Cellulose-based ionic liquids as an adsorbent for high selective recovery of gold

Wanghuan Guo[a,b,c], Fan Yang[a,b,*], Zhigang Zhao[a,b], Qiuxia Liao[a,b], Chunqing Cai[a,b],
Yang Zhang[a,b], Ruixi Bai[a,b]

[a] Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, China
[b] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China
[c] College of Chemistry and Materials, Fujian Normal University, Fuzhou, Fujian 350007, China

ABSTRACT

To achieve an adsorbent that has better absorption and extraction performance, carboxymethyl-diethylammo-niumethyl cellulose (CMDEAEC), a low-cost cellulose-based ionic liquid that possesses a nanoscale particle size and good swellability to increase the contact area, was prepared through a one-step reaction. The chemically modified cellulose was verified by Fourier transform infrared spectroscopy, elemental analysis and scanning electron microscopy. As an adsorbent, CMDEAEC was used for selective recovery of metal ions. The effects of pH, adsorbent dose, initial concentration, and contact time on metal ion adsorption were examined. CMDEAEC was found to exhibit selectivity only for Au(III). Additionally, the adsorption process follows the Langmuir isotherm model and the pseudo-second-order kinetics model. Furthermore, the desorption of ions from CMDEAEC and the regeneration capacity of CMDEAEC were investigated. In conclusion, as an efficient, low-cost, easily obtained and environmentally friendly adsorbent, CMDEAEC is expected to be used for the selective recovery of gold.

1. Introduction

Gold, as a type of precious metal, has specific properties, such as being lustrous, ductile, noncorrosive and highly stable (Lin et al., 2015; Majavu et al., 2016; Mowafy and Mohamed, 2016; Xue et al., 2016). Therefore, it has been widely used in the jewelry industry, in electronics, as corrosion-resistant materials, as chemical catalysts and in various chemical processes in recent years (Khogare et al., 2016; Liu et al., 2012). However, the demand for gold has increased markedly with the growth of the electronics industry (Nakajima and Sakaguchi, 1993; Nguyen et al., 2015; Parajuli et al., 2008). On the other hand, the frequent replacement of electronic devices causes the accumulation of large amounts of e-wastes. E-wastes have higher abundance of gold element than its own respective ores, which brings a potential for the profitable recovery of gold (Kinoshita et al., 2013; Yang et al., 2014a). Therefore, the recovery of gold from e-wastes has received significant attention and widespread interest (El-Safty et al., 2015; Lin et al., 2015).

Liquid-liquid extraction and solid-phase extraction have been extensively used for the recovery of precious metals (Cui and Zhang,

2008). Various problems in liquid–liquid extraction need to be overcome, such as organic solvents VOCs pollution, difficulty of separation and organic solvent entrainment loss (Gupta et al., 2014). These problems can result in significant loss of value. To solve these problems, an increasing number of ionic liquids are being proposed in liquid–liquid extraction (Jenkin et al., 2016; Yang et al., 2014b). For example, tricaprylylmethylammonium chloride (Aliquat-336) showed good extraction capacity for metal ions (Wei et al., 2016). Nonetheless, Aliquat-336 needed be combined with other extractant to separate precious metal ions. The extraction cost of ionic liquids is too high to be well applied to practical extraction process. Therefore, solid-phase extraction is one of the most appropriate methods for the separation and recovery of precious metal ions from aqueous solution (Els et al., 2000). Ion exchange of solid-phase extraction using chromatographic columns, which makes it more selective than liquid–liquid extraction. However, the kinetics indicates that sorption is too slow. For example, the kinetics of solid phase resin, bis-(2,4,4-trimethylpentyl)-monothiphosphinic acid (Cyanex-302) encapsulated in microcapsules of Ca alginate gel, shows that the adsorption equilibrium time is long (Ruhela et al., 2012). In addition, the secondary resources of gold could be leached

with hydrochloric acid and oxidant to obtain gold (III) chloride solution (Tuncuk et al., 2012). Hence, developing new green cheap and efficient adsorbents for the selective recovery of gold from acidic chloride solutions is extremely important from economic and environmental perspectives (Awual et al., 2013).

In this paper, diethylaminoethyl cellulose, as the main raw material, not only is cheap but also can be produced in large quantities. The nitrogen atom of the diethylaminoethyl cellulose grafting carboxymethyl group generates cellulose-based ionic liquid carboxymethyl-diethylammoniumethyl cellulose (CMDEAEC), which possesses a nanoscale particle size and good swellability, as shown in the SEM test. The physical and chemical properties of the adsorbent have changed after chemical modification. Especially the extraction and separation performance for metal ions increased greatly. Synthetic CMDEAEC can be used for the selective recovery of gold ions from aqueous solutions. In addition, the effects of pH, adsorbent dose, initial concentrations, and contact time on metal ion adsorption are discussed in detail. CMDEAEC shows higher selectivity and better adsorption efficiency for Au(III) than those of reported adsorbents (Erim et al., 2013; Sanchez et al., 2001). The adsorption isotherms, adsorption kinetics, desorption and regeneration capacity of CMDEAEC are also evaluated.

2. Materials and methods

2.1. Materials

Diethylaminoethyl-52 cellulose (DEAEC) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. Bromoacetic acid, dimethyl sulfoxide (DMSO) and nitric acid were obtained from Aladdin Industrial Corporation, Shanghai, China. Sodium carbonate anhydrous, sodium hydroxide, absolute ethanol, ammonia solution, hydrochloric acid, sulfuric acid and thiourea were supplied by Sinopharm Chemical Reagent Co., Ltd. Lithium bis(trifluoromethanesulphonyl)imide (LiTf$_2$N) was purchased from Shanghai Dibai Chemicals Technology Co., Ltd. Chloroauric acid was purchased from Chengdu Xiya Chemicals Technology Co., Ltd. Standard aqueous solutions (1000 mg/L) of Au (III), Cu(II), Ga(III), Gd(III), Pb(II) and Te(IV) were supplied by the General Research Institute for Nonferrous Metals. All solvents and reagents were used without further purification.

2.2. Synthesis of CMDEAEC

The CMDEAEC adsorbent synthesis was carried out according to the method described by Naoki Haraguchi and Parbhej Ahamed with some modifications (Haraguchi et al., 2012). Before the experiment, DEAEC was subjected to freeze-drying pretreatment for 48 h. First, DEAEC and sodium carbonate were added to DMSO while stirring for 15 min to form a homogeneous mixture. Then, bromoacetic acid was added to the homogeneous mixture with rapid stirring. After 24 h of stirring at 110 °C, the product was filtered, washed using ethanol, 0.1 mol/L hydrochloric acid and deionized water and freeze-dried for 72 h. Lastly, the dried synthesized sample was ground into powder form, and this

final product was denoted as the CMDEAEC adsorbent. The synthesis scheme of CMDEAEC is shown in Fig. 1. To characterize the structure of CMDEAEC, [CMDEAEC][Tf$_2$N] was synthesized. CMDEAEC and LiTf$_2$N were added to deionized water, and the mixture was oscillated for 24 h to ensure that ion exchange was complete. Then, the product was washed with deionized water 3 times. [CMDEAEC][Tf$_2$N] was obtained after drying in vacuum at 80 °C for 12 h.

2.3. Characterization methods

A Nicolet iS50 Fourier transform infrared spectroscopy (FT-IR) were used to verify the presence of functional groups in the samples. The contents of carbon, hydrogen, nitrogen and sulfur in samples were analyzed by Vario EL cube elemental analyzer. The morphology and size of the samples was observed by Hitachi S-4800 scanning electron microscope (SEM) operating at 5 kV.

2.4. Adsorption and desorption experiments

2.4.1. Adsorption experiments

An aqueous solution containing metal ions was prepared by diluting the standard solutions with deionized water. For the effect of pH, the initial pH was adjusted by dropwise addition of 0.1 mol/L HCl and NH$_3$·H$_2$O The pH was tested in a range of 1.0–3.5 in order to avoid precipitation of metal ions during adsorption. The concentration of Cl$^-$ in solution was adjusted to 0.1 mol/L by HCl and NH$_4$Cl, which took into account of the concentration of Cl$^-$ in the standard solutions. Five milliliters of an acid solution containing 5 mg/L metal ions was added to a known amount of the adsorbents in a 15 mL centrifuge tube, followed by stirring in a thermostatic bath at 25 °C to attain equilibrium. After adsorption, the solution was filtered through a poly(tetrafluoroethylene) membrane filter. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo scientific ICP 6500 series) was used to determine the concentration of metal ions in the filtrate. The adsorption percentage A (%) and the equilibrium adsorption capacity Q_e (mg/g) for each metal ion were calculated according to the following equations:

$$A(\%) = \frac{C_i - C_e}{C_i} \times 100$$

$$Q_e = \frac{(C_i - C_e)V}{m}$$

where C_i (mg/L) and C_e (mg/L) are the initial and equilibrium metal ion concentrations, respectively. V (L) is the volume of the adsorbate aqueous solution, and m (g) is the mass of the adsorbent.

2.4.2. Desorption experiments

After adsorption, the solution was separated as much as possible by suction filtration to obtain the adsorbent. Then the adsorbent was dried in vacuum at 80 °C for 12 h. Ten milliliters of desorption solution was added to the drying adsorbent in a 15 mL centrifuge tube, followed by stirring in a thermostatic bath at 25 °C to attain equilibrium. After
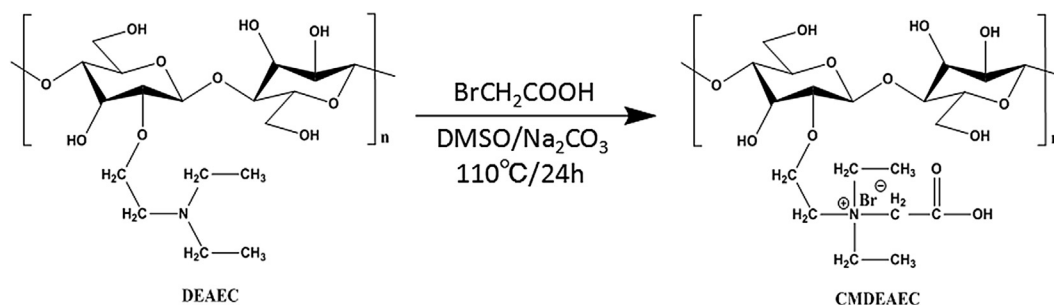

Fig. 1. Synthesis scheme of carboxymethyl-diethylammoniumethyl cellulose (CMDEAEC).