Sulfoethyl functionalized silica nanoparticle as an adsorbent to selectively adsorb silver ions from aqueous solutions

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ABSTRACT

A novel adsorbent was fabricated via grafting sulfoethyl groups on silica nanoparticles to achieve selective adsorption of silver ions from aqueous solution. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA) were used to characterize the adsorbent. The influence of pH, initial concentration, adsorption time and interfering metal ions was investigated. The adsorption equilibrium time was about 60 min and the adsorption capacity for silver ion was 21.9 mg g^{-1} at pH 6. The adsorption isotherms fitted well with the Langmuir isotherm and the obtained kinetic data support a pseudo-second order adsorption behavior for the functionalized silica nanoparticles. The adsorption mechanism is the chelating interaction. The functionalized silica nanoparticle showed good selectivity to adsorb the silver ions from aqueous solution. The adsorbent could be of great potential as a new class of adsorbent for silver ions.

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1. Introduction

Silver is a precious metal that has been widely used in photography industry, electrical and electronic equipment and medical products [1]. However, silver ion is highly toxic to aquatic organisms and can accumulate in human body which can lead to serious problems [2]. Therefore, it is of particular importance to develop effective methods for separating and recovering silver from industrial effluent and waste water.

Traditional methods of recovering silver ions include precipitation, electrolysis and adsorption [3]. Adsorption is of special interest because of easy operation, economy, simple maintenance and high efficiency [4]. A number of materials have been developed as adsorbents for the removal and recovery of silver ions [5–7]. Among these adsorbents, chelating sorbent containing complexing groups has received more attention, as they can be used for removal of metal ions with high selectivity [8]. There have been many papers on the immobilization of chelating ligands on the adsorbent for separating and recovering of metal ions from aqueous solution [9–11].

In recent years, nanoparticles have received more attention because of their unique physico-chemical properties [12]. Compared with other materials, nanoparticles as sorbents offer a remarkable

higher surface area-to-volume ratio [13]. Nanosilica is a significant example of nanosorbent since it provides considerable properties such as possible reuse, fast reaction rate, non-toxicity, mechanical, thermal and chemical resistance, and most importantly it can be easily modified with various desirable functional groups to achieve selective adsorption [14]. Furthermore, silica is also abundant and economical. These series of excellent properties of silica nanoparticles (SNPs) make them good candidates for developing chelating adsorbent for silver ions removal.

In this work, we functionalized silica nanoparticles with sulfoethyl groups for selectively adsorbing silver ions from aqueous solution. The functionalized SNPs were characterized by TEM, FT-IR, XPS and TGA. The influences of contact time, solution pH, initial concentration and interfering metal ions on the adsorption performance were investigated. Furthermore, the selectivity of the adsorbent was examined, and the primary adsorption mechanism, adsorption kinetics and isotherms were also studied.
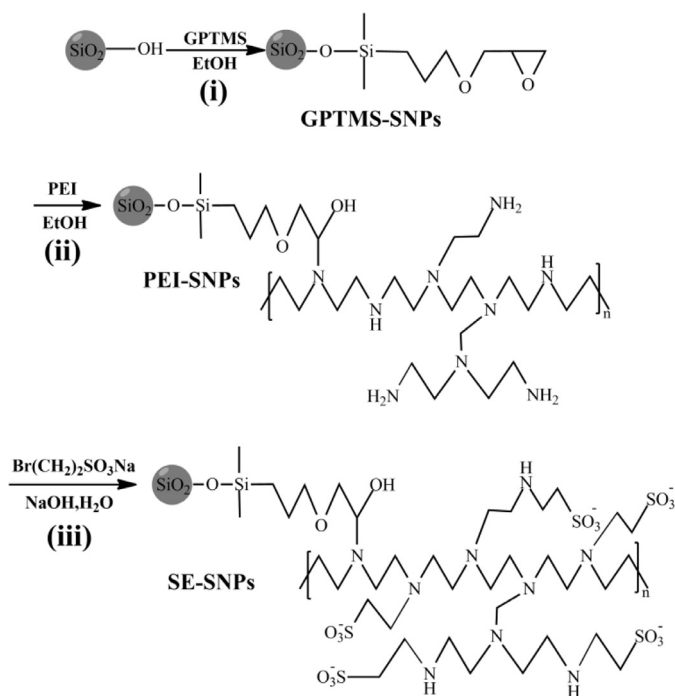
2. Experimental

2.1. Materials

Silica nanoparticles, 3-glycidyloxypropyltrimethoxysilane (GPTMS), branched polyethyleneimine (PEI) and sodium 2-bromoethanesulfonate were purchased from Aladdin Chemistry Co. Ltd. Ethanol was purchased by Sinopharm Chemical Reagent Co.,

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Scheme 1. Preparation of sulfoethyl functionalized silica nanoparticles.

Ltd. (China). All chemicals were analytical grade and used without any further treatment. All standard stock solutions of metal ions were prepared by dissolving appropriate amount of nitrate salts with deionized water. These standard solutions were adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions to achieve the desired pH value before using.

2.2. Preparation of sulfoethyl functionalized silica nanoparticles

The preparation process of the functionalized adsorbent was presented in Scheme 1. SNPs (5.0 g), 3-glycidyloxypropyltrimethoxysilane (10 mL), and ethanol (40 mL) were added to a 100 mL three-necked flask. The mixture was stirred and refluxed for 24 h. Then the suspension was centrifuged, the precipitate was washed with ethanol for five times and dried at 60 °C overnight to give GPTMS-SNPs. The amine-functionalized SNPs were prepared as follows. GPTMS-SNPs (4.5 g) were stirred in 40 mL of ethanol solution containing PEI (100 mg mL^{-1}) under reflux for 24 h. Then the mixture was centrifuged, the solid (labeled as PEI-SNPs) was washed with deionized water to remove physically adsorbed PEI and dried at 60 °C. Finally, 5.5 g of PEI-SNPs and 10 g of sodium 2-bromoethanesulfonate were added to 40 mL of deionized water. The mixture was stirred for 12 h at 70 °C, then 1.5 g of NaOH in 10 mL of water was added to the mixture, and stirred for 12 h at 70 °C, the resulting solid was washed and dried under vacuum, defined to SE-SNPs.

2.3. Adsorption experiments

Adsorption experiments were carried out in a ZD-85 thermostat steam bath vibrator at a shaking speed of 300 rpm, using 15 mL centrifugal tube. Generally, 20 mg SE-SNPs was added into 10 mL Ag$^+$ solution with desired initial concentrations and pH, followed with oscillation at 25 °C for 2 h After adsorption, SE-SNPs were separated from solution by filtration and the supernatant was determined by inductively coupled plasma atomic emission spectrometry. The amount of silver adsorbed per unit mass of adsorbent (q) and adsorption percent (R) were calculated from the fol-

lowing equations:

$$q = V(C_0 - C_t)/m \tag{1}$$

$$R = 100(C_0 - C_t)/C_0 \tag{2}$$

where m(g) represents the mass of SE-SNPs and V (L) is the volume of Ag$^+$ solution. C_0 and C_t (mg L^{-1}) are the initial and final concentration of Ag$^+$ solution, respectively. All the adsorption experiments were performed at least three times.

The effect of solution pH on Ag$^+$ adsorption was studied by varying the pH from 2 to 6, the initial Ag$^+$ concentration used was 50 mg L^{-1}, whereas other parameters like solution temperature, agitation speed and adsorbent dosage remained constant. To study the adsorption isotherms, 20 mg of SE-SNPs were added into 10 mL of Ag$^+$ solutions of different initial concentrations (20–90 mg L^{-1}) at pH 6. After the system reached adsorption equilibrium, the concentrations of Ag$^+$ in the supernatant solutions were determined to calculate q at equilibrium. Kinetic experiments were performed with a certain Ag$^+$ concentration (50 mg L^{-1}) and pH 6. The adsorption process was rapidly stopped by vacuum filtration at different time intervals (10–180 min), and the concentrations of Ag$^+$ in filtrate solutions were determined. Ashley Bibby performed the same operation in experiment to study the adsorption kinetics [15]. The selectivity of the adsorbent toward silver(I), copper(II), nickel(II), cobalt(II), manganese(II), barium(II), lead(II), zinc(II), cadmium(II) and magnesium(II) was studied. 20 mg of SE-SNPs was added into a series of centrifuge tubes containing 10.0 mL of single metal solution (50 mg L^{-1}) at pH 6. The mixture was shaken for 2 h and filtrated, then the concentration of the metal ions in the supernatant was determined.

2.4. Characterization

The size and morphology of silica nanoparticles were characterized by transmission electron microscope (TEM, JEM-2100). The Fourier transform infrared (FTIR) spectroscopy was collected using spectrum one FT-IR spectrometer (Irprestige-21) with a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on a ESCALab220I-XL (VG Scientific, UK) equipped with a monochromatized Al K-alpha radiation source (1486.6 eV). The binding energies were referenced to the C 1 s line at 284.6 eV from adventitious carbon. TGA measurements were performed on PerkinElmer TGA-7(USA) thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. The zeta potential of TSC-SNC in the aqueous solution was measured using a Zeta Plus potentiometer (Brookhaven, USA).

3. Results and discussion

3.1. Characterization of sulfoethyl functionalized silica nanoparticles

The size and morphology of SNPs and SE-SNPs were obtained by TEM at 150,000 × magnification and the images are shown in Fig. 1. It is noted that the average size of SNPs is 16.3 nm, and there is no obvious change in size and morphology after modified.

Fig. 2 shows the Fourier transform infrared spectra of GPTMS-SNPs, PEI-SNPs and SE-SNPs. The O−H stretching vibration band at 3430 cm^{-1} and the O−H deformation vibration band at 1630 cm^{-1} are due to the adsorbed water and silanol groups. The characteristic adsorption peaks at 1100 cm^{-1} and 470 cm^{-1} are attributed to Si−O−Si stretching vibration and bending vibration, respectively. In the FTIR spectrum of GPTMS-SNPs, the C−H stretching vibration at 2920 cm^{-1} and 2845 cm^{-1} indicated that organic silane was grafted onto the surface of silica nanoparticles. For PEI-SNPs, the 3600–3000 cm^{-1} band is broader, because the –NH$_2$ band at