Monolayer grafting of APTES modified graphene oxide on silica coated magnetite: Synthesis, characterization and application in heavy oil removal

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Abstract. Petroleum industries have been creating negative environmental and ecological impacts due to the formation of oilfield produced water (OPW) during refining processes. Graphene oxide (GO) as a chemical demulsifier was found non-recyclable; hence, it could cause environmental pollution. Thus, magnetic graphene oxide (M-GO) was proposed to prevent any possible contamination. In this work, GO, and M-GO were successfully synthesized and the produced M-GO composites were found coated with silica-coated magnetite (Fe₃O₄@SiO₂) nanoparticles. As such, they possess excellent superparamagnetic properties. The demulsification tests demonstrated that 0.25 wt% of M-GO aqueous suspension achieved 98.53% of demulsification efficiency on the as-prepared crude oil-water emulsion, which was more superior than GO as the suspending oil flocules attached to M-GO can be separated effectively using magnetic separation. The optimizations of the demulsification process were conducted, and significant findings were included as the major novelty of this work. The recycling tests have proven that M-GO can be reused to perform demulsification effectively for ten times. Despite being able to reduce the demulsification costs in the industry, this research suggests that the excellent properties of M-GO can minimize the risk of polluting the environment due to leakage of demulsifier through the application of magnetic separation.

1. Introduction

In the petroleum industry, large amounts of sewages such as sludge, oil, and water are generated from different activities and processes at different stages. For instance, oilfield produced water (OPW) can mainly be found from the refinery sector of the petroleum industry, as vast volumes of water are required in the oil refineries [1]. OPW is known as an oil-in-water emulsion (O/W emulsion), and it is the largest waste stream that contains several organic and inorganic compounds, such as suspended solids, oil, and grease (O&G), water-soluble metals, and salts in the petroleum industry. Oils and greases are the primary contaminants in the wastewater produced from the petroleum industry. In offshore oil recovery operations, the produced water...
can affect the ecological resources and functions, cause environmental pollutions, destroy the natural landscape, and threaten aquatic resources and human health if OPW is discharged to the underground or surface water environment without proper treatment [2, 3]. OPW can even increase the lethal or sublethal effect of cellular functions, and it is also the root of high toxicity to the catalysts in the refining process and the corrosion of production facilities, pipe surface and distillation equipment. Oil-in-water emulsions with oil droplet size larger than 20 µm can be treated easily using physical treatments such as gravity separation, centrifugation, and ultrasonic application. In contrast, O/W emulsions with emulsified oil droplets (oil droplet size smaller than 20 µm) are difficult to be treated by common physical treatments due to its high stability of the oil-water interface protective film [4]. Thus, O/W emulsions in the wastewater (OPW) are immensely unsolicited in the petroleum industry, and they have to be treated by an effective demulsification process. Demulsification techniques such as membrane, chemical, biological, and electrical demulsification are reported to have some shortcomings such as long separation time, low separation efficiency, high cost, the formation of pollutants, fouling issues and poor recyclability [5]. Consequently, new sustainable methods focusing on economic savings and environmental preservation are essential to be invented for oily wastewater (OPW) treatment [6, 7].

Graphene oxide (GO) possesses small size (nano), large specific surface area, and intrinsic optical properties. As a result, many industry experts and researchers have been inventing useful applications of GO [8]. For instance, nano-size GO was proposed for biomedical applications [8]. GO is also an excellent amphiphilic surfactant which can reduce the interfacial energy between the interfaces of oil and water [9, 10]. In emulsion systems, GO can be applied in both emulsion stabilization [11] and demulsification processes [12]. It was discovered that GO could demulsify O/W emulsions effectively by causing repulsion force (nonbonding π-π interactions) between oxygenated functional groups of GO and the aromatic rings of asphaltene in the interlayer space [13]. GO as a chemical demulsifier can demulsify oil-in-water emulsion efficiently at low costs, and it can be synthesized efficiently using Hummers method. However, the Hummers method may lead to the liberation of toxic gases such as dinitrogen tetroxide (N₂O₄) and nitrogen dioxide (NO₂) [14]. Then, sodium nitrate (NaNO₃) was found to be replaceable by a mixture of sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) in the Hummers method to produce exceptional quality of GO without production of toxic gases [15].

Consequently, the modified Hummers method (Tour method) became more widely accepted due to its strengths, such as equivalent conductivity, able to produce GO on a large scale and emit zero toxic gases. However, nano-size GO could not be recycled effortlessly when they are well dispersed in a solvent, leading to the causes of negative ecological and environmental impacts and the threats of human health if they are released to the surface along with the treated water [13]. Various kinds of synthesis methods of magnetic-functionalized GO using γ-Fe₂O₃/Fe₃O₄ compounds were invented to further develop the recyclability and reusability of GO for industrial applications, and they were reported to be successful [16-18]. Therefore, it is proposed to decorate GO nanosheets with magnetic nanoparticles (MNs) in order to produce recyclable magnetic GO nanosheets for the demulsification of OPW, and it is expected to be feasible, high efficiency, and cost-effective. Magnetic functional particles with interfacial activities can accumulate at the interlayer space between oil and water, and impart their magnetic properties on the dispersed droplets. As a result, they can separate droplets from multiple phases with the aid of an external magnetic field.

Additionally, some influential parameters in chemical demulsification process that can be altered to increase or decrease the stability of the emulsion. It was stated that the hydrophilic-lipophilic deviation (HLD) value could be shifted from negative (O/W emulsion) to approximately zero through increasing the salinity of emulsions, hence improving the demulsification effectiveness [19]. The impacts of pH of water on the stability of emulsion usually depend on the brine compositions and oil phase in the emulsion [20]. Generally, the surfactant hydrophilicity increases as the pH value of emulsion increases. It was reported that O/W
emulsions are more likely to be generated in basic conditions (high pH), whereas W/O emulsions are prone to be generated in acidic conditions (low pH) [21]. Asphaltic interfacial films are stronger in acidic environments, whereas resinous films are more rigid in the alkaline environment. Nevertheless, extremely low pH (too acidic) environment may cause corrosion of equipment in the treatment plants which results in unnecessary extra cost; hence, precautions have to be taken to achieve optimal pH for demulsification.

Hence, this research aims to study the synthesis of recyclable magnetic graphene oxide (M-GO) by utilizing co-precipitation and a series of cross-linking reactions, including Stöber process. The effect of influential parameters such as salinity and pH of emulsion on the demulsification performance of M-GO has been investigated. Moreover, the recyclability of M-GO has also been tested and proved to reduce the demulsification cost and contamination through the application of magnetic separation after performing the demulsification process.

2. Experimental

2.1 Materials and chemicals

The chemicals H$_2$SO$_4$, H$_3$PO$_4$, KMnO$_4$, H$_2$O$_2$, NaOH, n-Hexane, and NH$_4$OH were purchased from Merck and used without further treatment. Graphite (<20 μm, synthetic powder), ethanol, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl), N-hydroxysuccinimide (NHS), FeCl$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, sodium citrate (Na$_3$C$_6$H$_5$O$_7$), tetraethyl orthosilicate (TEOS), toluene and (3-aminopropyl) triethoxysilane (3-APTES) were purchased from Sigma-Aldrich and used as received. The crude oil sample used to prepare synthetic O/W emulsion was provided by Miri Crude Oil Terminal (MCOT, Malaysia).

2.2 Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) nanosheets were synthesized from graphite powder according to the modified Hummers method (Tour method) [15] with some modifications. Graphene oxide (GO) nanosheets were synthesized from graphite powder according to the modified Hummers method (Tour method) (Marcano, D. C. et al., 2010). Briefly, 0.75 g graphite powder was added into a mixture of acid solutions consisted of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (90:10 mL) in a 500 mL beaker and stirred at room temperature for 0.5 h. 4.5 g of KMnO$_4$ was then added gradually into the mixture underwater bath stirred for another 0.5 h. Then, the mixture was stirred at 50 ºC for another 2 h. The resultant mixture was then ultra-sonicated for 1 h for further exfoliation. The solution was allowed to cool down to room temperature, and 200 mL of deionized ice water was added into the mixture. 3 mL of 30% H$_2$O$_2$ was then added into the mixture to remove excessive KMnO$_4$ and the colour of the mixture became brilliant yellow. The reaction was conducted underwater bath conditions, and 0.5 h of stirring was used to achieve a completed reaction. The mixture was centrifuged (4000 rpm, 20 min) and the supernatant was removed, 10% HCl aqueous solution was used to wash the remained solids (GO), followed by the subsequent centrifugation. This cycle was repeated for 4 times until the pH value of the suspension was nearly 6. Then, the final product (GO solid) was dried in a vacuum oven (TVAC-92) at 60 ºC under 0.05 MPa for 16 h.

2.3 Synthesis of magnetite nanoparticles (MNP)

As shown in Figure 1a, the synthesis of magnetic particles (Fe$_3$O$_4$) was achieved based on a co-precipitation method [22] with some modifications. Briefly, 0.02 mol (5.41 g) of FeCl$_2$·6H$_2$O and 0.01 mol (1.99 g) of FeCl$_3$·4H$_2$O were added into 100 mL of degassed deionized water in a 250 mL three-neck flask under a nitrogen atmosphere with constant agitation at room temperature for 1 h. While keeping the constant flow of nitrogen gas into the three-neck flask, the 5M NaOH
solution was added into the reaction solution gradually, until the resultant dispersion pH reached 11, according to Equation (1):

\[
\text{Fe}^{2+}(aq) + 2\text{Fe}^{3+}(aq) + 8\text{OH}^{-}(aq) \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}(l)
\]  

(1)

After the system was stirred for 4 h, the produced insoluble precipitates \( \text{Fe}_3\text{O}_4 \) were separated from the solution using a strong magnet. Lastly, the precipitates were dried in a vacuum oven (TVAC-92) for 12 h at 60 ºC and pressurized under 0.05 MPa after they were repeatedly washed with degassed deionized water four times.

2.4 Synthesis of mesoporous \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) core-shell microspheres

The preparation of silica-coated \( \text{Fe}_3\text{O}_4 \) was completed based on the \( \text{Fe}_3\text{O}_4 \) Stöber process [23]. 2 g of the magnetic \( \text{Fe}_3\text{O}_4 \) nanoparticles were added and dispersed into 200 mL of 0.5 M sodium citrate in order to reduce aggregation. The dispersed \( \text{Fe}_3\text{O}_4 \) nanoparticles were isolated using a magnet and then added into a 400 mL mixture of ethanol (75 vol. %), water (23.5 vol. %), and ammonia solution (1.5 vol. %). Then, a 16 mL mixture of TEOS and ethanol solution (4:12 mL) was gradually added to the dispersion under mild agitation at 40 ºC in a water bath for 24 h. The as-prepared particles were repeatedly washed with ethanol and water, and subsequently dried at 80 ºC in the vacuum oven for 24 h under 0.05 MPa.

2.5 \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) surface functionalization

The core-shell microspheres were functionalized with 3-APTES. 1 g of produced silica-coated \( \text{Fe}_3\text{O}_4 \) nanoparticles was added into 20 mL of toluene and mixed under vigorous stirring for 0.5 h. 20 mL of toluene was used to dilute 10 mL of 3-APTES, and they were gradually added into the mixture under constant agitation in the water bath and \( \text{N}_2 \) atmosphere at 120 ºC for 5 h. Then, the produced amino-functionalized magnetite \( \text{Fe}_3\text{O}_4@\text{SiO}_2—\text{NH}_2 \) nanoparticles were collected using a magnet after cooling down to room temperature. Lastly, the nanoparticles were washed by ethanol and toluene and dried in a vacuum oven (60 ºC, 0.05 MPa, 12 h).

2.6 Fabrication of GO onto \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) core-shell microspheres

The preparation progressions of M-GO were demonstrated in Figure 1a. Firstly, 0.1 g of produced GO was dispersed in 100 mL of deionized water. The resulting dispersion was sonicated using Probe type Ultrasonic Liquid Processor (SONOMECHANICS LSP-500, 500 W, 20 kHz) at a 40% amplitude for 1 h in order to achieve a GO suspension with a concentration of 1 mg/mL. Then, 40 mg of NHS and 50 mg of EDC.HCl was added to the GO suspension. By using the \( \text{NaOH} \) solution, the pH of the suspension was adjusted to ~5.5. In order to obtain a homogeneous suspension, the mixture was mechanically stirred for 0.5 h, followed by another 0.5 h of sonication. Then, 0.3 g of prepared amino-functionalized \( \text{Fe}_3\text{O}_4 \) nanoparticles were added into the GO suspension and ultra-sonicated for 0.5 h, followed by mechanical stirring for 1 h at 80 ºC for the grafting reaction [17]. The synthesized M-GO was washed with deionized water and separated using a magnet. Lastly, the M-GO solids dried in a vacuum oven (60 ºC, 0.05 MPa, 12 h). The mechanism of synthesis of M-GO through cross-linking reaction as illustrated in Figure 1b.
Figure 1. Mechanism of synthesis of desired nanoparticles and magnetic graphene oxide (M-GO). (a) Amino functionalized Fe$_3$O$_4$@SiO$_2$ Nanoparticles, (b) M-GO.

2.7 Preparation of crude oil-in-water emulsion

10 g of crude oil sample obtained from MCOT was directly added into 190 g of deionized water in a glass bottle. The mixture was then homogenized by a high-speed homogenizer (Silverson L5M) at 6000 rpm for 30 min; and eventually, a crude oil-in-water emulsion with 5.0 wt% oil content was formed. The prepared emulsion was further used for the demulsification test, recycling test of M-GO, and to investigate the effect of influential parameters on the demulsification efficiency of M-GO.

2.8 Characterization methods

An attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (Agilent Technologies, Cary 630 FTIR) was used to identify the presence of functional groups in the
produced GO, various magnetic nanoparticles obtained from each stage and M-GO. The FTIR spectra and characteristic peaks of the samples were obtained and recorded in a computer at a wavelength range between 550 and 4000 cm\(^{-1}\) at ambient temperature and pressure.

Zetasizer Nano-ZS (Malvern Instruments, UK) was used to conduct DLS analysis and zeta potential measurement on the produced GO, various nanoparticles, and M-GO. 30 mg of produced GO solid was added and homogenized in 300 mL of deionized water by Silverson L5M Homogenizer at 2000 rpm for 10 min. For DLS analysis, three samples (GO suspension without sonication (GO1), GO suspension with 15 min sonication (GO2), and GO suspension with 60 min sonication (GO3)) were measured in this analysis to investigate the effect of the ultra-sonication technique on the oxidation and exfoliation degree of GO. Besides, the measurements of zeta potential for produced GO, various magnetic nanoparticles obtained from each stage, and M-GO will be performed in aqueous solutions at pH of \(\sim 7\).

The morphology and physical structure of various magnetic nanoparticles and M-GO were observed by a scanning electron microscope (SEM, Hitachi S-3000N) at an essential magnification at ambient temperature. Dried solid samples were observed on an aluminium stub, and the images were obtained subsequently. An X-ray diffractometer (XRD, STOE Stadi-P diffractometer) was used to investigate the phase and crystal structure of the as-prepared magnetic nanoparticles.

The thermal characteristics of GO and M-GO were analyzed by the thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) using a simultaneous thermal analyzer (METTLER TOLEDO, Switzerland). Briefly, 10 mg of samples were weighed into the ceramic crucible with a constant purging of pure nitrogen at a rate of 100 mL/min and heated from 25 ºC to 800 ºC at a heating rate of 10 ºC/min.

The magnetic hysteresis loops of various magnetic nanoparticles and M-GO were investigated using the vibrating sample magnetometer (Lake Shore 7400 Series VSM system) at room temperature to determine their magnetization.

### 2.9 Demulsification test

The mechanism of demulsification processes, as illustrated in Figure S1. 0.1 wt% of M-GO aqueous suspension was shaken and added into the as-prepared oil-in-water emulsion. The M-GO dosage can be determined based on the concentration of mass. Thorough agitation was required to achieve the demulsification, and the mixture was allowed to settle at room temperature for the oil and water separation. An as-prepared emulsion without any addition of M-GO was employed as a reference for comparison afterwards. A magnet was then used to quicken the residual oil flocules separation from the water phase. Subsequently, a separatory funnel was used to separate the separated water samples from the newly formed mixture.

The demulsification efficiency can be calculated by measuring the remaining oil content in the sample of separated water. The treated separated water was collected from a separatory funnel. Hexane was used to extract the residual oil from the separated water. The residual oil content possesses a linear relation with the absorbance of hexane-diluted-oil, and it was analyzed by UV-visible Spectrophotometer, Lambda 25 UV/Vis Double Beam (Perkin Elmer, USA) at a wavelength of 570 nm (1 cm path length). Each of the tests with the exact dosage of M-GO was conducted three times to get the average values for higher accuracy, and the demulsification efficiency was calculated using Equation (2) and Equation (3):

\[
c = \frac{m_o}{V_w}
\]

\[
\text{DE(\%)} = \frac{c_o - c_i}{c_o} \times 100\%
\]

Where \(m_o\) is mass of the oil, \(V_w\) is the water samples volume (in mL); \(c, c_o, \) and \(c_i\) (mg/mL) are the oil concentration, oil concentration of emulsion and oil concentration of separated water.
respectively. DE is the calculated demulsification efficiency of M-GO by determining the oil removal percentage from the original emulsion.

2.10 Effect of influential parameters on demulsification efficiency

0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.25 wt % M-GO aqueous suspensions were used to perform demulsification on the as-prepared emulsion respectively to determine the effect of dosage of M-GO on the demulsification performance. O/W emulsions with different pH values (2, 4, 6, 8, and 10) were prepared, and the demulsification efficiencies achieved by 0.25 wt% M-GO aqueous suspensions were compared to investigate on the effect of emulsion pH on the demulsification efficiency. Also, 0.1 wt% of M-GO aqueous suspensions were added into O/W emulsions with different salinity (0 - 0.5 M NaCl) at neutral pH to determine the impact of salinity of O/W emulsion on the demulsification efficiency.

2.11 Recycling and reuse of M-GO

The produced M-GO was expected to be recycled and reused for demulsification. The recyclability of M-GO was investigated in the optimal condition of pH value at 4, with a 0.25 wt% dosage of M-GO added on the O/W emulsion with initial oil concentration at 50 mg/mL. The M-GO was separated and collected using a magnet after performing demulsification. Successively, the collected M-GO was washed by toluene 3 times repeatedly in order to remove the asphaltene molecules which were previously adsorbed onto the M-GO surface. M-GO was then collected and dried in a vacuum dryer at 60 ºC for 6 h. Finally, the M-GO was used for the same demulsification test, and the first cycle of the recycling tests was completed. Numerous cycles of recycling tests were performed until the oil content in the separated water was above 10 mg/mL after the demulsification test.

3.0 Results and discussion

3.1 Characterization of graphene oxide, various nanoparticles, and magnetic graphene oxid

3.1 (a) Fourier transform infrared (FTIR) spectra. The FTIR spectra of graphite and the produced GO are shown in Figure 2. From the FTIR spectrum of graphite, a broad absorption band is exhibited at 3559.6 cm\(^{-1}\), which is corresponded to O-H stretching vibration. A broad peak between 3200 cm\(^{-1}\) and 3400 cm\(^{-1}\) was also observed, which indicated the presence of the C-OH stretch of the hydroxyl functional group and –OH stretching vibrational mode from the carboxylic acid group in the GO sample [24]. The apparent broad peak at 3213 cm\(^{-1}\) is corresponded to the water molecules adsorbed onto the GO surface. The narrow peak at 1718.3 cm\(^{-1}\) is attributed to the C=O stretch of the carboxyl group of GO, whereas the peak at 1628.8 cm\(^{-1}\) indicates the presence of C=C stretches from the incompletely oxidized (sp\(^2\) character) graphitic domain in the GO sample. Furthermore, there are a total of 3 characteristic peaks shown in the fingerprint region of the IR spectra, which are 1155.5 cm\(^{-1}\), 1028.7 cm\(^{-1}\) and 872.2 cm\(^{-1}\). Both of the peaks at 1155.5 cm\(^{-1}\) and 1028.7 cm\(^{-1}\) correspond to the C-O stretch of an epoxy group and C-O stretching vibration of the carboxylic acid group in the GO samples, respectively [25]. The peak at 872.2 cm\(^{-1}\) was corresponded to the out of plane wagging vibration of C-H stretches of the GO [26]. The presence of epoxy and carboxyl groups in the FTIR spectra of GO specifies that the initial extended conjugated π-orbital system of the graphite (precursor) was destroyed, followed by the insertion of oxygen-containing groups into the carbon skeleton during the oxidation process, hence proving the completion of the oxidation process of graphite into GO [27].
As shown in Figure 3, the IR spectrum of all nanomaterials showed a predominant peak at ~600 cm$^{-1}$, which indicated the characteristic of Fe-O vibrational stretch from the magnetite (Fe$_3$O$_4$) phase. The IR spectrum of Fe$_3$O$_4$@SiO$_2$, Fe$_3$O$_4$@SiO$_2$-NH$_2$, and Fe$_3$O$_4$@SiO$_2$-GO nanoparticles showed stable broadband at ~1058 cm$^{-1}$, which was attributed to the Si-O-Si asymmetric stretching vibration or the Fe-O-Si stretching vibration at the silica coating layer, proving that the layer of silica was coated onto the surface of Fe$_3$O$_4$. A minor peak at 2907 cm$^{-1}$, which is attributed to the vibrational stretching of –CH$_2$ groups of aminopropyl from the 3-APTES, was observed after the silane treatment (addition of 3-APTES) on the Fe$_3$O$_4$@SiO$_2$ nanoparticles. The characteristics peaks showed the vibrational stretching and bending of amino groups at 1528 cm$^{-1}$ and 650 cm$^{-1}$. This has indicated that the 3-APTES was successfully grafted onto the surface of silica-coated Fe$_3$O$_4$ nanoparticles. The IR spectrum of M-GO in Figure 4a has shown apparent peaks at 1625-1655 cm$^{-1}$, 1401 cm$^{-1}$ and 1066 cm$^{-1}$, which were attributed to the characteristic bending of –OH from hydroxyl groups, a vibration of -C=O from carbonyl groups and stretching of C-O-C from alkoxy groups of GO respectively. A strong broad peak at 3354-3332 cm$^{-1}$, which is likely attributed to the vibrational stretching of N-H in the amide group (CO-NH$_2$) of MGO and the stretching of –OH from hydroxyl groups have determined the existence of amino-functionalized magnetic particles on the GO surface.

3.1 (b) Dynamic light scattering (DLS) analysis. A full DLS analysis was applied to analyze the polydispersity index (PDI), average crystallite size, and size distribution of the GO nanosheets dispersed in deionized water. With the application of the ultra-sonication technique, the optimal average particle diameter size of the GO3 sample was determined to be 215.7 nm with a PDI value of 0.3 as shown in Table 1. Hence, the application of sonication plays a significant role in controlling the size and the dispersity of GO in its solvent (water). The size measurement of Fe$_3$O$_4$ and produced M-GO was conducted using DLS analysis with the application of ultra-sonication technique, and their size was determined to be 37 nm and 304 nm, respectively, each having PDI values of 0.3 and 0.294.
**Figure 3.** FTIR spectra of (a) M-GO, (b) amino functionalized Fe$_3$O$_4$@SiO$_2$ NPs, (c) Fe$_3$O$_4$@SiO$_2$ NPs, and (d) Fe$_3$O$_4$ NPs.

| Table 1. Results of DLS analysis on different GO samples. |
|-----------------------------------------------------------|
| **Sonication Duration (min)** | **Sample** | **Average Particle Diameter (d.nm)** | **PDI value** | **Average Size Distribution** |
|------------------------------|------------|--------------------------------------|---------------|-------------------------------|
|                              |            |                                      |               | Size (d.nm) | Intensity (%) | Volume (%) |
| 0                            | GO1        | 703.3                                | 0.546         | 404.2       | 100           | 100        |
| 15                           | GO2        | 353.6                                | 0.371         | 356.8       | 84.9          | 16.5       |
|                              |            |                                      |               | 4635        | 11.8          | 82.1       |
|                              |            |                                      |               | 77.65       | 3.3           | 1.4        |
| 60                           | GO3        | 215.7                                | 0.301         | 222.9       | 95.4          | 28.6       |
|                              |            |                                      |               | 5072        | 4.6           | 71.4       |
3.1 (c) Zeta potential measurement. Zeta potential measurements of all products were also completed. As shown in Figure 4, the average surface zeta potential of GO and Fe$_3$O$_4$ were determined to be -47 mV and +5.17 mV correspondingly. The coating of the silica layer on the surface of the magnetite was confirmed because the zeta potential value of Fe$_3$O$_4$@SiO$_2$ became -26.8 mV due to the negatively charged silica surface layer [28]. Then, the Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles became positively charged with its zeta potential value of +1.53 mV due to the amino groups’ protonation on the silica surface. It was determined that the molecules of 3-APTES were successfully grafted onto the silica layer of magnetite. After the cross-linking reaction between GO and produced Fe$_3$O$_4$@SiO$_2$-NH$_2$, the surface charge of the produced M-GO was measured as -18.2 mV. As compared to GO (-47 mV), the zeta potential value of M-GO is smaller due to the influence of unreached amino groups and acylamino groups on the silica layer [29]. Thus, it has convincingly evidenced that the synthesis of M-GO was successful.

![Figure 4. Zeta potential measurements.](image)

3.1 (d) Scanning electron microscope (SEM). Scanning electron microscope (SEM) analysis was performed to investigate the morphology and structure of the Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ nanoparticles, and M-GO, as shown in Figure S2, and a factor of 5000 magnified all the images. The SEM image of Fe$_3$O$_4$ shown in Figure S2a indicates that the synthesized spherical Fe$_3$O$_4$ nanoparticles were highly aggregated into clusters due to their magnetism [30]. In Figure S2b, it can be observed that the spherical Fe$_3$O$_4$ nanoparticles were coated by nonporous silica layers, hence forming near-spherical core-shell Fe$_3$O$_4$@SiO$_2$ nanoparticles. The decreased of the degree of aggregation was evidenced by the bunches of Fe$_3$O$_4$ nanoparticles were separated and became more dispersed after wrapped by the nonporous silica layer. The SEM image of M-GO shown in Figure S2c indicates that the magnetic nanoparticles were decorated in uniform bunches and well dispersed on the GO sheets. Therefore, it is suggested that M-GO was successfully formed.

3.1 (e) X-ray diffraction (XRD) analysis. X-ray diffraction analysis was conducted to determine further the phase and structure of GO, Fe$_3$O$_4$ nanoparticles and M-GO, and the summary of the results is shown in Table 2. A characteristic diffraction peak of GO was observed at 2θ value of 10.3º (assigned to (001) plane), corresponding to the 0.75 nm interlayer spacing of GO, which is comparatively larger than the typical interlayer spacing of graphite as the GO layers are loosely
stacked [31]. From the XRD measurement of synthesized magnetic nanoparticles, numerous well-defined significant peaks at 2θ value of 30.3º, 35.6º, 42.8º, 53.4º, 57.3º, 62.7º which can be assigned to the (220), (311), (400), (422), (511) and (440) plane reflections correspondingly were found to be consistent with the XRD patterns of Fe₃O₄ nanoparticles (JCPDS card No. 19-0629) [32]. The fitted lattice constant of unit cell dimension (a) was found to be 8.37 Å, suggesting the good agreement at the cubic spinel crystal structure of Fe₃O₄ nanoparticles [30]. Besides, the diffraction peaks observed from the XRD measurement of M-GO were found to match well with the characteristic peaks of GO and Fe₃O₄ nanoparticles, which indicated the existence of Fe₃O₄ particles in the M-GO composites [33]. Nevertheless, a small amount of maghemite (γ-Fe₂O₃) may exist amongst the Fe₃O₄ nanoparticles due to defection. Similar results were also obtained by other research [34].

Table 2. Summary of results of XRD measurements of GO, Fe₃O₄ and M-GO.

| Sample                    | Diffraction Peak (2θ) | Reflection (Plane) |
|---------------------------|-----------------------|--------------------|
| Graphene oxide            | 10.3°                 | (001)              |
| Magnetite (Fe₃O₄)         | 30.3°                 | (220)              |
|                           | 35.7°                 | (311)              |
|                           | 42.8°                 | (400)              |
|                           | 53.4°                 | (422)              |
|                           | 57.3°                 | (511)              |
|                           | 62.7°                 | (440)              |
| Magnetic graphene oxide   | 30.1°                 | (220)              |
| (M-GO)                    | 35.3°                 | (311)              |
|                           | 43.1°                 | (400)              |
|                           | 52.9°                 | (422)              |
|                           | 57.1°                 | (511)              |
|                           | 62.7°                 | (440)              |

3.1 (f) Simultaneous thermal analyzer (STA). Thermogravimetric Analysis (TGA) is the analytical technique that was used to characterize the reaction progress of GO, Fe₃O₄, and M-GO during thermal reduction. Also, derivative weight loss curves were generated to reveal the most significant weight loss point, and the Differential Scanning Calorimetric (DSC) were analyzes for the samples. Based on the TGA curve of GO shown in Figure 5a, the GO sample became thermally unstable and resulted in losing weight when the heating temperature was increased at a rate of 10 ºC/min. This has proven that GO has low thermal stability due to the weak Van der Waals forces interaction between its structure [35]. Three main stages of the GO weight loss can be observed. The first apparent gradual weight loss occurred below 100 ºC, which is corresponded to the evaporation of absorbed water molecules from the GO surface [36]. The main weight loss was observed between 100 ºC and 350 ºC, which was attributed to the decomposition of the oxygen functional gr
|oups from the GO surface, resulting in the yield of steam, carbon monoxide (CO) and carbon dioxide (CO₂) [37]. It was shown that the pyrolysis of the oxygen-containing functional groups (hydroxyl, epoxy, carboxyl, and carbonyl groups) had caused the increase in a weight loss of GO from 43% to 76% in the temperature range from 150 ºC to 350 ºC. The oxygen to carbon ratio of the GO was significantly decreased as most of the oxygen functional groups were removed. The third gradual weight loss was observed between 350 ºC and 800 ºC, which is ascribed to the pyrolysis of the GO carbon skeleton and oxygen functionalities that were more stable [36]. Figure 6a has shown the DSC curve of GO samples, and a few distinct endothermic and exothermic peaks were observed. The first endothermic peak was observed between 110 ºC
and 130 ºC, which is corresponded to the vaporization of water molecules. A sharp exothermic peak was observed at 150 ºC, which can be attributed to the significant weight loss due to the decomposition of oxygen functionalities such as epoxide and carboxyl groups of GO. The DSC curve also demonstrated the exothermic nature of the pyrolysis of the carbon skeleton in the temperature at 400 - 500 ºC.

Figure 5b has shown the TGA curve of Fe$_3$O$_4$ nanoparticles in a temperature range between 25 ºC and 800 ºC under the nitrogen atmosphere. 10% weight loss of Fe$_3$O$_4$ was observed at 25 – 110 ºC, which has indicated the removal of absorbed water molecules from the Fe$_3$O$_4$ surface. Another weight loss (~3%) occurred at 110 – 310 ºC was observed, and it corresponded to the removal of water molecules bonded with Fe$_3$O$_4$ surface and chemical absorbed water molecules [38]. A minor gradual weight loss (~1%) occurred at 310 - 800 ºC was observed, which can be ascribed to the phase transition of magnetite to maghemite due to the higher stability of FeO when the temperature is 600 ºC and above [39]. No major exothermic peaks can be observed from the DSC curve of Fe$_3$O$_4$ in Figure 6b, and its small weight loss (~15%) has determined that magnetites are highly thermally stable materials.

As shown in Figure 5c, the TGA curve of M-GO demonstrated a weight-loss trend similar to GO. Nevertheless, the amount of weight loss of M-GO at any given temperature is much lesser than that of GO. At 150 ºC, the total weight loss of GO is 44%; however, the total weight loss of M-GO is only 10.4%. Additionally, only 18.17% weight of GO residue existed while 69.15% of the original weight of M-GO was left at 800 ºC, indicating that M-GO has distinctively higher thermal stability as compared to GO due to the coating of Fe$_3$O$_4$ nanoparticles on the GO sheet [40]. As shown in Figure 6c, no abrupt exothermic or endothermic peaks can be observed from the DSC curve of M-GO. Hence, it was determined that M-GO are thermally stable materials [41].

**Figure 5.** Thermogravimetric weight loss (TGA) curves of (a) GO, (b) Fe$_3$O$_4$ and (c) M-GO.
3.1 (g) Vibrating sample magnetometer (VSM) test. The magnetic properties of various magnetic nanoparticles and M-GO were investigated by Lake Shore 7400 Series VSM system. The magnetic hysteresis loops of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$, amino-functionalized Fe$_3$O$_4$@SiO$_2$ and M-GO has shown in Figure 7 confirmed that they possessed excellent superparamagnetism as the magnetic remanence values of all samples were determined to be 0 emu/g, which indicated that there was no residual magnetization after the removal of external magnetic field [30]. The saturation magnetization of amino-functionalized Fe$_3$O$_4$@SiO$_2$ particles was reduced to 46.67 emu/g, while that for the original Fe$_3$O$_4$ nanoparticles was 51.73 emu/g initially. This was ascribed to the coating of nonporous silica layer on Fe$_3$O$_4$ surface, and the decoration of amino groups on the silica layer [40]. The saturation magnetization of M-GO was then decreased to 32.67 emu/g due to the presence of non-magnetic GO in the M-GO composite. In other words, the considerably high saturation magnetization of M-GO particles has confirmed the attachment of Fe$_3$O$_4$ nanoparticles on the GO sheets [42]. Figure S3 has also shown the magnetic separation of M-GO particles, and it was observed that all M-GO particles were rapidly attracted to the applied magnetic field, followed by the quick re-dispersion of M-GO particles with a slight agitation after the removal of the magnetic field. Thus, it was indicated that M-GO particles which possess excellent magnetic properties are suitable for the practical demulsification. Similar results were reported by other researchers as well [41].
3.2 Demulsification test

The bottle test method was applied to investigate on the demulsification performance of GO and M-GO in destroying the interfacial film of O/W emulsion. Two bottles containing the same oil content of O/W emulsion were prepared and stored under ambient conditions for 6 h. The emulsions remained stable in each bottle, and there was no distinct phase separation. Subsequently, 0.1 wt% of the produced GO and M-GO aqueous solution was added into the prepared O/W emulsion in bottle 1 and bottle 2 respectively, with mechanical vibration. An immediate color change of the emulsion was observed in the first ten seconds after the vibration, indicating the breaking of the emulsion stability in both bottles. Small oil floccules from the emulsion were coalesced and formed large oil droplets, resulting in floating onto the top of the water phase to form the oil phase. As shown in Figure S4, very obvious phase separations were accomplished within 5 min after the addition of GO and M-GO into the emulsion correspondingly.

On the other hand, a very light yellow color was exhibited by the newly formed water phase in bottle 1 as shown in Figure S4a. This could be attributed to the suspension of tiny oil floccules and GO in the water phase. In contrast, magnetic separation was conducted on bottle 2, and the M-GO nanoparticles were isolated along with absorbed oil droplets at the bottom of the bottle for further recycling purpose as shown in Figure S4b.

The collected water was then separated into different bottles, with each bottle will then be investigated to determine the demulsification efficiency of GO and M-GO. The residual oil content of the separated water was obtained by correlating its absorbance to the generated calibration curve by using a UV-visible spectrophotometer absorbance test at a wavelength of 570 nm. The oil content of the emulsion in each bottle was determined to reduce from 50 mg/mL to ~4 mg/mL (bottle 1) and from 50 mg/mL to ~2.2 mg/mL (bottle 2) in the treated water phase. GO is an efficient and low-cost chemical demulsifier as it has achieved a 91.97% of demulsification
efficiency with only 0.1 wt% addition. Additionally, M-GO has been proved to be more efficient than GO in performing demulsification as it has achieved a higher demulsification efficiency of 95.59% with the same dosage of addition into the O/W emulsion with same initial oil content.

3.3 The demulsification mechanism

GO is consisted of a flexible planar sheet which has a network of hydrophobic polyaromatic islands of benzene rings on the basal plane and hydrophilic polar oxygen functionalities decorated on the periphery [43]. Therefore, GO is an amphiphatic absorbent/surfactant that can be utilized in an application in emulsion systems such as demulsification processes and emulsion stabilization [12, 44]. In the emulsion system, the crude oil-in-water emulsion stability is dependent on the electrical double layer repulsive force between the protective film and oil droplets (Figures 12a1-b1) [45]. Thus, reducing the repulsive force or extinguishing the viscoelastic film is crucial in demulsifying the stable emulsion at the oil/water interfaces. Amphipathic GO nanosheets with a hydrophobic basal plane and hydrophilic edges can well disperse in the water phase [46]. As GO is added into an oil-in-water emulsion, it can be uniformly dispersed in the water phase caused by strong mechanical agitation (Figures 12b2-b3). Then, the GO in the emulsion can contact to the asphaltenes/resins molecules when it reaches the oil/water interfaces [13]. Due to the strong interaction (attraction) between asphaltenes/resins and GO (Figure S5a2), the cortical protective films of the oil droplets in emulsion are partially destroyed with the aid of collision between water and oil, which ultimately resulted in the formation of a non-continuous protective film at the O/W interface (Figure S5b4). Subsequently, the partially protected oil droplets can ‘escape’ from the partial destroyed protective film by coalescing with other oil droplets (Figure S5b5). The small oil droplets start to coalesce and aggregate to become big oil droplets and eventually an oil phase is formed and floated up to the liquid surface (Figure S5a3 and Figure S5b6). With the mechanisms mentioned above, the dispersed oil droplets are successfully separated from the water phase.

Asphaltenes and resins are structurally similar to GO as they both have massive delocalized π systems, which are attributed to their conjugated aromatic rings. π-π interactions are commonly known as non-covalent interactions, and they can be utilized to interpret either self-assembly or strong adsorptions of molecules with delocalized π systems [47]. Generally, there is a π-donor and a π-acceptor among the molecules in stacking interactions. Resins and asphaltenes possess more negative electron affinity than GO, which explains that resins and asphaltenes can easily acquire electrons from GO. Thus, it is very likely that GO acts as a π-donor, whereas resins and asphaltenes are the π-acceptors. When polarized π orbitals of GO interact with the π-conjugated system of resins/asphaltenes, strong π-π interactions will be formed between them. Furthermore, the adsorption strength is also further enhanced due to the σ-π interaction between the lowest unoccupied molecular orbital (antibonding) of resins/asphaltenes and the electron-rich functional groups in GO. The analysis of non-covalent interaction has determined that the strong affinity between asphaltenes/resins and M-GO are caused by the strong π-π interactions and σ-π interactions (between the hexagonal rings of GO and the asphaltenes/resins aliphatic side chain).

With the aid of magnetic NPs attached to the amino-functionalized GO, the sedimentation of the small oil flocules in the water phase can be improved through using a magnet. As the M-GO has strongly interacted with the oil droplets, most of them can be brought into the oil phase after the demulsification process. Hence, it is evident that both the demulsification efficiency and kinetics can be enhanced with the aid of the external magnetic field. As illustrated in Figure S4, a magnet was used to enhance the sedimentation of oil flocules and M-GO and form a colorless water phase within 5 min. With the aid of an external magnetic field, it was proved that the fine oil flocules were also separated efficiently from the water phase along with M-GO. GO only achieved 91.97% while M-GO has achieved 95.59% of demulsification efficiency with 0.1 wt% dosage added into the O/W emulsions with the same initial oil content. Therefore, M-GO is
The interfacial activity of GO is highly sensitive to the pH value of the solvent, and it was reported that the pH-dependent behaviour of GO is mainly attributed to the deprotonation degree of its carboxyl groups at the edges [48]. Thus, the effect of pH value of emulsion on the demulsification performance of M-GO was investigated. Two central regions can be observed from the results shown in Figure S6a. In the first region (pH 2–4), the lowest separated water oil concentration was reduced from 50 mg/mL to ~0.7 mg/mL (98.6% demulsification efficiency) in acidic condition with pH value at 4 while the oil concentration was decreased to ~1.85 mg/mL (96.3% demulsification efficiency) at a pH value of 2 with 0.25 wt% of M-GO addition. It was observed that M-GO sheets are less hydrophilic at lower pH as they tended to rise to the oil phase along with the absorbed oil droplets after demulsification. Some M-GO sheets that were initially isolated at the bottom of the bottle (with an application of magnetic separation) started to rise to the oil-water interface or float in the separated water phase when the pH value was lowered below 4, which results in higher remaining oil concentration [13]. In the second region (pH 4–10), it was shown that the surface activity level of M-GO increases at acidic conditions [21]. 0.25 wt% M-GO was only able to reduce the oil concentration from 50 mg/mL to 4.29 mg/mL at pH ~10, with a demulsification efficiency of 91.42% while the demulsification efficiency increased obviously when the pH value was lowered down gradually. In other words, M-GO performed better in demulsification in acidic conditions than alkaline conditions. Therefore, the pH value at 4 was suggested to be the optimal condition for demulsification performed by M-GO.

3.4 (b) Effect of salinity of emulsion. The salinity of emulsion was reported to have considerable impacts on the demulsification performance [19]. The improvement in the effectiveness of the demulsification performance of M-GO was then investigated based on the increasing salinity of the produced O/W emulsion at neutral pH. The results shown in Figure S6b has depicted that the demulsification efficiency was increased as the salinity of O/W emulsion increased. The demulsification efficiency of 0.1 wt% M-GO was increased from 95.59% to 98.12% when the salinity of O/W emulsion was increased to 0.5 M NaCl. It was mainly due to the “salting-out” effect which reduced the stabilizing surfactants’ hydrophilicity hence resulting in lower O/W emulsion interfacial tension [49].

3.4 (C) Effect of dosage of M-GO addition on the demulsification performance. The demulsification efficiency can be impacted significantly by the dosage of added M-GO. The results showed that ~88% of oil removal was achieved with 0.01 wt% M-GO addition as the oil concentration was reduced from 50 mg/mL to 6.1 mg/mL. Furthermore, 98.53% of demulsification efficiency (0.74 mg/mL in oil concentration) was achieved with a 0.25 wt% M-GO addition. As shown in Figure S6c, it can be observed that M-GO possesses better demulsification ability as compared to GO. A higher and optimal dosage of M-GO exhibits higher demulsification efficiency as more possible surface areas are exposed to the emulsion. Also, it was concluded that an external magnetic field could effectively eliminate the residual oil by combining extremely small oil floccules in the emulsion with M-GO distributed in the separated water hence resulting in better demulsification.

3.5 Recyclability of magnetic graphene oxide

Since M-GO was determined to possess superparamagnetic properties, it was expected to be recyclable and reusable after performing demulsification with the application of magnetic separation. During the separation process between the oil and water phase, it was observed that the M-GO absorbed the asphaltene, and was isolated to the bottom of the bottle due to the applied magnetic field. Toluene was used to remove the adsorbed oil for the reactivation of M-GO as the adsorbed oil (asphaltenes/resins) may remain on the M-GO surface after demulsification. As
shown in Figure S6d, the recycling tests were successfully repeated for 10 times. In the first 5 cycles, M-GO was able to reduce the oil concentration in the water phase from 50 mg/mL (high concentration O/W emulsion) to <1 mg/mL, achieving ~98% of demulsification efficiency. The demulsification efficiency of M-GO started to decrease from the sixth cycle onwards. In the last cycle, the oil concentration was only reduced to 9.4 mg/mL, and the demulsification efficiency was dropped to 81.19%. It was suggested that the toluene was not able to remove the adsorbed oil molecules that were firmly attached to the M-GO surfaces after multiple cycles of demulsification. As a result, magnetic demulsifier M-GO was proved to be recyclable and reusable for demulsification due to its outstanding magnetic properties, leading to the advantages of low chemical cost and reduction in adverse environmental impacts in industrial petroleum applications as compared to the other conventional non-recyclable chemical demulsifier.

4. Conclusions and recommendations

GO, and M-GO were successfully synthesized by conducting modified Hummers method, surface functionalizations of GO and magnetite, and the cross-linking reactions of GO with magnetic nanoparticles correspondingly. Subsequently, the properties of obtained GO, various magnetic nanoparticles, and M-GO were investigated by several characterizations. In summary, it was determined that the produced M-GO composites which contain important oxygen functionalities such as carboxyl groups were successfully coated with silica-coated magnetite (Fe₃O₄@SiO₂) nanoparticles and they possess excellent superparamagnetic properties. A comprehensive understanding of the mechanisms of formation of GO and M-GO and the demulsification of crude oil-in-water emulsion were also presented. The demulsification tests demonstrated that 0.25 wt% of M-GO aqueous suspension could achieve a 98.53% of demulsification efficiency within 5 min on the high concentration (5 wt%) as-prepared crude oil-in-water emulsion. The demulsification performance of M-GO was found to be superior, in comparison to GO as the suspending tiny oil floccules that were attached to M-GO can be separated from the water phase more effectively using magnetic separation. The optimizations of the demulsification process were also conducted to investigate the effect of dosage, pH and salinity and significant findings were presented. Also, the recycling tests have proven that the M-GO can be reused to perform demulsification effectively for 10 times. In addition to being able to reduce the demulsification costs in the industry, the excellent properties of M-GO can also minimize the risk of polluting the environment due to leakage of demulsifier through the application of magnetic separation for recycling purposes.

A water bath is suggested for the synthesis of GO instead of an ice bath, as a more constant reaction temperature could be achieved. Also, the non-covalent interaction (NCI) analysis is recommended to further investigate the inherent interaction between M-GO and asphaltene molecules during the demulsification process in future work.

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This article was not published and is not under consideration for publication anywhere else. We also do not have any conflicts of interest to disclose.

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