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Polymer Mixed Matrix Membrane with Graphene Oxide for Humic Acid Performances

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This study investigates the performance of polymer mixed matrix membrane integrated with graphene oxide (GO) towards humic acid application. Enhancement of antifouling property of polysulfone (PSf) polymer membrane can be done by integrating strong GO hydrophilicity towards hydrophobic PSf membrane. In this work GO additives were synthesized from graphite powder using variable stirring times. Meanwhile five different samples with different GO composition was fabricated via phase inversion techniques to investigate the effect of GO towards polymer mixed matrix membrane. Performances test was completed through the pure water permeability test, humic acid rejection test and anti-fouling analysis. Analysis of the results show that hydrophilic properties of the membrane increased with increasing of GO composition. Similar pattern also was observed for permeation, rejection and antifouling performances with increasing GO contents all these performances were also increased. However, concentration of GO also must be controlled to avoid the pore blockage due to GO particles agglomeration especially at higher GO concentration.

1. Introduction

Contamination of water has becoming serious problems nowadays that need to be tackled urgently due to uncontrolled industry and human activities. Contamination of clean water from river and other various sources will increased the acidity and it will cause the higher concentrations of nutrients, sediments, salts, chemical, trace metal and other toxins as well as disturb the whole life in the earth, human eco-system and life-sustainability resources (Palaniappan et al., 2010). Generally, clean water is crucially needed in almost all applications such as energy production, domestic usage, recreation, agriculture, medical and most industry to produce the quality production i.e. food and pharmaceutical industries. Basically, clean water is commonly used to control, reduce and remove toxic from the body or to keep the body healthy. In fact, clean water also is important as human drinking sources to ensure stability of fluid body circulation and stability of respiratory activity inside human body (Gleick and Iwra, 2009).
Nowadays, Membrane technology is known as one of the most efficient technologies that capable to treat water to the level of Nano-contamination and one of the most preferred technologies in treating wastewater problem (Qadir et al., 2016). The characteristics of membrane that consists of thin layer structure with tailored pore size that able to meet the to the level of microfiltration, ultrafiltration, Nano-filtration and reverse osmosis (Harun et al., 2013b) applications has made this membrane application widely used in most of water treatment process. Membranes are react as separation that offer improved energy efficiency, and membranes are use in separation

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processes such as water purification, gas separations and many more (Mckeown, 2016). In this current work, PSf polymer mixed matrix membrane embedded with synthesized graphene oxide was investigated towards ultrafiltration performance. Basically PSf is quite intensively used as polymer membrane materials due to its good mechanical conductivity, thermal stabilities, superior film ability, anti-compactions, strong chemical reaction and it's also low cost material (Rezaee et al., 2015). In However, due to its hydrophobic nature (Harun et al., 2013a) the usage PSf membrane always associated to the fouling problem. Fouling can described as accumulation of feed solution constituents at or in the membrane causing escalate in resistance of permeate flow (Jamalludin et al., 2013); result in loss of the membrane performance either chemically or physically. Therefore, enhancement of polymer mixed matrix membrane using inorganic hydrophilic additives is always preferred as is more practically can be implemented, cheap and involved simple technique (Qadir et al., 2016). There are various additive of membrane can be mixed or added into the membrane structure for different needs and purposes. In fact the used of small portion of additives materials that give strong effect to the membrane properties is more preferable to be used. Thus the used of GO additives synthesized from graphite was proposed in this work. By varying stirring times the synthesized of GO from graphite also can be controlled.

2. Experimental

2.1 Materials

Polymer/GO membrane was produced from polysulfone (PSf) reacted as main polymer material, N-methyl-2-pyrrolidone (NMP) was performed as solvent, Polyethylene Glycols (PEG) was performed to build pores in membrane and GO was synthesized via modified hummers' method (Shin et al., 2016) as an additive embedded onto membrane.

2.2 Experimental Procedure

Preparation of PSf/GO membranes was completed using by phase inversion via casting method (Jamalludin et al., 2013). Phase inversion method by immersion precipitation was conducted for preparing asymmetric ultrafiltration membranes (Garcia-ivars et al., 2014). Dope solution was prepared by PSf in N-methyl-2-pyrrolidone (NMP) which reacts as a solvent and stirred for 4 h. Then, PEG and GO were acted as an additive at same concentration (0.7 g) but with the different time stirring of synthesization of graphene oxide was subsequently added with continuous stirring and heating 60 ^{o}C until the dope solution was completely homogenous and dissolved. Afterward, the dope solution was poured into the bottle and the bubbles were released in ultra-sonication for 1 h. After the bubbles in solution completely released, the dope solution were cast by using a flat sheet membrane casting system, and then submerged in a coagulation bath of distilled water. Finally, the flat sheet membranes were dried for 24 h or more (Zaini et al., 2013).

2.3 Membrane performance

The pure water flux, rejection and fouling test was measured using the membrane permeation testing unit. The flat sheet membrane was cut to a circular disk before it was installed in the membrane cell. The permeation flux was conducted with a pressure of 5 bar at the beginning, testing until the distilled water flowed under steady conditions. Then, 2 bar of pressure were applied to determine the value of pure water flux and rejection. The value of pure water flux was recorded every 10 min. The rejection measurement was carried out using humic acid (HA) solution at a pressure of 2 bar. The concentration of HA used was 0.2 g/L of HA (Riduan et al., 2016).

2.4 Pure Water Flux (PWF)

The pure water flux was measured using Eq(1) at pressure of 2 bar. Meanwhile, the rejection result of humic acid was calculated using Eq(2). The higher rejection value shows the most effective membrane.

$$PWF = \frac{Q}{A \times \Delta t} \tag{1}$$

where PWF is the pure water flux ($Lm^{-2}h^{-1}$), Q is the permeate volume (L), A is the membrane area (m^2), and t is the time(h).

$$R\% - \left[1 - \left(\frac{C_p}{C_F}\right)\right] \times 100 \tag{2}$$

where C_P is solute concentration in permeate stream and C_F is solute concentration in feed stream (Riduan et al., 2016).

2.5 Fouling Analysis

Membrane fouling can be determined by resistance during the filtration process. Fouling resistance occurred due to the cake layer formation on the membrane surface, pore blocking and adsorption into membrane surface or bio-fouling. Darcy's law was applied to determine fouling resistance as expressed in Eq(3):

$$J_{WF} = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_{cp} + R_a)} \quad (3)$$

where J_{WF} is the pure water, μ is the viscosity (Pa s), and ΔP is the trans pressure-membrane (Pa). Meanwhile, R_t is the total of membrane resistance (m^{-1}) of intrinsic membrane resistance R_m, due to the concentration polarization R_{cp}, cake layer formation on the membrane surface R_c and adsorption R_a (Riduan et al., 2016).

3. Results and Discussion

3.1 Water permeability test

Figure 1 shows the results of pure water flux performance of PSf/GO membranes based GO concentration. Basically, the ability of the membrane was investigated and measured through the permeation testing unit within 10 min. The membrane denoted as sample 1 until sample 6 was prepared with 2 h stirring times. Overall comparison shows that the addition of GO can increase membrane pure water flux rate. Current reviews by Wei et al. (2014) reported that, the total flux through GO is composed of contributions from the pristine and oxidized regions respectively, i.e. However there is a slight reduction of flux rate from sample 4 to sample 8, which could be due to the high tendency agglomeration effect of GO which is still in the metastable condition. As increasing stirring time of GO the synthesization effect is obviously shown with higher water flux value is given by 10 h stirring of GO with flux value at 133.613 L/m^2h this result is aligned with the porosity value that demonstrated GO (8 h). This result is in line with the porosity values that show higher porosity will contribute to the better permeation performance. This result is in agreement with other previous studies as reported by Wei et al. (2014). Another recent papers by Geim et al. that claim that thin film GO sheets are capable of a high water permeate while presenting an extremely restricted porosity (Muscatello et al., 2016).

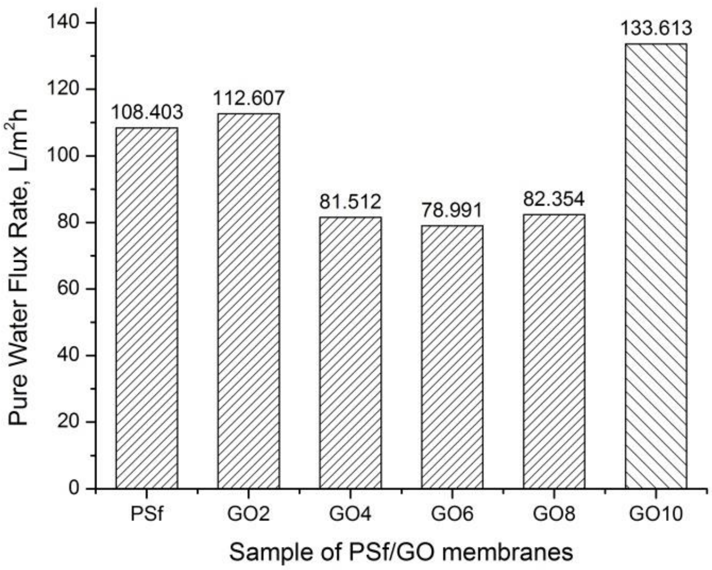

Figure 1: Pure Water Flux Rate of PSf/GO membranes

3.2 Humic acid (HA) rejection opposite

Rejection testing of the fabricated membrane was accessed based on the humid acid solute concentration in the permeate stream. Figure 2 shows the result of the rejection test of PSf/GO membranes at different concentration. Initial concentration of HA was measured using the UV spectrophotometer rejection testing machine. The initial measured solute concentration value of HA was 2.898 with UV absorbance measured at

254 nm. Results show that the rejection value is in the trade off pattern compared with permeation results. This is in line with other studies by Harun et al. (2013a) and agreed well with basic theory of membranes permeation and rejection concept (Harun et al., 2013a). This lowest rejection result can be linked to the highest permeation result that can be correlated to effect of GO inside the membrane structure especially in metastable condition of GO. As demonstrated by other works (Zaini et al., 2013), higher concentration of inorganic additive particles also can prevent the HA from entering the porous which can sometimes can build the pore blocking as can be seen in sample 2. The higher value percentage of humic acid rejection was given by sample 3 with value at 99.4 %. Thus, it revealed that the membrane pore size can prevent the humic acid (HA) from entering the pore length which can sometimes can create pore blocking (Zhang et al., 2011). Commonly the appropriate range of additive to have good distribution across the structure (Harun et al., 2013a).

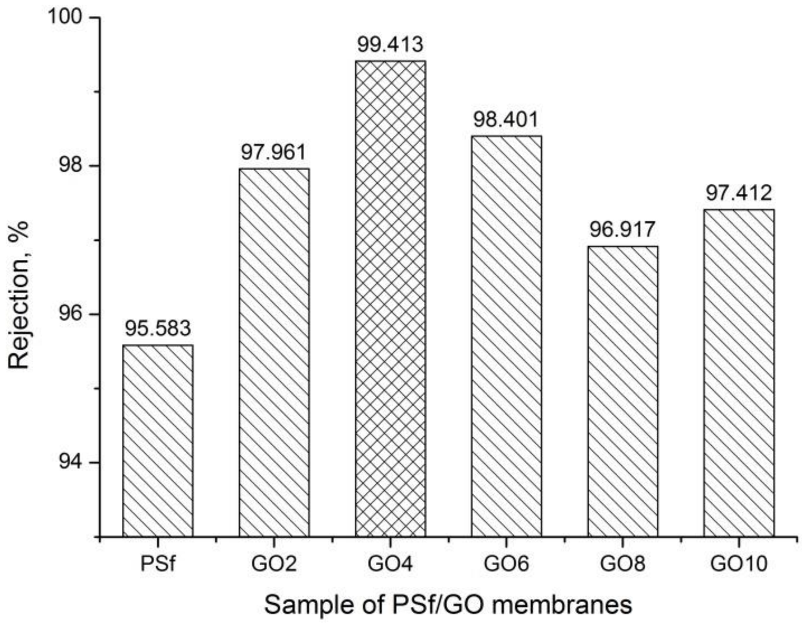

Figure 2: Humic Acid (HA) rejection for PSf/GO membranes

3.3 Anti-fouling analysis

Result of normalized flux ratio (J/Jo) is presented in Figure 3 for different synthesized times of graphene oxide (GO). In measuring this value, filtration of PSf/GO membranes at 120 min using humic acid (HA) as loading medium was performance. The graph below show the normalized flux ratio was reduced over time started at 10 min for the first filtration until the end 120 min. Sample 4 (6 h synthesized) show the lowest drop in normalized flux compared to other PSf/GO membranes. Meanwhile sample 3 show the highest drop in flux after 120 min this can be relate to metastable condition of GO that tend to be in hydrophobic condition and easily can trap foulants. Second highest drop shown by the sample 5 and 6, this could be due to agglomeration of particles that able to block foulants from pass through the membranes.

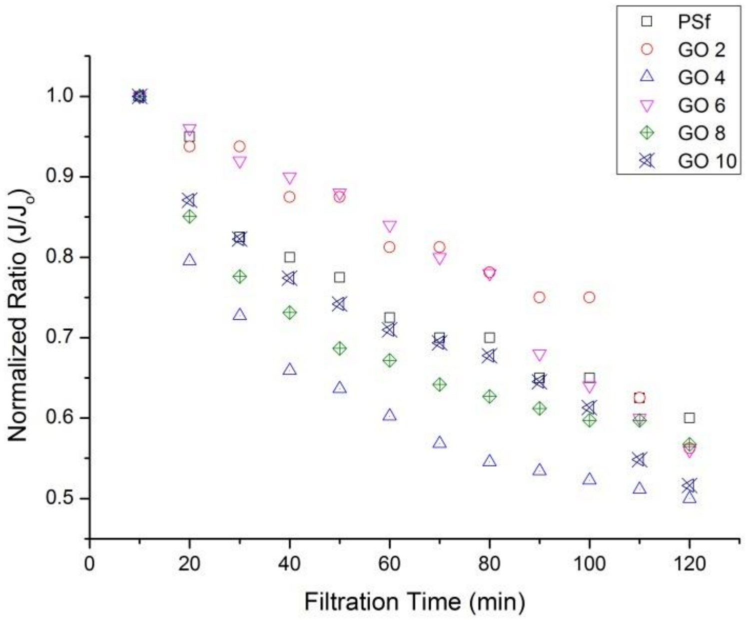

Figure 3: Normalized flux ratio at different time synthesized of PSf/GO membranes

4. Conclusion

Synthesization of Graphene oxide (GO) was successfully conducted using Hummer's method in this study and then GO was embedded with the polymer membrane via phase inversion techniques. The effect of GO synthesization from graphite incorporated into polymer membrane was investigated, observed and studied based on the permeation and rejection of humic acid performance onto the PSf/GO membranes. Results showed that polymer mixed matrix membrane incorporated with graphite strongly influenced by the duration synthesized of GO. Stable GO able to provide better hydrophilicity and showed better permeation value. Meanwhile higher concentration of additive along together metastable condition of GO tend to be hydrophobic has tendency to create pore blockage and foulants accumulation, as presented by normalized flux ratio results.

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