ARTICLE IN PRESS

Materials Letters xxx (2016) xxx-xxx

Contents lists available at ScienceDirect



Materials Letters



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

Synthesis of quaternized chitosan-coated magnetic nanoparticles for oil-water separation

Shuang Zhang^a, Ting Lü^{a,*}, Dongming Qi^b, Zhihai Cao^b, Dong Zhang^a, Hongting Zhao^{a,*}

^a Institute of Environmental Materials and Applications, College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China ^b Engineering Research Center of Eco-Dyeing and Finishing of Textiles of Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China

ARTICLE INFO

Article history: Received 9 October 2016 Received in revised form 27 December 2016 Accepted 28 December 2016 Available online xxxx

Keywords: Magnetic nanoparticles Composite materials Polymers Oil-water separation Reusability

ABSTRACT

In this letter, we reported successful development of a class of novel quaternized chitosan (QC)-coated magnetic nanoparticles (MNPs) for oil-water separation. Fe_3O_4 MNPs were coated with silica and 3-aminopropyltriethoxysilane (APTES), followed by QC grafting to yield QC-coated MNPs. Results showed that Fe_3O_4 and $Fe_3O_4@SiO_2$ MNPs exhibited negligible oil-water separation effect and APTES coating onto $Fe_3O_4@SiO_2$ MNPs could only improve its separation efficiency under acidic condition. However, QC-coated MNPs not only exhibited excellent oil-water separation performance at various pH levels, but also could be reused up to 8 times without showing significant decrease in separation efficiency. Results suggested QC-coated MNP could potentially be used as a class of promising materials for oil-water separation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Oily wastewater discharge and crude oil leakage accidents have posed severe threat to environment and human health [1,2]. Generally, in oily wastewater, a substantial portion of oil is present in emulsified form, which is extremely difficult to separate from water phase [3]. Thus, it is urgent to develop cost-effective methods to separate the emulsified oil from aqueous environment.

Currently, adsorption is probably one of the most commonly used methods in practice. However, majority of the spent oil-absorbing materials were difficult to be regenerated and the re-collection processes were not convenient and economic. Nowadays, Fe₃O₄ magnetic nanoparticles (MNPs) have attracted increasing attentions due to their high surface area and the advantage of easy separation [4]; however, the surface property of Fe₃O₄ MNPs should be further modified in order to improve their efficiency of oil-water separation.

Chitosan has been selected as an ideal substrate material for various applications such as drug delivery [5], wastewater treatment [6]. As compared with chitosan, quaternized-chitosan (QC) has permanent cationic charges [7], and hence it is presumably easier to interact with the negatively charged oil droplets via electrostatic interaction. Thus, it is assumed that QC-coated MNPs

* Corresponding authors. *E-mail addresses:* lvting@hdu.edu.cn (T. Lü), info-iem@hdu.edu.cn (H. Zhao).

http://dx.doi.org/10.1016/j.matlet.2016.12.092 0167-577X/© 2016 Elsevier B.V. All rights reserved. might have greater potentials to efficiently remove emulsified oil droplets from aqueous media.

In this study, Fe₃O₄ MNPs were prepared by a coprecipitation method, followed by surface coating with silica and 3-aminopropyltriethoxysilane (APTES); subsequently, QC-coated MNPs were synthesized by grafting QC onto APTES-coated MNPs. Finally, oil-water separation efficiencies of the synthesized MNPs were investigated in detail as a function of dosage, pH value and reusability.

2. Experimental

 Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -APTES MNPs were prepared by using the method as previously described [8]. $Fe_3O_4@SiO_2$ -APTES MNPs were added to aqueous glutaraldehyde solution and stirred for 3 h. The MNPs were then collected and washed with water 5 times. Subsequently, the MNPs were dispersed in aqueous QC solution, followed by magnetic stirring for 2 h. The synthesized QC-coated MNPs were rinsed with water several times and dispersed in water for further use.

Sample morphology was examined by transmission electron microscopy (TEM, JSM-1200EX) and scanning electron microscope (SEM, SIRION-100). X-ray powder diffraction patterns were obtained with an X-ray diffractometer (XRD, D8 Discover). Fourier transform infrared spectra (FTIR, Nicolet 6700) were recorded between 4000 and 400 cm⁻¹. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (TGA/DSC 1, Mettler

Please cite this article in press as: S. Zhang et al., Synthesis of quaternized chitosan-coated magnetic nanoparticles for oil-water separation, Materials Letters (2016), http://dx.doi.org/10.1016/j.matlet.2016.12.092

Toledo) with a heating rate of 10 °C/min to 800 °C. Zeta potential was measured by using a zeta potential analyzer (Nano-Z Zetasizer, Malvern). Brunauer-Emmett-Teller (BET, Autosorb IQ) surface areas of the nanoparticles were determined by N_2 adsorption/desorption. Water transmittance was recorded by a UV-vis spectrometer (UV-2450, Shimadzu) at a wavelength of 610 nm.

Diesel-in-water emulsion containing 0.2 wt% of diesel was prepared by powerful sonication for 5 min. A certain amount of MNPs were added to the emulsion and the mixture was shaken by hand for 20 s. Upon applying an external magnetic field, the MNPs coated diesel droplets were moved to the vial wall. The water transmittance was then determined to assess demulsification efficiency. After demulsification test, the spent MNPs were washed with ethanol 3 times to remove the attached oil. The regenerated MNPs were then reused in the next cycle of oil-water separation.

3. Results and discussion

TEM images of Fe₃O₄ and Fe₃O₄@SiO₂ MNPs are shown in Fig. 1a-b. Fe₃O₄ MNPs exhibit nonspherical shape with a size of \sim 12 nm (Fig. 1a). It can be seen from Fig. 1b that a thin layer of silica was successfully coated on Fe₃O₄ MNPs, and some aggregates could be observed after surface coating. Fig. 1c-d shows the SEM images of Fe₃O₄ and Fe₃O₄@SiO₂ MNPs. It can be seen that, after silica coating, the surface of MNPs became rough. BET surface area of Fe₃O₄ and Fe₃O₄@SiO₂ MNPs were measured to be 112.0 and 207.9 m²/g, respectively.

XRD experiments were carried out to determine the crystalline structures of MNPs and the results are shown in Fig. 2a. For Fe₃O₄ MNPs, diffraction peaks at 30.3°, 35.5°, 43.2°, 53.5°, 57.2° and 63.0° related to their corresponding indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed, indicating a cubic spinel structure. Such a XRD pattern can be indexed to JCPDS No. 75-0033. Similar XRD peak positions and half-peak width were also observed for Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-APTES and Fe₃O₄@SiO₂-QC, indicating the stability of the crystalline phase of Fe₃O₄ nanoparticles during surface coating [9]. In addition, a broad diffraction band between 20° and 25° was observed after surface coating with silica,

further confirming the existence of amorphous silica shell on Fe₃O₄ MNPs [10].

FTIR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-APTES and Fe₃-O₄@SiO₂-QC MNPs are shown in Fig. 2b. The absorption peaks at 576 cm⁻¹, corresponding to the Fe-O vibration, were observed for all MNPs. On the other hand, new characteristic peaks at 1102, 789 and 465 cm⁻¹ were observed for Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-APTES and Fe₃O₄@SiO₂-QC MNPs, which could be assigned to the vibrations of SiO₂. For Fe₃O₄@SiO₂-APTES and Fe₃O₄@SiO₂-QC MNPs, the characteristic absorption peaks of APTES and QC were not obvious. However, the successful APTES coating and QC grafting were confirmed by the results of TGA and zeta potential (Fig. 2c-d).

As compared with Fe₃O₄, Fe₃O₄@SiO₂ MNPs, the TGA curve of $Fe_{2}O_{4}@SiO_{2}$ -APTES MNPs showed a major weight loss (4.4 wt%) from 250 to 550 °C due to the decomposition of organic groups of APTES (Fig. 2c), suggesting the percentage of APTES anchored on MNPs was ~5.2 wt%; meanwhile, the TGA curve of Fe₃O₄@SiO₂-QC MNPs exhibited a weight loss (3.1 wt%) from 250 to 350 °C. Based upon the weight loss of QC and Fe₃O₄@SiO₂-APTES between 250 and 350 °C, the grafting ratio of QC was estimated to be 3.8 wt %. Zeta potential results (Fig. 2d) showed that Fe₃O₄ MNPs were positively charged at pH 4, while negatively charged at pH 7 and 10; however, Fe₃O₄@SiO₂ MNPs were always negatively charged at pH of 4, 7 and 10, suggesting the successful surface coverage of silica layer on MNPs. After coating with APTES, the surface charge of MNPs became positive at pH 4 and 7, due to the protonation of aminopropyl groups, consistent with previous reports [11]. QC-coated MNPs were always positively charged at various pH levels, suggesting the successful QC grafting onto MNPs surface.

Fig. 2e illustrates the magnetic separation process of $Fe_3O_4@$ -SiO₂-QC MNPs. In the absence of an external magnetic field, MNPs could be well dispersed in water. However, when external magnetic field was introduced, MNPs could rapidly move to the vial wall within 20 s, suggesting good feasibility of magnetic separation.

The performances of synthesized MNPs for oil-water separation were investigated at various pH levels (Fig. 3a-c). It was found that



Fig. 1. TEM and SEM images of Fe₃O₄ (a, c) and Fe₃O₄@SiO₂ (b, d) MNPs.

Please cite this article in press as: S. Zhang et al., Synthesis of quaternized chitosan-coated magnetic nanoparticles for oil-water separation, Materials Letters (2016), http://dx.doi.org/10.1016/j.matlet.2016.12.092

Download English Version:

https://daneshyari.com/en/article/5463046

Download Persian Version:

https://daneshyari.com/article/5463046

Daneshyari.com