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Oily wastewater treatment using modified microfiltration membrane

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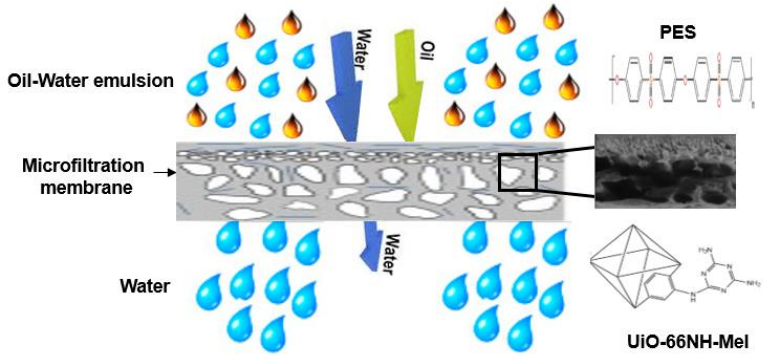
GRAPHICAL ABSTRACT



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ABSTRACT

A new polyethersulfone (PES) microfiltration (MF) membrane was fabricated via phase inversion method using a melamine-modified zirconium-based metal-organic framework (MOF). The wettability and permeability of the membrane were measured using water contact angle and pure water flux (PWF), respectively. By introducing the MOF additive (0.1 wt. %) to the membrane matrix, the performance of the membrane in the separation of the oil-water mixture (different oil concentrations of 300 and 500 mg/L) was enhanced. The flux recovery ratio (FRR) of the modified membrane was significantly increased to 90.76 % compared to that in the bare membrane (20.41 %). Furthermore, the antifouling property was considerably improved.

1. Introduction

Today, environmental pollution made by filtering and repulsing of residuum, became one of the most important problems of the civic aquarium ecosystem in the world. There are different types of pollutants including emerging pollution (e.g., herbicides and pest remain), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbon (PAHs), persistent organic pollutants (POPs), and low concentration oil compounds (Kumar et al. 2018).

Frequent leaks of oil to seas and from urban industries caused several problems for the aquatic ecosystem and human health, and made serious concerns for the environment (Schrope. 2011; Wang et al. 2018). Marine resources are so vulnerable to this disaster (Lahann. 2008).

Separation of oil-water mixture become a newfound subject in research and industrial societies. For the separation, in place burn and vacuum suction have been introduced (Kleindienst et al. 2015), but they are expensive and partly inefficient, which can cause the second pollution. In contrast, employing a selective method for removal the precious oil from the mixture can be attractive (Ma et al. 2016). For seeking suitable materials, the degree of hydrophilicity (and/or hydrophobicity) should be considered by determining the surface wettability (Chu et al. 2015; Ma et al., 2016). Membrane technology has found many interests in filtration and recycling wastewater via efficient isolation of viruses, organic macromolecules, and colloidal pollutants (Miao et al. 2016). There are some limiting issues in applying polymeric membranes such as weak mechanical strength, low anti-jamming ability, and short-time operation. For recovery of the membranes, repeatedly clean-up and their replacing are inevitable, which imposes high energy and cost (Zhu et al. 2014). Since membrane ultrafiltration is not capable to remove pollutants with low concentration, next-generation membrane technologies with structure multi-functionality have developed (Ren et al. 2019).

It has been found that by introducing nanomaterials, with high wettability, to polymeric membranes the performance of the composite membranes improved. For example, TiO_2 nanoparticles (Wang et al. 2019), carbon nanotubes (Wang et al. 2018), and C_3N_4 (Shi et al. 2019) have been employed for this purpose. In an oil-water mixture, a selective separation can be achieved as a hydrophilic membrane allows the penetration of only one phase (i.e., water). Besides

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wettability, smaller and controllable pores in membranes play beneficial roles in efficient oil-water separation. However, improved anti-fouling, high flux, and perfect detachment efficiency can be expected by utilizing these strategies (Lee at al. 2019).

In the last decade, metal-organic frameworks (MOFs), which are formed from metallic nodes and organic linkers, have considered as a proper platform for guest-host chemistry (Furukawa at al. 2013). These solid materials are preferred to other current porous materials like zeolites and carbon base materials (Dechnik at al. 2017). They have some incredible properties including ordered and adjustable pores, high variety in structures (lots of different metallic ions and ligands) and geometries, and structural stability. According to the literature, the introduction of MOFs to organic membranes was promising (Denny Jr et al. 2016), particularly in gas separation (Dietzel et al. 2009). Although many attentions have been focused on the applications of MOFs for gas adsorption and separation (Rowsell et al. 2004), there are limited reports using MOFs for separating liquids. In recent years, MOF-based mix matrix membranes have been introduced for wastewater purification (Maroofi and Mahmoodi. 2019).

In the current study, the effect of melamine-modified MOF (UiO-66-NH-Mel) as an additive on the performance of the PES-based membrane in oily wastewater separation was evaluated. For this purpose, the characteristics of the membrane such as wettability, morphology, antifouling behavior in different feed concentrations (300 and 500 mg/L) were examined.

2. Materials and methods

2.1. Materials

Dimethylacetamide (DMAc) as a solvent and polyethersulfone (PES) (MW= 58000 g/mol, ultrason E6020P) as the main polymer were purchased from BASF, Germany. Polyvinylpolypyrrolidone (PVP) (MW=25000 g/mol, Merck Germany) was used as a pore maker. 2-Aminoterephthalic acid as an organic ligand, zirconium chloride as a metal source, dimethylformamide (DMF) as a solvent were all supplied from Merck Germany. All chemicals were used with no further purification. In all experiments, distilled water has been used.

2.2. Preparation of modified UiO-66-NH_2 with Melamine (Mel) at room temperature

The post-synthesis modification (PSM) of UiO-66-NH2 was carried out according to our previous report (Sadeghi et al. 2017). In brief, UiO-66-NH_2 (0.1 g, 0.3 mmol NH_2) was dissolved in 6 mL DMF and sonicated for about 5 min. Cyanuric chloride or 2,4,6-trichloro-1,3,5-triazine (0.022 g, 0.12 mmol) was added into the solution and stirred at room temperature for 24 h. NH_3 (0.12 mmol) was added to the solution and stirred at room temperature for 24 h. The resulting solid was centrifuged, washed with DMF (3 ×) and methanol (3 ×), and dried at 150 °C in an oven for 5 h.

2.3. Preparation of mixed matrix membrane

For the preparation of the membrane casting solution, all chemicals were mixed together according to the compositions in Table 1. The content of PVP and PES (12 wt. %) were fixed, while different additive loadings were used.

Table 1. The casting solution composition for membrane preparation.

Membrane type	PES, wt. %	PVP, wt. %	DMA, wt. %	MOF, wt. %
M_1	12	1	87	-
M_2	12	1	86.9	0.1
M_3	12	1	86.5	0.5

Based on blending methods, three different casting solutions were prepared (i.e., bare PES and PES with 0.1 and 0.5 wt. % modified UiO 66-NH2). The solutions were stridden up for 24 h to form a uniform clear solution. The solutions were then sonicated (DT 102 H Bandelin ultrasonic, Germany) for 30 min to make sure all air bubbles have been removed. Casting knife and glassy plates were used to prepare the flat sheet membranes with a thickness of 150 µm. After pushing casting solutions, without any evaporation, the plates were put in distilled water in order to form a polymeric membrane (8-12 seconds). After that, the polymeric membranes were transferred to fresh distilled water and kept for 24 h to ensure phase inversion has been completed. For membrane drying, they were wrapped in filter paper for 24 h.

2.4. Characterizations techniques

The characteristics and morphology of the membranes were investigated by water contact angle (WCA, contact angle meter XCA-50), scanning electron microscopy (SEM, Philips-XL30, The Netherland), and the value of chemical oxygen demanded.

2.5. Membrane setup and performance

The performance of the membranes was evaluated using a dead-end setup (150 mL volume, 12.56 cm^2 effective touching surface, made of stainless steel) illustrated in Fig. 1. The setup was fitted out by nitrogen cylinder as driving force. Constant starring was applied to the cell content to avoid any polarization. At the beginning of the experiment, the pressure was set out on 4 bar, then after steady-state, it reduced to 3 bar and the data was recorded. All examinations were run at room temperature. The membrane pure water flux (PWF) was determined with a gravimetric method through Eq. 1:

$$J_{w.1} = \frac{M}{A\Delta t} \quad (1)$$

where, $J_{W.1}$ is the permeated volume (kg/(m^2.h)), M is the permeated weight (kg), A is effective membrane area (m^2), and ΔT is testing time (h). In order to measure the membrane porosity, a specific random area (2×2 cm) of each membrane was cut and weighed, and then submerged in distilled water for 24 h, and weighed again. The porosity of each membrane was determined using Eq. 2:

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times L \times dW} \quad (2)$$

Fig. 1. The dead-end setup schematic shape.

2.6. Fouling effects

For the purpose of membrane's anti-fouling properties and reusability, a milk powder solution (1000 mg/L) has been used as a good foulant (simulated protein solution). Firstly, distilled water was tested for a total time of 60 minutes, then the milk powder solution was examined for 90 minutes. After this step, the membrane was washed and kept in distilled water for 15 min and then the second examination was feed again for 60 minutes (distilled water–milk powder–distilled water). The flux recovery ratio (FRR) was determined with Eq. 3:

$$FRR = \left(\frac{Jw2}{Jw1}\right) \times 100 \quad (3)$$

In connection to exact evaluation, different types of resistances, e.g., total, reversible, and irreversible resistance have been calculated based on the following equations, total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}):

$$R_t(\%) = (1 - \frac{j_p}{j_{w.1}}) \times 100 \quad (4)$$

$$R_r(\%) = \left(\frac{j_{w.2} - j_p}{j_{w.1}}\right) \times 100 \quad (5)$$

$$R_{ir}(\%) = (\frac{j_{w.1} - j_{w.2}}{j_{w.1}}) \times 100 = R_t - R_r \quad (6)$$

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2.7. Preparation of oil-water emulsion

To consider membrane behavior in contact with oily foulants, simulated oily wastewater (diesel oil, SAF 40) were prepared with different concentrations of oil (300 and 500 mg/L). It stirred for 45 min, then sonicated for 25 min, and stirred again for 45 min to obtain a homogeneous solution. The feed was stirred (400 rpm) during the examination to inhabit the concentration polarization.

2.8. Oil rejection

The oil rejection ratio was evaluated using a chemical oxygen demand (COD) method (Rice et al. 2012):

$$R\% = (1 - \frac{C_P}{C_F}) \times 100 \quad (7)$$

where, C_p and C_f are the oil concentration in permeate and feed, respectively.

3. Results and discussion

3.1. Characterization of the MOFs

The FT-IR spectra of UiO-66-NH_2 and the modified UiO-66-NH_2 are represented in Fig. 2. It revealed peak characteristic of N-H stretching, C=O stretching, C-O stretching in 3400, 1650, 1257 (and 1160 cm^{-1}), respectively. The Zr-O band can be seen in 660-590-480 cm^{-1} (Sadeghi et al. 2017).

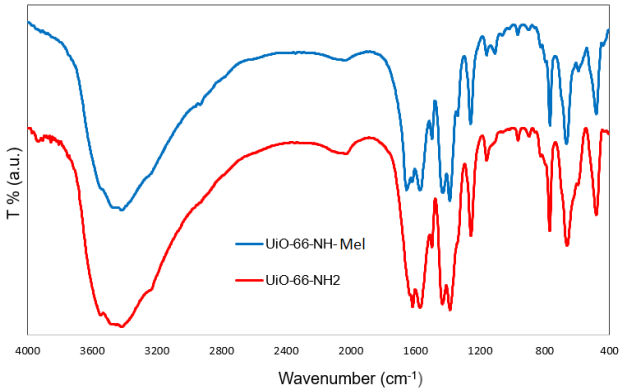

Fig. 2. FTIR spectra of MOF and modified MOF.

3.2. Membrane hydrophilicity and pure water flux

It is known that by adding hydrophilic nanoparticles, the water contact angle (WCA) of membranes is decreased. As shown in Fig. 3, the WCA decreased from 79.8° to 68.98° by adding the modified MOF (M2). Flux is one of the main characters of membrane performance. In the presence of the modified MOF, a notable increment in the flux was observed due to the hydrophilic nature of the MOF. In higher additive percentages (M3), the flux showed a reduction trend because of undesirable agglomeration of the MOF particles.

3.3. Morphology analysis

Fig. 4 illustrates the SEM cross-section images of the membranes film. A notable difference in the membrane textures is related to the compositions and quantity of the components in the membranes. Moreover, the formation of a dense top layer and spongy sublayer is due to the presence of the MOF. By the addition of a hydrophilic additive to the PES polymer matrix, hydrogen bonding formed between the additive and the matrix prevented the fast migration of the additives to the top layer during the phase inversion. It also created a porous sublayer due to the existence of the porous additive. In higher additive loading (M3) agglomeration plays a major role in the formation of the porous sublayer.

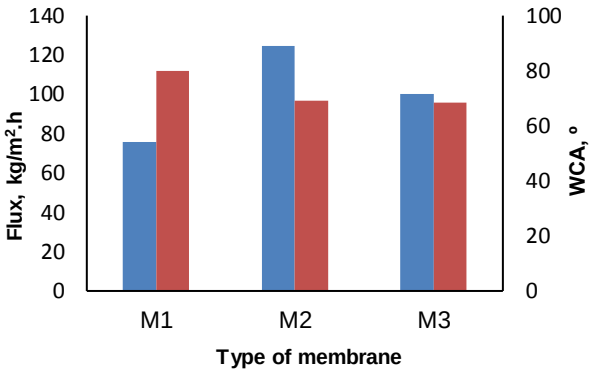

Fig. 3. The pure water flux (PWF) and water contact angle of the prepared membranes.

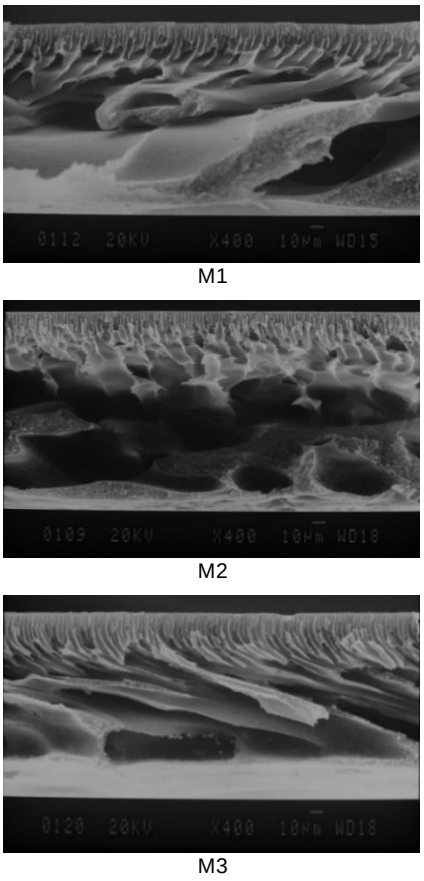

Fig. 4. The SEM cross-section of prepared membranes.

The effect of additives on the porosity of the membrane can be seen in Fig. 5. A higher porosity was observed for the membrane with optimal additive loading (M2), while in higher loading (M3) the agglomeration caused pore blocking and flux reduction.

3.4. Fouling behaviour

The fouling behavior was studied by three-frequent step, i.e., distilled water-milk powder solution-distilled water (Fig. 6). The most interesting finding was observed for the modified membranes (M2 and M3), which showed the most self-cleaning ability against fouling, in comparison with the bare membrane. In order for precise evaluation of these behaviors, the FRR results are represented in Fig. 7. The most anti-fouling property and recovery ability in M2 are related to the existence of additives in the membrane matrix. By introducing a higher amount of additive, the FRR was decreased due to the agglomeration.

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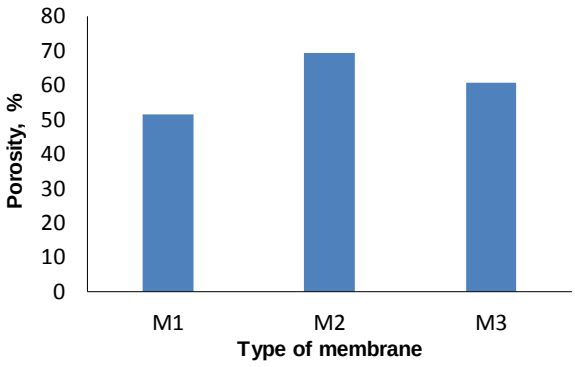

Fig. 5. The porosity of the prepared membranes.

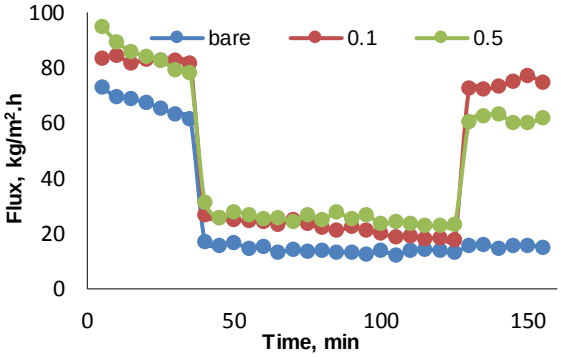

Fig. 6. Three frequent analyze (distilled water, milk powder solution, distilled water).

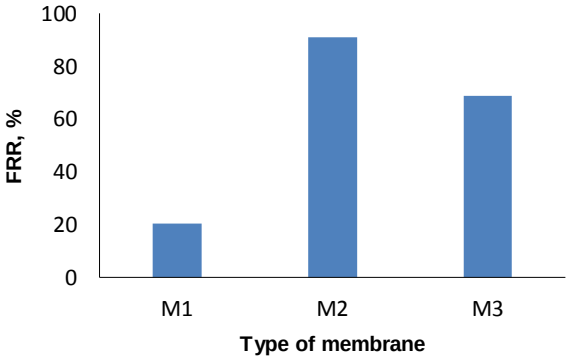

Fig. 7. The FRR results of the membranes.

3.5. Oil test in different concentrations

Fig. 8 is illustrates the simulated oily wastewater separation in different concentrations (300, 500 mg/L) as it can be obtained from the graph pure water flux reduction for optimal membrane (0.1 wt. % M_2) was about 8 % and for 0.5 wt. % was 58 %. This can be explained as good dispersion of NPs on membrane matrix and hydrophilicity improvement, caused hydrophobic against rejection (COD removal 96.2 %).

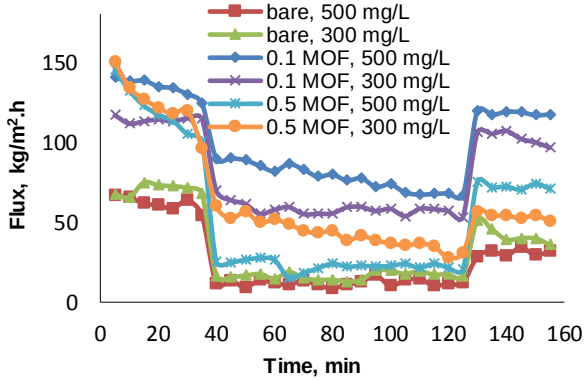

Fig. 8. Three-frequent step for the membranes in different feed concentrations.

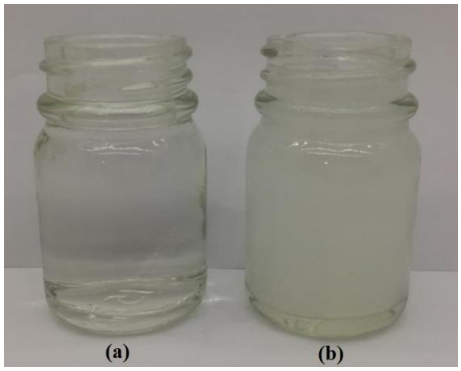

Fig. 9. The feed and permeation solution for the optimal modified membrane (a: permeated solution, b: feed solution (500 mg/L).

4. Conclusions

In this study, blended modified MOF to the membrane matrix, showed notable improvement in the membrane behavior and performance. The optimal value of the MOF was found to be 0.1 wt. %. The optimally modified membrane exhibited high PWF (124.73 kg/m^2.h) and high antifouling ability resulting from the embedded hydrophilic porous additive. Moreover, significant improvement in the long-term filtration performance observed for the membrane with modified MOF. Further studies can be helpful to establish an accurate formulation for the composite membrane in the purification of oily wastewater.

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