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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, VSM, 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. (Panatdasirisuk et al., 2017). Oily 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 (electroflotation, 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 finely 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 Sillanpä, 2015; Mohammadzadeh Kakhki, 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 polystyrene (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, carbocylic, 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 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 4000–450 cm^{-1}. The SEM-EDX analysis was performed using scanning electronic 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 $FeCl_3.6H_2O$, 19.88 g of $FeCl_2.4H_2O$, 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 $FeCl_3.6H_2O$, 19.88 g of $FeCl_2.4H_2O$, 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.

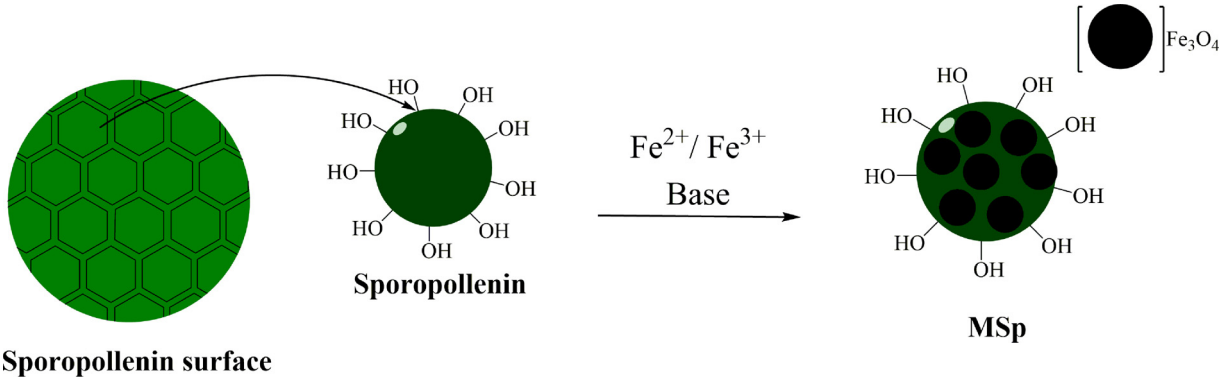

Fig. 1. Schematic route for the synthesis of MSp adsorbent.