COMPOSITE CHRISTIAN ALBRECHT UNIVERSITY-1 MEMBRANE ON ALUMINA HOLLOW FIBER FOR DESALINATION APPLICATIONS

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ABSTRACT

Depletion of fresh water sources seems to be concerning as a lot of factors lead to it such as population growth, urbanization, industrialization and climate change. Membrane technology seems to be the key to save the sources from continuingly depleting. This study was aimed to develop metal organic framework (MOF) based membrane for desalination process. Christian-Albrechts-University-1 (CAU-1) is an excellent choice of MOF as it is water stable and can be utilized in desalination application. It was synthesized using solvothermal technique by differentiating the precursor concentration (0.05 M, 0.1 M, 0.5 M) and further post-treatment process using methanol was carried out to remove guest molecules. The problem with CAU-1 is to produce defect-free layer on alumina support. Perfluorinated polymer (PF) layer need to be added to improve the surface as well as the permeation performances. Series of characterization and performance tests were conducted to evaluate the parameter effects. Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM) and contact angle were performed to achieve better understanding in changes that occur to CAU-1 membrane properties. FESEM images showed that CAU-1 membrane was successfully produced on alumina hollow fiber support with thicknesses ranging from 1.3 – 2.7 µm. FTIR and XRD results showed that the presence of guest molecules does really gives significant effect to the CAU-1 framework. Guest molecules in CAU-1 framework interrupts the amine peak that should be presence in range 3500 – 3300 cm^{-1}. The removal of guest molecules does help in defining the peak in XRD. Forward osmosis (FO) performance of untreated 0.5 M CAU-1 (M6) membrane manage to achieve water flux of 18 L m^{-2} h^{-1} and reverse solute of 0.0792 kg m^{-2} h^{-1}. The configuration of the FO process was changed by facing the active layer towards the draw solution. Results obtained were surprisingly different than it should be as it follows reverse osmosis concept. The water molecules flows from higher concentration gradient to lower concentration gradient. M6 membrane possesses flux value of 4.05 L m^{-2} h^{-1} and salt rejection of 75% for sodium chloride. The addition of PF layer does significantly improve the structural integrity of CAU-1 framework as it heals micro-defect present in CAU-1. In FO performance, treated 0.5 M CAU-1 (M5) membrane with PF layer showed the highest flux of 11.15 L m^{-2} h^{-1} and the reverse solute of 0.00084 kg m^{-2} h^{-1}. For the active layer facing draw process, M5 membrane with PF layer managed to get flux up to 5.16 L m^{-2} h^{-1} and salt rejection up to 95.98%. It can be concluded that the presence of guest molecules and addition of polymer layer can improve the performance of CAU-1 membrane.

ABSTRAK

Pengurangan sumber air bersih menjadi perkara yang merisaukan kerana banyak faktor yang menjadi punca seperti contoh pertambahan populasi, pembandaran, pengilangan, dan perubahan cuaca. Teknologi membran menjadi kunci untuk menyelamatkan sumber ini daripada terus berkurang. Kajian ini dijalankan bertujuan untuk mewujudkan membran berasaskan kerangka logam organik (MOF) untuk proses penyahgaraman. Christian-Albrechts-University-1 (CAU-1) menjadi pilihan terbaik sebagai MOF memandangkan ia stabil di dalam air dan boleh digunakan untuk proses penyahgaraman. Ia disintesis melalui teknik pemanasan pelarut dengan membezakan kepekatan pemula (0.05 M, 0.1 M, 0.5 M) dan proses rawatan selanjutnya dijalankan menggunakan metanol untuk menyingkirkan molekul asing. Masalah yang dihadapi oleh CAU-1 ialah penghasilan lapisan yang sempurna di atas fiber alumina berongga. Lapisan polimer berfluorin (PF) perlu ditambah bagi penambahbaikan permukaan dan juga prestasi kebolehtelapan. Berberapa siri pencirian dan prestasi dijalankan untuk menilai kesan parameter. Mikroskop imbasan elektron pancaran medan (FESEM), spektroskopi infra merah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), mikroskop daya atom (AFM) dan sudut sentuh dilaksanakan untuk mencapai pemahaman yang mendalam tentang perubahan yang berlaku pada membran CAU-1. Imej FESEM menunjukkan membran CAU-1 berjaya dihasilkan di atas gentian berongga alumina dengan ketebalan di dalam julat 1.3 – 2.7 µm. Keputusan FTIR dan XRD menunjukkan kehadiran molekul asing memberikan impak signifikan terhadap membran CAU-1. Molekul asing di dalam kerangka CAU-1 mengganggu kewujudan puncak amina yang sepatutnya hadir di dalam lingkungan 3500 – 3300 cm^{-1}. Penyingkiran molekul asing membantu mengenal pasti puncak di dalam XRD. Osmosis hadapan (FO) untuk membran tidak dirawat 0.5 M CAU-1 (M6) berjaya untuk mencapai fluks air 18 L m^{-2} h^{-1} dan bahan fluks larut terbalik 0.0792 kg m^{-2} h^{-1}. Konfigurasi proses FO ditukar dengan menghadapkan lapisan aktif terhadap larutan berkepekatan tinggi. Keputusan yang diperoleh adalah mengejutkan kerana ia berbeza daripada sepatutnya dan mengikut konsep osmosis songsang. Molekul air bergerak dari larutan berkepekatan tinggi kepada larutan berkepekatan rendah. Membran M6 mencatat nilai fluks 4.05 L m^{-2} h^{-1} dan penolakan garam 75% untuk natrium klorida. Penambahan lapisan PF meningkatkan struktur berintegriti kerangka CAU-1 secara signifikan kerana ia memulihkan kecacatan mikro yang terdapat pada CAU-1. Di dalam prestasi FO, membran dirawat 0.5 M CAU-1 (M5) dengan lapisan PF menunjukkan fluks tertinggi 11.15 L m^{-2} h^{-1} dan bahan fluks larut terbalik 0.00084 kg m^{-2} h^{-1}. Untuk lapisan aktif menghadap larutan berkepekatan tinggi, membran M5 dengan lapisan PF memperoleh fluks sehingga 5.16 L m^{-2} h^{-1} dan penolakan garam sebanyak 95.98%. Ia boleh disimpulkan bahawa kehadiran molekul asing dan penambahan lapisan polimer mampu untuk meningkatkan prestasi membran CAU-1.

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LIST OF ABBREVIATIONS

BSA	-	Bovine serum albumin
CAU	-	Christian-Albrechts-Universitat
CFV	-	Cross flow velocity
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
GHG	-	Greenhouse gases
HT	-	High throughput
INC	-	Integrated nanocatalyst
MED	-	Multi-effect distillation
MOF	-	Metal organic framework
MSF	-	Multi stage flash
MVC	-	Mechanical vapour compression
MF	-	Microfiltration
NF	-	Nanofiltration
PA	-	Polyamide
PAN	-	Polyamide
PES	-	Polyethersulfone
RO	-	Reverse osmosis
ROASL	-	Reverse osmosis assisted sweeping liquid
T	-	Temperature
TMP	-	Trans-membrane pressure
UF	-	Ultrafiltration
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	Percentage
°C	-	Degree celcius
M	-	Molarity
$\$/m^3$	-	High cost unit per metre volume
Å	-	Angstrom
µm	-	Micrometer
mm	-	Milimeter
nm	-	Nanometer
pH	-	pH value
mg/mL	-	Milligram per mililiter
MPa	-	Megapascal
cm^3/g	-	Centimetre cubic per gram
$\Delta\pi$	-	Osmotic pressure difference
Jω	-	Solvent transport
Jś	-	Solute flux
kV	-	Kilovolt
ΔP	-	Trans-membrane pressure difference

CHAPTER 1

INTRODUCTION

1.1 Research Background

Fresh water supplies have been depleted due to various reasons, i.e. population growth, urbanization, industrialization and climate change [1–4]. Efforts have been focused on finding technologies to overcome the problem. In this context, seawater desalination using membrane technology has been regarded as the promising option for clean water supplies. Seawater is an unlimited water source that can accommodate the needs of growing global population [3]. In fact, this technology has been extensively used in the middle-east countries to produce clean water supply [5]. Seawater desalination technologies should enable 99.5% rejection of salt from seawater, as high sodium content can lead to body dehydration [6]. There are many conventional methods that have been used in the desalination application such as multi-effect distillation (MED) [7], mechanical vapour compression (MVC) [8], multi-stage flash (MSF) [9], solar distillation [10] and chemical approach such as ion-exchange desalination [11]. It has been known that these technologies are energy extensive [5]. High usage of energy will resulted in high cost expenditure, huge emission of greenhouse gases (GHG), disposal of brine concentration accumulated from the process and other environmental impact [12].

A part of the aforementioned technologies, membrane technology has gained an interest for seawater desalination. Membranes are considered favourable for desalination because of its high efficiency, high selectivity, low energy consumption and ease of operation [1]. Typically, polymer materials are used in membranes production as they displays good rejection and good separation performance [13]. However, some of the polymer membranes are suffering from low mechanical strength, thermal and chemical degradation, shorter lifespan and susceptible to bio-fouling [14]. Recently, ceramic material has captured the attention of researchers and industries due to its characteristics and sustainability. In comparison, ceramic membrane offers a number of advantages than polymeric membrane in fluid separation [15]. It provides thermal and chemical stability, good mechanical strength, higher life longevity and anti-swelling properties [16]. Although ceramic membrane shows exceptional characteristics, it shows ineffective performance in removing salt from seawater [16]. The performance of the ceramic membrane itself can be enhanced by embedding other materials onto the surface of the membrane. Microporous materials such as metal organic frameworks (MOFs) seems to be the most suitable candidate to improve the characteristic and performance of the ceramic membrane [17].

Recently, MOFs have gained considerable attention among researchers due to its vast functionality and great future progress. These materials are made up of organic ligand (linker) molecules, usually consists of phosphonate or carboxylate group, and inorganic metal or metal cluster such as aluminium [18], zinc [17], zirconium [19] or other type of metal. The characteristics of MOFs can possibly enhance the performance of ceramic membrane in term of seawater desalination [20]. Highly porous structure, tuneable pore size and functionality, large specific surface area and high thermal and chemical stability make MOF as a versatile framework structure [15–18]. These frameworks are considered special for its tuneable properties as the pore size and functionality of the MOFs are possible to be changed by applying isoreticular synthesis. The properties of the MOFs can be fine-tuned by post-synthetic modification applied to the established inorganic building blocks [21]. Regarding the potential progress of the MOFs, it has been utilize in varieties of application such as desalination [6], heavy metal removal [16], gas storage [24], photocatalytic [25] and many more applications yet to be discover.

Even though MOF is considered as one of the versatile materials for separation application, producing a defect-free MOF surface is still a great challenge. One way to produce a defect free MOF is by applying polymer on MOF. Friebe et al. states that the presence of polymer on the MOF can either heal the micro-defect presence in MOF or interact with it [27]. Polymer can be explained as a long, repeating chains of monomers. It possess a unique properties as how they are bonded together or what type of molecules that is bonded to the polymer. The organic structure of polymer eases the MOF to interact with certain kind of polymer. This is due to the presence of organic linker inside the MOF. It increases the compatibility between polymer and the MOF.

1.2 Problem Statement

CAU-1 is considered as one of the excellent materials in MOF study. There are several advantages of making CAU-1 as a desalination membrane. First, CAU-1 is considered as water-stable materials which is great for desalination application. It possess robust coordination bonds which strengthen the framework when subjected to water molecules. Next, CAU-1 has small pore opening of 1 – 0.45 nm and small triangular gates of 0.3 – 0.4 nm to pass through the structures. This small opening leads to the selective permeation of water molecules while retaining the salts which have higher radii in ion sizes. It also possess large Langmuir surface area and high pore volume which fulfil the criteria for membrane selection. However, there were no study conducted on CAU-1 as a membrane for desalination application. Most of the study were subjected to gas separation applications and not as a membrane when dealing with CAU-1 MOF. This problem was tackled in this study by forming the CAU-1 as a membrane on alumina hollow fiber. Information on incorporating CAU-1 MOF on alumina hollow fiber is scarce and works need to be done in order to produce functionalized membranes on alumina hollow fiber.

Inorganic membrane and MOFs need to have compatibility in order for the MOFs to adhere well on the membrane surface. In this research, same material-based between MOF and ceramic membrane is used in order to increase compatibility between both materials. Aluminum is a type of element that has high abundance and easy to process. In term of MOF synthesizing, aluminum is selected because it can produced a highly porous and stable structure. The interconnection of aluminum-centered octahedral enables the formation of plentiful single and dual dimensional inorganic sub-networks. The same charge number (+3) of the ceramic material (alumina) and CAU-1 (Al-based MOF) increase the compatibility between both structures and the surface attachment will be significantly better.

Although MOF is considered as one of the great materials in separation process, fabricating defect-free MOFs on the surface of the ceramic membrane are relatively hard to achieve. Poor membrane substrate interaction is a typical issue facing by MOFs. Technique of implying MOFs onto the surface of the membrane need to be correctly done so that defect-free MOFs can be form along the ceramic support. If there are pin holes or cracks exists along the surface of the MOFs, the performance of the modified membrane will eventually disrupted and desired separation cannot be achieve. The additional layer of polymer will help to heal those micro-defect present on the MOF. Furthermore, the interaction between both MOF and polymer layer might give benefits to the performance of the membrane in terms of water flux and salt rejection. It will also help in controlling the pore flexibility of the MOF which influence the separation process.

1.3 Objectives of Study

The objectives of this research are as follows:

1. To assess the deposition characteristics of CAU-1 MOF membrane on the outer surface of alumina hollow fiber.
2. To evaluate the performance of CAU-1 MOF membrane under dead-end filtration, forward osmosis (FO) and reverse osmosis assisted sweeping liquid (ROASL).
3. To study the interaction of polymer curable resin with CAU-1 MOF membrane for its physical characteristics and performances in FO and ROASL.

1.4 Scope of Study

a) Scope of Objective 1

I. Fabrication of thin layer CAU-1 MOF membrane using different synthesis concentration (0.05 M, 0.1 M, 0.5 M) on the outer surface of alumina hollow fibers using solvothermal synthesis method with synthesis time of 5h and temperature of 120°C.
II. Removal of guest molecules inside the pore structure by stirring the membrane inside 100 ml methanol solution for 72 hours.
III. Characterization of CAU-1 MOF membrane was conducted using field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR), X-ray powder diffraction (XRD) and contact angle.

b) Scope of Objective 2

I. To evaluate the water permeation flux and solute rejection of CAU-1 MOF membrane using dead-end process.
II. FO performance evaluation process was done on CAU-1 MOF membrane using the same variation and it was done using the FO setup.
III. To investigate the effect of active layer position towards higher salt concentration solution using ROASL setup.
IV. To measure two different salts (NaCl and $MgSO_4$) in ROASL performance test to compare the significance of using two different draw solutions.

c) Scope of Objective 3

I. To study the effect of using perfluorinated polymer (PF) by incorporating it on the surface of selected CAU-1 MOF membrane (M3 and M5) via dip coating method.
II. To characterized the composite CAU-1 membranes using FTIR, XRD, FESEM, contact angle and AFM.

III. To evaluate composite CAU-1 membranes performance using FO process and ROASL process.

1.5 Significance of Study

Recently, clean water shortage has been a severe global problem and fast action need to be taken to overcome this situation. Membrane technology seems to be the promising solution in encountering the water scarcity problem. This research is to provide alternative method for clean water production. Membrane-based seawater desalination can be used to produce drinkable clean water and avoid demand. Salts inside seawater need to be reduced or removed first in order for the water to be consumable. MOF membrane supported on alumina hollow fiber is expected to remove salt content from seawater does making it drinkable. This state of art can be used in water-stress area and it can give contribution towards the community.

Conventional technologies have been used for decades in middle-east countries to desalinate seawater. It provides clean consumable water for industries, agriculture and community. Although these technologies help a lot in seawater desalination but the processes are energy-extensive and not environmental friendly. Seawater desalination based on membrane technology seems to be promising as it only consumes low energy usage, environmental friendly and low cost expenditure. This technology surely evades the environmental problem as no greenhouse gases (GHG) emission and the concentrated brine collected from the process will be release back to the sources. Besides, it also helps to build a greener environment and produce better human living. This is the first time ever CAU-1 MOF is used as membrane for desalination. Breakthrough discovery such as ROASL process was proposed to make membrane technological innovation.

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LIST OF PUBLICATIONS

Journal with Impact Factor

1. **M. Z. Mohd Pauzi.,** N. M. Mahpoz., N. Abdullah., M. A. Rahman., K. H. Abas., A. Abd Aziz., M. H. Padzillah., M. H. D. Othman., J. Jaafar.., and A. F. Ismail.”Feasibility study of CAU-1 deposited on alumina hollow fiber for desalination applications,” *Seperation and Purification Tecnology,* pp. 247-257. https://doi.org/10.1016/j.seppur.2019.02.021., 2019. **(Q1, IF: 5.107)**