

Demulsification of Crude Oil in Water (O/W) Emulsions using Graphene Oxide

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Abstract. Implementation of nanotechnology in oil and gas industries, particularly for enhanced oil recovery (EOR) has recently gained interest. In this work, graphene oxide (GO) has been synthesized and used as nano-demulsifier for crude oil in water (O/W) emulsions. GO was synthesized by using modified Hummers' method and characterized using X-Ray diffractometer (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. Subsequently, the nano-demulsifier's performances were tested to Field D crude oil-water emulsions by varying nano-demulsifier concentrations and contact time. The performances of GO for demulsification of crude oil-in-water emulsions were then determined by measuring the oil contents in water using a UV-Vis spectrophotometer. Demulsification tests indicated that the optimum GO concentration was around 20-40 ppm, while the optimum contact time was 30 min. The residual oil content in the separated water was as low as 100 ppm. This might be due to the amphiphilic properties of GO. It indicates that the GO is a promising demulsifier and by further understanding the intrinsic interaction between GO and crude oil, the performances of GO can be easily tailored in the future.

1. Introduction

Demulsification is a complicated process as oilfield emulsions is a stable liquid-liquid colloidal suspension. However, the demulsification of O/W emulsions can be accelerated by several methods such as thermal, electrical, mechanical and filtration methods. Among those, chemical-based demulsification method is more preferred owing to the simplicity of the process. Seeking for highly efficient, rapid, universal, and low-cost demulsification materials to break the crude oil-water emulsion(O/W) and emulsified oily wastewater at ambient condition has been the goal of the petroleum industry [1].

Field D is one of the offshore field in Malaysia that carried out enhanced oil recovery (EOR) development project by using enhance water alternating gas (EWAG). The is due to the abundance of gas with adequate water and gas injection facilities. An emulsion study has been conducted on Field D where surfactant M was added. However, based on the current analysis, it was found that the level of oil in the water is still higher than the targeted value. Therefore, it is important to ensure that the concentration of oil in water is as low as possible prior discharged to wastewater treatment system at platform to avoid auxiliary process that incurred high cost.



The use of nanotechnology in the petroleum industry has gained enormous interest in the recent years whereby most investigations have shown that nanoparticles are promising for future enhanced oil recovery (EOR). Nanotechnology is now chosen as an alternative method for viscosity reduction (aluminium oxide, copper (II) oxide, iron oxide), interfacial reduction (silica oxide, polyacrylamide micro-gel nano sphere), wettability alteration (tin oxide, silica oxide, alumina coated silica) and enhance sweep efficiency (polymer coated nanoparticles) [2].

Recently, graphene oxide (GO) has found its application in separating oil from oil in water emulsion by behaving as a highly efficient demulsifier [3]. In general, GO comprises of oxygen-containing functional groups including, epoxide, hydroxyl, carbonyl and carboxyl. The presence of these oxygen-containing functional groups provided potential advantages for using GO in numerous applications. The polar oxygen functional groups in GO sheet render it strongly hydrophilic, which gave GO good dispersibility in many solvents, particularly in water. This material is hydrophilic and forms stable suspension in water and other solvents, as GO has many hydrophilic functional groups such as carboxyl and hydroxyl [3]. Due to behaving strongly hydrophilic with these properties they will consequently form a stable oil in water emulsion.

Demulsification starts with the flocculation of water droplets that tend to clump together and forming aggregates called 'flocs'. These droplets are close enough to each other but may not coalesce as coalescence only takes place when there is a weak emulsifier film that surrounds the water droplets [1]. Such factors that affect the rate of flocculation; water content in the emulsion (high), temperature of the emulsion (high), viscosity of the oil (low), density difference between oil and water (high), and application of electrostatic field. Subsequently, coalescence takes place in demulsification whereby water droplets start to coalesce together to form a larger drop eventually leading to a decrease in the presence of water droplets until completion of this process [5].

Such factors that improve the coalescence process; rate of flocculation (high), absence of mechanically strong films, interfacial tension (high), water cut (high), interfacial viscosity (low), temperature of the emulsion (high), and application of chemical demulsifier [6]. Sedimentation or creaming can also take place during demulsification in which either water droplets settle down in an emulsion or rising of oil droplets in the water phase. Both these two processes result from the density difference between oil and water and may not cause in destabilizing emulsion. Incomplete emulsion droplets may accumulate at the oil/ water interface and likely form an emulsion pad [6]. These emulsion pads are caused by ineffective or insufficient demulsifier, other chemical that nullify demulsifier's effect, low temperature and presence of accumulating solids. Several problems may arise due to the presence of these pads, like reduction in the retention time, increases the BS&W, increase residual oil in water, and equipment upset frequency [7]. Meanwhile, this research aims to synthesize and characterize GO by using modified Hummers' method and study its performances as nano-based demulsifier for demulsification of oil in water emulsion.

2. Methodology

2.1 Chemicals and Materials

Crude oil sample was obtained from Field D. Synthetic brine (produced and sea water) was prepared according to the Field D formulation. The chemicals used for preparing synthetic brine calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), potassium chloride (KCl), barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), and sodium chloride (NaCl). The chemicals used for preparing GO were graphite, sodium nitrate (NaNO_3), concentrated sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30% w/w), hydrochloric acid (HCl, 37%). All chemicals were purchased from Merck, R&M Chemicals, Syterm and used without further purification.

2.2 Preparation and Characterization of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized by using modified Hummers' method which involved oxidation

and exfoliation of graphite [7]. The gel-like formed GO solution was dried in an oven for 24 hours at 60 °C to form GO nano-demulsifier. The GO nano-demulsifier was then characterized using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer) in the range from 400 cm⁻¹ to 4000 cm⁻¹ to confirm the presence of oxygen-containing functional group. X-ray diffractometer (XRD, Rigaku) was also used to observe the crystal structure of GO. The emission current and accelerating voltage used were 40 mA and 40 kV. Data was collected using Cu-K radiation in the range of 2θ from 5° to 50°.

2.3 Preparation of Emulsion

Crude oil was retrieved from Field D and kept inside a sampling bottle for further laboratory analysis. The sampling bottle contained with crude oil was dipped inside a water bath at a reservoir condition temperature (54 °C). Brine solution (produced water, PW and sea water, SW) was then prepared according to the Field D formulations. A pre-determined amount of CaCl₂·2H₂O, MgCl₂·6H₂O, KCl, BaCl₂·2H₂O, SrCl₂·6H₂O and NaCl were added into a beaker and continuously stirred to form a homogeneous brine solution. NaHCO₃ was then added into the brine solution prior to lab analysis. An O/W emulsion has been prepared using M surfactant based on the formulations used in pilot study for Field D EWAG. The emulsion test was conducted at pilot condition with 80% water cut by mixing 20 ml of crude oil with 80 ml of brine solution. The brine formulation was based on the the combination of seawater (SW) and produced water (PW) at a ratio of SW:PW = 40:60. SW was first mixed with M surfactant at a ratio of 8 ml of M to 400 ml of SW. Then, the new integrated SW with surfactant was mixed with PW to form the brine solutions, which then mixed with crude oil. All sample tubes were shake for 2 minutes and then placed in water bath for 5 minutes at 54 °C.

2.4 Demulsification Test

The concentrations of GO nano-demulsifier and contact time in O/W emulsion during demulsification tes were varied from 20 to 100 ppm and 30-240 minute, respectively. The concentration of oil in the brine solutions was then determined using a UV–Vis spectrophotometer.

3. Results and Discussions

3.1 Characterization of Graphene Oxide

XRD is used to identify crystalline phases and determine the structural properties of GO [9]. Figure 1 compares XRD spectra for graphite and GO. It can be seen that a sharp and intense peak was observed at 2θ=26.4, which indicates that graphite is a highly crystalline material. Upon oxidation and exfoliation process, the peak at 2θ= 26.4 disappeared and lower angle peak was observed at 2θ=9.58. There is a little broad at bottom of the peak which might indicates to non-uniform strain condition affect by grain size or hardness factors.

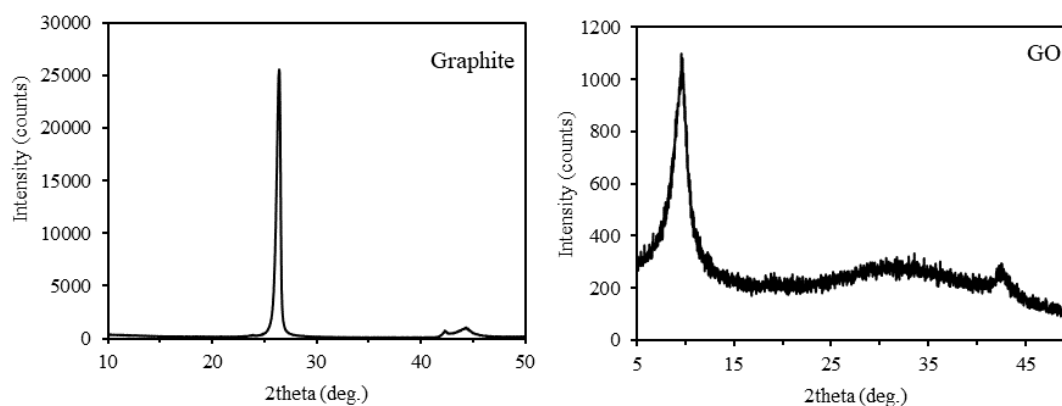


Figure 1. XRD data of graphite and GO

Figure 2 compares the FTIR spectrum for graphite and GO. It can be seen that no functional group is observed for graphite. However, upon the oxidation process of graphite, several new functional groups appeared. The broad spectrum observed at around 3178.3 cm^{-1} is due to O-H stretching vibrations, which might be attributed to adsorbed water on GO. The spectrum at 1716.96 cm^{-1} is known as the stretching vibrations of COOH group, corresponding to carbonyl and carboxyl groups, whereas the spectrum at 1622.56 cm^{-1} is attributed to in-plane vibration (C – O stretching vibration of C – OH). The spectrum at 1043 cm^{-1} is attributed to (C – O – C) stretching vibrations mode. The appearance of these functional groups confirms the formation of GO.

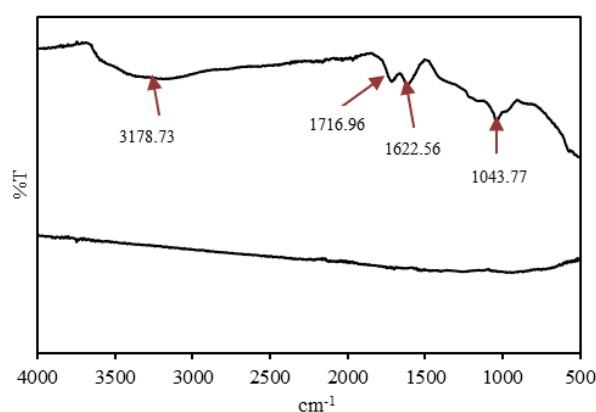


Figure 2. FTIR spectrum for graphite and GO

3.2 Performance Study of Graphene Oxide (GO) demulsifier

Figure 3 shows the demulsification performance of GO nano-demulsifier at various concentrations and contact time. It has been found that GO can effectively break the emulsion even at a very low concentration owing to the nano properties. At 20 ppm of GO concentration and 30 min of contact time, the concentration of O/W was found to be 90.5 ppm. As the contact time of GO nano-demulsifier was increased, the concentration of O/W decrease slightly. This indicates that the demulsification of O/W can be achieved at a shorter time using GO.

Interestingly, it was found that as the concentration of GO nano-demulsifier used increases to 100 ppm, the value of O/W was higher. This indicates that the adsorption of oil was lowered although more GO was used. This might be because as the amount of GO added increased, GO cannot be fully dispersed in the solution. Therefore, the contact area for demulsification to occur decreased.

Oil content in Field D's emulsion was observed to reduce significantly when GO nano-demulsifier was added, where the lowest oil content corresponding to the maximum demulsification efficiency was achieved between 20-40 ppm of GO. When the dosage of GO exceeds the threshold, the oil content in the water was higher. This probably be due to the subsequent distribution of GO dispersion after demulsification. Because GO is more distributed in the water phase, the adsorbed oil on the GO surface causes a slight increase of oil in the separated water samples.

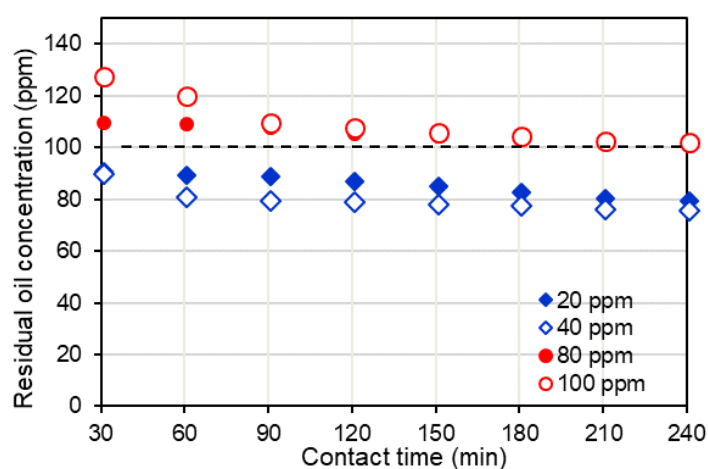


Figure 3. Residual oil content with graphene oxide as nano-demulsifier

3.3. Observation Study of Graphene Oxide

Figure 4 visualizes the demulsification study at selected contact time. It was observed that longer contact time leads to a better separation efficiency. Higher oil adsorption was observed at the beginning, where nearly more than 75% emulsion were separated during the first 30 min. By increasing the contact time to 240 min, better separation of emulsions was observed. As GO concentrations increased, high amount of solid residue was observed to settle at the bottom of separating funnel. These solid residues occurred as some part of the emulsion presence elements might adhere and attracted to GO adsorbent and eventually breaking down the emulsion into two layers.

When GO nano-demulsifier was applied into the emulsion, abundance of irregular oil floccules in the water phase with larger sizes than that in original emulsion was observed. Such findings denote that GO suspension can interact with fine oil drops in emulsion after they contact each other, eventually lead to clear colors of the emulsion just after immediate addition of GO suspension. GO dispersion promote combining of fine oil drops in emulsion to form big oil drops [14]. After completely shaking, oil floccules aggregate quickly to form accumulated floating oil phase on the water surface. The demulsification mechanism involved could be related with the presence of repulsive force that form such stability of the crude oil-water emulsion. The repulsive force normally comprising of molecules likely asphaltenes, resins, and naphthenic acid located at the interface of oil and water. In order to break the stable emulsion, such alternatives implemented should focusing on decreasing the repulsive force and destruct the viscoelastic film situated at oil-water interface [15].
























C. Time Conc.	Emulsion	30 min	60 min	120 min	240 min
20 ppm					
40 ppm					
60 ppm					
80 ppm					
100 ppm					

Figure 4. Visualization of O/W demulsification using various GO concentrations and contact times

4. Conclusions

From the results obtained, it has been found that GO nano-demulsifier can effectively break the crude oil in water emulsion. Lower concentration of GO and shorter contact time were preferred due to better demulsification efficiency. The residual oil content in the separated water was found to be as low as 100 ppm that might be due to the amphiphilic properties of GO. By further understanding the intrinsic interaction between GO and crude oil, the performances of GO can be easily tailored in the future to achieve the targeted value of OW content.

Acknowledgments

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