ORIGINAL RESEARCH PAPER

Synthesis of $NiFe_2O_4$/sawdust nanocomposite for oil-water separation

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ABSTRACT

Magnetic nanocomposites have the ability to remove water pollutants such as dyes, oils and organic solvents. In this study, $NiFe_2O_4$/sawdust nanocomposite was synthesized for removing oil pollutants. The oil-adsorbing nanocomposite could be easily separated from water by magnet bar. The XRD results show tetragonal phase proving the composite formation. The FESEM pictures successfully reveal the growth of $NiFe_2O_4$ on the sawdust template. The FTIR bands at 422 cm^{-1} and 615 cm^{-1}correspond to the metal oxygen stretching band. VSM hysteresis loop proves the superparamagnetism of the composite. In addition contact angle depicts hydrophobic properties of the resulted nanocomposite. More importantly, as-prepared nanocomposite exhibited high oil adsorption capacity and good reusability. Our studies show easy synthesis and fast method for oil removal from water. Facile synthesis procedure, high oil adsorption capacity, fast and simple magnetic separation and reusability of nanoadsorbent are among the benefits of these composite. This approach will open up new fields of studies in polluted-water treatment.

Keywords: *Magnetic nanocomposite, Sawdust adsorbent, Reusability, Oil removal.*

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INTRODUCTION

With the growing demand for the removal of oily wastewater due to their catastrophic effects on the environment and human health, various researches have been devoted to develop simple and efficient methods for removal of oil from the aqueous surface [1-5]. So far considerable efforts have been made for oil-water separation. Among these techniques, adsorption has drawn much interest because of its low cost, easy operation, and fewer toxic byproduct [6, 7]. A broad variety of absorbents have been reported for oil removal including silica aerogels [8, 9], carbon nanotubes [10-13], sponges [14, 15], mesh films [16, 17], magnetic nanomaterials [18,19] and so on. Magnetic nanocomposites have attracted significant attention as oil adsorbing agent especially the superhydrophobic composites due to their high performance for oil-water separation.[20, 21].

To develop these kinds of magnetic materials, many investigations have been focused on combining magnetic and hydrophobic features of materials to fabricate efficient adsorbents, such as magnetic bulk materials [22], superhydrophobic sponges [23, 24], magnetic nanocomposites and magnetic polymer nanocomposites [25, 26] accidental oil spills and oily wastewater discharges

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produced during industrial activities and can have dramatic impacts on the environment. The limitations of current clean-up techniques have inspired researchers to study the application of nanotechnology for oil remediation. Previously, we reported excellent oil-removal efficiency of a reference MC252 oil using polyvinylpyrrolidone (PVP. The previous oil removal process have their own limitations including complex process, high cost and low oil adsorption capacity. Although numerous studies have been done on oil-water separation, but there is no report about applying $NiFe_2O_4$/sawdust magnetic nanocomposite for this purpose.

In this study,novel magnetic $NiFe_2O_4$/sawdust nanocomposite was fabricated for oil removal from water. The wood sawdust was modified by a hydrothermal method. As-prepared nanocomposite adsorbed oil from water quickly due to its hydrophobic and oleophilicproperties. In comparison with former oil-removal methods, as-produced composite demonstrated significant advantages, including easy synthesis procedure, fast magnetic separation and simple recycling. Therefore, our magnetic nanocomposite is a good candidate in the purification of oily wastewater.

EXPERIMENTAL

Materials

Wood sawdust was purchased from local markets in Tehran. Nickel chloride hexahydrate ($NiCl_2.6H_2O$98% Merck), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$ 99.5% Merck), Potassium nitrate (KNO_3 99% Merck), Sodium hydroxide (NaOH 99% Merck) and vinyltriethoxysilane (98% Merck) were all supplied from Merck. All reagents were analytically pure and used without further purification. Three types of oil were utilized in oil-water separation test including lubricating oil, pump oil, and frying oil.

Synthesis

The provided sawdust was rinsed with deionized water, dried at room temperature and sieved through 100 mesh screen.1 g of sawdust was added to 20 mL the aqueous solution of $FeSO_4$(0.2 M) and 20 mL of $NiCl_2$ (0.1M) and then transferred to the Teflon-lined stainless-steel autoclave and heated to 90°C for 10 h. The collected nanoparticles were washed with deionized water and dried at 90°C for 24 h. Vinyltriethoxysilane ethanol solution (95 mL anhydrous ethanol, 5 mL H_2O and 1 mL glacial acetic acid) was added to the nanoparticles and stirred for 4 h. Finally the mixture was dried at 110 ^{0}C. (Fig.1).

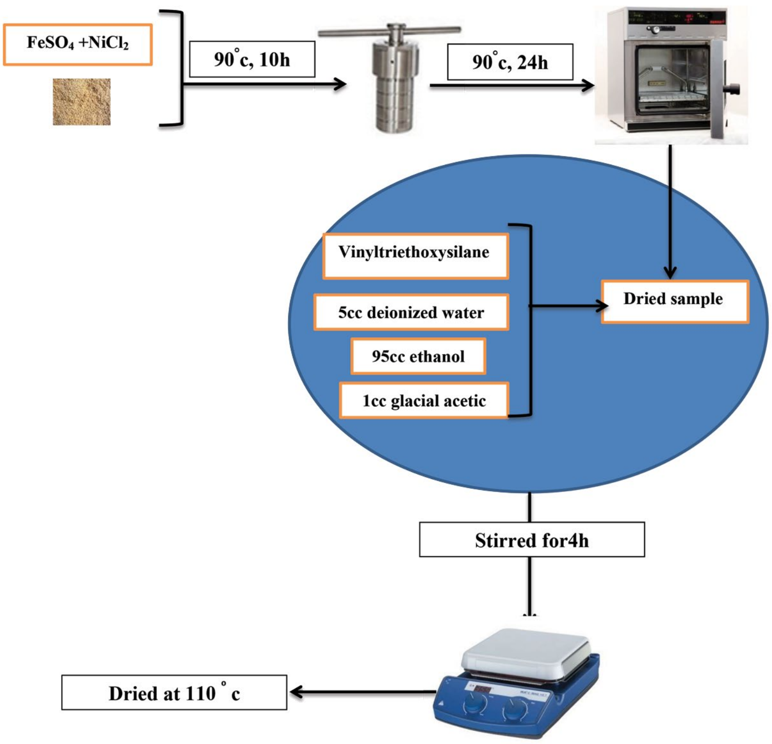

Fig. 1. Illustration synthesis procedure of $NiFe_2O_4$/sawdust nanocomposite.

Oil-water separation test

The oil adsorption capacity of $NiFe_2O_4$/sawdust magnetic nanocomposite was calculated by weight measurements according to this equation $Q= (m_2-m_1)/m_1$. In which m_1 and m_2 are the weights of modified sawdust before and after oil adsorption, respectively. Q is the oil adsorption capacity of magnetic nanocomposite. Oil-water separation test was done for three types of oil (lubricating oil, pump oil, and frying oil) at different periods of time, after 5,10, 15 and 20 minutes. Magneticnanocomposite were scattered on the surface of the oil-water mixture. Finally, by magnetic separation, the oil-adsorbing composites were easily separated from water. The adsorbed oil was removed from modified sawdust by vigorous stirring in ethanol solution for 10 min. Modified sawdust could be reused after drying in the oven at 110°C for 12 h. The adsorption/desorption cycle was repeated to investigate the reusability of the as-prepared composites.

Characterization of $NiFe_2O_4$/sawdust magnetic nanocomposite

The morphology observation of the specimen was carried out by field-emission scanning electron microscopy (FESEM, TESCAN MIRAΠ). The composition of as-prepared magnetic nanocomposite was analyzed by X-ray diffraction (XRD, PW1730 PHILIPS) and Fourier transforms Infrared spectroscopy (FTIR, Bruker Tensor27). Water contact angle was measured by a contact angle meter to investigate the surface wettability of the modified sawdust (CA, CA-EF20, Fars Eor Tech). The magnetic properties were also measured by a vibrating sample magnetometer at room temperature. (VSM, LBKFB, Meghnatis Daghigh Kavir Co).

RESULTS AND DISCUSSION

Contact angel study

To assess the hydrophobic properties of treated sawdust, the CA was measured as shown in Fig.2. There are two important factors for evaluating the hydrophobicity of a surface: the microstructure and chemical composition of a solid surface. As shown in Fig.2, when a droplet of water was dropped on the modified sawdust, the static contact angel was around 140.7. Although the value of prepared template is lower than superhydrophobic (150), it has a good capacity for adsorbing oil from water.

Fig. 2. Optical image of a water droplet on $NiFe_2O_4$/ sawdust nanocomposite.

XRD study

XRD pattern of sawdust/$NiFe_2O_4$ nanocomposite demonstrates the formation of nickel ferrite. The miller indices (111), (331), (400), (422) and (440) which matched with the JCPDS NO (00-054-0964) prove the formation of $NiFe_2O_4$ (Fig.2). The peak at 22.6° is related to the cellulose crystal structure with the miller indices of (110) [27]. The crystalline size of nanocomposite was calculated from Scherrer equation: D=kλ/βcos. In this equation D is the crystalline size, k (the shape factor) is equal to 0.8, λ is the X-ray wavelength, β is the FWHM (full width at half the maximum intensity) and is the Bragg angle. The crystallite size of nanocomposite is about 19.85nm.

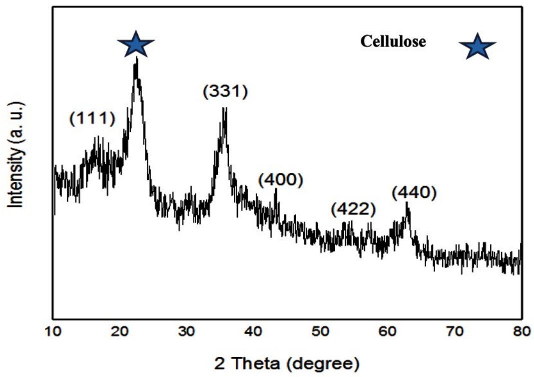

Fig. 3. XRD pattern of $NiFe_2O_4$ /Sawdust nanocomposite.

FTIR Study

The FTIR spectra of magnetic NiFe2O4/ Sawdust nanocomposite and untreated sawdust are represented in Fig.4. O-H stretch vibration, aliphatic C-H stretching vibration, and C-O stretching vibration are indicated by the bands at 3421, 2921, and 1459 cm^{-1}, respectively[28]. The bands of untreated sawdust depict cellulose(889 cm^{-1}) and hemicelluloses (1731cm^{-1} and 1039 cm^{-1})

[29].The band around 1259 cm^{-1} is corresponded to lignin[30]. After modifying the sawdust, two bands around 422 cm^{-1} and 615 cm^{-1} could be related to stretching vibrations of Fe-O bands at tetrahedron and octahedron sites, Si-O-Si bands are 1112 cm^{-1} and 1051cm^{-1} revealing the adsorption of silica substance on the surface of nanomagnetic composite[31].The band around 2899 cm^{-1} is related to aliphatic C-H stretching vibration. [32].

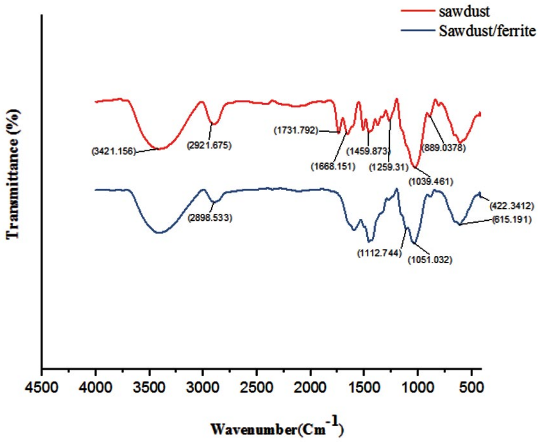

Fig. 4.FTIR spectrum of sawdust and $NiFe_2O_4$ /Sawdust nanocomposite.

FESEM study

To investigate the morphology and structure of the prepared adsorbent, FESEM micrographs were taken (Fig.5). As shown in Fig. 5a. c. e, it is obvious that the surface of untreated sawdust is clean and containing interconnected pores [33]. Fig.5b. d. f illustrates that after modification procedure, when a layer of $NiFe_2O_4$ nanoparticles was adsorbed on the substrate of sawdust template. Thus, the precipitation of these magnetic nanoparticles could enhance the surface of the matrix. Nanocomposite agglomeration is caused by magnetic $NiFe_2O_4$ phase. The average nanoparticle size is about 27.96 nm, which is in good accordance with hysteresis curve in Fig.6.

VSM study

From the curve in Fig.5, it is understandable that the treated sawdust shows superpararmagnetic behavior. The room temperature saturation magnetization (M_s) of the treated sawdust is 48.6 emu/g, while the M_s of $NiFe_2O_4$ nanoparticles is about 67 emu/g. This decrease in M_s could be attributed to the nanomagnetic sawdust template.[34].

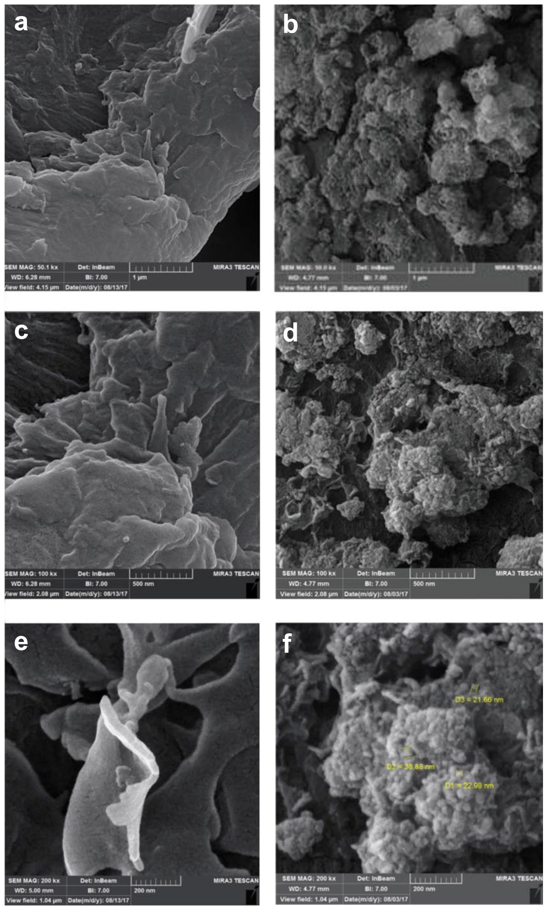

Fig. 5. a. c. e FESEM image of raw sawdust b. d. f $NiFe_2O_4$ / sawdust nanocomposite.

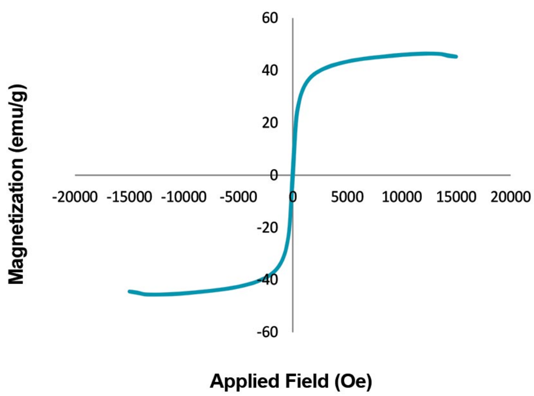

Fig. 6. Hysteresis loop of $NiFe_2O_4$/sawdust at room temperature.

Oil-water separation test

Oil-water separation tests were conducted in four periods of time, including 5, 10, 15, 20 min. It is proved that, the oil adsorption capacity (Q) increased directly by the time. The results of this test indicate that the maximum oil adsorption capacity of the as-produced nonadsorbent was obtained from pump oil due to its high density (Fig.6). By increasing of oil density, the oil adsorption capacity will be increased as well. As shown in Fig.7, after 10 oil-removal cycles, no significant changes were observed in oil adsorption capacity of $NiFe_2O_4$/sawdust nanocomposite. The results prove that the modified sawdust possesses high oil adsorption capacity and reusability, which could be attributed to good chemical stability of as-prepared nanoadsorbents.

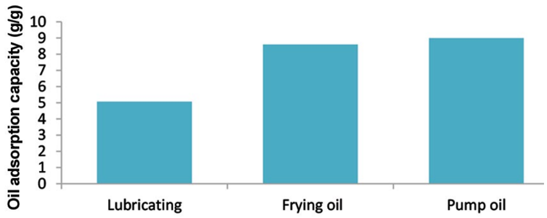

Fig. 7. Oil adsorption capacity of $NiFe_2O_4$/sawdust magnetic nanocomposite for three types of oil.

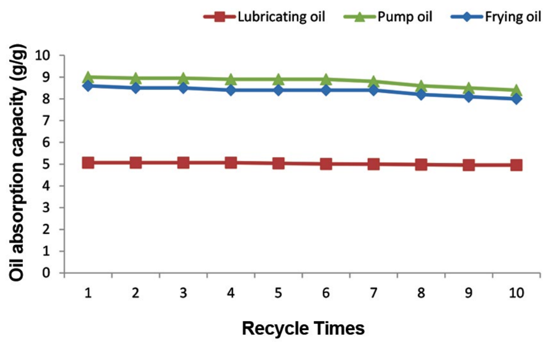

Fig. 8. Oil adsorption capacity of modified sawdust for three types of oil after 10 oil removal cycles.

CONCLUSION

In summary, $NiFe_2O_4$/sawdust magnetic nanocomposite was synthesized by hydrothermal method. The obtained composite was characterized with X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), contact angle measurement (CA), vibrating sample magnetometer (VSM) and field-emission scanning spectroscopy (FESEM). The adsorption capacity was evaluated by weight measurements. It is observed that the maximum oil adsorption capacity of composite was 9 (g/g) corresponding to pump oil. The most important aim of this project was about reusability of the modified sawdust. It is proved that the as-prepared magnetic nanocomposite could be reused after 10 adsorption/desorption cycles. Facile synthesis procedure, high oil adsorption capacity, fast and simple magnetic separation and reusability of nanoadsorbent are among the benefits of these composite. This approach will open up new fields of studies in polluted-water treatment.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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