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Selective recovery of silver from aqueous solutions by poly (glycidyl methacrylate) microsphere modified with trithiocyanuric acid

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ABSTRACT

The poly (glycidyl methacrylate) microsphere was modified with trithiocyanuric acid to achieve selective adsorption of silver ions from aqueous solutions. X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the microsphere. In this study, the effects of pH, initial silver ions concentration and contact time on silver ions adsorption, reusability and selectivity of the microsphere were investigated. Experimental results showed that the removal rate of silver ions reached 96.40% under pH 5, the adsorption equilibrium time was about 14 h and the maximum adsorption capacity was 217.17 mg/g at pH 5. Besides, the microsphere has an excellent selectivity for silver ions among Zn (II), Ni(II), Co(III) and Ge(IIII). The adsorption isotherm of Ag^{+} on T-PGMA fitted the Langmuir isotherm model well and the adsorption kinetics followed the pseudo-second-order model, suggesting that the main adsorption is chemical monolayer adsorption. Moreover, the microsphere has a high reusability and the absorbability was slightly decreased from 96.29% to 94.01% after four cycles. All the experimental data indicated that the microsphere is very promising for silver ions adsorption from aqueous solutions.

1. Introduction

Silver has always played an significant role in industrial and various aspects of human life [1]. Due to the unique physical and chemical properties [2], silver is widely used in biomedicine, photography, battery industry, electronics industries, clothing, photonics, catalysis, jewelry and other important areas [3–6]. Some reports evidenced that thousands tons of silver have been consumed every year. Thus, silver ion was discharge into wastewater by various industrial activities [4,7]. With the circulation of water, silver ions mixed into the groundwater or exposed to the air, causing disease, organ failure, behavioral changes and oxidative stress to human beings and many other creatures [8–10]. On the one hand, there is a shortage of silver resources [11]. On the other hand, the global demand for silver continues to escalate [12]. Hence it is important to recover silver from water.

Generally, the recovery methods for silver from aqueous solutions include electrolysis, ion exchange, solvent extraction, chemical precipitation, membrane technique and adsorption [13–15]. Adsorption is recognized as a promising method to remove silver ions because of its high efficiency, simplicity, reusability, cost-effectiveness and environmental friendliness [16]. Many sorbents have been developed for the recovering of silver ions, such as silica gel, cellulose, chitin nanomaterials and polymer materials [17–19]. In contrast, polymer materials are promising for its high uptake capacity, excellent selectivity and better stability [19].

Polymer materials have received widespread attention as a new type of sorbent for the removal of metal ions [20]. Poly (glycidyl methacrylate)(PGMA) is one of the polymer materials due to its good mechanical strength, acid and base resistance, and high reactivity of the epoxy group [21]. Moreover, its epoxy group can be covalently react with ligand by a single chemical reaction step [22,23].The introduction of a chelating group to conventional polymer is important for extending their applications. Thus, the functionalized PGMA will meet the practical application in many fields, such as for chromatography, sensing and sorption.

In this paper, a new adsorbent was synthesized via modifying poly (glycidyl methacrylate) microsphere with trithiocyanuric acid for the recovery of silver ion from aqueous solutions. The adsorbent was characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). The effects of pH, initial silver ions concentration and contact time were investigated. Meanwhile, selectivity, reusability, adsorption kinetics, adsorption isotherms and adsorption mechanism were also examined. It has the advantages of high selectivity and large adsorption capacity.

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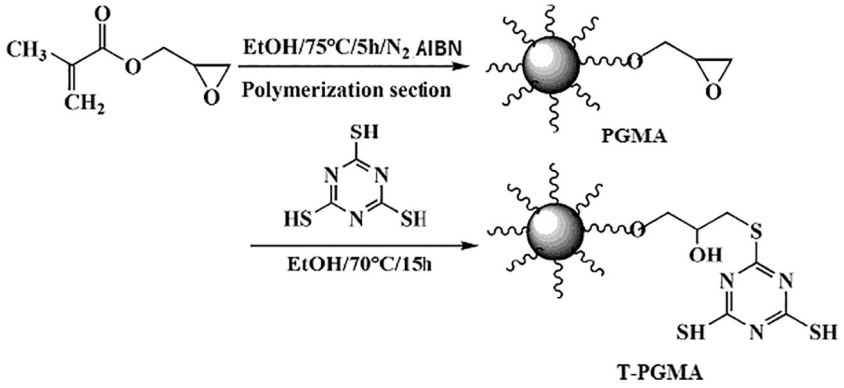

Scheme 1. The modified process of PGMA with trithiocyanuric acid.

2. Experimental section

2.1. Materials

Glycidyl methacrylate (GMA), polyvinylpyrrolidone (PVP), Azobisisobutyronitrile (ABIN), Trithiocyanuric acid (TCY) were purchased from Aladdin Chemistry Co. Ltd. Ethanol was purchased by Sinopharm Chemical Reagent Co. Ltd. (China). Silver Nitrate was purchased from shanghai Regent Chemical Reagent Co. Ltd. All of the chemicals were analytical reagent. The pH value of standard solutions was adjusted by HNO_3 and NaOH solutions.

2.2. The modified process of PGMA with trithiocyanuric acid

The modified process of PGMA with trithiocyanuric acid (TCY) has been showed in Scheme 1. Firstly, glycidyl methacrylate (10 g), PVP (3 g), ABIN (0.12 g) and ethanol (150 mL) were added into a 250 mL three necked round-bottomed flask. The mixture was stirred and refluxed for 5 h at 70 °C under nitrogen. Then, the suspension was centrifuged (8000 rpm, 15 min) and the precipitate was washed by ethanol for five times and dried at 70 °C for 12 h. The obtained product was referred as PGMA. Secondly, the mixture of PGMA (5 g), TCY (5 g) and ethanol (100 mL) were stirred and refluxed for 15 h at 70 °C. After centrifuged and washed by deionized water, the final product was defined to T-PGMA.

2.3. Adsorption experiments

The adsorption experiments of silver ions on T-PGMA were carried out in a ZD-85 thermostat vibrator at 300 rpm and 28 °C. 10 mg of T-PGMA sorbent was added into 15 mL silver solution with different initial concentration and pH. After 14 h, the mixture was centrifuged at 8000 rpm for 15 min. The concentration of silver ions in the supernatant was determined by inductively coupled plasma optical emission spectrometer (ICP-OES). The adsorption kinetics experiments were carried out in different time (5 min–1080 min), and the selective adsorption experiments of silver ions with the coexisting ions of Zn(II), Ni(II), Co (III) and Ge(IIII) were also investigated. In addition, the reusability of T-PGMA was also studied. The removal rate (R) and equilibrium adsorption capacity (q) of silver ion adsorbed on T-PGMA were showed by Eqs. (1) and (2), respectively.

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

$$q = \frac{(C_0 - C_t)}{m} V \quad (2)$$

where m (mg) represents the mass of T-PGMA sorbent and V (mL) represents the volume of the silver ion solution. R (%) and q (mg/g) are the removal rate and the equilibrium adsorption capacity of silver ion, respectively. C_0 (mg/L) and C_t (mg/L) are the initial and residual concentration of silver ion, respectively.

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50, USA) was recorded from 400 to 4000 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) was performed with ESCALab220I-XL (VG Scientific) from UK and equipped with a 1486.6 eV radiation source of monochromatized Al K-alpha. The scanning electron microscope (SEM, Phenom pro X, Netherlands.) has a magnification range of 20–100,000× and an acceleration voltage of 2–20 kV. The concentration of silver ion was measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Leeman prodigy 7, USA).

3. Results and discussion

3.1. Characterization

The Fourier transform infrared spectra of PGMA and T-PGMA were showed in Fig. 1. The peaks at 2935 cm^{-1}, 1723 cm^{-1}, 1145 $cm^{-1}$and 758 cm^{-1} in the spectra of PGMA were attributed to the C—H, C═O, C—O and C-O-C stretching vibration, respectively. The bands at 845 cm^{-1} and 905 cm^{-1} were corresponded to the epoxy groups of the PGMA microspheres. And the two peaks at 845 and 905 cm^{-1} disappeared after ring-opening reaction with TCY. In the spectra of T-PGMA, new peaks at 3435 cm^{-1}, 1648 cm^{-1}, 1484 cm^{-1} and 610 cm^{-1} were the bonds of O—H, C═N, C—N and C—S, respectively. The results

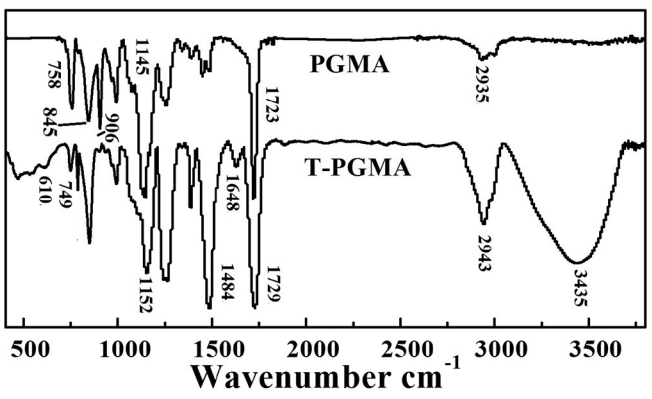

Fig. 1. FT-IR spectra of PGMA and T-PGMA.