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Study on the influence of thiolation on the adsorption and magnetic recovery of superparamagnetic nanoadsorbents for Cd^{2+} removal

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ABSTRACT

In the study, the influence resulting from thiol-functionalization on Fe_3O_4-based superparamagnetic nanoadsorbents was investigated in detail, involving various physicochemical properties, especially, the contradiction between adsorption performance and magnetic recovery. The experimental results demonstrated clearly that the aqueous dispersibility and stability of the Fe_3O_4-SH nanoparticles were positively related with the thiolation while the magnetic response and recovery efficiency in aqueous solution had negative correlations with the amount of SH-groups on the surface. In addition, the adsorption performances for Cd^{2+} using the Fe_3O_4-SH nanoparticles with different thiolation degrees were also studied comprehensively, which were all sensitive to pH and ionic strength and varied with a similar trend. Meanwhile, the adsorption kinetics and isotherms manifested that the initial adsorption rates and adsorption capacities could also be positively correlated with higher thiolation degree on the nanoadsorbent surface.

1. Introduction

Cadmium (Cd), as a kind of non-essential heavy metal to all living organisms, is identified as one of the most toxic contaminants to plants, animals, and human beings in the environment [1–3]. With the industrial development these years, massive Cd contaminants have been discharged into our aquatic environment, triggering a serious environmental problems threatening human health and ecological security due to the enrichment of Cd in the environmental waters into living bodies to cause irreversible damages [4–7]. As a result, nowadays various treatment technologies have been developed to remove Cd contaminants from aquatic environments, such as chemical precipitation, evaporation, ion-exchange, adsorption, electrodialysis and reverse osmosis, *etc* [4,8–12]. Among them, adsorption has been one of the most utilized methods due to its low cost, effectiveness and convenience of subsequent processing [13–17]. Up to now, Fe_3O_4-based superparamagnetic nanoparticles, have attracted great attention as Cd adsorbents, in terms of their high surface areas and specific magnetic recovery, which overcomes the separation difficulty after use [18–21]. Therefore, thiolation, used to modify Fe_3O_4 nanoparticles with SH-groups on surface, has been studied widely to improve the stability and adsorption performance of the magnetic nanoadsorbents in the wastewater treatments involving Cd contaminants. Typically, SH-groups could be added on Fe_3O_4 surface through graft or coating of materials with thiols [22–24]. For instance, Bach et al. [25] obtained successfully the Fe_3O_4-SH nanoparticles through one-step process, using ammonium hydroxide (3-mercaptopropyl) trimethoxysilane (MPTMS) as the thiolation agent. Yantasee et al. [24] demonstrated that thiolated Fe_3O_4 showed great adsorption capacity and selectivity for Cd^{2+}, vastly overmatching common commercial adsorbents. In general, the thiol-functionalization could improve effectively the adsorption ability of Fe_3O_4-based adsorbents for aqueous Cd^{2+}. However, the SH-groups on Fe_3O_4 surface could severely weaken the magnetic response of these nanoadsorbents, resulting in a sharp conflict between the magnetic recovery and adsorption capacity [20,26]. Hitherto, the adsorption performances of various Fe_3O_4-SH nanoadsorbents for heavy metal contaminants have been extensively researched, while the concrete effect of thiolation on the physicochemical properties, adsorbability and magnetic recovery of Fe_3O_4-based nanosorbents, as well as the relationship between them, has been rarely explored yet. Nevertheless, they are critical for the thorough understanding of the Cd^{2+} adsorption behaviors of Fe_3O_4-SH nanoparticles and providing scientific guidance for the

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increasing of thiolation efficiency in order to be successfully applied in the heavy metals decontamination in polluted waters. Hence, the core goal of our study was to explore the Cd^{2+} adsorption processes using the Fe_3O_4-SH nanoparticles with different thiolation degrees and investigate the effect of the amount of SH-groups on superparamagnetic nanoadsorbent properties, magnetic recovery and adsorption capacity. The work started with the preparation of Fe_3O_4-SH with different thiolation degrees by the grafting of MPTMS onto the surface, followed by elaborate characterization to explore the variations within various properties, including morphology, surface charge, dispersibility, *etc*, as well as the magnetic recovery performance in particular. Then the adsorption processes of these nanoadsorbents were traced and compared comprehensively using aqueous Cd^{2+} as subjects, including the adsorption kinetics and isothermals as well as the effect of initial pH and ionic strength, focusing on the adsorption diversities stemming from thiolation.

2. Experimental section

2.1. Materials and reagents

The chemical regents used in this study were all of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared with deionized water with a resistivity of 18 MΩ cm. The working solutions of Cd^{2+} were all prepared using cadmium nitrate ($Cd(NO_3)_2$).

2.2. Preparation of superparamagnetic nanoadsorbents

2.2.1. Preparation of bare Fe_3O_4

1 mmol $FeCl_3{\cdot}6H_2O$ and 0.5 mmol $FeCl_2{\cdot}4H_2O$ was dissolved in 50 ml distilled water and then rapidly mixed with 10 ml 0.5 mol/L NaOH solution, followed by 3 h incubation at 60 °C under nitrogen atmosphere with vigorous stirring. At last the bare Fe_3O_4 could be collected from suspension with a 0.6 T permanent magnet after several washing steps.

Preparation of Fe_3O_4-SH: 0.5 g bare Fe_3O_4 prepared was dispersed in 100 ml of 1:1 water/ethanol solution with 2.5 g MPTMS under reflux for 5 h with nitrogen protection at 90 °C and pH of 10.0, 11.0 and 12.0, corresponding to Fe_3O_4-SH with 1.36, 3.12 and 4.73 mmol/g thiol, respectively. Finally the thiolated Fe_3O_4 nanoadsorbents were isolated using a 0.6 T permanent magnet from the solution and washed repeatedly with deionized water to eliminate the residues on surface.

2.2.2. Determination of thiolation degrees

The thiolation degrees on the prepared nanoadsorbents were determined through an indirect method dependent on the molar weight of Si. In a typical procedure, 0.1 g Fe_3O_4-SH was dissolved by 1 mol/L HCl solution and the Si concentration c_{Si} (mmol/L) was detected in solution after diluted with deionized water to 100 ml, whose value was equal with the thiolation degree D_t (mmol/g).

2.3. Adsorption and magnetic recovery

0.1 g Fe_3O_4-SH nanoparticles were added to 100 ml Cd^{2+} solution in a 250 ml flask, which was then placed in a shaker at 175 rpm at 30 °C. The supernatant was sampled at specified time intervals and the nanoadsorbents were separated by means of a permanent magnet before the residual concentration of Cd^{2+} in the supernatant was determined. The adsorption capacity q (mmol/g) and removal efficiency η were determined according to Eqs. (1) and (2).

$$q = (c_0 - c_h) \times (0.1g/0.1L) \tag{1}$$

$$\eta = (c_0 - c_h)/c_h \times 100\% \tag{2}$$

Where c_0 (mmol/L) and c_h (mmol/L) were the initial and residual concentrations of Cd^{2+} in solution, respectively.

In the magnetic recovery experiments, 30 ml suspension with 0.1 g well dispersed nanoparticles was under the field of a 0.6 T permanent magnet and the supernatant was sampled at given time intervals with the pH adjusted to 1.0 by 1 mol/L HCl to dissolve the residual nanoparticles. Then the Fe ion concentration in the sample was detected after diluted with deionized water to 100 ml to figure out the recovery efficiency η_r according to Eq. (3):

$$\eta_r = (c_{Fe0} - c_{Fe1})/c_{Fe0} \times 100\% \tag{3}$$

Where c_{Fe0} (g/L) and c_{Fe1} (g/L) were the Fe concentrations in the supernatant before (as control) and after magnetic removal.

All experiments in this study were triplicated with the variations among parallel experiments were less than 5%.

2.4. Assays

In this study, X-ray photoelectron spectra (XPS) of samples were recorded on a spectrometer instrument (PHI-5300, Perkin–Elmer, USA) with 1147.5 eV pass energy in an ultrahigh vacuum. Fourier-transform infrared (FTIR) analysis was carried on a FTIR spectrometer (Nicoletis 10, ThermoScientific, USA) with samples in KBr pellets and in the frequency range of 4000–400 cm^{-1} at 25 °C. The zeta potentials and size distributions of nanoparticles were measured by a zeta potentiometer (Zetasizer Nano ZSP, Malvern, UK) in a 10 mg/L suspension at 25 °C. X-ray diffraction (XRD) patterns were obtained depending on an X-ray power diffractometer (D8, BRUKER, Germany) with Cu-Kα radiation. Transmission electron microscopy (TEM) photos of nanoparticles were recorded on an electron microscope (FEI Quanta200, FEI, US) using 200 kV accelerating voltage of on specimens obtained by dropping the sample dispersed in deionized water on a copper grid and letting them to naturally dry. The magnetism of samples was analyzed by a vibrating sample magnetometer (730T, Lakeshore, USA). The pH values of working solutions were determined by a pH meter (SevenEasy, Mettler, Switzerland). The concentrations of Cd, Fe and Si in solutions were all detected by an inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument (IRIS, Thermo Elemental, USA).

3. Results and discussion

3.1. Effect of thiolation on nanoparticle properties

As shown in Fig. 1, multiple measurements had been taken to analyze the effect of thiol-functionalization on the properties of the superparamagnetic nanoparticles. The wide-scan XPS spectra of the bare Fe_3O_4 and Fe_3O_4-SH with different thiolation degrees are listed in Fig. 1a, where the peaks representing Fe, O could all be observed easily as well as that for the calibration electron (C1s). However, in contrast with that of bare Fe_3O_4, the characteristic peaks assigned for sulphur element (S2p at 163.6 eV) and silicon element (Si2p at 101.8 eV) were found in the spectra for all of Fe_3O_4-SH nanoparticles, which could be unanimously interpreted that SH-groups had anchored onto the Fe_3O_4 surface. FTIR spectra of the nanoparticles displayed in Fig. 1b witness that thiolation treatments had resulted in chemical changes on Fe_3O_4 surface through the appearance of new characteristic bands. As shown, the bands at 1123, 1079 and 987 cm^{-1} assigned to the Si—O—H and Si—O—Si groups appeared on the spectra of all Fe_3O_4-SH, indicating that the silane framework had been grafted successfully onto the nanoparticle surface by Fe-O-Si bonds. And the adsorption band at 2584 cm^{-1}, ascribed to the S—H stretching of MPTMS moieties,