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Tannin-immobilized mesoporous silica bead (BT–SiO_2) as an effective adsorbent of Cr(III) in aqueous solutions

Xin Huang[a], Xuepin Liao[a,*], Bi Shi[b]

[a] *Department of Biomass Chemistry and Engineering, Sichuan University, Chengdu 610065, PR China*
[b] *National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, PR China*

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ABSTRACT

This study describes a new approach for the preparation of tannin-immobilized adsorbent by using mesoporous silica bead as the supporting matrix. Bayberry tannin-immobilized mesoporous silica bead (BT–SiO_2) was characterized by powder X-ray diffraction to verify the crystallinity, field-emission scanning electron microscopy to observe the surface morphology, and surface area and porosity analyzer to measure the mesoporous porous structure. Subsequently, the adsorption experiments to Cr(III) were applied to evaluate the adsorption performances of BT–SiO_2. It was found that the adsorption of Cr(III) onto BT–SiO_2 was pH-dependent, and the maximum adsorption capacity was obtained in the pH range of 5.0–5.5. The adsorption capacity was 1.30 mmol g^{-1} at 303 K and pH 5.5 when the initial concentration of Cr(III) was 2.0 mmol L^{-1}. Based on proton nuclear magnetic resonance (HNMR) analyses, the adsorption mechanism of Cr(III) on BT–SiO_2 was proved to be a chelating interaction. The adsorption kinetic data can be well described using pseudo-first-order model and the equilibrium data can be well fitted by the Langmuir isothermal model. Importantly, no bayberry tannin was leached out during the adsorption process and BT–SiO_2 can simultaneously remove coexisting metal ions from aqueous solutions. In conclusion, this study provides a new strategy for the preparation of tannin-immobilized adsorbents that are highly effective in removal of heavy metals from aqueous solutions.

1. Introduction

Chromium [Cr(III)] compounds are widely used in modern industries, such as leather making, metal finishing, and petroleum refining [1,2], which inevitably results in a large quantity of Cr(III)-contaminated industrial effluents. Waters containing a high concentration of Cr(III) are extremely harmful to human beings because they are non-biodegradable in living tissues and would induce toxic and carcinogenic health effects on humans [3]. Therefore, the removal of Cr(III) from aqueous solutions arouses great attention. Many methods have been established for the removal of metal ions from aqueous solutions, such as chemical precipitation, membrane separation, electrolytic reduction, ion exchange, and adsorption [4–9]. Among these methods, adsorption is more useful and economical method for the removal of metal ions at low concentration (<100 mg L^{-1}) in aqueous solutions [10,11]. Accordingly, great effort has been put into the development of new adsorbents that are able to effectively remove Cr(III) ions from aqueous solutions [3,12,13].

More recently, tannin has emerged as a potential alternative for the removal of heavy metals from aqueous solutions [14,15]. Tannins are natural plant extracts and contain high content of multiple adjacent phenolic hydroxyls in their molecules, and thus they have strong chelating ability towards many heavy metal ions including Cr(III), Pb(II), Hg(II), Cd(II) and Au(II) [16–18]. Since tannins are water-soluble compounds, they often need to be immobilized onto water-insoluble matrixes such as agarose [19], cellulose [20], hydrotalcite [21], and collagen fiber [22]. Our previous investigation indicated that tannin-immobilized collagen fiber exhibited outstanding adsorption capacity to many metal ions [22–24]. However, in this adsorbent, a part of phenolic hydroxyls of tannins have interacted with collagen fibers through hydrogen bonds, and hence the adsorption capacity of tannins to metal ions was not fully represented. Therefore, new approaches for the immobilization of tannins should be developed to improve the adsorption capacity of tannin-immobilized adsorbents as well as its adsorption kinetics.

Silica matrix has received great attention since it shows excellent swelling resistance in different solvents and a good mechanical, thermal and chemical stability [25]. So it is possible to obtain tannin-immobilized adsorbents with excellent physical and chemical properties by using silica as a supporting matrix. On the basis of this idea, we designed a new adsorbent for the removal of Cr(III) ions by immobilizing bayberry tannin onto mesoporous silica

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* Corresponding author. Tel.: +86 28 85400382; fax: +86 28 85400356.
E-mail address: xpliao@scu.edu.cn (X. Liao).

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(SiO_2) bead. Bayberry tannin-immobilized mesoporous silica bead (BT–SiO_2) is expected to have fast adsorption rate and high adsorption capacity towards Cr(III) ions due to the permanent mesopore structure of SiO_2 bead and abundant accessible multiple adjacent phenolic hydroxyls of bayberry tannin. In this study, the adsorption behaviors of this new adsorbent to Cr(III) ions were investigated. In addition, the adsorption mechanism of BT–SiO_2 to Cr(III) ions was also studied using proton nuclear magnetic resonance (HNMR).

2. Materials and methods

2.1. Reagents

Bayberry tannin (BT) was obtained from the barks of *myrica esculenta* by extraction with an acetone–water solution (1:1, v/v), followed by spray drying [26]. The tannin content of the extract was 76.3% determined using hide powder method, a national standard method of China (Code: GB2615-81) [27]. $Cr(NO_3)_3{\cdot}6H_2O$ and all other chemicals were analytical grade reagents. The stock solution of Cr(III) (10.0 mmol L^{-1}) was prepared by dissolving $Cr(NO_3)_3{\cdot}6H_2O$ into deionized water, and it was diluted to an appropriate concentration when used. Diluted HNO_3 and NaOH solutions were used for adjusting the initial pH of solutions.

2.2. Preparation of adsorbents

2.2.1. Preparation of aminated mesoporous SiO_2 beads
Aminated mesoporous SiO_2 beads were prepared following a methodology similar to that described by Cheng et al. [28]. Briefly, 4.0 mL of cyclohexane, 1.0 mL of n-hexanol, and 1.0 mL of TritonX-100 were added into 300.0 mL deionized water under constant stirring. After 5–10 min, a fine emulsion was formed. 9.0 mL of tetraethyl orthosilicate (TEOS, silica source) and 3.0 mL of 3-aminopropyl-triethoxysilane (APES, aminating agent) were subsequently added into the emulsion and kept vigorous stirring for 12 h. Then a proper amount of ammonia ($NH_3{\cdot}H_2O$) was dropped in so as to promote the hydrolysis of TEOS and APES. After stirring for 12 h, 2 mL of acetone, used as an emulsion breaker, was added into the emulsion, followed by vigorous stirring for another 12 h. Finally, snow-white mesoporous SiO_2 beads were obtained by filtration, extensively washed with deionized water, and then dried at 373 K.

2.2.2. Preparation of BT–SiO_2 adsorbent
1.0 g of BT was dissolved in 100 mL of deionized water and mixed with 1.0 g of aminated mesoporous SiO_2 beads prepared in Section 2.2.1. The mixture was stirred at 298 K for 2 h, and then 4 mL of glutaraldehyde (50%, w/w) was dropped into the mixture. Afterwards, the mixture was first stirred at 298 K for 24 h. Subsequently, brown BT–SiO_2 adsorbent was obtained by filtration, fully washed with deionized water and dried in vacuum at 323 K for 12 h. BT grafting degree of BT–SiO_2 was calculated according to the concentration difference of BT before and after the immobilization, measured by using ultraviolet visible (UV–vis). Additionally, the preparation of BT–SiO_2 adsorbent was repeated several times, and it showed good reproducibility.

2.2.3. Characterization of adsorbent
Specific surface area, pore size and pore size distribution of the samples were determined with surface area and porosity analyzer (TriStar 3000, Micromeritics, US) using nitrogen as the adsorption gas. Powder X-ray diffraction (XRD) spectra were obtained from X-ray diffractometer (X'pert ProMPD, Philips, Holland). Surface morphologies were examined by field-emission scanning electron microscopy (Fe-SEM, S-4800, Hitachi, Japan). The pH-dependence of the zeta potential of BT–SiO_2 was measured instrumentally (Laser Zee3.0, Pen Kem Inc.) and the pH corresponding to zero point of charge (pH_{zpc}) of BT–SiO_2 was determined.

2.2.4. Adsorption experiments
2.2.4.1. Effect of initial pH on the adsorption capacity of BT–SiO_2 to Cr(III). Adsorption experiments were carried out in 100 mL of 1.0 and 2.0 mmol L^{-1} Cr(III) solution, in which the adsorbent dose was 0.1 g. The pH of the solutions, ranged from 2.5 to 5.5, was adjusted using diluted HNO_3 solution and NaOH solution. The adsorption process was conducted at 303 K with constant stirring for 24 h. Then, the suspension was filtered and the concentration of Cr(III) in filtrate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 2100 DV, PerkinElmer, US). The adsorption capacity of Cr(III) onto BT–SiO_2 was calculated from the concentration difference of Cr(III) before and after the adsorption. The adsorption of Cr(III) onto commercial SiO_2 was also carried out as a control experiment.

2.2.4.2. HNMR studies. In order to investigate the adsorption mechanism of BT–SiO_2 to Cr(III), proton nuclear magnetic resonance (HNMR) technique was employed. Considering the complexity of molecular structure of BT, pyrogallic acid was used as a model compound to simulate the interaction between BT and Cr(III). The HNMR spectrum of pyrogallic acid–Cr(III) reaction product was measured by Bruker DPX400 NMR instrument using DMSO-*d*6 as solvent. For comparison, the HNMR analysis of pyrogallic acid was also performed.

2.2.4.3. Adsorption isotherm studies. Adsorption experiments were carried out in 100 mL of Cr(III) solution, where the initial concentrations of Cr(III) ranged from 0.1 to 4.0 mmol L^{-1} and the dose of BT–SiO_2 was 1.0 g L^{-1}. The pH of the solutions was 5.5 and the adsorption process was kept at 303 K for 24 h. The adsorption process was also conducted in the presence of $NaNO_3$ with concentration of 10 and 100 mmol L^{-1}, respectively. The adsorption capacity at equilibrium was calculated by the mass balance of Cr(III) before and after adsorption.

2.2.4.4. Adsorption kinetics studies. 0.1 g of BT–SiO_2 was suspended in 100 mL of 1.0 mmol L^{-1} Cr(III) solution. The pH of the solutions was adjusted to 5.5 and the adsorption process was conducted at 303 K with constant stirring. The concentration of Cr(III) was analyzed at a regular interval during adsorption process.

2.2.4.5. Effect of adsorbent dose on the adsorption of Cr(III). The adsorption experiments was carried out in 100 mL of 1.0 mmol L^{-1} Cr(III) solution, in which the adsorbent dose varied from 0.01 to 0.4 g. After 2 h of adsorption, the concentration of Cr(III) in the solutions was analyzed by ICP-AES

2.2.4.6. Effect of coexisting metal ions on the adsorption of Cr(III). Desired amounts of BT–SiO_2 (0.1, 0.2 and 0.3 g) was added into 100 mL mixture solution of $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Al(NO_3)_3$, and $Ca(NO_3)_2$, in which the concentrations of all metal ions were 0.1 mmol L^{-1} and the initial pH of the solutions was 5.5. After 2 h of adsorption, the concentrations of Cr(III) and other metal ions in the solutions were analyzed by ICP-AES.

2.2.4.7. Stability of BT–SiO_2 adsorbent. In view of practical application, the BT immobilized onto SiO_2 beads should be stable during the adsorption process. Thus, a precise and sensitive spectrophotometric procedure described by Butler et al. was used to quantitatively analyze the BT leaked from the adsorbent [29]. This method is based on the reduction of ferric ion to ferrous ion in the presence of tannin, followed by the formation of a ferricyanide–ferrous ion complex, called Prussian blue. The mixture