Iron oxide decorated graphene oxide embedded polysulfone mixed-matrix membrane: Comparison of different types mixed-matrix membranes on antifouling and performance

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Abstract. Polymeric membrane is widely adopted for water treatment due to its stability in thermal and chemical resistance, smaller footprints and relatively low cost. However, polymer membrane always suffers the poor performance due to its hydrophobic nature. In the recent years, nanomaterials were introduced into membrane matrices to increase the hydrophilicity. In this study, three different types of nanomaterial, iron oxide (Fe₃O₄), graphene oxide (GO), and iron oxide-decorated graphene oxide (Fe₃O₄/GO) were embedded in the polysulfone (PSf) mixed-matrix membranes (MMM). This study investigated the effect of three different nanomaterials on the membrane characteristics, performance, and antifouling properties. Membrane characterization, performance, and antifouling was carried out by pore size, porosity, contact angle analysis, zeta potential analysis, flux measurements and flux recovery ratio respectively. First, GO, Fe₃O₄ and Fe₃O₄/GO nanomaterials were synthesized using Hummers method, co-precipitation method, and co-precipitation method in the presence of GO. After that, membranes were fabricated using phase inversion method. In this study, Fe₃O₄/GO-PSf MMM (76.35%) and GO-PSf MMM (64.39%) showed enhanced porosity as compared to the pure PSf membrane (56.89%) due to the presence of abundance hydrophilic group in GO nanoplates. However, the Fe₃O₄-PSf MMM show slightly lower porosity (53.82%). Contact angle analysis also revealed that Fe₃O₄-PSf MMM (71.47°), GO-PSf MMM (69.17°), Fe₃O₄/GO-PSf MMM (69.97°) showed improved hydrophilicity as compared to the pure PSf membrane (78.80°). Experiment also demonstrated that all MMMs exhibit high negatively surface zeta potential as compared to pure PSf membrane. The membrane performances were investigated using pure water flux and congo red (CR) dye removal. Study showed that Fe₃O₄/GO-PSf MMM give the best membrane performance with the flux of 112.47 L/m².h and CR dye removal of 97%±2. Fouling analysis reveal that all MMMs exhibit high flux recovery ratio (>80%) as compare to pure PSf membrane.

Keywords: Iron Oxide-decorated Graphene Oxide, Graphene Oxide, Nanomaterial, Polysulfone, Mixed-matrix membrane,
1. Introduction
In the study field of membrane separation, the issue of membrane fouling has been addressing over time as it is a common and inherent problem arose from the filtration process [1]. The presence of pores or gaps within the membrane layer has led to the contamination of particles in the membrane during separation process. The transport motion of fluid is significantly disrupted as the contamination of particles has become the resistance factor in filtration. Generally, there are various types of pattern in membrane fouling. For instance, the deposition of proteins, inorganic molecules in the form of metal salts and particulate are the examples of foulants during filtration [2]. Some foulants that are non-removable are restrained in the membrane and reduce the efficiency of membrane. This problem is deteriorated when it comes to polymeric membranes that possess high hydrophobicity of the membrane property. The hydrophobic characteristic will reduce the water flux during filtration which indicates that most of the particles are trapped in the membrane matrixes and restricted to pass across the membranes. Moreover, the fouling problem in the membranes has restricted the transport process of particles and consequently a higher pressure must be induced to ease the filtration process [3]. The higher operating pressure required indicates that the energy consumption is higher. The procedure of chemical cleaning has to be carried out more frequent. This will shorten the life span of membranes and hence reduce the flux during filtration. Eventually, the replacement of membranes must be carried out frequently and the maintenance and operating cost has increased. Thus, the performance and efficiency of the membranes have reduced [4]. From the problem arose, it has been reported that membrane fabrication and its modification with nanoparticles as well as additives may be the solution of the fouling issue. The enhancement of hydrophilicity property in the membrane is completed by adding in various types of nanofillers, non-solvent additive or amphiphilic additives in many research studies [3, 5]. Furthermore, the fabricated nanocomposite membrane that is modified with nanomaterials is anticipated to resist the fouling during filtration. The enhancement of membrane property is expected to improve the water flux and possess antifouling property after the modification. Hence this study investigate the effect of three different types of nanomaterials towards the alteration of membrane performance in flux, rejection and antifouling. Three different types of MMM, GO-PSf MMM, Fe₃O₄-PSf MMM and Fe₃O₄/GO-PSf MMM with the pure PSf membrane as control set.

2. Methodology

2.1 Nanomaterial synthesis

2.1.1 Iron oxide nanoparticles (Fe₃O₄ NPs). Ferrous sulphate heptahydrate (FeSO₄.7H₂O) and ferric chloride hexahydrate (FeCl₃.6H₂O) were ordered from Bendosen, Malaysia and Merck, Germany respectively. Ammonium hydroxide (NH₄OH) with 30% of ammonia in water was supplied by R&M Chemicals, Malaysia. Fe₃O₄ nanoparticles were synthesised by the co-precipitation method. Initially, FeCl₃.6H₂O and FeSO₄.7H₂O were dissolved in absolute ethanol and pure water respectively. After both solutions had completely dissolved, FeSO₄.7H₂O solution was added slowly to the FeCl₃.6H₂O solution. The final mixture was heated to 35±5 °C followed by the addition of NH₄OH to reach the desired pH. The solution mixture continued to be stirred vigorously under heating at 60±5 °C for two hours. The resulting solution was then left to cool followed by washing steps. Repeated washing was carried out with pure water. The product was dried overnight at 75°C in an oven.

2.1.2 Synthesis of graphene oxide nanoplates (GO) and iron oxide decorated graphene oxide nanohybrid (Fe₃O₄-GO). GO was synthesized via Hummers method using graphite flakes as raw material [6, 7]. Fe₃O₄/GO nanohybrid was synthesized via co-precipitation mixing FeSO₄.7H₂O and FeCl₃.6H₂O in the presence of GO as mentioned in the previous study [8].
2.2 Membrane fabrication
Mixed-matrix membrane was prepared using phase inversion method. The composition of the membrane casting solution was prepared according to Table 1. It was prepared according to the method mentioned in the previous study [9]. The prepared membrane casting solution was sonicated and kept overnight to remove the air bubbles [10]. The prepared casting solution was slowly poured on a clean glass plate. Then the solution was casted on the glass plate by using Filmographe Doctor Blade 36003 (Braive Instrument, Germany). The thickness of the blade was fixed at 0.2 mm. After that, the casting solution was immersed into pure water. The solidified membrane was stored for few hours to ensure the solidification process complete. In this study, 3 different nanomaterials were doped into the membrane as shown in Table 1. The study was carried at constant 0.4 wt% nanomaterial to the weight of polymer.

| Membrane Name | Type of Nanomaterial | Nanomaterial (wt%) | PSf:NMP:Nanofiller |
|---------------|----------------------|-------------------|--------------------|
| PSf (pure)    | M0                   | 0                 | 15:85:0.00         |
| Fe₃O₄/GO-PSf MMM | M5-0.4             | Fe₃O₄/GO          | 0.4                | 15:85:0.40 |
| Fe₃O₄-PSf MMM  | M-Fe₃O₄             | Fe₃O₄             | 0.4                | 15:85:0.40 |
| GO-PSf MMM     | M-GO                | GO                | 0.4                | 15:85:0.40 |

2.3 Membrane characterization

2.3.1 Pore size and porosity calculation. The porosity of the membrane (ε) and the membrane pore size(rₘ) were determined by Eq (1) and, Eq (2), respectively [11, 12].

\[
\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times \rho}
\]

\[
r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta Q}{\varepsilon \times A \times \Delta P}}
\]

The parameter for the Eq (1) and Eq (2) was as follow, where \(\omega_1\) and \(\omega_2\) is the wet and dry membrane weight measured in kg, A is the surface area of the membrane (m²), l is the thickness of the membrane (m) fixed at 0.2 mm, \(\rho\) is the water density (999 kg/m³), \(\eta\) is the water viscosity (8.9×10⁻⁴ Pa s), \(Q\) is the volume of permeated pure water per unit time (m³/s), and \(\Delta P\) is the operating pressure (0.1 MPa).

2.3.2 Contact angle. The membrane wettability or hydrophilicity analysis was characterized by the static contact angle of the membrane surface. It was measured based on the sessile drop technique using a Drop Shape Analysis System goniometer, model DSA100, (Kruss GmbH, Germany).

2.3.3 Membrane surface zeta potential. The surface charge of the fabricated membrane was assessed by zeta potential measurement using Malvern Zeta Sizer Nano ZS (Malvern Instruments, UK). By applying a field strength of 25 V/cm, the zeta potential of PSf membrane surface in 0.1 mM NaCl at pH 7 was measured using 300-350 nm latex particles as the tracer particle (DTS1235 Malvern, UK).

2.3.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Nanoparticles leaching test was evaluated by Inductively Coupled Plasma Mass Spectrometry analysis (PerkinElmer, Model ELAN 9000). The permeate solution collected from Fe₃O₄ and Fe₃O₄/GO membranes filtrate were used to test the presence of iron ions.
2.4 Membrane performances

2.4.1 Membrane flux and rejection measurement. Permeation test was carried out using a stirred cell filtration system (Sterlitech TM HP4750, USA) with an effective membrane area of 14.60 cm². CR solution of 20 ppm [13] was used as the feed solution during membrane performance study. The permeation flux was determined by Eq (3).

\[ F(\text{Flux}) = \frac{V}{At} \]  

(3)

The parameter \( F \) (L/m².h) is defined as the permeation flux, \( V \) (L) is defined as the permeate volume, \( A \) (m²) is defined as the effective membrane area and \( t \) (hour) is time of the permeation. The absorbance of CR was measured using UV-vis spectrophotometer at the wavelength of 497 nm. The CR rejection was calculated according to Eq (4).

\[ R(\%) = \left(1 - \frac{C_p}{C_f}\right)\times100\% \]  

(4)

The parameter \( R \) (%) is known as the rejection percentage of CR, \( C_p \) (mg/l) is the final concentration or permeate concentration and \( C_f \) (mg/l) is the initial concentration or the feed concentration.

2.4.2 Membrane flux recovery. The membrane recovery performance was measured using the flux recovery ratio as shown in Eq. (5). To calculate the flux recovery ratio value, the initial water flux \( (J_w) \) were taken first. After that, the permeation test for 2 hours was carried out using the CR model solution and the permeate flux was recorded \( (J_a) \). The membrane was then gently washed with water and immersed in the water for 30 minutes before the testing of the water flux \( (J_{w1}) \).

\[ FRR = \left(\frac{J_{w1}}{J_w}\right)\times100 \]  

(5)

3. Result and discussion

3.1 Membrane analysis

3.1.1 Pore size and porosity, contact angle and surface zeta potential

Analysis of pore size and porosity measurements, contact angle and surface zeta potential for different types of MMMs (PSf-Fe₃O₄, PSf-GO, and PSf-Fe₃O₄/GO MMM) and pure PSf membrane (M0) are given in Table 2. From Table 2, M5-0.4 and M-GO shown enhancement in terms of porosity and pore size as compare to M0 membrane. The increase of porosity and pore size was probably due to the presence of abundance hydrophilic group in the GO nanoplates [14]. However, M-Fe₃O₄ is showing reduction in porosity and pore size. This could possibly due to the aggregation problem that caused by single type nanomaterial [15]. It is hypothesized that the aggregation problem in M-Fe₃O₄ is more dominant than the hydrophilic properties of the nanomaterial. The contact angle value decreased for all types of MMMs. The decrement in contact angle could be explained by the presence of hydrophilic functional group in the polymer [14]. From Table 2, M5-0.4 MMM and M-GO has the lower contact angle value at 69.97° and 69.17° respectively as compared to M0 (78.80°), and M-Fe₃O₄ (71.47°). The slightly higher contact angle value of M-Fe₃O₄ are directing on the higher tendency of aggregation issues. All the MMMs possessed higher negativity surface charge as compare to pure PSf membrane while M5-0.4 MMM possessed the highest negativity surface charge. The improvement was due to incorporation of nanomaterial into membrane matrices that induce an increase of membrane surface charge [9].
Table 2. Characteristics of different type MMM

| Membrane Type | Porosity (%) | Pore Size (µm) | Contact Angle (°) | Surface zeta Potential (mV) |
|---------------|--------------|----------------|-------------------|--------------------------|
| M0            | 56.89        | 0.0331         | 78.80             | -4.00                    |
| M5-0.4        | 76.35        | 0.0347         | 69.97             | -24.67                   |
| M-Fe304       | 53.82        | 0.0300         | 71.47             | -18.30                   |
| M-GO          | 64.39        | 0.0333         | 69.16             | -18.40                   |

3.1.2 Nanoparticles Leaching Study. ICP-MS was conducted to test if any trace of iron ions could be detected. Table 3 shows the ICP analysis result for membrane M-Fe$_3$O$_4$ and M5-0.4. Permeate from pure water filtration using M-Fe$_3$O$_4$ and M5-0.4 membrane were analysed in order to verify that the permeate was free from iron compounds. There was no trace of iron detected. According to the results, it was confirmed that none of the iron has passed through the polymeric membranes during the filtration process. The findings reveal that the incorporation of different nanomaterials were stable and will not detached.

Table 3. ICP analysis results for M-Fe$_3$O$_4$ and M5-0.4

| Sample                  | Concentration of Fe (ppm) | Remarks                        |
|-------------------------|---------------------------|--------------------------------|
| Permeate for M-Fe$_3$O$_4$ | 0.00                      | No leaching of Fe from the membrane |
| Permeate for M5-0.4      | 0.00                      | No leaching of Fe from the membrane |

3.1.3 Membrane Performance and Fouling Study. Comparison between all the MMMs and the M0 was made by evaluating the permeation flux, CR rejection and flux recovery ratio. From Figure 1, M5-0.4 and M-GO are showing higher permeation compared to M0 membrane. The incorporation of Fe$_3$O$_4$/GO nanohybrid and GO nanoplates in polymer matrix are showing a good improvement in terms of permeation flux. The increment in permeation flux was due to the enhancement of membrane hydrophilicity that discussed previously. However, the M-Fe$_3$O$_4$ are showing lower permeation flux as compared to M0 membrane. Both findings are having a good agreement with the contact angle, pore size and porosity analysis reported in Section 3.1.1. Although the M-Fe$_3$O$_4$ show slight improvement in the hydrophilicity, but the aggregation problem (causing lower pore size and porosity) has become the dominant effect causing lower flux. In this study, the maximum permeation flux was achieved by using M5-0.4 MMM. The M5-0.4 MMM achieved 112.47 L/m$^2$.bar flux while M0 membrane has 51.82 L/m$^2$.bar. The increment of the permeation flux was 2 times higher. The result show that by incorporating nanomaterials, it helps to improve the flux. Figure 1 also present the rejection capability of M0, M5-0.4, M-Fe$_3$O$_4$, and M-GO membranes in removing CR. As shown in Figure 1, all the membranes are showing relatively higher CR rejection which is higher than 85%. This is due to the higher negativity surface charge after the addition of nanomaterials [7]. Besides that, Figure 1 also show the flux recovery ratio of all the fabricated membrane. According to the results, the FRR of all MMMs are higher than M0 membrane. This could be due to the nature of antifouling behaviour of the nanomaterials. The M0 are having the lowest FRR recovery due to the hydrophobic nature of the polymer itself. The analysis also reveals that M5-0.4 and M-GO is among the membrane with higher antifouling property. Based on these three analyses, it reveals that M5-0.4 and M-GO is a better membrane as compare to M0.
4. Conclusion
Iron oxide polysulfone mixed-matrix membrane, iron oxide decorated graphene oxide polysulfone mixed-matrix membrane, and graphene oxide polysulfone mixed-matrix membrane were successfully fabricated using phase inversion method. The findings from this study shown that the graphene oxide polysulfone mixed-matrix membrane and iron oxide decorated graphene oxide polysulfone mixed-matrix membrane are showing a better property (hydrophilicity, membrane performance, antifouling property) as compare to pure polysulfone membrane. However, the iron oxide polysulfone mixed-matrix membrane only show a slight improvement by considering all the analyses. The iron oxide polysulfone mixed-matrix membrane showed greater antifouling property as compare to pure polysulfone membrane but slight decrement of the membrane performance. As a conclusion, iron oxide decorated graphene oxide polysulfone mixed-matrix membrane appear as the better membrane in psychochemical properties, performances and antifouling property. Iron oxide decorated graphene oxide polysulfone mixed-matrix membrane showed two times increase of permeate flux at 112.47 L/m².h as compare to pure polysulfone membrane (51.82 L/m².h), 97± 2% of congo red removal and flux recovery ratio higher than 80%.

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