.0 M.

e) The effect of pH on the affinity of the complexing agent towards $MgCl_2$ was studied using 0.02 M $MgCl_2$ at different pH (3.0, 5.0, 7.0 and 9.0) and fixed amount of 0.5mL 1w/v% PSS was added. Using the best TFC which showing the better water flux from previous experiment, water flux and Mg (II) rejection were determined using dead-end filtration system,

f) Determination of the best complexing agent loading based on the best pH selected from previous experiment. The loading of the PSS was varied at 0.1, 0.5. 1.0, 2.5 and 5.0 w/w % in 500 mL of 1.0 M $MgCl_2$ DS. Using ultrapure water as feed in FO, water flux and RSF are determined under AL-FS configuration.

g) Study on copper removal in FO using the best selected TFC and PSS-$MgCl_2$ complex with the best pH and loading as draw solution. By using 1000, 2500 and 5000 ppm of Cu^{2+} ion from $CuSO_4$ solution as feed, water flux and Cu (II) rejection were determined.

1.5 Significance of the Study

The potential of FO has raised this emerging technology for applicability in various applications such as sea water desalination and wastewater treatment. This research is basically focusing on the heavy metals removal application particularly Cu (II) using FO. Industries that has Cu (II) in its wastewater such as electroplating, alloy and pigment manufacturing and many more can be profited from this research. Inorganic DS like $MgCl_2$ was commonly used in many FO application. Optimization of FO limitation on the DS plays an important role for the system to run at its most efficient way. Innovative approach to reduce the effect of RSF by applying the concept of complexation may lift the drawback of the $MgCl_2$ DS. Based on the outcomes of this study, an effective pre-treatment of wastewater laden with heavy metal is proposed. The contamination of heavy metal beyond standard limit into the freshwater stream can be avoided and eventually will be benefiting the environment, the country and humankind.

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LIST OF PUBLICATIONS

Indexed Paper

1. M.F. Hamid, N. Abdullah, N. Yusof, N.M. Ismail, A.F. Ismail, W.N.W. Salleh, J. Jaafar, F. Aziz, W.J. Lau, Effects of surface charge of thin-film composite membrane on copper (II) ion removal by using nanofiltration and forward osmosis process, J. Water Process Eng. 33 (2020) 101032. doi:10.1016/J.JWPE.2019.101032. **(Q1; IF:3.73)**

Conference

2. M.F. Hamid, N. Yusof, N.M. Ismail, M.A. Azali, Role of Membrane Surface Charge and Complexation-Ultrafiltration for Heavy Metals Removal: A Mini Review, J. Appl. Membr. Sci. Technol. 24 (2020) 39–49. doi:10.11113/amst.v24n1.170. **(Non-indexed).**