Fabrication of Composite Magnetic HAP/GO-PES Membrane for Iron Removal

Luqman Bin Roslan, Dr. Nur Hidayati Bt. Othman

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—Polymeric based membrane usually having problems with fouling and hydrophilicity of it surface. Thus, a new material which is graphene oxide (GO) was introduced to reduce the fouling effect. GO which obtained from the modified Hummers method is bind to the polymeric membrane. The magnetic NPs and hydroxyapatite (HAP) was added into the GO-PES membrane to form GO-MHAP-PES membrane. The membranes were fabricated using phase inversion technique and embedded with various percentage of GO (0.5, 1.0, 1.5 and 2.0 wt%). The effect of GO-MHAP-PES membrane morphology and performance were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), water contact angle, and Fourier Transform infrared (FTIR). The fabricated membrane display higher rejection rate compared to the bare.**

Keywords*—*Graphene oxide, Magnetic nanoparticle, Phase inversion technique

I. INTRODUCTION

Heavy metals are defined as metallic elements that have a relatively high density compared to water. Besides, heavy metal defined as a highly electronegative metals with a density greater than 5 g/cm3 [1]. Heavy metals is a major concern because it able to affect human and ecosystem since it is toxic, persistence and non-degradable [2]. Sources of heavy metals include mining industry, foundries, smelters, chemical plant waste, and emission gas from vehicle or factories and agriculture activities.

In the past decade, many research and technologies have been done to remove heavy metals such as utilization of adsorbent, membrane filtration, chemical precipitation, centrifuges, and electro- dialysis. Among them, membrane filtration technologies seem to be the most efficient to control and removed heavy metal efficiently. Besides, it also capable to remove suspended solid, organic and inorganic effluent. There are several types of process available in membrane filtration, which is ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO), and nanofiltration (NF). All of the processes are classified according to their capability to remove particles according to contaminant size.

The introduction to the membrane technologies is one of the technologies used in water treatment industry. Although membranes have a capability in delivering high efficiency water separation, low cost operation and simple operation, membrane also has its limitations. Their limitation is fouling and hydrophilicity especially polymer based membrane. These problems can be reduced by modifying the membrane surface by using hydrophilic polymers, adding nanoparticles (NPs) or apply the organic coating [3].

Thus, this study was conducted to modify the existing polymeric membrane with presence of graphene oxide (GO) and addition of magnetic nanoparticles (mNPs) in order to decrease membrane fouling, enhanced rejection rate and increase it capability to absorb heavy metal. The presence of mNPs is to enhance the surface area of the membrane. Presence of mNPs will yields different characteristics from bulk metals, in which the nano-size particulates would exhibit greater physical and chemical properties [4].

Therefore, the main objective in this study is to compare the performance of polymeric membrane and polymeric membrane with addition of mNPs and GO.

II. METHODOLOGY

A. *Materials and Chemicals*

Graphite powder (Mw=12.01, COMAK) was used in the experiment. Chemical such as polyethersulfone (PES), N,N-Dimethylacetamide (DMAc) are purchased from Sigma Aldrich and used as polymer and solvent to prepare cast solution. On the other hand, sulphuric acid (H2SO4) (95%-98%, R&M Chemicals), sodium nitrate (NaNO3) (84.99 g/mol, SYSTERM), potassium permanganate (KMnO4) (158.05 g/mol, R&M Chemicals), hydrogen peroxide (H2O2) (30%, Merck) were used in GO preparation. Diluted hydrochloric acid (HCL) and deionized water were prepared in the lab.

For synthesis of hydroxyapatite (HAP) and magnetic nanoparticle (mNPs) was iron (II) chloride tetrahydrate (FeCl2.4H2O), iron (III) chloride hexahydrate (FeCl3.6H2O), nitrogen (N2) gas, hydrazine hydrate (H6N2O), calcium nitrate tetrahydrate (Ca(NO3)2.4H2O) and diammonium phosphate ((NH4)2HPO4).

B. *Synthesis of GO and Magnetic HAP*

Preparation of GO from raw graphite powder and Hummer's method was applied. In order to produce 10 g of GO, it need 10 g of graphite powder, 5 g of Sodium Nitrate (NaNO3), 60 g of Potassium Permanganate (KMNO4) and 400 ml of Sulphuric acid (H2SO4).

Firstly, 10 g of graphite powder together with 5 g sodium nitrate (NaNO3) were diluted in 400 ml of sulphuric acid (H2SO4) in 2000 ml beaker. The mixture were stirred continuously at 350 rpm in the ice bath condition to maintain it temperature below 15°C for one hour. After one hour stirred, the mixture was continuously stirred for another two hour. In between two hour period, 60 g of potassium permanganate (KMNO4) is added in a small portion and temperature was maintained below 15℃. After two hour, the beaker was removed from ice bath condition and left stirred for another 22 hours in a room temperature condition. Next, the mixture was heated to 70 ℃ and stirred for three hours. The temperature increased to 90℃ with added 200 ml distilled water and left stirred for one hour.

The reaction will stop instantly when 60 ml of hydrogen peroxide was added. The mixture then was cooled enough to proceed with washing using Hydrochloric acid (HCl) and distilled water for several times. The HCl was prepared from saturated HCl using dilution technique. 160 ml of HCl was mixed with 1840 ml distilled water and produced diluted HCl. Acetone was added into the mixture at the end of washing period. The mixtures were split into several tubes for centrifuged. The mixtures were centrifuged at 10,000 rpm at 15℃. The centrifuged mixtures were placed in the petri dishes. Lastly, the petri dishes were dried in oven for 24 hours at 60℃.

In order to synthesis magnetic HAP with GO, this steps were followed. Firstly, 2.7 g GO was dispersed in 750 mL water by sonication for one hour to convert carboxylic acid group into carboxylate anions. Then, FeCl2.4H2O (19.05 g) and FeCl3.6H2O (48.75 g) were dissolved in 600 mL pure water solution, which were added dropwise to GO solution at room temperature under a nitrogen flow (40 mL/min) with vigorous stirring. Done completing ion exchange, 28% of ammonia solution was added gradually (with dropping rate 10d/min) in order to achieve solution of pH 10 for synthesis of magnetic Fe3O4 nanoparticle (clear black deposited obtained). After 15 minutes 150 mL of Ca(NO3)2.4H2O (33.7 mmol) and 150 mL of (NH4)2HPO4 (20 mmol) solutions whose pH were all modified to 11 were gradually poured in simultaneously to the precipitate solution achieved before for 30 minutes with mechanical stirring. The produced pure suspension was heated at 90℃ for two hour. Right after that, the mixture were cooled to room temperature and left for 12-24 hours without stirring. Lastly, the black deposited was separated by a magnet and washed frequently by deionized water until it reached neutral. Dried in the oven at 90℃ and grinded with mortar. Magnetic hydroxyapatite with graphene oxide GO-MHAP was the final product.

C. *Synthesis of GO-PES Membrane*

Referring to Table 1 and Table 2, it shows the composition and amount needed to synthesize GO-MHAP-PES membrane.

Firstly, polyvinylpyrrolidone (PVP), GO were added into the bottle filled with N,N-Dimethylacetamide (DMAc) solution. The bottle need to be stirred until the solutions inside is homogenous. Next, the mixed solutions need to proceed with sonication process for 30 minutes. After sonication, PES is poured into the bottle and stirred homogenously before proceed with 30 minutes sonication process. The synthesized membranes named as Bare PES, GO-MHAP-PES-0.1, GO-MHAP-PES-0.5, GO-MHAP-PES-1.0, GO-MHAP-PES-1.5 and GO-MHAP-PES 2.0.

Table 1 : Composition of Membrane

Membrane	PES (wt%)	DMAc (wt%)	GO-MHAP (wt%)	PVP
Bare PES	17	82	0	1
GO-MHAP-PES-0.5	17	81.5	0.5	1
GO-MHAP-PES-1.0	17	81	1.0	1
GO-MHAP-PES-1.5	17	80.5	1.5	1
GO-MHAP-PES-2.0	17	80	2.0	1

Table 2 : Membrane Dope

Membrane	PES (g)	DMAc (ml)	GO-MHAP (g)	PVP (g)
Bare PES	77.9	400	0	4.59
GO-MHAP-PES-0.5	78.4	400	2.306	4.61
GO-MHAP-PES-1.0	78.9	400	4.642	4.64
GO-MHAP-PES-1.5	79.4	400	7.0	4.67
GO-MHAP-PES-2.0	79.9	400	9.4	4.7

D. *Membrane Characterization*

1) *Fourier Transform Infrared Spectroscopy (FT-IR)*

Fourier Transform Infrared Spectroscopy (FT-IR) is the devices used to obtain the data on absorption or emission of infrared spectrum of solid, liquid and gas. FT-IR (Pelkin Elmer) used to analyzed the GO, PES and MHAPGO. FT-IR will show the results in form of transmittance vs wavelength.

2) *X-ray diffraction (XRD)*

X-ray diffraction (XRD) is the device used to confirm the FT-IR result. Rigaku model XRD is used where the GO powder is placed on the plate and placed in the holder of the device. The crystalline structure of the GO can be seen by using XRD. The measurement is performed in scanning range of 40 Kv, 40 mA, 5-80°, (2°/min).
.

3) *Water Contact Angle*

Water contact angle goniometer (AST Product INC VCA-3000s) model is used to measure the water contact angle measurement. Hydrophilicity of the membrane is when the water contact angle is higher than 90° and less hydrophilicity is when water contact angle is less than 90°. The device work when 5μL of water drop placed on the membrane surface’s and the needle tip is placed on top of the water drop. After that, a digital camera will magnify the image of water droplet. The measurement is taken three times and the average reading is record.

E. *Membrane Performance*

1) *Pure Water Flux*

This is the test to measure the permeate flow volume that passed through membrane. The test is conduct in a lab scale, which involved a dead end mode and tubular shape mode. Firstly, the membrane is compacted under six bar of ultrapure water until the flux reached equilibrium. The test is conducted for one hour where permeate volume are taken at 10 minutes interval. Then, the fluxes are calculated using this equation:

$$J = \frac{V}{A\Delta t} \quad (1)$$

Where J is pure water flux (L/m^2h), V is volume of permeated pure water (L), A is Effective area of membrane (m^2), Δt is differential time (hour).

2) *Water with Heavy Metal*

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (2)$$

Where, R is the rejection rate in percentage. C_p is the concentration of permeate solution (mg/l) and C_f is the concentration of the feed solution (mg/l).

III. RESULTS AND DISCUSSION

A. *Characterization of GO*

Fig.1 show the X-ray powder diffraction (XRD) pattern for graphite, GO and GO-MHAP.

As shown in the Fig.1 the diffraction peak of GO appeared at 2θ=10°. According to Mahmoudi etc.al. [5], the GO peak is at 2θ= 10.89°. Besides, GO peak spectrum also is confirmed at 2θ= 11°, according to Ionita etc.al. report [6]. Besides that, this result also compared with other studies which show that GO peak is at 2θ= 9.98° and 42.26° [7].

On the other hand, as stated by [8], graphite peak (green) is at 2θ= 26.5°. The peak is shifted to lower 2θ value which is at 10.8° and 23.9° which correspond to GO (red). This action happens due to complete oxidization of graphite.

Next, the crystalline structure of GO-MHAP shown in blue colour shows the peak presence at 2θ values 18.27°, 30.1°, 35.4°, 43.05°, 56.94°, 62.51°, and 73.95°. Furthermore, the very slight diffraction peak at 2θ value 10.0° show the crystal structure of GO. The diffraction peak of GO 2θ = 10.0° obviously reduced whereby GO-MHAP peak at 2θ = 42° was completely disappeared.

This statement is supported by report wrote by Chai etc.al.[9], the crystal structure of GO at peak 2θ= 10.80° and 42.22° indicate that graphite is fully oxidized to GO. However, the mNPs peak is obviously not clearly seen because of lower concentration of Fe_3O_4 used. In contrast, results obtained by Kassaee et al. [10], the higher concentration of Fe_3O_4 used show diffraction of Fe_3O_4 – Go peaks at 2θ= 13.37°, 23.71° and 42.24°. The peak at 2θ= 13.37° refer to peak of GO which shift because of interaction between Fe_3O_4 and GO [11]. Based on other literature studies, the peaks at 2θ= 23.71° and 42.24° referring to reduction of GO.

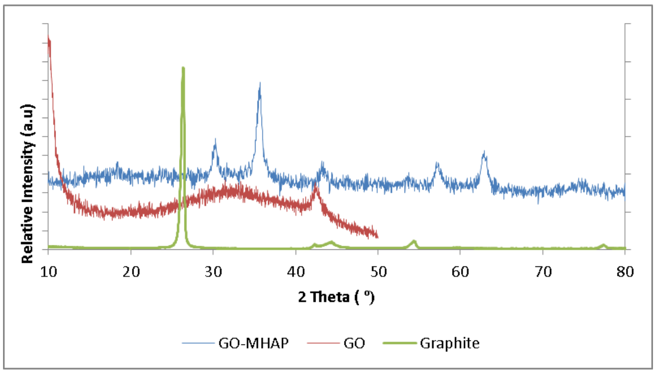

Figure 1: XRD pattern of the graphene oxide (GO) (red), graphite (green) and graphene oxide-magnetic hydroxyapatite (GO-MHAP) (blue).

From fig.2, the FT-IR spectrum of the GO shows that at peak 1618 cm^{-1} correspond to un-oxidized sp^2 C=C bond in the graphitic lattice structure, while the peak at 1044 cm^{-1} is the C-O stretching vibration [12]. Meanwhile the intense peak at 1721 cm^{-1} is referring to stretching vibration of –C=O bond from the carboxylic group and the broad peak at 3318 cm^{-1} referring to the stretching vibration of O-H bond from the synthesized GO [13]. Unlike GO, graphite spectrum do not have an oxygenous groups such as COOH, O-H and epoxide groups.

Further explained on GO from Ionita et.al [6], the FTIR spectrum of GO at 1736 cm^{-1} indicate C=O stretching vibration of COOH group. The peak at 1640 cm^{-1} attributed to C=C stretching mode of GO sp^2 network. Meanwhile, O-H functional group is at around 3000-3700 cm^{-1} which stretching from GO surface and to water obstructed in GO layer.

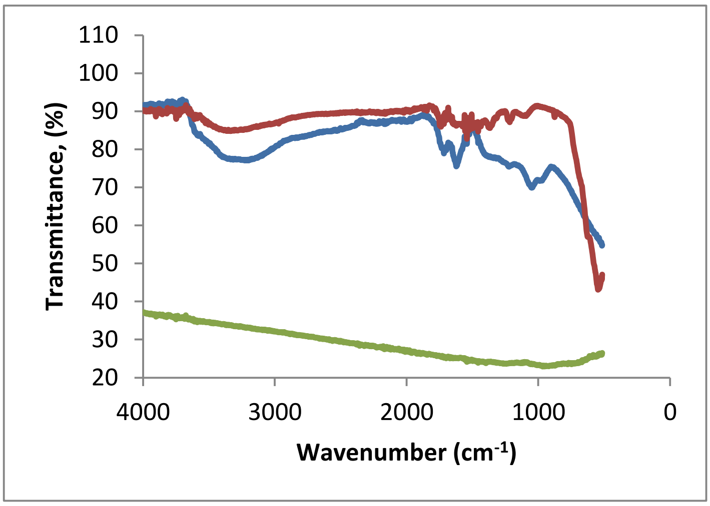

Figure 2: FTIR pattern of the graphene oxide (GO) (blue), graphite (green) and graphene oxide-magnetic hydroxyapatite (GO-MHAP) (red).

B. *Pure Water Flux and Water Contact Angle*

The data obtained from the test is used to construct water flux against time graph of each membrane at difference pressure.

First of all, the experiment is conducted to alter the hydrophilicity of the typical polymer membrane by adding nanoparticles that will increase it affinity toward water which is GO and magnetic nanoparticles.

From the pure water flux results in figure 3 and figure 4, the hydrophilicity of the membrane have improved compared to polymer membrane. In this experiment, the concentration of GO-MHAP were varied (0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%). Those concentrations have changed the performance of membrane to be more hydrophilic. As shown in figure 3 and figure 4, clearly seen that the bare membrane show the least water permeates compared to the rest of membrane at difference pressure condition. Besides, the increasing in GO-MHAP concentration not necessarily will provide the better performance for membrane. Membrane GO-MHAP-PES 1.5 wt% is the optimum membrane that allowed water to pass through it compared to membrane GO-MHAP-PES 2.0 wt%. This situation also is affect by the contact angle of the membrane. Bare membrane has higher water contact angle compared to GO-MHAP-PES membrane.

In figure 6, GO-MHAP-PES 1.5 wt% has slightly lower water contact angle than GO-MHAP-PES 2.0 wt% membrane. Thus, GO-MHAP-PES 2.0 wt% membrane has slightly less water flux than GO-MHAP-PES 1.5 wt% membrane. In addition to that, these phenomenon also due to addition and irregular positioning of GO nano-plate and decreased in functional groups on membrane surface [14] [3].

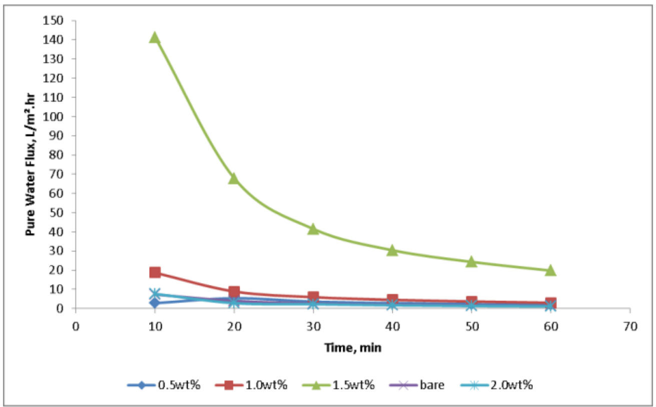

Fig. 3: Pure water flux, (L/m^2.hr) against time at pressure 1 bar. It shows the permeability of the membrane as the GO percentage increase.

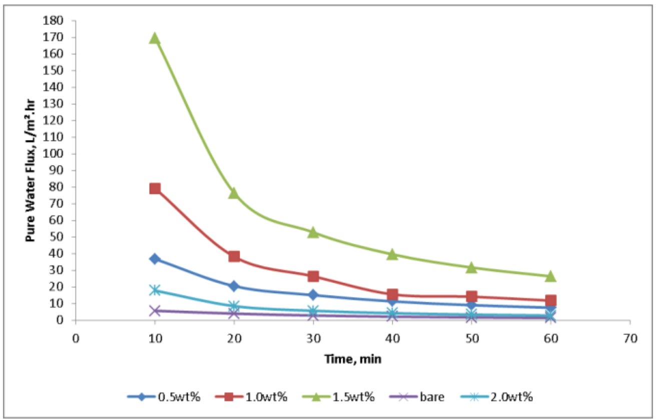

Fig. 4: Pure water flux, (L/m^2.hr) against time at pressure 2 bar. It shows the permeability of the membrane as the GO percentage increase.

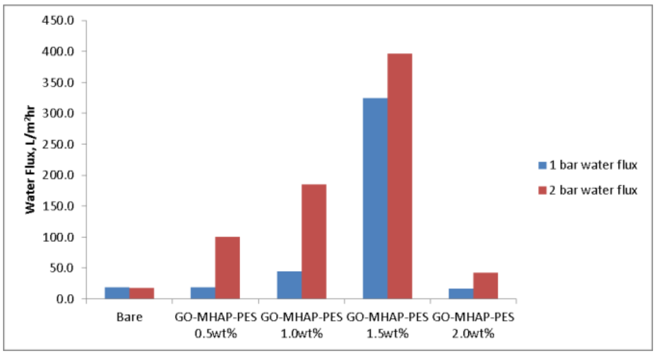

Fig. 5: Total Pure water flux, (L/m^2.hr) at 1 hour for every membrane.

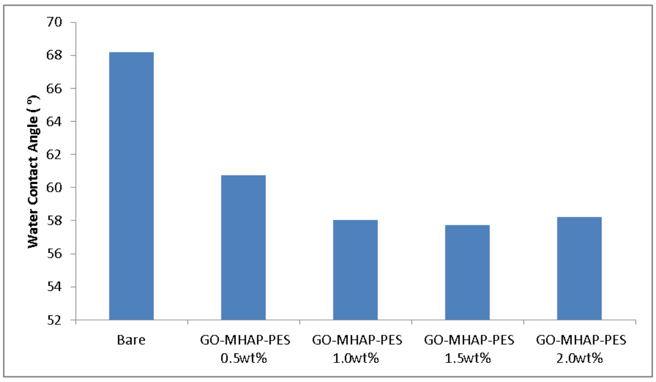

Fig. 6: Summary of pure water flux at pressure 1 bar and 2 bar with contact angle of each membrane.

C. Iron removal

In this experiment, iron was choose to analyze the performance of the fabricated membrane toward heavy metal removal. The stock solution of 200 ppm iron Fe^{2+} was prepared. The membranes were test under 2 bar pressure.

Table 3: Rejection Rate of Fabricated Membrane

Membrane	Rejection Rate (%)
Bare PES	42.6
GO-MHAP-PES 0.5wt%	62.3
GO-MHAP-PES 1.0wt%	82.5
GO-MHAP-PES 1.5wt%	96.5
GO-MHAP-PES 2.0wt%	97.9

Referring to figure 7, the trend of the rejection increased as the concentration the GO-MHAP-PES membrane increased. Bare PES membrane show the least rejection rate compared to other membrane with presence of GO-MHAP-PES. Bare PES membrane was lack of the magnetic nanoparticles which is GO-MHAP that act magnet to attract the Fe^{2+} ions in GO-MHAP-PES membrane. Thus, it obviously shows that with the presence of the GO-MHAP will further enhanced the capability of the membrane to trap heavy metal. The highest rejection rate was achieved by GO-MHAP-PES 1.5wt% and GO-MHAP-PES 2.0wt% membranes. GO-MHAP in PES membrane provides the active sites, which increase the effectiveness of PES membrane toward iron rejection. The Fe rejection rate is at 96.5% and 97.9% demonstrate by GO-MHAP-PES 1.5wt% and GO-MHAP-PES 2.0wt%.

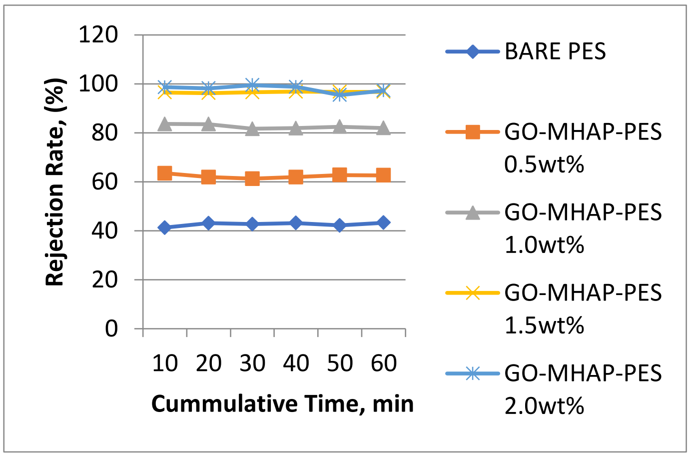

Figure 7: Rejection Rate of the Membrane

IV. CONCLUSION

As a conclusion to the experiment of fabrication of magnetic nanocomposite GO-MHAP-PES membrane is to show the increased in affinity of the polymer membrane PES toward water and its effectiveness to remove iron.

Synthesize of the GO by Hummer’s method and GO-MHAP was successfully done. The characterization of the GO and GO-MHAP were done and it proven the nanoparticles by X-ray diffraction (XRD) and Fourier transform infrared (FTIR).

GO-MHAP-PES membrane was successfully fabricated and achieved the objectives of the experiment. There were five membranes fabricated, Bare PES, GO-MHAP-PES 0.5wt%, GO-MHAP-PES 1.0wt%, GO-MHAP-PES 1.5wt% and GO-MHAP-PES 2.0wt%. The modified membrane was proved to have more affinity toward water compared to Bare PES. Water contact of Bare PES is 68º bigger compared to modified membrane. Lower water contact angle referred to more hydrophilic and higher water contact angle was vice versa. The hydrophilicity of the membranes was shown in pure water flux test. GO-MHAP-PES 1.5wt% produced the highest water flux accompany by GO-MHAP-PES 1.0wt%, GO-MHAP-PES 0.5wt%, GO-MHAP-PES 2.0wt% and Bare PES.

Next is iron removal. The rejection rate of iron with stock solution 200 ppm and at pressure two bar condition was tested. The highest rejection rate obtained by GO-MHAP-PES 1.5wt% and GO-MHAP-PES 2.0wt% was 96.5% and 97.9%. High Fe rejection rate was influence by it hydrophilicity and the presence of GO-MHAP. Thus, GO-MHAP-PES membrane was the suitable membrane for iron removal.

ACKNOWLEDGMENT

In the name of Allah S.W.T, with all the possibilities that been given to me to complete this final year project on fabrication of composite magnetic hydroxyapatite (HAP)-graphene oxide (GO)-polyetersulfone (PES) membrane (mHAP-GO-PES). Special thanks to my supervisor Dr. Nur Hidayati Bt. Othman, Oil and Gas Engineering lecturer of Universiti Teknologi MARA (UiTM) for her comments, ideas, guidance and times to help me in doing the project.

Finally yet importantly, I want to thanks my seniors for guidance and assist me in completing this project. Moreover, I have improved my lab skills and knowledge toward my project. Last but not least, special thank to all parties that participated directly or indirectly to make this project possible.

References

1. Agarwal, S.K., *Heavy metal pollution*. Vol. 4. 2009: APH publishing.
2. He, K., et al., *Comparison of soil heavy metal pollution caused by e-waste recycling activities and traditional industrial operations.* Environmental Science and Pollution Research, 2017. **24**(10): p. 9387-9398.
3. Igbinigun, E., et al., *Graphene oxide functionalized polyethersulfone membrane to reduce organic fouling.* Journal of Membrane Science, 2016. **514**: p. 518-526.
4. Chung, Y.T., et al., *Development of polysulfone-nanohybrid membranes using ZnO-GO composite for enhanced antifouling and antibacterial control.* Desalination, 2017. **402**: p. 123-132.
5. Mahmoudi, E., et al., *Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanoplates.* Chemical Engineering Journal, 2015. **277**: p. 1-10.
6. Ionita, M., et al., *Improving the thermal and mechanical properties of polysulfone by incorporation of graphene oxide.* Composites Part B: Engineering, 2014. **59**: p. 133-139.
7. Stobinski, L., et al., *Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods.* Journal of Electron Spectroscopy and Related Phenomena, 2014. **195**: p. 145-154.
8. Asgar, H., et al., *Synthesis of graphene via ultra-sonic exfoliation of graphite oxide and its electrochemical characterization.* Materials Chemistry and Physics, 2018. **206**: p. 7-11.
9. Chai, P., et al., *Preparation of novel polysulfone-Fe3O4/GO mixed-matrix membrane for humic acid rejection.* Journal of Water Process Engineering, 2017. **15**: p. 83-88.
10. Kassaee, M., E. Motamedi, and M. Majdi, *Magnetic Fe3O4-graphene oxide/polystyrene: Fabrication and characterization of a promising nanocomposite.* Chemical Engineering Journal, 2011. **172**(1): p. 540-549.
11. Shen, X., et al., *One-pot solvothermal syntheses and magnetic properties of graphene-based magnetic nanocomposites.* Journal of Alloys and Compounds, 2010. **506**(1): p. 136-140.
12. Hu, M. and B. Mi, *Enabling graphene oxide nanosheets as water separation membranes.* Environmental science & technology, 2013. **47**(8): p. 3715-3723.
13. Gao, W., et al., *Engineered graphite oxide materials for application in water purification.* ACS applied materials & interfaces, 2011. **3**(6): p. 1821-1826.
14. Rezaee, R., et al., *Fabrication and characterization of a polysulfone-graphene oxide nanocomposite membrane for arsenate rejection from water.* Journal of Environmental Health Science and Engineering, 2015. **13**(1): p. 61.