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Adsorption of heavy metal ions from aqueous solution by polyrhodanine-encapsulated magnetic nanoparticles

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ABSTRACT

Polyrhodanine-coated γ-Fe_2O_3 nanoparticles, synthesized by one-step chemical oxidation polymerization, were applied to the process of removal of heavy metal ions from aqueous solution. Factors influencing the uptake of heavy metal ions such as solution pH, initial metal ion concentration, contact time, and species of metal ions were investigated systematically by batch experiments. The adsorption equilibrium study exhibited that the Hg(II) ion adsorption of polyrhodanine-coated magnetic nanoparticles followed a Freundlich isotherm model than a Langmuir model. The kinetic data of adsorption of Hg(II) ion on the synthesized adsorbents were best described by a pseudo-second-order equation, indicating their chemical adsorption. In addition, the synthesized nano-adsorbents can be repeatedly used with help of an external magnetic field due to their magnetic properties. This work demonstrates that the magnetic polyrhodanine nanoparticles can be considered as a potential recyclable adsorbent for hazardous metal ions from wastewater.

1. Introduction

Water pollution by heavy metal ions has become a serious environmental issue especially due to their toxicity and tendency to bioaccumulation [1,2]. The heavy metal ions are not only toxic to living organisms in water, but also cause harmful effects to land animals including humans through food chain transfers. In living organisms, heavy metal ions can particularly bind to nucleic acids, proteins, and small metabolites. The contaminated organic cells are altered or missed their biological functions with losing the homeostatic control of essential metals, resulting in fatal health problems [3,4]. Therefore, it is necessary to eliminate such hazardous heavy metal ion in wastewater before discharging it into the ecosystem.

Several techniques, such as ion exchange [5], chemical precipitation [6], membrane processes [7,8], electro-dialysis [9], and adsorption [10–12] have been developed for the removal of heavy metals from aqueous media. Among these purification methods, the adsorption process using adequate adsorbents is considered as one of the most efficient and economical techniques in the viewpoint of simple design and facile handling. Numerous efforts have been contributed to the development of effective adsorbents like activated carbon [13], chitosan [4,14], zeolite [15], polymer [16,17], functionalized silica [18–21], and clay [22–25]. Besides, there is also a huge interest to adsorption on metallic and coated surfaces in the field of petroleum science [26–28].

Polyrhodanine has attracted considerable attention in various application fields such as anticorrosion [29], antibacterial [30,31], and antihistaminic agents [32]. In addition, they can be used for detecting or adsorbing of metal ions because the rhodanine monomeric unit has a metal-binding functional groups [33–37]. According to the hard and soft acids and bases (HSAB) theory introduced by Pearson, oxygen, nitrogen, and sulfur atoms are regarded as metal-binding atoms with strong affinity for heavy metal ions like lead, cadmium, mercury, etc. [38]. Polyrhodanine can be expected as a promising candidate for efficient adsorbent of heavy metal ions because it contains oxygen, nitrogen, and sulfur atoms in its monomeric structure.

We previously reported the facile one-step chemical oxidation polymerization for the preparation of magnetic γ-Fe_2O_3/polyrhodanine nanoparticles [39]. In the present work, the synthesized magnetic polyrhodanine nanoparticles were evaluated in their heavy metal ions adsorption performances. The various papers related to the heavy metal removal using magnetic nano- or microparticles have been reported [40–45]. It is anticipated that the polyrhodanine-encapsulated magnetic nanoparticles (PR-MNPs) prepared under one-pot synthesis system have some advantages for heavy metal removal such as easy recovery by an external magnetic field and excellent metal-binding activity due to its magnetic property and large surface area, respectively. The adsorption mechanism and kinetics of the PR-MNPs were systematically

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investigated with various experimental parameters such as solution pH, initial metal ion concentration, contact time, and species of metal ions. In order to study the adsorption behavior of the PR-MNPs, adsorption isotherm models and kinetic models were applied to the experimental data. The PR-MNPs could be easily recycled based on their magnetic properties; the recyclability of the PR-MNPs was also investigated.

2. Material and methods

2.1. Materials

Rhodanine (97%), iron chloride ($FeCl_3$) (97%), and sodium borohydride ($NaBH_4$) (99%) were purchased from Aldrich (Milwaukee, WI) and used without further purification. For heavy metal adsorption properties, mercury nitrate monohydrate ($Hg(NO_3)_2{\cdot}H_2O$) (98%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$) (98%), manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$) (98%), and chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$) (99%) were purchased from Aldrich (Milwaukee, WI). The hydrochloric acid (37%), nitric acid (70%), and ammonia solution (37%) were also bought from Aldrich (Milwaukee, WI) for control of solution pH.

2.2. Fabrication of polyrhodanine-encapsulated magnetic nanoparticles (PR-MNPs)

The PR-MNPs were fabricated using previously reported one-step process [39]. In a typical procedure, 100 ml of an aqueous solution containing 7.5 mM of rhodanine was heated to 90 °C. After the solution was heated, iron chloride (6.2 mM) and sodium borohydride (26 mM) were sequentially injected into the rhodanine dissolved water. After then, the reactor was sealed up and vigorously stirred. The iron ions became magnetic γ-Fe_2O_3 nanoparticles, and then the rhodanine monomer was polymerized on the surface of magnetic nanoparticles with vigorous stirring for 10 h. After polymerization, the synthesized PR-MNPs were obtained by external magnetic field and washed several times with more than 100 mL of distilled water to remove the residual reagents.

2.3. Effects of pH and initial metal ion concentration on adsorption of Hg(II) ions

In this work, the all the tested PR-MNPs were the fresh one except for the recycling test. Five milligrams of fabricated PR-MNPs was dispersed in 10 mL of mercury nitrate solution at serial pH values (2.0–8.0). The pH value was adjusted with 0.1 M of nitric acid and 0.1 M of ammonia solution. The prepared samples were shaken for 12 h at 350 rpm with mechanical shaker (VS-101 Green Sseriker, Vision Scientific Co.). The residual concentration of the mercury ion was measured by inductively coupled plasma (ICP) analysis after the adsorbent was recovered from the solution by an external magnetic field. Furthermore, the relationship between adsorption capacity and initial concentration of metal ion was also investigated. Five milligrams of magnetic polyrhodanine nanoparticles was added into each flask containing 10 mL of Hg(II) ion solutions with various initial metal ion concentrations (from 1 mg/L to 80 mg/L). All the flasks were shaken at 350 rpm in a rotary shaker for 12 h. The adsorbed amount of metal ions onto the PR-MNPs was calculated according to the following equations:

$$q = \frac{C_0 - C}{C_0} \times 100(\%) \tag{1}$$

$$Q_e = \frac{(C_0 - C_e) \times V}{W} \tag{2}$$

where q is the adsorptivity (%), Q_e is the equilibrium adsorption capacity of adsorbent in mg (metal)/g (adsorbent), C_o and C is the concentration of metal ions before and after adsorption in mg/L, C_e is the equilibrium concentration of metal ions in mg/L, V is the volume of metal ions solution in liter scale, and W is the weight of the adsorbent in gram scale. The C_e values were defined as the remained Hg(II) ion concentration after 12 h of shaking time because it was determined that the adsorption of Hg(II) ions onto the PR-MNPs sufficiently reached an equilibrium state for 12 h based on the experimental data.

2.4. Effect of contact time to adsorption capacity of Hg(II), Cd(II), Mn(II) and Cr(III) ions onto the PR-MNPs

Typically, 5.0 mg of the PR-MNPs was added into 10 mL of Hg(II) ion solution (80 mg/L) at a pH value of 4.0. Then, the prepared samples were shaken at 350 rpm using a mechanical shaker at 25 °C. After a desired time, the PR-MNPs were removed from the solution using an external magnetic field. The residual Hg(II) ion concentration was determined by inductively coupled plasma (ICP) analysis. The analysis of the batch adsorption of the metal ion was carried out as a function of contact time (from 30 min to 12 h). The adsorption capacities of Cd(II), Mn(II), and Cr(III) ions were also determined similarly. For accurate adsorption results, all the adsorption data were analyzed three times and the results were averaged.

2.5. Recycling experiment of PR-MNPs to Hg(II) ions

Five milligrams of the PR-MNPs was added into 10 mL of Hg(II) ion solution (80 mg/L) at a pH value of 4.0. Then, prepared samples were shaken at 350 rpm using a mechanical shaker at 25 °C. After 4 h, the PR-MNPs were harvested from the solution using an external magnetic field and the residual metal ion concentration was determined using inductively coupled plasma (ICP) analysis. In order to regenerate the metal-binding property of the PR-MNPs, the recovered PR-MNPs were dispersed to 10 mL of 0.1 M hydrochloric acid solution and shaken for 3 h. Then, the PR-MNPs were collected using an external magnetic field and washed repeatedly with excessive amount of deionized water (pH 7) to neutralize the acidic condition. After drying in a vacuum oven at room temperature, the PR-MNPs were re-added into the fresh mercury ion solution to investigate the potential to be a recyclable heavy metal ion removal agent. The recovery rate was calculated according to the following equation:

$$\mathrm{Re} = \frac{Q_r}{Q_o} \times 100(\%) \tag{3}$$

where Re is the recovery rate (%), Q_o is the uptake of metal ions by the fresh PR-MNPs in mg (metal)/g (adsorbent), and Q_r is the uptake of metal ions after recovery procedure in mg(metal)/g (adsorbent).

2.6. Characterization

The image of transmission electron microscope (TEM) was obtained with a JEOL JEM-200CX (JEOL, Japan). Acceleration voltage for TEM was 200 kV. The X-ray diffraction (XRD) patterns of the PR-MNPs were obtained with a D5005 powder X-ray diffractometry (Bruker, Germany) with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 1 deg/min. The X-ray photoelectron spectra were performed with an AXIS-His X-ray photoelectron spectroscopy (XPS) analyzer (KRATOS). The magnetic properties of the PR-MNPs were measured using a SQUID magnetometer at 300 K between −20 and +20 kOe (Quantum Design MPMS5). The UV–vis spectra were taken with a Perkin-Elmer Lambda-20 spectrometer (Perkin-Elmer, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Bomem MB 100 spectrometer (Quebec, Canada) in the absorption modes at a resolution of 4 cm^{-1} and 32 scans. ICP