Copper Ions Removal by PSF-Si Spiral Wound Membranes of Different Porosity

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Abstract. Effluent discharged from various industries is one of the point sources of pollutions that affect the water quality. The effluent contains a high concentration of hazardous compounds of metal ions. Membrane technology using ultrafiltration membrane had proven successful in treating physical and organic impurities from water and wastewater. The importance of this study was to clarify the effectiveness of additive concentration in nanofiltration membrane for heavy metals removal. The physicochemical characteristics and copper ions removal efficiencies were determined for a different amount of silica extracted from sugarcane bagasse as an additive added to polysulfone polymer membranes. The PSF-Si membranes were fabricated via the phase inversion technique. The results show that silica in the formulation and fabrication of polysulfone membrane gives added value to membrane porosity, water content, and hydrophilicity. The most effective membrane in removing copper ions was the membranes with the lowest silica content, which is PSF-21 Si-2. The PSF-21 Si-2 membrane is hydrophilic, attracts a large amount of water, and gives a pure water flux of 56 L/m²hr to pass through the membrane. Moreover, the copper rejection increased from 92% to 98% as the copper concentration increased for the best membrane formulation PSF-21 Si-2.

1. Introduction

Untreated or partially treated effluent discharge containing heavy metals into the environment have become a major ecological problem in developing countries. Urbanisation, industrialisation, agricultural expansion, and rapid population growth have increased water usage and accelerates pollution of the biosphere, especially water. Numerous industries, including semiconductor, petrochemical, electronic, metal processing, food processing, automotive and paint manufacturing, release excessive heavy metals into water bodies [1]. One of the main sources of waterway pollution is industrial waste containing metals. The heavy metal ions released into the water can contribute to chronic hazardous health problems such as mutagenicity and carcinogenicity towards humans and environmental effects [1, 2]. Due to their adverse effect, the regulatory agencies are forced to implement increasingly stringent standards for environment protection [2]. An extensive range of wastewater treatment technologies has been applied

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throughout the previous decades. Among them are coagulation, adsorption by activated carbon, flocculation, biosorption, and others [3]. Practically, most of these treatments present many disadvantages such as metal-specific, inadequate metal removal, generation of a secondary pollutant, high capital cost, labour intensive, and ineffective to treat a variety of wastewater [1, 3]. Therefore, alternative treatment technologies for heavy metals removal are being investigated and developed. Heavy metals removal by membrane technology has recently attracted worldwide researcher and development spending due to flexibility, low energy requirement, high effectiveness of pollutants removal, and environmental compatibility [3, 4].

Recently the membrane has been produced from polymer materials, and it is vital in the membranes process. This membrane process has its challenge due to its higher selectivity. The physical and chemical properties of polymer materials used in the membrane may influence fabricated membrane selectivity [5]. Polysulfone (PSF) is often and commonly used because of its flexibility in producing a wide range of pore-sized membranes. It is easy for fabrication and manufacturing, has good thermal stability, has excellent chemical tolerance, high mechanical resistance, and a broad range of tolerated pH because of its hydrophobic [1]. However, its high hydrophobicity contributes to a low permeation rate and fouling tendency. Modifying PSF membrane by introducing a suitable additive can be applied in membrane formulation and fabrication to increase surface hydrophilicity [3]. The additives added to the dope solution included surfactant [6], mineral filler [7], or nonsolvent [8]. Those additives affected membrane-based polymer crystallinity, anti-bacterial properties, porous structure, hydrophilicity, membrane charge, and surface roughness [3, 8]. This study was conducted to investigate different amounts of silica as a pore generating agent added to the polysulfone membrane. The efficiencies of modified PSF spiral wound membranes in copper ions removal need to be discovered.

2. Methodologies

2.1. Membrane Materials
Polysulfone was purchased from Sigma-Aldrich Company with a molecular weight of 60,000 g/mol. The N, N-dimethylacetamide (DMAc) as solvents for the dope solution was supplied by MERCK, Malaysia. This solvent was used due to its ability to dissolve various polymers and precipitated swiftly when immersed in water to provide porosity. For the additive, the sugarcane bagasse from nearby plantations was hydrolysed, refluxed, precipitated, and washed to extract the pure silica.

2.2. Formulation and Fabrication of Membrane
The polymer, Polysulfone, solvent, N, N-dimethylacetamide, and additive, silica sugarcane bagasse, was weighed using weighing balance accurately to ensure the optimum formulation. The concentration of silica sugarcane bagasse additive was varied from 2 wt.% to the maximum concentration based on a cloud point of 8 wt.% [1]. The mixtures are prepared for blending in the stirred flange flask using a mechanical stirrer. The homogenous dope solution was allowed to cool for about one day to obtain ample release of bubbles before the casting process. Fabrication of flat sheet membrane was done via phase inversion method by the pneumatically controlled casting unit Model: TR31-A for flat sheet [1]. Casting dope was poured onto the surface of the glass plate and then spread by stainless-steel knife to get a 300μm thickness of casting film. Next, the casting film was deep in a pure water coagulation bath to precipitate and separate from the glass plate. Lastly, the fabricated flat sheet membrane was soaked in a deionised water bath for 24 hours at room temperature to complete the exchange between the solvent and nonsolvent.

The module configuration is based on a spiral wound module. Flat sheet membranes were attached by their bottom and face the feed stream. The three layers of flat sheet membrane were configured alternately with feed spacer and permeate spacer. The layer was wrapped around the inner core approximately 20 cm long and 3 cm diameter, with five circular holes. These circular holes received permeate stream that passes through the membrane and is collected in the permeate tank. Figure 1 shows the schematic diagram of the PSF-Si spiral wound membrane filtration system, which contains the membrane cell, feed tank, valves, flow meter, pressure gauges, an inlet port, outlet port, and pipes. This setup was designed to test the efficiency of the membrane for copper rejection. In this system, the feed
stream from the feed tank penetrates the membrane cells, while the produced retentate returns into the feed tank. On the other hand, the permeate stream was collected into a permeate tank and undergo permeate flux testing. The cross-flow filtration was applied in this system, where the feed stream flows tangential to a membrane, generating a pressure differential across the membrane. As a result, permeate stream was not recirculated into the system.

![Figure 1. The Schematic Diagram of PSF-Si Spiral Wound Membrane](image)

2.3. Characterization of Membrane

2.3.1. The contact angle of membrane
A contact angle measuring instrument from DSA, KRUSS, Germany, measured the contact angle between water and membrane. First, approximately 4uL of deionized water was poured onto the membrane surface using a microsyringe. Then, the value of the water contact angle was recorded after 3 seconds. Next, the contact angle measurement was carried out for at least five reading at different locations of the membrane surface sample. Finally, the five reading was averaged to yield the contact angle to minimize the experimental.

2.3.2. Equilibrium Water Content and porosity.
The equilibrium water content (EWC) was evaluated by (1):

\[ ECW = \frac{W_w - W_d}{W_w} \times 100\% \]  

(1)

The mass loss of wet membrane from the drying process were determined for analysis of fabricated membrane porosity. The initial weight of the wet membrane was recorded after the surface of the membrane was washed with water. After reached the constant mass, the membrane dried and weighed. The membrane porosity was determined using formula (2):

\[ \varepsilon = \frac{W_w - W_d}{\rho \times V} \times 100\% \]  

(2)
Where $W_w$ is the mass of membrane sample at wet status, $W_d$ is the mass of membrane sample at dry status, $\rho$ is density of pure water, and $V$ is the volume of a membrane in wet status.

2.4. Performance of Membrane

A membrane cell gripping the 225 cm$^2$ effective membrane was used to test the fabricated membrane's water permeability. Firstly, the membranes were exposed to deionized water for approximately 1.5 hours under 6 bars pressure. Then, the pure water flux testing was carried out at room temperature in a 2.0 m/s and 6 bars cross-flow filtration velocity and velocity, respectively. The permeability of the membrane can be calculated by using equation (3):

$$J_w = \frac{V}{t \times A}$$

(3)

The unit for permeate flux is L/m$^2$.hr. $V$, $t$, and $A$ are permeate volume, time, and effective membrane area, respectively. The triplicate experiments were carried out using compressed nitrogen gas and copper solutions of different feed stream concentrations of 3, 6, 9, or 12 mg/L. The 620 nm wavelength of UV–Vis spectrophotometer double beam was used to measure the permeate stream concentration of copper in the solution was analysed. The copper rejection was calculated based on the formula in equation (4):

$$\% R = \frac{C_f - C_p}{C_f} \times 100\%$$

(4)

$C_f$ and $C_p$ (mg/L) were concentrations of heavy metals copper in the permeate and the feed solutions, respectively.

The studied of membrane fouling behaviour was carried out as follows. First, pure water flux of the membrane $J_{w1}$ (L/(m$^2$h)) was measured at 6 bars. Then, the aqueous solution of copper at various concentrations of 3, 6, 9, or 12 mg/L was fed into the spiral wound ultrafiltration membrane system. After 30 min filtration process, the membrane was rinsed for about 10 min with pure water. Next, the membrane pure water flux $J_{w2}$ (L/(m$^2$h)) was tested. In order to evaluate membrane antifouling property, the flux recovery ratio (FRR) was calculated using (5):

$$FRR = \frac{J_{w1}}{J_{w2}} \times 100\%$$

(5)

3. Results and Discussions

3.1. Membrane Characteristics

Table 1 shows the contact angles, equilibrium water content, and porosity, and PSF-Si membranes. The results indicate that the number pores distribution in the membranes of 4 wt.% and 6 wt.%. Silica is smaller than that in the membrane of PSF-21 Si-2 and PSF-21 Si-8. The highest addition of silica in the membrane is categorized by the greeters well-distributed numeral of pores. The results indicated that the equilibrium content of water increased with the increasing amount of silica. The membrane wettability was tested on both side bottom and top of the membrane for inactive and active surfaces. A similar trend was exhibited for the contact angle, where the highest is membrane PSF-21 Si-8. The contact angle values determined on the active sides of the membrane were higher than those on the inactive sides. Membrane PSF-21 Si-2 showed the greatest hydrophilicity with the lowers value of contact angle. In contrast, the membrane with the highest Silica content exhibited the lowest hydrophilicity from all membranes.
Table 1. The Contact angle, equilibrium water content (EWC), and porosity (ε) of membrane

| Membranes  | Contact Angle Top | Contact Angle Bottom | EWC (%) | Porosity (%) |
|------------|-------------------|-----------------------|---------|--------------|
| PSF-21 Si-2 | 75.0              | 70.2                  | 75.2    | 51.5         |
| PSF-21 Si-4 | 75.2              | 70.4                  | 76.1    | 46.2         |
| PSF-21 Si-6 | 75.9              | 70.5                  | 76.5    | 48.4         |
| PSF-21 Si-8 | 77.2              | 70.8                  | 78.7    | 66.0         |

3.2. Membrane Performance

Figure 2 presents the PSF-21 membranes' pure water flux after filtration of copper ions solutions for different membrane porosity. The result shows that the increasing amount of pore generating agent, silica, causes increasing in pure water flux except for membrane PSF-21 Si-4. The pure water flux for the PSF-21 Si-4 membrane was slightly lower than other membranes. This indicates a non-linear correlation between the amount of silica as a pore generating agent and membrane pure water flux after filtration of copper solution. The highest pure water flux, 125 L/m²h was measured for the membrane with the greatest silica content as a pore generating agent, which is PSF-21 Si-8.

![Figure 2. Pure water flux of the PSF-Si membranes.](image-url)

The percentage rejection of copper ions by the PSF-21 membranes versus the initial concentration of the feed solution is presented in Figure 3. The efficiency of copper ion removal for the membranes containing 2, 6, and 8 wt.% silica show a similar trend where the efficiency increases with increasing initial copper concentration. In contrast with the previous study [9], the PSF-21 membranes show more efficient copper rejection at a higher heavy metal concentration of feed solution. In the study, the cellulose membrane is more effective at lower concentrations of heavy metals.

However, with the increasing amount of silica as a pore generating agent, the percentage of copper rejection decreases. The highest efficiency of copper ions removal of all concentrations was found for the membrane of the lowest silica content. For the membrane containing 4 wt.% Silica, the correlation between copper rejection and initial copper concentration is inimitable. For this membrane, the copper rejection for the lowest 3 mg/L and the highest 12 mg/L feed solution is similar for the other membranes. Whereas, for 6 and 9 mg/L copper feed solutions, the performance of PSF 21- Si-4 is diverse. The feed solution of 6 mg/L is the lowest, while 9 mg/L is the highest (98%) among all membranes. Thus, the
efficiency of copper ion removal using PSF-Si membrane is better than published results [10]. In the study, the PVDF membrane containing 1.00 wt% pore generating agent could remove 93.1% of copper ion from an aqueous solution during filtration.

Figure 4 shows the flux recovery ratios (FRR) for the PSF-Si membranes after copper ion filtration. For the membranes of the highest (PSF-21 Si-8) and lowest (PSF-21 Si-2) amount of silica as a pore-generating agent, the results of FRR are similar after copper solution filtration. For example, the lowest FRR, 77.8%, was obtained for PFS-21 Si-4, whereas the highest FRR is 97.8% for PFS-21 Si-6 after filtration of a copper solution.

![Graph 3](image3.png)

**Figure 3.** Percentage of Copper rejection for filtration with PSF-Si Membranes.

![Graph 4](image4.png)

**Figure 4.** The flux recovery ratio of PSF-Si membranes after filtration of copper solution.
4. Conclusions
Formulation of PSF-21 membranes by the addition of various amounts of Silica (Si) into the fabrication of membrane was able to produce various porosity of membranes. The membrane porosity has a beneficial effect on the equilibrium water content. The greatest pure water flux for the PSF-21 membrane is 125 L/m²h with the greatest porosity. Modification of membrane with silica as pore generating agent can enhance the contact angle of the membrane, hence increasing the pure water flux. The highest efficiency of filtration was found for the membranes of the lowest content of Silica which is PSF-21 Si-2.

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