Journal of Environmental Chemical Engineering 5 (2017) 5250–5259

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Research paper

Simple and green fabrication of recyclable magnetic highly hydrophobic sorbents derived from waste orange peels for removal of oil and organic solvents from water surface

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ARTICLE INFO

Keywords:
Hydrophobic coating
Magnetic
Oil-water separation
Orange peel absorbent
Oil absorption capacity
Recyclability

ABSTRACT

This study presents the preparation and characterization of natural waste material (orange peel) derived low cost, bio-based, recyclable, highly hydrophobic/superoleophilic magnetic sorbents to treat environmental pollution caused by oils and organic contaminants from water. Orange peels were dried, powdered and converted into magnetic and highly hydrophobic/superoleophilic sorbents by the incorporation of Fe_3O_4 nanoparticles using co-precipitation approach and subsequently modifying with low surface energy polydimethylsiloxane (non-fluorinated hydrophobic reagent) layers. SEM, EDS, XRD, FTIR, XPS, TGA, VSM and contact angle measurements analysis were used for characterization of the developed materials. The as-prepared sorbents exhibit strong magnetic behavior with saturation magnetization (Ms) value of 14.9 emu/g, excellent hydrophobicity with water contact angle of 149.2° and very high capacity for the selective absorption of various oils and organic solvents from oil contaminated water. It has high absorption capacity up to 5.11 and 6.90 times its original weight for diesel oil and engine oil respectively, along with high recyclability of more than eight cycles and the advantage of magnetic separation from water surface after absorption of oils. Thus, the orange peel waste derived absorbent with magnetic and high hydrophobic properties is a promising alternative for the capture of oil and organic pollutants from water.

1. Introduction

Water pollution due to oil and organic liquids is increasing with the rapid expansion of industrial activity such as oil-production, oil-deliveries, oil refining, oil spillage and discharge of industrial oily waste water [1]. The frequent occurrence of organic solvent and oil spill are of serious concern, leading to adverse impact on ecosystems and immeasurable loss to our living environment [2,3]. When oil gets spilled into the water, oil film is formed over the water surface that separates the aquatic environment from the atmosphere, which are responsible for pollution in the natural environment and ecological damage [1,4,5]. Hence, in order to protect the environment, an efficient removal of organic solvents and oil spills from water surface is urgently needed.

Various traditional methods have been reported for selective removal of oil and organic solvents from water including fabric based membranes, sorbent materials, chemical dispersants, mechanical extraction, in situ burning, bioremediation etc. [1,6–9]. Among these methods, sorption is a simple, effective and economically viable approach, widely used to remediate oily and other inorganic and organic contaminants from water [10–16]. A considerable number of absorbent materials like cellulose aerogels [17], film [18], carbon nanotubes [19], foam [20], sponge [21] and superamphiphobic filter [22] have been synthesized and used for removing oil from water. However, these materials have limited applications because of their high cost, environmental incompatibility and low recyclability.

Since an oil spillage can cause water pollution over huge area (for example, 1 ton of oil can spread rapidly on the surface of water to form a film of 12 km^2 of area), oil adsorbent materials, which can be quickly distributed and collected without affecting the aquatic life and without causing any secondary pollution, are more desirable. Invariably, large quantity of absorbent is needed for removing spilled oil released into the ecosystem [10]. In the recent past, some of the absorbents materials have been developed that have superhydrophobic, superpoleophilic and magnetic property in order to improve absorption efficiency and easy recyclability. Li et al. [23] prepared low cost biosorbent based on yellow horn shell residues treated by ionic liquid (IL) for oil removal from water. However, the maximum sorption efficiency of IL-treated shell residues was low, around 0.39–0.61 g/g. Zhang et al. [24] tried to

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http://dx.doi.org/10.1016/j.jece.2017.09.060
Received 23 May 2017; Received in revised form 26 September 2017; Accepted 27 September 2017

mimic the hierarchical structure similar to micromorphology of lotus leaf and synthesized superhydrophobic particles using dopamine, Ag nanoparticles and 1H,1H,2H,2H-perfluorodecanethiol. Yang et al. [25] prepared Fe_3O_4@Polydopamine (Fe_3O_4@PDA) core shell composite microsphere and incorporated superhydrophobicity to it using 1H,1H,2H,2H-perfluorodecyltrichlorosilane. Though, the developed superhydrophobic composites showed effective oil-water separation properties, fluorinated compounds were used in order to generate superhydrophobicity, which are expensive, environmentally undesirable and nonbiodegradable. In addition to this, fluorinated compounds may also cause environmental contamination as they can easily react with other materials [1]. These compounds are also found to impede nerve growth in children [26]. Thus the development of eco-friendly and economical approach for the preparation of superhydrophobic absorbents is required to obtain desirable oil-water separation ability, which is the primary motivation of this work.

Waste orange peel powder (WOPP) have excellent capacities of absorbing and retaining water and oils, consisting of superamphiphilic constituents such as starch and cellulose. Thus WOPP can be a suitable candidate as a base material for separation of oil-water mixtures after its suitable modification to prepare superhydrophobic/superoleophilic materials. The reason for the selection of orange peel is that it is easily available (orange-juice and soft-drinks industries) and has negligible price. Application of waste orange peel in the form of useful sorbent not only minimizes the environmental pollution but also can help in remediating water pollution. WOPPs based adsorbent is already reported to remediate heavy metals and other pollutants [27,28]. Therefore, we propose to extend the uses of WOPPs by the fabrication of cost-effectively, environment friendly and hydrophobic/oleophilic sorbents from waste orange peel for separation of various oil-water mixtures. Herein, we report a low cost, recyclable, environment friendly and magnetic orange peel particles (MOPPs) as an absorbent composed with high hydrophobicity and superoleophilicity by the simple and inexpensive (without using any sophisticated equipment) fabrication process using non-fluorinated hydrophobic reagent. The absorption efficiency towards various common organic solvents and oils, water repelling ability and recyclability of MOPPs were studied. In addition, regeneration of the used absorbents was also evaluated.

2. Experimental section

2.1. Materials

The orange peel used for this experiment was obtained from a local fruit juice shop in Kanpur, India. It was washed, dried, cut, grinded and sieved through 100 mesh sieve after collection. Isopropanol (99%) and ethanol (99.9%) were purchased from Merck. Liquid ammonia (25% NH_3) and toluene (99.5%) were purchased from Fisher Scientific. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥ 98%) was purchased from Molychem and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, ≥ 98%) was supplied by RFCL limited. Polydimethylsiloxane (PDMS,) was supplied by Dow Corning Corporation (Sylgard, 184). All chemicals were of analytic reagent grade and used without further treatment. Deionized water was used throughout the study.

2.2. Procedures for fabrication of MOPPs

2.2.1. Preparation of orange peel particles

The synthesis process of hydrophobic and superoleophilic modified magnetic orange peel particles (MOPPs) has been shown in Fig. 1. The orange peel was first washed and cut into small pieces, dried in oven at 80 °C for 24 h. Then it was grinded to make it in powder form and sieved through 100-mesh screen to obtain particles in the range of 0.1 − 0.2 mm. The powdered orange peel was washed with DI water and dried in an oven at 80 °C for 12 h. The powdered peel was added to isopropanol and stirred for 24 h at room temperature and then rinsed with isopropanol for two times. After that it was washed with DI water until the filtrate became colorless and then dried at 80 °C for 12 h.

2.2.2. Synthesis of PDMS coated magnetic orange peel particles

$FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were mixed in 40 ml of DI water and in the molar proportion of 2:1 and stirred for 1 h in a flask. 5 ml of $NH_3 \cdot H_2O$ was added to the solution and was kept at 60 °C for 2 h in an oven. 4 g of powered orange peel was added to the solution and mixed well. The mixture was kept at 80 °C for 2 h in the oven. The magnetic orange peel particles were collected using external magnet, rinsed with DI water for three times and dried at 90 °C for 12 h. Final recovery of the magnetic peel particle was 4.4 g, which was used for further modification. A separate solution was prepared by adding 2 g of Polydimethylsiloxane (PDMS) in 50 ml of toluene and stirring the solution for 2 h at room temperature. Subsequently, 4 g of the magnetic peel particle was added to the solution and further stirred for 2 h at room temperature. The final magnetic orange peel particles (MOPPs) were collected using external magnetic field and dried at 120 °C for 1 h and 150 °C for 1 h.

2.3. Characterizations

The surface morphology and elemental composition of untreated orange peel particles (OPPs) and modified magnetic orange peel particles (MOPPs) were investigated by field emission scanning electron microscope (FESEM, Zeiss, Germany, supra-40VP) equipped with an energy dispersive X-ray detector (EDS). A sputtering coater was used to place a thin layer of gold film to increase the conductivity of the samples before the morphological analysis. Brunauer-Emmett-Teller (BET) surface area of the MOPPs was determined from nitrogen adsorption isotherms using an autosorb Quantachrome instrument. The crystalline structure of the modified MOPPs was measured using PANalytical XRD device with Cu-Kα radiation ($\lambda = 1.5405$ Å) at a scan rate (2θ) of 2° min^{-1}, an accelerating voltage of 45 kV and an applied current of 40 mA ranging from 20 to 80°. The X-ray photoelectron spectroscopy (XPS) measurement was done using XPS instrument (PHI 5000 Versa Prob II, FEI Inc.). Fourier Transformed infrared spectroscopy (FTIR) analysis was done using FTIR spectrometer (KBP pellet method) in the range of 500 to 4000 cm^{-1} in order to identify the presence of functional group on the modified MOPPs. The measurement of magnetization was done at room temperature using vibrating sample magnetometer (EV7 VSM, USA). Thermogravimetric analysis (TGA) of the samples were carried out using instrument TA2100 (TA instruments, USA) at a heating rate of 10 °C per minute under N_2 environment in the range of 20 to 1000 °C.

2.4. Evaluation of hydrophobicity of modified MOPPs and surface energy calculation

Hydrophobicity of the modified MOPPs were evaluated using water contact angle measurement. For the water contact angle measurement, the particles were places on a glass slide and pressed into a flat film to get a flat surface. The measurement of contact angle was done by the commercial goniometer (OCA 20, dataphysics, Germany) instrument using sessile water drop method with 5 μl volume of DI water drop at room temperature. The measurements were taken for five times at different locations and the average of these measurements were used to calculate final water contact angle.

Surface energy estimation was done using contact angle measurement [29,30]. A three-phase interface line is formed when a drop of liquid is formed on the surface. The balance of equilibrium forces between the surface tensions at the three-phase contact line is expressed by Young's equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$$

Where γ_s is the surface free energy of a solid, γ_{sl} is the interfacial tension

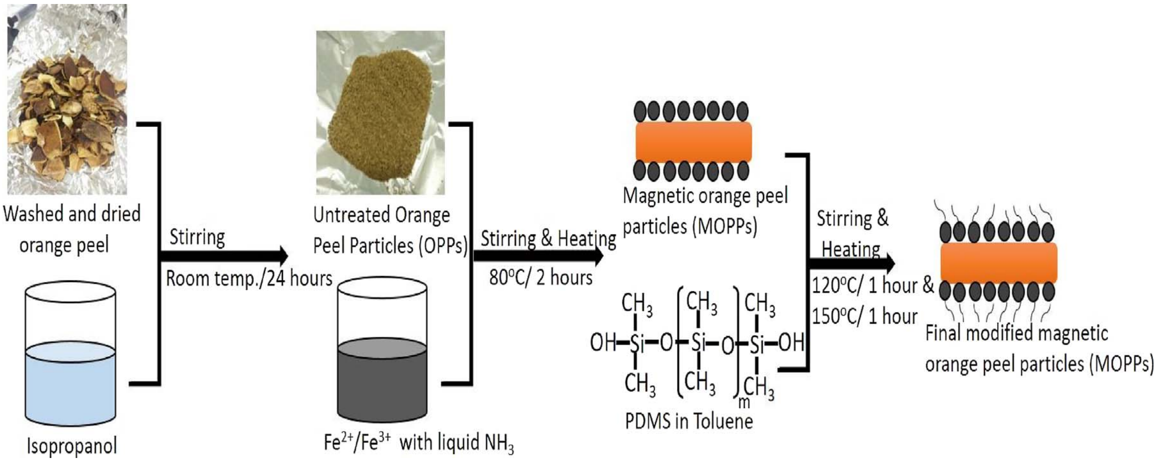

Fig. 1. Schematic diagram for the synthesis of highly hydrophobic modified magnetic orange peel particles (MOPPs) from waste materials (orange peel).

between solid and liquid, γ_l is the surface tension of the liquid, is the angle between liquid-air interface and the surface. The total surface tension of a solid is contributed by two surface tension component, polar γ_s^p and non-polar γ_s^d (dispersive) [29].

2.5. Absorption capacity and recyclability study

The study for the oil absorption capacity was done by weight measurement as illustrated in Fig. 2. Water was kept in a beaker and small volume of oil was poured on the surface of water. A certain amount of the modified MOPPs was smoothly placed on the surface of oil-water mixture. The particles were left undisturbed for 10 min in the completely wetted condition. After that the absorbed oil together with the modified MOPPs were separated using magnet bar. Their weight was measured using an electronic balance with an accuracy of 0.1 mg. All the absorption experiments were done at room temperature and were repeated for three times and their mean values were used for the analysis. The formula used for calculating absorption capacity (Q) was:

$$Q = \frac{m_2 - m_1}{m_1}$$

Where, m_1 and m_2 are weight of the particles before and after the absorption of oil respectively. For the regeneration of particles, the oil absorbed particles were ultrasonically washed in ethanol and dried in an oven at 120 °C for 2 h. It was observed that the particles could be used for several times for the separation of oil from water surface. Their reusability was investigated by measuring contact angles and calculating absorption capacity for each cycle.

3. Results and discussion

3.1. Morphology and structure of Fe_3O_4/PDMS coated orange peel particles

The fabrication process of superhydrophobic and superoleophilic magnetic orange peel particles has been illustrated in Fig. 1. After converting orange peel into fine particles, they were coated with Fe_3O_4 and modified with PDMS to incorporate desired properties. The fabrication process used was very inexpensive and very simple (without using an inert medium or any sophisticated equipment). To determine surface morphology, chemical properties, and component analysis, characterization of modified magnetic MOPPs by different methods was performed. For the surface to have superhydrophobic property, the essential requirement is the presence of hierarchical structure at the surface [31].

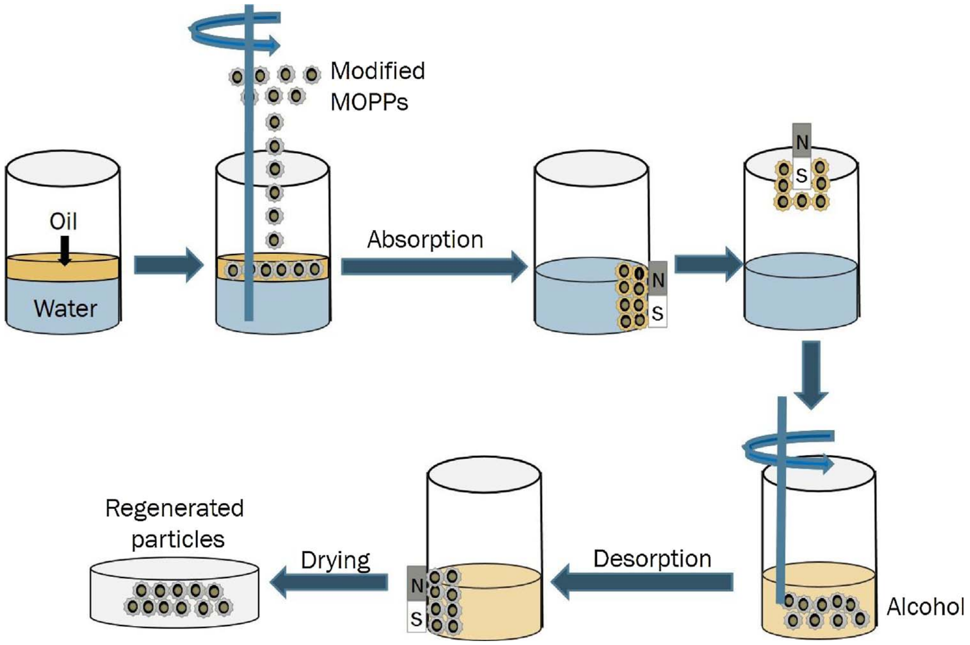

Fig. 2. Illustration for the removal oil from the surface of water by using hydrophobic and superoleophilic MOPPs under the external magnetic field and their recycle route.

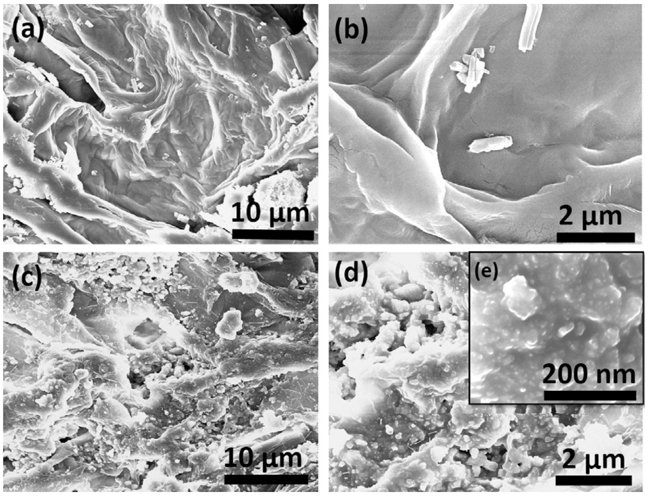

Fig. 3. SEM images of untreated orange peel particles in (a) low and (b) high magnification and SEM images of modified magnetic orange peel particles in (c) low, (d) high and (e) very high magnification.

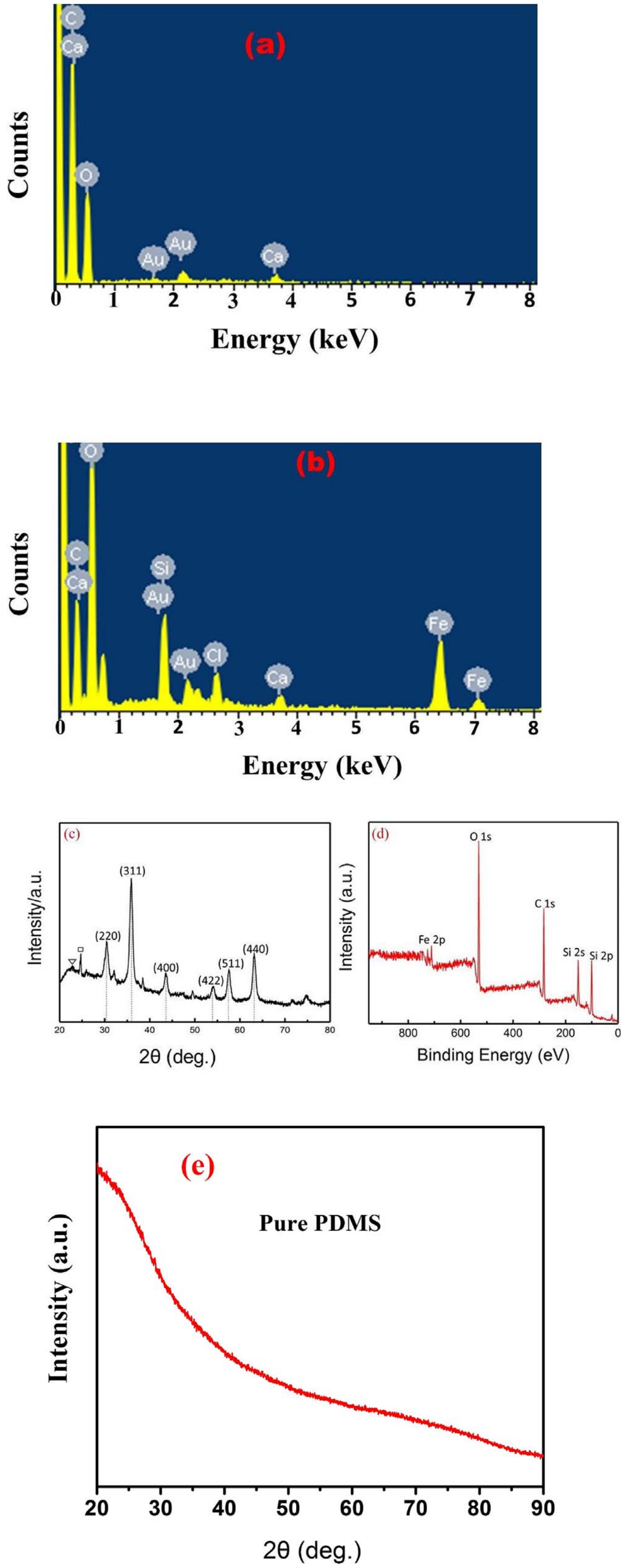

Fig. 4. Magnified EDS spectra of (a) untreated orange peel particles and (b) modified magnetic orange peel particles (c) XRD pattern and (d) XPS survey spectrum of modified magnetic orange peel particles (MOPPs). (e) XRD pattern of pure PDMS.

The surface morphologies of untreated OPPs and modified MOPPs were analyzed through FESEM as shown in Fig. 3. The low and high magnification SEM image of untreated OPPs are shown in Fig. 3(a) and (b), respectively. The surface of untreated OPPs was clean and smooth. Fig. 3c–e shows the SEM images of treated MOPPs under high and low magnification. It can be observed from the figures that the roughness of modified MOPPs is higher than the untreated OPPs. It has been reported that the wetting properties of a solid surface with respect to water or oil droplets depend on the surface roughness and surface chemistry [30]. Surface roughness is one of the key factors in obtaining hydrophobicity because water droplets can be repelled by air pockets between the water and a hydrophobic surface [32]. Zhang et al. [33] reported the similar influence of surface roughness on the hydrophobicity and superoleophilicity of the polyethylene coated copper mesh for separation of different types of oil/water mixtures.

To analyse the elemental component on the surface, EDS analysis was done. The content of every element in OPPs and MOPPs are shown in Fig. 4 (a) and (b) respectively. The EDS results strongly suggest that surface of MOPPs was covered with a layer of PDMS films which is indicated by the presence of a Si peak, as shown in Fig. 4 (b), after the coating treatment with PDMS. Fig. 4 (b) confirmed the presence of C, O, Ca, Au, Cl, Fe and Si elements on the surface of modified MOPPs. In contrast, there were no Si and Fe peaks for unmodified OPPs as shown in Fig. 2 (a), indicating the successful incorporation of Fe_3O_4 with PDMS coating on the surface of OPPs. The peak corresponding to the Au element in the EDS spectra arises from the gold coating on the samples during the analysis [34], and the peak of Cl may be due to the impurity during the preparation of Fe_3O_4. In addition, the peak of Ca is because of the occurrence of Ca as a mineral in the top layer of orange peel [35]. The BET surface area of the MOPPs is 4.46 m^2/g. The observed small value of measured surface area of MOPPs is attributed to the collapsing of cellulose chains during the dehydration process using vacuum drying (conditions of sample preparation before the N_2 adsorption in the BET test). During this vacuum drying process all the pores in the intermolecular structure may be clogged after the elimination of intramolecular water molecules [36,37]. Therefore, only external BET surface area of MOPPs was measured and we observed low surface area value. A similar result has also been observed for Oil palm empty fruit bunch fiber by other workers [37]. Which have low surface area (0.3463 m^2/g), but high sorption capacity for crude oil.

The crystalline structure of the as prepared modified MOPPs was characterized by X-ray diffraction technique and to determine the composition of the final particles accurately, the characterization was done using X-ray photoelectron spectroscopy (XPS). Fig. 4(c) presents the XRD pattern, which shows the formation of magnetite (Fe_3O_4) and maghemite (ϒ-Fe_2O_3), confirmed by comparing XRD pattern experimentally obtained at the corresponding standards of cubic iron oxide

(JCPDS Card No. 88-0866 and 39–1346). The reflection peaks assigned to the diffraction from crystallographic planes of cubic structure of Fe_3O_4 represented by Miller indices: (2 0), (3 1), (4 0), (4 2), (5 1) and (4 0) indicate the presence of Fe_3O_4 compound. These demonstrated that Fe_3O_4 nanoparticles have been successfully precipitated on the surface of OPPs. The diffraction peak at 22.6° indicates the crystalline region of the cellulose [38]. The diffraction peak at 24.1° corresponds to the crystalline region of Fe_2O_3. The presence of small amount of Fe_2O_3 can be attributed to fact that the reaction of magnetite formation was carried out in open environment (not in inert medium) leading to the formation of small amount of Fe_2O_3. The purity of the final product was indicated by the absence of other peaks. In addition, the X-ray diffraction pattern of pure PDMS was analysed at similar conditions of modified MOPPs. The obtained result is shown in Fig. 4 (e). Pure PDMS showed no significant crystalline peak for the silicon (Si) in the XRD pattern which indicates its amorphous nature.

The chemical composition of modified MOPPs was further investigated accurately by X-ray photoelectron spectroscopy. As shown in Fig. 4(d), the characteristic signals of C, O, Fe and Si elements were clearly present in the XPS spectra of modified MOPPs. The peaks at 711.2 eV and 725.2 eV were ascribed to $Fe2p_{3/2}$ and $Fe2p_{1/2}$, respectively. The peaks at 525.2 eV and 276 eV were due to O 1 s of the oxygen atom and C 1 s of the carbon atom, respectively. Furthermore, the peaks at 100.8 eV and 152 eV were related to Si 2p and Si 2 s of the silicon atom, respectively. The peak of Si2p in the XPS spectrum was attributed to the Si-O in the PDMS. No additional peak was observed indicating none of the impurities were generated.

In order to investigate the functional group present in the coating and understand the chemical modification underwent by untreated OPPs after treatment with Fe_3O_4 and PDMS, FTIR spectroscopy characterization was carried out. Spectroscopic analysis (FTIR and EDS) shows the successful binding organic matrix to the metal surface. The FTIR absorption spectra of untreated orange peel particles (OPPs) and orange peel particles after treatment (modified MOPPs) are shown in Fig. 5(a) with several characteristic peaks related to vibrations and deformation of the functional group within the range 500 cm^{-1} to 4000 cm^{-1}. The disappearance of peaks at 3422 and 1739 (originally presented in OPPs) on MOPPs revealed the combination of Fe (of Fe_3O_4) with OH groups of OPPs. The newer peak at 567 cm^{-1} assigned to Fe-O group on MOPPs indicated the presence of magnetic nanoparticles on the surface of OPPs [39]. The peak at 800 cm^{-1} resulted from the asymmetric deform of Si-$(CH_3)_2$ bending vibration [40]. The peaks at 3422, 2927, 1631 and 1430 cm^{-1} were related to O—H stretch vibration, $-CH_3$ asymmetric, O—H bending vibration and C—O stretching vibrations, respectively. The peaks corresponding to major cell wall components such as cellulose (890 cm^{-1}), hemicellulose (1739 and 1024 cm^{-1}) and lignin (1240 cm^{-1}) were also observed in the spectra [41]. After the modification of untreated OPPs to modified MOPPs, peaks at 622 and 567 cm^{-1} were observed corresponding to the stretching vibrations of Fe-O bond at the tetrahedral site, suggesting the presence of magnetic compound [42]. The presence of peaks at 1113 and 1050 cm^{-1} related to Si-O-Si groups indicated the adsorption of silica polymer onto the surface of the particles. The presence of $-CH_2$ group was confirmed by the absorption band at 2899 cm^{-1}. The absorption band at 1258 and 800 cm^{-1} were related to stretching vibration of Si-C and asymmetric stretching vibration of Si-O-Si bond [43]. The peak corresponding to 1617 cm^{-1} was assigned to C=O symmetry stretching.

The crosslinking between OPPs with PDMS and Fe_3O_4 is attributed to the hydrophilic nature of the surface of OPPs due to the presence of numerous hydroxyl groups. When the OPPs were dipped into the PDMS, the hydrophilic nature trapped the Si-O inside the OPPs sample due to the interaction of hydroxyl group. Hence PDMS bonded to the OPPs through the O—H bonds [40]. In addition, atoms of Fe in the Fe_3O_4 nanoparticles are present in the form of Fe^{2+} and Fe^{3+}. It was expected that O in the PDMS was electronegative in nature and thus adsorb atoms of Fe through the electrostatic interactions [40].

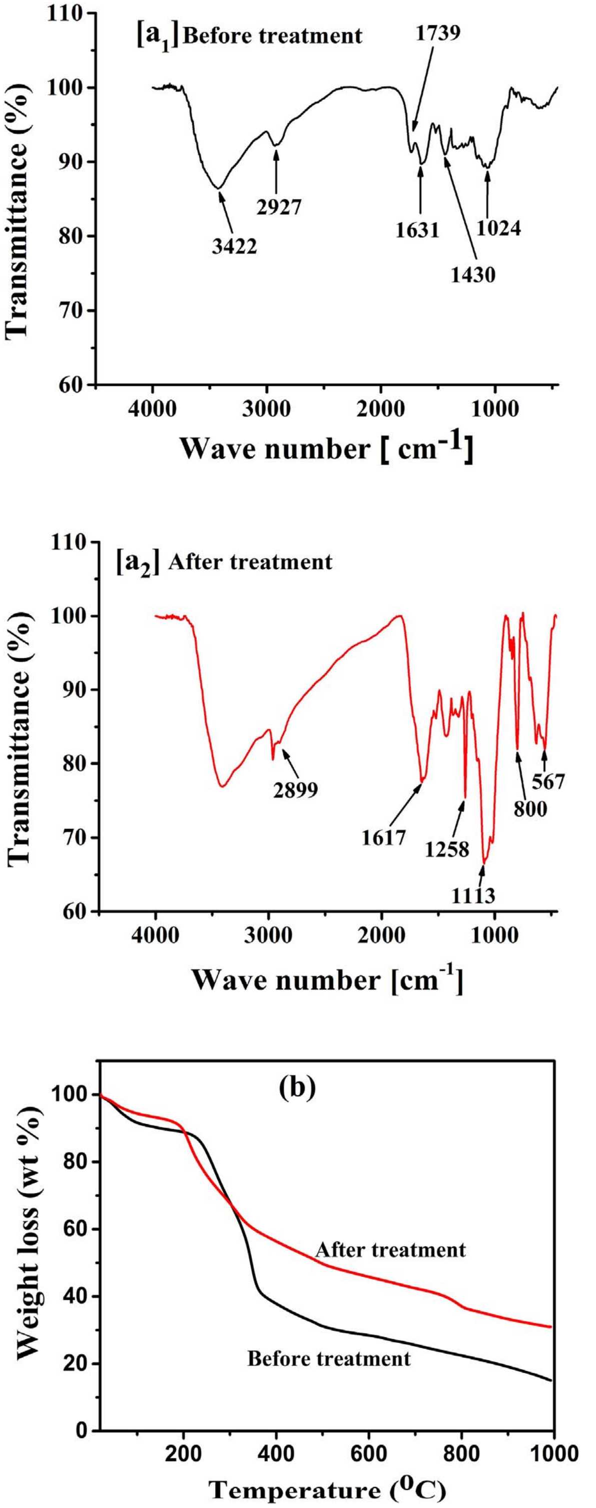

Fig. 5. (a) FTIR spectra of untreated orange peel particles (a_1-before treatment) and final modified orange peel particles (a_{-2} after treatment) and (b) TGA curves of orange peel particles before treatment and after treatment.

The thermogravimetric analysis (TGA) of the untreated OPPs and modified MOPPs is shown in Fig. 5(b). It can be observed that the weight loss of the treated material occurred in three stages from 20 to 200 °C, 200–350 °C, and 350–1000 °C. In the first stage, there was a loss of almost 10% in the range of 20–200 °C, which is attributed to the release of water that is physically absorbed on the surface of the

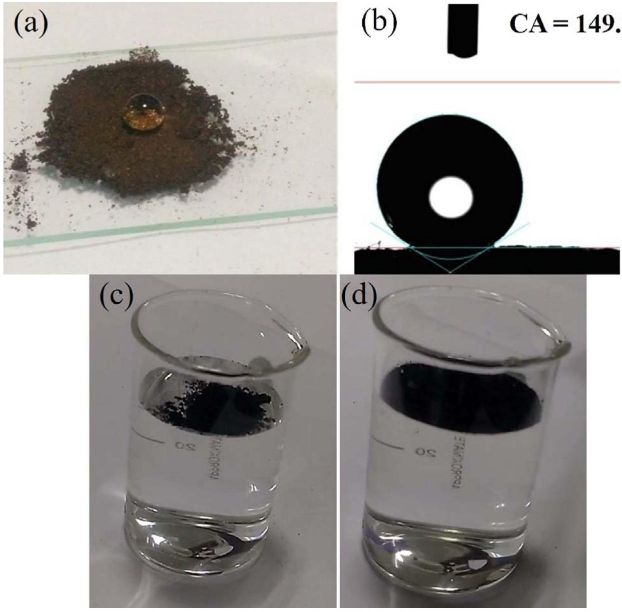

Fig. 6. (a) Digital photograph image of water droplet placed on the surface of modified MOPPs, (b) optical image of water droplet placed on that surface, (C) digital photograph image of modified MOPPs on the surface of water before and (d) after vigorous agitation.

particles. With the temperature increasing to 350 °C significant weight losses (60%) for the MOPPs appeared [44]. In general, oil absorption experiment performed at room temperature, which is not higher than 100 °C. These results indicate good thermal stability of the MOPPs for practical application of oil/water separation in relevant environmental conditions [45].

3.2. Wetting behaviour study and stability of modified MOPPs

The modified MOPPs prepared by the application of PDMS in combination with the Fe_3O_4 nanoparticles, displayed an excellent hydrophobic property as shown in Fig. 6. In the case of the pristine orange peel particles, the water contact angle was 0° (water droplets absorbed) that can be justified by the presence of sufficient hydroxyl group on the orange peel surface. A water drop was placed on the bed of the modified MOPPs, and its contact was determined to be of 149.2°. The high value of contact angle clearly suggests an excellent hydrophobicity of the final modified particles after PDMS modification (Fig. 6(a) and 6(b)). This may be associated to the low surface energy of the modified MOPPs.

The surface free energy was determined by measuring the contact angle of three different liquids (water, glycerol and ethylene glycol). The three test liquids with their different components of energy have been listed in Table 1. Three measurement values were taken for each sample and an average value was taken for the calculation. The contact angles for water, glycerol and ethylene glycol were 149.2°, 142.2° and 136.7° respectively. The polar component of the free surface energy of solid came out to be 0.296 mN/m and dispersion component came out to be 2.684 mN/m. The total free surface energy of the solid was found out to be 2.98 mN/m. The very low free surface energy of the particles supports the fact that the final particles are highly hydrophobic.

Table 1
Surface free energy of liquids used in free surface energy calculation of MOPPs.

Liquid	Surface tension, γ_l (Nm)	Polar component, γ_l^p (Nm)	Dispersion component, γ_l^d(Nm)
Water	72.8	43.7	29.1
Glycerol	63.4	26	37.4
Ethylene glycol	47.7	21.4	26.3

Furthermore, the wettability of MOPPs was also evaluated with diesel oil. We noticed that in contrast to water when a drop of diesel oil was placed over the bed of modified MOPPs, it was quickly absorbed by the particles leading to complete wettability. The oil contact angle was near to 0° (**See Video S1**). This observation strongly indicates that the modified MOPPs is superpoleophilic. Therefore, the MOPPs exhibit highly hydrophobic and superpoleophilic properties simultaneously. A similar pattern for the identification of superpoleophilic property of the nanocomposites has been reported earlier [46].

Moreover, the modified MOPPs displayed an unsinkable property even under vigorous stirring and no particle sunk to the bottom of the water as illustrated in Fig. 6c–d (**See Video S2**). After being collected by a magnet bar, the weight of particles was measured, there is no any significant change in weight, confirming the water repelling property of the particle surface. This unsinkable property of the modified MOPPs might be explained by the superhydrophobic PDMS coating, which repelled the water surface overcoming its own weight [47,48].

Furthermore, the modified MOPPs exhibited a stable superhydrophobic property even after floating on the water surface and an aqueous solution of 0.1 M NaCl for 24 h respectively as shown in Fig. 7. It was also noticed that PDMS coated MOPPs were stable and their highly hydrophobic property was intact even after floating on the surface of corrosive media for a long period of time (24 h).

To analyse the stability of modified MOPPs in acidic and alkali medium, the particles were left over the surface of an aqueous solution with pH values ranging from 1 to 13 for 24 h. Subsequently, the particles were collected, and contact angle measurements were made. Fig. 7 (e) shows the measured contact angle against the pH value of the solution. It is evident from the figure that the highly hydrophobic coating was intact in different mediums. However, it is noted that slight decrease in the contact angle was observed at a pH value of over 13. These results showed that the final developed particles could be proved to be of immense importance under oceanic conditions. With the increase in the large-scale contamination caused by spillage of oil in the environment, there is a great challenge in developing the suitable and low cost oil absorbent. Our findings may provide an effective method to develop low cost, environment friendly, and suitable material that can be produced on the industrial scale to deal with frequent and large-scale contamination caused by oil spills in the future.

3.3. Magnetic properties study

The magnetic properties of pristine orange peel particles and final modified MOPPs were studied by VSM technique at room temperature with the maximum applied magnetic field up to 18 KOe. The hysteresis curves for both the materials are shown in Fig. 8. It can be clearly observed that the hysteresis curve for pristine orange peel particles was 0.055 emu/g which was close to zero, indicating the diamagnetic behaviour of the original particles. On the other hand, the modified MOPPs exhibited ferromagnetic behaviour with saturation magnetization (Ms) was 14.9 emu/g, measured at room temperature. The saturation magnetization (Ms) of the modified MOPPs was smaller compared to the Fe_3O_4 nanoparticles (Ms = 92emu/g at 300 K) [49], but still was strong enough to be separated by simple bar magnet [42]. In addition, we observed that MOPPs maintain its Ms value after heat treatment in a drying oven at 60 °C for 24 h. Thus, the prepared MOPPs are promising materials, with stable magnetic property.

3.4. Oil absorption capacity analysis and kinetics of oil sorption

The highly hydrophobic and superoleophilic modified MOPPs could be used for the selective absorbance of floating oils from the water surface. In order to investigate this property, a specific experiment was conducted as illustrated in Fig. 9 (**See Video S3**). A few drops of diesel

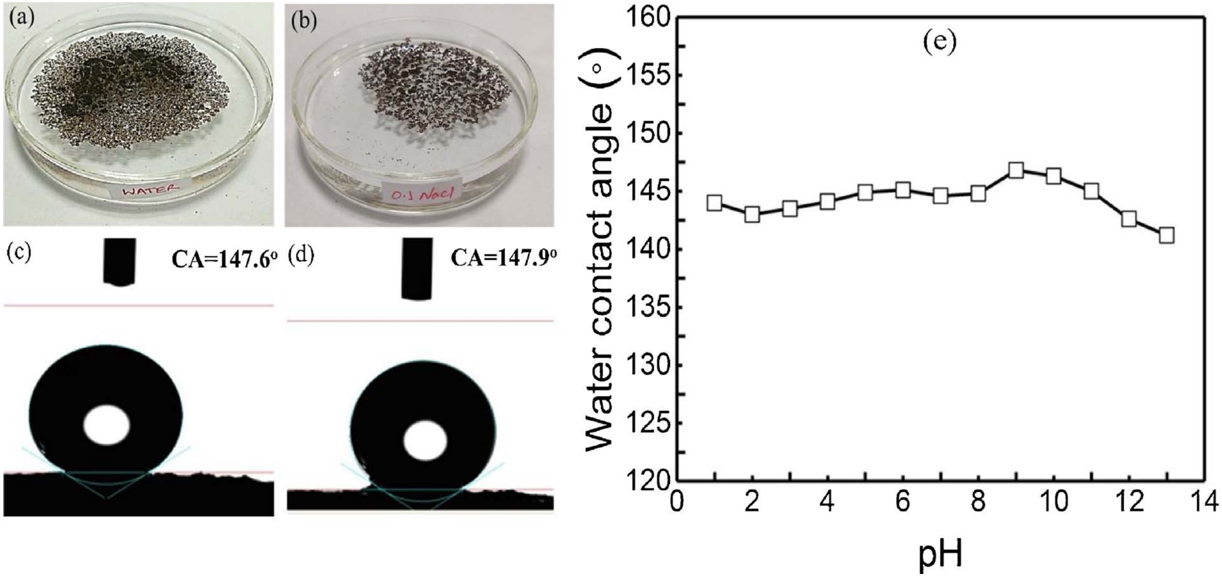

Fig. 7. Digital photograph image of modified MOPPs after floating for 24 h on (a) water surface, (b) aqueous solution of 0.1 M NaCl, and their optical image after floating for 24 h on (c) water surface and (d) aqueous solution of 0.1 M NaCl, (e) water contact angles of modified MOPPs after floating over the aqueous solution for 24 h with pH ranging from 1 to 13.

oil dyed with Sudan Blue II were dropped onto the surface of the water. As expected, the oil drops quickly spread over the water surface forming a thin layer. When a certain amount of modified MOPPs was manually added over the water surface containing a film of dyed diesel oil, the particles quickly absorbed the diesel oil and the oil surface was divided into pieces, which prevented the spreading of spilled oil over water. Moreover, the diesel oil was collected around the absorbent particles because of the superoleophilic nature of the particles which could be very useful in quickly reducing the water area polluted by oil leading to the safety of the aquatic organism during large scale oil spillage as fast as possible. After the oil got absorbed, the oil containing particles were easily moved collected with the help of a magnet because of their strong magnetic property. Thus the separation of MOPPs after absorption of oils from the water surface not only reduced the requirement of manpower but also made the recovery process very fast, proving to be very handy for practical applications. The recycling and further utilization of the particles were also ensured by their complete recovery with the help of a magnet.

The main absorption mechanism for the products (MOPPs) during oil/water separation is ascribed as follows: MOPPs preferentially absorb oils from oil/water mixtures because of its superoleophilic surface nature due to the PDMS coating. When the MOPPs was put into the contact of oil, the first adsorption is processed by the molecular diffusion. After some seconds, oils are driven into the bulk of MOPPs through the pores due to the similar surface energies between oils and PDMS coating. The PDMS coating is the main factor for enhanced oil

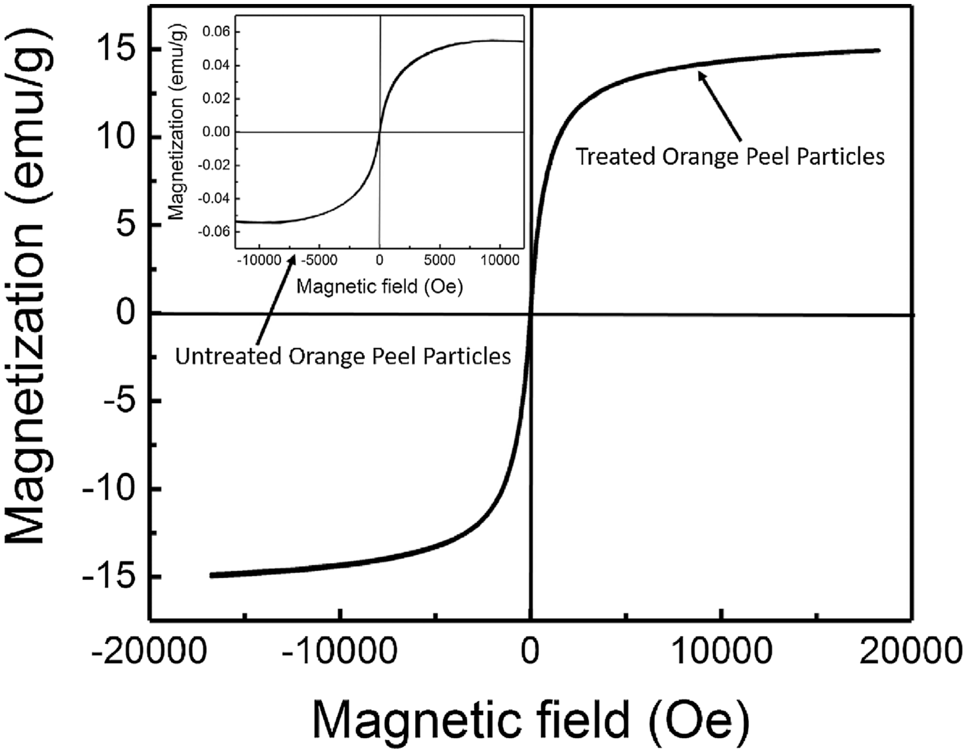

Fig. 8. VSM measurement result of pristine orange peel particles and PDMS coated magnetic orange peel particles.

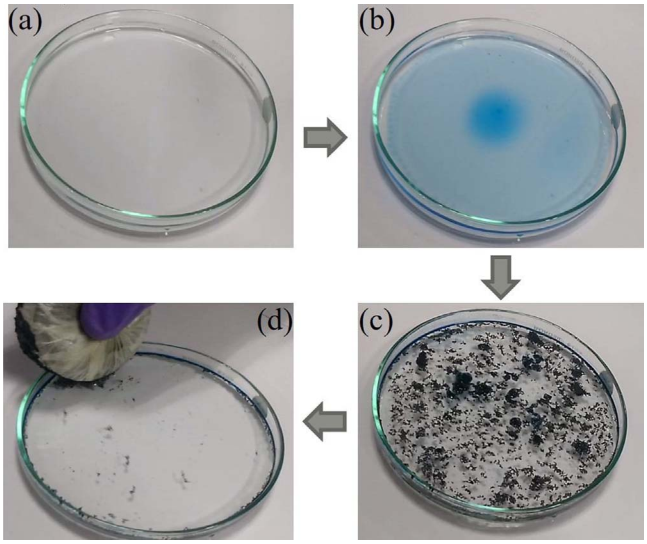

Fig. 9. Diesel oil removal from the water surface with the help of hydrophobic and superoleophilic magnetic orange peel particles under the magnetic field. The diesel oil was coloured with blue dye for clarity.

sorption with high selectivity. Thus the MOPPs surface is wetted by oils and organic solvents spontaneously. On the contrary, water is strongly repelled by the MOPPs surface due to large gap of surface energies between water (72 mN/m) and PDMS coating (20.4 mN/m) [45]. The oils were stored in the bulk of MOPPs through the pores, while water is completely repelled by the hydrophobic surface, resulting in effective separation of oil/water mixture through selective absorption approach.

The optimum removal time (t_m) to achieve maximum absorption was investigated by plotting absorption capacity (Q) for the diesel oil with removal time as shown in Fig. 10(a). It can be observed that initially the absorption capacity increased with removal time but after 60 min it was almost constant. Also, for the removal time of 10 min it was 5.11 g/g and for the 60 min it was 6.34 g/g. It was noted that increasing the time of removal to 50 min does not cause further increase in the absorption capacity. Therefore, 10 min was selected to be the optimum removal time and this optimum removal time was used for further experiments.

In addition, to understand the rate of diesel oil sorption with MOPPs, the experimental data were further analysed using pseudo-first-order and pseudo-second-order kinetic models, as represented by the following Eqs. (1) and (2), respectively [50].

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

Table 2
Parameters for pseudo-first-order and pseudo-second- order kinetic models.

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
q_e ($g\,g^{-1}$)	K_1 ($g\,g^{-1}\,min^{-1}$)	R^2	q_e ($g\,g^{-1}$)	K_2 ($g\,g^{-1}\,min^{-1}$)	R^2
5.37	0.297	0.91	6.37	5.6×10^{-2}	0.99

Table 3
Physical properties of various types of experimental oils.

Experimental oil	Density at 25 °C (g/cm^3)	Viscosity at 25 °C (cP)	Surface tension (mN/m)
Diesel Oil	0.835	6.5	12.8
Engine Oil	0.890	61.2	31.0
Olive Oil	0.905	34.1	32
Hexadacane	0.770	2.6	27.47
Vegetable Oil	0.910	32.3	14.3
Decane	0.730	0.859	23.83
Toluene	0.867	0.56	28.52

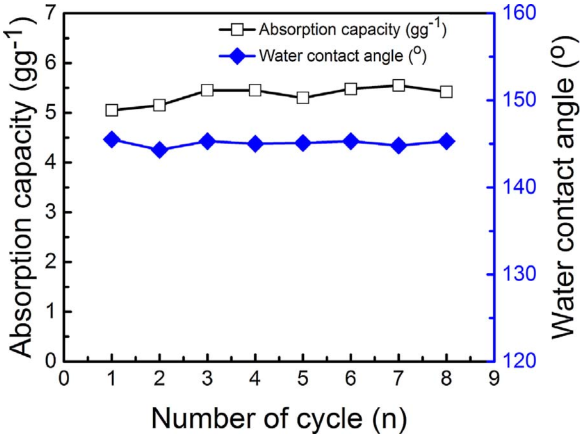

Fig. 11. Water contact angle and oil-absorption capacity of the modified MOPPs after different water-oil separation cycles.

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right) \tag{2}$$

Where q_t and q_e are the amounts of oil sorbed at time t (s) and at equilibrium, respectively, in g^{-1}. k_1 is the pseudo-first-order rate constant (min^{-1}) and k_2 is the pseudo-second-order rate constant (min^{-1}). The slope and intercepts of the plot ln (q_e-q_t) versus t (using Eq. (1)) were used to determine k_1(min^{-1}) and theoretical value of q_e.

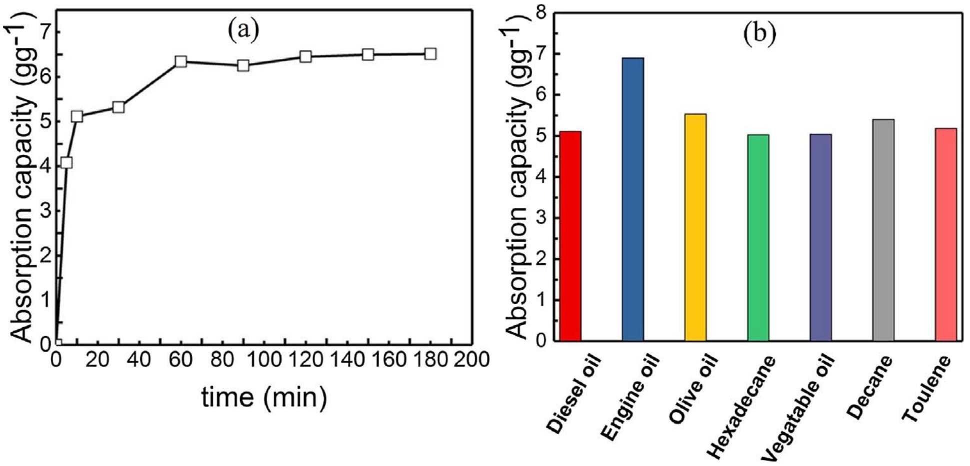

Fig. 10. (a) Oil-absorption capacity (Q) for the PDMS modified MOPPs as a function of removal time and (b) absorption capacities of the modified MOPPs for different oils and organic solvents in terms of weight of the particles.

Table 4
Comparative study of absorption capacity of diesel oil of different absorbents:.

Absorbent	Feedstock	Technique used	Absorption capacity (g/g)	References
Yellow horn shell residues treated by ionic liquid	Yellow horn shell, Ionic liquid	Microwave irradiation	0.39–0.61	[23]
Fe_3O_4 coated with PS	Fe_3O_4, Styrene	Emulsion polymerisation	3	[46]
Fe_3O_4@poly (St/DVB) modified with poly (MMA/St/DVB)	Fe_3O_4, Poly (styrene, divinylbenzene), Poly (methyl methacrylate/styrene/divinylbenzene)	Emulsion polymerisation, secondary polymerisation	3.63	[51]
Magnetic Silica modified with vinyl-tri-methoxy-silane	Fe_3O_4, Tetraethylorthosilicate, vinyltrimethoxysilane	Sol-gel	3.78	[52]
Fe_3O_4/PS composites with a rough surface	Fe_3O_4, Styrene, divinylbenzene	Solvent thermal, emulsion polymerisation	2.49	[53]
Magnetic orange peel modified with PDMS	OPPs, Fe_3O_4, PDMS	Co-precipitation, Dip coating	5.11	This study

Similarly, the rate constant k_2 and theoretical value of q_e were calculated from slope and intercept of the linear plot of t/q_t against t (using Eq. (2)). The values of these kinetic parameters (k_1, k_2 and q_e) and regression coefficient (R^2) of both models for oil sorption on MOPPs were listed in Table 2. From the Table 2, it can be seen that the theoretical values (q_e) of the both kinetic models are not showing a big difference from the experimental value. However, pseudo-second-order kinetic model resulted in a higher regression coefficient value ($R^2 = 0.99$) as compared to the pseudo-first-order model ($R^2 = 0.91$). Therefore, the pseudo-second-order kinetic model was more suitable for describing the sorption of oil on MOPPs. A similar observation has been reported earlier for separation diesel oil using magnetic polyaniline nanocomposite [50].

Oil-absorption capacity was also examined for different oils and organic solvents as shown in Fig. 10(b).

The maximum absorption capacities of MOPPs for decane, diesel oil, engine oil, hexadecane, olive oil, toluene, vegetable oil were 5.4, 5.11, 6.905, 5.03, 5.53, 5.18 and 5.04 g/g, respectively. It can be seen that the modified MOPPs exhibited highest oil-absorption capacity of 6.905 g/g for engine oil due to its high viscosity. The characteristics of the experimental oils and organic solvent based on density, viscosity and surface tension is shown in Table 3. As the viscosity of the oil increases, the adherence of oil to the surface of the absorbent also increases leading to higher oil-absorbing capacity. As a result, oil can be effectively and selectively absorbed by the absorbent particles making them an ideal candidate for oil-water separation through absorbent material.

3.5. Regeneration study

The regeneration cycles of the absorbent material in oil-water separation have a compelling effect on the operating cost. Although the oil-absorption capacity of porous absorbent materials is high due to the capillary forces [51], they have the difficulty of completely removing the absorbed oil from the pore sites, and thus reduces the availability of possible sites for oil-absorption for repeated use and thus significantly affects the recyclability of the absorbents. However, the regeneration of oil-absorbed modified MOPPs was quite easier in comparison to the typical porous materials. The oil-absorbed modified MOPPs could be economically regenerated by ultrasonically washing in ethanol for 10 min and drying in an oven for 1 h at 120 °C. The relationship between oil-absorption capacity, water contact angle and the number of cycles of the regenerated material is shown in Fig. 11. The regenerated particles exhibited remarkable recyclability in the removal of diesel oil from water.

The oil absorption capacity and water contact angle of the absorbent particles were unchanged even after the 8th cycle of regeneration. Even after the 8th cycle of regeneration, the oil-absorption capacity of the modified MOPPs was 5.42 g/g for the diesel oil, which was higher than most of the absorbent as illustrated in Table 4. Also, no major change in the water contact angle was observed even after the 8th cycle of regeneration of the absorbent particles, and it remained over 144°. These results suggested that the developed absorbent material possess excellent reusability and chemical stability. In addition, the as-prepared particle has other advantages like low cost, environment friendliness, scalable fabrication, operational convenience, high selectivity for oil, corrosive resistance, thermal stability, simple regeneration method and great recyclability. Based on the above remarkable properties of the prepared PDMS modified MOPPS, it inferred that the material reported in this work has immense potential to solve oil-spillage problems.

4. Conclusions

In summary, the present work introduces a simple and environment friendly method for the fast and facile removal of oil from the water surface with the help of highly hydrophobic and superoleophilic magnetic orange peel particles under external magnetic field. These modified MOPPs with properties like low cost, scalable fabrication, environment friendliness, unsinkability, operational convenience, high selectivity for oil, thermal stability, corrosive resistance, simple regeneration method and excellent recyclability were synthesized by modifying Fe_3O_4 coated orange peel particle with low surface energy PDMS layers. The modified MOPPs showed an excellent oil-absorption capacity up to 5.11 and 6.90 times its original weight for diesel oil and engine oil respectively, along with good stability in corrosive media for a long time. The oil-absorption capacity and highly hydrophobic property were intact even after eight cycles of regeneration, making the modified MOPPs suitable for practical applications. Hence, this kind of low-cost magnetic absorbent might be promising substitute material in solving the problem of oil spills as well as improving the utility value of the natural waste resource.

Acknowledgements-

This work is supported by the Science and Engineering research board (SERB), Department of Science and Technology (DST), and Council of Scientific and Industrial Research (CSIR) Government of India. AKS gratefully acknowledges Science and Engineering Research Board (SERB) for the SERB-National Post-Doctoral Fellowship (PDF/2016/002638).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jece.2017.09.060.

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