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Functional nanomaterials: Study on aqueous Hg(II) adsorption by magnetic $Fe_3O_4@SiO_2$-SH nanoparticles

Zhuoxing Wang[a], Jiang Xu[b,*], Yunjun Hu[a], Heng Zhao[b], Junliang Zhou[b], Yu Liu[a], Zimo Lou[a], Xinhua Xu[a]

[a] *Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China*
[b] *State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China*

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ABSTRACT

A selective adsorbent for Hg(II) was prepared by coating Fe_3O_4 nanoparticles with SiO_2 which was further functionalized with thiol (–SH) group. The new adsorbent ($Fe_3O_4@SiO_2$-SH) was shown to adsorb aqueous Hg(II) species in a wide range of pH (1.0–8.0) conditions. The Hg(II) adsorption capacity q_e was more than 90.0 mg g^{-1} at pH > 3.0, and was slightly decreased to 84.6 mg g^{-1} under strong acidic conditions due to the electrostatic repulsion. The Langmuir isotherm model fitted the adsorption data better than the Freundlich, Temkin, and Dubinin-Radushkevich isotherms models. The maximum adsorption capacity of $Fe_3O_4@SiO_2$-SH for Hg(II) was 132.0 mg g^{-1}. The adsorption kinetics were shown to follow the pseudo-second-order kinetic model, and the kinetic constant k_2 was 2.4×10^{-3} g mg^{-1} min^{-1}. The magnetic retrieve of the newly-developed adsorbent was easily carried out via an external magnetic field, enabling both excellent adsorbent utilization and adsorption efficiency at high Hg(II) concentrations.

1. Introduction

In the recent decades, the threat and risk of heavy metal pollution have become a major environmental concern due to the rapid economic and industrial development globally [1]. The exposure and accumulation of heavy metals will probably cause various adverse health effects to humans, including the mental and neurological function impairments [2,3]. Mercury is a typical hypertoxic heavy metal and hazardous substance to cause accidental pollution events, such as Minamata disease in Japan [4,5]. Since Hg(II) has great mobility and trends to dissolve in lipids to form alkyl mercury with a higher toxicity, how to effectively remove aqueous Hg(II) has been a major challenge in water and wastewater treatment [5–7].

A variety of treatment technologies have been used to remove Hg(II) from wastewater, such as chemical precipitation, adsorption, ion exchange and bioremediation [7–11]. The adsorption method has been widely studied due to its cost-effective, efficient, and simple removal of Hg(II). Activated carbon, zeolite, agricultural wastes, and other various materials have been used to adsorb aqueous Hg(II) [2,12–15]. Recently, in order to retrieve and recycle the adsorbents, Fe_3O_4 nanoparticles with magnetic property, high surface area, and large adsorption capacity have been developed to remove heavy metals from aqueous solutions, which can be easily separated and recycled via an external magnetic field [16–22]. However, bare Fe_3O_4 nanoparticles are easily oxidized in air and corroded in acidic environment, and also prone to aggregation via magnetic force [23,24]. As a result, the magnetic property and adsorption capacity will be significantly reduced. Thus, surface protection and modification of Fe_3O_4 nanoparticles are required to inhibit the aggregation, which will also endow the nanoparticles with high dispersity, antioxidant ability, and acid/alkali resistance. For example, Tween-20 and reduced graphite oxide were used to stabilize gold nanoparticles and Fe_3O_4 nanoparticles, respectively, achieving rapid and efficient removal of mercury species [25]. Ferromagnetic sorbents based on nickel nanowires also exhibited efficient uptake of Hg(II) from water [26]. Besides, silica (SiO_2) is another excellent support to stabilize nanoparticles, with higher Hg(II) adsorption capacity of SiO_2-coated magnetic nanoparticles being observed [27]. Moreover, the adsorption capacity and selectivity of the adsorbent will be greatly enhanced via the introduction of an active functional group [28,29]. Thiol (SH) group and oligonucleotide functionalized adsorbent both have been reported to selectively capture Hg(II) from aqueous system [30–32].

The objective of this study was to develop SiO_2-coated and SH-functionalized magnetic nanoparticles ($Fe_3O_4@SiO_2$-SH) to effectively remove aqueous Hg(II). SiO_2 was used to stabilize the Fe_3O_4 nanoparticles and inhibit their aggregation, while the SH group was applied to functionalize the $Fe_3O_4@SiO_2$ nanoparticles so as to obtain selective and rapid Hg(II) adsorption. The micromorphology and

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* Corresponding author. Tel.: +86 21 62238962; fax: +86 21 62231809.
E-mail address: jxu@sklec.ecnu.edu.cn, xujiang@hotmail.com (J. Xu).

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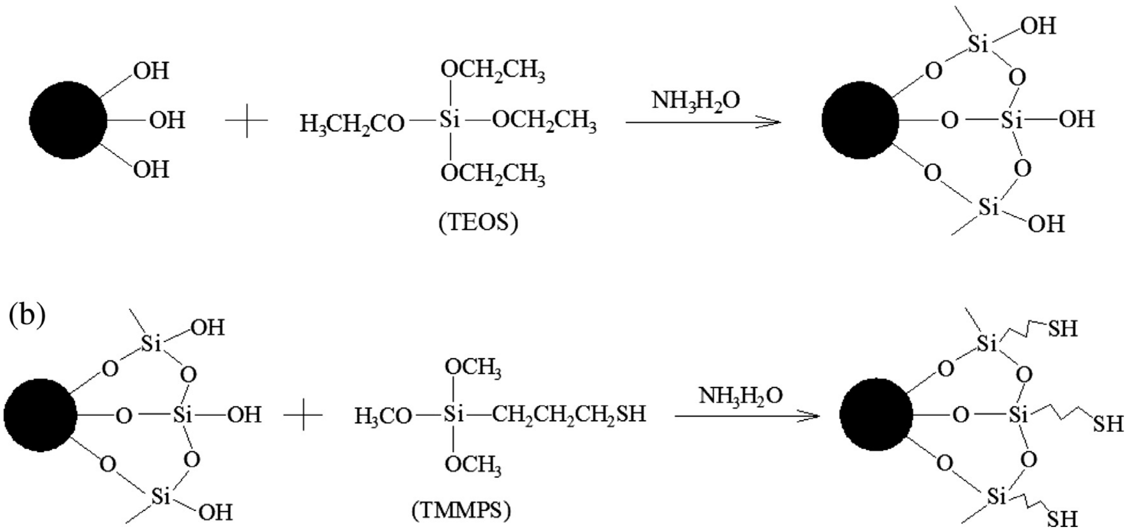

Fig. 1. Schematic of Fe_3O_4@SiO_2-SH nanocomposites preparation.

surface functional groups of prepared Fe_3O_4@SiO_2-SH were analyzed. The effects of reaction time, initial pH, and Hg(II) concentration on Hg(II) adsorption by Fe_3O_4@SiO_2-SH were investigated in detail. Furthermore, the adsorption isotherm and kinetics were discussed.

2. Materials and methods

2.1. Materials

$HgCl_2$, $FeCl_3$•$6H_2O$, $FeSO_4$•$7H_2O$, NH_3•H_2O, NaOH, HCl, tetraethoxysilane (TEOS), polyethylene glycol 4000 (PEG), and methyl alcohol were of analytical grade and purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China. Trimethoxysilylpropanethiol (TMMPS) was obtained from Aladdin Reagent Co., Ltd., Shanghai, China.

2.2. Preparation

The Fe_3O_4@SiO_2-SH nanoparticles were prepared in three steps: superparamagnetic Fe_3O_4 nanoparticles synthesis via chemical coprecipitation, SiO_2 coating on Fe_3O_4 nanoparticles by sol-gel method, and SH modification on Fe_3O_4@SiO_2. The synthesis process is illustrated in Fig. 1.

At room temperature, $FeCl_3$•$6H_2O$ (8.66 g) and $FeSO_4$•$7H_2O$ (5.56 g) at the molar ratio of 1.6:1.0 were firstly dissolved into 100 mL deionized water under a nitrogen atmosphere, which was evenly mixed with 100 mL PEG surfactant solution under ultrasonication and stirring (400 rpm). NH_3•H_2O was slowly dropped into the mixed solution until pH was increased to 11.0. Then the reaction was allowed to continue in a thermostatic water bath for 2 h at 60 °C, and Fe_3O_4 nanoparticles were formed according to Eq. 1.

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \tag{1}$$

The product was washed three times with deionized water and dried for 10 h in a vacuum oven at 60 °C. The prepared Fe_3O_4 nanoparticles (2.0 g) were ultrasonically dispersed into 50 mL deionized water at 25 °C. Then 5 mL NH_3•H_2O and 80 mL methanol solution containing 1.80 mL TEOS were added to the Fe_3O_4 suspension. The reaction mixture was stirred under ultrasonication for 15 min, and continued for 4 h without ultrasonication to form SiO_2-coated Fe_3O_4 (Fig. 1a). The nanocomposites were washed three times and dried in a vacuum oven at 60 °C for 12 h.

The Fe_3O_4@SiO_2 (1.0 g) was ultrasonically dispersed into 150 mL glycerol under a nitrogen atmosphere. Then 1.5 mL NH_3•H_2O and 50 mL methanol solution containing 0.8 mL TMMPS were added under stirring at 80 °C. After 1 h, the nitrogen-blowing was stopped, and the solution was continuously stirred for another 5 h. As shown in Fig. 1b, Fe_3O_4@SiO_2-SH was prepared. The fresh Fe_3O_4@SiO_2-SH was alternatively washed with methanol and deionized water until pH 7.0, and finally dried in a vacuum at 60 °C for 12 h.

2.3. Batch experiments and analytical methods

Hg(II) solutions of different concentrations (from 5 to 100 mg L^{-1}) were prepared, with their pH being adjusted by a buffer solution. Batch experiments were performed in glass flasks (100 mL) containing the freshly synthetized Fe_3O_4@SiO_2-SH and 50 mL of Hg(II) solution in a waterbath constant temperature vibrator (25 °C, 120 rpm). The supernatants (5 mL) were collected after 24 h and filtered through 0.22 μm membrane filters. The reaction time, initial Hg(II) concentration, and initial solution pH was changed to investigate their effects on Hg(II) adsorption.

2.4. Analytical methods

The aqueous Hg(II) concentration was analyzed by atomic fluorescence spectrophotometer (AFS-230E). Transmission electron microscopy (TEM, JEOL 2010, operated at 200 kV voltage) was used to obtain the nanoparticle structure and size. Fourier transform infrared analysis (Nexus670 FTIR spectrometer, acquired in the 4000–400 cm^{-1} wavenumber) was used to analyze the surface functional groups on the Fe_3O_4@SiO_2-SH nanoparticles.

3. Results and discussions

3.1. Characteristics of Fe_3O_4@SiO_2-SH nanocomposites

The geometric structures of bare Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2-SH nanoparticles were characterize by SEM and TEM. As shown in Fig 2a and b, most of the bare Fe_3O_4 nanoparticles were spherical, and the particle size was about 15–25 nm in the TEM image, the prepared Fe_3O_4 nanoparticles were more homogeneous and dispersed than the previous study [33]. Although the distribution was uniform, a portion of Fe_3O_4 nanoparticles were overlapped and aggregated due to the magnetic force, large surface area and