



# Amino ionic liquids-modified magnetic core/shell nanocomposite as an efficient adsorbent for dye removal



Jingjing Cheng, Lijuan Shi<sup>\*</sup>, Jianjun Lu<sup>\*</sup>

Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China

## ARTICLE INFO

### Article history:

Received 24 November 2015

Received in revised form 12 January 2016

Accepted 5 February 2016

Available online 11 February 2016

### Keywords:

Amino ionic liquids

$\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2$  microspheres

Mesoporous core/shell structure

Dye removal

Magnetic separation

## ABSTRACT

Amino ionic liquids modified superparamagnetic mesoporous core/shell nanocomposite ( $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$ ) was synthesized to remove orange II and amaranth from water. Due to the multiple active sites of the introduced ionic liquids, the adsorbent presents superior adsorption performance and instantaneous adsorption capacity. The maximum adsorption capacities are reached at pH 2 due to the protonation of amino groups, which are 153.06 and 84.40  $\text{mg g}^{-1}$  for orange II and amaranth, respectively. The good stability, rapid adsorption kinetics, large adsorption capacity, and high separation efficiency make  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$  an efficient adsorbent for removing anionic contaminant from water.

© 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## Introduction

Dyes have been widely used in industries like paper, pharmaceutical, food, cosmetic, textile, leather and so on. With the development of the industries above, the removal of dyes from wastewater has received worldwide concern because dyes may disrupt the ecological system and harm human health with a small amount [1–3]. Lots of technologies, such as chemical oxidation, photo-catalytic degradation, biological treatment, membrane filtration, ion-exchange, and adsorption [4–9], have been developed for the treatment of dyes. Among these techniques, adsorption has received much attention due to its merits of simplicity, high efficiency, and no secondary pollution.

Many substances, including active carbon, zeolites, polymers, biomass materials [10–13], etc., have been used as adsorbents. Magnetic nanomaterials with functional surfaces have been suggested as efficient and environmental friendly adsorbents owing to the large removal capacity, fast kinetics, and high separation efficiency [14–19]. In recent years, modification of magnetic nanoparticles with a series of polymers and small organic compounds has been extensively investigated [20–27]. Compared with conventional organic compounds, ionic liquids (ILs) are

receiving much attention owing to their unique physicochemical properties, such as high thermal and chemical stability, and excellent designability [28,29]. Currently, kinds of ILs have been used to remove pollutants from water and have presented good performances [30–32], but several drawbacks like large consumption, tedious separation procedures, and difficult recycling have restricted their applications. In order to overcome these problems, supported ILs formed by immobilizing ILs on solid materials become excellent candidates. Recently, a lot of efforts have been made to prepare ILs functionalized magnetic materials [33,34]. However, these common ILs were immobilized mainly by immersion, which presents a few of drawbacks such as poor stability, uneven distribution, and small load volumes. In response, ILs immobilized by chemical method has been developed recently [35].

Herein, amino-functional ILs-modified nanoporous magnetic core/shell nanocomposite  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$  was successfully synthesized to remove anionic dyes effectively. The structure and properties of  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$  were characterized. Meanwhile, the adsorption kinetics and isotherms of  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$  were studied in detail. The fast adsorption kinetics, large adsorption capacity, rapid separation process, and no secondary pollution in the adsorption process make  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2@\text{DHIM-NH}_2$  serve as a highly efficient adsorbent for the removal of anion contaminants from water.

<sup>\*</sup> Corresponding authors. Tel.: +86 351 6010190.

E-mail addresses: [shilijuan@tyut.edu.cn](mailto:shilijuan@tyut.edu.cn) (L. Shi), [lujianjunktz@tyut.edu.cn](mailto:lujianjunktz@tyut.edu.cn) (J. Lu).

## Experimental

### Materials and reagents

Orange II (85%) and amaranth (98%) were obtained from Aladdin Chemical Reagent Co., Ltd. The dye molecular structures are shown in Table 1. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium acetate ( $\text{CH}_3\text{COONa}$ , 99.0%), ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ , 98.0%), tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazol ( $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_3\text{Si}$ ), 3-chloropropylamine hydrochloride ( $\text{C}_3\text{H}_8\text{ClN} \cdot \text{HCl}$ , 98%), and  $\text{DMSO-d}_6$  (99.8%) were purchased from Beijing J&K Scientific Ltd.  $\text{CH}_3\text{CH}_2\text{OH}$  (99.8%),  $\text{HCl}$  (37 wt%),  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (28 wt%),  $\text{NH}_4\text{NO}_3$  (96.0%),  $\text{KHCO}_3$  (99.5%),  $\text{NaOH}$  (96.0%), and pentane were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd. Deionized water was used in all experiments.

### Characterization

Transmission electron microscopy (TEM) observations were performed on a JEM-2010 (Japan) with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were gained by a JSM-7001F. The X-ray diffraction (XRD) patterns were recorded with a DX-2700 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation over the angular range from  $20^\circ$  to  $80^\circ$ . Fourier infra-red (FT-IR) spectra were recorded with an IR spectrophotometer Bruker VERTEX 70 FT-IR (Germany).  $\text{N}_2$  adsorption/desorption analysis was measured at a liquid nitrogen temperature (77 K) using a 3H-2000PS2 specific surface area and pore size analyzer. Thermogravimetric analysis (TGA) was performed on a 209F3 (NETZSCH, Germany) from  $100^\circ\text{C}$  to  $900^\circ\text{C}$  at a ramp rate of  $10^\circ\text{C min}^{-1}$ . The dynamic light scattering (DLS) and surface zeta potential were measured using a Nano-ZS90 (Malvern, United Kingdom). The magnetic properties were analyzed by a vibrating sample magnetometer (MPMS SQUID VSM).  $^1\text{H}$  NMR spectra were run on a Bruker Advance 400 spectrometer equipped with a pulse field gradient module (Z-axis) using a 5 mm BBO probe. The instrument was operated at a frequency of 400.13 MHz at  $25 \pm 0.1^\circ\text{C}$ . The absorbance was recorded on a Unico Uv4802 UV/vis spectrophotometer.

### Synthesis of $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2$ magnetic mesoporous microspheres

#### Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

The magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by solvothermal method [36]. 2.16 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in

80 mL ethylene glycol under magnetic stirring and a yellow clear solution was obtained after stirring for 30 min. Then 5.76 g sodium acetate was added to the solution. After stirring for 50 min, the resultant homogeneous yellow solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at  $200^\circ\text{C}$  for 8 h. After cooled to room temperature, the black magnetic particles were collected by a magnet, followed by washing with ethanol for 6 times. The product was dried in vacuum at  $60^\circ\text{C}$  for 12 h.

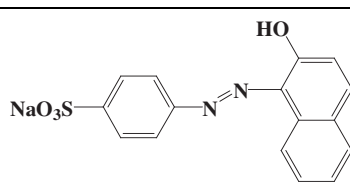
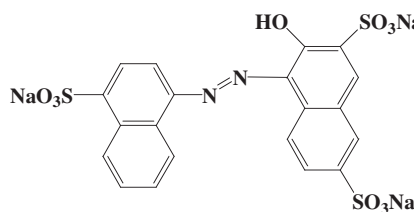
#### Synthesis of $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2$ microspheres

The core/shell  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2$  microspheres were prepared according to the method reported previously [37,38]. Briefly, 0.10 g  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were treated with 0.1 M  $\text{HCl}$  aqueous solution (50 mL) by ultrasonication for 10 min. After separated and washed with deionized water, the magnetic nanoparticles were homogeneously dispersed in a mixture of ethanol (80 mL), deionized water (20 mL), and concentrated ammonia aqueous solution (1.0 mL, 28 wt%), followed by the addition of TEOS (0.03 g, 0.144 mmol). After mechanistically stirring at room temperature for 6 h, the  $\text{Fe}_3\text{O}_4@n\text{SiO}_2$  microspheres were separated and washed with ethanol and water. The product was re-dispersed in a mixed solution containing CTAB (0.30 g, 0.823 mmol), deionized water (80 mL), concentrated ammonia aqueous solution (1.00 g, 28 wt%), and ethanol (60 mL). And the dispersion was homogenized to form a uniform dispersion with the help of ultrasonic vibration and mechanical mixing. Subsequently, 0.40 g TEOS (1.90 mmol) was added dropwise to the dispersion above under continuous stirring and the reaction was allowed to proceed for 6 h. Then the product was collected with a magnet and washed repeated with ethanol and water to remove nonmagnetic by-products. Finally, the purified microspheres were re-dispersed in 65 mL ethanol (95%) containing 0.13 g  $\text{NH}_4\text{NO}_3$ , and the mixture was stirred at  $60^\circ\text{C}$  for 15 min to remove the template CTAB. Microspheres were recovered by a magnet and washed with cold ethanol, and the treatment above was repeated twice to obtain  $\text{Fe}_3\text{O}_4@n\text{SiO}_2@m\text{SiO}_2$  microspheres. The product was dried in vacuum at  $80^\circ\text{C}$  for 24 h.

#### Preparation of amino-functional ILS

The compound was prepared using a similar procedure reported previously [39]. A mixture of *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazol (5.489 g, 20 mmol) and 3-chloropropylamine hydrochloride (3.120 g, 24 mmol) were added into 30 mL dry ethanol, followed by refluxing at  $80^\circ\text{C}$  for 24 h under nitrogen.

**Table 1**  
Characteristics and structures of anionic dyes.

Generic name	M.W.	$\lambda_{\text{max}}$ (nm)	Molecular structure
Orange II	350.32	484	
Amaranth	604.47	520	

Download English Version:

<https://daneshyari.com/en/article/227793>

Download Persian Version:

<https://daneshyari.com/article/227793>

[Daneshyari.com](https://daneshyari.com)