Polyethersulfone Membranes Prepared with 3-Aminopropyltriethoxysilane Modified Alumina Nanoparticles for Cu(II) Removal from Water

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ABSTRACT: In this study, 3-aminopropyltriethoxysilane (APTES) modified γ-alumina nanoparticles were utilized to improve the copper removal efficiency of polyethersulfone (PES) membranes. Alumina nanoparticles were first modified by APTES silane coupling agent before impregnating into PES composite membranes. The PES membranes were fabricated by incorporating three different amounts of modified nanoparticles by a phase inversion process. The prepared membranes were characterized using field emission scanning electron microscopy, Fourier transform infrared, X-ray diffraction, thermogravimetric analysis (TGA), dynamic mechanical analysis, water contact angle, water flux, and porosity measurements. The Cu(II) removal and adsorption capacity of the membranes were also analyzed. The addition of nanoparticles increased the thermal stability, hydrophilicity, total porosity, Brunauer–Emmett–Teller surface area, and glass transition temperature of the membranes. TGA confirmed a suitable uptake of the nanoparticles during the membrane fabrication process. The water permeation of the membranes also increased significantly. Membranes synthesized with 4 wt % nanoparticles showed the highest rejection for copper ions of 87%. Adsorption isotherms were tested using Langmuir and Freundlich models, where the Freundlich isotherm model resulted in the best fitting.

1. INTRODUCTION

Heavy metal ions are among the most dangerous water pollutants, even at low concentrations. Although copper is considered to be a vital micronutrient for humans, excess accumulation of copper in the human body poses a dangerous health risk and may cause headache, depression, nausea, learning problems, and kidney and liver damage.1,2 Currently, several physiochemical and biological approaches, such as precipitation, coagulation, adsorption, ion exchange, biological treatment, and membrane processes, are employed to remove heavy metals from polluted waters.3 Among these methods, adsorption is the most widely used mechanism because of its high effectiveness, low cost, and versatility.4,5 Nanostructured materials, usually in the form of inorganic nanoparticles, are known as efficient adsorbents because of their high specific surface area and high chemical affinity toward heavy metals.6 However, difficulty in regeneration and separation of nano-adsorbents from treated water remains a challenging issue.4,7 Incorporating nano-adsorbents into porous polymeric materials has been shown to be a promising approach to address the aforementioned issue and improve the removal efficiency of the membranes.7–9 The membranes themselves might also act as the auxiliary adsorbent in enhancing the overall adsorption capacity.7

Different types of nanoparticles have been utilized to improve the heavy metal ions removal performance of membranes,10 of which metal oxide nanoparticles have shown the most promising results.11–13 Metal oxide nanoparticles, such as MnO2,11 ZrO2,14 and Fe3O4,1,9,12,15 have been extensively utilized to synthesize nanocomposite membranes in order to improve the membrane performance for the removal of heavy metal ions from water. Among these nanoparticles, aluminum oxide (alumina) is one of the most promising adsorbents because of its high affinity toward heavy metal ions in aqueous solutions.4,16–18 A majority of the research on impregnating polymeric membranes with alumina nanoparticles has been focused on flux improvement and fouling mitigation.14,19–21 Although many studies investigated the use of alumina nanoparticles in polyethersulfone (PES) membranes for the removal of contaminants, such as dye and nitrate,22–24 only few studies investigated the use of alumina/PES membranes for the removal of heavy metal ions from water.7

Recently, the incorporation of modified nanoparticles into polymeric materials has attracted great interests. One common...
method to modify the nanoparticles is treating them by silane coupling agents, such as methacryloxy methylendemethyl diethoxysilane and 3-aminopropyltriethoxysilane (APTES).\textsuperscript{25,26} Silane coupling agents are extensively used in inorganic polymer composites such as mineral-filled polymer composites.\textsuperscript{27,28} Choosing the appropriate silane group can modify the surface of an inorganic material from hydrophilic to hydrophobic, increase its affinity to the functional groups of the polymer matrix,\textsuperscript{29,30} and decrease the agglomeration of nanoparticles.\textsuperscript{31}

In this study, alumina nanoparticles, treated by APTES, are used to fabricate novel PES membranes to remove Cu(II) ions from water. The morphology and physiochemical properties of the modified nanoparticles and membranes were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), dynamic mechanical analyzer (DMA), porosity, and water contact angle (WCA). The performance of the membranes was tested in terms of Cu(II) ion removal from water as well as pure water flux (PWF) measurements.

2. RESULTS AND DISCUSSION

2.1. IR Spectroscopy (FTIR). The modification of alumina with APTES occurs by the reaction of the hydroxyl groups of Al$_2$O$_3$ nanoparticles with the silane functional group of APTES.\textsuperscript{25} To investigate the modification efficiency of the nanoparticles, FTIR spectroscopy was used. The IR spectra of nonmodified γ-alumina nanoparticles and APTES modified nanoparticles are shown in Figure 1.

The broad adsorption peak in the range of 980−1220 cm$^{-1}$ corresponds to Al−O−Si and Si−O−Si bonds of the silane coupling agent. The frequency of Al−O−Al bonds in the alumina structure is also in this range.\textsuperscript{27} The wide peak in the range of 3000−3550 cm$^{-1}$ can be assigned to O−H bond and adsorbed water on Al$_2$O$_3$ surface.\textsuperscript{25,27,32} APTES modified nanoparticles display two additional bands at 1600 and 2950 cm$^{-1}$. The peak at 1600 cm$^{-1}$ can be attributed to the N−H vibrations, indicating the presence of R−NH$_2$ groups at the surface of modified nanoparticles.\textsuperscript{32} Also the peak at 2950 cm$^{-1}$ can be assigned to C−H stretching vibrations.\textsuperscript{33} These results confirm the presence of the silane coupling agent at the surface of the treated nanoparticles.

2.2. Membrane Characterization. The presence of alumina nanoparticles in the membrane structure was confirmed by XRD analysis. The XRD spectra of neat PES membrane and PES/alumina nanocomposite membranes are shown in Figure 2. As it can be seen, the PES polymer is primarily amorphous and shows one main peak at 2θ = 18.2°, which is similar to the reported peak for pure PES.\textsuperscript{34} For the alumina/PES nanocomposite membranes, two new peaks at 2θ = 46° and 68° were observed. These peaks are characteristic of γ-alumina.\textsuperscript{35} This proves the presence of γ-alumina nanoparticles in the PES membrane matrix. These results show that the γ-alumina nanoparticles have been distributed into the polymer matrix, and also, with the addition of nanoparticles, the nano-enhanced membranes remained amorphous.

The glass transition temperature of the membranes (T$_g$) was measured using a DMA. The glass transition temperature depicts the transition of the polymer from glassy behavior to rubbery state, which results in a considerable decrease in the stiffness of the polymer.\textsuperscript{36} The T$_g$ of the membranes can be determined from the peak of the loss modulus. As it can be seen in Figure 3, adding nanoparticles into the polymer membranes shifts the maximum peak of the loss modulus to higher temperatures. For the neat polymeric membrane (M 0), the glass transition temperature was determined as 218 °C. The nanocomposite membranes showed significantly higher glass transition temperatures, which were 224, 233, and 244 °C for M 3, M 4, and M 5 samples, respectively. The presence of the modified nanoparticles in the polymer matrix makes interfacial strong bonds between the polymer matrix and the nanoparticles and also restricts the movement of the polymeric chain.\textsuperscript{36} This explains the increase in the glass transition temperature by incorporating nanoparticles.

Thermogravimetric analysis (TGA) was used to confirm the distribution of the alumina nanoparticles and evaluate the thermal stability of the fabricated membranes. Figure 4 shows the TGA curves for neat polymeric and composite membranes. TGA curves for the composite membranes show a small shift compared to neat PES membranes, which indicates that the thermal stability of PES membranes containing alumina nanoparticles was enhanced. The residual weight ratios for...
M 3, M 4, and M 5 samples are 9.8, 14.2, and 17.5%, respectively. Comparing the residual weight ratios with the nominal concentration of nanoparticles in the membranes, that is, 14% (M 3), 18% (M 4), and 21% (M 5), indicates that the nanoparticles were reasonably distributed in the polymer matrix. However, some amount of alumina particles leached out to the coagulation bath during the membrane formation.

Figure 5 presents the FESEM images of the cross section of the synthesized membranes. The cross sections of the membranes show a typical asymmetric structure consisting of a thin dense layer supported by a large finger-like sublayer. Also, large macro-voids are formed beneath the finger-like pores. This structure contributes to the higher flux of the membrane while also maintaining its salutre rejection, as discussed in the following sections. In addition, it can be seen that the nanocomposite membranes contain slightly larger macro-voids in the sublayer compared to neat PES membranes, which is in accordance with the total porosity and Brunauer–Emmett–Teller (BET) surface area results (Table 2). Generally, the growth of sublayer macro-voids leads to a higher total porosity.

The total porosity, presented in Table 1, shows that the nanocomposite membranes possess higher total porosity compared to neat PES membranes. The membrane porosity increased with increasing the nanoparticle amounts in the matrix from 66% for neat polymeric membranes to 82% in the case of M 5 samples. It has been reported that the interaction between nanoparticles and the polymer solution leads to easier diffusion of solvent molecules from the polymer matrix to the coagulation bath. In addition, the diffusion rate of the

| membrane sample | porosity (%) | WCA | PWF (kg/m² h) | surface area (m²/g) |
|-----------------|--------------|-----|---------------|---------------------|
| M 0             | 68           | 69  | 29.1          | 20.6                |
| M 3             | 73           | 54  | 44.1          | 32.3                |
| M 4             | 78           | 47  | 54.3          | 35.5                |
| M 5             | 81           | 44  | 48.6          | 29.1                |
| γ-Al₂O₃          | 58.1         |     |               |                     |

Figure 5. SEM cross-sectional images of (a) M 0, (b) M 3, (c) M 4, and (d) M 5 membranes.
solvent [dimethylacetamide (DMAc)] from the membrane into the coagulation bath can also increase through the addition of nanoparticles. As a result, the nanocomposite membranes have a higher amount of total porosity as well as BET surface area compared to the neat polymeric membrane. The BET surface area of the membranes, shown in Table 2, increased from 20.6 cm$^2$/g for neat polymeric membrane to 35.5 cm$^2$/gr for M 3 samples. This can be explained by the presence and dispersion of nanoparticles with high surface area in the membrane structure. Figure 6c confirms the suitable dispersion of alumina nanoparticles in the matrix of the membranes. The uniform distribution of the nanoparticles is favorable because it increases the contact area of the passing water through the membrane and the surface of the particles, which subsequently increases the surface adsorption of the copper ions. Interestingly, M 5 samples exhibit less amount of surface area compared to M 4 and M 3 samples. This can be attributed to the agglomeration of the nanoparticles, as depicted in Figure 6b. Agglomeration may also lead to blocking of some pores in the structure and consequently lowering the available surface area of the membranes.

Contact angle measurement is a commonly used method to characterize the hydrophobicity and hydrophilicity of membranes. High contact angles indicate that the membrane is more hydrophobic and vice versa for lower contact angles. Table 1 shows the WCA of the PES membranes decreasing from 69$^\circ$ to 44$^\circ$ with increasing the nanoparticle amount in the matrix. The hydroxyl content of the membrane surface increases because of the incorporation of alumina nanoparticles into the membrane surface, leading to increased hydrophilicity of the membrane surface.

### Table 2. Equilibrium Constants of Langmuir and Freundlich Isotherms for Cu(II) Adsorption

| Membrane Sample | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_F$ (mg/g) | $n$ | $R^2$ |
|-----------------|--------------|------------|-------|--------------|-----|-------|
| M 3             | 34.01        | 0.068      | 0.972 | 6.68         | 0.426 | 0.994 |
| M 4             | 39.37        | 0.168      | 0.961 | 16.88        | 0.183 | 0.991 |
| M 5             | 44.84        | 0.401      | 0.974 | 26.99        | 0.1149 | 0.996 |

2.3. Adsorption Study. Figure 7 shows the equilibrium adsorption of Cu(II) versus time for the membranes synthesized in this work. The results show that by increasing the alumina concentration in the membranes, the adsorption

![Figure 6](image1.png)  
Figure 6. Higher magnification SEM cross-sectional image of (a) M 4 membrane showing incorporation of the nanoparticles in the polymer matrix, (b) M 5 showing the agglomeration of nanoparticles, (c) energy-dispersive X-ray map scanning spectra for the cross section of M 4 sample.

![Figure 7](image2.png)  
Figure 7. Equilibrium adsorption of the membranes as a function of time (initial copper concentration = mg/L).
capacity increases significantly. The highest Cu(II) adsorption capacity of each membrane was 18.7, 24.7, and 31.8 mg/g for M 3, M 4, and M 5 membranes, respectively. The increase in the adsorption capacity of the membranes can be attributed to the increased number of active sites for the adsorption of copper ions as a result of increasing the amount of alumina in the membranes, as well as the increased surface area of the membranes.

Langmuir and Freundlich equilibrium adsorption isotherms were applied to the adsorption data. Table 2 presents the Langmuir and Freundlich isotherm parameters for Cu(II) adsorption on the nano-enhanced membranes. Langmuir isotherm, which indicates a monolayer adsorption on homogenous adsorption sites, is expressed by eq 1

\[
q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e}
\]

where \(q_e\) is the equilibrium adsorption (mg/g), \(C_e\) is the equilibrium concentration in the aqueous phase (g/L), \(q_{\text{max}}\) is the adsorption capacity (mg/g), and \(b\) is the equilibrium constant (L/mg).

The Freundlich isotherm corresponds to a multilayer adsorption on a heterogeneous surface and is formulated by eq 2

\[
q_e = k \cdot C_e^n
\]

where \(k\) and \(n\) are the relative adsorption constant and adsorption intensity parameter, respectively. On the basis of the obtained data, the Freundlich model showed a better fit with the equilibrium data (\(R^2 = 0.99\)), which indicates a multilayer coverage and heterogeneous adsorption on the membrane surface.

2.4. Filtration Performance. The results of membrane performance to remove Cu(II) are shown in Figure 8. It can be seen that neat PES membranes exhibit the lowest amount of copper removal, whereas the membranes containing 4 wt % of alumina nanoparticles (M 4) exhibit the highest Cu(II) at 87%. The dispersed modified alumina nanoparticles in the polymer matrix act as active sites to adsorb copper ions and prevent copper ions from passing through the membrane.

However, the nanocomposite membranes with the highest content of nanoparticles (M 5) showed lower copper removal compared to M 4 because of the agglomeration of the nanoparticles, discussed earlier. Because the adsorption of the copper ions on the surface of alumina nanoparticles is the main mechanism for copper removal, dispersion of the nanoparticles in the polymer matrix plays an important role in the membrane performance. Agglomeration of nanoparticles decreases the effectiveness of the nano-enhanced membranes by decreasing the available surface area of the nanoparticles, leading to the lower rejection performance.7,12 This is in accordance with the decreased available BET surface area of the M 5 sample.

The PWF along with WCAs of the membranes are shown in Figure 9. It can be seen that the membranes with a higher amount of nanoparticles exhibit higher flux and lower WCAs. This can be explained by the combination of the increased hydrophilicity of the surface at lower surface contact angles and the higher porosity of the membranes with higher nanoparticles content. Several studies have reported an increase in water flux through the membranes because of the increased hydrophilicity, porosity, and the mean pore size of membranes incorporating nanoparticles.14,42,43 However, by increasing the nanoparticles amount from 4 to 5 wt %, the PWF decreased because of the agglomeration of the nanoparticles. Agglomeration of nanoparticles in the membranes can lead to the blocking of the surface pores and result in lower permeability in accordance with similar results reported by others.7,12,44

It should be noted that reverse osmosis and nanofiltration have been investigated and used extensively to remove heavy metal ions from water. Although these techniques are able to remove heavy metals from water very efficiently, high operational pressure, high energy consumption, and low flux are the main drawbacks of these systems.45 The developed nanocomposite membrane in this study is an attempt to mitigate these issues. The synthesized membranes combine adsorption and membrane technology, and because the pore size is bigger than nanofiltration and reverse osmosis, the operational pressure is very lower and the water flux is higher.

2.5. Reusability. The membrane with the best performance of copper removal in the filtration experiment (M 4) was

![Figure 8. Copper removal (%) from aqueous solution for PES and nano-enhanced membranes.](image1)

![Figure 9. PWF and WCA of the synthesized membranes.](image2)
chosen for the usability study. Ethylenediaminetetraacetic acid (EDTA) was utilized as a cleaning agent because it has been reported that it is able to permanently remove copper ions from membrane adsorption sites because of the high formation constant of $[\text{Cu(EDTA)}]^2\cdot 7$. As it can be seen in Figure 10, the M 4 membrane can be reused after 4 cycles with only 5% reduction of copper removal (compared to initial copper removal capability). This confirms that the performance of synthesized membranes in copper removal was not reduced significantly, even after four cycles of filtration process.

3. CONCLUSIONS

APTES modified alumina nanoparticles ($\gamma$-Al$_2$O$_3$) were incorporated in PES membranes to enhance the removal of Cu(II) ions from aqueous solutions. The morphology and performance of the nanocomposite membranes were analyzed extensively. It was revealed that by adding the modified nanoparticles to the PES membranes, the hydrophilicity, total porosity, BET surface area, thermal stability, and glass transition temperature were all improved. The combination of higher porosity and lower hydrophobicity of the membrane surface led to a significantly higher water flux. Moreover, the copper ion removal increased from 11%, in the case of neat polymer membranes, to 87% for the nanocomposite membrane containing 4 wt % of modified alumina nanoparticles. Batch adsorption studies showed that the adsorption of copper ions on the membranes fits the Freundlich model, which corresponds to heterogeneous adsorption sites.

4. EXPERIMENTAL SECTION

4.1. Materials. PES (Ultrasor E6020P, 58 000 g/mol, BASF Company, Germany) was used as the base polymer. Polyvinyl pyrrolidone (PVP) with a 25 000 g/mol molecular weight and DMAc were purchased from Sigma-Aldrich. $\gamma$-Al$_2$O$_3$ nanoparticles with a surface area of 58 m$^2$/g were purchased from U.S. Research Nanomaterials (Texas, USA). APTES was purchased from Sigma-Aldrich and was used for surface modification of $\gamma$-Al$_2$O$_3$ nanoparticles. Copper nitrate ($\text{Cu(NO}_3\text{)}_2$) was purchased from Sigma-Aldrich and was used to prepare feed solutions containing specific concentration of Cu(II). Necessary dilutions were performed with Milli-Q water having resistivity higher than 18 M$\Omega$ cm.

4.2. Surface Modification of Alumina Nanoparticles. To increase the stability of the nanoparticles in the casting solution, surface modification of alumina nanoparticles with APTES silane coupling agent was carried out. Certain amounts of alumina nanoparticles were added to anhydrous ethanol under nitrogen purging followed by 60 and 30 min bath and probe sonication. Subsequently, 4 wt % of APTES was added to the mixture under nitrogen atmosphere. After stirring for 6 h at 70 °C, the particles were separated from the solution by centrifuging at 10 000 rpm for 20 min. Finally, the Al$_2$O$_3$ particles were dried in an oven for 24 h at 50 °C.

4.3. FTIR Study. FTIR spectroscopy was used to confirm the chemical modification of alumina nanoparticles. FTIR spectra of APTES modified alumina nanoparticles and nonmodified alumina nanoparticles were measured using Bruker Eco-ATR spectrophotometer from 4000 to 400 cm$^{-1}$. Each spectrum was captured by averaging 400 scans with a resolution of 2 cm$^{-1}$.

4.4. Preparation of PES/Alumina Mixed Matrix Membranes. Table 3 shows the compositions of doped solutions prepared to fabricate nanocomposite membranes. PES flat membranes were synthesized by phase inversion via the immersion precipitation method. A homogenous mixture of alumina nanoparticles and DMAc was prepared by adding predetermined amounts of nanoparticles into the DMAc and sonication for 1 h. Afterward, measured amounts of PES and PVP were dissolved into the mixture while stirring at 400 rpm for 24 h. Finally, the solutions were mixed by an acoustic mixer for 1 h before casting.

The solutions were cast onto a glass substrate at room temperature with a thickness of 200 $\mu$m using the doctor blade technique and an automatic film applicator at a speed of 60 mm/s. The casting was subsequently moved into distilled water and stored for 24 h. The prepared membranes were washed and dried between two sheets of filter paper and subsequently vacuum dried for 24 h at 50 °C.

4.5. Static Cu(II) Adsorption Study. Batch adsorption tests were performed to calculate the static adsorption of Cu(II) ions on the PES/alumina mixed matrix membranes. Copper solutions with different initial concentrations in the range of 20–80 mg/L were prepared by dissolving Cu(NO$_3$)$_2$ in deionized water. The tests were carried out by adding 0.05 g of sliced membranes into vessels containing 100 mL of Cu(II) solutions. The vessels were then placed in a shaker and agitated at room temperature for 48 h. The equilibrium concentration of Cu(II) in the solutions was determined by a flame atomic adsorption spectrometer (ICE 3000 Thermo Fisher). The copper ion adsorption of the membranes (mg/g) were calculated by eq 3

$$q_e = \frac{(C_0 - C_e)V}{M_m}$$

Table 3. Compositions of the Casting Solutions

| membrane sample | PES (wt %) | PVP (wt %) | DMAc (wt %) | Al$_2$O$_3$ (wt %) |
|-----------------|------------|------------|-------------|-------------------|
| M 0             | 18         | 1          | 81          | 0                 |
| M 3             | 18         | 1          | 78          | 3                 |
| M 4             | 18         | 1          | 77          | 4                 |
| M 5             | 18         | 1          | 76          | 5                 |
where $q_0$ is the equilibrium adsorbed amount of copper ion per membrane weight (mg/g), $C_0$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of Cu(II) in the solution, $V$ is the volume of the copper solution (L), and $M_m$ is the mass of the membrane (g).

### 4.6. Membrane Characterization

#### 4.6.1. XRD Analysis

To determine the crystal phase composition of the alumina nanoparticles, PES, and alumina/PES membranes, XRD analysis was conducted using an Advance Bruker-D8 Discover diffractometer ($K_{a1} = 1.5406 Å$, 2θ range from 5° to 80°). The detector was LYNXEYE-XE operating at an accelerating voltage of 40.0 kV and emission current of 40.0 mA.

#### 4.6.2. Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a useful technique to measure the glass transition temperature of the membranes. Neat polymeric and nanocomposite membranes were investigated using a TA Instruments Q800 dynamic mechanical analyzer. A preload of 0.005 N was applied to keep the samples flat during the test. The membrane samples were heated at the rate of 3 °C min$^{-1}$ from 25 to 280 °C while oscillating at a frequency of 1 Hz at an amplitude of 10 μm. Glass transition temperature of the synthesized membranes were determined from the peak of the loss modulus.

#### 4.6.3. TGA Thermal Analysis

To investigate the thermal stability and dispersion of the alumina nanoparticles in the membranes, TGA was conducted under air atmosphere over a temperature range of 25–1000 °C at a heating rate of 10 °C min$^{-1}$.

#### 4.6.4. Contact Angle Measurements

The contact angle of the prepared membranes was measured using a contact angle measuring instrument (Rame-Hart goniometer model 250). Sessile droplet method and image analysis of the droplet on the surface were used to measure the equilibrium WCA. A 6 μL water droplet was deposited on the membrane surface and the contact angle was measured after 5 s. The contact angle was measured at three different points on the membrane surface and the average value was reported.

#### 4.6.5. Membrane Porosity

In order to determine the total porosity of the synthesized membranes, membrane samples were cut to a certain dimension and soaked in distilled water for 24 h. The surface of the membrane samples was wiped with filter paper and the samples were immediately weighed. After that, the membranes were dried in a vacuum oven at 50 °C for 24 h and weighed again.

The total porosity of the synthesized membranes was determined by the following equation

$$\text{Porosity (\%)} = \frac{W_w - W_d}{\rho_w \times V} \times 100$$

where $W_w$ and $W_d$ are the weights of wet and dry membranes (g), and $\rho_w$ and $V$ are water density (g/cm³) and membrane pieces volume (cm³), respectively. The results were reported as an average number of three measurements for each membrane sample.

#### 4.6.6. BET Surface Area

The gas adsorption–desorption technique was used to measure the surface area of the synthesized membranes. Nitrogen sorption analyses were obtained with a surface-area analyzer (Micromeritics ASAP 2020) using standard continuous procedures at 77.15 K on the membrane samples that had been degassed at 333 K under a high vacuum for 6 h. The surface area was calculated according to the BET model over a relative pressure range of 0.05–0.90.

#### 4.6.7. Scanning Electron Microscopy

FESEM (Hitachi, S-8400) was used to analyze the morphology of the membranes. In order to minimize the stress on the sample and prevent deformation of the membrane cross section and pore structure during fracturing, a modified freeze fracture method (Cryo-snap method) was used to break the samples. In this method, the specimen is embedded into ice before breaking. The dried cut samples were iridium sputtered and were investigated under the microscope at 5 kV.

#### 4.6.8. Filtration Process

Water flux of the membranes was measured using a batch-type dead-end stirred cell (Millipore, UFSC05001) at a fixed speed of 400 rpm. The effective area of the membrane in the filtration cell was 13.4 cm². Prior to the water flux determination, the membrane sample was first pressurized at 4 bar for 1 h to minimize compaction effects. After compaction, transmembrane pressure was set to 3.5 bar and the permeate flux was calculated by eq 5

$$\text{Pure water flux (kg/m² h)} = \frac{Q}{A \times \Delta t}$$

where $Q$, $A$, and $\Delta t$ are the quantity of permeate (kg), membrane area (m²), and sampling time (h), respectively.

In order to evaluate the membrane performance in removing Cu(II) from water, feed solutions containing initial Cu(II) concentration of 20 mg/L were employed. The permeate was collected every 10 min and its concentration was measured. Copper ion removal was calculated using eq 6

$$\text{Copper removal (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where $C_p$ and $C_f$ are the copper ion concentrations (mg/L) in the permeate and feed, respectively.

#### 4.6.9. Membrane Usability

The membrane with the best performance was chosen for reusability test. The membrane used for copper removal test was regenerated by dipping and stirring for 1 h in the 10 mM EDTA solution. Then the membrane was washed with plenty of deionized water and reused for the filtration test. This procedure were repeated four times with the duration of 100 min for each filtration cycle.

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**Notes**

The authors declare no competing financial interest.

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