



Efficient and selective adsorption of multi-metal ions using sulfonated cellulose as adsorbent



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ARTICLE INFO

Article history:

Received 8 March 2016

Received in revised form 18 May 2016

Accepted 19 May 2016

Available online 20 May 2016

Keywords:

Sulfonated cellulose

Metal ions

Adsorption

Removal efficiency

Desorption

ABSTRACT

Contamination of heavy metal in wastewater has caused great concerns on human life and health. Developing an efficient material to eliminate the heavy metal ions has been a popular topic in recent years. In this work, sulfonated cellulose (SC) was explored as efficient adsorbent for metal ions in solution. Thermo gravimetric analyzer (TGA), X-ray diffraction (XRD) and Fourier-transform infrared spectrometer (FTIR) first analyzed the characterizations of SC. Subsequently, effects of solution pH, adsorbent loading, temperature and initial metal ion concentration on adsorption performance were investigated. The results showed that sulfonated modification of cellulose could decrease the crystallinity and thermostability of cellulose. Due to its excellent performance of adsorption to metal ions, SC could reach adsorption equilibrium status within as short as 2 min. In multi-component solution, SC can orderly removes Fe³⁺, Pb²⁺ and Cu²⁺ with excellent selectivity and high efficiency. In addition, SC is a kind of green and renewable adsorbent because it can be easily regenerated by treatment with acid or chelating liquors. The mechanism study shows that the sulfonic group play a major role in the adsorption process.

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1. Introduction

The rapid industrialization has generated heavy metal contamination, wherein fossil fuel combustion, mining and smelting activities have intensified the invasion of heavy metal into surface and body of underground water (Singha & Guleria, 2014). Accumulated heavy metals can do harm to environment and human health even at a quite low concentration. To reduce negative effects of heavy metals in water body, many technologies, such as precipitation, chemical oxidation/reduction, membrane filtration, ion-exchange and adsorption, have been employed to remediate heavy metals (Bessbousse, Rhlalou, Verchère, & Lebrun, 2008; Ji et al., 2012; Sakai, Matsuoka, Zinchenko, & Murata, 2009; Zewail & Yousef, 2015). Among these methods, adsorption received more attentions due to its high efficiency, technical flexibility and cost-effective, and adsorbents prepared by cellulose and its derivatives has been broadly investigated because of their renewability, sustainability and biodegradability.

Formerly, a variety of chemically modified cellulose have been prepared as adsorbent to remove different metal ions. For example,

the cellulose, modified by using maleic anhydride, removes Hg²⁺ from water with a moderate adsorption capacity (172.5 mg g⁻¹) (Zhou, Jin, Hu, Zhang, & Ma, 2012). In addition, Hokkanen investigated the adsorption properties of aminopropyltriethoxy-silane (APS) modified cellulose in aqueous solutions containing Ni²⁺, Cu²⁺ and Cd²⁺ ions, and the maximum removal capacity for Ni²⁺, Cu²⁺ and Cd²⁺ ions were 2.734, 3.150 and 4.195 mmol g⁻¹, respectively (Hokkanen et al., 2014). Compared to the other cellulose derivatives, sulfonated cellulose possess the advantages of low cost, easy preparation and low toxicity.

In our previous work (Dong, Zhang, Pang, Liu, & Zhang, 2013), we have demonstrated that sulfonated cellulose is good adsorbent for Pb²⁺ from solution. In this paper, we further investigated competitive adsorption mechanism of multi-metal ions using sulfonated cellulose. These efforts were devoted to further elucidate the adsorption mechanism of sulfonated cellulose and to develop novel adsorbent with excellent performance.

2. Experimental

2.1. Material and chemicals

Microcrystalline cellulose (MCC) was provided by Shanhe pharmaceutical Co., Ltd. of Anhui Province. Sulphur trioxide pyri-

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dine complex (SO₃-Py) was purchased from Hubei Prosperity Galaxy Chemical Co., Ltd. *N,N*-Dimethylformamide (DMF, chromatographic grade) was obtained from Tianjin Chemicals Co., Ltd. Iron chloride hexahydrate (99%), copper nitrate trihydrate (99%), lead nitrate (99%) and disodium edetate (99%) were purchased from Tianjin Daomao Chemical Reagent Company. All chemicals were used as received without further purification.

2.2. Sulfonation of cellulose

The MCC was dispersed in DMF and stirred (800 rpm) at 40 °C for 30 min. Then, SO₃-Py was added to the solution and stirred vigorously. The modified samples were collected by filtration through ash-free filter paper (Whatman No. 1442 070) on a Buchner funnel and thoroughly washed with absolute ethyl alcohol. Finally, the collected samples were vacuum-dried at 40 °C for 48 h.

2.3. Determination of the sulfonation degree of cellulose (DS)

The DS was determined by elemental analysis of sulfur in a Carlo Erba EA 1108 CHNS analyzer. Elemental analysis of the samples was carried out by triplicate and the mean values are reported. All the determinations showed relative standard deviations below 2%. The DS was calculated according to Eq. (1):

$$DS = (S\%/C\%)/(32/72) \quad (1)$$

where S% and C% are the percentage of sulfur and carbon on dry basis respectively; 32 is the atomic weight of sulfur and 72 is the total molecular weight of carbon on glucose unit. All the sulfonated cellulose sample used in this paper with a DS of 0.56.

2.4. Adsorption of heavy metal ions by SC

Metal ions solution were prepared by dissolution of Pb(NO₃)₂, Cu(NO₃)₂ and FeCl₃ in ultrapure water. The solution pH was adjusted by 0.1 M HCl solution. A certain amount of SC and 25 mL of metal ions solution were added in a flask. Then, the solutions were vigorously mixed (800 rpm) at specified temperature. The equilibrium solutions were centrifuged and the supernatant concentration were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 2000DV). In the case of binary and ternary metal ions adsorption, designated metal ions were added with identical concentration (100 mg L⁻¹).

The amount of metal ions adsorbed on SC at adsorption equilibrium was calculated according to Eq. (2):

$$q_e = (C_0 - C_e) \times V/m \quad (2)$$

where q_e is the amount of adopted metal at equilibrium; C_0 and C_e are the initial and equilibrium concentration of metal ions in the solution, respectively; V is the volume of the solution; and m is the amount of SC added in the solution.

The removal efficiency (R %) of the adsorbent was calculated according to Eq. (3):

$$R(\%) = (C_0 - C_e)/C_0 \times 100 \quad (3)$$

2.5. Desorption and regeneration

Desorption experiments were conducted using eluents including 0.1 M HCl, 0.1 M HNO₃ and 0.1 M Na₂EDTA. Firstly, adsorption was performed using 50 mg SC in 100 mg L⁻¹ metal ions solutions (25 mL) at room temperature for 30 min. Then the spent adsorbents were filtrated from solutions through ash-free filter paper (Whatman No. 1442 070) on a Buchner funnel. Desorption treatment was then carried out by adding 25 mL of desorption eluent

to the adsorbent and vigorously stirred (800 rpm) for 2 h. The desorbed adsorbent was washed thoroughly with distilled water and subjected to the next cycle. The regeneration performances were examined by adsorption-desorption process for four cycles for Pb²⁺ ions and the concentration of ions was measured at each step by inductively coupled plasma emission spectrometer as described above.

The regeneration efficiency (R_E %) of adsorbent was calculated according to Eq. (4):

$$R_E(\%) = (C_0 - C_r)/(C_0 - C_e) \times 100 \quad (4)$$

where C_r is the equilibrium concentration of metal ions in the solution after desorption.

2.6. Characterization of SC

Fourier transform infrared spectroscopy (FTIR) was used to analyze groups in the samples obtained by the KBr pellet technique. Samples were grounded, mixed with KBr, and pressed in an evacuated die under suitable pressure. The spectrum was scanned with wavenumber from 400 to 4000 cm⁻¹.

X-ray diffraction spectroscopy (XRD) with Cu K_α radiation generated at 45 kV and 40 mA was used to measure the crystal structure of cellulose. XRD spectra were obtained at a rate of 2 °C/min from 5° to 45°. Thermogravimetric analysis (TGA) were performed under nitrogen purge (TA-Instruments Q-50 thermogravimetric analysis system). The samples were heated from 25 °C to 500 °C at rate of 20 °C/min.

Based on the procedure described by Sun and Gunasekaran (2009), we calculated zeta potentials by measuring the electrophoretic mobility with a particle size analyzer (90Plus, Brookhaven, Long Island, NY, USA). The prepared samples were diluted with distilled water. Their concentration typically ranged between 10⁻⁵ and 10⁻² volume fraction prior to zeta potential measurement.

3. Results and discussion

3.1. Characteristics of SC

3.1.1. Crystallinity structure of SC

Cellulose is composed of compact crystalline zone and loose amorphous zone. The ratio between the two zones varies, and significantly affect the reactivity of hydroxyl groups, size and distribution of micropores and adsorption capacity. Characterization of supramolecular alignment of cellulose and its derivatives has been successfully achieved using XRD (Cunha et al., 2007). Thus, the crystalline structure of the original and sulfonated cellulose was analyzed by XRD, whereby illustrated release of free hydroxyl groups and internal permeability derived from sulfonated modification (Fig. 1). Compared to the original cellulose, the relative peak intensity of SC declined significantly due to abundant substitution of hydroxyls of cellulose with sulfonic acid group (Khalil-Abad, Yazdanshenas, & Nateghi, 2009). Accordingly, crystallinity of sulfonated cellulose (37.8%) was significantly reduced compared to that of the original cellulose (63.1%). These results suggested that the sulfonated modification could effectively deconstruct crystalline region and release massive free hydroxyls.

3.1.2. Thermostability of SC

Thermal properties of adsorbent can be used to evaluate the thermal stability and applicable temperature, which were analyzed using TG with temperature ranged from 25 to 500 °C (Fig. 2). Compared to the original cellulose, the temperature of substantial weight loss of SC was greatly lowered, which demonstrated the

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