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Selective adsorption of Ag(I) ions with poly(vinyl alcohol) modified with thiourea (TU–PVA)

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ABSTRACT

A novel poly(vinyl alcohol) modified with thiourea adsorbent (TU–PVA) was successfully prepared and characterized. The spectrum of FT–IR implies that the thiourea group has been modified on the primary hydroxyl of PVA in TU–PVA. The adsorption behavior for Ag(I) ions on TU–PVA follows the Langmuir model, and the adsorption kinetic data are fitted with the pseudo–second-order model. The maximum adsorption capacity for Ag (I) ions on TU–PVA calculated by the Langmuir model was 66.93 $mg\cdot g^{-1}$. Thermodynamic parameters indicate that the adsorption process for Ag(I) ions on TU–PVA is spontaneous and endothermic in nature. The selectivity coefficient of Ag(I) ions and other metal cations onto TU–PVA indicated an overall preference for Ag(I) ions, and the selectivity and adsorption capacity was much higher than that of poly(vinyl alcohol). The selective adsorption mechanism of Ag(I) ions on TU–PVA was coordinated. The study of repeating and selectivity adsorption indicates that TU–PVA exhibits good durability and selectivity for Ag(I) ions. Thus, the adsorbent has potential application in recycling of Ag(I) ions in complex wastewater.

1. Introduction

Silver has significant industrial uses and plays an important role in daily life because of its superior malleability, ductility, electrical and thermal conductivity, photosensitivity, and antimicrobial properties. However, the earth resources of silver are extremely scarce and are mainly found with lead, copper, and antimony deposits. Substantial amounts of silver are lost in effluents discharged from various industries, requiring the removal and recycling of Ag(I) ions from wastewater (Donia et al., 2007; Wang et al., 2009). Common methods can be used to remove and recycle Ag(I) ions from industrial wastewater, including precipitation (Rivera et al., 2007), metallic replacement (Liu et al., 2015), ion exchange (Virolainen et al., 2015), electrodeposition (Matias et al., 2015), and adsorption (Zhang et al., 2015a; Petrova et al., 2015). Among these methods, adsorption exhibits the greatest potential for reducing the concentration of Ag(I) ions because of the low energy consumption and simplicity of the process However, the common adsorbents used for metal ions cannot effectively extract Ag(I) ions from complex wastewater, which contains other high-concentration metal ions, particularly when Ag(I) ions are within trace levels of concentration ($< 100\ mg\ L^{-1}$). Therefore, the adsorbent showing good selectivity toward Ag(I) ions plays an important role in the separation and enrichment of Ag(I) ions (de Almeida Neto et al., 2013).

Numerous polymers and their derivatives as adsorbents have drawn considerable interest because of their potential for application in the removal and recycling of heavy metal ions. These polymers and their derivatives include chitosan (Petrova et al., 2015; Djerahov et al., 2016; Alshehri et al., 2016), polyacrylamide (Desai and Murthy, 2012), pyrazine (Lu et al., 1997), poly(vinyl pyrrolidone) (Gasparotto et al., 2011; Sionkowska et al., 2009), pyrazine derivatives (Huang et al., 2016; Zhang et al., 2015b), and poly(vinyl alcohol) (PVA) (Hallaji et al., 2015; Rad et al., 2014; Majidnia et al., 2015). Polymers with nitrogen radical exhibit good adsorption for metal ions; however, they cannot show an excellent selectivity for Ag(I) ions because their coordination ability with Ag(I) ions is not significantly stronger than that of other metal ions. PVA, which exhibits cost efficiency, chemical stability, and nontoxicity, is widely used in adhesives, biological catalysts, and emulsifiers. However, PVA without nitrogen and sulfur functional groups show poor adsorption for metal ions. Tongsai et al. (Jamnongkan et al., 2014) used a PVA hydrogel to remove copper ions from an aqueous solution. Modified and composite materials on PVA were used in adsorption experiments for metal ions. Lu et al. (Lu et al., 2014) synthesized a hydrophilic poly(vinyl alcohol-*co*-ethylene) nanofiber membrane functionalized with iminodiacetic acid for the removal of Cu(II), Ni(II), Co(II), Zn(II), and Mg(II) ions. Song et al. (2015) fabricated polyacrylonitrile/PVA fiber, which shows good selectivity toward Ag(I)

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ions in a multiple-metal ion solution. Yehua et al. (Zhu et al., 2014) studied the removal of Co(II) from radioactive wastewater by blending chitosan with PVA. Irani et al. (2012) used a mesoporous poly (vinyl alcohol)/tetraethylorthosilicate/aminopropyl triethoxysilane composite nanofiber prepared by sol-gel/electrospinning for cadmium removal. Keshtkar et al. (Keshtkar et al., 2013) used 3-mercaptopropyltrimethoxysilane as the -SH functional group and 3-aminopropyltriethoxysilane (APTES) as the -NH_2 functional group to modify PVA/silica membranes for the adsorption of copper ions in wastewater. Similarly, these materials exhibit no excellent selectivity for the specific metal ion. Thus, a polymer adsorbent is expected to be easily modified at a low cost and with high selectivity toward Ag(I) ions.

Numerous studies indicate that materials containing sulfur radical have a special affinity for Ag(I) ions. In accordance with the hard and soft acids and bases (HSAB) concept, their coordination is highly strong when Ag(I) ion (soft acid) reacts with sulfur radical (soft base). Therefore, a polymer adsorbent modified with a sulfur radical can also adsorb Ag(I) ions. However, there are few reports on the PVA polymer material-modified thiourea.

In the present study, we synthesized a new PVA adsorbent modified with thiourea (TU–PVA). The TU–PVA adsorbent was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT–IR), thermal gravimetric analysis (TGA), and X-ray diffraction (XRD). In addition, the selectivity and reusability of the sorbent toward Ag(I) ions. as well as the isotherms and kinetics during adsorption, were investigated.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA, 1750 ± 50 polymerization degrees, Mw = 81,000–96,000, hydrolysis 98.5%–99.4%) was purchased from Xiangzhong Chemical Reagent Development Center, Hunan, China. Glutaraldehyde (GA, 50% aqueous solution), hydrochloric acid (HCl, 37% reagent grade), and $AgNO_3$ were supplied by Shanghai ShenBo Chemical Co., Ltd. Thiourea (TU) was obtained from Tianjin Tianli Chemical Reagent Co., Ltd.,China. All reagents were of analytical grade and used without further purification.

2.2. Analytical instrumentation

Fourier-transform infrared spectroscopy (FT–IR) was used to characterize and analyze the adsorbent. Their spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer with an attenuated total reflectance accessory, in the wavelength range of 4000–400 cm^{-1}. XRD was conducted to determine the crystalline structures of the composites by using a PerkinElmer PHI-5400 diffractometer, employing a CuKα radiation wavelength of 1.54 λm. The data were taken within the Bragg range of 3°–90° (2θ), with a step size of 0.02°. The morphology and composition of the synthesized composites were analyzed using a field-emission scanning electron microscope (Hitachi S-4800, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscope (EDX). TGA and differential scanning calorimetry were conducted using a Simultaneous Thermal Analyzer STA 409PC (NETZSCH, Germany) at temperatures ranging from 30 °C to 600 °C with 20 mL min^{-1} flow of nitrogen and a heating rate of 10 °C min^{-1}. The absorbance of Ag(I) ions was detected using a TAS-990 atomic absorption spectrophotometer (AAS; Purkinje General, Beijing) at 328.1 nm.

2.3. Preparation of the TU–PVA adsorbent

PVA solution (10%) was prepared by dissolving the PVA powder in deionized water at 363 K. The solution was then cooled to room temperature, with its pH adjusted to 3.0 by adding 0.5 $mol·L^{-1}$ HCl. The acidified PVA solution was slowly dropped into a glutaraldehyde solution (2.56 $mol·L^{-1}$, 100 mL) in a 250 mL beaker. The mixture was stirred for 12 h at 343 K. The white powder was then washed to remove any unreacted fraction with ethanol and deionized water. In the subsequent step, the white powder and the acidified thiourea solution (1.0 $mol·L^{-1}$, 100 mL) were thoroughly mixed and heated at 333 K to react for 12 h. The synthesized white powder was washed with deionized water, dried, and labeled as TU–PVA.

2.4. Adsorption experiments

Batch adsorption experiments were conducted in 100 mL Erlenmeyer flasks. Adsorbent concentration was kept constant at 0.1 g in a 25.0 mL solution. The pH of the sample solution was adjusted by adding 0.1 $mol·L^{-1}$ HNO_3 and then maintained in the 5.0 ± 0.1 range. The initial and equilibrium concentration of the Ag(I) ions were measured using an AAS. The adsorption capacity (q) and removal efficiency (η) of the Ag(I) ions were calculated using Eqs. (1) and (2), respectively:

$$q = (C_0 - C) \times \frac{V}{m} \tag{1}$$

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \tag{2}$$

where q is the adsorption capacity of Ag(I) ions at time t or at the equilibrium ($mg·g^{-1}$). C_0 is the initial Ag(I) ion concentration of the solution ($mg·L^{-1}$), C is the Ag(I) ions concentration of the solution at time t or at the adsorption equilibrium ($mg·L^{-1}$), m is the mass of the adsorbent sample used (g), and V is the volume of the solution used (L).

2.5. Adsorption selectivity experiments

In this study, Ni(II), Cu(II), Pb(II), and Zn(II) ions were chosen as competitive metal ions to prove the Ag(I) specificity of TU–PVA and PVA. Mixed solutions containing Ag(I), Ni(II), Cu(II), Pb(II), and Zn(II) ions (100.0 $mg·L^{-1}$ for each) were used to perform the competitive adsorption test. After adsorption equilibrium, the concentration of each ion in the remaining solution was measured with an AAS. Distribution coefficients (K_d) of Cu(II), Ni(II), Pb(II), and Zn(II) ions with respect to Ag(I) were calculated using Eq. (3) (Ren et al., 2008a).

$$K_{\mathrm{d}} = \frac{q_{\mathrm{e}}}{C_{\mathrm{e}}} \tag{3}$$

where K_{d} is the distribution coefficient ($L·g^{-1}$), q_{e} is the equilibrium adsorption capacity of metal ions ($mg·g^{-1}$), and C_{e} is the equilibrium concentrations of metal ions ($mg·L^{-1}$). The selectivity coefficient (k) for the binding of Ag(I) in the presence of a competitor species can be calculated using Eq. (4).

$$k = \frac{K_{\mathrm{adsorption-metal}}}{K_{\mathrm{interferent-metal}}} \tag{4}$$

2.6. Desorption experiments

Desorption experiments were conducted in 100 mL Erlenmeyer flasks. The concentration of TU–PVA adsorbing Ag(I) ions was kept constant at 0.1 g in a 20.0 mL eluting solution (a mixed solution of 1.0 $mol·L^{-1}$ nitric acid and 0.5 $mol·L^{-1}$ thiourea). The solution was then oscillated in an oscillator for about 8 h at 25 °C. The concentration of Ag(I) ions in the filtrate was measured using an AAS.