Effect of Demulsification on Anionic-Stabilized Oil-in-Water Emulsion Using Graphene Oxide

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***Abstract*—Emulsion problem is one of the problem in oil and gas industry that needs further attention. Although there are many method to break emulsion, and a few demulsifier had been recognized, finding the right demulsifier that gives the best outcome at low cost and high separation rate remains a problem. Graphene Oxide (GO), due to its amphiphilic behavior is recognized as one of the potential demulsifier. In this study, GO was synthesized by using modified Hummer's method and was characterized by using XRD, FTIR and zeta sizer. Then, the effect of GO as demulsifier in breaking emulsion at different water cut was investigated by using demulsification test and result shows that different water cut will results in different trend and different optimum GO dosage. Water cut 1:2 showing increase in concentration of GO will increase the final volume of water separated. However, the best performance of GO in separating emulsion is at water cut 1:3 with over 98% separation. Also, performance of GO in different pH was further investigated. It was found out that GO can perform well in acidic condition, although in this study the result might be affected by anionic condition of emulsion. Although the performance of GO in alkali condition was not as good as in acidic condition, there are still separation occurring although the trend was rather hard to determine. To further examine the result, concentration of oil in separated waster was measured using UV Vis and result shows that oil concentration of each tests correspond to the rate of separation. Zeta potential at different pH was conducted and it was confirmed that anionic surfactant causes decrease in value of zeta potential thus explains the separation even in alkali condition.**

Keywords— graphene oxide, emulsion, emulsion stability, demulsification.

I. INTRODUCTION

Emulsion can be defined as a biphasic system of two immiscible liquids, one of which the dispersed phase is finely and uniformly dispersed as globules throughout the second continuous phase.(Khan et al., 2011) The dispersed phase or also known as discontinuous phase or internal phase refers to the material that makes up the droplet while dispersing phase or also known as continuous phase or external phase refers to materials that make up the surrounding (McClements, 2007). According to Augustina & Sylvester (2015), there are three main condition for formation of emulsion; (1) two immiscible liquid such as oil and water in contact (2) presence of emulsifying agent such as asphaltene or resin and (3) sufficient energy of agitation to disperse one liquid into another.

(Kokal & Wingrove, 2000) mentioned that presence of emulsion can cause operational problems such as tripping of equipment and pressure drop in flow lines. According to D (2012), treatment methods for emulsion in crude oil including application of heat, application of electricity, application of chemical, polymers and natural treatment. Application of chemical is also known as demulsification process. Many types of demulsifier had been recognized while some are still in research status. For example, (Nour, Abu Hassan, & Yunus, 2007) concluded that amine demulsifier group is the most effective in breaking emulsion compared to polyhydric and acid demulsifer.

Graphene oxide (GO) is one of the potential demulsifier due to its amphiphilic properties. (Fang et al., 2016) suggests that GO was able to reduce the interfacial tension of emulsion while (J. Liu et al., 2015) in their study fund that GO can help in demulsification up to 99.99% and can perform well even in acidic condition. This study focus on the effect of addition of GO on emulsion with variation of different water cut and pH.

II. METHODOLOGY

A. Materials

For preparation of GO, graphite powder was obtained from COMAK. Sodium nitrate,$NaNO_3$ (84.99g/mol) and hydrochloric acid, HCl (12% concentration) obtained from SYSTERM. Concentrated sulfuric acid, H_2SO_4 (98.08g/mol), potassium permanganate, $KMnO_4$ (158.03g/mol) and hydrogen peroxide, H_2O_2 (39% concentration) were all obtained from R&M Chemicals. For preparation of synthetic oil, toluene (92.14g/mol) and n-heptane (100.21g/mol) both purchased from SYSTERM while surfactant used was Sodium Lauryl Sulphate (SDS) from R&M Chemicals.

B. Synthesize of Graphene Oxide

Synthesize of GO was done by using modified Hummer's method(Gupta, Rajaura, & Sharma, 2015). Graphite powder and sodium nitrate were added into concentrated sulfuric acid in ice bath condition and were stirred for one hour. Within the next two hour of stirring under ice bath condition, potassium permanganate was added slowly in small doses into the mixture. The mixture was kept stirred for another two hour under ice bath condition. After that, the mixture was stirred at room temperature. After 20 hours, the mixture was heated to 70°C while stirred for three hour. Along these three hour, 100ml of distilled water is inserted into the mixture. After that, the mixture was heated up to 90°C while stirred and another 100ml of distilled water is inserted into the mixture along the one hour. Hydrogen peroxide is added into the mixture to stop the reaction. Resulting mixture was washed with hydrochloric acid and distilled water for three times before they were centrifuged and dried in the oven.

C. Characterization of Graphene Oxide

Characterization of GO was done by using FTIR and XRD. FTIR was done to determine the functional group present at wavelength 400-4000cm^{-1}. XRD was done at 2θ. The size of GO was measured by using zeta sizer.

D. Preparation of Emulsion

Synthetic crude was prepared by using n-heptane and toluene in 7:3 ratio(Hajivand & Vaziri, 2015). For every tube, different amount of oil and water was used to obtain different water cut (1:1, 1:2, 1:3 and 1:4). Emulsion was introduced into the system by adding surfactant.

To have neutral system, distilled water was used as water phase. To have acidic system that is at pH 2 and pH 5, hydrochloric acid was used as water phase. pH 9 and pH 12 that is alkali phase was prepared by using sodium hydroxide.

E. Demulsification Test

Dispersion of GO was done in distilled water (0g, 0.02g, 0.04g, 0.08g, 0.15g)(Fang et al., 2016) where 0g of GO acts as baseline. 0.5mL of different concentration of GO was inserted into each tube. All test tube with oil and water phase were shaked by 100 times hand shake(Xia, Lu, & Cao, 2004) before time taken for separation to occur and final volume of separated water was recorded. The percentage of separation will be calculated by the formula(Nour et al., 2007):

$$Separation = \frac{Volume\ Separated\ Water}{Total\ Volume\ of\ Water}\ X\ 100$$

F. Emulsion Analysis

The emulsion formed was further analyzed by using polarizing microscope, UV Vis spectrometer and zeta potential. Polarizing microscope was used to observe difference after GO had been used. UV Vis spectroscopy was used to measure the concentration of oil in separated water and zeta potential was used to confirm the effect of addition of GO into the system.

III. RESULTS AND DISCUSSION

A. Characterization of Graphene Oxide

In Figure 1(a), there is only one peak that most likely appear due to impurities. In Figure 1(b), there were new peak introduced prooving that graphite powder had been oxidized. The peak at 3242.28cm^{-1} indicates the presence of O-H hydroxyl group(Bykkam & Rao, 2013)(Szymanowski & Hiron, 1984)(Eluyemi et al., 2016). A stretching vibration peak of C=O carbonyl had appeared at 1716.45cm^{-1} (Eluyemi et al., 2016)(Zhang et al., 2010)and peak at 1049.85cm^{-1} indicates stretching vibration peak assigned to alkoxyl group with functional group C-O(Zhang et al., 2010). The peak at 1623.23cm^{-1} refers to skeletal vibration of unoxidized graphene domain

Finding suggested that introduction of oxygen functionalities in GO was because the substance had been oxidized by very strong oxidizing agent.

. In Figure 2(a), XRD pattern for graphite flakes shows a sharp peak at 2θ=26.3°, with interlayer distance of 0.338nm. XRD pattern for GO in Figure 2(b) shows that the peak had shifted to 2θ=10.02 with interlayer distance of 0.882nm.(Akgül, Alver, & Tanriverdi, 2016)(Bykkam & Rao, 2013)(C. Liu, He, Xie, & Yang, 2015)

B. Demulsification Performance of GO

i) At different water cut

The data for water cut 1:1 can be seen in Figure 3 (a). In the first set whereby no GO was added, the first appearance of separation line is observed 60seconds after the emulsion was formed with 20% separation. Comparing to when GO is added to the emulsion, first appearance can be seen as early as 30seconds after emulsion was formed. However, despite the early appearance, the rate of separation during the early stages is considered quite low. There are inconsistency of how amount GO affected time of separation at this water cut but it cannot be denied that introducing GO into the system does increase the rate of separation. Final product after 600 second also shows that presence of GO increase the final volume of water separated.

The effect of GO on rate of separation in water cut 1:2 is more obvious compared to in water cut 1:1. In Figure 3 (b), the separation lines start to appear with separation of 65.62% as early as 90second. When GO is added to the emulsion, for GO concentration 0.02g/L, at 90 second, the separation had increased to 74.99%. As the concentration of GO further increase, the time taken for first appearance of separation lines decrease to 30 seconds, implying that the separation has increase. Without any GO added to the system as demulsifier, the separation did not even reach 89.99%. Introducing GO to the system had quickened the time taken for separation to occur. For example, for separation of 89.99% to occur, using GO concentration of 0.02g/L will take 330second. As the concentration of GO increase to 0.04g/L, the time taken had decreased to 300second. Further increasing the concentration of GO to 0.08g/L, the time taken further decreased to 240second, and finally, the fastest time taken was 180second, when GO concentration of 0.15g/L was used. Apart from faster separation, it can also be concluded that using GO as demulsifier had caused higher separation whereby we can see that the final volume of water separated is higher when GO is used. Also, from the figure, we can see that without using GO, the final volume of water separated is only 84.36% while addition of 0.02g/L and 0.04g/L GO will results in total of 89.99% separation. Highest separation will be by using 0.08g/L and 0.15g/L concentration of GO with separation of 91.87%.

For water cut 1:3, the final separation for baseline (without GO) is around 90% as shown in Figure 3 (c). When GO is added to the system, the highest separation is 93.33% that is when using GO of 0.04g/L and 0.08g/L. This also shows different separation trend from water cut of 1:2. In water cut 1:2, as concentration of GO increase, the separation increase thus using higher amount of GO is advisable. However, for water cut 1:3, the optimum amount of GO will be at concentration of 0.04g/L and 0.08g/L. Apart from slightly low separation result, the result shows that the rate of separation to be higher when GO is introduced to the system. This can be seen as without GO, the rate of separation did not even reach 91.67%, while introducing 0.02g/L GO, 91.67% separation was obtained in 240second. Further increasing GO concentration to 0.04g/L, the time taken to reach 91.67% separation reduced to 180second and when GO concentration of 0.08g/L is used, the time taken is only 90second. However, as GO concentration further increase to 0.15g/L, there is a change in trend where the time taken to reach 91.67% separation increase to 180second. This trend also confirms that the optimum GO concentration for watercut 1:3 is not the one with highest GO concentration, instead, the optimum will be GO with concentration of 0.08g/L.

From Figure 3 (d), the time taken for first appearance of separation line for water cut 1:4, despite GO being added or not, was as early as 30second. However, to determine which concentration of GO is the most optimum is a bit difficult because of inconsistency in trend of final volume of water separated. This can be seen when the final separation for when GO is not added is 87.5% while adding 0.02g/L of GO will results in separation of 93.75%. Next, it was observed that using 0.04g/L of GO results in slightly lower separation of 92.19% while 0.08g/L GO will results in the highest separation of 96.88%. Lastly, when 0.15g/L GO was used, final separation of water is 93.75%.

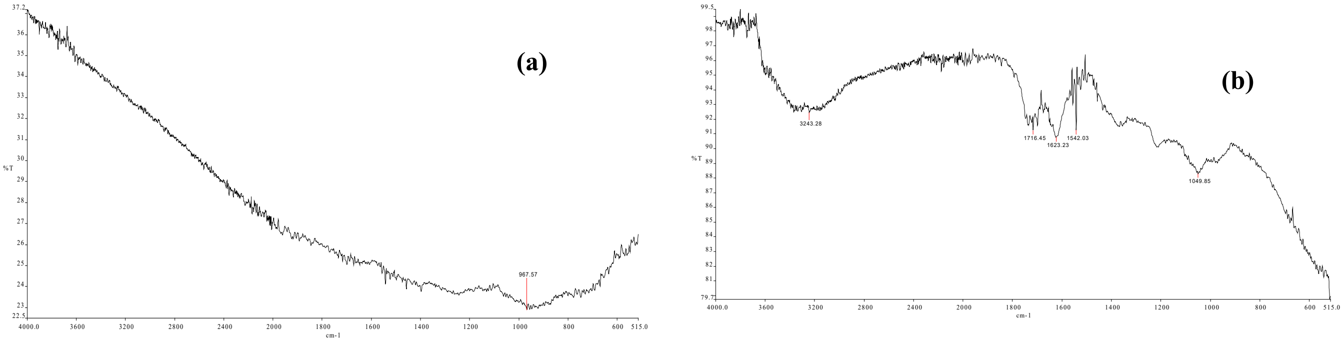

Fig. 1 Fourier Transfor Infrared Spectroscopy of (a) graphite flakes (b) GO

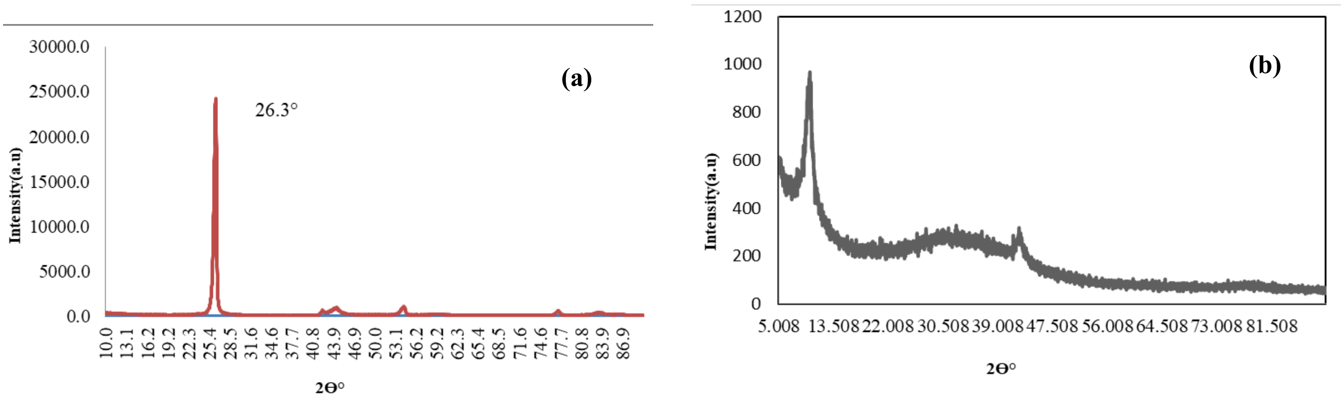

Fig. 2 X-Ray Diffractometer of (a) graphite flakes (b) GO

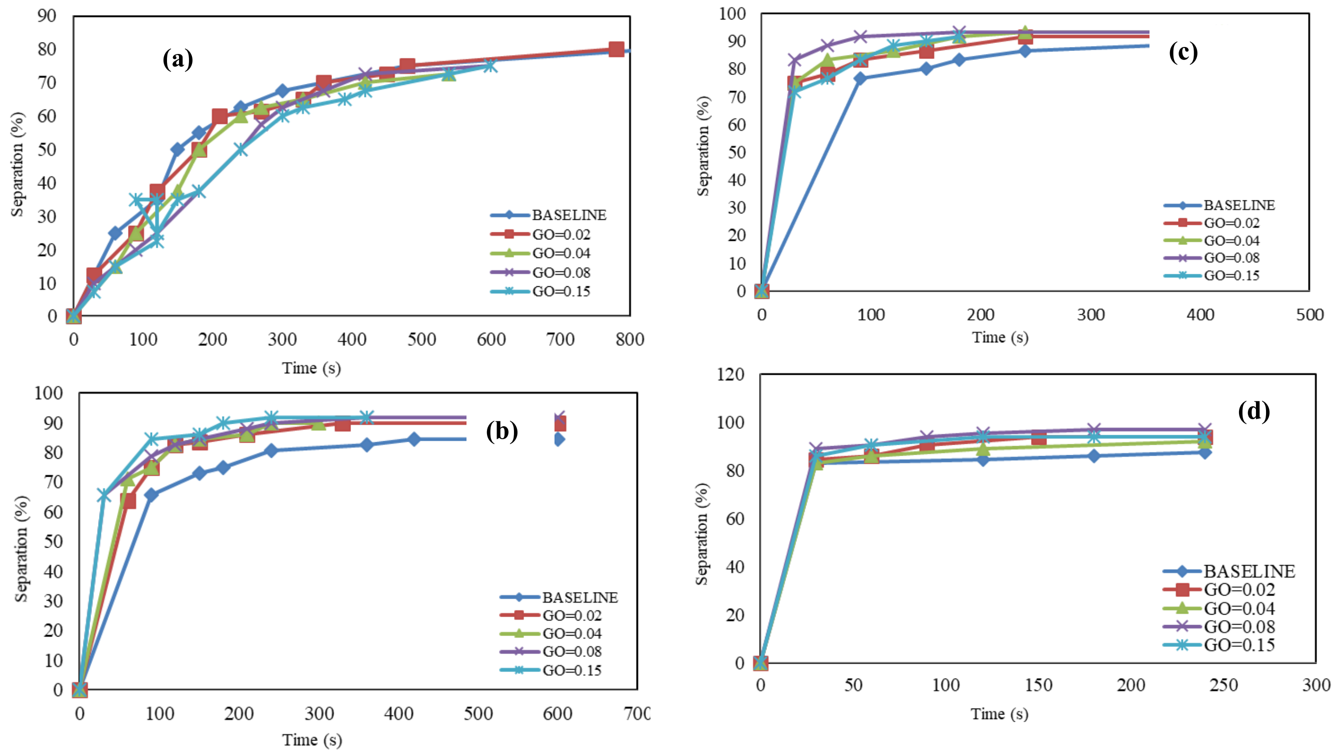

Fig. 3 Separation at (a) water cut 1:1 (b) water cut 1:2 (c) water cut 1:3 and (d) water cut 1:4

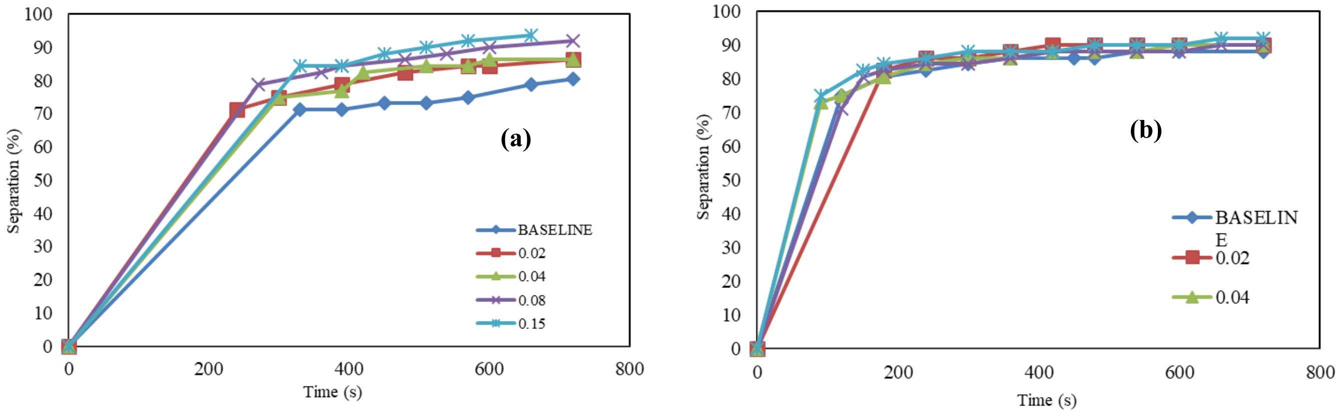

Fig. 4 Separation at (a) acidic condition(pH 2) and (b) alkali condition (pH 12)

ii) At Different pH

At strong acidic condition, it was predicted that GO will not be functioning at maximum rate. However, when experiment was done at pH 2, despite the low pH value, it was found out that introducing GO to the system still affect the separation. Without GO, the final separation was only around 80.61%. As medium concentration of GO was inserted, the rate of separation increase to 86.24%. Highest GO concentration of 0.15g/L results in highest final volume of water separated. GO was predicted to be most effective around pH 5. Although it was indeed true that introducing GO to the system had increase the rate of separation, it does not mean as GO increase the separation also increase as the trend that happen at pH 2. Rather than that, the most optimum concentration of GO to be used at this pH value is o.o2g/L. Further increasing the concentration of GO will not result in increase in separation as the volume of separated water at 600 minutes are the same for GO concentration of 0.04, 0.08 and 0.15 g/L. Trend for separation in acidic condition is shown in Figure 4(a)

The optimum amount of GO for high separation rate at pH 9 is hard to predict. This is because the highest separation within the first 600 minutes occurs at GO concentration of 0.02g/L and 0.08g/L that is 95.61% separation. In pH 12, there are inconsistencies in the time taken for first separation line to appear as without GO, the time taken is around 120 second. Introducing 0.02g/L GO into the system actually make it worse as line only starts to appear at 180 second. However, when the concentration of GO is 0.04g/L, separation line can be seen as early as 90 second. Comparing the total volume of water separated, at 720 second, tube with 0.15g/L had already achieved 91.86% separation whereas without using GO, only 88.11% separation can be achieved. However, it was observed that when GO concentration is medium such as 0.02g/L,0.04g/L and 0.08g/L, the separation is the same. The separation over time for alkali condition is shown in Figure 4 (b).

iii) Total Separation

GO is more effective in water cut 1:2, 1:3 and 1:4, whereas application of GO in water cut 1:1 is not really effective in terms of separation. However, the optimum amount of GO is different for each water cut. For water cut 1:1, the optimum GO concentration is at 0.04g/L and 0.02g/L with separation of 85%. At water cut 1:2, as the concentration of GO increase, the separation increase with highest separation when 0.15g/L of GO is used, reaching up until 93.74%. For water cut 1:3, the optimum GO concentration is at 0.08g/L with separation of 98.33%. Finally, for water cut 1:4, increasing the GO concentration will also increase the separation. However, at 0.04g/L GO, the rate of separation if slightly lower with only 93.75% separation.

The final volume of water separated for pH 2 is the highest. The trend for pH 2 is also considered good because as the concentration of GO increase, the separation increase before reaching the same separation after 0.08g/L of GO. At pH 5, the trend is the same except for slight decrease in 0.04g/L GO. At ph7, the trend is increasing although the increament is not as high as in pH 2. At pH 9, there is inconsistency of separation while in pH 12, the separation exists but effect of GO is hardly seen as the difference of separation at different GO concentration is very small.

C. Emulsion Analysis

Although there are inconsistency in terms of how Go dosage affect the separation trend at water cut 1:1, percentage of final separation match the percentage of oil concentration present in the water. From Figure 6(a) we can see that at highest separation of 85%, the percentage of oil concentration is the lowest at 7% while at lowest separation at 72.5%, there are higher oil concentration of 11%. For water cut 1:2, Figure 6(b) shows the reverse effect of GO concentration on oil concentration and separation. At lowest GO concentration, the separation is the lowest at 86.2%, and the measured oil concentration in the separated water is the highest at 5.5%. At GO concentration of 0.08g/L and 0.15g/L, the separation rate is only slightly different. However, at GO concentration 0.08g/L, the oil concentration is higher compared to GO concentration of 0.15g/L. This proves that 0.15g/L is the most efficient GO concentration as it gives higher separation that results in lower oil concentration. For water cut 1:3, when there is no GO in the system, the rate of separation is the lowest at 88.33% and the oil concentration is separated water is the highest at 6.8%. At GO concentration of 0.02g/L until 0.08g/L, the separation continue to increase and the oil concentration in separated water continue to decrease. However, at GO concentration of 0.15g/L, the separation slighty decrease and the oil concentration slightly increase and this might occur due to distribution of GO in the system(J. Liu et al., 2015). From Figure 6(c), optimum concentration of GO was at 0.08g/L because of the highest separation and lowest oil content. For water cut 1:4 as shown in Figure 6(d), the trend for separation is increasing, thus with increase of GO concentration, the oil concentration in separated water decrease. However, there is an abnormalities at GO concentration of 0.04g/L where it is the only concentration when separation rate decrease. This may be due to insimilarity of how GO is distributed in the system. To further confirm, the oil concentration was measured and it was confirmed that at the time separation rate was low, the oil concentration was discovered high.

Figure 5(a) shows the emulsion without addition of GO and Figure 5(b) shows the emulsion with addition of GO. It was clear that the droplets before addition of GO is smaller compared to droplets after GO was added. This proves that addition of GO had helped in accumulating the droplets together and helps in separation rate.

The dispersion of GO in different pH was considered well-dispersed because the zeta potential values that are higher than 40mV, except in pH 2 and pH 12 of highly acidic and highly alkali medium. As explained by (Li, Müller, Gilje, Kaner, & Wallace, 2008), electrostatic repulsion mechanism that make GO colloids stable could also enable the formation of well dispersed graphene colloid.

Research by Katepalli, (2014) explains that even the presence of very low concentration of anionic surfactant can cause changes on zeta potential, whereby, anionic surfactant will decrease the value of zeta potential due to the chemical reaction of negative head of surfactant and positive charge of surface area. This explains the very low negative value of SDS surfactant in various pH condition as shown in Figure 7 (c), ranging from -97.3mV to -112mV.

From Figure 7, the zeta potential of both oil and GO become more negative as pH increase before starts to increase after pH 7. This causes the electric repulsion between GO and oil to not be a problem, thus resulting in proper demulsification as happened in other pH condition

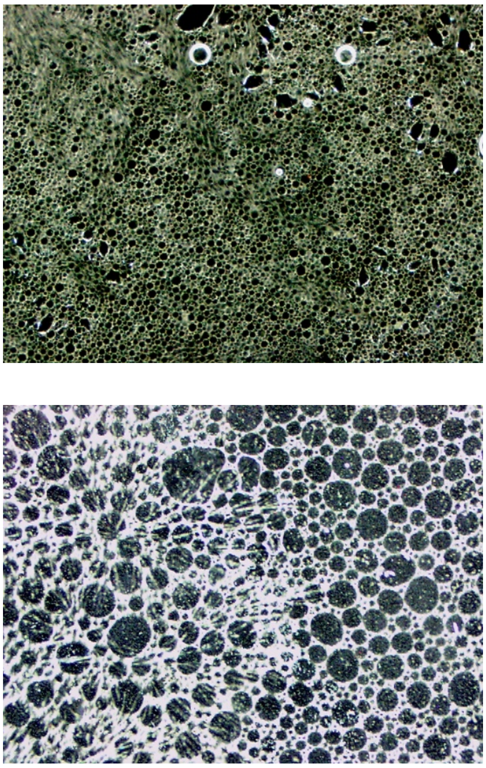

Fig. 5 Polarizing Microscopic Image of emulsion (a) without GO and (b) with GO

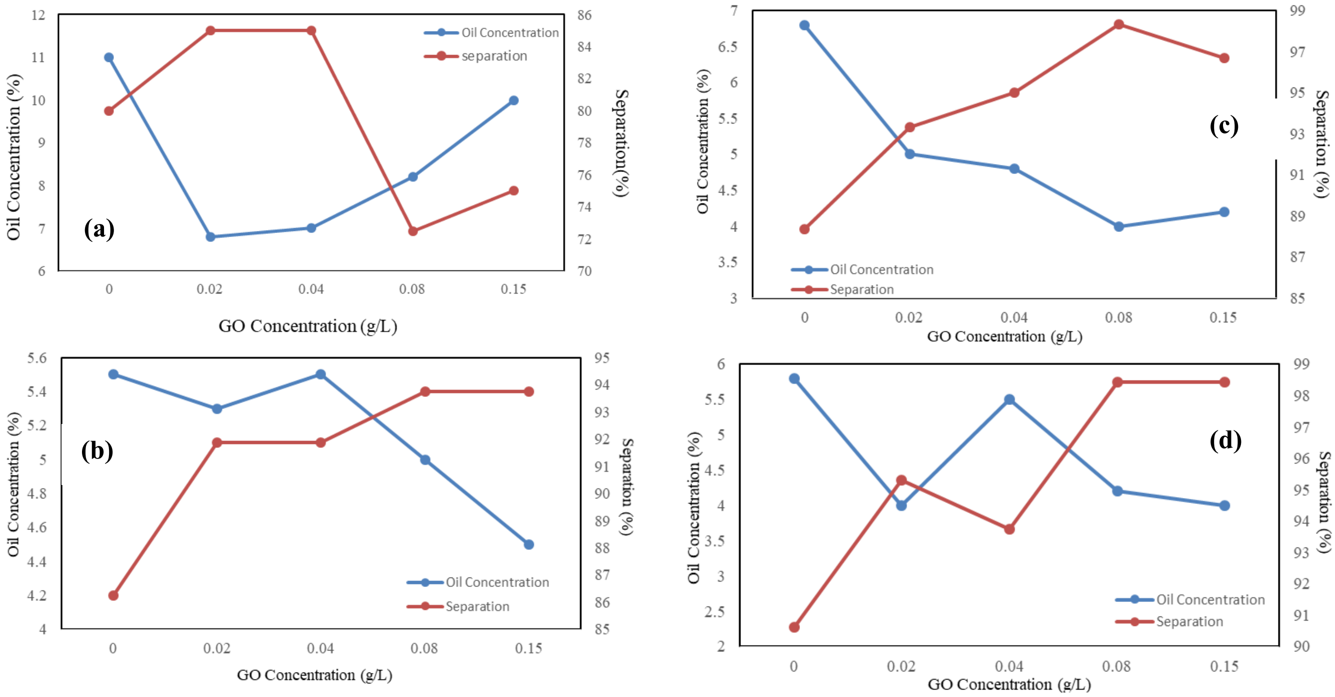

Fig. 6 UV Vis Spectroscopy of (a)water cut 1:1 (b) water cut 1:2 (c) water cut 1:3 and (d) water cut 1:4

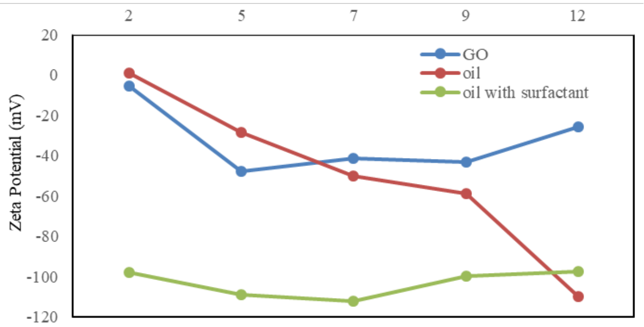

Fig. 7 Zeta Potential of GO and oil at different pH

IV. Conclusion

It was confirmed that GO can act as a very good demulsifying agent. Result shows that GO was able to increase the separation of emulsion up until 96.88% separation at very short time. Different water cut has different optimum GO concentration. GO can also perform well in acidic and alkali condition. However, it was believed that the result was affected by types of surfactant used. To apply GO to any real life field, it is important to test GO with real crude test to obtain even more accurate result.

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