



Effect of Magnetic Graphene Oxide on Heavy Oil Demulsification

Aqilah Dollah^{1*}, Nurfarahain Abu Bakar¹, Nur Hidayati Othman¹, Siti Nurliyana Che Mohamed Hussein¹, Nur Shuhadah Japperi¹

¹School of Chemical Engineering, College of Engineering
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, MALAYSIA

DOI: <https://doi.org/10.30880/ijie.2022.14.05.017>

Received 26 June 2022; Accepted 15 August 2022; Available online 25 August 2022

Abstract: Chemical demulsification is the most efficient demulsification approach that can attain the desired separation efficiency and meet the environmental regulation standards whilst impose minimal economic burden on the petroleum industry. However, current demulsification methods using chemical demulsifiers suffer from significant secondary pollution, particularly after the demulsification process. Therefore, in this work, magnetic graphene oxide (MGO) was synthesized by a one-step co-precipitation method from graphene oxide (GO). The properties of MGO were then characterized by X-ray diffraction and Fourier transform infrared. MGO was successfully synthesized and used as the demulsifier for diluted heavy oil emulsions. Different MGO concentrations (40, 80, 120, 160, and 200 ppm) were used at different water cuts (20:80, 30:70, 40:60, 50:50, and 60:40 v/v%). Demulsification tests using the bottle test method indicated that MGO could separate the emulsions up to 99.98% efficiency due to the high surface area-to-volume ratio of nanoparticles and magnetic features, which enhanced the adsorptive capacity for separating water from the oil. The residual oil content in the separated water was then analyzed by an ultraviolet-visible spectrophotometer. The oil concentration in the separated water reduced to 398.8 mg/ml, corresponding to a demulsification efficiency of 99.98% observed at 40 ppm MGO concentration. The interfacial tension of the emulsions during demulsification was also analyzed, where the interfacial tension decreased with increasing MGO concentration.

Keywords: Chemical demulsification, oil emulsion, magnetic graphene oxide, bottle test, interfacial tension

1. Introduction

In the oil and gas industry, crude oil and brine/water emulsification always occurs during production and processing. Emulsion is formed due to the extraction of crude oil mixed with water. [1] stated that these emulsions could be classified based on continuous and dispersed phases. Commonly encountered emulsions are oil-in-water (O/W) emulsions and water-in-oil (W/O) emulsions.

Emulsion is a dispersion of one liquid throughout another immiscible liquid in the form of small droplets, which can be stabilized by an emulsifying agent. Natural emulsifiers, such as surface-active agents or surfactants, consist of hydrophilic and hydrophobic parts that are only attracted to water and oil, respectively. Due to this molecular structure, surfactants form interfacial films at the oil/water interface of the emulsions. The interfacial rheological properties, solubility, and adsorption-desorption kinetics of the surfactants determine the stability of the interfacial film [2]. Interfacial films act as a barrier against the coalescence and flocculation of oil and water droplets. Thus, to separate these emulsions, omission, variation, or neutralization can be done on the emulsifying agents [3]. Failure to separate these emulsions could result in several difficulties, such as damage to surface separation equipment and pipeline corrosion [4].

Chemical demulsifiers are mostly used in treating crude oil emulsions. This is because chemical demulsifiers can reduce the kinetic stability of interfacial films during demulsification by changing the interfacial rheological properties of the emulsions. For example, asphaltene is an emulsifier in crude oil. The emulsifier has sufficient functional groups

*Corresponding author: aqilah7097@uitm.edu.my

2022 UTHM Publisher. All rights reserved.

penerbit.uthm.edu.my/ojs/index.php/ijie

that form an interfacial layer with good mechanical strength. Demulsification occurs when demulsifying materials break the interfacial layer of asphaltene.

Graphene-based materials have been discovered as potential adsorbents due to their amphiphilicity and unique interfacial behavior [5]. Graphene oxide (GO) is also rich with surface-active agents, hydroxyl, and carboxyl. Therefore, GO can provide fast and excellent separation efficiency. However, previous research claimed that GO is less likely to be used alone during adsorption due to high hydrophilicity and easy dispersion in an aqueous solution. Hence, it is difficult to separate GO from an aqueous solution after demulsification [6].

GO can also contaminate the water or crude oil in the refinery because GO is stable in aqueous and oil phases [7]. Thus, the addition of magnetic nanoparticles to minimize the contamination by GO will be beneficial in the long run. In this study, GO was modified through the functionalization with iron oxide (Fe_3O_4) to form magnetic graphene oxide (MGO) nanoparticles. As GO is dispersible in an aqueous solution and difficult to separate, the magnetic property could aid the post-treatment separation and the nanoparticles could be reused [8]. The functional group of Fe_3O_4 can be added to the adsorbent, enhancing its adsorption capacity. Magnetic nanoparticles are capable of magnetic separation, environmental remediation, and other applications in most fields, which have caught the interest of researchers on the subject.

MGO nanocomposite possesses high adsorption capacity, which can easily separate oil from the water phase when an external magnetic field is introduced. The separation using MGO requires less energy compared to other separation methods, such as filtration and centrifugation [9]. In this work, MGO was used to break diluted heavy oil emulsions. The rheological properties and demulsification efficiency at different MGO concentrations for different water cuts of diluted heavy oil emulsions were then investigated.

2. Materials and Methods

2.1 Materials

Graphite powder was obtained from Merck. Sodium nitrate (NaNO_3), concentrated sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), 5% of hydrochloric acid (HCl), and acetone were used to synthesize GO. Meanwhile, ferric chloride (FeCl_3), ferrous chloride (FeCl_2), and 28% ammonia solution were used for preparing MGO. Bertam heavy crude oil samples, sodium chloride (NaCl), potassium chloride (KCl), magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), potassium dihydrogen phosphate (KH_2PO_4), toluene, and distilled water were utilized to produce synthetic brine. The properties of Bertam heavy crude oil are presented in Table 1.

Table 1 - Chemical and physical properties of Bertam heavy crude oil

Properties	Value
Oil density (g/cm^3)	0.988
Kinematic viscosity, (50 °C, cP)	17,751
Saturate (% wt.)	3.0
Aromatic (% wt.)	63.4
Resin (% wt.)	12.9
Asphaltene (% wt.)	20.7

2.2 Synthesis of GO

GO was synthesized from graphite powder according to the modified Hummer's method [10], which involved oxidation and exfoliation of graphite. In this method, 10 g of graphite powder and 5 g of NaNO_3 were added into a 500 ml beaker. Then, 200 ml of concentrated H_2SO_4 was added to the mixture. The mixture was stirred for 1 h at a temperature below 15 °C and a stirring speed of 350 rpm in an ice bath. After that, 60 g of KMnO_4 was added quarterly to the mixture and stirred continuously for 2 h at a temperature below 15 °C. Later, the ice bath was removed, and the mixture was kept stirred for 2 h at room temperature.

The mixture was then heated to 70 °C and 100 ml of distilled water was added slowly within 2 h. Next, the mixture was heated to 90 °C and another 100 ml of distilled water was added within 1 h while stirring. Then, 60 ml of H_2O_2 was added to the mixture to remove excess KMnO_4 and constantly stirred for 1 h. After completion, the solution was left overnight. The mixture was washed with 5% of HCl to remove the supernatant, followed by washing with distilled water to obtain an alkaline solution with pH 10. The mixture was centrifuged to separate water and solids. After that, the GO solution was washed with acetone to produce fine particles of GO. Finally, the washed GO solution was dried in an oven at 60 °C for 24 h to produce GO.

2.3 Preparation of MGO

MGO was prepared by the chemical co-precipitation method [11]. Approximately 1.8 g of synthesized GO was dispersed in 500 ml of high-purity water and ultrasonicated for 2 h to obtain a clear dispersion of GO. Then, 32.5 g of FeCl₃ and 12.7 g of FeCl₂ were added slowly to 400 ml of H₂O. The mixed solution was added slowly to the GO solution under nitrogen flow at 50 ml/min with vigorous stirring. The 28% ammonia solution was added slowly to precipitate Fe²⁺ and Fe³⁺ ions to synthesize magnetite particles until the pH of the solution reached 10. The solution was cooled at room temperature after being rapidly stirred for 30 min with constant mechanical stirring. An external magnetic field was then applied to the dark black-colored solution to separate MGO from the solution. After that, the separated MGO was washed with high-purity water five times and dried in the oven at 60 °C for 24 h to produce MGO.

2.4 Preparation of Diluted Heavy Oil Emulsions

Synthetic brine was prepared by mixing 10 g of NaCl, 0.29 g of KCl, 0.42 g of MgSO₄·7H₂O, 0.83 g of KH₂PO₄, and 0.42 g of NaNO₃ into 1 L of distilled water. Heavy crude oil was obtained from Bertam oil field with the properties of 11° API. The crude oil was diluted with 20% by volume of toluene. Diluted heavy oil emulsions were prepared by dispersing the oil phase into the water phase in a 500 ml beaker. Synthetic brine and crude oil were used as the continuous and dispersed phases, respectively. These two phases were vigorously stirred at room temperature until they became completely homogeneous. The emulsions were prepared at different water-to-crude oil ratios of 80:20, 70:30, and 50:50 (% , v/v).

2.5 Demulsification Test

The bottle test was conducted to estimate the efficiency of MGO toward diluted heavy oil emulsions. MGO was dissolved in distilled water (1 g/L) and added to the test tube of 20 mg/L MGO suspension in 30 ml of the previously prepared emulsions. Then, the mixture was shaken vigorously for 1 min. The test tubes were placed in a water bath for 10–15 min at 60 °C. Water separation was observed for 30 min, depending on the efficiency of the demulsifier. Next, the separated water was removed from the newly formed oil phase using a separating funnel. The demulsification efficiency of MGO was determined by measuring the residual oil content in the separated water sample. The sample was analyzed by an ultraviolet-visible (UV-Vis) spectrophotometer at a wavelength of 350 nm with a 1 cm path length [12]. The initial oil concentration was calculated using the following equation:

$$C_o = \left(\frac{m_o}{V_m} \right) \times 10^3 \quad (1)$$

where C_o (mg/L) is the oil concentration, m_o (mg) is the corresponding mass of oil in the standard sample, and V_w (ml) is the water volume. The demulsification efficiency, E (%) was calculated from the measured residual oil content using the following equation:

$$E = \left(\frac{C_o - C_i}{C_o} \right) \quad (2)$$

where C_o and C_i are the initial and residual oil content in the separated water sample, respectively. The interfacial tension of the mixture was then observed using a goniometer with the pendant drop shape method to test the demulsification efficiency.

3. Results and Discussion

3.1 Characterization of M-GO

Fourier transform infrared (FTIR) spectroscopy was used to determine the functional groups on the surface of MGO and the binding mechanism of pollutants [13]. The FTIR spectra of all the studied compounds are shown in Fig. 1. The MGO high points are located at 1,634 cm⁻¹ and 589 cm⁻¹ in relation to Fe-O vibration, indicating the symmetric stretching of Fe₃O₄ nanoparticles. This finding is consistent with work by [8]. The wide band at 3,197 cm⁻¹ in the FTIR spectra includes the stretching vibration of the hydroxyl group and N-H bond, while the peaks at 1,673 cm⁻¹ and 1,018 cm⁻¹ are attributed to C=O of the -NH=C=O and C-OH bond stretching, respectively. X-ray diffraction (XRD) measurement is an effective technique to determine the phase and structure of MGO by providing data about the physical and chemical forms of MGO nanocomposites.

The XRD spectrograms of MGO are presented in Fig. 2. From the figure, several well-defined diffraction peaks could be observed at 2θ values of 30.10°, 35.49°, 43.39°, 53.37°, 57.25°, and 62.98°, which can be indexed as the 449, 704, 424, 419, 456, and 481 plane reflections of magnetic nanoparticles, respectively. Five major peaks observed in the

pattern of MGO in Fig. 2 are similar to iron oxide, indicating its dominance in the binary mixture. The high peak at the start of 2θ of 10° of the GO patterns is due to air scattering during the analysis.

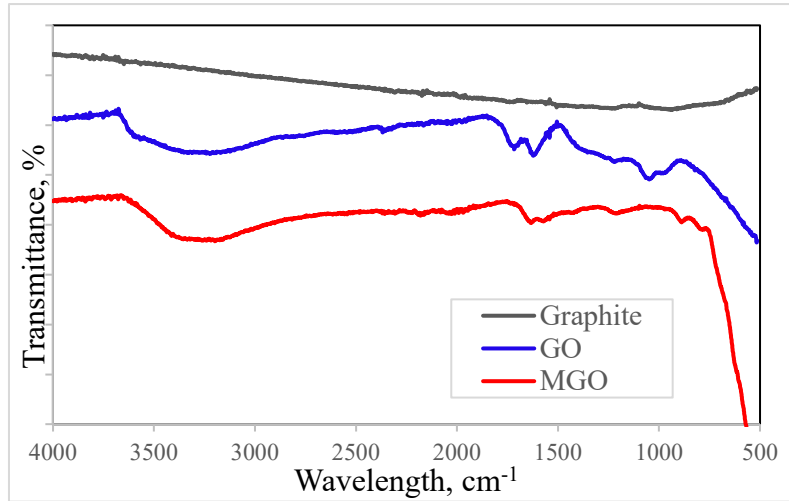


Fig. 1 - FTIR spectra of graphite, GO, and MGO

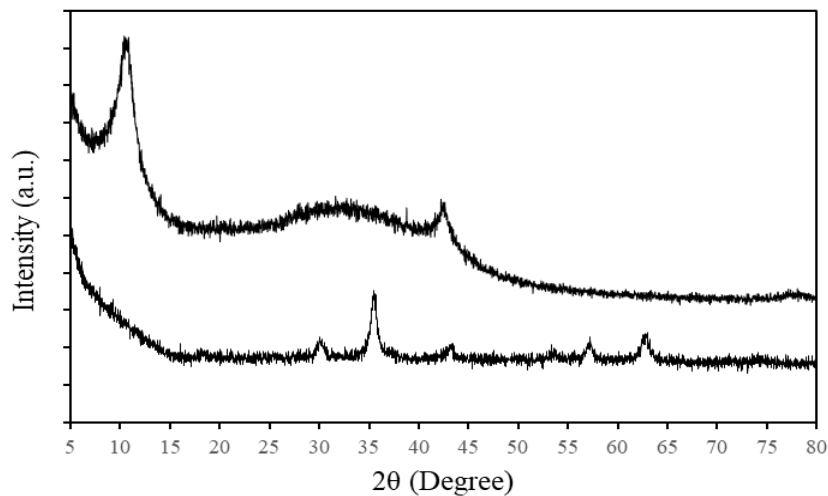


Fig. 2 - X-ray diffraction spectrograms of GO and MGO

3.2 Demulsification Performance of MGO Demulsifier

The demulsification of the prepared emulsions could be visually observed through the bottle test method. It is a simple and intuitive method to evaluate the performance of MGO as a demulsifier [14]. The demulsification process driven by MGO nanoparticles is shown in Fig. 3. Different MGO concentrations were added to 30 ml of diluted heavy oil emulsions inside the test tubes and observed for 30 min. Fig. 3(a) shows the initial condition of the emulsions prior to adding different concentrations of MGO into the test tubes. The emulsions were prepared with three different oil-to-water ratios of 20:80 v/v% in Fig. 3(b), 30:70 v/v% in Fig. 3(c), and 50:50 v/v% in Fig. 3(d). The separation of diluted heavy oil from water by various MGO concentrations could be seen from the bottle test method. It is believed that the color of the separated water after demulsification by various MGO concentrations is the color that originated from MGO nanoparticles [15]. The cloudiness of the separated water is due to the diluted heavy oil that tends to stick to the wall of the plastic test tubes.

The demulsification efficiency of the emulsions was determined by the residual oil concentration in the separated water based on the UV-Vis analysis. As shown in Fig. 4, for emulsions with 80% water cut, the residual oil concentration in the separated water reduced to 398.8 mg/ml, corresponding to a demulsification efficiency of 99.7% with 40 ppm MGO concentration. It was found that the best demulsification performance was acquired at the concentrations of 80–200 ppm with the corresponding demulsification efficiencies from 99.97% to 99.99%. Overall, the residual oil concentration decreased with increasing MGO concentration. The best demulsification efficiencies for the emulsions were 99.98%–99.99% for emulsions with 70% water cut at 80–200 ppm MGO concentration. For emulsions with 50%

water cut, the best demulsification efficiencies were 99.91%–99.99% for MGO concentrations of 120–200 ppm. The results in Fig. 5 indicate that MGO nanoparticles could be used as an effective demulsifier for breaking the emulsions.

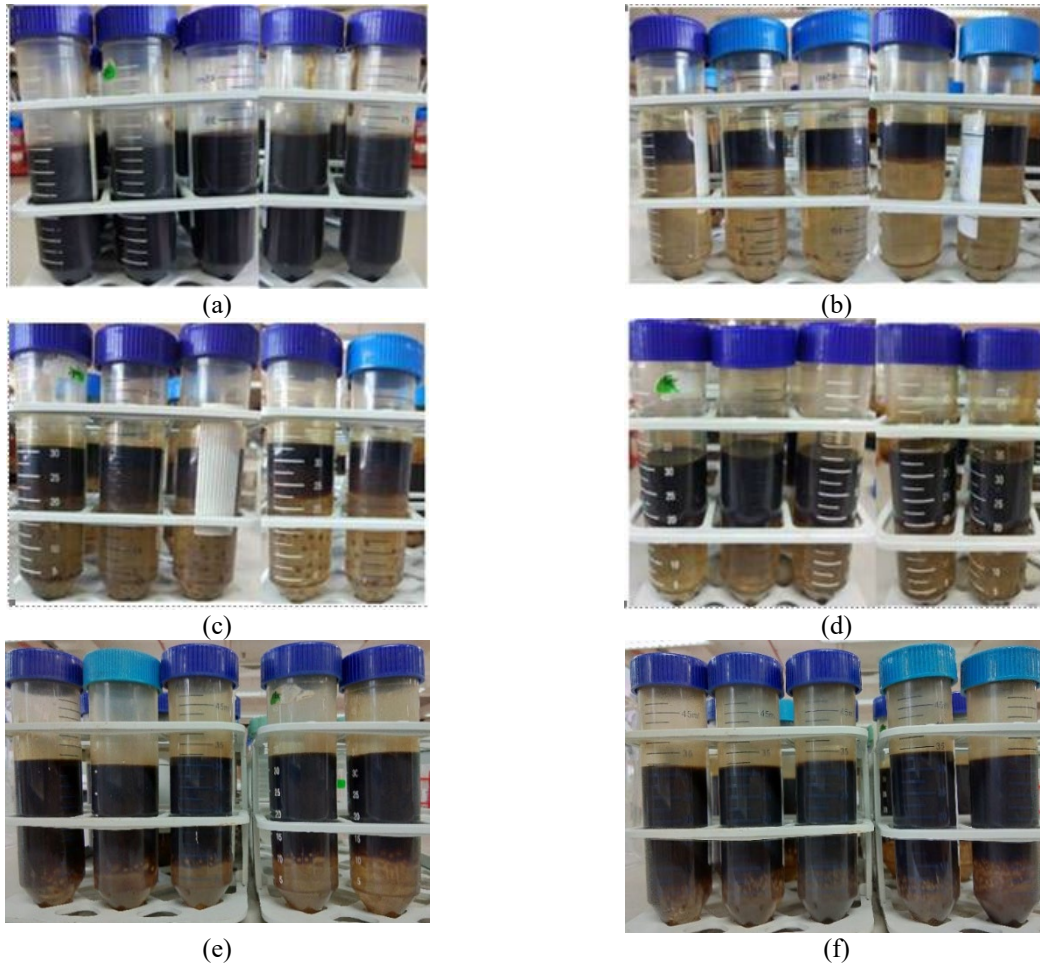


Fig. 3 - Visual observation of the demulsification process after MGO was introduced from the right at 40, 80, 120, 160, and 200 ppm for (a) the initial condition of emulsion before MGO addition, (b) emulsion at 20% of oil, (c) emulsion at 30% of oil, (d) emulsion at 40% of oil, (e) emulsion at 50% of oil, and (f) emulsion at 60% of oil

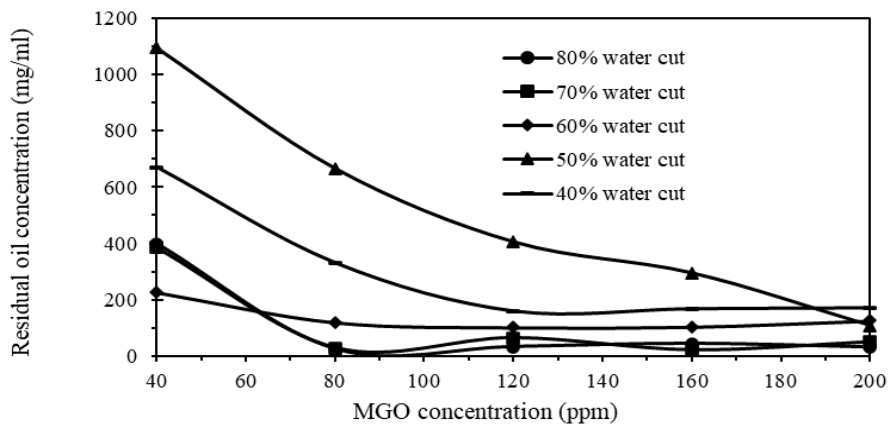


Fig. 4 - Effect of MGO concentration on the residual oil concentration at different water cuts

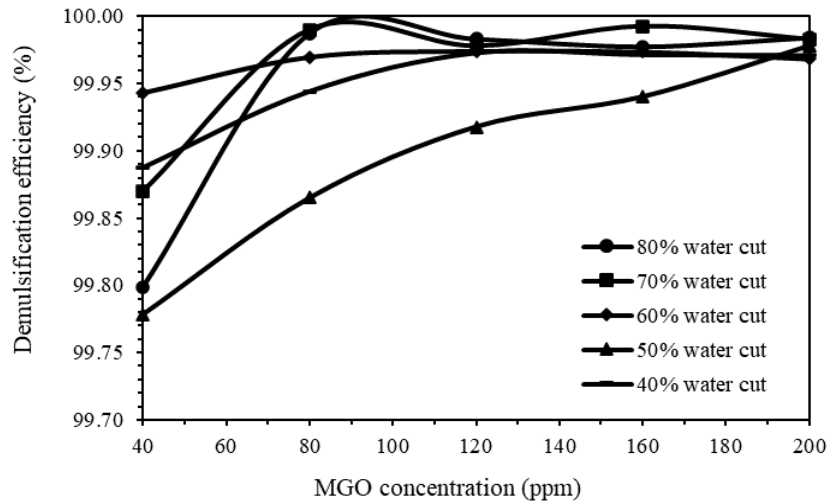


Fig. 5 - Effect of MGO concentration on the demulsification efficiency at different water cuts

3.3 Interfacial Rheology

The interfacial tension was determined as a function of MGO concentration. The interfacial tension of each emulsion with different MGO concentrations was measured using the pendant drop method of a goniometer. The drop shape used to calculate the interfacial tension is shown in Table 2. [16] stated that the interfacial tension of emulsions decreased gradually with the increase of demulsifier concentration in the solution. The result is consistent with the values obtained from the pendant drop shape analysis [17]. The relationship between the MGO concentration and interfacial tension is shown in Fig. 6. From the figure, the interfacial tension of the emulsions decreased with increasing MGO concentration. This finding confirms that MGO nanoparticles have excellent interfacial activity and can diffuse into the oil/water interface to reduce the interfacial tension of the emulsions.

Table 2 - Effect of various MGO concentrations on the interfacial tension of emulsions at different water cuts

MGO Concentration (ppm)	Water Cut (v/v, %)				
	20:80	30:70	40:60	50:50	60:40
0					
40					
80					
120					
160					

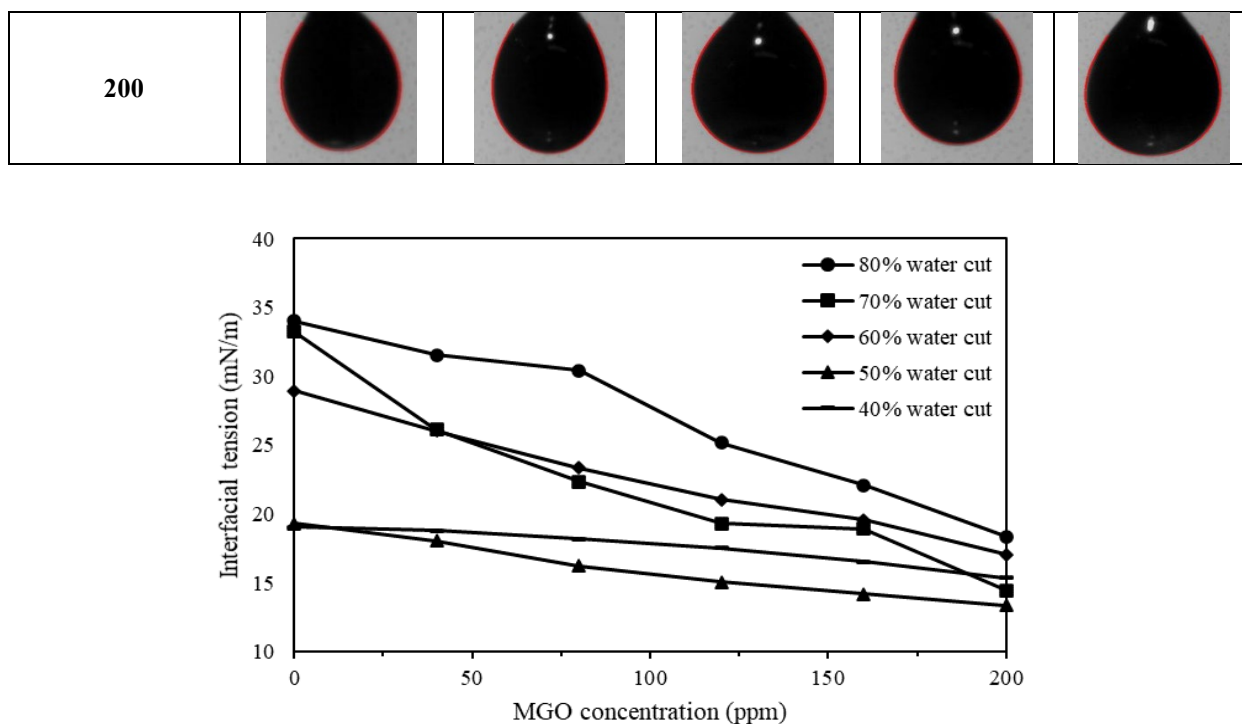


Fig. 6 - Effect of MGO concentration on the interfacial tension at different water cuts

4. Conclusions

In this study, MGO was applied as a magnetic demulsifier. MGO is a rapid and highly efficient demulsifier for breaking up diluted heavy oil emulsions. From the results, the stability of the emulsions decreased significantly with the addition of MGO and the demulsification process could be completed within several minutes. MGO could also reduce the interfacial tension of the emulsions, implying that MGO nanoparticles are interfacially active. MGO offers excellent demulsification performance because it can be separated from the separated water by applying an external magnetic field, which can also eliminate small oil floccules in the separated water. Furthermore, MGO can be reused until its function deteriorates.

Acknowledgements

The authors gratefully acknowledge the assistance of the Ministry of Higher Education Malaysia and Universiti Teknologi MARA (UiTM) in providing the research grant (Project Number: 600-IRMI/FRGS 5/3 (400/2019)).

References

- [1] Ali, N., Bilal, M., Khan, A., Ali, F., Yang, Y., Khan, M., Adil, S. F., & Iqbal, H. M. N. (2020). Dynamics of oil-water interface demulsification using multifunctional magnetic hybrid and assembly materials. *Journal of Molecular Liquids*, 312, 113434. <https://doi.org/10.1016/j.molliq.2020.113434>
- [2] Alsabagh, A. M., Hassan, M. E., Desouky, S. E. M., Nasser, N. M., Elsharaky, E. A., & Abdelhamid, M. M. (2016). Demulsification of W/O emulsion at petroleum field and reservoir conditions using some demulsifiers based on polyethylene and propylene oxides. *Egyptian Journal of Petroleum*, 25(4), 585–595. <https://doi.org/10.1016/j.ejpe.2016.05.008>
- [3] Wai, M. M., Khe, C. S., Yau, X. H., Liu, W. W., Sokkalingam, R., Jumbri, K., & Lwin, N. (2019). Optimization and characterization of magnetite-reduced graphene oxide nanocomposites for demulsification of crude oil in water emulsion. *RSC Advances*, 9(41), 24003–24014. <https://doi.org/10.1039/c9ra03304a>
- [4] Javadian, S., & Sadrpoor, S. M. (2020). Demulsification of water in oil emulsion by surface modified SiO₂ nanoparticle. *Journal of Petroleum Science and Engineering*, 184, 106547. <https://doi.org/10.1016/j.petrol.2019.106547>
- [5] Lan, T., Zeng, H., & Tang, T. (2019). Molecular dynamics study on the mechanism of graphene oxide to destabilize oil/water emulsion. *The Journal of Physical Chemistry C*, 123(37), 22989–22999. <https://doi.org/10.1021/acs.jpcc.9b05906>
- [6] Sun, J., Liang, Q., Han, Q., Zhang, X., & Ding, M. (2015). One-step synthesis of magnetic graphene oxide nanocomposite and its application in magnetic solid phase extraction of heavy metal ions from biological samples.

- Talanta, 132, 557–563. <https://doi.org/10.1016/j.talanta.2014.09.043>
- [7] Liu, J., Wang, H., Li, X., Jia, W., Zhao, Y., & Ren, S. (2017). Recyclable magnetic graphene oxide for rapid and efficient demulsification of crude oil-in-water emulsion. *Fuel*, 189, 79–87. <https://doi.org/10.1016/j.fuel.2016.10.066>
- [8] Sherlala, A. I. A., Raman, A. A. A., & Bello, M. M. (2019). Synthesis and characterization of magnetic graphene oxide for arsenic removal from aqueous solution. *Environmental Technology (United Kingdom)*, 40(12), 1508–1516. <https://doi.org/10.1080/09593330.2018.1424259>
- [9] Lingamdinne, L. P., Koduru, J. R., & Karri, R. R. (2019). A comprehensive review of applications of magnetic graphene oxide based nanocomposites for sustainable water purification. *Journal of Environmental Management*, 231, 622–634. <https://doi.org/10.1016/j.jenvman.2018.10.063>
- [10] Othman, N. H., Jahari, A. F., Alias, N. H., Jarni, H. H., Shahrudin, M. Z., Irfan, M. F., Dollah, A., & Halim, N. H. (2018). Demulsification of crude oil in water (O/W) emulsions using graphene oxide. *IOP Conference Series: Materials Science and Engineering*, 458, 012023. <https://doi.org/10.1088/1757-899X/458/1/012023>
- [11] Othman, N. H., Alias, N. H., Shahrudin, M. Z., Abu Bakar, N. F., Nik Him, N. R., & Lau, W. J. (2018). Adsorption kinetics of methylene blue dyes onto magnetic graphene oxide. *Journal of Environmental Chemical Engineering*, 6(2), 2803–2811. <https://doi.org/10.1016/j.jece.2018.04.024>
- [12] Chen, Y., Tian, G., Liang, H., & Liang, Y. (2019). Synthesis of magnetically responsive hyperbranched polyamidoamine based on the graphene oxide: Application as demulsifier for oil-in-water emulsions. *International Journal of Energy Research*, 43(9), 4756–4765. <https://doi.org/10.1002/er.4614>
- [13] Yau, X. H., Khe, C. S., Mohamed Saheed, M. S., Lai, C. W., You, K. Y., & Tan, W. K. (2020). Magnetically recoverable magnetite-reduced graphene oxide as a demulsifier for surfactant stabilized crude oil-in-water emulsion. *PLoS ONE*, 15(4). <https://doi.org/10.1371/journal.pone.0232490>
- [14] Salam, K. K., Alade, A. O., Arinkoola, A. O., & Opawale, A. (2013). Improving the demulsification process of heavy crude oil emulsion through blending with diluent. *Journal of Petroleum Engineering*, 2013, 1–6. <https://doi.org/10.1155/2013/793101>
- [15] Ain, Q. U., Farooq, M. U., & Jalees, M. I. (2020). Application of magnetic graphene oxide for water purification: Heavy metals removal and disinfection. *Journal of Water Process Engineering*, 33, 101044. <https://doi.org/10.1016/j.jwpe.2019.101044>
- [16] Adewunmi, A. A., Kamal, M. S., & Solling, T. I. (2021). Application of magnetic nanoparticles in demulsification: A review on synthesis, performance, recyclability, and challenges. *Journal of Petroleum Science and Engineering*, 196, 107680. <https://doi.org/10.1016/j.petrol.2020.107680>
- [17] Wang, H., Liu, J., Xu, H., Ma, Z., Jia, W., & Ren, S. (2016). Demulsification of heavy oil-in-water emulsions by reduced graphene oxide nanosheets. *RSC Advances*, 6(108), 106297–106307. <https://doi.org/10.1039/c6ra18898b>