



Porous cellulose spheres: Preparation, modification and adsorption properties



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HIGHLIGHTS

- Porous cellulose spheres (PCS) were precipitated from a cellulose ionic liquid.
- Modified PCS (SPCS) were used to remove heavy metal ions from aqueous solution.
- Adsorption behavior of Pb²⁺ on SPCS fit the kinetic models.
- The maximum adsorption capacity reached 150.6 mg g⁻¹.

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ABSTRACT

Porous cellulose spheres (PCS) were fabricated by precipitating the spheres from a cellulose ionic liquid solution, followed by freezing, solvent exchange, and drying. PCS had low crystallinity and a large surface area that facilitated modification with trisodium trimetaphosphate (STMP) to introduce phosphate ester groups into the porous structure of the heterogeneous system. The STMP-modified PCS (SPCS) were used to remove heavy metal ions from aqueous solution. With increasing STMP dosage, the adsorption capacity of SPCS obviously improved due to chelation between Pb²⁺ and phosphate ester groups. The kinetic adsorption and isotherm data matched the pseudo-second order model and the Langmuir model well. The maximum adsorption capacity reached 150.6 mg g⁻¹ for SPCS. SPCS were competitive with other adsorbents because the phosphate ester groups and porous structure contributed to Pb²⁺ adsorption. Moreover, SPCS can be regenerated with ethylenediamine tetraacetic acid disodium salt (EDTA) solution for repetitive adsorption of Pb²⁺.

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1. Introduction

Cellulose, one of the most abundant natural polymers, is composed of β-1,4 linked D-glucose units with many hydroxyl groups. Cellulose is regarded as an attractive renewable resource due to its low cost, renewability, biodegradability, nontoxicity, and biocompatibility (Qiao et al., 2016; Liu et al., 2015; Mahmoudian et al., 2012); however, the application of cellulose is generally constrained by its high crystallinity and supramolecular structure resulting from its inter- and intramolecular hydrogen bond network (Husson et al., 2011).

Great effort has been committed to finding direct solvent systems that dissolve cellulose by destroying its crystallinity and hydrogen bond network. The highly active free hydroxyl groups could then be homogeneously modified to introduce new functionalities that impart special properties to cellulose. During the past few decades, many cellulose solvents have been developed including N, N-dimethylacetamide (DMAC)/lithium chloride (LiCl); dimethyl sulfoxide (DMSO)/paraformaldehyde; N-methyl-morpholine-N-oxide (NMMO)/H₂O; and NaOH/urea (Liu et al., 2015); as well as molten salt hydrates, such as LiClO₄·3H₂O and LiSCN·2H₂O (Kuang et al., 2008). However, these solvent systems are restrictive due to toxicity, cost, uncontrollable side reactions, difficult solvent recovery, or instability in processing.

Since Swatloski et al. (2002) reported that the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was an outstanding nonderivatizing solvent for cellulose, ILs have become

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the new solvent for processing and modification of cellulose (Chen et al., 2013). Imidazolium-based ILs are nonflammable, nonvolatile, easy to recycle, chemically and thermally stable, and have been gradually accepted as cellulose solvents (Zhang et al., 2014). The IL 1-allyl-3-methylimidazolium-chloride ([AMIM]Cl) was used as a reaction medium for homogenous functionalization of cellulose in the preparation of cellulose acetate butyrate and cellulose acetate propionate (Huang et al., 2011); and sugarcane bagasse was homogeneously modified with maleic anhydride in [BMIM]Cl without the use of catalysts (Chen et al., 2013). More excitingly, ILs have been used to transform cellulose into a broad variety of new, eco-friendly materials. Cellulose II powders were prepared from α -cellulose extracted from maize cobs by dissolution and regeneration of the α -cellulose in [BMIM]Cl, using either water, acetone, or boiling water as the antisolvent for precipitation of cellulose from solution (Azubuike et al., 2012). Regenerated cellulose films were fabricated using cellulose from different sources (pine, cotton, bamboo) as the raw material and the IL 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) as the solvent (Pang et al., 2015). Porous cellulose materials have been obtained using a process of freezing the cellulose solution in the IL, followed by solvent exchange and freeze-drying under vacuum (Liu et al., 2015).

Water pollution of heavy metals from discharged industrial effluent has recently become a serious environmental problem, as most heavy metals have toxic effects on organisms and accumulate in biota (Park et al., 2016). Inappropriate discharge of heavy metals into the ecosystem can result in potential threats to human health and the environment (Shaker and Albishri, 2014). In this work, cellulose spheres were fabricated by dropwise addition of a solution of cellulose in [BMIM]Cl into water. The hydrous spheres were freeze-dried to prepare dispersed porous cellulose spheres (PCS), which were different from the monolithic porous cellulose of Liu et al. (2015). PCS were modified with trisodium trimetaphosphate (STMP) to introduce phosphate ester groups into the porous structure of the heterogeneous system. The porous structure and low crystallinity of the PCS made the modification easy and effective, and also altered the modification of cellulose from its typical homogeneous pattern to heterogeneous. PCS with a porous structure and functionalized with phosphate ester groups could be used to remove metal ions from aqueous solution. Here, Pb^{2+} ions were chosen as the model heavy metal ions for evaluation of the adsorption capacity of these adsorbents from cellulose. This work presented a facile approach to endowing cellulose with a new function while simultaneously maintaining the porous structure to strengthen this function.

2. Experimental

2.1. Materials

Cellulose was procured from Canfor Pulp Limited Partnership (Vancouver, BC, Canada). Ionic liquid (IL), [BMIM]Cl, was provided by the Centre for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). All other reagents were commercially available and of analytical grade.

2.2. Preparation of porous cellulose spheres (PCS) and solid cellulose spheres (SCS)

[BMIM]Cl IL (12.5 g) was heated at 130 °C and cellulose (0.5 g) slowly added and allowed to completely dissolve for 2 h. Under vigorous stirring at room temperature, the cellulose IL solution was added dropwise, at the rate of 1 mL min⁻¹, into water to obtain cellulose spheres. The cellulose spheres were washed several times with water to remove the IL, until testing with AgNO₃ solution

showed no Cl⁻ was present. The cellulose spheres were divided into two parts: One part was dried overnight at 30 °C to form solid cellulose spheres (SCS); the other part was frozen at -10 °C for 5–6 h. The frozen spheres were immersed three times in ethanol for about 2 h each time, and then dried overnight at 30 °C to form porous cellulose spheres (PCS).

2.3. Modification of PCS and SCS with trisodium trimetaphosphate (STMP)

Cellulose/SCS/PCS (0.1 g) was placed in 200 mL NaOH solution (5%), and STMP (0.93, 1.86 or 2.79 g) added with vigorous stirring. The reaction was processed at 30 °C for 2 h. Since the molar mass of cellulose (i.e. anhydroglucose unit) is 162, the mole ratios of STMP/cellulose were about 5, 10, and 15, respectively. The modified products were washed in water several times, and then washed three times with ethanol before drying for testing. The STMP-modified cellulose, SCS, and PCS were respectively labeled as SC-15, SCS-15, SPCS-5, SPCS-10, and SPCS-15, with the numbers indicating the STMP/cellulose mole ratio. The process for preparation of SCS, PCS, and SPCS, along with photographs, is shown in Fig. 1 (a); and the mechanisms for modification of PCS and adsorption of metal ions are exhibited in Fig. 1 (b).

2.4. Characterization

The external and fracture surfaces of SCS, PCS, and SPCS were viewed using a Hitachi S-4800 scanning electron microscope. Porous PCS and SPCS were cooled in liquid nitrogen, broken, and the fracture surfaces vacuum coated with gold for SEM.

X-ray diffraction (XRD) patterns for cellulose, PCS, and SPCS were recorded in the reflection mode over the angular range of 10–50° (2 θ) at ambient temperature using a Bruker D8-S4 Pioneer operated at a CuK α wavelength of 1.542 Å.

FTIR analysis of PCS and SPCS was performed on a BIO-RAD FTS3000 IR Spectrum Scanner. The sample powders were evenly dispersed in KBr and pressed into transparent sheets for testing.

Thermogravimetric analysis of PCS and SPCS was measured on an STA 409 PC thermal analyzer (NETZSCH, Germany). The approximately 10 mg samples were heated from room temperature to 800 °C at a heating rate of 15 °C min⁻¹ in a nitrogen atmosphere.

Adsorption capacity was measured (Chang et al., 2012) by immersing dried PCS or SPCS-15 (weight = w_0) in water or ethanol for 0.5 h at room temperature and then filtering. The composites were weighed (w) when liquid no longer dripped from the filter paper. The adsorption capacity was calculated as follows:

$$\text{Liquid Adsorption Capacity} = \frac{w - w_0}{w_0} \quad (1)$$

2.5. Adsorption experiments

Adsorption experiments were conducted (Feng et al., 2016) using glass bottles containing 0.5 g L⁻¹ of the adsorbents and PbNO₃ solution (0.2 g L⁻¹ Pb²⁺). The glass bottles were placed on a slow moving platform shaker for a certain length of time for adsorption at 30 °C. The concentration of Pb²⁺ in the solutions was analyzed using an atomic adsorption spectrometer (Thermo Scientific iCE 3000).

The adsorption isotherm, where the concentration of the adsorbent was 0.5 g L⁻¹ and the Pb²⁺ concentration changed from 0.2 to 0.5 g L⁻¹, was studied as well. These experiments were carried out at 30 °C in bottles shaken for 10 h on a rotary shaker at 100 rpm to reach the adsorption equilibrium.

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