

Synthesis of an Eco-friendly and Reusable Magnetic Ferrofluid using Orange Peel Extract for Oil Spill Cleanup

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Abstract:

Oil spills pose a huge threat to the marine ecosystem. The Exxon Valdez oil spill and the Deepwater Horizon oil spill have caused extensive damage to marine habitats, fishing and tourism industries, and even humans. Current oil spill cleanup methods include booms and skimmers, in-situ burning and chemical dispersants, which are inefficient and expensive. Recently, oil-based ferrofluids have gained traction to be applied in oil spill cleanup, but it is uneconomical to purify and obtain oleic acid (OA), one of the most frequently used surfactants in the synthesis of ferrofluids. A novel, eco-friendly oil-based magnetite ferrofluid was synthesised via co-precipitation, and its surfactant was derived from orange peels (OP), a common fruit waste with high potential to be used as capping agents due to their high fatty acid content. The hydrophobicity of magnetite particles with OA and OP surfactants were examined through water contact angle measurements. This paper demonstrates the simple application of OA- and OP-ferrofluids in the removal of spilled motor oil from water. The oil removal capacities of the ferrofluids were investigated. At 1 vol%, OP-ferrofluid's oil removal capacity of 59.7 g/g is comparable to that of OA-ferrofluid, and even outperforms other magnetic sorbents fabricated by other researchers and the commercial polypropylene. The oil removal capacity of OP-ferrofluid was maintained above 50 g/g throughout 5 progressive cycles of oil removal, unlike OA-ferrofluid. The facile synthesis, high oil removal capacity and magnetic property of OP-ferrofluid show that it has great potential to be used as an eco-friendly and reusable material for rapid and efficient oil-water separation.

1. Introduction

1.1. Literature Review

Marine oil spills pose a serious threat to the ecosystem of the sea. They are mainly caused by occasional accidental episodes of supertankers, oil rig drilling and natural events (Bayat et al., 2005). A notable example of oil spills is the Deepwater Horizon oil spill which occurred in 2010, spilling over 200 million tonnes of crude oil into the ocean (Kurtz, 2013) and causing massive damage to the marine ecosystem. Cleaning up oil spills is of paramount importance because oil can coat different parts of mangrove plants and block sunlight from reaching submerged aquatic plants, eventually leading to plant death (Andersen et al., 2008). Moreover, oil spills have adverse effects on animals, killing them by physical smothering or ambient toxicity of polycyclic aromatic hydrocarbons (PAH) present in crude oil (Forde, 2002). In the long run,

bioaccumulation and biomagnification of PAHs up the marine food chain can poison humans who consume seafood (Laegdsgaard & Johnson, 2001).

Current methods of cleaning up oil spills include booms and skimmers, in-situ burning, chemical dispersants, bioremediation, and the use of synthetic sorbents (Karakasi & Moutsatsou, 2010). However, booms and skimmers are ineffective and expensive (Abdullah et al., 2019), in-situ burning releases large amount of toxic gases (Allen & Ferek, 1993), chemical dispersants are not only expensive but environmentally unfriendly (Page et al., 2002) and bioremediation is very slow (Atlas, 1995). Synthetic sorbents such as polypropylene are used commercially as they are hydrophobic and have high oil sorption capacities (Bayat et al., 2005), but their low biodegradability is a major environmental concern (Tokiwa et al., 2009). Furthermore, synthetic sorbents are derived from fossil fuels, a non-renewable resource, hence, it is imperative to develop a novel, eco-friendly and cost-effective solution for oil spills.

Recently, magnetic materials such as core-shell Fe_2O_3 nanoparticles (Zhu et al., 2010) and monodisperse Fe_3O_4 nanoparticles (Atta et al., 2017) have been found to provide a fast separation of oil from water by applying an external magnetic field. However, there is a tendency for iron oxide nanoparticles to agglomerate due to their high surface area to volume ratio (Imran et al., 2018).

An oil-based ferrofluid is a smart colloidal suspension of magnetite nanoparticles in an oil medium which possesses unique magnetic and fluid properties (Sangeetha et al., 2013). Being superhydrophobic and superoleophilic, they are able to attract contaminant oil via strong dispersion forces while completely repelling water molecules (Rashin et al., 2014). After use, oil-based ferrofluids can be easily retrieved from the ocean via the application of a magnetic field. In addition, oil-based ferrofluids can maintain good dispersion stability even under the influence of external fields (Zhu et al., 2012). Hence, the magnetite nanoparticles in a colloidal suspension do not aggregate, dissociate or chemically react with the surroundings (Atta et al., 2015). Ferrofluids thus show great potential to be reused for multiple cycles.

The most common surfactant used to synthesise oil-based ferrofluids is oleic acid (OA) (Zhang et al., 2006). OA has a hydrophilic end which is able to attach to the surface of magnetite nanoparticles (Tsai et al., 2010) and a long hydrophobic chain containing a cis-double bond, providing the greatest steric hindrance to maximise the distance between magnetite nanoparticles (Harris et al., 2015), preventing agglomeration. However, since pure oleic acid is usually obtained via fractional distillation, its synthesis process is energy intensive (Elkacmi et al., 2016) and uneconomical.

On the other hand, orange peels are an environmentally friendly natural waste material commonly discarded after orange juice has been extracted (Olea-Mejia et al., 2017). The

world's orange production is estimated to be about 60 million tonnes per year (Munagapati & Kim, 2016), demonstrating its high accessibility and availability. Orange peel extract has great potential to be a source of cheap, eco-friendly and effective alternative surfactant for magnetite nanoparticles as it contains fatty acids with similar molecular structures as oleic acid, such as palmitic acid, stearic acid and linoleic acid (Islam et al., 2012). To date, there have been no studies regarding the synthesis of oil-based ferrofluids using natural extracts for oil spill cleanup.

1.2. Objectives and Hypotheses

The objectives of this study are to synthesise a ferrofluid using orange peel extract as a surfactant via a co-precipitation method and compare its oil removal capacity and reusability across 5 progressive cycles of oil removal and regeneration with conventional ferrofluid synthesised using oleic acid.

It is hypothesised that ferrofluid can be synthesised using orange peel extract via a co-precipitation method. The oil removal capacity and reusability of this ferrofluid across 5 progressive cycles of oil removal and regeneration will be comparable to conventional ferrofluid synthesised with oleic acid.

2. Materials and Methods

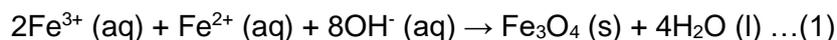
2.1. Materials

Iron(III) chloride hexahydrate and iron(II) sulfate heptahydrate were purchased from GCE Chemicals. Oleic acid was procured from Sigma Aldrich. Corn oil and motor oil were purchased from the supermarket and the petrol kiosk respectively. Orange peels were collected from fruit stalls.

2.2. Synthesis of Ferrofluid using Orange Peel Extract and Oleic Acid

Orange peels were washed with deionised water, dried, and crushed. 20g of orange peels were then soaked in 100ml of hexane for 2 days. The mixture was filtered before orange peel extract was obtained using a rotary evaporator to remove the hexane solvent. 1g of orange peel extract was then dissolved in 25ml of isopropanol. Subsequently, 2.70g of iron(III) chloride hexahydrate and 1.39g of iron(II) sulfate heptahydrate were dissolved in 50ml of deionized water and mixed with orange peel extract in isopropanol. 25% (w/w) aqueous ammonia was added dropwise into the solution with stirring to induce the co-precipitation of magnetite coated with orange peel extract (OP-magnetite). A magnet was used to separate the OP-magnetite which was washed until neutral pH and dried at 60°C until constant mass. The chemical reaction for the co-precipitation of magnetite is shown in equation (1). Varying masses of OP-magnetite (0.259g, 0.517g, 0.776g) were then added to 5ml of corn oil to obtain

1 vol%, 2 vol% and 3 vol% ferrofluids respectively, where vol% represents (v/v). The ferrofluid synthesised using orange peel extract (OP-ferrofluid) was then sonicated for 1h.



The conventional synthesis of ferrofluid using oleic acid was adapted from Rashin et al., (2014). 40ml of deionised water was added to pure magnetite before 1.5ml of 25% (w/w) aqueous ammonia was added to adjust the pH to 9. 7ml of oleic acid was added and the mixture was stirred at 80°C for 1 h. The chemical reaction for the formation of the oleate ion is shown in equation (2). Since oleic acid is insoluble in water, it is converted into the soluble oleate ion so that it can be attached to the surface of the magnetite via electrostatic attraction (Tsai et al., 2010). The excess water and oleic acid were washed off using absolute ethanol before the magnetite coated with oleic acid (OA-magnetite) was dried in the oven until constant mass. Varying masses of OA-magnetite (0.259g, 0.517g, 0.776g) were then added to 5ml of corn oil to obtain 1 vol%, 2 vol% and 3 vol% ferrofluids respectively. The ferrofluids synthesised using oleic acid (OA-ferrofluid) was then sonicated for 1h.

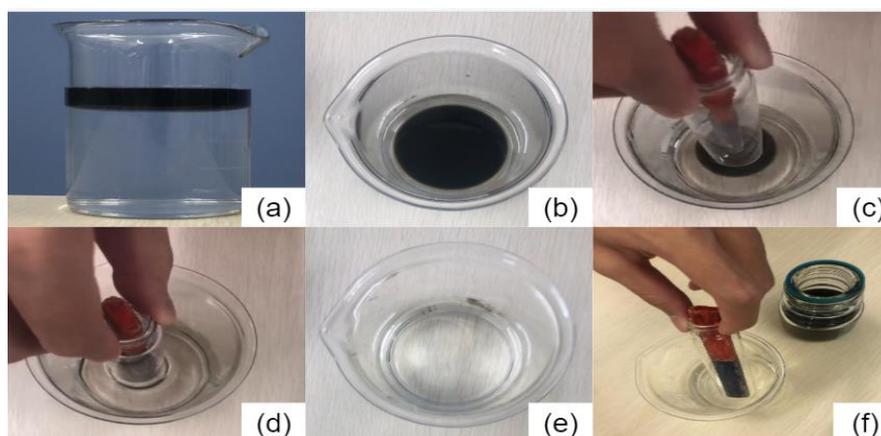


Water contact angle measurements were conducted on both magnetites using UBS digital microscope while ferrofluids were characterised by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and zeta potential measurements using a Malvern Zetasizer.

2.3. Oil Removal Tests for OP- and OA-Ferrofluids

Artificial seawater was prepared by dissolving 56 g of sodium chloride, 17 g of magnesium chloride, 8.19g of magnesium sulfate, 2.5 g of calcium sulfate and 2 g of potassium chloride in 2 litres of deionised water. 0.500g of motor oil and 0.050g of 1 vol% OP-ferrofluid were added to 50ml of artificial seawater. The mixture was shaken on an orbital shaker for 5 min before a magnet encased in a glass vial was used to retrieve the mixture of ferrofluid and motor oil (Figure 1). The same procedure without the addition of a ferrofluid was used as the control experiment.

Figure 1: Optical images showing the process of oil removal: (a) and (b) Side and top views of motor oil with ferrofluid added, (c) Magnet dipped into mixture, (d) Magnetised oil attracted by magnet, (e) and (f) Cleaned seawater and retrieved oil



Next, the seawater and the remaining motor oil was transferred to a separating funnel, before 50ml of hexane was added to extract the motor oil. The seawater was drained off and a rotary evaporator was used to remove the hexane solvent. The mass of motor oil remaining was monitored until the mass remained constant. The above procedure was repeated for 2 vol% and 3 vol% OP-ferrofluids, as well as OA-ferrofluids. The oil removal capacity of the ferrofluids was calculated using the following formula:

$$Q_o = \frac{m_i - m_f}{m_m}$$

where Q_o is the oil removal capacity/g/g, m_i is the initial mass of motor oil/g, m_f is the final mass of motor oil/g and m_m is the mass of magnetite used/g.

2.4. Reusability of OP- and OA-Ferrofluids

After each oil removal test, the glass vial with the magnet was soaked in 200ml of hexane to dissolve the oil. The solution was decanted using a magnet to retrieve the OP- or OA-magnetite, which was dried and added to corn oil to obtain a new OP- or OA-ferrofluid. The regenerated ferrofluids were tested on their ability to remove motor oil for a total of 5 cycles.

3. Results and Discussions

3.1. Characterisation of OP- and OA-Ferrofluids

3.1.1. By Transmission Electron Microscopy (TEM)

ImageJ (an open source image processing software) was used to determine the particle size of magnetite in the ferrofluids. Figure 2 shows that OA-magnetite particles are monodispersed and spherical in shape with an average size of 12.8 nm. Figure 3 shows that OP-magnetite particles are less dispersed and are cubic in shape with an average size of 17.4 nm.

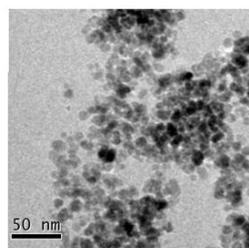


Figure 2: TEM image of OA-ferrofluid

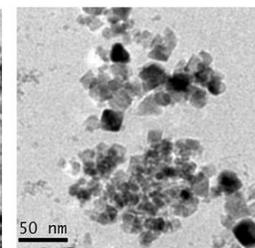


Figure 3: TEM image of OP-ferrofluid

3.1.2. By X-Ray Diffraction (XRD)

The X-Ray Diffraction (XRD) pattern of the OP magnetite nanoparticles (Figure 4) exhibits 2 theta peaks at 13.08°, 30.28°, 35.79°, 43.47°, 53.52°, 57.50° and 62.97° corresponding to crystal planes of (111), (220), (311), (400), (422), (511) and (440) respectively, which is similar to that reported by Loh et al., (2008), confirming that magnetite had been successfully synthesised. OA magnetite displays similar peaks.

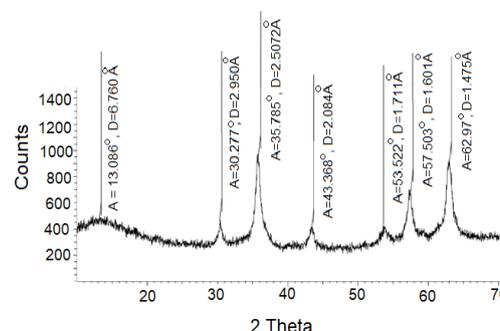


Figure 4: XRD pattern of OP magnetite

3.1.3. Water Contact Angle

The water contact angles of OA- and OP-magnetite were measured using a Dino-Lite digital microscope. When the contact angle is more than 90°, the material is hydrophobic (Förch, Schönherr & Jenkins, 2009). Figures 5, 6 and 7 reveal that the water contact angles of both OA- and OP-magnetite are about 136° (Figure 7), exceeding 90°. This suggests that both the OA- and OP- magnetite are hydrophobic.

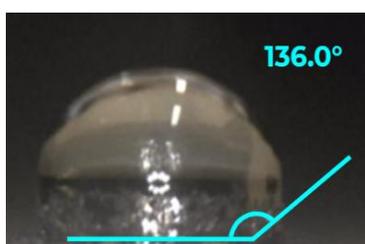


Figure 5: Water contact angle of OA-magnetite

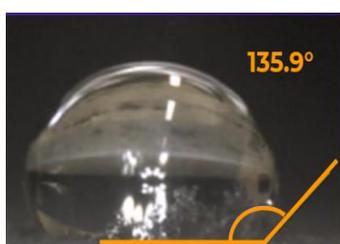


Figure 6: Water contact angle of OP-magnetite

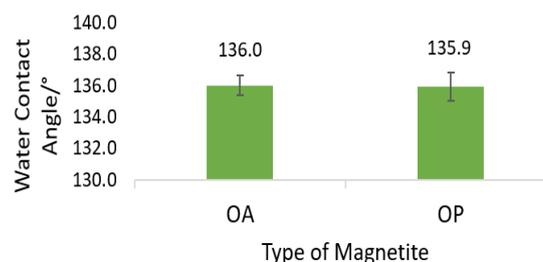


Figure 7: Water contact angles of OA- and OP-magnetite. N=6

3.1.4. Zeta Potential

The zeta potential (ZP) of a colloidal suspension can be used to measure its stability as it indicates the level of repulsion between particles similarly charged in dispersion, and it was measured using Laser Doppler Electrophoresis. For values of ZP between 0 mV and ± 5 mV, the dispersed phase strongly tends to precipitate; values from ± 10 mV to ± 30 mV indicate an incipient instability; from ± 30 mV to ± 40 mV a moderate stability; from ± 40 mV to ± 60 mV a good stability, and ZP values higher than ± 60 mV indicate an excellent stability (Souza et al., 2012). Table 1 shows that both OA- and OP-ferrofluids demonstrate excellent stability, suggesting that the presence of surfactants have successfully prevented agglomeration of the magnetite particles in ferrofluid.

Table 1: Zeta potentials of OA- and OP-ferrofluids

	Zeta Potential/mV
OA-Ferrofluid	-90
OP-Ferrofluid	-61

3.1.5 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectrum of OA-magnetite (Figure 8) reveals two bands at 2929 cm^{-1} and 2852 cm^{-1} corresponding to the asymmetric and symmetric $-\text{CH}_2$ stretch respectively. The band at 1430 cm^{-1} corresponds to the $-\text{CH}$ bend. The band at 1712 cm^{-1} can be attributed to asymmetric stretch of $-\text{C}=\text{O}$ group while the bands at 1575 cm^{-1} and 1521 cm^{-1} correspond to asymmetric and symmetric $-\text{COO}^-$ stretch respectively. The presence of these two bands is due to the complexation between the iron(II)/iron(III) ions and carboxylate ions of oleic acid. This confirms the successful attachment of oleic acid to the magnetite surface.

Similarly, Figure 9 reveals bands at 2925 cm⁻¹ and 2851 cm⁻¹ corresponding to the asymmetric and symmetric -CH₂ stretches, 1735 cm⁻¹ corresponding to the asymmetric -C=O stretch and 1429 cm⁻¹ corresponding to the -CH bend. In addition, the band at 1517 cm⁻¹ and 1625 cm⁻¹ can be attributed to the aromatic C-C stretch and the bands at 1268 cm⁻¹, 1107 cm⁻¹ and 1077 cm⁻¹ correspond to the -C-O stretch. This suggests that in OP-magnetite, there is a greater variety of different molecules being coated onto the magnetite. Possible molecules present in the surfactant of OP-magnetite include linalool (Farhat et al., 2011) and 4-acetoxy-3-methoxystyrene (Erukainure et al., 2016), which are found in orange peel extract.

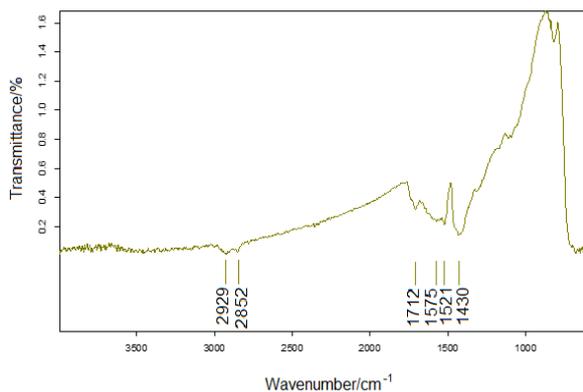


Figure 8: FTIR spectrum of OA-magnetite

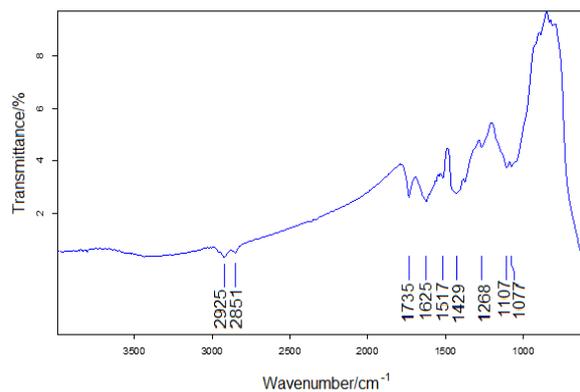


Figure 9: FTIR spectrum of OP-magnetite

3.2. Oil Removal Tests for OP- and OA-Ferrofluids

When the ferrofluid is added to the motor oil, the non-polar, hydrophobic chains of the contaminant oil molecules are attracted to the long hydrocarbon tails of the fatty acids, which serve as surfactants, and the carrier oil (corn oil) molecules via London dispersion forces which arise from the instantaneous dipoles that occur from momentary shifts in charge, caused by the constant movement of electrons (Figure 10). In contrast, the interactions between oil and water molecules are weak because oil molecules are not able to form hydrogen bonds with water molecules. The stronger association among the polar water molecules leads to a greater tendency for the ferrofluid and the motor oil to group together. As the magnetic ferrofluid attaches to the oil molecules, it causes the oil molecules to be magnetic. With the simple use of a magnet, the magnetic ferrofluid along with the contaminant oil can be easily separated from water.

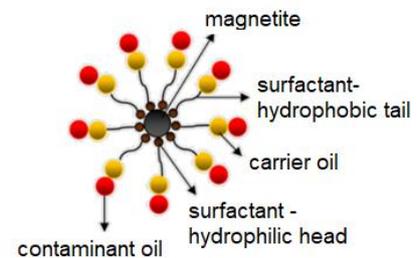


Figure 10: Proposed mechanism of oil removal (Rashin et al., 2014)

Figure 11 shows that the oil removal capacity of the OP-ferrofluids are slightly lower than that of the OA-ferrofluids. The Mann-Whitney U-Test on both 1vol% ferrofluids gives a p-value of

0.211 (>0.05), suggesting that there is no significant difference in the results. Thus, 1 vol% OP-ferrofluid is comparable to 1 vol% OA-ferrofluid in terms of oil removal. This could possibly be due to the fact that the molecules containing heteratom functional groups present in orange peel extract were extracted from non-polar hexane and hence tend to be relatively large molecules with large electron clouds that can be easily polarized to generate strong dispersion forces between the surfactant and the motor oil. Furthermore, the polar components of these surfactants may form permanent dipole-permanent dipole interactions with various substances in motor oil, such as phenols and aldehydes in additives (Lu & Kaplan, 2008).

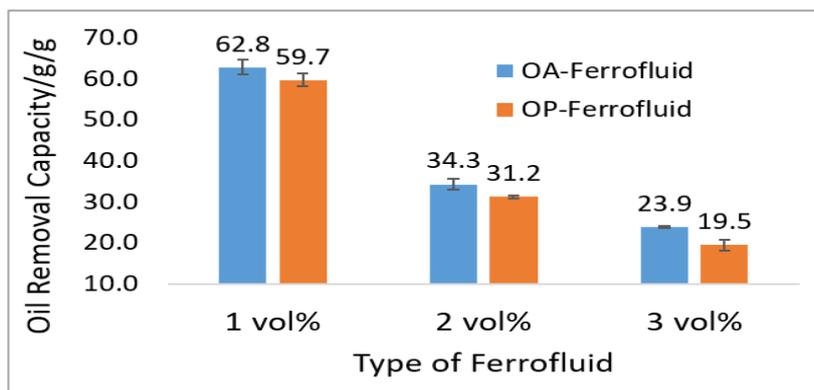


Figure 11: Oil removal capacities of OA- and OP-ferrofluids. N=5

It can also be observed that 1 vol% ferrofluids outperform 2 vol% and 3 vol% ferrofluids in terms of oil removal capacity. This could be due to the higher chance of agglomeration when there is a larger number of magnetite particles per unit volume of the ferrofluid when the concentration of magnetite increases, leading to decreased surface area to volume ratio for the attraction of contaminant oil molecules. Therefore, 1 vol% OA- and OP-ferrofluids were selected for future tests.

Table 2 shows that both ferrofluids have higher oil removal capacities than magnetic absorbents reported in literature and commercial polypropylene, suggesting that OP-ferrofluid has great potential to be used as an eco-friendly and effective method to clean up oil spills.

Table 2: Comparison of motor oil removal capacities of different absorbents

Type of Adsorbent	Motor Oil Removal Capacity/g/g	Reference
1 vol% OA-ferrofluid	63	This study
1 vol% OP-ferrofluid	60	This study
Magnetic hexagonal boron nitride	53	Leyva et al., 2018
Magnetic exfoliated graphite	45-52	Pavlova et al., 2018
Magnetic polystyrene/magnetite/graphite aerogel	40	Zhou et al., 2015
Magnetic polyurethane sponge	32-40	Jiang et al., 2020
Commercial polypropylene	10-20	Senanurakwarkul et al., 2013

3.3. Reusability of OP- and OA-Ferrofluids

After 5 cycles of oil removal, it is observed that OP-ferrofluid experiences a less substantial drop in effectiveness than OA-ferrofluid (Figure 12). At Cycle 4, the oil removal capacity of OP-ferrofluid exceeded that of OA-ferrofluid. While the oil removal of OA-ferrofluid plummeted to 37.9 g/g (24% decrease) in Cycle 5, oil removal capacity of OP-ferrofluid remains above 50 g/g (4% decrease). FTIR spectroscopy was conducted to find out why.

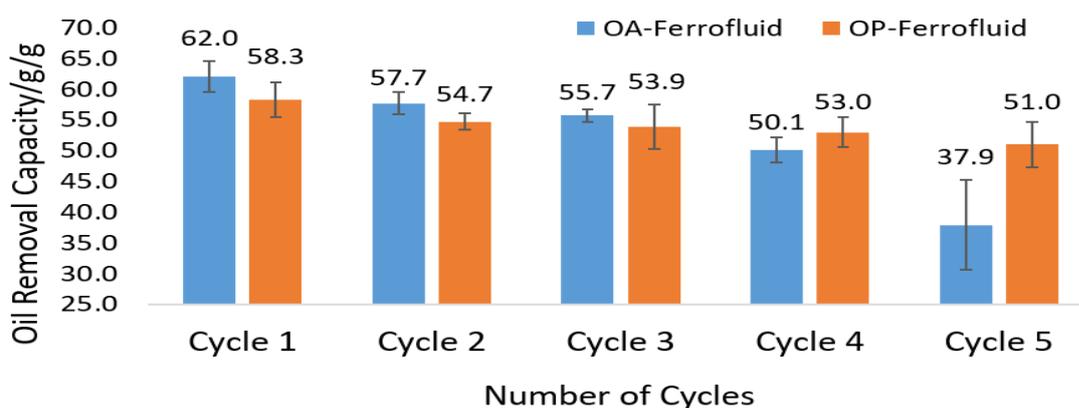


Figure 12: Regeneration of OA- and OP-ferrofluids for progressive cycles of oil removal. N=5.

The FTIR spectrum of OA-magnetite at the end of Cycle 4 (Figure 13) shows an absence of a distinctive peak at about 2900 cm^{-1} , which corresponds to the C-H stretch. This could suggest that after cycles of oil removal, the oleic acid surfactant had been washed off. Since the dispersion forces between long hydrocarbon chains of oleic acid and motor oil are relatively strong, when OA-ferrofluid is desorbed using hexane, there is a high tendency for the oleic acid molecules to be detached from magnetite along with the motor oil molecules which dissolve in hexane. A lower amount of surfactant increases the chances of agglomeration of magnetite particles, so they cannot be evenly dispersed in the carrier oil, leading to a decrease in surface area to volume ratio to attract motor oil. This explains the absence of a C-H peak and the lowered oil removal capacity. On

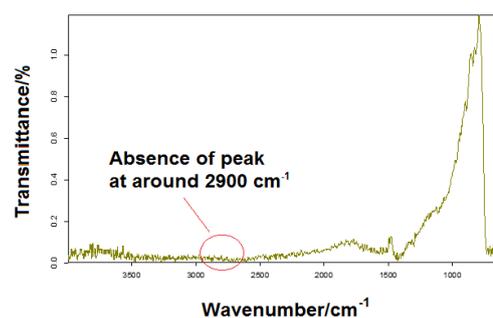


Figure 13: FTIR spectrum of OA-ferrofluid at the end of Cycle 4

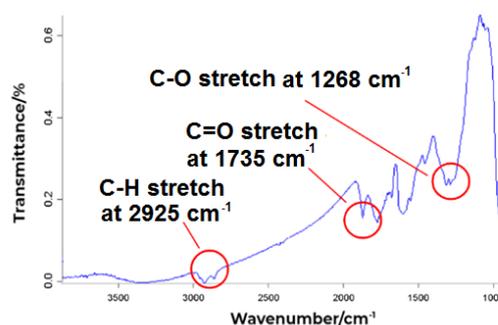


Figure 14: FTIR spectrum of OP-ferrofluid at the end of Cycle 4

the other hand, the FTIR spectrum of OP-magnetite (Figure 14) reveals a distinctive peak at 2925 cm^{-1} corresponding to the C-H stretch, hence suggesting that the -C-H group is still present within the surfactant, along with other heteroatom functional groups such as the -C=O

group (1735 cm^{-1}) and the -C-O group (1268 cm^{-1}). This is because for OP-ferrofluid, the interactions between the motor oil molecules and the surfactant molecules, some of which have slight polar properties, are relatively weaker. Hence, it is easier to desorb OP-ferrofluid using a non-polar solvent like hexane. Since the surfactant is not fully washed off, magnetite particles are prevented from agglomerating.

4. Conclusions and Future Work

OP-ferrofluid was successfully synthesised using orange peel extracts via a co-precipitation method. 1 vol% OP-ferrofluid was most effective in removing motor oil from water, with the oil removal capacity being comparable to that of 1 vol% OA-ferrofluid and higher than many magnetic absorbents reported by other researches, as well as commercial polypropylene. The magnetic property of OP-ferrofluid allows for a rapid and simple method of recovery by the use of a magnet, enabling it to be recycled effectively. OP-ferrofluid can be reused for at least 5 progressive cycles of oil removal without a significant drop in effectiveness, potentially saving cost and making the use of it in cleaning oil spills even more eco-friendly.

A model on how the OP-ferrofluid could be used to clean up oil spill was proposed (Figure 15). This model can be designed to be fully automated using robotics technology. An electromagnet is used to attract and separate the ferrofluid-contaminant oil mixture from seawater. It is then transported to a collection well using a conveyor belt where the contaminant oil can be retrieved and reused. As the

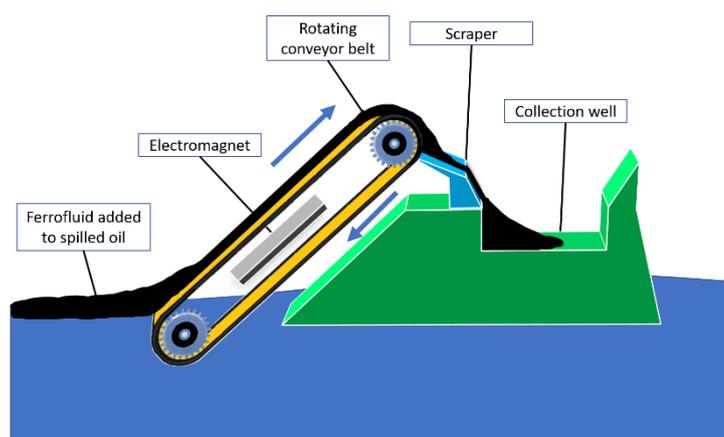


Figure 15: Proposed model for the application of OP-ferrofluid in oil spill cleanup

boat with the proposed mechanism moves through the ocean, large areas of oil spills can be cleaned at an extremely fast rate. Such a system facilitates the rapid and efficient use of OP-ferrofluid when cleaning up real-life oil spills.

In the future, the use of other plant extracts to synthesise ferrofluid could be investigated. It would also be interesting to determine the identity of the biomolecules from orange peel extract which have coated onto the magnetite using High Performance Liquid Chromatography. The oil removal capacity of OP-ferrofluid on other types of organic pollutants such as diesel oil, polycyclic aromatic hydrocarbons and microplastics could also be explored. Finally, the proposed model could be tested to assess its feasibility in the real-life context.

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