Investigation of GO-MNP-HAP Hollow Fibre and Disc Membrane for Oily Wastewater Treatment

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***Abstract*— The membrane separation technology has been seen as an alternative wastewater treatment toward the conventional treatment. However, the membrane separation also has several disadvantages such as fouling and generally low selectivity. Thus, a new material which is graphene oxide magneticnanoparticles hydroxyapatite (GO-MNP-HAP) was introduced. GO-MNP-HAP was synthesized through the modified Hummer's method and chemical in situ method. The GO-MNP-Hap was coated on to the surface of ceramic supported hollow fibre and disc membrane to reduce the fouling effet of the membrane. The characterization of the GO-MNP-HAP hollow fibre and disc membrane was investigated by using, X-ray diffraction (XRD), and Fourier Transform infrared (FTIR) The performance study of the GO-MNP-HAP ceramic supported membrane was evaluated through oily wastewater rejection at different concentration. The GO-MNP-HAP coated membrane display higher permeate flux varied from 1201.58 L/m^2.h to 16689.10 L/m^2.h and oil rejection rate up to 98% compared to the bare membrane.**

Keywords*— Graphene oxide, Magnetic nanoparticle, Hummer's method

I. INTRODUCTION

In the oil and gas industry, the production of the wastewater especially oily wastewater is tremendously higher that the production of the oil and gas itself. Commonly, the oily wastewater has a high content of hydrocarbon that mixed well with the water. The oily wastewater is extremely toxically and can give harm to human health and as it will contaminate the clean water resources if being directly discharged. In order to be reused or discharge to the environment, the oily wastewater need to undergo specific wastewater treatment to remove the oil content in the water that strictly need to meets the National Wastewater Discharge requirement.

There are several conventional techniques and technology that being introduced for the oily wastewater treatment like hydrocyclone, induced air floatation, biological treatment, centrifugal separation and coagulation-flocculation. The conventional techniques provide some good advantages for the water treatment but it limited by the low of operation efficiency and required high total and operating [1]. Therefore, the membrane technology was introduced as an alternative technology to improve the oily wastewater treatment. Membrane is semipermeable selective barrier that act as the filter that trap oil, suspended and colloidal particles, dissolved ionic and non-ionic substance from the wastewater. The membranes process separation has some advantages such as environmentally friendly due to no requirement of chemical during the process, low energy consumption, capable to produce high quality of permentate and low in operational cost. The membrane can be categorized into microfiltration (MF), ultrafitration (UF), nanofitration (NF) and reverse osmosis (RO) based on their membrane pore size. Ultrafiltration (UF) is one of the most effective methods for oily wastewater treatment in comparison with the traditional separation methods because of high oil removal efficiency, no chemical additives, low energy costs and small space occupancy [2]. The application of microfiltration and ultrafiltration membranes in oily water treatment were the most common based on the past researches. Abadi et al conducted a research on Tehran refinery oily wastewater treatment by using tubular ceramic (α-Al_2O_3) microfiltration (MF) membrane [3]. C. Wu et al studied on the on the performance of polyvinylalcohol (PVA) ultrafiltration for oily wastewater treatment by using pilot-scale continuous cross-flow membrane system [4]. The membrane produce more than 95% recovery ratio and demonstrates anti-fouling characteristic towards oil. Li et al proposed a purification of oily wastewater by using tubular ultrafiltration (UF) membrane with inorganic nano sized aluminia particles modification [5].

However, the application of membrane in oily wastewater treatment have some disadvantages such as fouling, short membrane life time and low in selectivity. The fouling is the main problem that encountered in the membrane system which can effects the performance of the membrane and the quality of the produced water from the process. Thus, in order to minimise this problem, some modification on the membrane surface has been done to improve the hydrophilic and performance of the membrane. The surface modification of a membrane comprises the attachment or binding of some additional interactions (affinity, responsiveness or catalytic properties) to enhance the performance of the membrane [6]. Therefore, several researches has been made on the modification of membrane surface to improve its performance. Othman et al synthesized graphene oxide (GO) by using modified Hummer's method and deposited on the aluminia hollow fibre substrate by using vacuum assisted method [1]. The performance of the membrane was investigate with the synthetic oil feed and its produce more than 90% rejection. Zhou et al modified the commercial Al_2O_3 MF membrane with nano-sized ZrO_2 for oily wastewater treatment. The modified membrane increase the hydropihilic of the membrane and increase its performance by produce rejection rate up to 97.8% [7].

In this work, the graphene oxide magnetic nanoparticles hydroxyapatite (GO-MNP-HAP) membrane was synthesized and deposited onto the ceramic hollow fibre and disc substrate using a vacuum suction method. The performance of the membrane to treat oily wastewater was then investigated.

II. METHODOLOGY

A. Materials

For graphene oxide (GO) synthesization, graphite powder (MW=12.01), sulphuric acid (H2SO4) (95% - 98 %), sodium

nitrate (NaNO3) (84.99 g/mol), potassium permanganate (KMnO4) (158.05 g/mol), hydrogen peroxide (H_2O_2) (30%), diluted hydrochloric acid and deionized water were used.

While iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate ($FeCl_2.6H_2O$), nitrogen (N_2) gas, hydrazine hydrate (H6N2O), calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) and diammonium phosphate ($(NH_4)_2.HPO_4$) were used for magnetic nanoparticles (MNP) and hydroxyapatite (HAP) synthesization. Ceramic hollow fibre and disc membrane were used for this experiment.

B. Synthesis of GO-MNP-HAP

1) GO Synthesization

The synthesizing of the graphene oxide from the graphite powder was prepared through the modified Hummer's method based on the recent studies of [1].

10g of graphite powder, 5g of Sodium nitrate ($NaNO_3$) and 400ml of Sulphuric acid (H_2SO_4) were diluted. The mixture was stirred at 350rpm in the ice bath condition and the temperature was kept under 15℃ for 1 hour. The mixture then was slowly added with the 60g of Potassium permanganate ($KMNO_4$) within 2 hours under continuous stirring at temperature below 15℃. The ice bath was removed and the mixture was kept stirred for 20 hours at room temperature until the dark brown colour was formed. The mixture was heated up and slowly added with 100ml H_2O to increase the temperature until 70℃ and kept constant for 3 hours. The mixture again was heated up and slowly added with 100ml to increase the temperature until 90℃ and kept constant for 1 hour.

. After that, 60ml of Hydrogen Peroxide was added into the mixture to stop the reaction and with the heat released. The mixture then repeatedly washed with the diluted HCl, distilled water and acetone. The mixture was centrifuged with 10000rpm at the room temperature for 25 minutes to separate the mixture until it formed gel like solution. The gel like solution was layered on the petri dishes and dried in the oven at 60℃ for 24 hours. The produced graphene oxide powder was labelled as GO.

2) GO-MNP-HAP Synthesization

The synthesizing of the GO-MNP-HAP was based on the modified method propose from the recent studies of [8] . Firstly, 0.9 GO with 250ml of distilled water was dispersed through the sonication for 1 hour in order to transform the carbocyclic acid groups to carboxylate anions. 6.35g of $FeCl_2.4H_2O$ and 16.25g of $FeCl_3.6H_2O$ was dissolved into 200ml of pure water solution. The mixture then was added drop wise into the GO solution at the room temperature along with the 40ml/min of nitrogen flow with a vigorous stirring at 300 rpm.

After the ion was completely exchange, 10ml of 28% of ammonia solution was added at the rate of 10 drop/min until the solution become pH 10 for the magnetite Fe_2O_4 NP synthetizing. The black precipitate was produced instantly. Then, after 15 minutes 50ml of $Ca(NO_3).4H_2O$ (33.7mmol) and 50ml of $(NH_4)2HPO_4$ (20mmol) solution whose pH adjusted to 11 were dropped simultaneously into the precipitate solution for 30 minutes under mechanical stirring. The pure suspension was heated until 90℃ and kept constant for 2 hours. The mixture was left cooled at room temperature for 12 to 24 hour. The precipitate was separated and washed repeatedly with distilled water until the pH neutral by using magnet. Then the precipitate was dried in the oven at 90℃ for 24 hours. The dried precipitate was grinded with the mortar to form powder. The powder then was labelled as the GO-MNP-HAP.

Fig 1 Separation of GO-MNP-HAP by using magnet.

C. Preparation of GO-MNP-HAP Hollow Fibre and Disc membrane

1) Preparation of GO-MNP-HAP Coating Solution

The GO-MNP-HAP coating solution was prepared by immersed 0.4g of GO-MNP-HAP powder into 200mL of deionized water. The solution then was left for ultrasonic for one hour to obtain homogenous solution. After ultrasonic treatment, the GO-MNP-HAP solution become homogenous

Fig 2 GO-MNP-HAP coating solution before utrasonic (left), after ultrasonic (right)

2) Preparation of GO-MNP-HAP Hollow Fibre membrane

The hollow membrane was modified with GO-MNP-HAP by deposited it via a vacuum suction method based on the method suggested by [1]. One end of the hollow fibre was sealed while the other one was connected with the vacuum pump as shown in **Fig 3**. Water was sucked into the fibre and flow directs GO-MNP-HAP flakes to the hollow fibre membrane, once the vacuum was applied to the fibre lumen for one hour. Then the GO-MNP-HAP hollow fibre membrane was left dried at room temperature for one hour and then was dried in the oven at 60℃ for 12 hours.

As shown in **Fig 4**, the hollow fibre changed colour from white to brownish colour after GO-MNP-HAP coating. That show that the GO-MNP-HAP was successfully deposited onto the surface of the hollow fibre. The GO-MNP-HAP coated hollow fibre then was tested with oil removal on dead end permeation test.

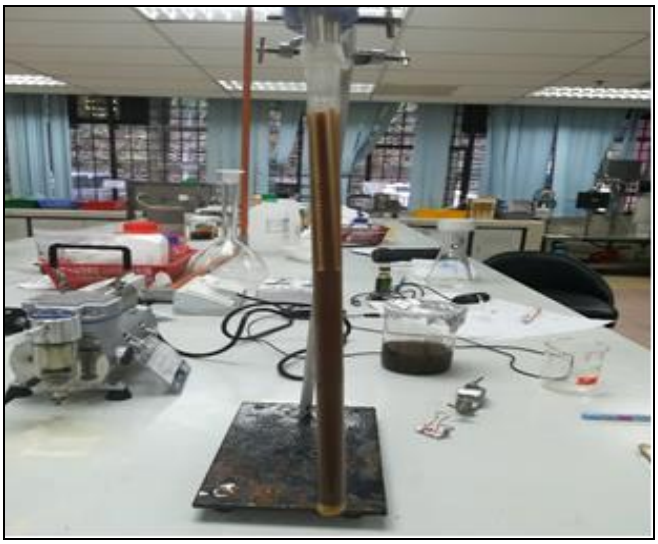

Fig 3 Vacuum suction set up

Fig 4 Hollow fibre membrane before coating (above), after GO-MNP-HAP coating (below**)**

3) Preparation of GO-MNP-HAP Disc membrane

The ceramic disc membrane was coated with GO-MNP-HAP via dip coating method suggested by recent studies of [9] . Next, the disc membrane was dip into GO-MNP-HAP aqueous solution at room temperature for about 30 second so that the GO-MNP-HAP membrane could totally deposited onto the surface of ceramic disc membrane. Then the GO-MNP-HAP disc membrane was left dried in the oven at 60 ℃ for 12 hours. **Fig 5** below show the dip coating method for disc membrane coating.

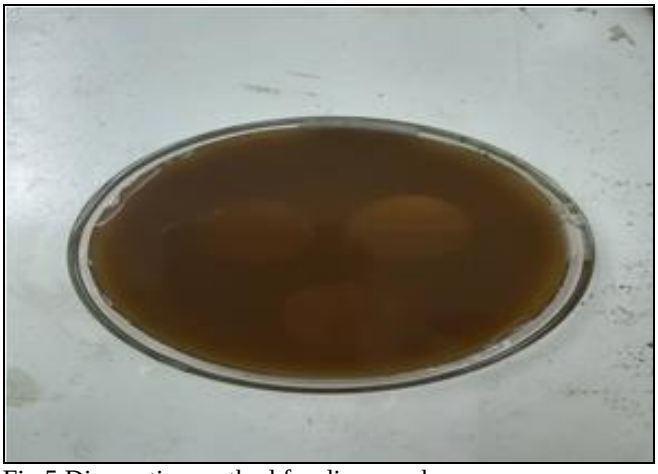

Fig 5 Dip coating method for disc membrane

As shown in **Fig 6**, the disc membrane turns to brownish colour after dip into the GO-MNP-HAP coating solution. This show that, the surface of the disc membrane was successfully coated with GO-MNP-HAP. The GO-MNP-HAP modified membrane then was tested with oily wastewater by using dead end permeation test.

Fig 6 Disc membrane before GO-MNP-HAP coating (left), after coating (right)

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4) Preparation of Oily Wastewater Calibration

The treatment of the oily wastewater was evaluated by using GO-MNP-HAP hollow fibre and disc membrane. The presence of surfactant, SDS in oily wastewater preparation was to promote the stabilization of oil in water. The stability of oily wastewater was observed every 1 hour for about 5 hour. From the **Fig 7** below, the oil in water was well mixed and did not form a distinct layer after left for 5 hours.

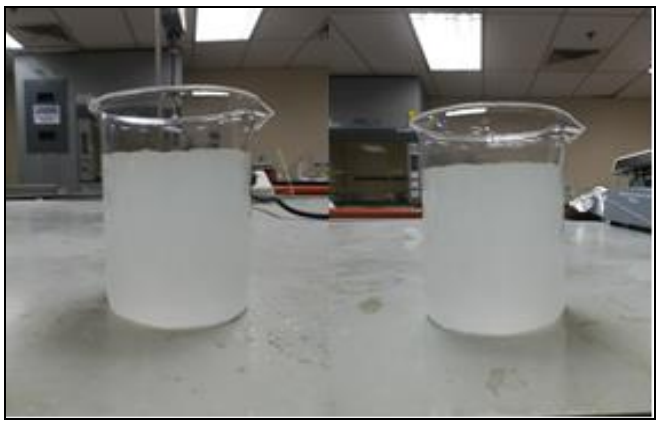

Fig 7 After left 1 hour (left), after 5 hour (right)

III. RESULTS AND DISCUSSION

A. Characterization of GO and GO-MNP-HAP

1) XRD Characterization

XRD analysis was used to characterize the crystalline nature. GO shows a diffraction peak at $2\Theta = 10.04°$. The result was consistent with studied by [9]. The diffraction peak of GO was mainly due to the oxidation of graphite. The increased interlayer spacing of the GO sample was due to the oxidation of graphite and this indicates that the oxygen bond was found between the interlayer. The changes of peak to 10.04° and increased d-spacing has proved that GO was successfully synthesized.

The crystalline structure of GO-MNP-HAP was identified with XRD. The diffraction peak of GO at $2\Theta=10.04^0$ was reduced while diffraction peak of GO at $2\Theta=42^0$ was totally disappears. This characterization was satisfy with the recent studies of [8].

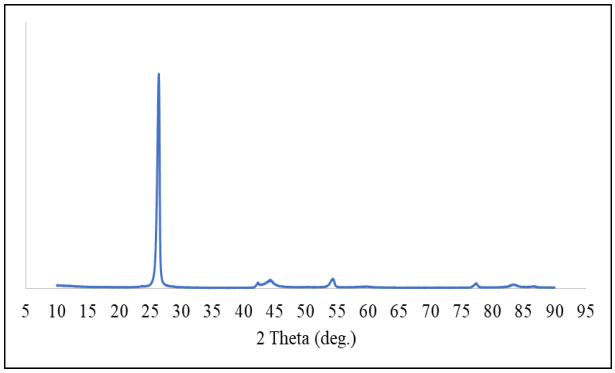

Fig 8 XRD pattern of graphite

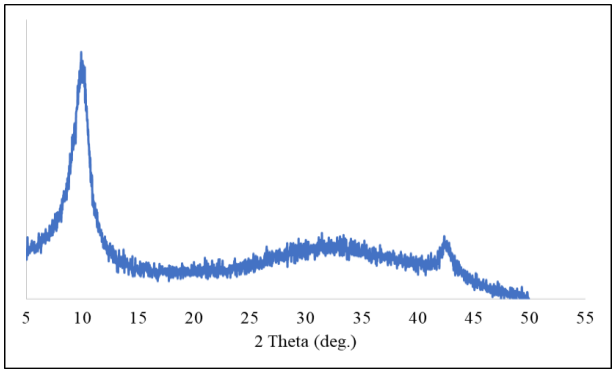

Fig 9 XRD pattern of GO

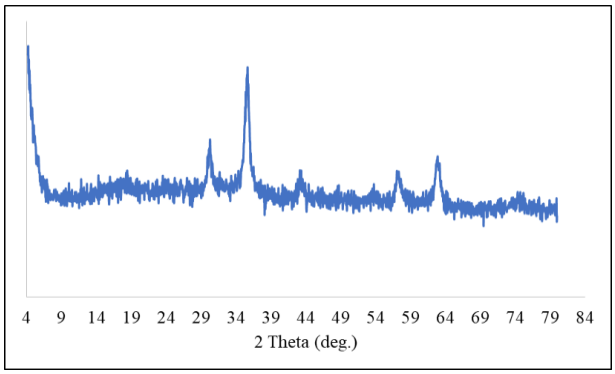

Fig 10 XRD pattern of GO-MNP-HAP

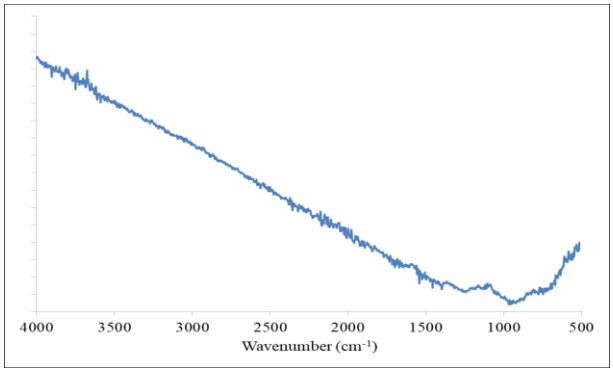

Fig 11 FTIR spectra of graphite

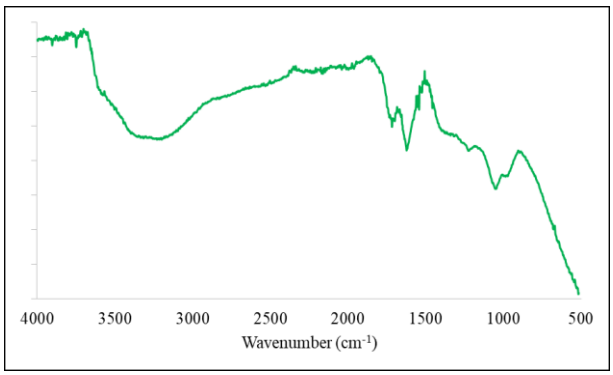

Fig 12 FTIR spectra of GO

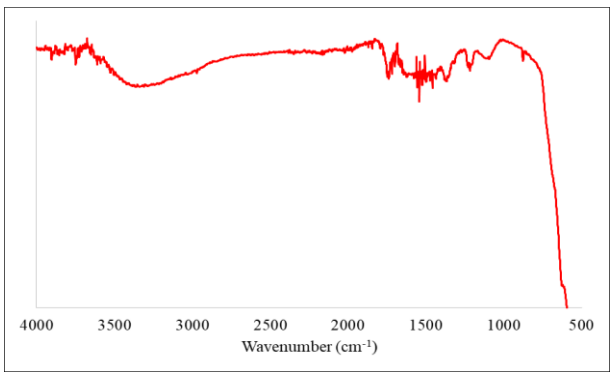

Fig 13 FTIR spectra of GO-MNP-HAP

2) FTIR Characterization

The FTIR spectra reveal the presence of can be attributed to the existence of functional groups. The FTIR spectra reveal the presence of C=C at 1716.55 cm^{-1} and 1622.72 cm^{-1} almost as similar study to [1]. While at **Fig 12** the peak at 1542.09 cm^{-1} corresponds to C-O-C stretch. Meanwhile, the peaks at 3228.92 cm^{-1} attributed to the existence of OH functional group. The peak at 1052.33 cm^{-1} is attributed to the C-O bond.

As shown in **Fig 13** the peak attributed to OH functional group decrease to 3335.55 cm^{-1} while the peak correspond to C-O-C stretch reduced to 1523.44 cm^{-1}. The changes in FTIR spectra confirm the synthesization of GO-MNP-HAP with the present of functional group.

B. Performance Study of GO-MNP-HAP Hollow Fibre and Disc membrane

The performance of both bare and GO-MNP-HAP modified ceramic membrane on oily wastewater separation were investigated by using dead-end permeation test. The experiment was performed at room temperature and pressurized to 1.5 bar with three different feed concentration, 100 ppm, 500 ppm and 1000 ppm of oily wastewater. The oily wastewater was pumped and introduced in the membrane module and pass through the membrane as permeate. Permeate was collected every 15 minutes for two hours. The permeate tested by using UV-VIS spectroscopy to be tested for oil rejection.

The permeation rate was calculated by using this equation:

1

$$J = \frac{Q}{A} = \frac{V}{A \times t}$$

Where, J is water flux in $L/m^2.hr$, V is the permeate in L, A is the effective membrane area m^2, T is time in hour, hr.

The concentration of the feed will change from higher concentration to low concentration after passed through the membrane. The rejection rate can be calculated by using a simple formula:

$$R = (1 - \frac{Cp}{Cf}) \times 100 \quad (2)$$

Where Cp is the concentration of the permeate that passed through the membrane, while Cf is the concentration of the feed.

1) *Pure Water Flux Study*

The pure water flux study was conducted on dead-end permeation test. The experiment was conducted at room temperature and pressurized at 1.0 bar and 1.5 bar. The test was conducted by using bare hollow fibre and disc membrane to evaluate the performance of the bare membrane separation on pure water flux. The average membrane surface are of the hollow fibre used is 0.000257 m^2 while average membrane surface are for disc membrane was 0.000103 m^2.

The feed tank was filled up with deionized water. The water was pushed through the disc membrane and pass through the membrane as permeate. The permeate was collected for every 15 minutes for two hours. The volume of permeate collected was recorded and the pure water flux against cumulative time graph was plotted as shown in **Fig 14** and **Fig 15**.

Both membrane produce same permeate flux trend rate. At 1.5 bar pressure, both membrane produce high permeate flux after 15 minutes of operation before the flux start to reduce. While at 1.0 bar, both membrane produce a constant flux for 2 hours.

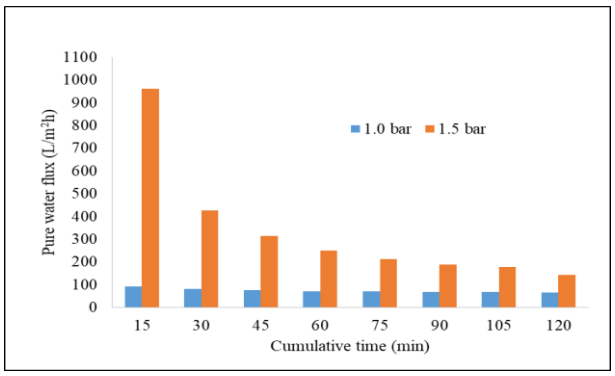

Fig 14 Pure water flux of bare hollow fibre at 1.0 and 1.5 bar

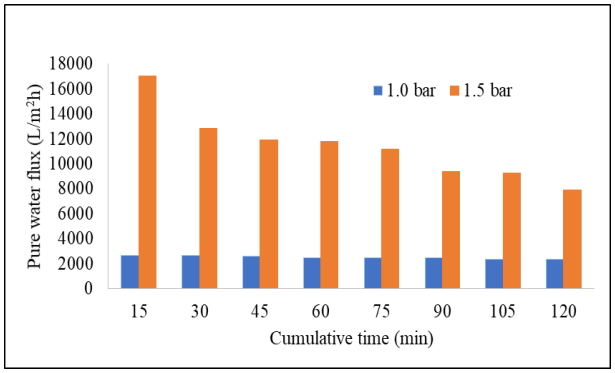

Fig 15 Pure water flux of disc membrane at 1.0 and 1.5 bar

C. *Oily Wastewater Separation Study*

The dead end permeation test was conducted to evaluate the performance of both unmodified and GO-MNP-HAP hollow fibre and disc membrane on oily wastewater separation. The experiment was carried out at room temperature and pressurized to 1.5 bar with three different feed concentration, 100 ppm, 500 ppm and 1000 ppm of oily wastewater. The oily wastewater was pumped and introduced in the dead end cell and pass through the membrane as permeate. The permeate was collected every 15 minutes for two hours and tested with UV-VIS spectroscopy to determine the oil rejection. The permeate flux and oil rejection for both bare and GO-MNP-HAP membrane was plotted against the cumulative time as shown in **Fig 16** until **Fig 21**.

From the graph below, both GO-MNP-HAP hollow fibre and disc membrane produce high permeate flux compare to the bare membrane. The permeate flux increases up to 50 % which indicate that the fouling effect of the membrane was minimised due to the presence of the GO-MNP-HAP surface coating. However, the permeate flux decreased as the operating time increase. This due to accumulation of oil deposited on the membrane surface. As the accumulation increase, the permeability of membrane gradually decrease cause reduction in permeate flux.

The GO-MNP-HAP modified membrane also show high oil rejection compared to the bare membrane. The highest rejection achieve by both hollow fibre and disc membrane were up to 98% of rejection. This indicate that the oil was totally removed from the water.

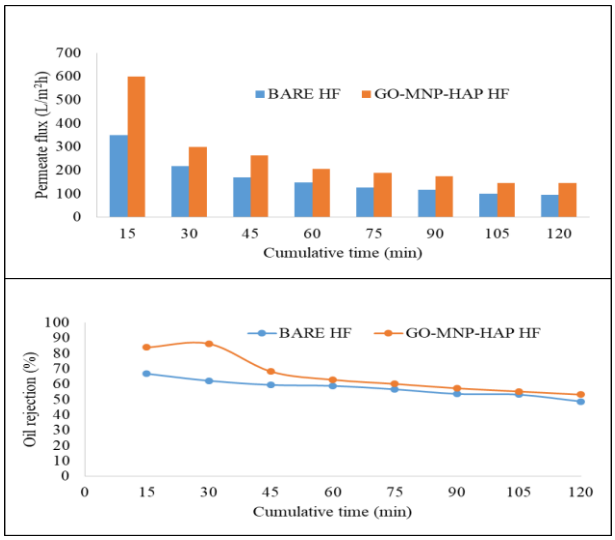

Fig 16 Permeate flux and oil rejection of bare and GO-MNP-HAP hollow fibre at 100 ppm

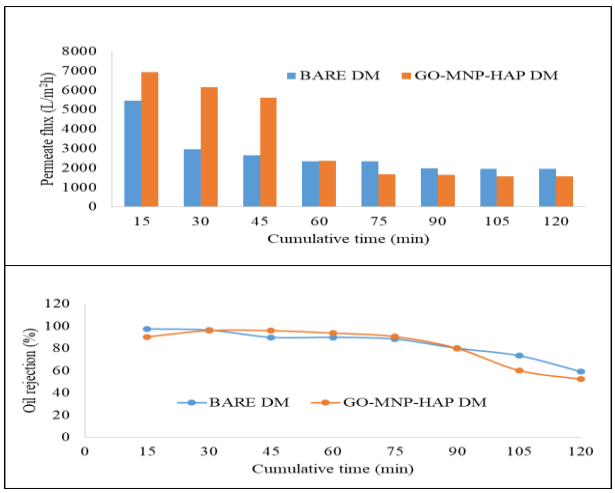

Fig 17 Permeate flux and oil rejection between bare and GO-MNP-HAP disc membrane at 100 ppm

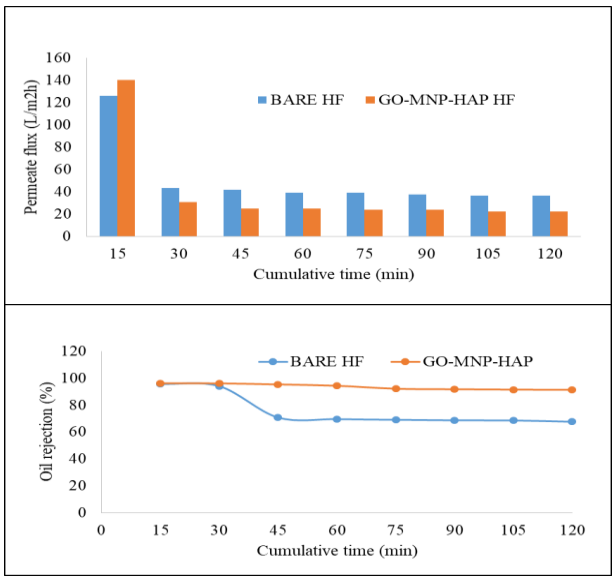

Fig 18 Permeate fluxx and oil rejection between bare and GO-MNP-HAP hollow fibre at 500 ppm

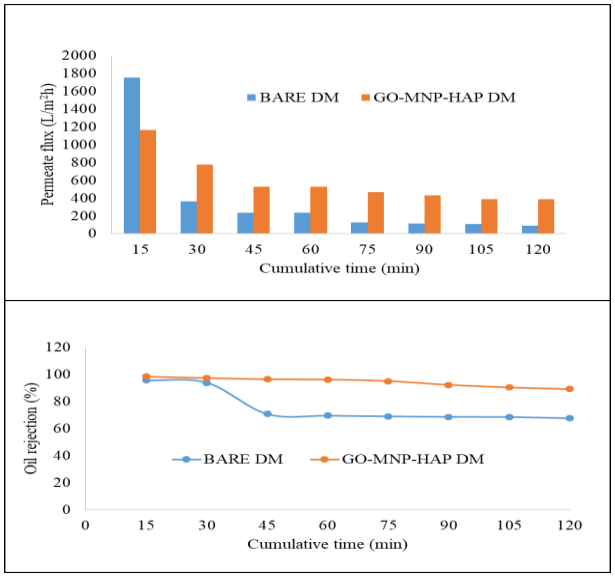

Fig 19 Permeate flux and oil rejection between bare and GO-MNP-HAP disc membrane at 500 ppm

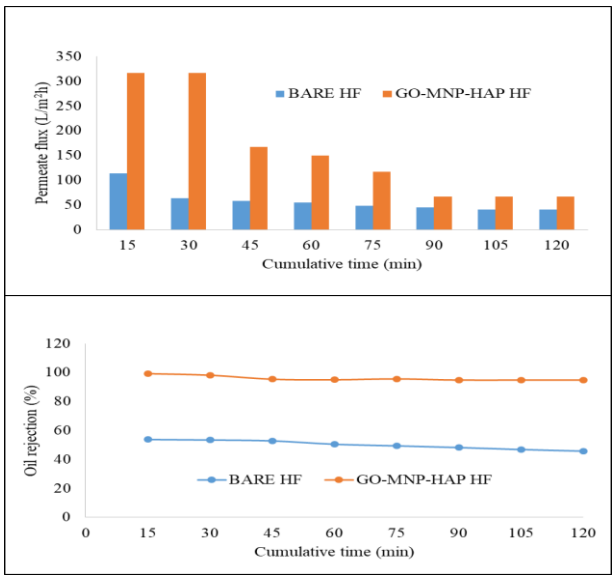

Fig 20 Permeate flux and oil rejection between bare and GO-MNP-HAP hollow fibre at 1000 ppm

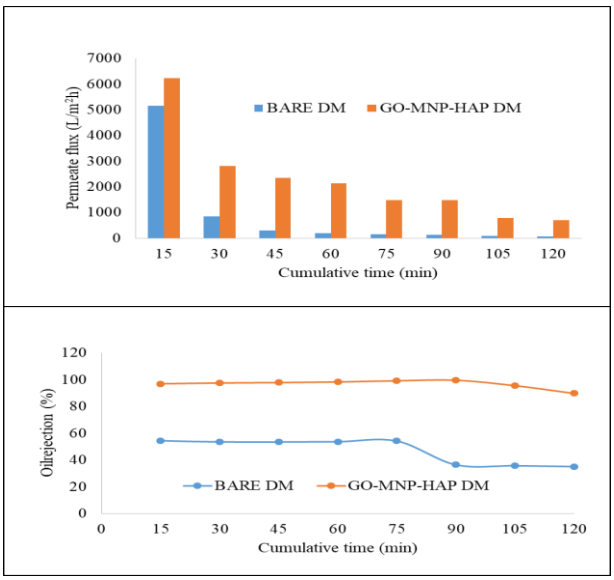

Fig 21 Permeate flux and oil rejection between bare and GO-MNP-HAP disc membrane at 1000 ppm

CONCLUSION

In this work, GO-MNP-HAP was successfully synthesized by using both Hummer's method and chemical in situ method. The GO-MNP-HAP hollow fibre and disc membrane was prepared by using vacuum suction method and dip coating method. From the characterization studies, the XRD pattern of graphite, GO, and GO-MNP-HAP show the peak changes that satisfy the recent studies of [8].. Both GO-MNP-HAP hollow fibre membrane produced average permeate flux each 1201.58 L/m^2.h and 16689.10 L/m^2.h and oil rejection up to 98%..The objectives of this study was successfully achieved. In conclusion, the GO-MNPHAP modified membrane can be a potential candidate for oily wastewater treatment both for onshore and offshore operations.

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