



# Preparation of novel polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane for humic acid rejection



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## ABSTRACT

In this study, novel polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane was prepared by embedding the iron-decorated graphene oxide (Fe<sub>3</sub>O<sub>4</sub>/GO) into polysulfone (PSf) polymer. First, graphene oxide (GO) nanoplates were synthesized using natural graphite powder according to the Hummers method. Fe<sub>3</sub>O<sub>4</sub>/GO was then prepared by mixing both GO and Fe<sub>3</sub>O<sub>4</sub> in the presence of ammonia hydroxide (NH<sub>4</sub>OH) according to co-precipitation method. A series of test, such as X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were performed to characterize the produced Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid. Mixed-matrix membrane was fabricated by casting the pre-mix PSf-Fe<sub>3</sub>O<sub>4</sub>/GO polymer solution mixture using phase inversion method. The performance of both neat PSf membrane and novel polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane were evaluated by measuring the membrane permeate flux and humic acid rejection. Experiment demonstrated that the novel polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane was having 3 times higher permeate flux than the neat PSf membrane despite the drop in humic acid rejection from 89 ± 2% to 84 ± 2%. However, polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane permeability was increased with the compensation of decreasing retention capacity due to pore size enlargement, higher porosity as well as higher hydrophilicity.

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## 1. Introduction

Membrane technology is a well-established technology used widely in wastewater treatment due to its high stability and efficiency, low energy requirements and easy operation [1]. However, membrane fouling set a limitation to the applications of this technology. Blending the membrane polymer solution with inorganic nanoparticles (NPs) had become one of the significant efforts that have been accomplished to resolve the membrane fouling problem. The most common inorganic NPs used to incorporated into membrane are TiO<sub>2</sub> [2], ZnO [3], Ag [4], and Fe<sub>3</sub>O<sub>4</sub> [5]. It has been reported that, incorporation of inorganic NPs into the membrane matrix can enhance the hydrophilicity and porosity of the membrane thus reduces the membrane fouling propensity [6]. However, incorporation of inorganic NPs into membrane matrix always hindered by poor dispersion or aggregation of NPs at higher

concentration [7] that could possibly lead to weak membrane structure formed. Therefore, it is necessary to avoid the aggregation of NPs in order to develop better membrane performance. Attributed to this, nano-hybrid has become the solution to avoid the aggregation of NPs in the membrane matrix. Nano-hybrid is defined as the combination of two different NPs that combine the special properties from both NPs. GO has been reported as one of the commonly used materials in producing nano-hybrid due to its 2D carbon nanostructure and high specific surface area [8,9] that allowed variety of NPs to be attached at the surface of GO. GO also regarded as one of the NPs that has a high hydrophilicity due to the presence of abundant oxygen-containing functional groups such as hydroxyl, carbonyl, and carboxyl and epoxy group [10]. Due to its unique properties, the presence of GO as one of the compounds in nano-hybrid will avoid aggregation of inorganic NPs in the membrane matrix while promoting the synergistic effect of both NPs. In this work, a novel PSf-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane was prepared via phase inversion method. The Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid was characterized by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) analysis while the fabricated Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane was characterized by Field Emission Scanning Electron Microscopy (FESEM), EDX mapping, porosity, pore size,

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and contact angle and the membrane performance was evaluated based on membrane permeability and humic acid (HA) rejection.

## 2. Materials and methods

### 2.1. Materials

GO nanosheets were synthesized using extra pure fine graphite (particle size <50 μm), sodium nitrate (NaNO<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (95–98 wt%), supplied by R&M Chemicals, Malaysia. Iron-decorated GO (Fe<sub>3</sub>O<sub>4</sub>/GO) nano-hybrid was synthesized using ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) and ferrous sulphate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) purchased from Merck, Germany and Bendosen, Malaysia respectively. Ammonium hydroxide supplied by R&M Chemicals, Malaysia was used as a reducing agent (NH<sub>4</sub>OH) during Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid synthesis. Asymmetric flat sheet membranes were fabricated from polysulfone (PSf) pellets and *N*-Methyl-2-pyrrolidone (NMP) obtained from GoodFellow, Malaysia and Merck, Germany, respectively. Synthetic humic acid (HA) powder obtained from Sigma-Aldrich, USA was used as the organic foulant during the experiment without further purification. Sodium hydroxide (NaOH) solution was used to improve the dissolution of HA in water.

### 2.2. Preparation of inorganic particles

#### 2.2.1. Graphene oxide synthesis

Graphene oxide (GO) was synthesized using natural graphite powder according to Hummers method [11,12]. Graphite powder (5 g), NaNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> were put together in a round flask. The mixture was then stirred for 30 min in an ice bath at the temperature of 10 °C. Next, KMnO<sub>4</sub> was added gradually under continuous stirring. The mixture was allowed to react below 10 °C for 2 h and then successively stirred at 35 °C for another 1 h. The mixture was then diluted with deionized water while temperature was kept below 100 °C. The solution was stirred for another one hour followed by further dilution with deionized water. H<sub>2</sub>O<sub>2</sub> was then added into the mixture to reduce the KMnO<sub>4</sub> residual until the colour of the mixture turned into brilliant yellow. Finally, the mixture was centrifuged and rinsed with hydrochloric acid (HCl) aqueous solution before sent to freeze dryer to obtain fine brown GO powders.

#### 2.2.2. Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid synthesis

Nano-hybrid Fe<sub>3</sub>O<sub>4</sub>/GO were synthesized by co-precipitation of FeCl<sub>3</sub>·6H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O in the presence of GO [13]. The aqueous solution of FeCl<sub>3</sub>·6H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O was prepared in 3:1 molar ratio separately. The weight ratio of iron (Fe) to GO was set to be 0.1:1. First, GO (1 g) was stirred and ultrasonicated in a mixture of deionized water and absolute ethanol. FeCl<sub>3</sub>·6H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O salt were also stirred in absolute ethanol and deionized water separately to obtain a homogeneous solution before added to the GO aqueous solution. The temperature of the mixing solution was raised to 60–70 °C and NH<sub>4</sub>OH was added gradually to increase the pH to 11. The mixture was allowed to react for 2 h before cooled down to room temperature. Repeating washing process was carried out with pure water until the pH of the resulting solution reach 7 ± 0.2. Final washing was done with absolute ethanol. The resulting product was dried overnight at 90–100 °C in an oven. The black powder obtained was sent for XRD and TEM analysis.

### 2.3. Membrane preparation

Phase inversion method was used for the fabrication of PSf-Fe<sub>3</sub>O<sub>4</sub>/GO mixed-matrix membrane. The membrane casting solution was prepared by dissolving pre-dried PSf into NMP solvent

at the weight percentage composition of 15:85. First, 1 wt% (0.15 g) Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid were ultrasonicated in NMP solution for 30 min followed with overnight stirring to obtain a homogeneous solution. PSf was dissolved in NMP and subjected to an initial stirring of 100 rpm at 65 °C for 4 h and 30 min to form a homogeneous solution. The homogeneous solution was then left overnight under stirring at 40 °C. Then, the homogeneous Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid solution was injected into the PSf/NMP aqueous solution. The final mixture was then ultrasonicated for another 30 min and was kept in dark overnight to remove the trapped air bubbles. The casting solution was poured equally on a clean glass plate and then cast manually at membrane thickness of 0.2 mm using the Filmographie Doctor Blade 360099003 (Braive Instrument, Germany). The nascent membrane on the glass plate was then solidified by immediately immersed into ultrapure water at room temperature. The immersion was left for a day to ensure complete solidification. Performance of the casted membrane was evaluated in terms of permeability and humic acid rejection.

### 2.4. Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid characterization

#### 2.4.1. X-ray diffraction (XRD)

XRD technique was used to identify the structure phase and crystal size of synthesized Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid. The XRD analysis was performed by BRUKER AXS D8 ADVANCE diffraction meter (Bruker AXS, GmbH). The system is equipped with a CuKα radiation (λ = 1.5406 Å) with scanning in range of 5–80° for 2θ angle. The average crystal size, D was estimated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where β is the peak width at half maximum (radian), K is the Scherrer constant (K = 0.89), λ is the X-ray wavelength (λ = 1.5406 Å), and θ is the Bragg diffraction angle (θ).

#### 2.4.2. Transmission electron microscope (TEM)

The particle size of Fe<sub>3</sub>O<sub>4</sub> was evaluated using the Transmission Electron Microscope (TEM, JEOL, JEM-2010). For the TEM observation, Fe<sub>3</sub>O<sub>4</sub>/GO nano-hybrid colloidal suspension was pipetted out and dropped on a 3 mm diameter, 400 mesh carbon-coated grid. The droplet was then wicked to dryness for 10 min before undergoing for TEM imaging.

### 2.5. Membrane characterization

#### 2.5.1. Field emission scanning electron microscopy (FESEM)

FESEM was used to examine the surface and cross sectional structures of the fabricated membranes using FESEM Merlin Compact (Zeiss, Germany). Membrane samples were cut into an appropriate size and mounted on the sample holder. Quorum, (Q150R S) was used to coat the outer surface of the membrane sample with a thin layer of platinum under vacuum to provide electrical conductivity. After platinum sputtering, the samples were examined under the electron microscope at 3.0 kV potential.

#### 2.5.2. Porosity and pore size estimation

Porosity (ε) and pore size (r<sub>m</sub>) of the fabricated membrane was determined by the gravimetric method as shown by Eq (2) and Guerout-Elford-Ferry equation, Eq. (3), respectively [14–17]

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times \ell \times \rho} \quad (2)$$

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta\ell Q}{\varepsilon \times A \times \Delta P}} \quad (3)$$

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