

# Mixed-Matrix Membranes Containing Metal Organic Frameworks (MOFs) for Separation of Dyes and Heavy Metals from Water

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## A-R-T-I-C-L-E-I-N-F-O

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## A-B-S-T-R-A-C-T

**Background & Aims of the Study:** In this study, Metal Organic Frameworks (MOFs) were synthesized as an additive for the preparation of mixed-matrix membranes. MOFs were investigated by FTIR, XRD and FE-SEM techniques.

**Materials & Methods:** Synthesized MOFs were prepared via the hydrothermal method. The effect of MOFs on the morphology and property of the polyethersulfone (PES) membranes was examined using scanning electron microscopy (FE-SEM). The membranes were characterized by rejection of salt solutions, removal of heavy metals and dyes rejection.

**Results:** Results show that membrane containing 5 wt% of MOFs provides better hydrophilicity, flux, antifouling and rejection properties and change on the aforementioned characteristic properties was studied for this membrane. The results suggested that the water flux of membrane increased to 190 L.m<sup>-2</sup> h<sup>-1</sup> which related to 7 wt% membrane as well as the highest rejection for different heavy metals and dyes were related to 5 wt% MOFs in mixed matrix membranes.

**Conclusion:** Based on the results, hydrophilicity, water flux, and antifouling properties were improved by hybrid membranes.

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## Background

Environmental contamination of water with heavy metals and dyes is a source of mounting concern for global public health, (1). To minimize the amount of metals released into the environment, the development of selective solid-phase sorbents is an essential pursuit for industrial applications and environmental remediation (2). Polymeric membranes are more effective, environmental friendly and energy saving technique in separation technology (3-11). Various types of polymeric membranes have been developed for gas and liquid separation (12-24). Polyethersulfone has many attractive properties as, it is a high-T<sub>g</sub> (glass-transition temperature) polymer of high mechanical, thermal and chemical resistances and shows wide range of tolerated pH, physiological neutrality and can be used for food, water and medical applications (25). Besides having many advantages, polyethersulfone (PES) membranes have a major drawback of fouling when used in water treatment, which leads to deposition of particles on the surface or in membrane pores leading to its fouling and consequently to reduced flow and membrane lifetime (26). Introducing hydrophilic nanoparticles into PES material through common blending method has demonstrated another strategy to enhance the hydrophilicity of PES membranes (27).

MOFs are branch of materials having many virtues such as thermal stability, discrete ordered structure, ultra-low densities, large internal surface area extending beyond 6000 m<sup>2</sup>/g, ease of synthesis and with broad-spectrum of properties suited for physical and chemical applications (28). The synthesis of metal-organic frameworks (MOFs) has attracted immense attention during the last two decades due to the possibility to obtain a large variety of aesthetically interesting structures that could also be of great interest for applications in a number of fields related to porous materials (29-

32). Metal-Organic Frameworks (MOFs) is gaining much more interest as nanofiller because of its high surface area and multiple potential applications (33). Because of the easy synthesis and low regeneration cost related to the usual physisorption mechanism, porous metal organic frameworks (MOFs) that adsorb heavy metals have received increasing attention in recent years in water purification (34,35). MOFs have emerged as an extensive class of crystalline materials with high porosity in nature. Precipitation process is a conventional method for removal heavy metals and others metals from aqueous solutions, while the most useful technique is filtration with membranes (36). The modifying agent added to the polymer solution includes surfactants, mineral fillers, or nonsolvent (37). These substances were added to increase hydrophilicity, increase or decrease the number of generated macropores, and increase the number of pores and improve connections between them (38,39).

**Aims of the study:** In this study, the MOFs was synthesized via the hydrothermal method and the structure, was characterized by X-ray powder diffraction (XRD), Field-Emission Scanning Electron Microscope (FESEM), and Fourier transform infrared spectroscopy (FTIR). Then, the effect of MOFs dispersed in the mixed matrix membrane on the membrane performance, the matrix structure and surface hydrophilicity was investigated by FESEM. In this research, a MOF-PES membrane for removal of hazardous materials such as Hg, Pb, Cd, Cr, Methylene blue, and Methylene orange is presented.

## Materials & Methods

### Materials

Terephthalic acid (H<sub>2</sub>BDC) was purchased from Merck. Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, Polyethersulfone (PES, Ultrason® E 6020 P) was supplied by Sigma-Aldrich. Methanol (synthetic grade, Merck, Mumbai) was used as received, N-methylpyrrolidone (NMP), N,N-

dimethylformamide (DMF), acetone, were purchased from Dae Jung, South Korea. Bovine serum albumin (BSA) was supplied by Sigma-Aldrich. Doubly distilled water was made in the laboratory and was used throughout the experiments.

### Characterizations

FTIR spectra were acquired using a QF-510A spectrophotometer in the range of 500–4000  $\text{cm}^{-1}$  to analyse the functional groups. Field Emission Scanning Electron Microscope (FE-SEM) images was obtained to study the surface structure, cross-section and morphology of prepared nanocomposite membranes a using HITACHI S-4160, operating 30kV. All samples were fractured in liquid nitrogen and then coated with a thin gold layer.

### Preparations of functionalized MOFs

Synthesized MOFs was prepared via the hydrothermal method.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.321 g, 1 mmol), terephthalic acid (H2BDC, 0.490 g, 1 mmol) were dissolved in 20 mL DMF at room temperature. The mixture was transferred into a

50 mL Teflon-lined autoclave, which was sealed and maintained at 120 °C for 24 h. The reaction mixture was allowed to cool to 25 °C, and washed several times with methanol.

### Preparations of the membranes

Flat-sheet polyethersulfone (PES) membranes were prepared by phase inversion technique. In this study, various ratios of MOFs (3 wt%, 5 wt%, 7 wt%) were used as additives. They were added to N-methyl-2-pyrrolidone (NMP) and stirred vigorously to provide a homogeneous solution. Polyetherulfone was then added to prepare a casting solution. Polyethylene glycol (PEG) was used as pore forming agent (10 wt%). The composition of the membranes and their abbreviations are listed in Table 1. These solutions were flatted on smooth glass plate by doctor blade with 200  $\mu\text{m}$  thickness. The casting film was immediately immersed into non-solvent (usually distilled water bath) and kept there for 24 hour until most of the solvent was removed.

Table 1) Compositions of casting solution for PSf membrane with MOF 1-NH<sub>2</sub> as additive

Sample	Polyethersulfone membrane (wt%)	PEG (wt%)	NMP (wt%)	MOFs (wt%)
at PES	18	10	72	0
3 wt%-MOFs	18	10	69	3
5 wt% MOFs	18	10	67	5
7 wt% MOFs	18	10	65	7

### Pure water flux

Pure water flux measurements were carried out by loading the membranes in a batch type, dead-end cell at a pressure of 0.5 MPa. A membrane with an effective surface area of 7.065  $\text{cm}^2$  was used as sample. Nitrogen gas was utilized to force the water through the membrane. Water flux was determined on the basis of permeate mass divided by effective surface area and filtration time, in  $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  unit. The water flux was calculated by the following equation (1):

$$J = \frac{V}{A \times t} \quad (1)$$

Where J is the permeation flux of the membrane for pure water ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ), V is the permeate volume measured (L), A is the effective membrane area ( $\text{m}^2$ ) and t is the permeation time (hour).

### Heavy metals and dyes removal

The membranes were characterized by rejection of salt solutions, removal of heavy metals and dyes rejection. The separation performance tests were carried out with a 50 ppm of heavy metal ( $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{HgCl}_2$ ) under 0.5 MPa operating pressures. The methylene blue (MB) and methyl orange (MO) rejections

were recorded using a UV spectrophotometer PG (china) with 1 cm quartz cell. The concentration of metal ions in the aqueous solutions was determined using a Shimadzu AA-670 atomic absorption spectrophotometer with a hollow cathode lamp using an air-acetylene flame.

The rejection R (%) was calculated by using equation (2):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

Where  $C_p$  and  $C_f$  are the concentration of permeate and feed solutions, respectively.

### Antifouling properties

Dynamic fouling test for the prepared membranes was conducted using, bovine serum albumin (BSA) solution in PBS (100 ppm, 50 mM, pH=7) buffer. Each membrane was pressed for an initial 20 min at 0.4 MPa. Pure water flux of the membrane,  $J_{w1}$  ( $L.m^{-2}.h^{-1}$ ), was determined over a period of 1 minute. After that, BSA was fed inside cell to be passed through the membrane for 30 minute. Then the membrane was washed with water and pure water flux  $J_{w2}$  ( $L.m^{-2}.h^{-1}$ ) was measured again. Finally, the membrane antifouling property was determined which named flux recovery ratio (FRR) according to Equation (3):

$$FRR(\%) = \frac{J_{w2}}{J_{w1}} \times 100 \quad (3)$$

To assess static protein adsorption of the membranes, surface of samples washed with phosphate buffered saline (PBS) solution for 2 hour and then put into tubes filled with BSA in PBS solution (5 ml of 100ppm). These tubes were put on water bath for 24 hour at 30°C to reach equilibrium. The amount of protein adsorbed on the membrane was calculated by adsorption intensity of solutions at 280 nm (recorded by a UV-Vis spectrometer).

## Results

Figure 1 indicates the IR spectrum of the synthesized Zn-BDC. Also, the XRD patterns for zinc MOFs are presented in Figure 2.

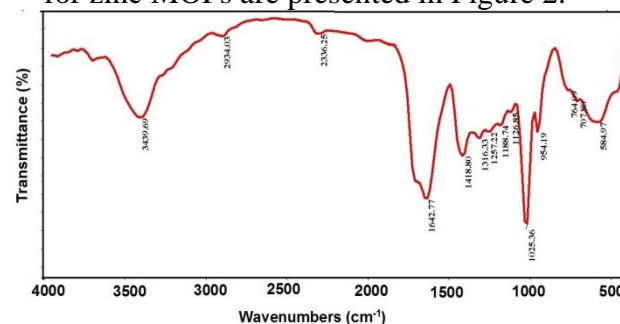


Figure 1) FT-IR spectra of MOFs

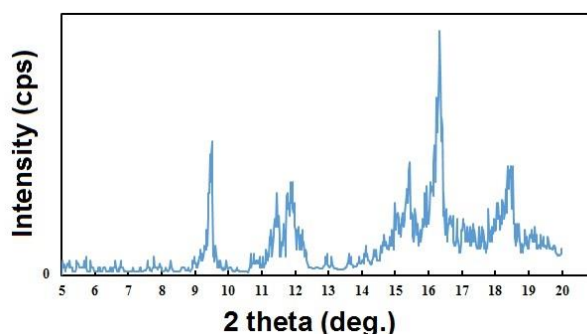


Figure 2) XRD diagrams for the prepared MOFs  
Scanning electron micrograph of MOFs is presented in Figure 3. Scanning electron microscopy is a technique that enables the study of the microstructure of nanoparticles of matter.

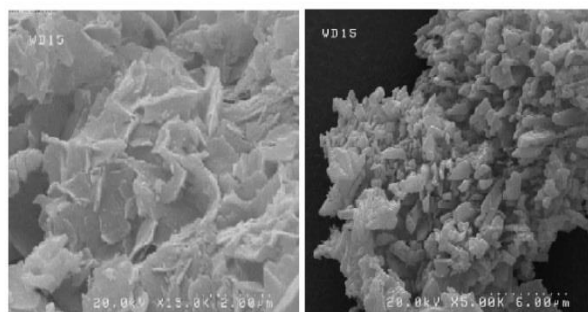


Figure 3) FE-SEM images of the MOFs  
To study the effect of MOFs on morphological changes of the membranes, the cross-sectional morphology was characterized using FE-SEM as shown in Figure 4. The effect of additive content on the membrane structure has been investigated using SEM analysis.

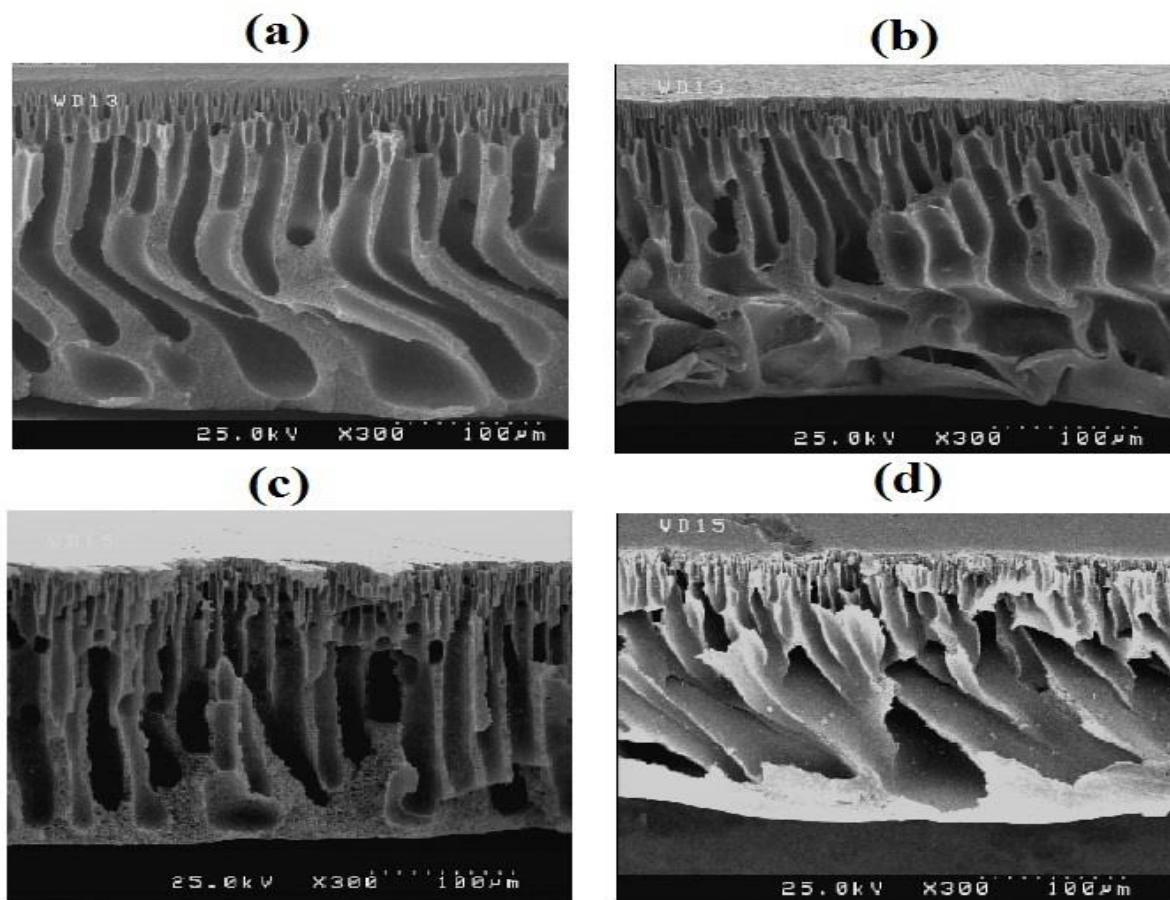


Figure 4) FE-SEM images of the cross section of membrane Neat (a), 3 wt% (b), 5 wt% (c), 7 wt% (d) from additive according to Table 1.

The permeated water flux through unmodified and modified membranes are shown in Figure 5 for different contents of additive to understand the effect of additives on membrane permeation, and mass transfer. It is seen that the highest mass transfer flux has been obtained for the membrane prepared with 7 wt. % of additive.

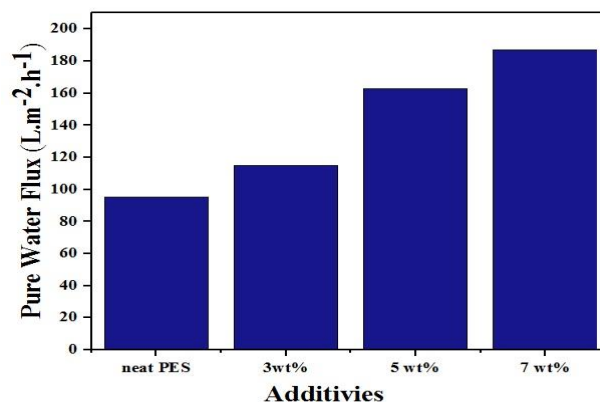


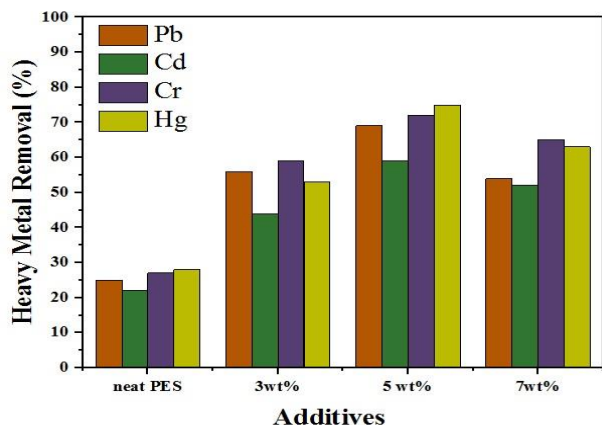
Figure 5) The pure water flux of PES composite membranes containing different percent of MOFs as additive in 5 bar pressure operating.

The fouling properties of the prepared membranes as well as the effect of MOFs percentage on flux recovery ratio, and adsorption intensity are listed in Table 2.

**Table 2) Flux recovery ratio (FRR) and static protein adsorption for the prepared membranes**

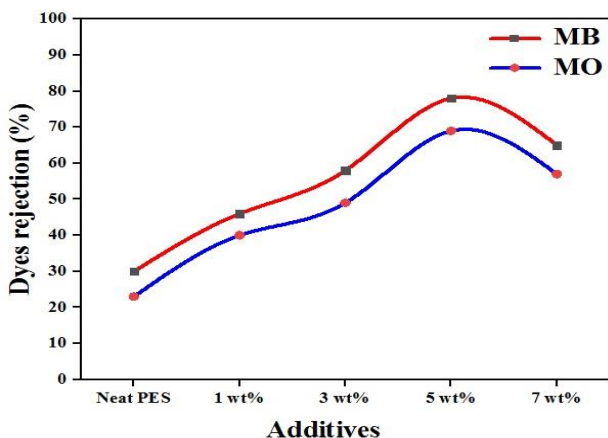
Membrane	$J_{w1}(L.m^{-2}.h^{-1})$	$J_{w2}(L.m^{-2}.h^{-1})$	Flux recovery ratio (%)	adsorption intensity (UV)
Neat PES	95.8	41.6	43.4	0.071
3 wt.% MOFs	115.6	85.2	73.7	0.079
5 wt.% MOFs	160.1	125.3	78.3	0.087
7 wt.% MOFs	189.7	134.2	70.8	0.082

The efficiency of membrane processes in removing of  $Pb^{+2}$ ,  $Cd^{+2}$ ,  $Cr^{+2}$  and  $Hg^{+2}$  from wastewater are represented in Figure 6.



**Figure 6) Performance of membrane in rejection of Heavy metal solutions including  $Pb^{+2}$ ,  $Cd^{+2}$ ,  $Cr^{+2}$  and  $Hg^{+2}$ .**

Figure 7 depicts the dye removal efficiency of the membranes for methylene blue (MB) and methyl orange (MO) organic dyes solution as a function of additive percentage.



**Figure 7) Dye rejection including (MO and MB) by unmodified and modified PES membranes.**

## Discussion

## Structural analysis

According to Figure 1, the IR spectrum of the synthesized Zn-BDC is dominated by the bands associated with organic part. In the paddlewheel structure, the carboxylate ion is coordinated to two Zn atoms and made a unit cell of crystal. The intense bands at  $1418.80\text{ cm}^{-1}$  appear in the spectrum which confirms the paddle-wheel type unit of MOF. IR spectra of MOF-5 show the expected strong characteristic adsorptions for the symmetric and asymmetric vibrations of BDC ( $1642.77$ ,  $1025.36$  and  $1418.80\text{ cm}^{-1}$ ) and adsorbed water ( $3,500\text{--}3,200\text{ cm}^{-1}$ ) (40).

X-ray diffraction (XRD) is an effective method to investigate crystalline properties of a synthesized material. According to Figure 2, the extremely high intensities of the diffraction peaks indicate the good crystallinity of sample. The peak of highest intensity in image at  $2\theta = 5.5^\circ$  is indexed as the d200 for zinc metals (40, 41). The SEM micrograph (Figure 3) show distribution of particles in MOFs as clusters of irregular shaped flakes arranged as flower-like clusters. SEM of MOFs, Figure 3 at the magnifications shown, show irregular flake particles. A high magnification Figure 3 confirm these flakes-like particles having irregular shapes (42).

## Membrane morphology

As shown in Fig. 4, a finger-like structure was formed when NMP/water was used as the solvent/nonsolvent pair with PES. The hydrophilic nature of MOFs increased the mass transfer rate between the solvent and the nonsolvent during phase inversion process and led to the formation of larger pore channels. This further demonstrated that addition of MOFs changed the structure of membrane. Gradually, it can be said that the presence of a large amount

of MOFs caused a remarkable hydrophilicity improvement in the prepared membranes and increased permeation rate of water molecules into the cast solution.

### Membrane Performance

#### Pure water fluxes

The achieved improvement in hydrophilicity (discussed later) was due to the presence of MOFs. As shown in Figure 5, water flux through unmodified and modified membranes were changed by increasing MOFs as an additive up to 7 wt%. For 5 bar pressure, the maximum and minimum rates of pure water flux was observed in 7 wt% MOFs and neat PES, respectively. This behavior could be explained in this manner which by increasing of polymer concentration in membrane formulation, the pore size of membrane decreased strongly. On the other hand, addition of MOFs amount in membrane causes larger channels, more porosity and subsequently makes them more hydrophilic in nature (43).

In this study, the fouling properties of membranes and the effect of MOFs on fouling, the dynamic fouling analysis (flux recovery ratio), static fouling analysis (surface protein adsorption) and rejection tests were done for prepared membrane. (Table 2). It was found that, the flux recovery ratio (FRR) increased from 43.4 % to 78.3%, when weight percent of MOFs increased from 0 to 5 wt.%, while for membranes with 7 wt.% MOFs obtained FRR (%) was 70.8%. This finding can be related to different parameters such as surface hydrophilicity and roughness. Surface roughness can play a key role due to protein molecules irreversible deposition into the surface pores. Static protein adsorption on the membranes surface decreased, which is in good agreement with FRR results and only a decrease was observed for membrane with 7 wt.% MOFs likely due to surface roughness which caused more adsorption of BSA.

The initial concentration of the used heavy metals for these experiments ( $\text{Pb}(\text{NO}_3)_2$ ,

$\text{Cd}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_2$  and  $\text{HgCl}_2$ ) was 50 ppm of metal ions. The percentage of heavy metal rejection improved by increasing additive (MOFs) from 0 to 5 wt%, while with further increase of MOFs in the membrane matrix, the removal of heavy metals decreased (see Figure 6). As mentioned in the previous section, two parameters (pore size and the extent of interaction between metal ions and functional groups on the MOFs surface) acted in the opposite direction (44). Therefore, it can be argued that the initial increase in rejection was due to more and stronger interactions; however, at higher percentage of additive, strengthening of the pore size is weakened the interactions effect, thus rejection of heavy metals decreased. The rejection of dyes was measured using a lab scale nanofiltration cell (operating pressure= 0.5 MPa, pH=7.0 and the dye concentration= 100 mg/L). As it can be observed in Figure 7, the MO rejection was more than the MB for all of the prepared membranes. As shown in Figure 7, the rejection performance in all of the MOFs modified membranes was better than the neat PES membrane that confirmed the effective filtration performance of the prepared nanocomposite membranes. The better rejection efficiency of the modified mixed matrix membranes can be related to the repulsion forces between negative surface of the membranes and negatively charged surface in the dye molecules (45). In other words, it can be concluded that rejection was improved by addition of MOFs to 5 wt.% and then decreased which could be related to contrast between pore size and the extent of interactions. The prepared mixed matrix membranes were negatively charged due to the presence of several carboxylic functional groups from MOFs additive. Increasing MOFs additive concentration from 1 wt.% to 5 wt.% improved dye removal while higher percentage of MOFs decreased removal efficiency slightly. This may be due to an increase in surface negative charge by MOFs to 5 wt% but higher percentage of MOFs increased the pore diameter

of the membrane and reduced removal efficiency. The results were in agreement with heavy metal removal and the highest dye removal was observed for the sample with 5 wt% MOFs additive concentration.

## Conclusion

In this study, metal organic frameworks (MOFs) was synthesized via the hydrothermal technique. This MOFs as additive was incorporated to the mixed matrix membrane. The surface and cross-section morphology of MOFs and the neat and the modified membranes were investigated by FE-SEM. Effect of MOFs on the performance's properties (heavy metals and dye removal) was investigated. Base on the results, hydrophilicity, water flux, and antifouling properties were improved by hybrid membranes. Addition of MOFs also improved the rejection of heavy metal and dyes more efficiently than neat PES membrane and membrane with 5 wt.% of MOFs suggested better properties. Additionally excellent heavy metal separation behavior was observed among rejection tests.

## Footnotes

### Conflict of Interest:

The authors declared no conflict of interest.

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