EFFECT OF DEMULSIFICATION OF OIL-IN-WATER EMULSION IN CATIONIC CONDITION USING GRAPHENE OXIDE

Muhammad Ikhmal bin Yahya and Aqilah binti Dollah

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—**Graphene oxide (GO) is an amphiphilic material capable of breaking oil-in-water emulsion at room temperature. Chemical demulsification are widely being used in the industry to treat oil-in-water emulsion which involves the use of chemical additives to rapidly enhance the emulsion breaking process. Hummer's method was used and successfully synthesized graphene oxide from graphite powder through strong oxidation process. Characterization of the GO produced was done using FTIR and XRD The performance of GO on separation of cationic surfactant stabilized emulsion was assessed experimentally. Results shows that GO successfully improves the demulsification process even under acidic condition but decrease in performance under alkaline condition.**

Keywords— Demulsification, Graphene oxide, emulsion, FTIR, XRD

I. INTRODUCTION

An emulsion is a stabilized mixture of two or more immiscible liquid, for example oil and water. Emulsion can be difficult to treat and can cause several operational problems in wet-crude handling facilities and also during separation process on surface facilities. Since oil is co-produced with water, it is very likely that formation of emulsion can occur along the production flowlines. The formation of emulsion occur due to the presence of oil and water in a single flowline along with the agitation caused when both of the liquid runs through the flowline. Apart from that, emulsion was also form due to the depletion in differential pressure. This phenomenon occur when the liquid exit the wellbore and onto to the surface. As the formation of emulsion occur, it will significantly reduce the differential pressure in the flowline and also slowdown the production. An Emulsion has a higher viscosity compared to when the liquid are in their original phase. These will lead to an increase in the use of demulsier and sometimes cause trip or upset in wet-crude handling facilities.

Emulsion is a serious threat to the production system. The formation of emulsion during oil production process or water treatment process is a very costly crisis, both in terms of the number of chemicals used for processing and treatment to meet product quality and the lost of production prior to emulsion incurred processing system shut-down. Formation of emulsion can cause difficulties during separation process where oil and water might fail to separate producing a less pure oil with high water content. Emulsion also carry fines and solid particles that can damage pipelines and other facilities through corrosions and erosions.

Radioactive materials are commonly found in a reservoir. Some of this material are likely to be produced along with sands, oil and water. This solids including sands can act as a stabilizer for the emulsion by accumulating on the wall of the emulsion droplets. This will strengthen the interfacial film and preventing separation of emulsion. Separation process of the oil is carried out inside a separator. At some point, when the emulsion is too stable, the separation process can fail resulting in all the solid particles to enter the production line. The presents of corrosive solid may cause damage to the valve and pump which is used to generate pressure to transport the clean oil. Valve and pump replacement can be very costly if the damage is too frequent due to the presence of the corrosive solid which failed to be separated. Emulsion also cause serious problem in the storage tank. The corrosiveness can damage the storage tank. Separation of emulsion will be harder in the storage tank as it was not build to separate emulsion.

The objectives of the study was to synthesized graphene oxide nanoparticles from graphite powder using modified Hummer's method and to study the performance of grapheme oxide nanoparticles as a demulsifying agent on a cationic surfactant stabilized synthetic oil-in-water emulsion at various watercut, pH and different concentration of GO used.

II. METHODOLOGY

A. *Materials*

For GO nanoparticle preparation, the materials used are graphite powder. Sodium nitrate ($NaNO_3$) was obtained from Systerm, sulphuric acid (H_2SO_4) obtained from R&M chemical and potassium permanganate ($KMNO_4$) also obtained from R&M chemical. Distilled water obtained from chemical lab, hydrogen peroxide (H_2O_2) obtained from Merck and hydrochloric acid (HCl) obtained from chemical lab.

For emulsion preparation, n-heptane and toluene was used as the synthetic oil. Distilled water was obtained from the chemical lab and Cetyl Trimethyl Ammonium Bromide (CTAB) used to stabilize the emulsion

B. *Preparation of Graphene Oxide (GO) Nanoparticle*

The graphene oxide was prepared using a modified Hummer's Method (Rattana et al., 2012). Initially, 10 g of graphite powder, 5 g of Sodium Nitrate ($NaNO_3$), 400 ml of Sulphuric Acid (H_2SO_4), and 60 g of Potassium Permanganate ($KMNO_4$) were measured accordingly. Then, 10 g of graphite powder and 5 g of $NaNO_3$ were diluted with 400 ml of H_2SO_4 inside a 2000 ml beaker and stirred using magnetic stirrer at 350 rpm. The mixture were cooled until below 15℃ inside an ice bath and left stirred for 1 hour. Under continuous stirring, 15 g of $KMNO_4$ were slowly added into the mixture every 30 minutes within the 2 hours period. The mixture was continued to be stirred for another 2 hours with the temperature was ensured to maintained below 15℃. Then the ice bath was removed and the mixture was continued to be stirred for 22 hours under room temperature. Next, the mixture was heated to

70℃ and stirred for 3 hours. 100 ml of H_2O was slowly added within the 3 hours. The mixture was then heated to 90℃ and kept stirred for 1 hour and another 100 ml H_2O was slowly added within the period. Next, 60 ml of Hydrogen Peroxide (H_2O_2) was added into the mixture to stop the reaction accompanied with the release of heat. After the resulting mixture cooled down, it was repeatedly washed with diluted Hydrochloric Acid (HCl) and distilled water 3 times, each for 24 hours. 160 ml of HCl was mixed with 1840 ml of distilled water to produced the diluted HCl and used for the washing method. After the washing is completed, the mixture was centrifuged at 25℃ temperature and 10,000 rpm for 25 minutes. After centrifuged, the producing supernatant was filtered and the produced solid precipitated was placed on a petri dishes and dried in an oven for 24 hours at a temperature of 65℃ - 70℃ to form grapheme oxide (GO).

C. *Emulsion preparation*

The Synthetic oil emulsion was prepared by mixing synthetic crude oil (mixture of n-heptane and toluene at a 7:3 ratio)(Hajivand & Vaziri, 2015) and distilled water at various ratios (1:1, 1:2, 1:3 and 1:4) and different pH value (2, 5, 7, 9, and 12). Different concentration of GO nanoparticle was added into the test tube (0g/L, 0.02g/L, 0.04g/L, 0.08g/L, and 0.15g/L)(Augustina & Sylvester, 2015)(Fang et al., 2016). The tube was sealed and the mixture was agitated vigorously by hand for 50 times until the mixture appear homogenous.

D. *Demulsification test*

The performance of the demulsifiers is carried out using bottle test to find the best amount of demulsifier used. The best demulsifier will be evaluate by determining which GO concentration can produce has the highest volume of water separated and time taken to achieved final separation. Percentage of separation can be calculated using formula,

$$\text{Percentage of water separation} = \frac{\textit{volume of water separated (mL)}}{\textit{Total volume of water (mL)}} \times 100\%$$

E. *Characterization of GO*

The functional group analysis was analysed using the Fourier Transfored Infrared (FTIR) spectrometer. The spectrum was measured with a Spectrum One made by perkin elmer. The FT-IR spectrometer is in a wavelength range of 500 cm^{-1} to 4000 cm^{-1}. The fuctional group was determined according to their specific group frequencies. Functional group of alkoxyl, carbonyl, and hydroxyl should exist in the grapheme oxide after being oxidized by strong oxidants.(Liu et al., 2015)

X-ray Diffraction (XRD) is a non-destructive technique used for characterizing crystalline material and provide information on structures, phases, preferred crystal orientation (texture), and grain size. The sample used can be in a form of liquid, powder or crystal. The equipment used was made by Rigaku's X-ray diffractometer. The interlayer distance calculation are as follows:

$$\text{Interlayer distances, d} = \frac{\lambda}{2\sin(\theta)}$$

Where,

λ is the wavelength of the X-ray beam, 0.154 nm
d is the layer distance between GO
θ is the diffraction angle

III. RESULTS AND DISCUSSION

A. *Characterization of Graphene Oxide*

Figure 1 shows the result of characterization of graphite powder using FTIR. In normal circumstances, graphite doesn't show any peak when analyzed using FTIR. IR spectra will show peaks of graphite powder beacuase it is not pure. In order to obtained a good FTIR result with zero peak, graphite flake need to be used.

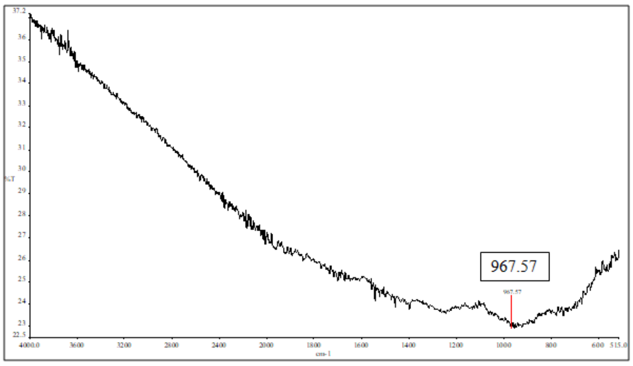


Figure 1: FTIR result for graphite powder

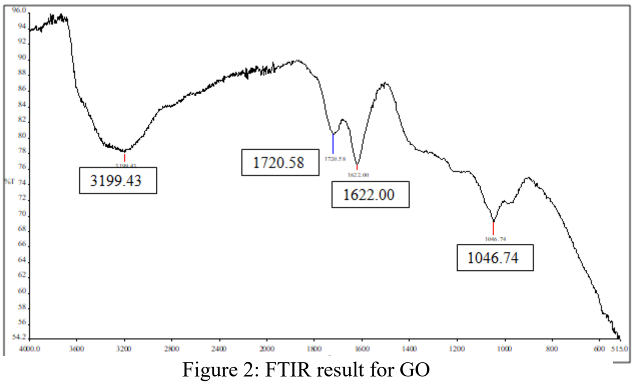


Figure 2: FTIR result for GO

Figure 2 shows the result of characterization of GO sample obtained using FTIR. It was found that several characteristic peaks appeared in the range of 500 to 4000 cm^{-1}. The most noticeable peak can be observed at 3199.43 cm^{-1} which is attributed to the C-OH strecthing vibration of a hydroxyl group. Second peak can be observed at 1720.58 cm-^{1} which is assigned to carbonyl groups C=O. The next peak appeared at 1622.00 cm^{-1} which is attributed to the C=C skeletal vibration of non-oxidized graphite. A third peak with comparable size to the second peak is located at 1046.74 cm^{-1} is attributed to the alkoxy C-O stretching vibration. There is also a small peak located at approximately 1750 cm^{-1} and is attributed to the C=O stretching vibrations of a carbonyl group. These functional group that appears in the FTIR confirmed that the GO synthesized were successfully introduced on the grapheme surface after a strong oxidation process. (Liu et al., 2015)

B. X-ray Diffraction (XRD)

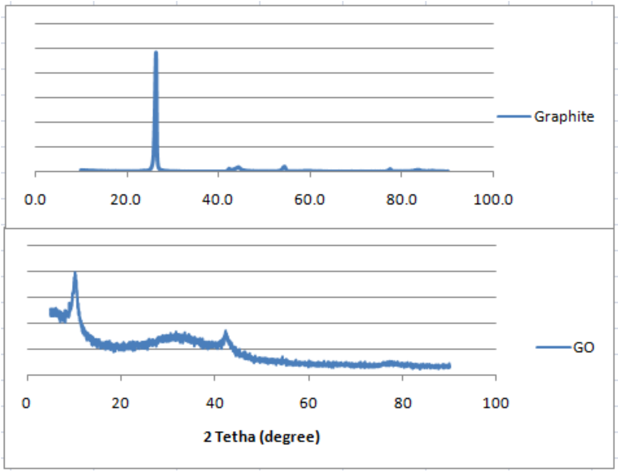


Figure 3: XRD result for graphite powder and GO

Figure 4.3 show the characterization of graphite powder and graphene oxide (GO) nanoparticle obtained from X-ray Diffraction (XRD). Graphene oxide was obtained through an oxidation process of graphite powder using a modified Hummer's Method. The interlayer distance obtained by graphite powder peaks at 0.33 nm (2θ = 26.40˚). This peak is then markedly expended to 2θ = 10.24˚ after oxidation process to form GO. The peak obtained at 0.88 nm (2θ = 10.24˚) confirmed the strong oxidation process from graphite powder to produce grapheme oxide. (Mu et al., 2013)

C. Demulsification Performance of Graphene Oxide on emulsion

1) GO performance based on watercut

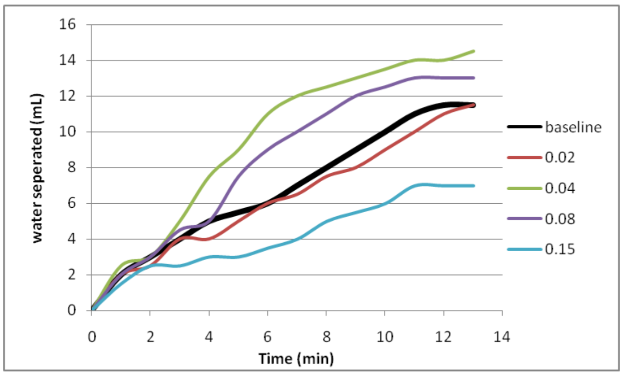


Figure 5: Emulsion separation at 1:1 ratio of oil and water

Figure 4 shows the difference between the amount of water separation of different concentrationof GO used after a period of time. Black represent the baseline or reference point of the demulsification process with zero concentration of GO added. Red represent 0.02 g/L of GO, Green is 0.04 g/L, Purple is 0.08 g/L and Blue is 0.15 g/L. From the graph, green and purple is higher than the baseline while red and blue are equal and lower respectively. This indicates that at 1:1 ratio of oil and water, only 0.04 g/L and 0.08 g/L concentration of GO seems to improves the amount of water separated from the emulsion at 4 mL and 6 mL more compare to the baseline. 0.08 g/L GO also achieved the same amount of separation of water at 9 mL at about 7 minutes faster compare to the baseline of the performance test. Percentage of water separation for baseline = 80%, 0.02 g/L = 82.5%, 0.04 g/L = 92.5%, 0.08 g/L = 95%, and for 0.15 g/L = 90%.

.

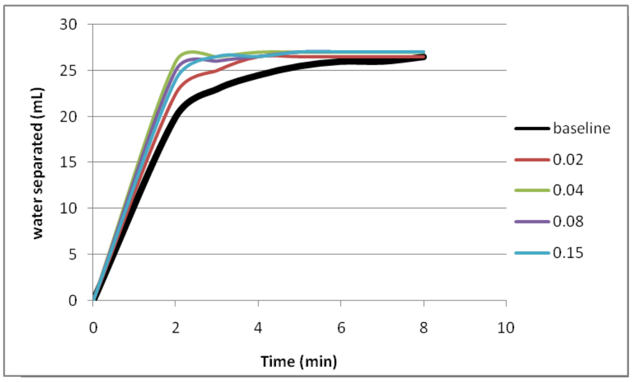


Figure 6: Emulsion separation at 1:2 ratio of oil and water

Figure 5 shows the emulsion separation at 1:2 ration of oil and water. From the graph, it can be observed that the presence of GO inside the emulsion does improves the separation performance of the emulsion in term of both time and the amount of water separated. The most effective concentration of GO for the 1:2 ratio emulsion is 0.15g/L which equal the amount of water separated for baseline at around 10 minutes faster and separates 3 mL of water more at the end of the performance test. The next best concentration of GO is 0.08 g/L which obtained the same amount of water separation as the baseline at around 9 minutes faster and separates about 2 mL more water compared to the baseline at the end of the test. 0.02 g/L and 0.04 g/L obtained the same amount of water separation at 22.5 mL which is also slightly more compare to the baseline of the performance test. Percentage of water separation for baseline = 86.2%, 0.02 g/L = 95.6%, 0.04 g/L = 82.5%, 0.08 g/L = 97.5% and 0.15 g/L = 97.5%

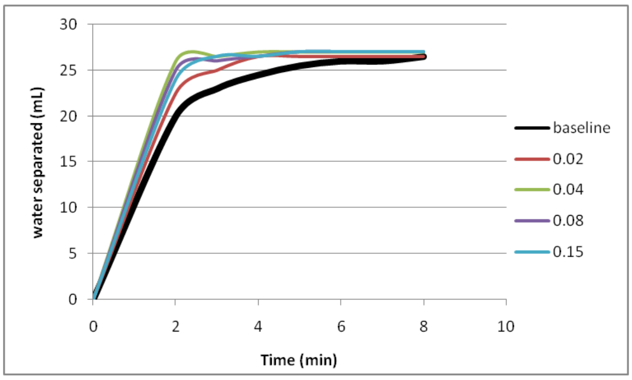


Figure 4: Emulsion separation at 1:3 ration of oil and water

Figure 6 shows the emulsion separation at 1:3 ratio of oil and water. From the graph plotted, it can be observed that the presence on GO in the emulsion considerably improves the time for separation of the emulsion while only slightly improves the amount of water separated from the emulsion. For 0.02 g/L concentration of GO, the amount of water separated from the emulsion equals the result obtained by the baseline but significantly improves the rate of separation as the time taken to reach final separation is much faster compare to the baseline result. As for 0.04 g/L, 0.08 g/L, and 0.15 g/L concentration of GO, the final separation is at 27 mL, 0.5 m e m it ac o th , 0. = 96

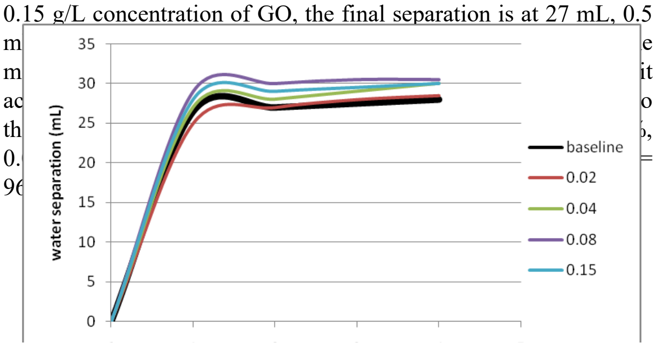


Figure 7: Emulsion separation at 1:4 of oil and water

Figure 7 show the emulsion separation at 1:4 ration of oil and water. From the graph plotted, it can be observed that all the coloured line are above the black line. Therefore it can be said that addition of GO in this ratio of oil in water emulsion does improves the separation performance of the emulsion. 0.02 g/L GO concentration is the least effective amount to separate the emulsion. By comparing the red line and the black line, we can see that red are much slower in the early phase of separation but is slightly ahead of the baseline at the end of separation with a 0.5 mL difference in the amount of water separated. As for 0.04 g/L and 0.15 g/L, both are faster than the baseline and has significantly higher amount of water separated which is 2 mL difference. 0.08 g/L is the best concentration of GO which has the highest amount of water separated at 30.5 mL and out-perform all the other concentration in term of rate of separation. Final percentage of water separation baseline = 90.6%, 0.02 g/L = 96.9%, 0.04 g/L = 98.4%, 0.08 g/L = 98.4%, and 0.15 g/L = 96.9%.

2) *GO performance at different pH*

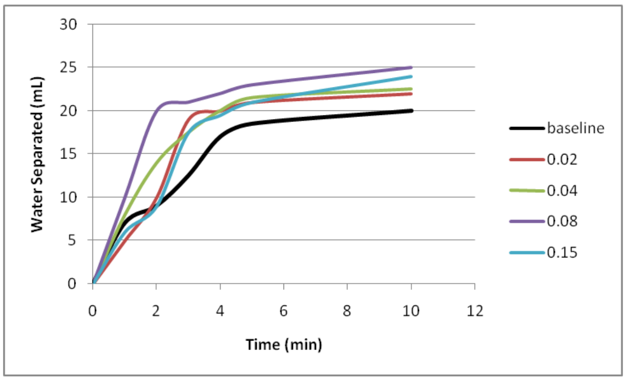


Figure 8: Emulsion separation at pH5

Figure 8 show the emulsion separation at pH5. From the graph plotted, it can be observed that all of the GO concentration added does improved the separation process of the emulsion with higher separation and faster time to separate the emulsion. 0.08 g/L GO has the highest volume of water separation at 25 mL, 5mL more compare to the baseline. The concentration achieved similar water separation 8 minutes faster compare to the baseline. The next best concentration of GO at this condition is at 0.15 g/L followed by 0.04 g/L and lastly 0.02 g/L produced the lowest and slowest rate of separation. Why?

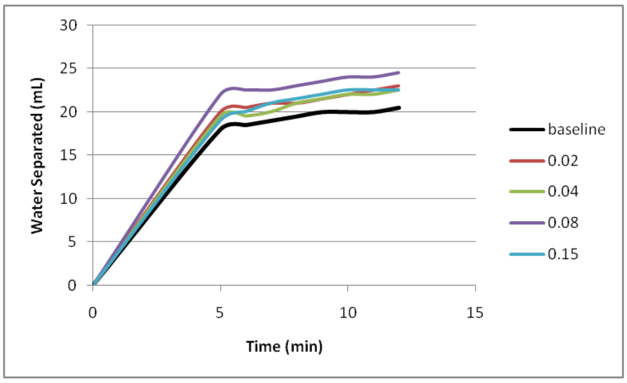


Figure 9: Emulsion separation at pH2

Figure 9 shows the emulsion separation at pH2. From the graph, it can be observed all of the GO concentration added slightly improves the separation process but at a much slower pace compare to when the emulsion is in pH5. This confirm that GO can perform under acidic condition but not as efficient as in normal condition. 0.08 g/L concentration of GO shows the highest volume of water separation and also the fastest time to separate. The amount of water separated is 4 mL more compare to the baseline result. The other concentration of GO produced an almost similar result, 2 mL of water separated more than the baseline.

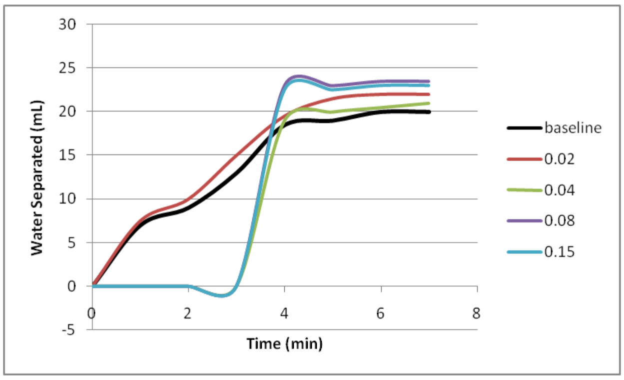


Figure 10: Emulsion separation at pH9

Figure 10 show the emulsion separation performance of GO at pH9. From the graph, an inconsistent result was obtained where some of the test remain unchanged at the early phase of separation. This was because of the inability to record the separation data due to the water separation remain unsighted in the early stage of separation. As time passed, the separation of water rapidly increase above the baseline. At the end of the separation process, all the emulsion with the addition of GO separate better compare to the baseline which is without the addition of GO. The final percentage of water separation for the baseline = 86.2%, 0.02 g/L = 93.7%, 0.04 g/L = 91.9%,0.08 g/L = 99.4% and for 0.15 g/L = 99.4%. The final result can be said to be inconsistent and confirmed that the performance of GO to separate oil-in-water emulsion are affected by the alkaline condition of the emulsion.

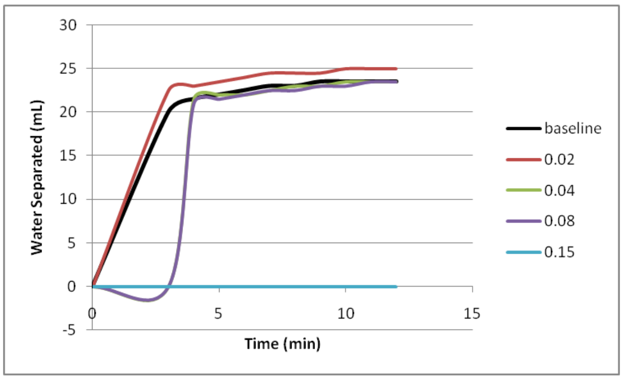


Figure 11: Emulsion separation at pH12

Figure 4.11 show the emulsion separation of GO at pH12. From the graph plotted, it can be observed that only 0.02 g/L concentration of GO show positive result which separate the emulsion better compare to the baseline. Other than that, all the other GO concentration result are either equal the baseline result of fail to separate the emulsion. This shows that at extreme alkaline condition the addition of GO fail to improve the demulsification performance of the emulsion. The addition of 0.15 g/L GO fail to separate the emulsion during the test time but does separate the emulsion after being left for 1 day. Why? The final percentage of separation after leaving for 1 day for the baseline is 91.9%, 0.02 g/L = 99.4%, 0.04 g/L = 93.7%, 0.08 g/L = 93.7 and 0.15 g/L = 99.4%.

D. *Visual study on the effect of GO on emulsion*

The emulsion prepared was observed under a polarizing microscope to deeply analyze and understand the demulsification process of synthetic oil-in-water emulsion driven by GO. The morphologies of emulsion with and without the addition of GO was analyze under a polarizing microscope at 4× magnification size. A few drop of emulsion was taken from the test tube using a droplet and placed on a glass slide surface.

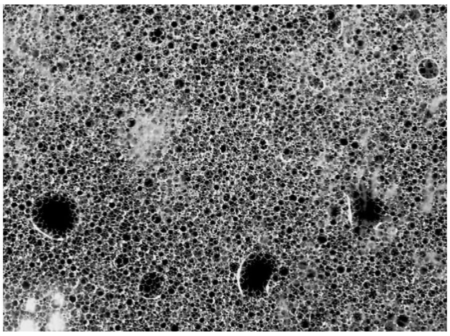


Figure 13: Emulsion without GO

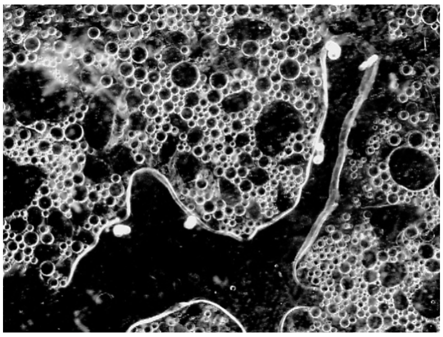


Figure 14: Emulsion with GO

Figure 4.12 show the image of oil-in-water emulsion without the presents of GO. The oil droplets is very small and was homogenously dispersed in the water phase. Figure 4.13 shows the emulsion with the addition of GO. As GO was introduces to the emulsion, the oil droplet start to flocculate to form larger oil droplets and began to separate from the water phase of the emulsion

E. *Effect of GO Dosage on Demulsification*

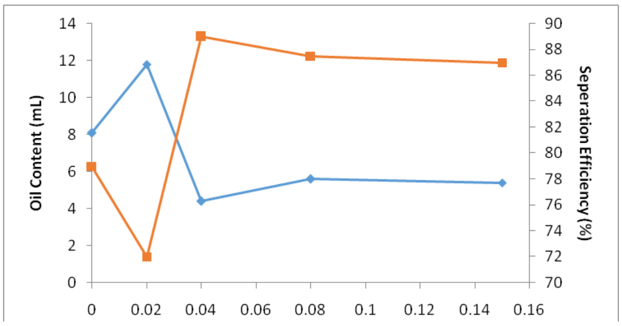


Figure 15: UV-vis result for 1:1 oil-water ratio

1) *Ultraviolet Visible Spectrometer*

Figure 16: UV-vis result for 1:3 oil-water ratio

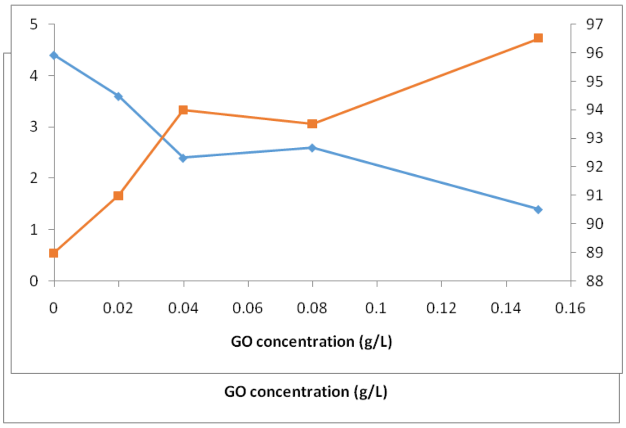
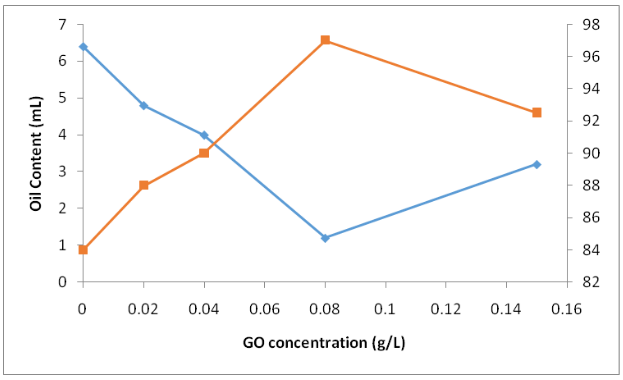


Figure 12: UV-vis result for 1:2 oil-water ratio



The demulsification performance of GO was evaluated using UV-vis spectrometer by determining the oil content in the separated water. The result shows that GO nanoparticle are well capable of separating the emulsion stabilized by cationic surfactant at different oil-water ratio as in figure 14-17. From the figures, the result indicate that the separation performance of the emulsion are better with higher GO concentration added. At 1:4 ratio emulsion. The highest dosage of GO added produced the highest percentage of separation with 96.7% which concludes that at higher watercut, higher concentration of GO gives better result. For 1:1 oil-water ratio, the highest separation is produced by the emulsion added with 0.04 g/L concentration of GO which the separation efficiency peaks at 89% of water. When the oil-water ratio is 1:2, addition of 0.08 g/L concentration GO produces the highest separation efficiency at 96% and also at 1:3 oil-water ratio, with the addition of 0.08 g/L gives the hight separation efficiency at 97%. 1:4 oil-water ratio produced highest separation efficiency at 96.7% with the addition of 0.15 g/L concentration of GO nanoparticles.

2) *Zeta Potential*

Figure 17: Zeta Potential result for GO and synthetic oil

Zeta potential test was carried out to clarify the effect of pH on GO. From the result obtained in figure 18, both oil and GO become more electronegative with the increase in pH value. This indicates that The electrostatic repulsion between oil and GO increases as

Figure 18: UV-vis result for 1:4 oil-water ratio

pH increases causing the demulsification performance to decrease at high pH condition.

IV. CONCLUSION

In conclusion, graphene oxide has been successfully synthesized from graphite powder using Hummer's method and confirmed by the functional group peaks in FTIR and correct diffraction angle from XRD. The result obtained from the performance test of GO to separate oil-in-water emulsion is positive and the test also finds out that GO can perform well under acidic condition but have decrease in performance when tested under alkaline condition. The findings in this work indicates that the GO is a highly efficient and universal chemical demulsifier to separate oil-in-water emulsion.

ACKNOWLEDGMENT

Thank you to my supervisor, Mdm. Aqilah binti Dollah for her guidance and dedication in helping me throughout the final year project period and Universiti Teknologi Mara for providing the necessary equipment and material needed to complete this project. Also a big thanks to my FYP colleagues for the teamwork that they have given and for pushing me out of my comfort zone and stop being a lazy and half-hearted person.

References

[1] Augustina, O., & Sylvester, O. (2015). Emulsion Treatment in the Oil Industry : A Case Study of Oredo Field.

[2] Fang, S., Chen, T., Chen, B., Xiong, Y., Zhu, Y., & Duan, M. (2016). Graphene oxide at oil-water interfaces: Adsorption, assembly & demulsification. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *511*, 47–54. https://doi.org/10.1016/j.colsurfa.2016.09.058

[3] Hajivand, P., & Vaziri, A. (2015). Optimization of demulsifier formulation for separation of water from crude oil emulsions. *Brazilian Journal of Chemical Engineering*, *32*(1), 107–118. https://doi.org/10.1590/0104-6632.20150321s00002755

[4] Liu, J., Li, X., Jia, W., Li, Z., Zhao, Y., & Ren, S. (2015). Demulsification of Crude Oil-in-Water Emulsions Driven by Graphene Oxide Nanosheets. *Energy and Fuels*, *29*(7), 4644–4653. https://doi.org/10.1021/acs.energyfuels.5b00966

[5] Mu, S. J., Su, Y. C., Xiao, L. H., Liu, S. D., Hu, T., & Tang, H. B. (2013). X-ray difraction pattern of graphite oxide. *Chinese Physics Letters*, *30*(9). https://doi.org/10.1088/0256-307X/30/9/096101

[6] Rattana, T., Chaiyakun, S., Witit-Anun, N., Nuntawong, N., Chindaudom, P., Oaew, S., … Limsuwan, P. (2012). Preparation and characterization of graphene oxide nanosheets. *Procedia Engineering*, *32*, 759–764. https://doi.org/10.1016/j.proeng.2012.02.009