Preparation and oil absorption properties of magnetic melamine sponge

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Abstract. The magnetic melamine sponge (MS-Fe₃O₄) with magnetic response and high hydrophobicity was fabricated by two-step method. First, the magnetic nano-particles were fixed on the skeleton of melamine sponge (MS) using 3-hydroxytyramine hydrochloride and 1-dodecanethiol, then hydrophobicity modified with octadecyltrichlorosilane (OTS). The structures and chemical compositions of MS and MS-Fe₃O₄ were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The wettability of the sample was obtained by using contact angle analysis system. MS-Fe₃O₄ endowed with outstanding selectivity and excellent oil absorption capacities, which can be widely used in absorbing various sorts of oil. The oil absorption capacities for crude oil, diesel oil, lubricating oil, soybean oil and peanut oil were 71g/g, 51g/g, 62g/g, 54g/g, 57g/g. In addition, MS-Fe₃O₄ showed excellent recyclability which can be forecasted as an ideal candidate for oil-water separation.

1. Introduction

The serious pollution caused by the leakage of petroleum and chemical products to the marine makes the removal and collection of organic pollutants on the surface of water become an important research topic[1]. As an efficient marine oil spill disposal method, oil absorption material has been widely used in marine oil spill pollution accident emergency treatment. Moreover, melamine sponge is a kind of material with high specific surface area, low density and easy to obtain. Chen et al. modified MS by solution impregnation method. Obtained sponges exhibited super hydrophobic properties and oil absorbency reached 73g/g[2]. Zhao et al. attached graphite on the surface of the MS. The modified sample was hydrophobic and had a strong oil absorption capacity, gasoline and diesel oil absorption rate higher than 105g/g[3].

Using Fe₃O₄ nano-particles modified sponge can make the sponge magnetic, which is conducive to the use of materials in the oil absorption and recovery. Liu et al. attached the Fe₃O₄ nano-particles to the surface of the sponge by the ultrasonic method, and then hydrophobic modification with dodecafluoroheptyl-propyl-trimethoxysilane[4]. The as-prepared sponge became magnetic but the Fe₃O₄ nano-particles was easy to fall off during repeated use. Wu et al. used chemical vapor deposition of tetraethoxysilane to create a magnetic, durable and super-hydrophobic polyurethane sponge. Deposited polyurethane sponges with Fe₃O₄ nano-particles and subsequently immersed in the fluoropolymer aqueous solution to hydrophobic modified[5]. But the practical application of the material was subject to complex synthetic methods and expensive precursor limitations.
Dopamine has outstanding adhesion properties and it can adhere functional nano-particles to the surface of the material\(^6\). Thiols can achieve reliable adhesion by increasing the adhesion activity of dopamine\(^7\). In this paper, we manufacture a magnetic sponge via a simple method through dipping melamine sponge in Fe\(_3\)O\(_4\) magnetic nano-particles, 3-hydroxytyramine hydrochloride and 1-dodecanethiol under ultrasonication, and then hydrophobicity modified with OTS.

2. Materials and methods

2.1. Materials

Melamine sponge, soybean oil and peanut oil were bought in the supermarket. Diesel, crude oil and lubricating oil were purchased from local gasoline station, Tianjin, China. FeCl\(_3\)·6H\(_2\)O, FeCl\(_2\)·4H\(_2\)O, anhydrous ethanol, 1-dodecanethiol, 3-hydroxytyramine hydrochloride were obtained from Tianjin Zhiyuan Chemical Reagent Co, China. Octadecyltrichlorosilane was purchased from Beijing Huawei Chemical Reagent Co, China. Distilled water was self-made. All the chemicals were used as received.

2.2. Preparation of MS-Fe\(_3\)O\(_4\)

In a typical synthesis process, 20mL of 0.5mol/L FeCl\(_3\)·6H\(_2\)O was mixed with 20mL of 0.5mol/L FeCl\(_2\)·4H\(_2\)O, then 120mL of 0.5mol/L NH\(_3\)·H\(_2\)O solution was gradually added into the mixture. Next the mixture was sealed in the magnetic stirring apparatus, stirring at 1000 rpm/min and heated at 30°C. After the mixture was discolored, the mixture was centrifuged and washed repeatedly with distilled water to remove the supernatant. Finally, the solution was dried at 60°C for 24h, and the Fe\(_3\)O\(_4\) nano-particles were obtained after grinding.

MS was cut into pieces of 1×1×1 cm, which was thoroughly cleaned first. 10mL of anhydrous ethanol was mixed with 10mL of distilled water, then 100mg Fe\(_3\)O\(_4\) nano-particles was put into the mixture. Next, MS, 50μL of 1-dodecanethiol and 40mg 3-hydroxytyramine hydrochloride were dipped into a homogeneous suspension under ultrasonication for 20min. The mixed solution was placed in a water bath shaker under 30°C for 12h. Finally, MS was dried in an oven at 60 °C.

Dry sponge immersed in 0.5% OTS anhydrous ethanol solution for 10min. After that, the sponge was dried in a oven and the residual solvents were removed at 60 °C.

2.3. Instrumentation

The microstructures were observed through the Scanning electron microscopy (SEM) images by using the Hitachi SU3500. A Fourier transform infrared spectrometer (FTIR, Bruker Tensor-37, Germany) was used to analyze the changes of functional groups on the surface of the sample. The X-ray diffraction patterns of MS and MS-Fe\(_3\)O\(_4\) were studied by X-ray diffractometer (XRD, Nippon Science D/MAX/2500PC, Japan). The wettability of sample was obtained by using the contact angle analysis system (KRUSS DSA100, Germany).

2.4. Oil-absorption experiments

MS-Fe\(_3\)O\(_4\) was put into 500mL beakers filled with different kinds of oil for 15min to test its oil absorption capacity. Then the saturated absorption of MS-Fe\(_3\)O\(_4\) was taken out and measured the weight after without oil drops down. The absorption capacity (S\(_S\)) of MS-Fe\(_3\)O\(_4\) in different varieties of oils was calculated with the equation: S\(_S\)=\((S_{St}-S_0)/S_0\), where S\(_0\) and S\(_{St}\) are the sponge weights before and after the oil absorption.

3. Result and discussion

The forms of MS and MS-Fe\(_3\)O\(_4\) can be seen in Fig.1a. The sponge was changed from white to black, which indicated that the surface of the sponge has been modified with a large number of magnetic nano-particles attached to the surface of the skeleton. The pore structure of MS-Fe\(_3\)O\(_4\) was clearly visible. It showed that the pore structure of MS-Fe\(_3\)O\(_4\) was not blocked and the normal spatial structure was maintained after modified. Imposed an external force to press MS and MS-Fe\(_3\)O\(_4\) into the water.
As shown in Fig.1b, MS rapidly absorbed water and then immersed in water. MS-Fe₃O₄ did not absorb water and floated on the water. Tested the magnetism of MS-Fe₃O₄, as shown in Fig.1c, MS-Fe₃O₄ in the diesel oil was easily absorbed on a magnet and the sample filled with diesel was tightly adsorbed on the magnet. As shown in Fig.1d, the wettability was obtained by using the contact angle (CA). Water droplet on MS-Fe₃O₄ surface maintained the spherical shape while oil droplet was immediately absorbed by the sponge as soon as it contacted with the sponge surface. Further CA measurement showed a water CA of 146° and an oil CA of 0°.

![Fig1. Appearance and characteristic diagrams of modified sample](image1)

The structures of nano-particles and the sample were observed by SEM. SEM of the prepared nanoparticles was shown in Fig.2a. The magnetic particles appeared spherical deposits with a uniform particle size (average particle size of 200 nm) and showed good nanoscale structure. SEM of MS was shown in Fig. 2b. It can be seen that MS exhibited a three-dimensional porous structure without any attachments on the surface of the skeleton. SEM of MS with nano-particles attached was shown in Fig. 2c. Fe₃O₄ nano-particles adhered to the surface of MS skeleton under the action of 1-dodecanethiol and 3-hydroxytyramine hydrochloride. SEM of MS-Fe₃O₄ was shown in Fig.2d. While for MS-Fe₃O₄, the highly porous structure of the sponge that can provide a large surface area and a high uptake capacity is retained. Meanwhile, OTS was packed on the sponge skeleton, forming a hierarchical rough structure.

![Fig2. SEM images of the samples](image2)

Fig.3 showed the FTIR of MS and MS-Fe₃O₄. The spectrum of MS displayed prominent peaks at 995, 1340 and 1482 cm⁻¹ that were assigned to triazine ring bending. Moreover, the strong peak at 3357 cm⁻¹ was associated with N-H stretching. Strong absorption peaks corresponding of -COH in MS-Fe₃O₄ appeared at 617 cm⁻¹ and 1449 cm⁻¹; the above absorption peaks indicated the binding of the alcohol groups to the material. The peak observed at 1119 cm⁻¹ was assigned to C-N stretching on primary amine R-NH₂; the above absorption peak indicated incorporation of amino groups with the material. Peaks at 1044 cm⁻¹ was attributed to Si-O-Si antisymmetry absorption. As well as, two short peaks at 2852 and 2923 cm⁻¹ were attributed to C-H stretching. The above described the combination of silicon-containing groups and material.

The existence of Fe₃O₄ magnetic nano-particles within MS-Fe₃O₄ was further researched by XRD. As shown in Fig.4, MS-Fe₃O₄ exhibited the same characteristic peaks of Fe₃O₄ powder (JCPDS Card No. 19-0629). The above described the combination of Fe₃O₄ nano-particles and material.
As shown in Fig. 5, tested the absorption magnification of MS-Fe₃O₄ for different oils. The oil absorption capacities for crude oil, diesel oil, lubricating oil, soybean oil and peanut oil were 71.63±4.65 g/g, 51.94±1.07 g/g, 62.76±2.64 g/g, 54.35±3.01 g/g, 57.4±2.65 g/g. The oil absorption of melamine sponge mainly depended on its inner pore, so the oil absorption rate was closely related to the density and viscosity of the oil. As shown in Fig. 6, tested its repeated absorption capacity of diesel oil. The diesel oil was squeezed from the MS-Fe₃O₄ by a convenient compression method. And oils absorbed sample was directly dried in an oven at 60°C for 6 h. The process was repeated 10 times to evaluate the reusability of MS-Fe₃O₄. Oil absorption rate of MS-Fe₃O₄ was decreased from 51.94±1.07 g/g to 44.91±2.31 g/g after 10 times of repeated use. There were two main reasons for the reduction in oil absorption. First of all, even if MS-Fe₃O₄ had been squeezed and dried, its internal still had residual diesel failed to discharge. As well as MS-Fe₃O₄ repeated squeezing caused the sponge skeleton structure damage. Although oil absorption capacity of MS-Fe₃O₄ had been reduced in the cycle, it still showed outstanding recycling performance.

MS-Fe₃O₄ can be used as an oil absorption material for selective absorption of oil from water. As shown in Fig. 7, MS-Fe₃O₄ can be lightly dominated by a magnet to separate oil-water mixtures and absorbed diesel oil quickly in several seconds, indicating outstanding absorption selectivity of the sample.
4. Conclusions

MS-Fe₃O₄ with magnetic response and high hydrophobicity was fabricated by two-step method. Nano-particles and silane coating were formed and firmly attached onto sample skeleton. By forming OTS on the skeleton of MS, MS-Fe₃O₄ possessed high hydrophobicity with CA exceeding 160°. MS-Fe₃O₄ can selectively absorb oil from oil-water mixture with high oil-absorption capacity up to 51-71 times of its own weight and excellent recyclability. As well as MS-Fe₃O₄ exhibited magnetic capability and gave the excellent separation performance with high absorption capacity using an external magnetic field. In summary, MS-Fe₃O₄ was an ideal oil absorption material because of its simple preparation and easy operation.

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