Synthesis and characterizations of magnetic bio-material sporopollenin for the removal of oil from aqueous environment

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ABSTRACT

There is an increasing global need for a simple and effective method to remove oil from water. This study details the synthesis of magnetic bio-polymer sporopollenin (MSp) and explores its use as an adsorbent for oil removal from water. The MSp was characterized using FT-IR, SEM, EDX, BET, TGA and water contact angle (WCA) measurements. The oil adsorption experiments were carried out in batch mode. The influence of adsorbent dosage, contact time and pH on oil adsorption efficiency was studied and then optimized for analysis. The optimized MSp was found to be an effective oil adsorbent, with a sorption capacity of 3.24 mg/mg. The effectiveness of MSp as an oil adsorbent is attributed to its hydrophobic surface that can be selectively adsorb oil while repelling water. The MSp is also reusable and able to maintain its sorption capacity even after five usage-regeneration cycles.

1. Introduction

The marine environment is increasingly exposed to the dangers of oil from spills from damaged ships or oil tankers, drilling rigs, and offshore oil platforms (Wang et al., 2012). Oil pollution can also occur in fresh water bodies due to damaged oil piping, or oily waste discharge from domestic and industries sources. The oil is highly toxic and causes injury and loss of life to humans and animals. For example, even small amounts of oil coated on the plumage of birds can affect their flight behaviour and compromise heat insulation. Birds attempting to remove the oil by preening themselves would inadvertently ingest the toxic oil, resulting in poisoning. (Panatasirisuk et al., 2017). Oil discharge in fresh water streams also renders the water unsuitable for drinking and use.

Being aware of the extent of damage of oil can cause to the environment, responsible parties have put tremendous effort in finding effective methods to remove oil from affected water bodies. Because even a little oil can spread over a very large volume of water, the treatment method must be low cost for it to be practicable. Several technologies already exist to separate oil from water, among them, various flotation methods (electrofloation, flotation with gas and dissolved air flotation), reverse osmosis, gravity separation, activated sludge treatment, filtration (micro and ultra), and membrane bioreactor (Santander et al., 2011). Among these methods, simple adsorption is the most attractive because of its high removal efficiency, cost-effectiveness, easy operation, and high regenerative ability of the adsorbents (Pintor et al., 2016).

To maximize the adsorption process, the adsorbent must have a large surface area on which the adsorbate can adhere to. At the same time, the mass of the adsorbent must be small to lower logistic cost. This high surface area to mass ratio is achieved in nanoparticles, where each grain is extremely divided so as to expose as much surface area as possible. However, the nanoparticles itself must be recollected after the treatment process, lest it becomes a secondary pollutant and this is an extremely difficult process. Magnetic nanoparticles (MNPs) are nanoparticles that are paramagnetic, and therefore can be easily collected just by using a simple magnet (Ghasemi and Sillanpää, 2015; Mohammadzadeh Kakhi, 2015). However, since MNPs are poor adsorbents for oil due to their hydrophilic nature, they must be modified with a hydrophobic component in order to make them useful for oil adsorption. Parallel works that have MNPs composited with organic polymers such as poly styrene (Chen et al., 2013) and epoxidized natural rubber (Venkatanarasimhan and Raghavachari, 2013) serve as a guideline to this study.

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Biopolymers are interesting modifier candidates for the removal of oil from water (Wu et al., 2008). Sporopollenin is an abundant biopolymer that is found in the outer membrane of moss, fern spores, and pollen grains (Ünlü and Ersoz, 2007). It is highly resistant to chemical, physical and microbiological degradation (Brooks and Shaw, 1978). The biopolymer contains hydroxyl, carboxylic, ketone, ether, and ester functional groups (Bernard et al., 2015) but its actual chemical structure still remains a debate (Hemsley et al., 1993; Moore et al., 2006). An earlier work suggested that sporopollenin is composed of polyalkyls (Guilford et al., 1988; Hayatsu et al., 1988) but recent works show that it might actually be a mixture of aliphatic and aromatic moieties (Jan de Leeuw et al., 2006; Wehling et al., 1989; Meychik et al., 2006). The hydrophobic regions of the biopolymer can selectively adsorb oil and repel water, making it useful as an oil adsorbent. Furthermore, the 2 μm thick perforated walls hollowed exine inner and the outer surface of sporopollenin is available for binding with guest molecule (Kamboh et al., 2016). MNPs can be modified with sporopollenin to give magnetic sporopollenin (MSp). MSp have already been used to adsorb a wide variety of pollutants such as metal ions (Ahmad et al., 2017; Kamboh and Yilmaz, 2013; Sargin and Arslan, 2016, 2015), phenol (Ayar et al., 2008), pesticides (Kamboh et al., 2016), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from contaminated waters (Thio et al., 2011).

Thus, this work deals with the synthesis of a potential nanoparticles incorporated into sporopollenin for oil decontamination from the aqueous environment. The oil adsorbent was characterized using several techniques such as FTIR, SEM, EDX, BET, contact angle measurement, VSM and TGA analyses. The sorption behaviour of the adsorbent towards oil was investigated through batch-type sorption experiments. In the sorption study, process parameters such as pH, dosage of adsorbent and contact time are investigated.

2. Experimental

2.1. Materials

All chemicals are analytical grade and purchased from Merck (Darmstadt, Germany) and used without further purification. All commercial grade solvents are stored over molecular sieves (4 Å, 8–12 mesh) from Aldrich (Steinheim, Germany) when not in use. Sporopollenin with size of 25 μm was purchased from Aldrich (Steinheim, Germany). If the pH of a solution needs adjusting, it was done using 0.1 M HCl and/or 0.1 M NaOH. Deionized water that was passed through a Milli-Q system (Lake End, UK) was used for the preparation of all the solutions. The oil sample used in this study is motorcycle engine oil (Yamalube 4 T MA SJ SAE20W50) that was purchased from a local workshop in Kuala Lumpur. The corn oil and palm oil were also purchased from a local store.

2.2. Instrumentation

Fourier Transform Infrared (FTIR) spectrometry (Spectrum 400 Perkin Elmer, Waltham, MA, USA) measurement was carried out using the ATR technique absorption mode with 4 scans at a resolution of 4 cm⁻¹ in the range of 400–450 cm⁻¹. The SEM-EDX analysis was performed using scanning electron microscopy (HITACHI SU8220), OXFORD Instrument (Oxfordshire, UK). The surface area and porosity of the adsorbent were measured through Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherm using Micromeritics Tristar II ASAP 2020, (GA, USA). The magnetic properties of MNP and MSp were measured using a vibrating sample magnetometer (VSM LakeShore 7400 series). Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere in the range of 30–900 °C at a heating rate of 20 °C/min using TGA 4000 (Perkin-Elmer, USA). Wettability analysis was performed using the TL 100 and TL101 (Gothenburg, Sweden) contact angle measurement instruments.

2.3. Synthesis procedure

2.3.1. Preparation of magnetic nanoparticle (MNP)

The preparation of MNP in this study was based on a previously reported method by Kamboh and Yilmaz (2013) with some modification (Kamboh and Yilmaz, 2013). Briefly, 13.32 g of FeCl₃·6H₂O, 19.88 g of FeCl₄·4H₂O, 5 mL of 5.0 M HCl, 40 mL of deionized water, and 5 mL of ethanol were added into a conical flask. The solution mixture was stirred for 2 h at room temperature until the salts are completely dissolved. Then, 100 mL of 1.0 M ammonia solution was added to the solution and stirring was continued for 2 h at room temperature. The formed MNP black precipitate was separated using a neodymium magnet and washed thoroughly with deionized water to remove impurities before being dried overnight in an oven at 60 °C.

2.3.2. Preparation of magnetic sporopollenin (MSP)

MSP was prepared as follows: 13.32 g of FeCl₃·6H₂O, 19.88 g of FeCl₄·4H₂O, 5 mL of 5.0 M HCl, 40 mL of deionized water, and 5 mL of ethanol were mixed and stirred at room temperature until complete dissolution of the salts. Then, 1.0 g of freshly prepared sporopollenin was dispersed in 30 mL of the solution and the mixture was stirred for 2 h at room temperature. The sporopollenin suspension was collected by filtration quickly washed with deionized water and transferred to 100 mL of 1.0 M ammonia solution. After 2 h stirring at room temperature, the suspended black MSp precipitate was collected using a neodymium magnet, washed thoroughly with deionized water and dried overnight under vacuum at room temperature. The process of MSp synthesis is illustrated in Fig. 1.

![Sporopollenin](Image)

**Fig. 1.** Schematic route for the synthesis of MSp adsorbent.
2.4. Oil adsorption experiment

50 mg of MSp is added into a petri dish containing 3 mL of lubricating oil in 20 mL of deionized water at 25 °C for 5 min. After 5 min, the adsorbent was recollected using a magnet. The oil adsorption capacity, $k$ was calculated by weight measurement using the following equation (Yu et al., 2015).

$$k' \text{(mg/mg)} = \frac{(W_2 - W_1)}{W_1}$$

where $W_1$ (mg) is the initial weight of the adsorbent before adsorption and $W_2$ (mg) is the final weight of the adsorbent after oil adsorption. The main parameters affecting the adsorption of oil i.e., pH of water, mass of adsorbent and adsorption time was optimized. Experiments for each parameter were run in triplicates.

After the adsorption experiment, the used MSp was ultrasonically washed with n-hexane to remove the adsorbed oil, and then it was dried in an oven at 90 °C for 24 h. The oil adsorption capacity of the regenerated adsorbent is again measured to determine its adsorption capacity.

3. Result and discussion

3.1. Characterisation

The FTIR spectra of the synthesized MNP, raw sporopollenin and MSp are shown in Fig. 2. In the spectrum of bare MNP (Fig. 2(A)), the strong absorption peak around 538 cm$^{-1}$ is associated with the Fe–O group. The bands at 3401 cm$^{-1}$ are associated with the hydroxyl group (Wang et al., 2013). The peaks at 1443 cm$^{-1}$, 2923 cm$^{-1}$ and 2884 cm$^{-1}$ in the spectrum for raw sporopollenin show in Fig. 2(B) result from C–H scissoring, asymmetric, and symmetric CH$2$ stretching; respectively. The peak at 1681 cm$^{-1}$ is associated with the C=O and 3461 cm$^{-1}$ associated with the O–H functional group. Finally, the presence of a peak at 545 cm$^{-1}$ in Fig. 3(C) in the spectrum for MSp is associated with the Fe–O bond, indicative of the successful magnetization process of sporopollenin. The peak at 3344 cm$^{-1}$ for MSp is broader than that of MNP and sporopollenin, due to the overlapping of hydroxyls groups of sporopollenin and MNP. The presence of these characteristic peaks is evidence of the successful synthesis of MSp (Kamboh and Yilmaz, 2013).

SEM is a surface diagnostic tool that is widely used to study the morphology of a compound. The differences in morphology of MNP and MSp are illustrated in Fig. 3. Fig. 3(A) reveals that the surface of MNP is hard and rigid (Cho et al., 2015). Raw sporopollenin has a round microcapsule form, and its surface has a uniform interconnected pore structure (Sener et al., 2014) as shown in Fig. 3(B). A high magnification SEM image of the MSp reveals the MNP embedded within the pores of sporopollenin (Fig. 3C) (Mahdavi et al., 2013). Thus, it is clearly showed the deposition of MNP at the surface of sporopollenin.

The elemental composition and the purity of MNP and MSp were examined using energy dispersive x-ray spectroscopy (EDX). Fig. 4 showed the elemental composition of MNP and MSp. For MNP (Fig. 4A), the iron (Fe) content is 75.5%, with the remaining content being oxygen (O) as expected. For MSp (Fig. 4B), a very high content of carbon (C) with 66% is expected due to the organic component, which is sporopollenin. The presence of iron (Fe) (8.3%) albeit small, confirm the modification of sporopollenin with MNP. No other elements were detected indicating the high degree of purity of the synthesized MSp.

BET analysis was carried out on both MNP and MSp to measure their surface area (Fig. 5A and B). Both samples have relatively high specific surface area being 3.73 m$^2$ g$^{-1}$ and 6.40 m$^2$ g$^{-1}$ for MNP and MSp respectively. The surface area can be used to estimate the pore size according to the relation $4V/S_{BET}$, where $V$ is adsorption total pore volume and $S_{BET}$ is the specific surface area of the samples. The calculated pore size approximately 4.15 nm for MNP and 32.0 nm for MSp. Table 1 tabulate the pore size, pore volume and $S_{BET}$ for MNP and MSp. The higher specific surface area of MSp is advantageous as it means that the adsorbent can adsorb more oil on its surface per unit mass.

The surface wettability of MNP and MSp was analysed using water contact angle measurements. The contact angle of water on MNP surface was measured to be 0° (Fig. 6A) and the water droplet was observed to spread out very quickly on the surface of MNP, indicating its super-hydrophilicity. This is due to the abundance of hydroxyl groups on the surface of MNP. In contrast, the MSp was found to be highly hydrophobic as the water contact angle was measured to be 123° (Fig. 6B). This can be explained by referring to the EDX results for MSp. The carbon content of MSp is high, being about 66% which is responsible for its hydrophobic behaviour. Being highly hydrophobic allows the MSp to effectively separate oil from water.

The magnetic behaviour of the synthesized magnetic adsorbents was studied using VSM analysis. Fig. 7 shows the magnetization curves of MNP and MSp. The VSM spectra show that both prepared nanoparticles...
possess superparamagnetic behaviour. The saturation magnetization value of MNP (Fig. 7A) and MSp (Fig. 7B) was found to be 63.30 emu g$^{-1}$ and 17.29 emu g$^{-1}$ respectively. The saturation magnetization of MSp is significantly lower than that for pure MNP due to sporopollenin layer shielding the MNP, thereby reducing magnetic interaction. The magnetization value of MSp is still acceptable and it can be separated easily from a solution using a magnet (Baharin et al., 2016).

The thermal stability of the adsorbents was investigated using TGA analysis and the results are shown in Fig. 8. The thermogram of MNPs (Fig. 8A) shows there was a loss of adsorbed water and hydroxyl groups (6.25%) at a temperature just below 100 °C. At temperatures 260 °C to 540 °C, another weight loss of 2.09% was observed due to the crystal phase transformation of magnetite to maghemite. The TGA curve profile for MSp (Fig. 8B) reveals three decomposition steps. The first step that occurs just below 100 °C can be attributed to the release of absorbed water molecules from the surface of MSp. The second step at around 200–650 °C is attributed to the decomposition of organic materials in MSp. After this step, the product is reduced to approximately 30% of the initial weight (Dyab et al., 2016). The final weight loss of 5% around 650–900 °C corresponds to the decomposition of the magnetic nanoparticles. The remaining 25% weight is the remaining undecomposed magnetic nanoparticles. This proves the successful phase transformation of magnetite to maghemite. The TGA curve profile for MSp (Fig. 8B) reveals three decomposition steps. The first step that occurs just below 100 °C can be attributed to the release of absorbed water molecules from the surface of MSp. The second step at around 200–650 °C is attributed to the decomposition of organic materials in MSp. After this step, the product is reduced to approximately 30% of the initial weight (Dyab et al., 2016). The final weight loss of 5% around 650–900 °C corresponds to the decomposition of the magnetic nanoparticles. The remaining 25% weight is the remaining undecomposed magnetic nanoparticles. This proves the successful
3.2. Comparison of adsorption capacity of MNP and MSp

MSp has the higher oil adsorption capacity (2.65 mg/mg) compared to that for MNP (1.08 mg/mg) (Fig. 9). This is expected since MNP is very hydrophilic and MSp is hydrophobic, which means that it favours interaction with other hydrophobic species such as oil. MSp also has a very high surface area for oil to adsorb on due to its porous structure. Therefore, MSp is chosen for use in the subsequent optimization study for the removal of oil from water.

3.3. The optimization of the parameters for efficient oil removal

3.3.1. Effect of solution pH

The effect of varying the oil-water pH from 3.0 to 13.0 on oil uptake was investigated and the results are shown in Fig. 10(A). The pH value of the oil-water mixture affects the oil emulsion breaking process (Schulz et al., 1998) and therefore must be taken into account. The $k'$ value of MSp was found to be 2.02 mg/mg at pH 3, followed by...
Table 2
Comparison of the oil-sorption capacity of MSp with other reported oil sorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Type of oil</th>
<th>Oil sorption capacities (mg/mg)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene coated magnetic nanocomposites (Fe3O4@PS)</td>
<td>Lubricant oil</td>
<td>3.0</td>
<td>(Chen et al., 2013)</td>
</tr>
<tr>
<td>Collagen-SPION nanobiocomposite</td>
<td>Lubricant oil</td>
<td>2.0</td>
<td>(Thanikaivelan et al., 2012)</td>
</tr>
<tr>
<td>MNP-FA</td>
<td>Lubricant oil</td>
<td>3.5</td>
<td>(Rozi et al., 2018)</td>
</tr>
<tr>
<td>Magnetic sporopollenin (MSp)</td>
<td>Lubricant oil</td>
<td>3.24</td>
<td>Current study</td>
</tr>
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<td>Current study</td>
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Fig. 12. The adsorption capacity of the MSp for the adsorption of selected oil.

2.48 mg/mg at pH 5 and 2.54 mg/mg at pH 7. The pH of the oil-water mixture can affect the nature of the adsorbent through protonation or deprotonation of the functional moieties. In acidic conditions, the hydrogen ions compete with the oil cations for binding sites on MSp resulting in a lower adsorption capacity for oil. The presence of excessive hydrogen ions could lead to the protonation of hydroxyl groups and also weaken the binding ability of carboxyl and carboxyl groups on sporopollenin (Ünlü and Ersoz, 2007). Therefore, a low pH is unfavourable for oil adsorption. The adsorption capacity for oil also decreased from 2.54 mg/mg at pH 7 to 2.29 mg/mg when the pH is increased to 13. This may be attributed to the destabilization of MSp at basic conditions. The optimum pH value for oil uptake using MSp is thus pH 7.

3.3.3. Effect of contact time

The effect of varying the contact time on the adsorbent dosage from 5 to 50 min on oil uptake was investigated and the results are shown in Fig. 10(C). The curve reveals that the maximum adsorption capacity is attained 5 min after introduction of the adsorbent. The maximum adsorption capacity at the beginning of the contact time is most likely due to a large number of vacant binding sites available for the oil adsorption. The oil uptake slightly decreases after 5 min to 20 min, likely due to the failure of some of the binding sites in MSp causing the oil to desorb again. Equilibrium is achieved after 20 min as the surface of MSp saturates with oil (Kayvani Fard et al., 2016). The optimum contact time for oil uptake using MSp is thus 5 min.

3.3.4. Reusability of the adsorbent

The reusability of the MSp on the oil uptake was examined for five adsorption-regeneration cycles. Reusing the MSp can significantly lower treatment cost at the expense of a slight drop in efficiency. Fig. 11 shows the relationship between the number of adsorption-regeneration cycles and the oil adsorption capacity. It was observed that the adsorption capacity of the MSp was still 3.2 mg/mg after three cycles and an accept Table 2.75 mg/mg after five cycles. The reduction in the adsorption capacity after the third cycle is mainly due to the incomplete regeneration of the adsorption sites on the MSp (Keshavarz et al., 2015).

3.5. Adsorption capacity of various oils

The adsorption capacity of MSp for various types of oil was also investigated. As can be seen in Fig. 12, the adsorption capacities for lubricating oil, palm oil, and corn oil are 3.24 mg/mg, 2.52 mg/mg and 2.34 mg/mg respectively. The adsorption capacity decreases in the order of lubricating oil > palm oil > corn oil due to the decreasing viscosity of the oil according to the type used (Wu et al., 2012).

3.6. Comparison of sorption capacities of MSp with other adsorbents

A comparison of oil removal capacity of MSp with other sorbents reported in the literature is given in Table 2. The data shows that the sorption capacity of MSp towards lubricant oil is relatively high compared to the other sorbents.

4. Conclusion

The newly fabricated highly hydrophobic MSp was successfully synthesized, characterized, and utilized for the removal of oil from aqueous environment. At optimum conditions, the MSp adsorbent has an oil sorption of 3.24 mg/mg after 5 min in an oil-water system at pH 7. The MSp is buoyant, and the spent adsorbent can be easily recycled using a magnet thus preventing the generation of secondary pollution. The MSp is also reusable for at least five adsorption-regeneration cycles. The MSp is thus a promising choice for removing oil pollutants from water.

Conflicts of interest

The authors have declared that no conflict of interest.

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