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Super-hydrophilic and in Water Superoleophobic Kaolin Modified Polysulfone (PSF) Microfiltration Membrane for Oily Water Purification: A Research

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Abstract: Surface modification of the polymeric membrane with nanoparticles has proven to be an effective method of preventing fouling. Kaolin modified membrane has good stability and pore size distribution, allowing it to function as a microfiltration membrane. In this work, performances of kaolin modified polysulfone membrane was compared with pristine polysulfone membrane. The best coating cycle for kaolin modified polysulfone membrane was determined by testing the oil and water contact angle on the membrane surface, porosity, morphology and chemical compound of the membrane. One-cycle kaolin modified polysulfone was chosen as the best membrane as it has the most well distributed pore on the surface compared to the two-cycle, three-cycle, four-cycle and five-cycle. One-cycle also has the highest porosity value which was 0.6446 while the lowest porosity value was cycle five. For both the flux and oil rejection, cycle one was proven to be better than the pristine membrane with value of 0.202 ± 0.042 ml/s and of 46.42 ± 1.85%. As a conclusion, this study has successfully produced kaolin modified polysulfone membrane with five different coating cycle which were cycle 1, cycle 2, cycle 3, cycle 4 and cycle 5 and the best kaolin coating cycle among all five was cycle 1.

Keywords: Microfiltration, Polymeric Membrane, Kaolin Nanoparticles

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1. Introduction

Membrane separation technologies are already widely used in industries such as biotechnology, pharmaceuticals, food processing, and wastewater treatment. Nowadays, various contaminants such as dyes, heavy metals, chemical residuals, and pharmaceutical compounds contribute to water pollution. To address this issue, membrane technology has evolved into a much better medium for treating water pollution. The methods include fabricating, classifying, and improving surface characterization to make it suitable for water treatment. The type of process that the membranes can perform is determined by the pore size of the membranes. There are three common types of membrane processes which are microfiltration, ultrafiltration and nanofiltration. Solutes that can be filtered in the microfiltration process have diameters greater than 100 nm, such as sand, algae, and certain bacteria [1].

Polymeric membrane which is polysulfone polymers are widely being used within the microfiltration process. This is because, they have several advantages which make them suitable for being selected as the membrane's base, such as having excellent properties either chemical or physical. For example, it has compressive strength, good thermal stability and also chemical inertness throughout the pH range [2]. But they also have disadvantages, such as their hydrophobic nature, which limits the separation performance. The hydrophobic nature has led to the membrane's fouling and also reducing the permeation flux. To improve the antifouling properties, membrane modification needs to be done which is the surface coating. Surface coating means that the membrane surface will be covered by a coated layer [3]. It is the simplest and least expensive method among the others, which leads to it being widely used in industrial operations.

The surface coating method will apply the hydrophilic material onto the membrane surface, creating a coating layer. Kaolin is one of the metal oxide nanoparticles that has a hydrophilic property and is readily dispersed in water. Kaolin has good physical and chemical properties such as crystal structure, mineralogy, and chemical composition [4]. It also has a quite affordable price compared to the other metal oxides. Kaolin is said to be functional in producing a smooth surface when it is used as the coating layer. The fabrication of kaolin-based membranes has improved the performance of the membrane within the wastewater treatment process.

This work aims feasibility studies to fabricate kaolin modified PSF microfiltration membrane via chemical modification with trimesoyl chloride, TMC and to test the performance of the modified microfiltration membrane for the treatment of oily wastewater.

2. Materials and Methods

Surface coating membrane modification method will be applied in order to produce kaolin modified polysulfone membrane. Different kaolin coating cycle will be used for surface modification, with addition of 0.25 wt% kaolin solution for every cycle. There will be five cycle of kaolin coating for the modified polysulfone membrane.

2.1 Materials

Materials that will be used for the kaolin modified PSF membrane fabrication including polysulfone (PSF) Udels P-3500 LCD MB3 polymer, kaolin nanoparticles from Kaolin (Malaysia) Sdn. Bhd., trimesoyl chloride, trimesoyl chloride SIGMA brand by VNK Supply & Services, Heptane MERCK brand by VNK Supply & Services and Foodie palm cooking oil by Foodie Group.

2.2 Methods

The PSF membrane substrate is treated by the sodium hydroxide aqueous solution (7.5 mol/L). The condition for the treatment is at 70^{o}C for 3 hours. After 3 hours, take out the membrane and wash with the Mili-Q water. Mili-Q water is a type of water that is already being purified by the Milipore Mili-Q lab water system. Then, immerse the membrane in 0.5 wt% TMC heptane solution for about half an hour at 25 °C. After the immersion is done, filter the kaolin solution (0.25wt%) using the treated membrane until the kaolin solution is completely filtered. The filtration is done using the vacuum pump filtration. This will lead to the kaolin coated on the membrane surface due to the chemical bonding as there will be reactions between the trimesoyl chloride and the hydroxyl groups on the hydroxylate PSF membrane and kaolin surface. Then wash again the membrane using the Mili-Q water [5]. Lastly, dry the modified kaolin membrane before using it. For the different kaolin coating cycle, repeat the method from the immersion step in TMC heptane solution until the drying steps.

2.3 Porosity

A gravimetric method is needed to measure the porosity of the modified polysulfone membrane. This method is a common one for measuring the membrane's porosity because of its directness, simplicity, and cost-effectiveness. Eq. 1 shows the calculation for the membrane's porosity.

$$\varepsilon = \frac{(m_2 - m_1)/\rho_2}{m_1/\rho_1 + (m_2 - m_1)/\rho_2} \qquad Eq. 1$$

Where m1 and m2 are the weight of the dry and wet membranes, respectively, ρ1 is the theoretical density of polysulfone (1.25 g/mL) and ρ2 is the density of water (1.00 g/mL).

2.4 Flux

Flux values of the sample was obtained after the permeation test was done. Flux can be calculated following the Eq. 2.

$$j = \frac{Q}{A\Delta t} \qquad Eq. 2$$

Where A is the effective area of the membrane in m^2, Δt refer to the permeation time in hour, and M is the permeate pure water's weight in kg.

2.5 Rejection Performance Test

The rejection performance test is performed to evaluate the membrane's anti-fouling properties as well as the water quality at the permeate. The rejection was calculated following Eq. 3.

$$R\,(\%) = [1 - \frac{c_p}{c_f}] \times 100\, Eq. 3$$

where,

c_p is the permeated concentration and c_f is the feed concentration.

3. Results and Discussion

The results consist of the characterization and performance tests for comparing the pristine and kaolin modified polysulfone membrane.

3.1 Morphology of Membrane Surface

The surface morphology of the pristine and kaolin modified polysulfone membranes were observed using a scanning electron microscope, SEM. All the membrane samples were coated with a gold layer before test. The characterization was done with magnification of 2000 X.

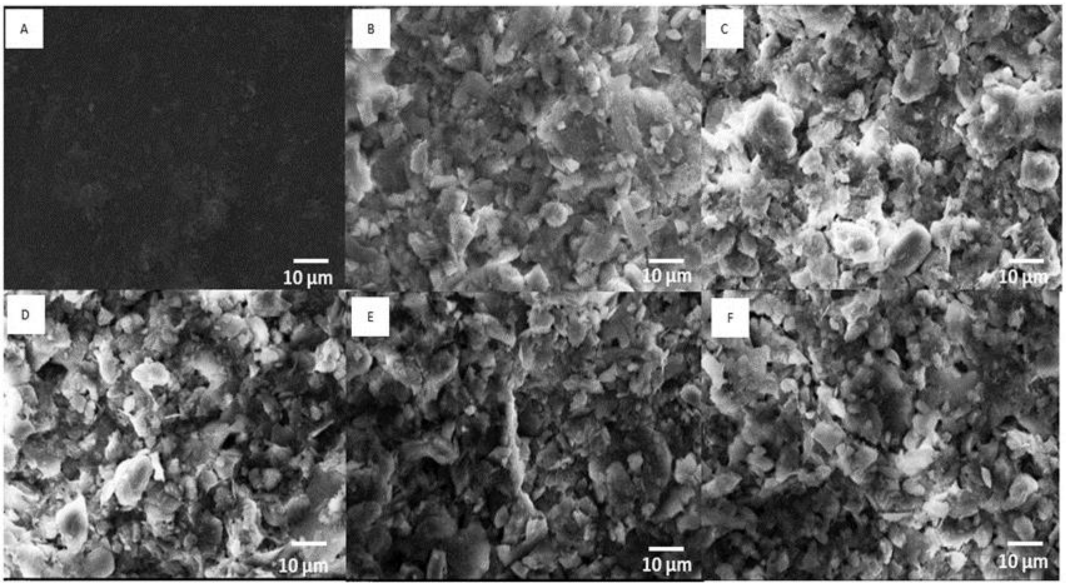

Figure 1: The surface morphology of A) pristine polysulfone membrane, B) kaolin modified membrane cycle 1, C) kaolin modified membrane cycle 2, D) kaolin modified membrane cycle 3, E) kaolin modified membrane cycle 4, and F) kaolin modified membrane cycle 5.

From Figure 1, it can be seen that when the cycle of kaolin coating increased, the membrane surface becoming more porous. After the images being analysed, cycle 1 kaolin modified polysulfone membrane has the most well distributed kaolin powder on its surface. The pore of cycle 1 kaolin modified membrane seems to be evenly distributed on the surface. The even distribution of the kaolin coating on this modified membrane means that there were presence of small-sized pores and it contributed to a higher membrane porosity [5].

3.2 Porosity of Membrane

The porosity of the membranes was being analysed using the gravimetric method. Porosity is the ratio of the pores' volume to the total volume of the membrane. When the membrane porosity is high, it means that the membrane also has high hydrophilic properties.

Table 1: Surface Porosity of Modified Membrane with Different Kaolin Coating Cycle

Membrane	Before (dry) (g)	After (wet, immerse 24 hours) (g)	Wet – dry (g)	Porosity, ε
Pristine	0.084	0.173	0.089	0.5698
Cycle 1	0.184	0.451	0.267	0.6446
Cycle 2	0.168	0.339	0.171	0.5599
Cycle 3	0.138	0.219	0.081	0.4232
Cycle 4	0.375	0.453	0.078	0.2063
Cycle 5	0.191	0.209	0.018	0.1054

Based on the table 1, it shows that the surface porosity of the membrane is decreased with an increase in kaolin coating cycle. Cycle one kaolin modified PSF membrane has the highest porosity value compared to the others. This makes it being the most hydrophilic than the other. One of the reasons on why the porosity of the membranes decreased over kaolin coating cycle was the kaolin coating might not attach to the membrane surface completely. This led to kaolin cracked during the immersion of the membranes for the gravimetric method.

3.3 Flux

Flux according to the membrane application was describe as how fast a mixture can be separated by the membrane. Flux usually was dependent to the membrane's pore size and porosity. It also dependent to the membrane fouling resistance.

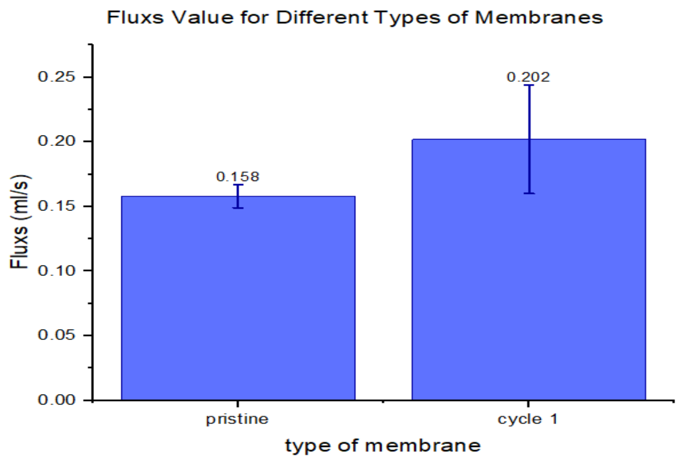

Figure 2: Graph for Pristine PSF membrane and Cycle 1 kaolin modified PSF membrane's flux.

According to the Figure 2, it is shows that cycle one has higher flux average compared to the pristine membrane. The average flux value for cycle one is 0.202 ml/s while for pristine membrane is 0.158ml/s. Its mean that cycle one kaolin modified membrane has faster permeated time. The improvement of the flux value can be explained by the increased of the hydrophilicity of the kaolin coating on the membrane surface. Based on the previous journal, if the membrane has higher porosity, it was often associated with higher flux [9].

3.4 Rejection

Via the oil emulsion permeation test, the oil rejection of the membrane also can be analysed. Oil rejection characteristics is very important in order to separate the oil from the water. The feed concentration of the oil emulsion used was 450 mg/L.

Table 2: The rejection values for different type of membranes

Membranes types	Concentration (mg/L)	Rejection (%)	Average (%)	Standard deviation (+/-)
Pristine a	203.00	54.89	37.06	12.61
Pristine b	321.67	28.52		
Pristine c	325.00	27.78		
Cycle 1 a	243.33	45.93	46.42	1.85
Cycle 1 b	250.00	44.44		
Cycle 1 c	230.00	48.89		

Table 2 shows the oil rejection efficiency for different types of membrane. Based on the table, the oil rejection efficiency of the cycle 1 kaolin modified PSF membrane, 46.42% was higher than the pristine membrane, 37.06% which signifies that the modified membrane's rejection efficiency was better than the pristine membrane. According to the results table, the rejection efficiency still not reached 50% which mean that the performance of the membranes is within a lower range. This might be because of the error that happened during the permeation test. When refer to previous research, it said that the attachment of the kaolin nanoparticles will reduce the pore size of the membrane which will enhance the oil rejection ability [11].

4. Conclusion

The fabrication of the kaolin modified membrane was done purposely for the purification of the synthetic oily wastewater. Compared to the pristine PSF membrane, the membrane that being modified with kaolin exhibited a better water absorption and oleophobic properties. The fabricated kaolin modified PSF membrane also exhibited better flux compared to the pristine which is approximately 0.261 ml/s. Based on the characterization of the kaolin modified membrane and pristine membrane, it showed that the modified membrane has greater properties. In conclusion, this study proved that the kaolin modified PSF membrane offers considerable advantages over the pristine PSF membrane for the synthetic oily wastewater purification.

Recommendations

In order to improve the data, there were a few recommendations that can be done. These recommendations include another permeation test should be done, so that the flux and oil rejection data can be improved into a better result. Permeation test usually was done in a long duration in order to get more significant flux values. As this research was obstructed by the limited time, another permeation test is difficult to be done.

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