A recyclable and regenerable magnetic chitosan absorbent for dye uptake

Weifeng Zhao [a,b], Xuelian Huang [a], Yilin Wang [a], Shudong Sun [a], Changsheng Zhao [a,*]

[a] College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, 610065 Chengdu, China
[b] Fiber and Polymer Technology, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), Teknikringen 56-58 SE-100 44, Stockholm, Sweden

ARTICLE INFO

ABSTRACT

A recyclable and regenerable magnetic polysaccharide absorbent for methylene blue (MB) removal was prepared by coating magnetic polyethyleneimine nanoparticles (PEI@MNPs) with sulfonated chitosan (SCS) and further cross-linked with glutaraldehyde. The driving force for coating is the electrostactic interaction between positively charged PEI and negatively charged SCS. Infrared spectra, zeta potential, thermal gravimetric analysis and X-ray diffraction demonstrated the successful synthesis of magnetic polysaccharide absorbent. The self-assembly of polysaccharide with magnetic nanopartices did not alter the saturation magnetization value of the absorbent confirmed by vibrating sample magnetometer. The nanoparticles showed fast removal (about 30 min reached equilibrium) of MB. In particular, the removal ability of MB after desorption did not reduce, demonstrating an excellent regeneration ability. Our study provides new insights into utilizing polysaccharides for environmental remediation and creating advanced magnetic materials for various promising applications.

1. Introduction

Nowadays, water pollution by dyes and heavy metal ions has become a serious issue for the environment. Among these pollutants from industries (Wang et al., 2012), methylene blue (MB) is one typical toxic dye with known harmful effects on human beings (Wang, Ding et al., 2015). The presence of MB in aquatic system even at a low concentration of 1 ppm could inhibit the sunlight transistence and affect the photosynthetic process of aquatic livings (Guo & Wilson, 2012). Therefore, removal of MB prior to its discharge into environment is needed to be considered. Cost-effective wastewater treatment techniques are required to reduce the concentration of MB under permissible levels. Among these techniques, dye adsorption based on magnetic separation technique has been receiving considerable attention owing to its low-cost, high efficiency, easy operation process and good mechanical stability (Chen et al., 2014).

Many polymers including synthetic polymers and natural polymers have been used with magnetic materials for MB removal due to the large amount of active sites in polymers. Polyacylic acid (PAA) is a commonly used synthetic polymer for MB removal. Mak et al. developed PAA/Fe$_3$O$_4$ nanoparticles for the adsorption of MB from an aqueous solution (Mak & Chen, 2004). Recently, a PAA functionalized magnetic Fe$_3$O$_4$ nanoparticle-graphene oxide nanocomposite (PAA/MGO) was synthesized, and the higher adsorption capacity of PAA/MGO was mainly attributed to the functionalization of PAA and its higher content of charged carboxyl groups than MGO (Zhang et al., 2015). However, these synthetic polymers cannot be degraded, which creates the secondary pollution after the removal of MB. Thus, the scientists turn their attention towards fabrication of magnetic adsorbents using natural polymers.

Among natural polymers, polysaccharides are abundant, biodegradable, hydrophilic and low-cost, therefore commonly used as adsorbent materials for wastewater treatment (Lu et al., 2015). It has been reported that pectin (Rakhshaee & Panahandeh, 2011), activated carbon/alginate (Ai, Li, & Li, 2011), GO/calcium alginate (Song, Wu, Zhong, Lin, & Chen, 2015), cellulose/GO (Shi, Li, Zhong, & Xu, 2014), corn straw (Zhao, Xia, Yang, Wang, & Zhao, 2014), carboxymethyl starch/poly(vinyl alcohol) (Gong, Zhang, Cheng, & Zhou, 2015) and β-cyclodextrin (Badruddoza, Hazel, Hidajat, & Uddin, 2010; Zhou et al., 2016) could been used to fabricate magnetic absorbents for MB removal. As an important family of polysaccharides, chitosan is also attracted much attention for MB removal. Uniform chitosan coated magnetic mesoporous sil-

ica nanoparticles with good adsorption capacity and magnetic response were synthesized to remove MB dyes (Li, Zhou, Nie, Song, & Chen, 2015). Zeng et al. (2015) synthesized a magnetic adsorbent of chitosan/organic rectorite-Fe_3O_4 intercalated composite microspheres for the removal of MB. In order to employ the promising properties of GO, a magnetic composite bioadsorbent composed of magnetic chitosan and GO was prepared as the magnetic adsorbent toward MB (Fan et al., 2012). For preparing a stable adsorbent, ethylenediaminetetraacetic dianhydride-modified magnetic chitosan complex was fabricated using glutaraldehyde as a cross-link agent for the MB removal (Xia et al., 2013). By using the same strategy, we hypothesize that a self-assembly of negatively charged polysaccharides and positively charged magnetic nanoparticles, and then followed by cross-linking, could produce recycled and regerated magnetic particles for MB removal.

The aim of this study is to fabricate a recyclable and regenerable magnetic adsorbent for MB removal by coating magnetic polyethyleneimine nanoparticle (PEI@MNP) with sulfonated chitosan (SCS) and further cross-linking with glutaraldehyde. SCS was firstly synthesized by a sulfonation of CS with HSO_3Cl. A solvothermal reaction was applied to produce PEI@MNP. After a self-assembly of SCS onto PEI@MNP by electrostatic interaction, the SCS was subsequently cross-linked by glutaraldehyde. As a consequence, the functional SCS is stabilized onto magnetic nanoparticles so that these magnetic hybrid materials could be regenerable and recyclable during wastewater treatments. Infrared spectra (IR), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and elemental analysis were applied to characterize SCS. Additionally, IR, zeta potential, thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) were used to follow the self-assembly and post cross-linking of SCS onto the magnetic nanoparticles. The magnetization of the magnetic particles was demonstrated by vibrating sample magnetometer (VSM). The adsorption, desorption and re-adsorption of the magnetic nanoparticles towards MB were also investigated.

2. Experimental

2.1. Chemicals

Chitosan (CS) with a degree of deacetylation of 95% and a viscosity of 100–200 mpa s was purchased from Aladin Inc. Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%, Aladin), polyethyleneimine (PEI, M.W. 10 000, Aladin), diethylene glycol (DEG, 99%, Aladin), acetic acid (99.8%, Aladdin), chlorosulfonic acid (HSO_3Cl, 99%, Kelong), ethanol (EtOH, 98%, Kelong), sodium hydroxide and normal saline solution (Kelong) were used as received. N,N-Dimethylformamide (DMF, 98%, Kelong) was distilled under vacuum prior to use. Deionized (DI) water was used throughout the study.

2.2. Preparation of magnetic polyethyleneimine (PEI) nanoparticles (PEI@MNPs)

The PEI@MNPs were synthesized by a modified solvothermal reaction. Firstly, 0.8 g of NaOH was added into 20 mL of DEG at 120 °C for 1 h under N_2, and cooled down to 70 °C to produce a NaOH/DEG stock solution. Then, 1 g of PEI and 1 g of $FeCl_3 \cdot 6H_2O$ were dispersed in 40 mL DEG, and heated to 220 °C under the protection of nitrogen flow and constant stirring. Afterwards, 5 mL of NaOH/DEG stock solution was injected rapidly into the hot mixture. The resulting mixture was kept at 220 °C for further 1 h, and then allowed to cool to room temperature. With the aid of a magnet, the black products were washed with DI water for several times to remove the solvent and unreacted chemicals, and then stored in normal saline solution.

2.3. Sulfonation of chitosan

10 g of CS was dissolved in acetic acid/DMF (w/w 1/10) at 60 °C for several hours, and the solution was then cooled down to 0 °C. Then HSO_3Cl/DMF (v/v 1/2) was added within 1 h under the protection of nitrogen gas, and the reaction was kept at 0 °C for 10 h. Sulfonated CS was extracted by diethyl ether, and then purified with ethanol. The product was then dried in a vacumm oven at 50 °C for 48 h.

2.4. Characterization of SCS

Fourier transform infrared (FTIR) spectra for the modified SCS was obtained using a FTIR spectrometer (Nicolet 560, America). ^1H NMR data were obtained with a BRUKER spectrometer (400 MHz). The molecular weight and molecular weight distribution were mesured by gel chromatography (HLC-8320GPC, Japan). Elemental analyses were performed on a CARLO ERBA 1106 elemental analyzer (Italy) for carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) with a carrier gas (He, at a flow rate of 100 mL min^{-1}) at a combustion temperature of 1000 °C using the solid samples.

2.5. Self-assembly and cross-linking of SCS onto magnetic nanoparticles

20 mL of PEI@MNPs (1 mg/mL) was added dropwise into 10 mL of SCS (5 mg/mL) aqueous solution. The self-assembly was carried out under shaking for 1 h. The obtained PEI@MNP/SCS was washed with 20 mL of DI water for 3–5 times to remove the excess SCS. For the cross-linking of SCS onto the magnetic nanoparticles, 1 mL of 50% glutaraldehyde solution was added to PEI@MNP/SCS, the cross-linking reaction was performed at 70 °C for 3 h, named as PEI@MNP/SCS$_{CL}$. In order to compare the effect of the acid addtion on the cross-linking of SCS, 100 μL of acetic acid was added during the cross-linking of PEI@MNP/SCS, and named as PEI@MNP/SCS$_{CLA}$. The preparation of PEI@MNP/SCS$_{CLA}$ was illustrated in Scheme 1.

2.6. Characterization of magnetic nanoparticles

ATR-FTIR analysis was performed on a Nicolet 560 instrument, equipped with a single-bounce attenuated total reflection cell, a detector, and a ZnSe single crystal. All the IR spectra were collected with a resolution of 4 cm^{-1} within a range of 4000–600 cm^{-1}. Prior to thermal analysis, all of the samples were pre-dried at 30 °C for at least 24 h under vacuum. TGA of the specimens was performed on a TG209F1 (Netzsch Co., Germany), and the samples were heated from 30 to 700 °C at a rate of 10 °C min^{-1}, protected by dry nitrogen. XRD measurement was performed on Empyrean X-ray diffraction device (PANalytical B.V., Netherland) by using $Cu_{K}\alpha$ radiation ($\lambda = 0.154$ Å). The operation voltage and current were kept at 40 kV and 35 mA, respectively. The 2θ range was 10–70° in steps of 0.03° with a count time of 0.2 s. The zeta potentials of magnetic nanoparticles were determined by dynamic light scattering (DLS) (ZETA-SIZER, MALVERN Nano-ZS90). The temperature was 25 °C and the scattering angle was 90°. The nanoparticle solution was diluted to 0.1 mg/mL prior to test. The TEM images were taken using a Tecnai G2 F20 S-TWIN (FEI, America) transmission electron microscope with a tungsten filament at an accelerating voltage of 200 kV. The magnetic properties of the nanoparticles were measured by a vibrating sample magnetometer (VSM) at room temperature over the magnetic density range from −10 to 10 kG.

2.7. Adsorption experiments

The dye removal was performed using methyl blue (MB) as a model dye. ~10 mg magnetic nanoparticles were dispersed into