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RESEARCH ARTICLE

Metal organic framework mixed-matrix membrane for arsenic removal

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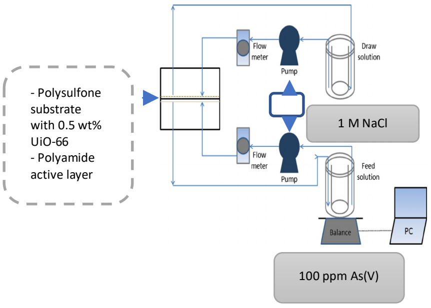
Graphical abstract



Abstract

Metal organic framework (MOF) is a recent class of porous materials that are built from metal cluster and organic linker. Among the discovered MOFs, UiO-66 has demonstrated both attributes of water stability and hydrophilic, making it suitable for wastewater treatment. In this study, 0.5 wt% UiO-66 was integrated into polysulfone membrane as nanofiller to form mixed-matrix membrane (MMM) with a thin-film composite, dense polyamide layer formed on top of the substrate layer that intended to remove 100 ppm of arsenic V from wastewater through forward osmosis. The successful synthetization of UiO-66 nanoparticle was proven by XRD and FESEM. The pure water permeability was significantly higher with the presence of LiCl in dope solution as pore former. It was found that the arsenic rejection achieved was 87.5% with satisfactory water flux and salt reverse flux.

Keywords: Metal organic framework, mixed-matrix membrane, wastewater treatment, forward osmosis

INTRODUCTION

Arsenic is a type of heavy metal that typically found in wastewater, generally used in agricultural, glass and electronics industry[1]. It is considered as a threat to humans due to its toxicity and carcinogenicity, not to mention that it has an accumulative effect, making it unsafe to be directly consumed[2]. According to Ministry of Health Malaysia, arsenic content in drinking water purposes should be diminished down to 0.01 mg/L for both raw and drinking water purposes within the satisfaction of World Health Organization. Arsenic in water bodies is existed in various concentrations, pH and forms such as arsenite (As^{3+}) and arsenate (As^{5+})[3]. A method of treatment in rejecting arsenic with wide variability is necessary to sustain the quality of product for drinking purpose.

Current treatment for arsenic includes coagulation-flocculation, batch adsorption, ion-exchange and membrane-based separation[4,5]. Membrane separation is considered as a promising technique for its high pollutant removal, cost effective and ease of operation. In order to reject arsenic from wastewater, nanofiltration (NF) range (1-10 nm) is suitable to be used, given that arsenic has high hydration diameter between 2.0-2.2 Å. Reverse osmosis (RO) range is also able to reject arsenic, but the relatively smaller pore size (< 1 nm) will compromise the water flux as the pore creates high resistance for water to pass through.

Forward osmosis (FO) is a movement of water from low to high concentration gradient by passing through a semi-permeable membrane driven by naturally occurring osmotic pressure. The opposite of FO is called RO, in which the external hydraulic pressure counters the osmotic pressure instead. FO is more advantageous than RO in terms of lower energy consumption and tendency for membrane fouling. [6]

The tiny aperture size and the reducing water permeability are the drawbacks of applying RO-like membrane in FO despite of its high rejection performance. The studies of NF-range membrane application in FO process are conducted as a solution to reduce the barrier for water to pass through while maintaining rejection efficiency of certain solutes such as heavy metals.

One of the challenges in traditional membrane is the trade-off between permeability and selectivity, especially when the separation mechanism is solely relied on the window size of the membrane. A large open pore allows more water molecules to pass through, though at the cost of solute passing through together causing low rejection. Mixed-matrix membrane is a promising solution to counterfeit the aforementioned problem by lowering the resistance for permeate diffusional pathways and increasing the resistance for solute[7].

Metal organic framework (MOF) is a class of porous materials that has been recently discovered. Built with metal cluster and organic linker, the combination of different types of those precursors can lead to variations of MOF structure, topology, stability and porosity[8]. In fact, MOF has been applied within many fields such as gas separation, catalysis, pervaporation and sensing[9–11]. Albeit so, when it comes to water treatment specifically, there has not been much for MOF to be deemed as suitable for usage, given that most of them do not demonstrate stability in water[12]. A zirconium-based MOF called UiO-66 (UiO stands for University of Oslo) that constructed into 12-coordination number, is proven to be stable in both water and certain range of pH, and also stable for prolong exposure[13–16].

Aside from its water stability, various factors that inflicted the sudden interest towards UiO-66 in wastewater application are its hydrophilic properties and moderate aperture size that can contribute to greater water flux when being used in membrane separation[11]. Previous studies regarding on UiO-66 MMM have shown improvement in water flux and salt rejection, compared to the neat polysulfone due to improvement upon the structure of active layer[17]. When being integrated as nanofiller in thin-film nanocomposite, a trend of water flux increment could be observed as the UiO-66 loading was increased while maintaining satisfactory selenium and arsenic removal [14]. This is because of the rejection that is contributed from surface charge properties that will enhance electrostatic repulsion via Donnan exclusion.

In current study, nanofiltration-like MMM (window size 1-10 nm) that consisted of polysulfone as the polymer matrix and UiO-66 as the nanofiller, was fabricated to treat arsenic through forward osmosis. The performance of membrane was studied and compared with neat TFC-polysulfone in terms of its effect towards arsenic rejection efficiency and pure water permeability. To the best of our knowledge, the application of UiO-66 MMM in wastewater treatment is still lacking because it is only recently studied, thus it is worth to be explored further.

EXPERIMENTAL

Materials and Methodology

Solvothermal synthesis of UiO-66 nanoparticles

The synthesis of UiO-66 nanoparticles took place via solvothermal method (high temperature and autogenous pressure). An equimolar of zirconium chloride ($ZrCl_4$, Sigma Aldrich, >99.5% purity) and 1,4-benzenedicarboxylic acid (BDC, Sigma Aldrich, 98%) were dissolved in a mixture of acetic acid (AA) and N,N-dimethylformamide (DMF) with volume ratio of 1:333. The mixture was then brought to sonication for 30 minutes before being placed into an oven at 120°C for 24 hours. The white particles formed at the bottom surface were recovered by filtration and washed with fresh DMF, followed by solvent exchange using methanol. The particles were recovered again and activated at 200°C in vacuum oven for overnight.

Phase inversion of polysulfone mixed-matrix membrane

Solid Udel polysulfone 3500 was first dried in the oven to remove moisture. Polyvinylpyrrolidone (PVP, Sigma Aldrich) and lithium chloride (LiCl, Sigma Aldrich) were dissolved in N-methyl-2-pyrrolidone (NMP). UiO-66 particles were added and brought to sonicate for 30 minutes until they were uniformly dispersed. A priming technique was used, where approximately 10 wt% from total solid polysulfone was added and stirred for 2 hours, followed by the remaining for 24 hours at 70°C. The composition of dope solution prescribed was shown in Table 1. After the dope has been completely homogenous, it was simultaneously degassed by a vacuum pump and stirrer by a blade that enclosed in a vessel with intention to remove bubbles and concurrently produce defect-free substrate. For membrane fabrication, the casting required glass rod, glass plate and tape in order to control the thickness around 70-90 µm as measured by micrometer gauge. Next, the casted dope was immediately immersed in water bath for 24 hours. The same procedure was likewise applied for fabrication of pure polysulfone substrate (without addition of UiO-66) to act as a negative control.

Table 1: Composition of UiO-66 MMM in wt.% (based on overall dope content).

Membrane id	UiO-66	Psf	LiCl	PVP	NMP
Psf-substrate	0	17	0	0.5	79.5
Psf-UiO-66-LiCl	0.5	17	3	0.5	79.5
Psf-UiO-66	0.5	17	0	0.5	82.0

Interfacial polymerization of polyamide TFC

The dry fabricated substrate was immersed in water bath for 3 minutes to provide moisture on the surface as well to remove trapped air inside the pores before being wiped prior to IP process. A 15 cm x 15 cm glass plate and clip were used to hold the substrate in order to prevent leakage. 2 wt% M-phenylenediamine (MPD) in distilled water was poured on top of substrate surface, left for 2 minutes and gently wiped with a tissue paper. 0.15 wt% trimesoyl chloride (TMC) in n-hexane was then poured and reacted with MPD monomer for 1 minute. The excess solution was discharged and the thin film was formed on the substrate surface. The TFC was stored in DI water until further application. The summary of TFC preparation was described in Fig. 1.

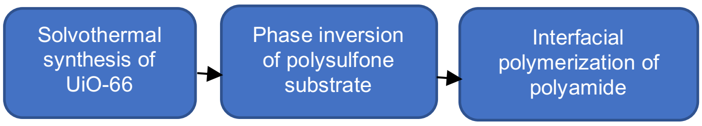


Fig. 1 Flow diagram of TFC-UiO-66 preparation technique.

Characterization

The crystallinity of UiO-66 powder and was determined by Bruker D8 X-ray diffractometer (XRD) using Cu Kα excitation radiation with 0.154 nm wavelength, 30 mA current and 40 kV voltage.

Field emission scanning electron microscope (FESEM) was used to study the surface morphology of UiO-66 nanoparticles. Meanwhile, for the parent Psf-UiO-66 and Psf-UiO-66-LiCl membranes, FESEM was used to capture the crossection morphology image. About 10 µL of ultra-diluted UiO-66/n-hexane solution was poured onto silicon wafer and the n-hexane was removed by air dried. Then, a thin platinum layer was placed on top of wafer to render conductivity.

The hydophilicity/hydrophobicity of UiO-66 powder was determined by Contact Angle Goniometer through sesile drop technique. The actual reading was taken from average of 10 repetition.

Membrane performance assessment

A cross-flow filtration unit was used to evaluate pure water permeability of substrates and TFC membrane. 5 bar of hydraulic pressure was applied to permeate the water through the membrane with 1.8 cm effective radius. The permeability was quantified by $L.m^{-2}.h^{-1}.bar^{-1}$, abbreviated as LMHB.

FO performance of TFC-MMM was determined by a lab scale FO filtration unit by determining water flux (A), solute flux (B) and reverse solute flux. The feed side of FO unit used was 10 mg/L As (V) while 1 M NaCl was used as the draw solution by using FO mode, whereby the selective PA layer was faced feed solution. The initial volumes for both sides were 1 L. The weight changes at draw side and conductivity at feed side were taken at 10 minutes interval until up to 80 minutes to determine forward flux and reverse flux respectively. TFC performance was calculated by equation (1);

$$\mathrm{PWP} = \frac{\frac{\Delta\,\mathrm{mfeed}}{\rho\mathrm{feed}}}{\Delta\,\mathrm{t} \times \mathrm{Am}} \tag{1}$$

where PWP is pure water permeability (LMHB), m_{feed} is feed solution weight loss (g), ρ_{feed} is feed solution density ($g.cm^{-3}$), Δt is time interval (min) and A_m is effective area of permeation cell (cm^2).

Arsenic rejection experiment

The arsenic rejection testing was conducted under RO mode. A cross-flow permeation cell was used by using 5 bar hydraulic pressure with 100 mg/L As (V) as the solute. To achieve stable permeation, the system was operated for 30 minutes before reading was taken. An atomic absorption spectroscopy (AAS) was used to identify the final concentration of As (V).

RESULTS AND DISCUSSION

The morphology by FESEM and crystallinity by XRD were expressed in Fig. 2 and Fig. 3 respectively. The FESEM image of UiO-

66 nanoparticle displayed octahedral 3D structure, where the octahedron edges were bonded by carboxylate functional groups[17]. Fig 2(c) and 2(d) displayed the cross-section images for Psf-UiO-66 and Psf-UiO-66-LiC respectively. Both of them demonstrated the formation of porous layer after phase inversion process. The morphological differences acquired in the membrane induced by kinetic effects by the presence of LiCl as pore forming agent, resulting into more porous structure. During phase inversion, LiCl leached out from the latter because they are water soluble, leaving behind voids that made the membrane became more porous. For XRD pattern, the peaks appeared at 7.4° and 8.5° were in-lined with as reported in the literature, confirming the well intergrown of crystal UiO-66 nanoparticle[18]. Nevertheless, there were additional peaks growth at 12° and henceforth. This could be resulted from incomplete removal of DMF solvent which formed noise in the image.

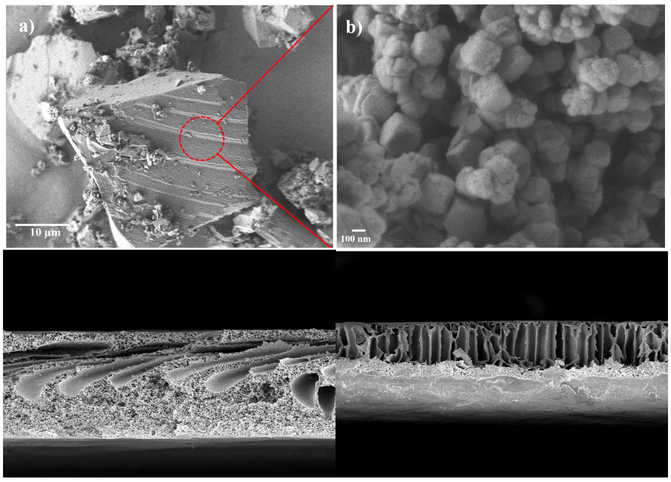


Fig. 2 FESEM images of UiO-66 nanoparticles and membrane a) under 2,000x, b) 50,000x magnification, c) Psf-UiO-66 and d) Psf-UiO-66-LiCl

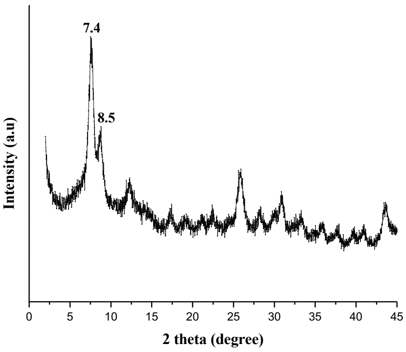


Fig. 3 XRD pattern of UiO-66 nanoparticle.

Effects of UiO-66 loading on the membrane performance

Pure water permeability, arsenic rejection and salt reverse flux were measured to determine the performance of fabricated membrane.

Fig. 4 displays the effects of different fabrication parameters of Psf-based MMM in response towards PWP. Psf substrates were first compared with Psf-UiO-66. It was found that the neat Psf demonstrated higher PWP than Psf-UiO-66, although the contact angle of neat Psf was higher. This might be due to the saturated phenomenon of UiO-66 nanoparticles into tiny pores of Psf, thus increasing the axial diffusion resistance for water, which was the diffusion across the membrane thickness. The permeability was tested again by using Psf-UiO-66-LiCl. The PWP had improved dramatically at 10 times larger than with absence of LiCl due to higher porosity morphology that allowed UiO-66 to be fitted in by preventing formation of macrovoid and aggregation of polymer in the dope solution[19]. This assumption was in agreement with other studies that discussed on the effects of LiCl as a pore forming agent[19]. For TFC-UiO-66-LiCl, the PWP was at 82.2 LMHB, a 63.4% reduction compared to without TFC. This was generally in sense because a dense, skin-like layer served as size-sieving mechanism was needed to reject solute while providing resistance for water to permeate.

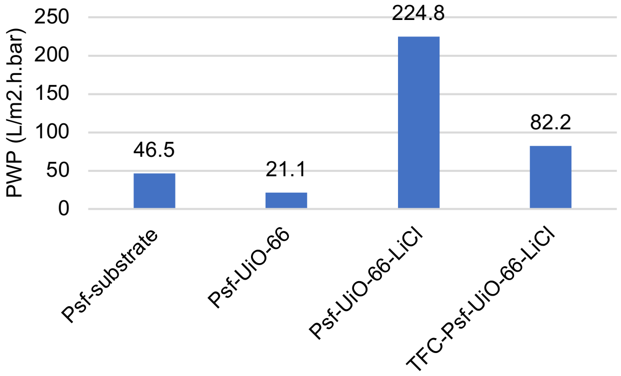


Fig. 4: PWP of Psf substrates and Psf-based mixed-matrix membrane.

Arsenic rejection testing

The rejection of arsenic was conducted by using TFC-UiO-66-LiCl, with PA layer on top of it with active layer faced feed solution. The results were expressed in Table 2. Based on rejection testing by RO mode, as much as 87.5% of As(V) had been rejected with 100 mg/L initial concentration. Theoretically, based on size exclusion, the rejection for divalent ion is higher than monovalent ion (such as Na+ and Cl-) because it has higher hydration diameter[14]. The solutes were able to be excluded on smaller window size of membrane surface. In this study however, the rejection of As(V) was found to be lower than monovalent ion as reported in previous study. A possible reason would be the lesser crystallinity of UiO-66 and noise formation which turned the nanoparticle into becoming more amorphous, resulting in less active site to interact with As solute[13,20,21]. Besides size exclusion, As(V) could also be rejected through electrostatic repulsion between negatively charged membrane and negatively charged solute[14,22]. Although UiO-66 was embedded in substrate layer, it did contribute to rejection performance by affecting interfacial polymerization of PA layer[17]. Due to its hydrophilic nature of UiO-66, the diffusion of MPD monomer became at greater rate and hence, affecting the ridge and valley top surface morphology of PA layer, leading to better performance[23].

Table 2: Performance of TFC-UiO-66-LiCl.

UiO-66 loading (wt%)	Contact angle (degree)	Rejection (%)	Water flux (LMHB)	Salt reverse flux (gMH)
0.5	61	87.5	5.8	6.6

Interestingly, although the contact angle of TFC-UiO-66-LiCl was higher than reported in the literature (indicates to be more hydrophobic), the water flux was more satisfactory (5.8 LMH compared to 2.8 LMH)[17]. This could be due to less severe to internal concentration polarization induced by lesser structural parameter value. The reverse salt flux acquired was 6.6 gMH, higher than as reported in literature, eventhough it had remained at moderate level[17].

The performance of TFC-UiO-66-LiCl was compared to commercially available cellulose triacetate (CTA) membrane manufactured by Hydration Technologies Inc. Jin *et al.* had carried out the performance of CTA embedded with polyester mesh to reject arsenic by FO and RO mode[24]. By using 10 ppm As (III) as the feed, as much 64% was rejected, much lower than the current study of 5.5 LMH water permeability. It was claimed that the unsatisfactory rejection was due to deformation of support and deterioration resulted from the presence of hydraulic pressure. Additionally, Mondal *et al.* explained that different arsenic valences could behave differently towards retention in membrane[22]. Due to absence of charge, As (III) interacted with functional group in membrane and thus diffused easily than negatively charged As (V).

CONCLUSION

In this study, UiO-66 has been synthesized and confirmed its formation through FESEM and XRD. In pure flux testing, the water permeability was significantly higher (approximately 10 times fold) when 3.0 wt% LiCl was added into the dope composition as pore forming agent through modification of porosity. For 100 ppm initial As (V) concentration, as much as 87.5% rejection was achieved in RO mode when 0.5 wt% UiO-66 was used as nanofiller. The hydrophilic properties of membrane contributed to satisfactory water flux.

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