Effect of Sodium Dodecyl Sulfate (SDS) on Polysulfone/Zeolite membrane for the removal of copper ions

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Abstract. The influence of anionic surfactant, Sodium Dodecyl Sulfate (SDS) on Polysulfone (PSf) polymer impregnated with zeolite adsorbent for removing copper ions from aqueous solution is the main focus of this paper. The flat sheet membrane was prepared via blending and phase inversion methods. Different amount of SDS (1 wt%, 3 wt%, 5 wt%, and 7 wt%) were added into the polymer casting solution. Batch adsorption and continuous filtration studies were carried out to study the effect of SDS dosage on PSf/zeolite membrane for the removal of copper ion. The membrane characterizations such as pure water flux (PWF), water contact angle (WCA) and mean pore size were investigated. From the study, it was found that the presence of a high amount of SDS could enhance adsorption efficiency (99 %) by shortening the equilibrium time with adsorption of 9.4 mg/g. Filtration study indicates that a lower amount of SDS (1 wt%) results in high rejection value (70 %) of copper metal ions from the solution. Besides, as the amount of SDS increase, the PWF increases from 0 L/m²h to 100 L/m²h, WCA decreases from 94.8° to 46.4° and the pore size of membrane increases from 0.082 μm to 2.530 μm.

1. Introduction
The demand for clean water is gradually increased as the world population increases rapidly. Water pollution caused by heavy metal has become the biggest challenge faced by the world as it is one of the most common toxic pollutants detected in water streams especially in industrial effluents (mining operations, paper, batteries, fertilizer and thermoplastics industries) [1][2]. Heavy metals are commonly defined as those with a specific density of more than 5 g/cm³ such as copper, chromium, mercury, cadmium, lead, nickel etc [3]. Copper is a type of heavy metals that have gained attention due to its toxicity and risky to the surroundings and human health when they are excessively emitted to the environment without proper treatment. Copper is an essential micronutrient that is vital to the body in small amounts [4]. However, human beings may present symptoms of temporary stomach and intestinal disorders to kidney or liver damage in high quantities, depending of the time of exposure [5]. It is therefore necessary to remove copper metal ion from the effluent before it is released into the environment in order to improve the quality of the water.

Conventional treatment techniques for the removal of heavy metal ions from wastewater included chemical precipitation, ion-exchange, coagulation-flocculation, adsorption, membrane filtration, etc [6-9]. Among these processes, adsorption and membrane filtration are widely used for the
immobilization and separation of metal species. Currently, a major focus has been placed on adsorptive membrane where it has dual function of membrane filtration and adsorption and it is found to be effective to remove traces amount of pollutants such as heavy metals [10]. In recent years, there has been increasing interest in using zeolite as an adsorbent to remove toxic heavy metals from aqueous solutions [11]. Zeolite is a low cost form of clay mineral, abundant availability, high surface area, non-toxic nature, great adsorption and a strong potential for ion exchange [12]. In this work, zeolite adsorbent is stuck on the surface of the Polysulfone (PSf) polymer membrane. PSf is a type of polymer that broadly utilized in membrane fabrication because of its high strength and rigidity [13].

Sodium Dodecyl Sulfate (SDS) is a type of anionic surfactant that can be found in pharmaceutical applications and detergent formulations and usually used in soil remediation [14]. SDS can be used to modify the zeolite surface to enhance the anion exchange capacity thus potentially remove cations, anions and organic compounds [15]. This paper aims to investigate the effects of different SDS amount on PSf/zeolite membrane in terms of the performance of copper removal by batch adsorption and continuous filtration experiment. In current work, PSf /zeolite membrane mix with SDS was prepared by the blending method and phase inversion technique. The pure water flux (PWF), water contact angle (WCA) and membrane pore size were determined.

2. Experimental

2.1. Materials
All chemical and reagents used were in analytical grade and used as received. Polysulfone (PSf) resin pellets (MW = 35,000 g/mol) and zeolite powder were purchased from Sigma Aldrich. N-methylpyrrolidone (NMP) (MW=10,000 g/mol) (Merck) and Sodium dodecyl sulfate (SDS) (Friendemann Schmidt) were used as the solvent and surfactant respectively. The copper (II) stock solution was prepared by using copper (II) chloride (CuCl₂·2H₂O) (R&M Chemicals). All solutions were prepared using distilled water.

2.2. Membrane preparation
The composition of the casting solutions for the prepared membranes is shown in Table 1. A solution was first produced by dissolving SDS in NMP solvent for 1 h under agitation at 300 rpm. It was followed by adding zeolite into the solution. The solution was then sonicated for 1 h to produce homogeneous casting solution with well-dispersed zeolite particles. Subsequently, PSf polymer was added slowly into the mixture which was stirred at 500 rpm and 70 °C for overnight. The resulting dope solution was once more sonicated and degassed for 1 h to get rid of air bubbles that exist in the solution. Afterward, the polymer solution was casted on a glass plate (250 μm thickness) using an automatic film applicator at room temperature. In order to allow the phase inversion phase to take place, the membrane was air-dried for 30 s and immersed in a water coagulation bath. Water was changed daily for 3 days to remove remaining NMP from the membrane. The detached membrane was finally dried at room temperature until it was used.

| Membrane | PSf (wt%) | Zeolite (wt%) | SDS (wt%) | NMP (wt%) |
|-----------|-----------|--------------|-----------|-----------|
| M0 (control) | 15  | -  | -  | 85  |
| M1 | 15  | 5  | 1  | 79  |
| M2 | 15  | 5  | 3  | 77  |
| M3 | 15  | 5  | 5  | 75  |
| M4 | 15  | 5  | 7  | 73  |
| M5 | 15  | 5  | 9  | 71  |
2.3. Batch adsorption experiment

Batch adsorption studies were performed to assess the behaviour of PSf/zeolite membrane in removing copper ions with and without the addition of SDS. The membrane was cut into small pieces and weighed (approximately 0.2 g). Then, it was added into a beaker containing 200 ml of copper solution with 10 mg/L initial concentration under stirring speed (500 rpm). The pH of the copper solution was set at 5.0 for preventing precipitation of Cu which occurred at pH greater than 6 [16]. The concentration of copper was measured for every time intervals of 1 h for the overall 7 hours experiment. Copper concentration was measured by atomic absorption spectroscopy (AAS) (Model: AA-6800 Shimadzu). Copper ion removal can be calculated using Equation (1)

\[
\text{Copper removal} \%(\%) = \left(1 - \frac{C_i}{C_f}\right) \times 100
\]  

(1)

where \(C_i\) and \(C_f\) are the final and initial concentration of copper solution (mg/L). In addition, the amount of copper adsorbed on the membrane (mg/g) was determined by using Equation (2):

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

(2)

where \(q_e\) is the amount of copper adsorbed per membrane weight at equilibrium (mg/g), \(C_0\) and \(C_e\) are the initial (mg/L) and equilibrium concentrations (mg/L) of copper in the solution, \(V\) is the volume (L) of the copper solution and \(M_m\) is the weight (g) of the dry membrane used in the experiment.

2.4. Continuous filtration adsorption experiment

Continuous filtration adsorption experiment was performed using a cross-flow membrane system at 1 bar pressure with 2 L copper feed solution (10 mg/L). The experiment began by placing the membrane to the membrane cell with an effective surface area of 3.154 x 10\(^{-3}\) m\(^2\). The permeate sample was collected after 1 h and the concentration of Cu (II) was analysed by using AAS machine.

2.5. Membrane Characterizations

The pure water flux (PWF) of the membrane was indicated by a cross-flow membrane rig system. Firstly, the membrane sample (3.154 x 10\(^{-3}\) m\(^2\)) was pressurized at 2 bar for 30 minutes to reduce the compaction effects. The permeation experiment was performed at 1 bar for 1 h. The PWF value of membranes can be calculated using Equation (3):

\[
J_w = \frac{Q}{A \times \Delta t}
\]  

(3)

where \(J_w\) is the pure water flux (L/m\(^2\)h), \(Q\) is the volume of collected permeate (L), \(A\) is effective membrane area (m\(^2\)) and \(\Delta t\) is sampling time (h).

The water contact angle (WCA) was analysed by a DropMeter A-100 contact angle system (Rame-Hart Model 300 Advanced Goniometer, USA). The samples were taped flatly onto a glass slide with a membrane surface facing upwards. The water was dropped on the surface of the membrane using microsyringe. For each membrane, ten points of different spots of the surface were measured to get the averaged water contact angle valued. The liquid-liquid displacement porometer (Porolux 1000, Germany) was used to investigate the pore size of the membrane. The membrane samples were cut and wetted with porefil liquid (surface tension of 16 dynes/cm) for an hour. Next, the nitrogen gas was pressurized on the membrane surface and the pore size of membrane was determined based on wet and dry of nitrogen curves.
3. Results and discussion

3.1. Batch adsorption experiment

The adsorption behaviour of copper ion on zeolite impregnated with PSf polymer at different SDS mass with respect to time is shown in Figure 1. From the results, no adsorption observed for M0. This is due to no zeolite adsorbent presence in the membrane. The presence of zeolite provides a significant role during adsorption owing to the existence of negatively charged groups, Si-O and Al-O on its surface that can attract the positive charge of copper metals [17]. It is also observed that all membranes except M0 achieve equilibrium and 99 % removal of copper after 7 hours adsorption period. The maximum adsorption capacity of copper on the zeolite membrane was 9.4 mg/g. At 1 hour experiment, M5 (9 wt% SDS) gives high removal efficiency of copper which is 92 % whereas M1 gives the lowest removal of copper which is 70 % without the addition of SDS surfactant. As can be seen in the results, once the amount of SDS increase, adsorption removal also increase. This is because SDS is an anionic surfactant that consists of a negative head that can also attract positive metal species [18]. Once it mixed with zeolite that has negative charge, strongest negatively charges of the membrane surface was formed. As a result, the modification of the zeolite membrane using SDS could enhance the adsorptive capacity for copper ions.

![Figure 1. Copper ion removal (%) versus time (h) for the adsorption of copper using PSf/zeolite membranes blend with SDS](image)

3.2. Continuous adsorption filtration experiment

The rejection of copper ions on the zeolite membrane was evaluated by carried out cross flow filtration experiment at low transmembrane pressure (TMP) of 1 bar as plotted in Figure 3. It shows that M2 with the lowest SDS amount (1 wt%) offers the highest percentage of rejection which is 70 % but the membrane with highest SDS (M5) amount (9 wt%) gives only 12 % rejection value. It is apparent that the rejection of copper ions reduced as the amount of SDS in the membrane increase. This is because of a large pore size of the membrane obtained. When the pressure was applied, many copper particles able to pass through the porous membrane then causes the decrement in rejection value of copper ions from the solution. In addition, M0 and M1 give zero rejection value of copper because of zero pure water flux (PWF) as shown in Figure 3.

3.3. Membrane characterizations

The results of pure water flux (PWF) and water contact angle (WCA) through PSf/zeolite membrane with SDS is illustrated in Figure 3. The increment of PWF of the membrane is following the order of M5 (100 L/m²h) > M4 (68 L/m²h) > M3 (40 L/m²h) > M2 (19 L/m²h) > M1 and M0 (0 L/m²h).
water permeability increased when SDS surfactant was blended with PSf/zeolite casting solution. As the amount of SDS increase, the PWF also increases. The existence of SDS makes the membrane more porous as it creates larger macro voids on the structure thus improving the hydrophilicity of the membrane [19]. This is proven by the water contact angle (WCA) analysis shown in Figure 3.

WCA has been measured to estimate the membrane’s surface wettability. Generally, the higher value of contact angle represents hydrophobic surface while the lower value represents hydrophilic surface characteristic [20]. The WCA values expected to be dependent on the SDS wt%. The decreasing trend of WCA is illustrated in Figure 3 after zeolite and SDS was added into PSf polymer. M5 membrane which contains the highest amount of SDS demonstrated the lowest WCA value of 46.4°. Apart from that, the PSf membrane, M0 showed the highest WCA value of 94.8° due to the hydrophobic nature of its material [21].
The pore size of each membrane was measured to determine the mean pore size distribution on the membrane surfaces. As presented in Table 2, M0 membrane that consists of PSf polymer only possesses the lowest pore size which is 0.082 μm. However, the pore size increased to 0.244 μm when the zeolite was mixed into the polymer solution. Besides, the membrane pore size become larger as the amount of SDS increase. The membrane pore size is shifted from ultrafiltration to microfiltration type with the presence of zeolite and SDS in the mixture. Basically, in the structure of the surfactant comprises of long hydrophobic alkali and hydrophilic ionic group (polar group). As the surfactant enters a watery media, the ionic head tends to water whereas the non-polar tail tends to absorb on a solid surface, air or organic phase. When the alkali chains close to polymer matrix (hydro-carbonic structure), they will join them together meanwhile the hydrophilic and polar portion will remain free. The aggregation of the polar groups in polymer structure causes repulsion between the polymer chains thus forming an open structure [22]. As a result, the porosity of the membrane increases.

| Membrane | Mean pore size (μm) |
|-----------|---------------------|
| M0        | 0.082               |
| M1        | 0.244               |
| M2        | 0.627               |
| M3        | 1.354               |
| M4        | 1.597               |
| M5        | 2.530               |

4. Conclusions
The flat sheet adsorptive membrane with PSf and zeolite adsorbent with the addition of SDS surfactant was successfully prepared by phase inversion approach for removing copper metals from aqueous solution. The results showed that surfactant plays an important role in influencing membrane performances. This study clearly indicated that the presence of SDS surfactants in the membrane improved the adsorption efficiency of copper metal (99% removal) by shortening the equilibrium time (1 hour). However, with a high amount of SDS, more copper particles will pass through the membrane resulting in lower rejection value of copper ions (12%). The finding of this study shows that at a low amount of SDS (1%), high filtration efficiency (70%) can be achieved. As the amount of SDS increases, the pure water flux (PWF) also increases and the membrane becomes more hydrophilic. Besides, the presence of SDS in the membrane matrix leads to a larger pore size of the membrane.

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