Recovery of silver from nickel electrolyte using corn stalk-based sulfur-bearing adsorbent

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ARTICLE INFO

ABSTRACT

A renewable and recyclable adsorbent was synthesized by introducing thiol (−C−SH), episulfide (C−S−C ring) and thion (−C═S) groups onto the surface of corn stalks with epithiochlorohydrine as a crosslinker (OCS-ET-TU). The adsorption capacity of OCS-ET-TU for $[AgCl_4]^{3-}$ reached to 79.94 mg·g^{-1} at the acid concentration of 1.0 mol·L^{-1} when the concentrations of Cu(II) and Ni(II) all reached to 10,000 mg·L^{-1}; the maximum selectivity coefficients of the OCS-ET-TU for Ag(I)/Cu(II) and Ag(I)/Ni(II) achieved to 2.95 and 3.37, respectively. The FT-IR and XPS results showed that $[AgCl_4]^{3-}$ as soft acid could easily interact with the sulfur-containing groups belonging to the OCS-ET-TU as soft base. The adsorption and regeneration results of corn stalk-based OCS-ET-TU presented that it can potentially apply for recovery of trace amount of silver anions. The investigation provides a new and high-efficient biomaterial to enrich Ag(I) from nickel electrolyte with high concentrations of copper, iron and nickel.

1. Introduction

Biomaterials, which have been researched for their excellent capacity to adsorb metal ions, are a general term of corn stalk, chitosan, fungi, lignite, banana peel, moss, peat, and so on (Babel and Kurniawan, 2003; Feng et al., 2016; Ji et al., 2016; Lou et al., 2015a, 2015b; Sun et al., 2014; Salman et al., 2011). In addition, biomaterials, which have the merits of renewable, low pollution, widely distributed, resource-rich, are also an important part of renewable energy. Efficient development and utilization of biomass could solve energy crisis, and avoid environmental pollution at the same time (Chen et al., 2011; Shen et al., 2014). Corn stalk (CS), as a byproduct agriculture, could be used as alternative materials to prepare various functional adsorbent (Hokkanen et al., 2016; Zhou et al., 2014). The low adsorption capacity of raw corn stalk may be due to intermolecular hydrogen bonds of cellulose. To improve the adsorption capacity of Ag(I), the chemical treatment plays a specific role in preparation of adsorbent which could enhance the sulfur content on the surface of corn stalk.

Silver, as a naturally occurring precious metal, plays an important role in industry and daily life. With increasing demand of silver, how to resolve silver stocks nervous problem has aroused great interest to

scientist. In recent years, recovery of silver from industrial water has caused highlight concern attribute to its decreasing natural resources. Therefore, a host of methods have been adopted to recover silver, for instance, chemical precipitation, ion exchange, redox and adsorption (Puente-Siller et al., 2013; Ünlü and Ersoz, 2006; Çoruh et al., 2010; Kuntyi et al., 2013; Moudir et al., 2013; Abd El-Ghaffar et al., 2009; Hong et al., 2017; Prado and Ruotolo, 2016; Wang et al., 2010). Among them, adsorption is considered as an effective method to collect low concentration of silver ions in solution due to its high selectivity and low energy consumption.

Thiourea, as functional monomer, was usually used for enriching precious or toxic metals from waste water in recent researches (Calla-Choque et al., 2016). For example, thiourea had been used as leaching agent for recovering the silver from abandoned cell phones, and the recovery rates was about 50% (Li et al., 2012). It was also reported that grafting thiourea onto the surface of poly(vinylidene fluoride) was an effective method for adsorbing Au(III) (Zhang et al., 2015). Besides, thiourea was grafted onto the surface of chitosan or other substrate materials for recovering copper or cadmium in solution (Liu et al., 2015; Wang et al., 2017). In a word, the experimental results of adsorbents modified by thiourea show excellent potentiality in recovering

precious or poisonous metals in industry wastewater. However, the biggest problem is how to efficaciously graft thiourea and obviously enhance the amount of sulfur groups as activated sites on the surface of corn stalk, which will in resolved in this study.

In this paper, aimed at improving the selectivity and adsorption capacity for silver coordination anions, thiol (−C−SH), episulfide (C−S−C ring), and thion (−C=S) groups were grafted onto the surface of carbonized corn stalk (OCS). In further order to confirm the stability and the capacity of the modified corn stalk adsorbent, adsorption and selective experiments were carried out, and all experimental details were shown in Section 2.3. Adsorption mechanisms were determined by the analysis of Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and the structure of the adsorbent unit calculated by Eqs. (6)–(8).

2. Experimental section

2.1. Reagents and instruments

Nickel chloride ($NiCl_2 \cdot 6H_2O$), silver nitrate ($AgNO_3$) and copper chloride ($CuCl_2 \cdot 2H_2O$) were used to prepare simulate nickel electrolyte which containing Ag(I)−Cu(II)−Ni(II). Corn stalk (CS) was collected from a local plantation field. The nickel electrolyte containing 24.75 mg·L^{-1} Ag, 90.0 g·L^{-1} Ni and 43.0 g·L^{-1} Cu was from Jinchuan Group Co., Ltd. All reagents were of analytical grade without further purification.

The concentration of metal ions in the aqueous phase was de-

for 24 h at 333 K and smashed into powder. Second, 10 g of the powder was put into 30 mL of concentrated sulfuric acid under vigorous stirring at 363 K for 12 h to produce the carbonized corn stalk (OCS).

2.2.2. Step 2: preparation of epithiochlorohydrine (ET)

At the condition of ice bath, thiourea was gradually added into the mixture of epichlorohydrin (EO) and deionized water. Next, it was stirred at 273 K for 2 h and then at room temperature for 2 h. Subsequently, the mixture was poured into separating funnel for achieving the organic phase, and then dried with calcium chloride. At last, the epithiochlorohydrine (ET) was obtained with rotary evaporators at the temperature of 343 K. Mass-to-charge ratios of the organic phase measured by GC–MS (45.13, 46.17, 73.42, 75.07, 108.16 m/z) are matched well with the databases (45.0, 46.0, 73.0, 75.0, 108.0 m/z) of Shanghai Institute of Organic Chemistry, Chinese Academy of Science.

2.2.3. Step 3: preparation of modified carbonized corn stalk (OCS-ET-TU)

Thiourea (1.52 g) was added into 35 mL of anhydrous ethanol, and was stirred for 2 h at 298 K. Next, after 3.0 g of sodium carbonate anhydrous was poured into the above solution, the epithiochlorohydrine (2.16 g) was gradually dropped into it, and stirred at 353 K for an additional 8 h. OCS (0.5 g) was then poured into the reaction mixture, and the solution continuously stirred for another 8 h at 383 K. At last, the product (OCS-ET-TU) was filtered, and extracted by acetone, and then dried at 323 K. Preparation of the OCS-ET-TU can be comprehended in detail in Eqs. (1)–(2).

$$(1)$$

$$(2)$$
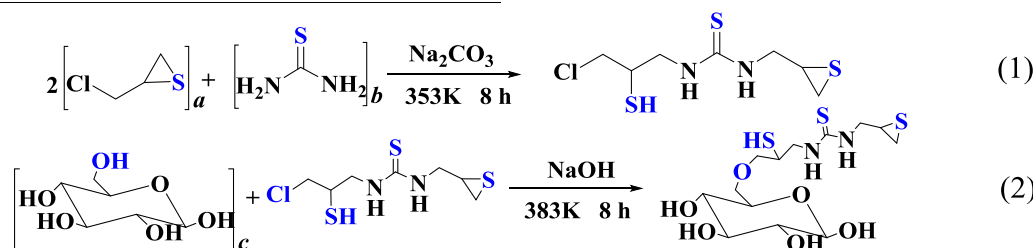
termined by a SHIMADZU AA-6880 atomic absorption spectrophotometer (SHIMADZU, Japan). Standard atomic absorption conditions for Ag are wave length 328.1 nm, air flow 15.0 L·min^{-1}, acetylene flow 2.2 L·min^{-1}. In addition, standard solution was stored in an amber glass bottle because silver is sensitive to light. SEM-EDX spectra were recorded using a Scanning Electron Microscope (S-4800, HITACHI), which equipped with energy-dispersive X-ray (Philips XL 30, Netherlands). Epithiochlorohydrine was identified by gas chromatography (TRACE GC Ultra TM) - mass spectrometry (Polaris Q). FTIR spectra were measured on a Spectrum One FT-IR spectrometer (Perkin-Elmer, USA). The content of C, N, H of the adsorbents was determined with a Flash EA 1112 elemental analyzer. Nitrogen adsorption isotherms were measured at −196 °C using Tristar 3020 volumetric adsorption analyzers manufactured by Micromeritics (Norcross, GA), and the specific surface area of samples were calculated by Brunauer–Emmett–Teller (BET) method. XPS spectra were measured by a thermo ESCALAB 250 X-ray photoelectron spectrometer with Al Kα X-ray source, and were fitted using the XPSPEAK4.1 software.

2.2. Preparation of modified carbonized corn stalk (OCS-ET-TU)

2.2.1. Step 1: preparation of carbonized corn stalk (OCS)

The preparation procedure of OCS was reported in our previous work (Lou et al., 2015a, 2015b). At first, the corn stalk (CS) was dried

In addition, to compare the affinity of −C−SH, and C−S−C groups originating from the epithiochlorohydrine to $[AgCl_4]^{3-}$, an adsorbent (abbreviated as OCS-EO-TU) was prepared following an identical procedure by replacing epithiochlorohydrine with epichlorohydrin.

2.3. Adsorption equilibrium experiment

All adsorption equilibrium experiments were individually conducted at 303 K for metal ions. The silver ion (Ag^+) could chelate with chloride ion (Cl^-) in the solution to form a series of $AgCl_i^{1-i}$ (i = 1, 2, 3, 4). The concentration of silver in the actual electrolyte nickel solution is about 15 mg·L^{-1}. Batch adsorption tests were all performed by taking 10 mg of adsorbent in 5 mL single solution ($[Cl^-]$ = 2.23 mol·L^{-1}, $[Ag(I)]$ = 15 mg·L^{-1}) or 5 mL simulate nickel electrolyte ($[Cl^-]$ = 2.23 mol·L^{-1}, $[Ag(I)]$ = 15 mg·L^{-1}, $[Cu(II)]$ = 10 g·L^{-1}, $[Ni(II)]$ = 10 g·L^{-1}) in the flask, and then the flasks were kept in a thermo-stated shaker at a speed of 180 rpm for 4 h. The concentration of metal ions in the treated solution was measured by AAS after filtration. The pH of solution controlled by HNO_3 plays an important role in the adsorption process. To research the influence of acid concentration, the experiments were performed by adjusting the initial acid concentration of solutions at different acid concentrations. The adsorption percentage for metal ions on the adsorbent was calculated according to Eq. (3), as well as the adsorption capacity in aqueous