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DEVELOPING SUPERHYDROPHOBIC/SUPEROLEOPHILIC POLYURETHANE SPONGE BASED ON FE_3O_4 PARTICLES FOR OIL - WATER SEPARATION

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Summary

Recently, the issue of oil and organic spills, driven by a growing human population, has become a significant concern globally, including in Vietnam. Researchers are increasingly focused on developing materials that can selectively absorb oils and organic solvents while repelling water. This project aimed to develop an oil-absorbing material by integrating stearic acid-modified Fe_3O_4 or Fe_3O_4 particles into a polyurethane (PU) foam base. The results demonstrated that the modified PU sponge exhibited superhydrophobic properties, with a water contact angle exceeding 150°, and superoleophilic characteristics, with an oil contact angle close to zero. With excellent oil selectivity, the modified PU sponge achieved diesel oil absorption capacity ranging from 44 to 53 times its weight, depending on the particle loading concentration.

Key words: Oil/water separation, superhydrophobic sponge, superoleophilic, stearic acid-modified Fe_3O_4 particles.

1. Introduction

Nowadays, the increasing demand for fossil fuels has led to the expansion of fossil fuel infrastructures, resulting in more oil spills and pollutant leaks. Consequently, the removal of oil, organic solvents, and gasoline from water has garnered significant attention over the years [1]. Various techniques have been employed to separate oil from water, including physical methods such as skimmers, booms, meshes, barriers, and absorbents; chemical methods using dispersants and solidifiers; and biological methods [2]. Although these traditional methods are easy to operate, they still have the disadvantages of low separation efficiency and low recycling rates in oily wastewater treatment. Therefore, the development of new oil - water separation materials with higher efficiency and higher recycling rates has become a hot trend in recent years [3, 4].

Inspired by the superhydrophobic/superoleophilic phenomena observed on lotus leaves, which have water contact angles greater than 150° and oil contact angles less than 10°, many researchers have created artificial superhydrophobic/superoleophilic surfaces for a wide range of applications, such as anti-corrosion coatings [5], anti-wax treatments [6], self-cleaning mechanisms [7], anti-fog solutions [8], anti-adhesion technologies, and water - oil separation [9]. To create superhydrophobic surfaces, it is necessary to combine surface roughness or structure with decreased surface energy [10].

Regarding absorbents, it is noted that conventional absorbents can absorb both water and oil, not just oil. To enhance their specificity, scientists have proposed transforming traditional absorbents from superhydrophilic to superhydrophobic through chemical modification and structural introduction. These superhydrophobic oil sorbents are the most effective remediation method for large oil spills compared to dispersants and skimmer devices. Therefore, significant research efforts have been directed toward the fabrication of superhydrophobic/superoleophilic materials for the separation of oil water mixtures. In general, superhydrophobic/superoleophilic sponges are fabricated using a two-step procedure that increases the surface roughness and reduces the surface energy of the sponge surfaces. Firstly, the surface roughness can be increased by coating sponge surfaces

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with micro/nano structures such as micro/nano particles (e.g., graphene, metal, metal oxides). In the 2nd step, the modified sponge with low surface energy materials is converted from superhydrophilic to superhydrophobic. Low surface energy materials can include fatty acids [11], organosilanes [12], polydimethylsiloxane [14], and graphene [15].

In this paper, we report a simple method to create a smart sponge with magnetic properties. It is easy to make in the laboratory using basic tools and inexpensive common chemicals.

2. Experiment

2.1. Materials

Stearic acid, high-density polyethylene, toluene, ethanol, acetone, H_2SO_4, NaOH, $FeSO_4.7H_2O$, $FeCl_3.6H_2O$ and NaOH are supplied by Xilong company (China), diesel oil is from BSR company (Vietnam).

2.2. Preparation of superhydrophobic steel surface

2.2.1. Formation of Fe_3O_4 powder

800 ml of 0.1 M NaOH is slowly added to a mixture of 100 ml of 0.1 M Fe^{2+} and 200 ml of 0.1 M Fe^{3+} with vigorous stirring for 15 minutes. After centrifugal filtration, the Fe_3O_4 powders are rinsed with water and dried in the oven at 60°C.

2.2.2. Preparation of superhydrophobic Fe_3O_4 powder

2 g of Fe_3O_4 was added to 50 ml of ethanol containing 0.15 g of stearic acid. This mixture was continuously shaken for 3 hours. After the reaction, the particles were rinsed with ethanol 3 times, shaking for 5 minutes each time. Finally, the stearic acid-coated Fe_3O_4 particles (AS-Fe_3O_4) were obtained by centrifugal filtration and dried in the oven at 60°C. The mechanism of AS modification is shown in Figure 1. During the process, AS contains -COOH groups, which react with the surface -OH groups of the Fe_3O_4 particles (due to the presence of a trace layer of water surrounding the particles). This reaction leads to the attachment of $-CH_3$ groups onto the Fe_3O_4 particles.

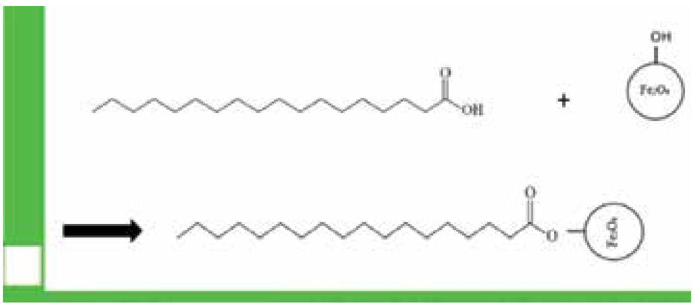


***Figure 1.** Mechanism of stearic acid modification on the Fe_3O_4 particle surface.*

2.2.3. Preparation of superhydrophobic polyurethane sponge

Typically, a polyurethane (PU) sponge (2 × 2 × 2 cm^3) was immersed in 15 ml of ethanol containing different concentrations ranging from 5 mg to 250 mg of Fe_3O_4 particles with or without chemical modification and shaken for 15 minutes. The Fe_3O_4-coated PU sponge was dried before being coated with HDPE or PDMS according to the procedures below.

For HDPE coating: The Fe_3O_4-coated sponge was immersed in 25 ml of toluene containing 2.5 g of high-density polyethylene (HDPE) for 5 minutes. Then, the modified PU sponge was dried in an oven at 50°C for 6 hours.

For PDMS coating: The Fe_3O_4-coated sponge was immediately dipped in 25 ml of ethyl acetate containing 0.25 g of PDMS and 0.025 g of curing agent for 10 minutes, then dried in the hood for about 12 hours.

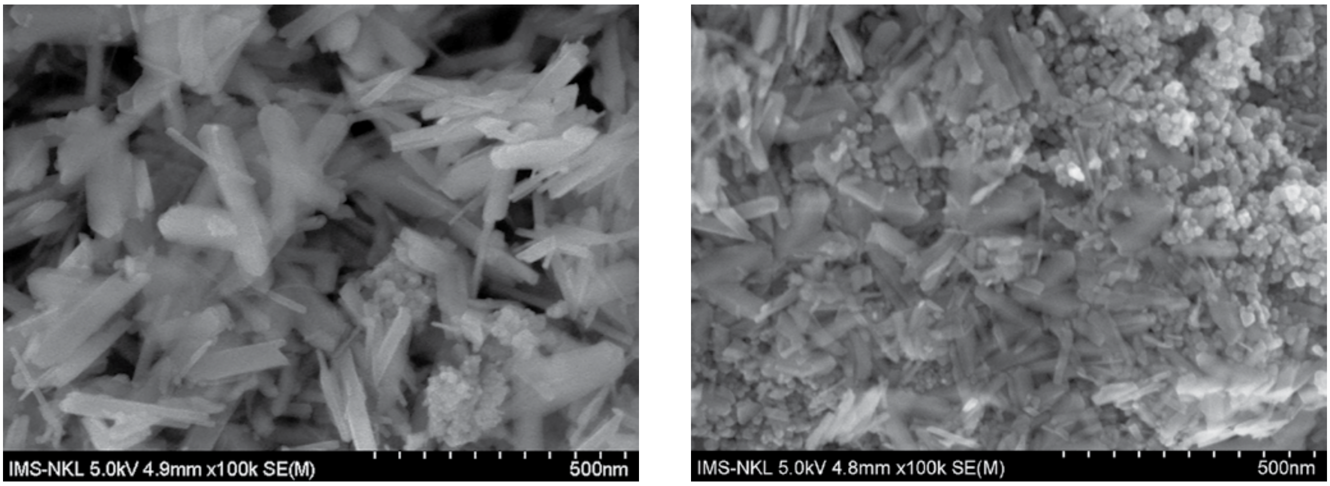
2.2.4. Materials characterisation

The morphology of Fe_3O_4 particles was characterised using a scanning electron microscopy (SEM, JEOL 7600F with EDS, Oxford Instruments). The FTIR methods were used to confirm the successful grafting of chemical modifications onto the Fe_3O_4 particle surface. The wetting properties of particles and PU surface were evaluated by measuring the static contact angle of water using an OCA-data physics instrument at three different positions on each surface, with a 5 µL distilled water droplet. Specifically, the powder Fe_3O_4 particles will be deposited onto a glass slide. Then, a 5 µL distilled water droplet will be placed on top, and the contact angle will be measured.

3. Results and discussion

3.1. Materials characterisation

Figure 2 illustrates the SEM images of pristine (Figure 2a) and chemically modified Fe_3O_4 particles with stearic acid (Figure 2b). In comparison to unmodified Fe_3O_4 particles, no thin chemical coating around the particles can be observed; the particles retain the same spin-like shape after modification. This indicates that the modification process did not



(a) (b)

Figure 2. *SEM images of pristine Fe_3O_4 (a) and (b) chemical modified-Fe_3O_4 particles with stearic acid. Insets are photos of corresponding water droplets.*

significantly damage the morphology of the particles. The insets of Figure 2 are photos of corresponding water droplets, which confirm that the wettability of the Fe_3O_4 surface particles changed from superhydrophilic to hydrophobic properties

Stearic acid is known for its composition of a non-polar, hydrophobic alkane chain and a hydrophilic carboxyl group. When Fe_3O_4 particles are combined with stearic acid, the -OH groups on the Fe_3O_4 surface react with the -COOH group of the stearic acid. This reaction results in the formation of a hydrophobic layer, denoted as $–(CH_2)_n$-CH_3, on the Fe_3O_4 particle surface.

The FTIR spectra of unmodified Fe_3O_4 particles (shown by the gray line in Figure 3) reveal a strong absorption peak at 3,412 cm^{-1}, indicating O-H stretching vibrations. This suggests that the surface of the pristine Fe_3O_4 particles contains numerous O-H groups, making them hydrophilic. A peak at 557 cm^{-1}, corresponding to the Fe-O skeleton, is also present and appears with lower intensity in the FTIR spectrum of Fe_3O_4 particles modified with stearic acid (blue line in Figure 3). In the modified spectrum, vibration absorption peaks at 1,794 cm^{-1}, 1,769 cm^{-1}, and 1,622 cm^{-1} are attributed to C=O bonds. Additionally, peaks at 1,447 cm^{-1} and 1,381 cm^{-1} correspond to C-H bonds of the $-CH_3$ group and peaks at 1,128 cm^{-1} and 1,048 cm^{-1} correspond to C-O bonds of the -COO group. This demonstrates that stearic acid can chemically bond to the surface of Fe_3O_4, altering its properties [11, 16, 17].

After modification, Fe_3O_4 particles transform from superhydrophilic (contact angle ~ 0°) to hydrophobic (contact angle ~ 135°C) as shown in Figure 4.

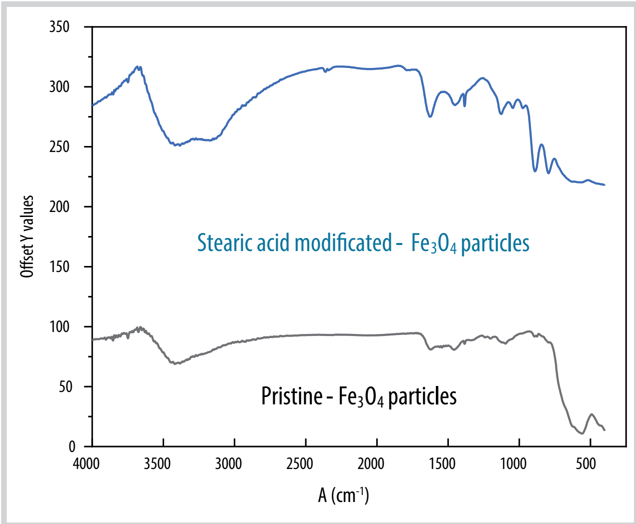


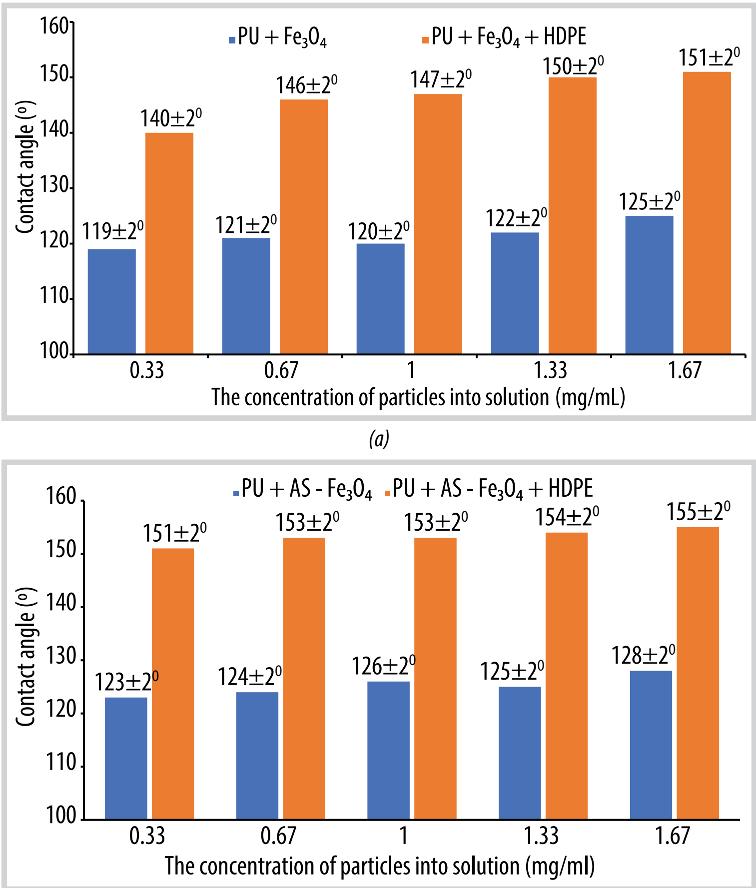
Figure 3. *FTIR spectra of as-prepared Fe_3O_4 particles, stearic acid-modified Fe_3O_4 particles.*

3.2. Wettability of modified sponge

In this section, the wettability of the sponge, both with and without modification, was characterised by contact angle measurement. The reason for introducing Fe_3O_4 particles into the PU sponge is to increase the robustness of the surface and integrate magnetic properties into the sponge. Figure 5 shows the water contact angle values on the pristine sponge modified with Fe_3O_4 particles (Figure 5a) and AS-Fe_3O_4 particles (Figure 5b), both of which were then coated with HDPE. It is noted that the PU sponge coated with Fe_3O_4 at different concentrations was hydrophobic, with a water contact angle of about 120° ± 2 (Figure 5a), while the sponge coated with AS-Fe_3O_4 particles became more hydrophobic, with a water contact angle of about 125° ± 2 at the same concentration. Moreover, adding HDPE coating to the PU sponge

(a) (b)

Figure 4. *Image of water droplet on Fe_3O_4 powder before (a) and after (b) modification.*



(b)

Figure 5. *Water contact angle on the sponge with Fe_3O_4 coating (blue column) and HDPE coating (orange column) (a) and with AS-Fe_3O_4 coating (blue column) and HDPE coating (orange column) (b) vs the concentration particle solution (mg/ml).*

(a) (b)

Figure 6. *Photograph of sponge used to test the hydrophobic and oleophilic behavior: (a) Sponge coated with modified HDPE-Fe_3O_4 coating (64%) vs. pristine sponge on the water surface; (b) Water droplet and diesel oil droplet on the sponge coated with modified HDPE-Fe_3O_4 coating (inset shows the corresponding water contact angle).*

containing Fe_3O_4 particles or AS-Fe_3O_4 particles further increased its hydrophobicity.

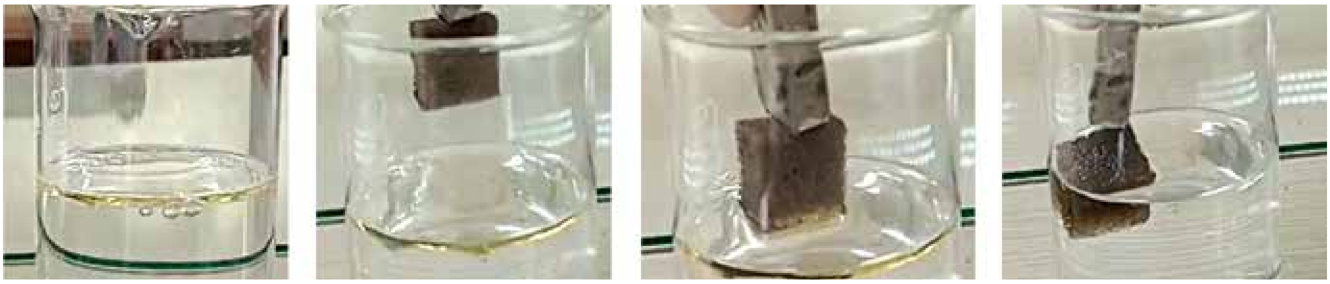
In the case of the Fe_3O_4-coated PU sponge with HDPE, the surface became superhydrophobic with a contact angle of more than 150° when the concentration of particles was greater than 1.33 mg/ml. However, in the case of the PU sponge coated with AS-Fe_3O_4 and HDPE, the surface became superhydrophobic at lower particle concentrations (> 0.33 mg/ml).

3.3. Superhydrophobic and oleophilic sponge for oil separation

To compare the hydrophobic properties between the pristine sponge and the modified sponge, both samples were deposited on the water surface, as shown in Figure 5a. The results show that the sponge coated with modified Fe_3O_4 particles floats on the surface of water, whereas the pristine sponge completely submerges. This is because the sponge becomes superhydrophobic with a contact angle of more than 152° ± 2 degrees after being coated with modified Fe_3O_4 particles. On the other hand, when a diesel oil droplet is deposited on the superhydrophobic sponge, the diesel oil completely spreads with a contact angle close to zero (contact angle ~ 0°), as shown in Figure 6b. The result is opposite with water droplets, which stay on the surface of the sponge due to the superhydrophobic properties with a contact angle > 150°. Therefore, after coating with Fe_3O_4 particles or modified Fe_3O_4 particles, the sponge becomes both superhydrophobic and superoleophilic. This implies that the modified sponge exhibits high selectivity for oil/water separation.

The oil/water separation experiment using the magnetic PU sponge was performed as follows. As shown in Figure 7, manipulated by a magnet bar, the magnetic PU sponge approached the oil/water mixture (diesel oil) and selectively and rapidly absorbed the floating oil on the water surface, leaving only water behind.

To test the capability of the modified



(a) (b) (c) (d)

***Figure 7.** The sequence image of oil/water separation experiment under magnetic actuation.*

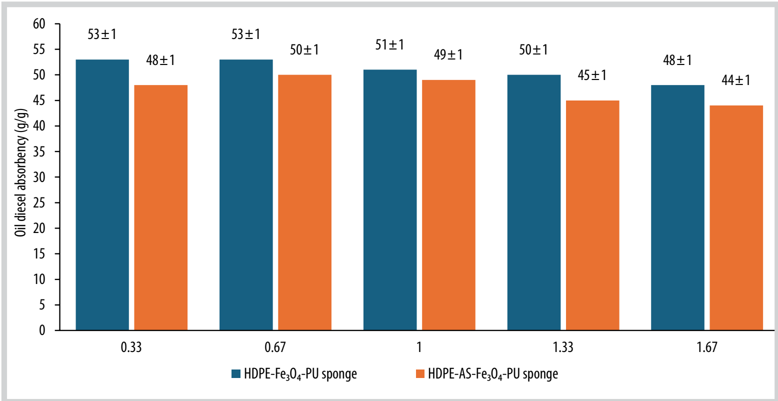


***Figure 8.** Oil mass absorption on modified PU sponge: with Fe_3O_4 particle and HDPE (HDPE-Fe_3O_4-PU sponge - blue column, with AS-Fe_3O_4 particles and HDPE sponge coating (HDPE-AS-Fe_3O_4-PU sponge - orange column).*

sponge to absorb oil from the water surface, the sample was placed into a beaker containing oil. Then, the modified sponge was added. To calculate the absorption capacity of the sponge, the weight of the sponge before and after absorbing the oil was measured as m_0 and m_1, respectively. The absorption capacity was calculated using the following equation [9], and the result of measurement is shown in Figure 8.

$$K = \frac{m_1 - m_0}{m_0} \quad [9]$$

Figure 8 shows that at the same particle coating level, the modified PU sponge with pristine Fe_3O_4 particles and an HDPE coating (HDPE-Fe_3O_4-PU) exhibits slightly higher diesel oil absorption, averaging 51 g/g, compared to the sponge with AS- Fe_3O_4 particles and an HDPE coating (HDPE-AS- Fe_3O_4-PU), which averages 46 g/g. However, the oil selectivity of the HDPE-AS-Fe_3O_4-PU sponge is marginally better than that of the HDPE-Fe_3O_4-PU sponge, likely due to its increased hydrophobicity, as demonstrated in Figure 5. Moreover, this sponge can be reused up to 10 times without scattering or deforming. To reuse the product, the process is straightforward: simply extract the oil by squeezing, and the product is ready for subsequent use.

The mass of the HDPE-Fe_3O_4-PU sponge (2 x 2 cm) is about 0.2 g. After the first use as a diesel oil (DO, d = 0.82 g/ml) absorbent, the volume of absorbed DO oil is about 12.44 ml. Therefore, a sponge with dimensions of 41 x 46 cm could absorb approximately 5.3 l of oil for the first use. In comparison, the Spilfyter Oil-Only Absorbent Pad, commonly used by most oil companies in Vietnam, can absorb 1.2 l of oil per use (once only). This research product shows great promise for oil absorption, likely due to its 3D structure, high oil absorption capacity, and high selectivity, with superior hydrophobic properties and a contact angle greater than 150°.

4. Conclusion

In summary, we fabricated a superhydrophobic PU sponge with magnetic properties through basic tools and inexpensive common chemicals. The smart PU sponge exhibited high absorption capacity and good oil selectivity. Therefore, this superhydrophobic and magnetic PU sponge has a high potential application in immiscible oil/water separation, such as in oil extraction or oil spill cleanup.

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