THIN FILM NANOCOMPOSITE MEMBRANES INCORPORATED ZIRCONIUM BASED METAL ORGANIC FRAMEWORKS FOR REMOVAL OF LEAD(II)

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DEDICATION

This thesis is dedicated to my family, especially to my mother and my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Contamination of heavy metals has attracted great attention in scientific community in which membrane technology by using thin film composite (TFC) membrane has shown a great potential for treating contaminated water. The presence of dense polyamide (PA) layer in TFC membrane often cause water transport to be hindered, yielding low flux at high pressure in which modifying TFC membranes by incorporating nanomaterials within thin active/selective layer serves as an interesting approach. This study aimed to develop and compare thin film nanocomposite (TFN) incorporated water-stable zirconium-based metal organic frameworks (MOFs) on the PA layer for removing lead (Pb) from water by different membrane processes. To investigate the effects of amine-functional groups of UiO-66 on physicochemical properties of the PA layer, TFN membranes with PA layer containing different loadings of UiO-66 or UiO-66-NH_2 were prepared and compared followed by their performance test for Pb(II) removal. The synthesized UiO-66 and UiO-66-NH_2 showed highly crystalline and uniform rhombic structures with particle size of 113-130 nm and 130-150 nm, respectively. Under field emission scanning electron microscopy analysis, the TFN membranes displayed thicker PA layer as compared to control membrane. Fourier transform infrared analysis revealed the successful fabrication of PA layer indicated by the strong amide peak. Atomic force microscopy analysis was similar for both TFN/UiO-66 and TFN/UiO-66-NH_2 which resulted in rougher membrane surface. Water contact angle analysis showed improved hydrophilicty of TFN membranes as compared to control membrane, in which the hydrophilicity of TFN/UiO-66-NH_2 was higher than TFN/UiO-66 membranes. Under nanofiltration (NF) process, it was found that the optimum loading of UiO-66 or UiO-66-NH_2 (0.01 wt%) has shown higher pure water flux than control membrane (4.45 L/m^2.h.bar), which was 6.26 L/m^2.h.bar and 8.63 L/m^2.h.bar, respectively. Basic salts rejections of $MgSO_4$, Na_2SO_4, $MgCl_2$ and NaCl revealed rejection of TFN membranes were at par with control membrane but at higher solute permeability. In terms of membrane performance for Pb(II) removal by NF process, increasing Pb(II) initial concentration caused decreased Pb(II) rejection for TFN/UiO-66 and TFN/UiO-66-NH_2. Presence of cadmium (Cd)/nickel (Ni) decreased the rejection of Pb(II) ascribed by the hydrated size and diffusion coefficients of metals. Interestingly, under forward osmosis (FO) process, Pb(II) initial concentration and presence of Cd/Ni did not influence the rejection of Pb(II) in which 99% rejection was achieved for all membranes. TFN membranes which were TFN/UiO-66 and TFN/UiO-66-NH_2 offered higher FO water flux, which was 16.51 L/m^2.h and 18.51 L/m^2.h, respectively as compared to 9.45 L/m^2.h for control membrane. In comparison to NF process using the same membrane, the rejection via FO process was 30% more efficient. Stability study demonstrated 10% reduction of permeability of TFN membranes as compared to 15% permeability drop for control membrane when subjected to $MgSO_4$ solution. The permeation and Pb(II) rejection from this study has proven that the incorporation of Zr-based MOFs (UiO-66 or UiO-66-NH_2) as additive has improved the properties of TFN membranes making it suitable to be used for water/wastewater treatment.

ABSTRAK

Pencemaran logam berat telah menarik perhatian utama komuniti di mana teknologi membran dengan menggunakan membran komposit filem tipis (TFC) telah menunjukkan potensi besar untuk merawat air yang tercemar. Kehadiran lapisan poliamida (PA) padat dalam membran TFC sering menyebabkan pengangkutan air terhalang, menghasilkan fluks rendah pada tekanan tinggi di mana mengubah membran TFC dengan memasukkan bahan nano dalam lapisan aktif/selektif nipis merupakan pendekatan yang menarik. Kajian ini bertujuan untuk membangunkan dan membandingkan nanokomposit filem tipis (TFN) yang menggabungkan kerangka organik logam berasaskan zirkonium (MOF) yang stabil pada air pada lapisan PA untuk penyingkiran plumbum (Pb). Untuk menyiasat kesan kumpulan berfungsi amina UiO-66 pada sifat fizikokimia lapisan PA, membran TFN dengan lapisan PA yang mengandungi muatan UiO-66 atau UiO-66-NH_2 yang berbeza telah disediakan dan dibandingkan diikuti ujian prestasi bagi penyingkiran Pb(II). UiO-66 dan UiO-66-NH_2 yang disintesis menunjukkan struktur rombus yang sangat kristal dan seragam dengan ukuran zarah masing-masing 113-130 nm dan 130-150 nm. Di bawah analisis mikroskop elektron pengimbas perlepasan medan, membran TFN menunjukkan lapisan PA yang lebih tebal berbanding membran kawalan. Analisis inframerah transformasi Fourier mendedahkan kejayaan pembuatan lapisan PA yang ditunjukkan oleh puncak amida yang kuat. Analisis mikroskop daya atom adalah serupa untuk kedua-dua TFN/UiO-66 dan TFN/UiO-66-NH_2 mengakibatkan permukaan membran lebih kasar. Analisis sudut sentuh air menunjukkan hidrofilik membran TFN adalah lebih baik berbanding dengan membran kawalan, di mana hidrofilik TFN/UiO-66-NH_2 lebih tinggi daripada membran TFN/UiO-66. Di bawah proses penapisan nano, didapati bahawa muatan optimum UiO-66 atau UiO-66-NH_2 (0,01 % berat) menunjukkan fluks air tulen yang lebih tinggi daripada membran kawalan (4,45 $L/m^2.j.bar$), iaitu masing-masing 6.26 $L/m^2.j.bar$ dan 8.63 $L/m^2.j.bar$,. Penolakan garam asas $MgSO_4$, Na_2SO_4, $MgCl_2$ dan NaCl mendedahkan penolakan membran TFN adalah setara dengan membran kawalan tetapi pada kebolehtelapan zat terlarut yang lebih tinggi. Dari segi prestasi membran untuk penyingkiran Pb (II) oleh proses NF, peningkatan kepekatan awal Pb (II) menyebabkan penurunan penolakan Pb (II) bagi TFN/ UiO-66 dan TFN/UiO-66-NH_2. Kehadiran kadmium (Cd)/nikel (Ni) menurunkan penolakan Pb (II) yang disebabkan oleh pekali ukuran dan resapan logam yang terhidrat. Menariknya, di bawah proses osmosis berhadapan (FO), kepekatan awal Pb (II) dan kehadiran Cd/Ni Pb (II) tidak mempengaruhi penolakan Pb (II) di mana penolakan 99% dicapai untuk semua membran. Membran TFN iaitu TFN/UiO-66 dan TFN/UiO-66-NH_2 menawarkan aliran air FO yang lebih tinggi, iaitu 16.51 $L/m^2.j$ dan 18.51 $L/m^2.j$, berbanding 9.45 $L/m^2.j$ daripada membran kawalan. Jika dibandingkan dengan proses NF menggunakan membran yang sama, penolakan melalui proses FO adalah 30% lebih cekap. Kajian kestabilan menunjukkan pengurangan kebolehtelapan membran TFN adalah 10% lebih rendah berbanding penurunan kebolehtelapan 15% membran kawalan apabila dikenakan larutan $MgSO_4$. Kebolehtelapan dan penolakan Pb (II) dari kajian ini telah membuktikan bahawa penggabungan MOFs berasaskan Zr (UiO-66 atau UiO-66-NH_2) sebagai bahan tambah meningkatkan sifat membran TFN menjadikan ia sesuai digunakan untuk rawatan air/air sisa.

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LIST OF ABBREVIATIONS

AAS	-	Atomic absorption spectrometer
AFM	-	Atomic force microscopy
AL-FS	-	Active layer-feed solution
As	-	Arsenic
ATR-FTIR	-	Attenuated reflection-fourier infrared
BDC	-	Benzene-1,4-dicarboxylic acid
BET	-	Brunauer, Emmett and Teller
Cd	-	Cadmium
CEUF	-	Complexation enhanced ultrafiltration
CP	-	Concentration polarization
Cr	-	Chromium
Cu	-	Copper
DI water	-	Deionized water
DMF	-	Dimethylformamide
DS	-	Draw solution
DS	-	Draw solution
EDX	-	Elemental Dispersive X-ray
Fe-SEM	-	Field scanning electron microscopy
FO	-	Forward osmosis
FS	-	Fees solution
HCl	-	Hydrochloric acid
Hg	-	Mercury
ICP	-	Internal concentration polarization
IEP	-	Isoelectric point
IP	-	Interfacial polymerization
KOH	-	Pottasium hydroxide
LbL	-	Layer by layer
MEUF	-	Micellar enhanced ultrafiltration
MF	-	Microfiltration
MgCl	-	Magnesium chloride

$MgSO_4$	-	Magnesium sulphate
MOFs	-	Metal organic frameworks
Na_2SO_4	-	Sodium sulphate
NaCl	-	Sodium chloride
NF	-	Nanofiltration
NH_2-BDC	-	Amino-Benzene-1,4-dicarboxylic acid
Ni	-	Nickel
NMOs	-	Nanosized metal oxides
NMP	-	N-methyl pyrollidone
PA	-	Polyamide layer
Pb	-	Lead
PIP	-	Piperazine
PSf	-	Polysulfone
PVP	-	Polyvinylpyrollidone
RO	-	Reverse osmosis
RSF	-	Reverse solute flux
Se	-	Selenium
SEM	-	Scanning electron miscroscopy
TFC	-	Thin film composite
TFN	-	Thin film nanocomposite
TMC	-	Trimesoyl chloride
UF	-	Ultrafiltration
UiO-66	-	University of Oslo-66
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction
Zn	-	Zinc
Zr	-	Zirconium
$ZrCl_4$	-	Zirconium chloride

LIST OF SYMBOLS

μL	-	micro litre
μm	-	micron meter
A	-	Area
Cf	-	Concentration in feed solution
cm_2	-	centimetre square
Cp	-	Concentration in permeate solution
Da	-	Dalton
Js	-	FO water flux
J_w	-	Water flux
kV	-	kilovolt
L	-	Litre
$L/m^2.h$	-	Litre per meter square per hour
M	-	molar
m^2	-	meter square
mg/L	-	milligram per litre
mL	-	millilitre
mV	-	megavolt
nm	-	nano meter
^{o}	-	degree
Pa	-	Pascal
ppm	-	part per million
q	-	quantity of Zr-MOFs
R	-	Rejection
Ra	-	surface roughness
Rq	-	Root mean square of Z data
t	-	Time
V	-	Volume

CHAPTER 1

INTRODUCTION

1.1 Clean Water Availability

Safe and readily available water, whether it is used for drinking purpose, domestic use, or food production or recreational purposes is important to the public health. In 2017, approximately 5.3 billion of people have safely consumed managed water service, however, there is still 2 billion of people consumed contaminated water as indicated by Figure 1.1 (Our World in Data, 2015). Briefly, contaminated water can transmit diseases such as cholera, typhoid, polio, dysentery with estimation of 1.2 million deaths of drinking polluted water in 2017 alone (Our World in Data, 2017). The availability of clean water is dwindling due to the increasing amount of water contaminants. The United Nations Educational, Scientific, and Cultural Organization disclosed that in 2017, 80% of agricultural and industrial wastes are being disposed into world's water, with the annual production of waste water is six times more than water available in all rivers in the world (UNESCO, 2017). Therefore, understanding and removing contaminants from water is crucial in finding solutions to overcome this issue.

As mentioned previously, industrial and agricultural wastes are the major contributor that contaminate water bodies. In certain cases, some industrial factories release waste effluent into the water ways while often pesticides and fertilizers from agricultural sectors contaminate water bodies during rain season where the contaminants readily penetrate to the water sources. The types of water contaminants are varies, from inorganic, organic or biological. Heavy metals contaminations in water has attract a great concern among scientists due to large number of industries player discharging their metal containing effluents into water bodies without any proper treatments.

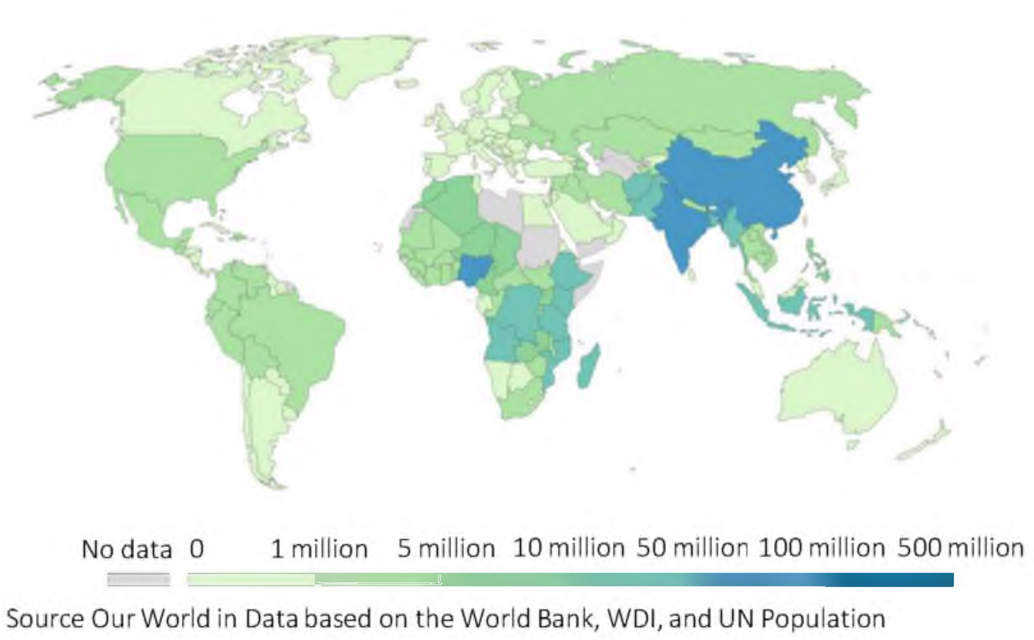

Figure 1.1 Number of people without access to safe water (Our World in Data, 2015)

Lead (Pb) is a type of heavy metals which is frequently emitted from manufacturing of battery storage, building construction, paint and ceramics, storage tank lining and pipework. In aquatic environment, Pb typically exists in the state of 2+ and 4+ where the speciation of lead compound solely relies on pH, dissolved oxygen and concentration of other organic and inorganic compound (UNEP, 2010). Unlike other heavy metals such as zinc, copper, cobalt, manganese and iron that play vital role in biochemical processes, Pb has no known beneficial role on living organism. Despite World Health Organization (WHO) has set the maximum contaminant level (MCL) of Pb in drinking water is 15 μg/L (Jamshidi Gohari, Lau, Matsuura, Halakoo, et al., 2013), the presence of as low as 10 μg/L of Pb had been reported to cause cognitive impairment, aggression and delinquency to children (Brinson & Brinson, 2008). Besides that, accumulation of Pb in body also causes disruption in the process of haemoglobin synthesis, renal function, nervous system, reproductive system and immune system. Due to the hazardous impacts posed by Pb, controlling or treating water laden with this metal has become a subject of interest among scientific community.

1.2 Membrane Technology for Lead Removal

There are various methods have been employed for removing Pb from water sources. These include ion exchange (Ahmed et al., 1998; Islam & Patel, 2009; Street et al., 2002; Trgo et al., 2006), precipitation (Eren, 2009; Esalah et al., 1999; Matlock et al., 2002; Rojas, 2014), coagulation-flocculation (Debora et al., 2013; Pang et al., 2011), and flotation (Drzymala et al., 2003; Ghazy et al., 2008). Nevertheless, incomplete Pb removal, high operational cost and generation of secondary waste are some of the limitations posed by the aforementioned (Barakat, 2011; Xiangtao Wang et al., 2012). Membrane technology is a versatile technique for removing various unwanted constituents, including metallic ions from wastewater. In principle, membrane acts as barrier that inhibits the passage of certain constituents while allowing other constituents to pass through (Figure 1.2). There are five membrane processes that can be used for water treatment; 1) microfiltration (MF), 2) ultrafiltration (UF), 3) nanofiltration (NF), 4) reverse osmosis (RO) and 5) forward osmosis (FO) in which the latter four have been reported to remove heavy metal ions.

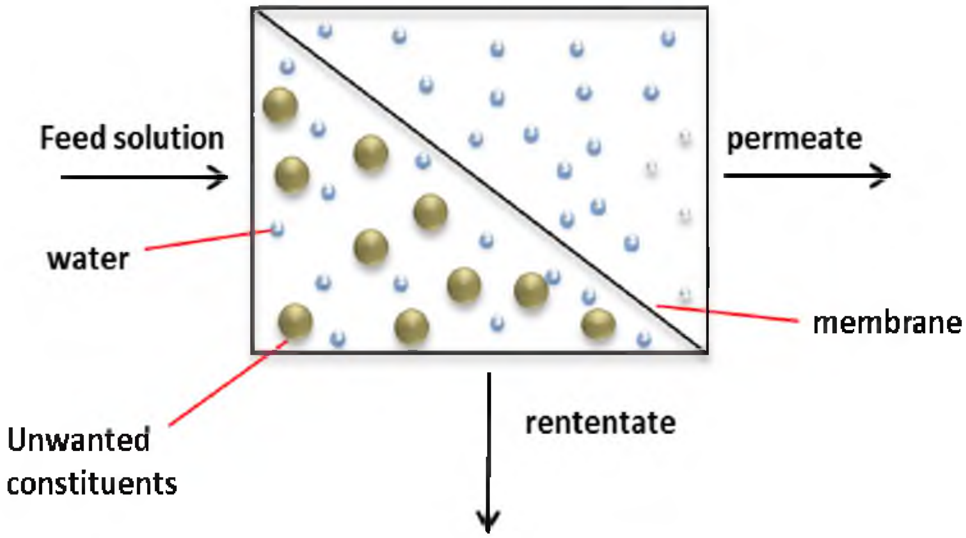

Figure 1.2 Basic principle of membrane technology

In comparison to UF membrane which require membrane with adsorptive feature, the state-of art of NF, FO and RO process for Pb often rely on thin film composite (TFC) membrane which comprised of ultrathin selective layer on porous polymeric substrates. The preparation of TFC is commonly conducted via interfacial polymerization (IP) reaction between two monomers- polyfunctional amine dissolved in aqueous solution and polyfunctional acid chloride dissolved in hydrocarbon solvent, followed by curing process to densify the polymerization properties of polyamide layer. Figure 1.3 illustrates the structure of thin film composite membrane.

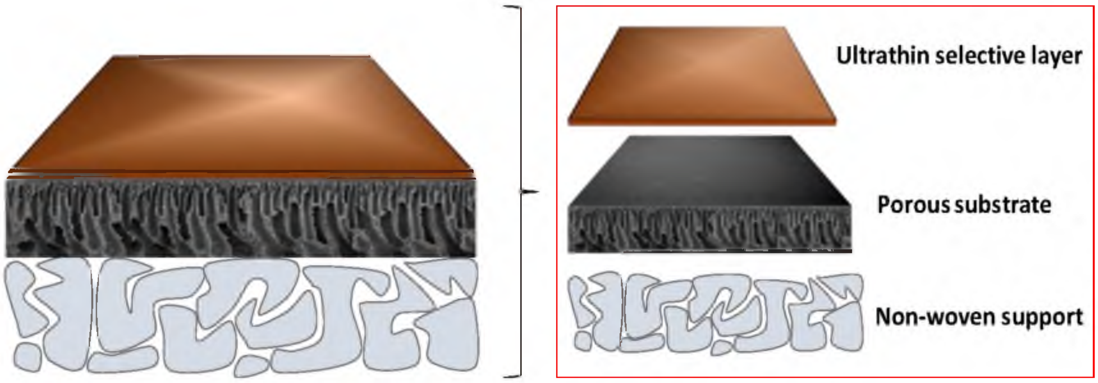

Figure 1.3 Components of thin film composite membrane

Despite all of the related published studies, the performance of TFC membrane could be further enhanced by incorporating nanomaterials into the dense layer of thin film. In this case, the term of this type of membrane changed to thin film nanocomposite (TFN) membranes. Various nanomaterials have been integrated during fabrication of TFN membranes; these includes graphene based materials (Lai et al., 2016; Mahdavi, Delnavaz and Vatanpour, 2017; Wang et al., 2017; Zhao et al., 2018), graphene quantum dots (Seyedpour et al., 2018), titanium dioxide (Emadzadeh et al., 2014; Ghanbari, Emadzadeh, Lau, Matsuura, et al., 2015), carbon nanotubes (Al-Hobaib et al., 2017; Han et al., 2015), metal nanocomposite materials (Ben-Sasson, Zodrow, et al., 2014; Lee et al., 2007; Ramezani Darabi et al., 2018), and silica nanoparticles (Abadikhah et al., 2018; Ang et al., 2019).

Metal organic frameworks (MOFs), a new type of porous materials which is widely used in gas separation has created a breakthrough for its studies in water/wastewater treatment application (Wang et al., 2016). MOFs is typically described as inorganic metal ions linked by organic ligands via coordination bonds (Rowsell & Yaghi, 2004). In general, the properties of MOFs are preferable for water treatment application ascribed by their high specific surface area, different particle structures, tunable properties, and distinct pore size and structure

Nevertheless, the use of MOFs membranes in water treatment is still in its infancy when compared with their applications for gas separation. MOFs-integrated membranes are advantageous because they can overcome the traditional filling problems of low affinity with the membrane, porosity blocking, and segregation (Kadhom et al., 2017). The hybrid MOFs structure with organic and inorganic parts is generally compatible with polymeric layers in membrane where MOFs particles can be more conveniently embedded into the TFC membrane with less gaps than those created by traditional inorganic fillers. There are also studies reported on incorporation of MOFs TFN membranes to treat water in different applications. For example, Lee et al. used A100 (aluminum terephthalate) and C300 (copper benzene-1,3,5-tricarboxylate) as water soluble MOFs, which were embedded and dissolved into the ultrafiltration membrane to increase its porosity (Lee et al., 2014). For reverse osmosis, Hu et al. (2011) reported two simulation studies that used Zeolitic Imidazolate Framework (ZIFs)—MOFs based on zeolite as membranes for water desalination. Xu et al. (2016) filled MIL-101(Cr) NPs into the TFC membrane to improve the desalination performance. Findings showed that the water flux increased by 44% comparing to the neat membrane just by adding 0.05% MIL-101 nanoparticles to the organic solution, while the salt rejection remained almost the same.

Another advantage is the low cost of the polymeric membranes and the vast selection range of linkers toward controlling MOFs shape, morphology, and surface chemistry, making it potentially possible to design membrane for specific applications (Wang et al., 2016). Hence, this research aimed to develop TFN membranes incorporated water-stable zirconium(Zr)-based MOFs for Pb(II) removal via membrane NF and FO processes. The physiochemical properties of the two types of

Zr-based MOFs (UiO-66 and UiO-66-NH_2) with and without functional amine (-NH_2) was be evaluated thoroughly. The performance of the membranes upon removing Pb(II) will be investigated under hydraulic pressure-driven NF process and osmotic pressure-driven FO process under various operational conditions. Leaching and stability study of the fabricated membranes at long operating hour were also conducted and evaluated.

1.3 Problem Statement

Thin film composite (TFC) membrane has been shown to be effectively remove heavy metals from water. This type of membrane which comprised of polyamide (PA) dense layer with thickness of few hundred nanometers which is supported by porous substrate (Shaffer et al., 2015). This is the active layer that responsible for salt rejection. However, due to the presence of dense PA layer, water transport is often hindered, yielding low flux at high pressure. In order to improve the properties of the membranes, modifying TFC membranes by incorporating nanomaterials within thin active/selective layer serves as an interesting approach (Zirehpour et al., 2017). Various types of nanomaterials have been studied comprising zeolite, silica, carbon nanotubes, pure metals and metal oxides to improve the TFN membranes properties (Lau et al., 2012).

Metal-Organic Frameworks (MOFs) are a class of nanomaterials consisting of an inorganic or metal core surrounded by an organic linker material (Champness, 2011). Nevertheless, due to lability of the bonding of ligand that surrounds the metal atom, most of the earlier reported of MOFs are susceptible to water content. With the improved understanding of MOFs towards water stability, many studies have reported such water stable/hydrophilic MOFs. High valence based MOFs such as UiO-66 (Ma et al., 2017), ZiF-8 (Sorribas et al., 2013) and HKUST (Nurasyikin Misdan et al., 2019) have been reported for desalination purpose using RO processes. The selection of this type of MOFs is mainly due to their excellent water stability in which their structures are not easily collapsed upon exposure to water molecules. Despite there were studies reported on the use of UiO-66 in thin film layer (Ma et al., 2017; He et al., 2017), different monomer leads to different types of polyamide layer. In addition, the impacts of adding two types of Zr-based MOFs where one have additional NH_2- groups to the physicochemical properties of NF-ranged TFN membranes have not yet being explored. Comparison between these two types of Zr-based MOFs is beneficial in providing the to which extent the presence of NH_2 group of Zr-based MOFs will influence the physicochemical changes of PA layer.

Another major issue faced by most membrane-based water separation processes is membrane fouling, caused due to the existence of varies contaminants in water. The effects of fouling aggravate over time, where the permeability of membrane declines in a long run. UiO-66 is the prototypical Zr-MOFs, having chemical formula of $Zr_6O_4(OH)_4(BDC)_6$ and possesses hydrophilic surface due to the presence of OH- functional groups. As most foulants are commonly hydrophobic in nature, thus, adding Zr-based MOFs with hydrophilic surface into TFN membranes can mitigate the adhesion of foulants, and hence improve the antifouling properties of the resultant membranes.

Despite to incorporation of additive into PA layer or substrate layer, the performance of TFC can be also influenced by difference modes of membrane processes. In addition, less information has been provided in term of the comparison between pressure driven and osmotic driven membrane process using same TFN membrane. Comparing the performance of TFN membranes using pressure driven membrane system (nanofiltration) and osmotic driven membrane system (forward osmosis) will provide better understandings in term of flux permeability, Pb(II) rejection and fouling propensity between different membrane processes. In addition, there is no comparative studies have been employed on the performance of TFN membranes incorporated with Zr-MOFs for Pb(II) removal under pressure-driven and osmotic-driven membrane processes.

1.4 Research Objectives

The main aim of this research work is to study the removal of lead (II) by thin film composite/Zr-metal organic framework (TFN/Zr-MOFs) membrane by NF and FO processes. The objectives of this study are:

1) To study the effects of different types and loading of Zr-based MOFs (UiO-66 and UiO-66-NH_2) to the physicochemical properties of PA layer of TFN/Zr-MOFs membranes.

2) To investigate the performance of TFN/Zr-MOFs membranes for removal of Pb(II) by using nanofiltration process and forward osmosis process based on water permeability, basic salt rejections, and Pb(II) rejections.

3) To evaluate the difference of the performance of TFN/Zr-MOFs when using hydraulic pressure-driven process and osmotic pressure-driven process for Pb(II) removal.

4) To evaluate the leaching and fouling impact to the stability of TFN/Zr-MOFs at longer operating hour.

1.5 Research Scopes

In order to achieve the aforementioned objectives, the following scopes of study are outlined:

1) Synthesizing two types of Zr- based MOFs which are UiO-66 and UiO-66-NH_2 via solvothermal method and characterizing their physicochemical properties

The aim of this phase is to synthesize and characterize two types of Zr-based MOFs which are UiO-66 and UiO-66-NH_2 by using high valence metal Zr^{4+} as precursor and 1,3-benzene dicarboxylic acid as ligand. The physiochemical properties of self-synthesised MOFs were evaluated via Fe-SEM (to evaluate the morphological structure of the prepared MOFs), X-ray diffraction analysis (to determine the crystallinity structure of MOFs and water stability), Attenuated total reflection-fourier transform infrared (ATR-FTIR) (to determine the presence of surface functional groups) and Brunauer, Emmet and Teller (BET) (to determine the specific surface area).

2) Fabricating TFN/Zr-MOFs membrane by incorporating different loading of UiO-66 or UiO-66-NH_2 ranging from 0.005 wt% to 0.1 wt% into the PA layer.

For this scope, PSf substrate was prepared by phase inversion technique, as followed by the optimized procedures. TFN membranes made of PSf substrates were prepared via in-situ interfacial polymerization by studying the effects of different loading of UiO-66 or UiO-66-NH_2 (0-0.1wt%) on the PA layer. The physiochemical properties of TFN membranes were evaluated by scanning electron microscope (SEM), elemental dispersive X-ray (EDX), Fourier transform infrared (FTIR), atomic force microscope (AFM), contact angle measurement, zeta potential analysis, pure water flux analysis and membrane conductivity.

3) Investigating the performance of TFN/Zr-MOFs membranes for removing of Pb(II) from aqueous solution by NF and FO process

The performance of two types of TFN/Zr-MOFs were firstly analyzed based on the water permeability and basic salt rejections (NaCl, MgCl, Na_2SO_4, $MgSO_4$) by using lab scale NF system. This followed by rejections of Pb(II) from aqueous solution by investigating the effects of pH (1.0-5.0), initial concentration (50ppm-500ppm) and presence of binary metal (Ni and Cd) were carried out where the final concentration of Pb(II) was measured by using atomic absorption spectrometer (AAS). For FO process, water flux and reverse solute flux (RSF) were carried out by using FO-cross flow membrane system in which the draw solution ($MgCl_2$ with concentration of 1.0M) and membrane orientation (active layer facing feed solution, AL-FS) were kept fixed.

4) Comparing the removal of Pb(II) using NF filtration process and FO filtration process.

In this scope, the performance TFN membranes upon removing Pb(II) was conducted at fixed operating conditions. The rejection of Pb(II) and water flux of the both types of TFN/Zr-MOFs membranes were measured and compared between both filtration processes.

5) Evaluating the effect of leaching and scaling compound to the stability of TFN/Zr-MOFs membranes

Leaching study was carried out by agitated the membrane and the amount of Zr-MOFs leached after overnight agitation was determined by AAS. 2000ppm $MgSO_4$ as scaling compound was used in order to study the effect of Pb(II) rejection in the presence of scaling compound. Both flux and rejection of solutes were measured and compared to the flux and rejection without scaling compound

1.6 Significance of Study

It is well known that membrane separation becoming important for various applications, TFN/Zr-MOFs membranes serve as another alternative measure for removal of heavy metals. This study is expected to provide better understandings on the underlying principle of the fabrication of TFN membranes for removal of heavy metals by considering the changes of incorporating different types of Zr-based MOFs into PA layer to the physicochemical morphologies, liquid separation characteristics, surface characteristics and comparative performance of pressure driven and osmotic driven membrane processes by using the developed membrane.

The primary outcomes of this study would benefit scientific community in the sense of filling the knowledge gap of nanotechnology and membrane technology for water/wastewater treatment. The approach of incorporating water stable MOFs which has good compatibility with polymer may combat the issues that are commonly faced by thin film composite membranes. In addition, as there are limited studies have been conducted on the comparative performance between pressure driven and osmotic driven membrane processes for heavy metals removal, thus this study may also provide better understanding in term metal rejection and fouling effects of the TFN membranes. As it is well known that addition of additive with hydrophilic surface will improve the antifouling properties of the membrane, however the life-span and performance of the membrane are also varied according to which type of membrane filtration processes are used.

In addition, from the perspective of Malaysian hazardous waste management and legislation policies, currently, the application of TFN/Zr-MOFs membranes will reduce the threat of heavy metals pollution towards surrounding environment and human health.

1.7 Organization of Thesis

This thesis consists 5 chapters. Chapter 1 describes brief research background about thin film composite and its applications as well as metal organic framework as additive in thin film composite. In addition, this chapter also elaborates the problem statements, objectives, scopes and rational of this study in detail.

Chapter 2 provides detailed information about heavy metal contaminations and type of membrane processes used for their removal from water. This chapter also gives information of the chronological development of thin film composite membrane and influence of additives to the performance of this type of membrane. Chapter 3 focuses on the experimental procedures involved in this study; from synthesis of metal organic frameworks, fabrication of thin film composite membrane, characterizations and performance analysis of the developed membrane.

Chapter 4 describes the results and discussion for the all experimental procedures which are sub-divided into subheadings. The physicochemical properties of the self-synthesized UiO-66 and UiO-66-NH_2 were firstly discussed followed by physicochemical properties of the TFN incorporated with different loadings of UiO-66 or UiO-66-NH_2. The physical properties of the prepared TFN membranes were firstly investigated by using Fe-SEM and AFM analyses while ATR-FTIR was conducted in order to evaluate their chemical properties The correlation of cross-linking between nanofillers and PA layer were analysed by using XPS analysis. For performance analysis, comparison of performance was firstly discussed between TFN/UiO-66 and TFN/UiO-66-NH_2 The results of the performance for Pb(II) removal by each membrane filtration processes were discussed and compared and the end of this chapter. Finally, the general conclusions of this study and some recommendations for future studies are drawn in chapter 5 followed by appendixes of this study.

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Journal with Impact Factor

1. **Abdullah, N**., Othman, F.E.C., Yusof, N., et al. (2020). Preparation of nanocomposite activated carbon nanofibers/manganese oxide and its adsorptive performance towards lead(II) from aqueous solution. *Journal of Water Process Engineering*. In Press. **(Q1, IF: 3.688)**

2. Hamid, M.F., **Abdullah, N**., Yusof, N., et al, (2020). Effects of surface charge of thin-film composite membrane on copper (II) ion removal by using nanofiltration and forward osmosis process, *Journal of Water Process Engineering* (In Press) **(Q1, IF: 3.688)**

3. Paiman, S.H., Rahman, M.A., Uchikoshi, T, Nordin, N.H.A.M., Alias,N., **Abdullah, N.,**et.al. (2020). In situ growth of α-Fe_2O_3 on Al_2O_3/YSZ Hollow Fiber Membrane for Oily Wastewater, *Separation and Purification Technology* (In Press) **(Q1, IF:4.551)**

4. **Abdullah,N**., Yusof, N., Lau., W.J.,Jaafar, J., Ismail,A.F. (2019). Recent trend of heavy metal removal from water/wastewater by membrane technologies, *Journal of Industrial and Engineering Chemistry, 76* (2019) 17-38. **(Q1,IF: 4.802)**

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1. **Abdullah, N.,** Yusof, N., et al. (2018). Effects of manganese(VI) oxide on polyacrylonitrile-based activated carbon nanofibers (ACNFs) and its preliminary study for adsorption of lead(II) ions. *Emergent Materials, 1,* 89-94.

2. **Abdullah, N.,** Tajuddin, M.H, Yusof, N., et al. (2017). Removal of lead(II) from aqueous solution using polyacrylonitrile/zinc oxide activated carbon nanofibers, *Malaysian Journal of Analytical Sciences, 21*, 619-626.

3. Ikhsan, S.N.W., **Abdullah, N.,** Yusof, N., et al. (2017). Polyethersulfone/HFO Mixed Matrix Membrane for Enhanced Oily Wastewater Rejection. *J. Applied Membrane Science & Technology, 20* (1), 11-17.

Book Chapter

1. **Abdullah, N**., Tajuddin, M.H., Yusof, N. *Forward Osmosis(FO) for Removal of Heavy Metal in Nanotechnology in Water and Wastewater Treatment*, Elsevier, BV, 2019.

2. **Abdullah, N**., Tajuddin, M.H., Yusof, N. *Carbon-based Polymer Nanocomposite for dyes and pigments removal in Carbon-based Polymer Nanocomposites for Environmental and Energy Applications*, Elsevier BV, 2018.