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PREPARATION OF SUPERHYDROPHOBIC MAGNETIC BIOMASS FOR OIL/WATER SEPARATION

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In order to explore the materials that can deal with oil spill and organic matter leakage in the sea, this study selected wood shavings and straw and other agricultural and forestry wastes to prepare adsorbents and used Fe_3O_4 and beeswax to modify them. The Fe_3O_4/beeswax coating enabled the biomass to be superhydrophobic with the water contact angle higher than 154 °. The separation of various oil/water mixtures with high purity was acquired using the prepared biomass. These natural fiber materials have the advantages of renewable, degradable, low cost and simple preparation methods. The modified material obtained has good hydrophobicity, durability and high temperature resistance, and can efficiently separate oil from oil-water mixture.

Keywords: superhydrophobic; beeswax; oil/water separation

1. Introduction

Recently, with the rapid development of the economy, human demand for energy is also increasing, and the amount of oil exploitation on land has not met the needs of production. However, the extraction and transportation process of offshore oil fields is more difficult, and the problem of oil spill pollution is becoming more and more serious [1]. The oil absorption method refers to the use of ultra-wettability of lipophilicity material, so that the oil sticks to the material for recovery, has the advantages of simple operation and low energy consumption. The adsorbent materials used to clean up oil spills fall into three main categories: (a) synthetic polymer materials, such as polypropylene[2], polyurethane[3], and rubber[4]; (b) Inorganic mineral materials, such as clay[5], zeolite[6], copper mesh[7], diatomite[8] and perlite[9]; (c) Natural fibre materials, such as bagasse[10], rice husk[11], sawdust[12], cotton[13], straw[14] and sponges[15].

As a major agricultural country, China produces hundreds of millions of tons of agricultural and forestry waste every year. Traditional incineration treatment can cause serious environmental pollution and waste of biomass energy. Therefore, the energy conversion of agricultural and forestry waste is one of the current research hotspots. Agricultural and forestry waste mainly comes from straw,

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sawdust and bark produced in the process of agricultural and forestry harvest and processing. Straw and sawdust contain a large amount of cellulose, hemicellulose and lignocellulose. Lignocellulose has the advantages of renewability, degradability, large pore size and low cost. Therefore, these natural fiber materials are one of the excellent materials for the preparation of adsorption materials. In fact, However, there are hydrophilic hydroxyl groups on the surface of unmodified biomass materials, which can absorb water and oil at the same time [16]. Unmodified materials not only have low adsorption capacity, but also easily lead to secondary pollution. Researchers have used the Young equation and the Cassie-Wenzel model to explain the lotus leaf effect in nature [17]. In other words, the self-cleaning effects of lotus leaves, cicada wings, gecko feet and butterfly wings are all due to the synergistic effect of micro-nano composite structures and low surface energy on their surfaces. After modification of micro and nano-scale rough structure and low surface energy, the surface of raw materials can be superhydrophobicity [18]. The superhydrophobic material has the characteristics of water contact angle greater than 150° and rolling angle less than 10 °, which can adsorb spilled oil on the surface of the material and effectively separate the oil/water mixture. The main preparation methods of superhydrophobic materials include spraying [19], electrospinning [20], impregnation [21], vapor deposition [22], chemical etching and photoetching [23]. Most of these methods require strict conditions and expensive reagents, which limits the application of superhydrophobic materials. Therefore, using cheap and easily available natural fiber materials and producing environmentally friendly superhydrophobic materials is a feasible way to achieve green development.

In this experiment, the physical adsorption method was used, and the materials selected were maize straw, sawdust, wheat straw and corncob with porous structure. Beeswax was used as a hydrophobic modifier to prepare reusable adsorption materials with super hydrophobic properties, which can be effectively applied to the recovery of different oils and organic solvents.

2. Materials and Methods

2.1 Materials

Maize straw (MS), sawdust (SW), wheat straw (WS) and corncob (COB) were purchased from a local market. Hydroxy acrylic resin was purchased from Jining Baiyi Chemical Co., LTD. Fe_3O_4 was purchased from Aladdin Chemical Company. Xylene, carbon tetrachloride, petroleum ether, normal hexane and anhydrous ethanol were purchased from Shanghai Macklin Biochemical Co., Ltd. Beeswax (BW), corn oil soybean oil and lube oil were obtained locally. All reagents were used without further purification.

2.2 Methods

The biomass samples were pretreated with anhydrous ethanol and dried in the oven in advance. The biomass samples were sifted, and the sizes were between 178 μm and 250 μm. 0.5 g hydroxy acrylic resin and 50 mL xylene were mixed in a beaker thoroughly until the hydroxy acrylic resin had been completely dissolved. Then 1 g cleaned samples were added in a beaker, and the mixture was blended under ultrasonic irradiation for 10 minutes. 0.2 g beeswax and 100 mL anhydrous ethanol were mixed in a beaker on a magnetic stirrer at 75 ℃. Then beeswax was completely dissolved in anhydrous ethanol, the cleaned biomass samples were added and kept heated for 5 minutes. After cooling, the obtained particles were dried in an oven at 50 ℃ for 24 h to obtain beeswax@ samples (BW@samples).

Then the magnetic superhydrophobic biomass materials were prepared, as shown in Fig. 1. The obtained pretreated biomass material and 0.5 g Fe_3O_4 were added in a beaker under ultrasound process for 20 minutes. The vacuum filter extracts the mixture, and the obtained Fe_3O_4@sample particles were placed in the fume hood to dry for later use. The following preparation process was the same as the second step. The mixture of 0.2 g beeswax and 100 mL anhydrous ethanol were placed on a magnetic stirrer, stirred to melt the beeswax at 75 ℃. Then beeswax was completely dissolved in anhydrous ethanol, the pretreated biomass samples were added and kept heated for 5 minutes. After cooling, the obtained Fe_3O_4@sample particles were dried in an oven at 50 ℃ for 24 h to obtain BW-coated Fe_3O_4@samples.

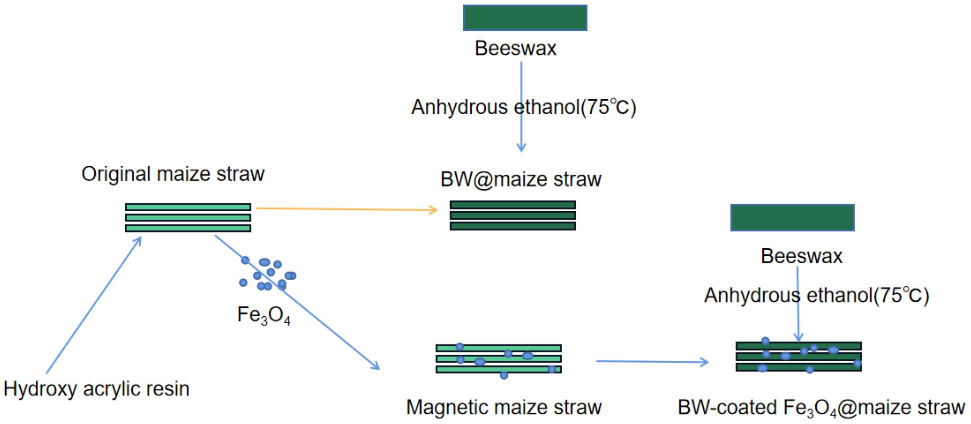

Fig. 1. Preparation process of magnetic superhydrophobic materials.

2.3 Measurement of oil-water selectivity and adsorption capacity

When measuring the oil-water selectivity of the material, the copper mesh is selected as the filter layer for separating the oil-water mixture. Carbon tetrachloride (served as heavy oil) and xylene (served as light oil) were used to simulate oil spills. 40 mL carbon tetrachloride (dyed by Sudan Ⅲ) and 40 mL deionized water (dyed by Methylene blue) were mixed in equal volume to form oil-water mixed solution of heavy oil. 40 mL of xylene (dyed by Sudan Ⅲ) and 40 mL of deionized water (dyed by Methylene blue) were mixed equally to form a light oil-water mixed solution. The adsorbent was filled in the copper mesh, and the filling layer was fixed in the gravity oil-water separation device, and the oil-water mixture was passed through the filling layer. When separating heavy oil, the separator is placed vertically. Conversely, when separating light oil, the separator should be tilted. The separation efficiency η (%) is calculated as follows: $\eta = M_2/M_1$, where M_1 and M_2 refer to the mass of oil before and after separation, respectively.

The water-in-oil emulsion was obtained by mixing 0.5 g Span 80, 1 mL deionized water and 100 mL soybean oil in a beaker and stirring the solution for 3 hours. The adsorbent was filled into the SPE column and fixed to the top and bottom of the packing using a hydrophobic sieve plate. Th oil flux (F_{oil}) was calculated using the formula: $F_{oil} = V/ST$, where V is the volume of oil obtained after separation, S is the effective area of adsorbent in SPE column, and T is the time required to complete oil-water separation. To measure the adsorption capacity of the material, 0.5 g of the adsorbent was held with the same mass of copper mesh and completely immersed into a beaker containing 50 mL of oil and organic solvents (carbon tetrachloride, xylene, corn oil, petroleum ether, n-hexane, and lubricating oil). After soaking for 30 minutes, remove the mesh from the beaker and let it sit for 10 minutes until no oil or organic solvent drips from the mesh. Subsequently, the mass of the adsorbent was weighted again by electronic analytical balance. The calculation formula of the maximum oil absorption Q (g/g) is $Q=(m_2-m_1)/m_1$. Where, m_1 is the mass (g) before oil absorption of the adsorbent and m_2 is the mass (g) after absorption of the adsorbent.

2.4 Characterization

Scanning electron microscopy (SEM, Quanta 200, FEI, USA) images were obtained on a scanning electron microscope to analyze the surface morphology of the samples. Fourier transform infrared spectroscopy (FTIR, Magna-IR 560, Thermo Nicolet, USA) was used to compare the absorption peaks of the samples to analyze the changes of surface groups. X-ray powder diffraction (XRD) showed the chemical composition of samples. The water contact angles (WCA) were measured with a 5 μL deionized water droplet by an optical contact angle measuring instrument (TST-200H, Shenzhen testing equipment CO., LED, China). All the contact angles were determined at 5 different points by averaging measurements on each sample surface.

3. Results and Discussions

3.1 Surface wettability and morphology

In order to explore the good hydrophobicity of the samples, the surface morphology of samples before and after modification was compared by SEM, as shown in Fig. 2.

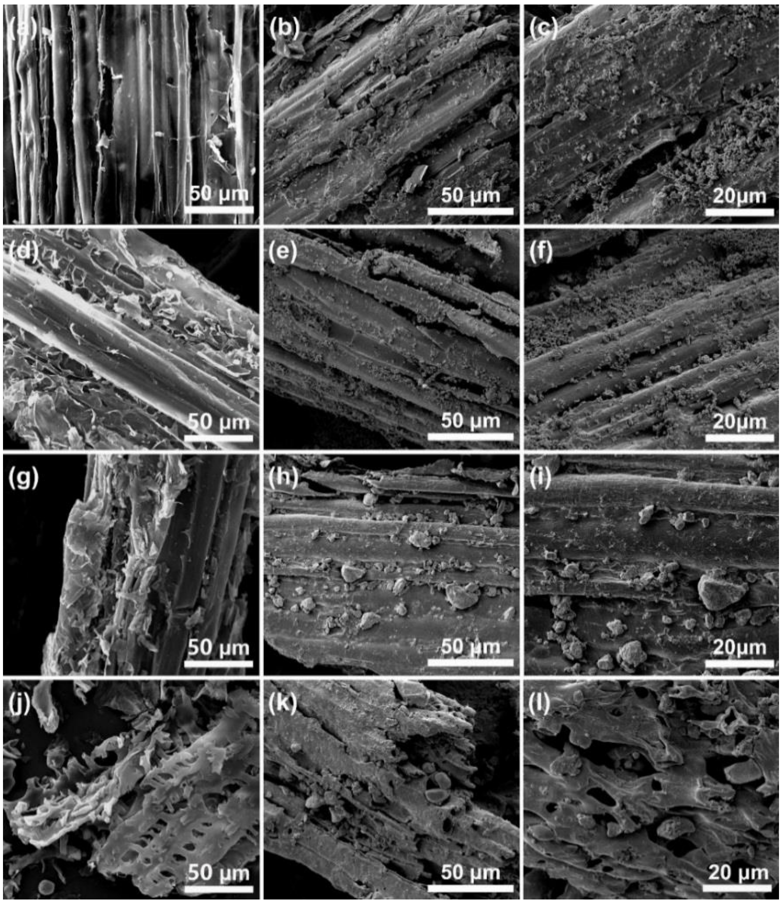

Fig. 2. SEM images of surface morphology of original and modified samples: (a), (b), (c), (d): original maize straw, original wheat straw, maize straw, sawdust, corncob; (e), (f), (g), (h): beeswax coated wheat straw, maize straw, sawdust, corncob; (i), (j), (k), (l): beeswax coated Fe_3O_4 coated wheat straw, maize straw, sawdust, corncob.

It can be clearly observed in Fig. 2 that the original wheat straw, maize straw, sawdust and corncob showed smooth surface and plicate layered structure. After the layered fiber materials were modified, the larger holes are retained, and the smaller ones are coated with beeswax to form a coating. After magnetic modification, Fe_3O_4 particles were evenly distributed on the surface of the sample, which makes the surface rough. The nano structure and beeswax layer make the surface of the materials hydrophobic. The coating prevents them from oxidizing and peeling-off and changes the gloss of the samples. Under a high-power scanning electron microscope, the coating appeared like papillary. SEM images of the biomass materials before and after modification showed that the structure of the material has not changed.

3.2 FTIR spectra analyses

The surface functional groups of the materials were probed by FTIR spectroscopy. The FTIR spectra of Fe_3O_4, the raw maize straw, BW@maize straw and BW-coated Fe_3O_4@maize straw in Fig. 3. The absorption peaks at 3429.25 cm^{-1}, 2937.43 cm^{-1}, 2860.28 cm^{-1} and 1460.04 cm^{-1} were attributed to the stretching vibration of methylene CH_2 groups of beeswax. Methylene is a hydrophobic functional group. In Fig. 3, the peak at 576.68 cm^{-1} was attributed to Fe-O vibrations, indicating that Fe_3O_4 was successfully coated on the material's surface. The absorption peak was located at 3429.25 cm^{-1}, which was attributed to the presence of hydroxyl group on the surface of the biomass material. In addition, the peak value of maize straw decreased significantly at 3429.25 cm^{-1} after beeswax modification, which proved that the number of hydrophilic hydroxyl groups were greatly decreased. This is because the surface of the material is modified by beeswax coating, and the hydrophobicity of the material surface increases accordingly. These results confirm that the material surface was modified by beeswax coating, and the hydrophobicity of the material surface increases accordingly.

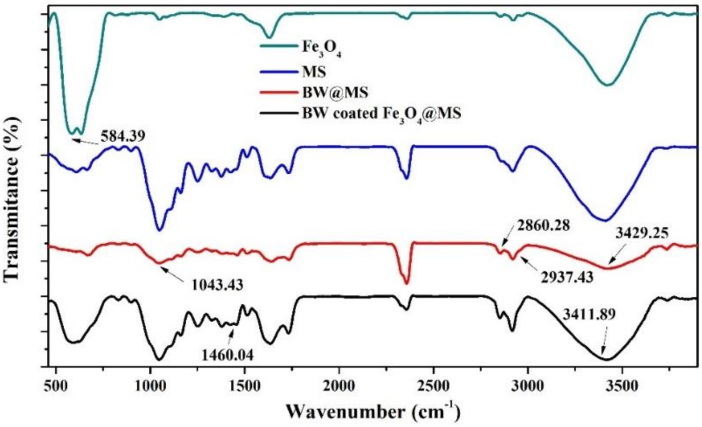

Fig. 3. FTIR spectroscopy of Fe_3O_4, the raw maize straw, BW@MS and BW-coated Fe_3O_4@MS.

3.3 X-ray diffraction spectra analyses

The X-ray diffraction spectra of the raw maize straw and BW-coated Fe_3O_4@MS were displayed in Fig. 4. The characteristic peaks appear at 30.2°, 35.5°, 43.5°, 53.7° and 57.4°, corresponding to the (220), (311), (400), (422), (511) and (440) crystal surfaces of Fe_3O_4 respectively. As can be seen from Fig. 4, Fe_3O_4 has been successfully coated on the surface of maize straw. In addition, the appropriate addition of Fe_3O_4 did not change the crystal structure of the biomass materials.

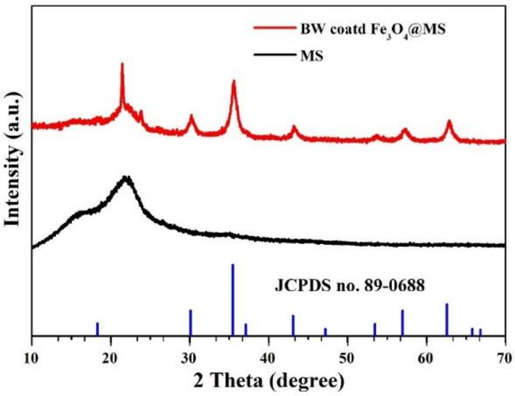

Fig. 4. XRD patterns of the raw maize straw and the BW-coated Fe_3O_4@MS.

3.4 Water contact angle measurements

Water contact angle (WCA) measurement results of BW-coated Fe_3O_4@sawdust, BW-coated Fe_3O_4@wheat straw, BW-coated Fe_3O_4@corncob and BW-coated Fe_3O_4@maize straw were shown in Fig. 5. The surface WCA values of the modified material were all greater than 150°, which fit to the superhydrophobic characteristics. Superhydrophobic characteristics can be demonstrated by tilting the material slightly and observing water droplets rolling off the surface of the material.

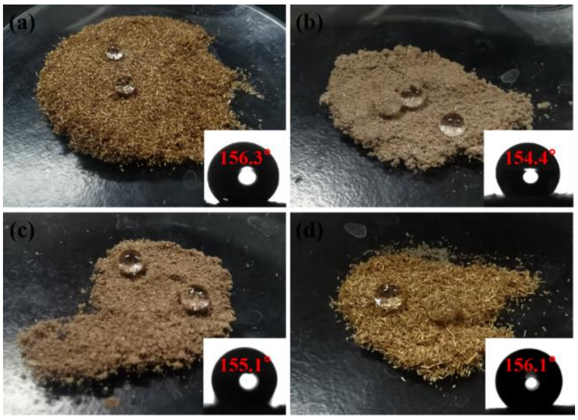

Fig. 5. (a) WCA of BW-coated Fe_3O_4@sawdust; (b) WCA of BW-coated Fe_3O_4@wheat straw; (c)BW-coated Fe_3O_4@corncob; (d)BW-coated Fe_3O_4@maize straw.

3.5 Oil/water selectivity

The oil/water mixture was separated by BW-coated Fe_3O_4 modified maize straw and observed the oil-water separation effect (Fig. 6). In this process, carbon tetrachloride density was bigger than that of water, so carbon tetrachloride enters the separation device first. Due to the superhydrophobicity of the sample, deionized water failed to pass through the sample filling layer. Fig. 6 showed that the mixture became clear when carbon tetrachloride was separated through BW-coated Fe_3O_4@MS filling layer and the solution was clarified, leaving only deionized water at the upper end of the separator (Fig. 6 (a) and (b) before separation and Fig. 6 (c) after separation).

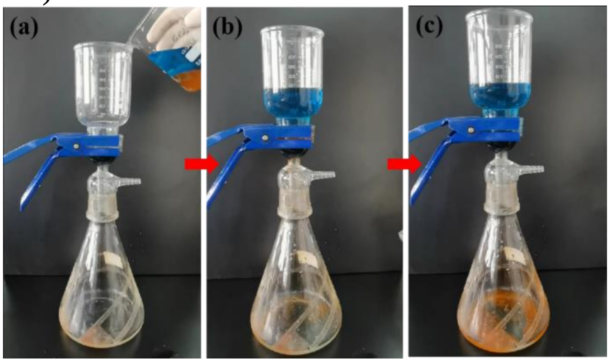

Fig. 6. Heavy oil/water separation process.

Similarly, oil/water separation experiments for xylene (light oil) were carried out (Fig. 7 (a) and (b) before separation and Fig. 7 (c) and (d) after separation). It should be noted that xylene was less dense than water and floated in the upper layers over water. Therefore, the oil/water separation device should be tilted to make xylene contact with the modified maize straw filling layer and be separated, so as to achieve oil/water separation.

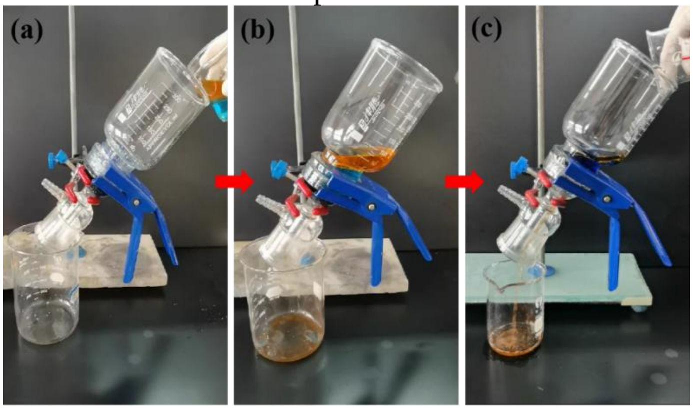

Fig. 7. Light oil/water separation process.

A solid phase extraction column was used to test the separation effect of water-in-oil emulsion (Fig. 8). 100 mL soybean oil, 1 mL deionized water and 0.5 g Span 80 were mixed by 3 hours to form a water-in-oil emulsion. Due to the action of gravity, the water-in-oil emulsion was slowly discharged through the adsorbent from the bottom exit of the SPE column, the water was separated, and the soybean oil drops into the sample bottle. When the sample bottle containing the water-in-oil emulsion was placed on the left side for comparison, it was obvious that the liquid in the right sample bottle became clear. The results indicated that BW-coated Fe_3O_4@MS could successfully separate oil and water in the water-in-oil emulsion with excellent separation performance.

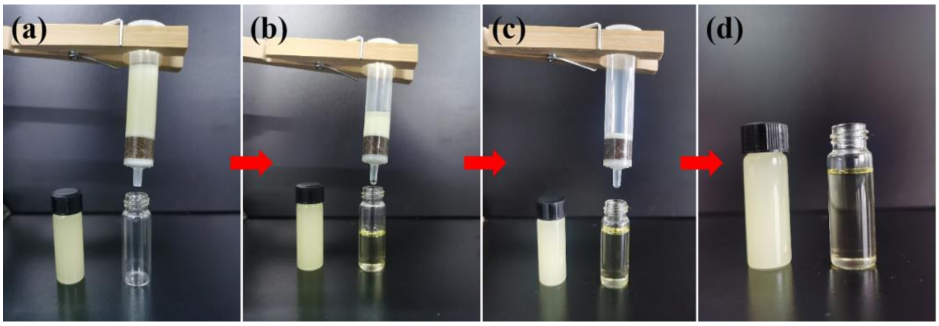

Fig. 8. The separation procedure for water-in-soy oil emulsion.

3.6 Retrievability

Fig. 9 illustrated the adsorption and recovery effects of magnetic superhydrophobic maize straw on heavy oil (Fig. 9(a)) and light oil (Fig. 9(b)). Xylene floated on the surface, carbon tetrachloride sink beneath the water layer. The prepared magnetic superhydrophobic maize straw was spread in deionized water, and the material could be observed to float evenly on the water surface, indicating that the modified maize straw showed good hydrophobic performance. The material was attracted by the magnet to collect in the direction of the oil drop. When the oil drop comes into contact with the superhydrophobic magnetic maize straw, it was quickly absorbed by the particles, realizing the recovery of the oil drop, and the water becomes clear again. In addition, after the oil-water separation experiment, the material was cleaned in petroleum ether and dried in an oven at 50 °C for 24 hours, which can be restored to use again.

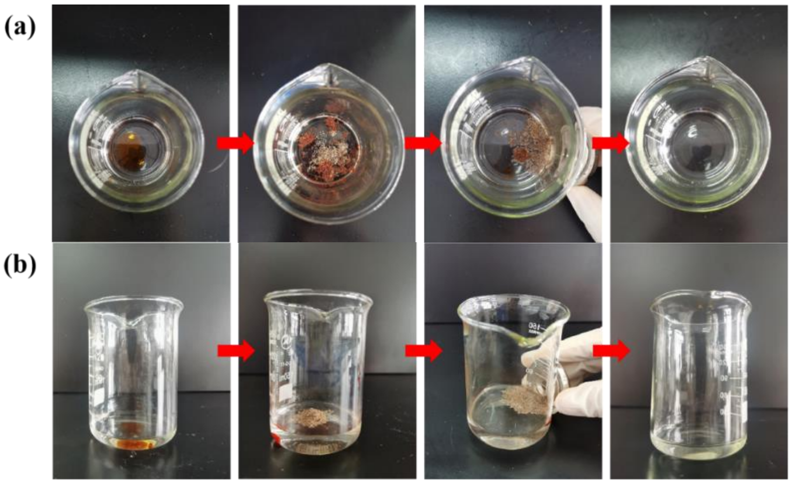

Fig. 9. (a) Heavy oil recovery process; (b) Light oil recovery process.

3.7 Oil absorption

Fig. 10 showed the adsorption of different oils and organic solvents on BW-coated Fe_3O_4@MS. The oil absorption capacity of the modified material to different oils and organic solvents can reach 7~15 times of its own weight, showing better adsorption performance. The difference in adsorption is mainly due to the volatility and viscosity of various oils and organic solvents. The reagents with high volatility and low viscosity are more likely to fall off from the adsorbent under the action of gravity, which makes the adsorption capacity decrease.

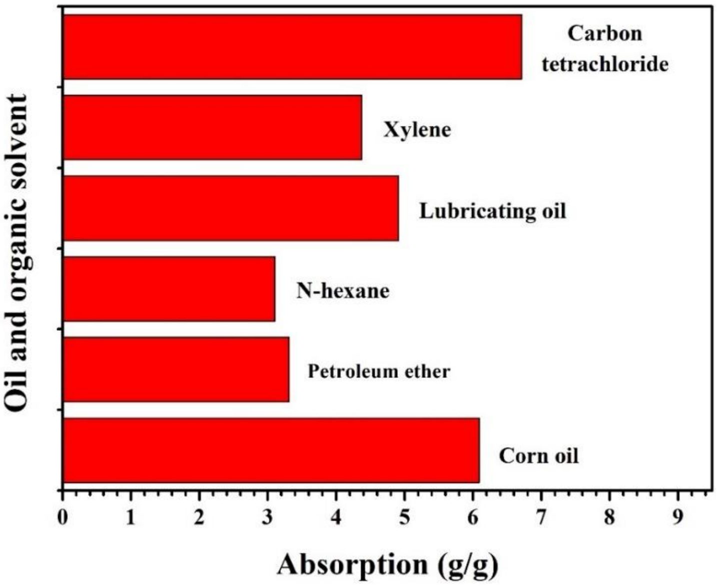

Fig. 10. Oil absorption of BW-coated Fe_3O_4@MS in different oils and organic solvents.

3.8 Durability and high temperature resistance

The durability of the modified materials was tested. The prepared materials were completely exposed to air for 30 days, during which WCA was tested every 5 days. As shown in Fig. 11a, the WCA value of the sample was still greater than 150° after 30 days. The test results show that the modified material has good durability in the air.

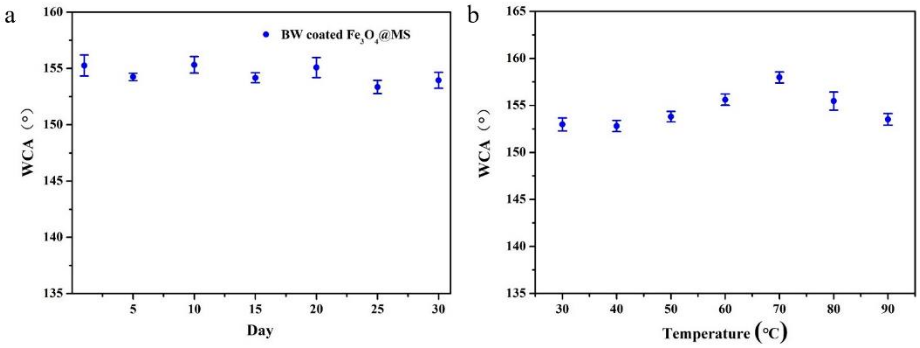

Fig. 11. a, the change of WCA value of modified material in the air; b, WCA of modified maize straw at different temperatures.

The high temperature resistance of the modified material was tested (Fig. 11b). Superhydrophobic materials should be stable at high temperatures. Therefore, the modified maize straw was dried at 30 ℃, 40 ℃, 50 ℃, 60 ℃, 70 ℃, 80 ℃ and 90 ℃ for 30 minutes, and then the material was placed on the contact angle measuring instrument to measure the WCA. Fig. 11b shows the WCA values of modified maize straw at different temperatures. According to the measurement results, the WCA of modified maize straw was greater than 150° and had no obvious change in the temperature range of 30° to 90°. These results showed that beeswax-coated-Fe_3O_4 modified maize straw has good high temperature resistance.

4. Conclusion

In summary, we modified crop waste through a two-step impregnation process. Magnetic materials with superhydrophobic properties were prepared by coating the surface with beeswax and Fe_3O_4. The coated biomass showed excellent filtration behaviors, realizing the removal and collection of organic contaminants from oil/water mixtures and emulsions. The resulting modified material had excellent adsorption capacity for different oils and organic solvents, and the oil absorption capacity could reach 7~15 times of its own weight, which could be used for oil recovery from water. After high temperature and durability tests, the material still showed good superhydrophobicity. The prepared magnetic coating provides a feasible solution for oil/water separation.

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