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Fabrication of mesoporous lignin-based biosorbent from rice straw and its application for heavy-metal-ion removal

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ABSTRACT

Lignocellulosic biomass offers the most abundant renewable resource in replacing traditional fossil resources. However, it is still a major challenge to directly convert the lignin component into value-added materials. The availability of plentiful hydroxyl groups in lignin macromolecules and its unique three-dimensional structure make it an ideal precursor for mesoporous biosorbents. In this work, we reported an environmentally friendly and economically feasible method for the fabrication of mesoporous lignin-based biosorbent (MLBB) from lignocellulosic biomass through a SO_3 micro-thermal-explosion process, as a byproduct of microcrystalline cellulose. BET analysis reveal the average pore-size distribution of 5.50 nm, the average pore value of 0.35 cm^3/g, and the specific surface area of 186 m^2/g. The physicochemical properties of MLBB were studied by FTIR, ATR-FTIR, X-ray photoelectron spectroscopy (XPS), and element analysis. These results Q4 Q5
showed that there are large amounts of sulfonic functional groups existing on the surface of this biosorbent. Pb(II) was used as a model heavy-metal-ion to demonstrate the technical feasibility for heavy-metal-ion removal. Considering that lignocellulosic biomass is a naturally abundant and renewable resource and SO_3 micro-thermal-explosion is a proven technique, this biosorbent can be easily produced at large scale and become a sustainable and reliable resource for wastewater treatment.

Introduction

Heavy-metal pollution has been drawing world-wide concerns, because heavy-metal-ions even in trace amount are hazardous to human health and ecosystem (Babel and Kurniawan, 2003;
Q6 Sud et al., 2008; Hlihor and Gavrilescu, 2009). Heavy-metal pollution resulting from the indiscriminate disposal of wastewater from many industries, such as mining, refining ores, tanneries, batteries, and paper industries, has becoming a global environment threat. Unlike organic pollutants, heavy-metal-ions are recalcitrant and accumulative in the environment and living tissues, causing diseases and disorders of living organisms even at low concentrations (Dabrowski et al., 2004; Hadi et al., 2013). Therefore, it is necessary to eliminate the toxic heavy-metal-ions from wastewater prior to their release into the environment.

Many techniques have been employed for the treatment of heavy-metal-ion contaminated wastewater, including chemical

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precipitation (Sun et al., 2003), ion exchange (Dabrowski et al., 2004; Metwally et al., 2013), chemical oxidation/reduction (Ortega et al., 2008), and membrane filtration (Jawor and Hoek, 2010). Among which, sorption technique is the most widely-used solution due to its simplicity and efficiency (Ngah and Hanafiah, 2008; O'Connell et al., 2008, Klapiszewski et al., 2015). Various sorbents, such as clay minerals (Dias and do Carmo, 2006), oxides (Zhao et al., 2011a, 2011b), and carbon materials (Cao et al., 2012; Stafiej and Pyrzynska, 2007), have been used in heavy-metal-ion removal. However, these materials often suffer from the shortcoming of high-costs. Therefore, developing more efficient, low-cost, and environment-friendly adsorbents is always being pursued.

Lignocellulosic biomass, as the most abundant renewable resource (Wyman, 1994; Lucas et al., 2008; Alonso et al., 2008; Lucas et al., 2010; Chen et al., 2014), which is predominantly composed of cellulose, hemicellulose, and lignin. Recently, numerous processing techniques have been developed on the lignin removal of lignocellulosic biomass and made great successes in recycling cellulose (Lynd et al., 1991; Huber et al., 2006; Taherzadeh and Karimi, 2007). However, it is still a major challenge to directly convert the lignin component into value-added materials mainly because lignin has evolved complex structural and chemical mechanisms for resisting chemical and biological assault (Ahvazi et al., 2011; Zhang et al., 2011). On the other hand, as a complex polymer of aromatic alcohols containing abundant functional groups, lignin shows potential capacities for the sorption of heavy-metal-ions (Celik and Demirbas, 2005; Conrad, 2008; Wu et al., 2008; Liu et al., 2013).

Up to now, various lignin-based biosorbents have been fabricated and successfully used to remove heavy-metal-ions from aqueous solutions (Wu et al., 2008; Liu et al., 2013; Li et al., 2015a, 2015b; Ge et al., 2016). It is envisioned that we can develop a conceptually new method for the synthesis of value-added mesoporous materials using the lignin component. The unique structure of the lignin may provide large surface area and large pore volume, and possess better diffusion, dispersion, and mass transfer behavior in the field of heavy-metal-ions removal (Zhang et al., 2008). Unfortunately, the intrinsic structure of lignin often has been wrecked during conventional pre-treatment processes of lignocellulosic biomass. Thus, it is still highly-desired to develop new effective strategy which can maintain the three-dimensional-structure of the lignin component in the recycle of cellulose component.

With regard to our continuing efforts toward environmentally friendly biomass disposal and resource recovery (Yao et al., 2011; Xu et al., 2011; Li et al., 2012a, 2012b), we proposed a facile and sustainable approach to fabricate mesoporous lignin-based biosorbent (MLBB) from lignocellulosic biomass as a byproduct in the recycle of cellulose, through a sulfur trioxide (SO_3) micro-thermal-explosion process. This approach can maintain the three-dimensional-structure of the lignin component in the recycle of cellulose component. Rice straw (RS), the largest agricultural byproduct around the world, was used as a model of lignocellulosic biomass. In-situ generated SO_3 gas diffused into the internal structure and reacted with the water contained in RS, initiating an internal physical explosion, then, dilute alkali solution was used to dissolve the lignin component. The physicochemical properties of MLBB were studied by FTIR, ATR-FTIR, scanning electron microscope (SEM), X-ray photoelectron spectrometry (XPS), BET and element analysis. Lead ion (Pb(II)), a typical heavy-metal-ion (Zhu et al., 2007; Peng et al., 2012; Guo et al., 2013; Li et al., 2015a, 2015b), was selected as a target heavy-metal-ion to evaluate the adsorption properties of this mesoporous adsorbent in heavy-metal-ion removal.

1. Materials and methods

1.1. Materials

RS, harvested in early October 2013, was collected from a suburb of Hefei, Anhui province, China. The RS was naturally air-dried to get rid of the surface water until the constant moisture was reached, with the moisture content of around 13 wt.%. The elemental compositions of the RS are shown in Table 1. Oleum (H_2SO_4), ammonium hydroxide ($NH_3{\cdot}H_2O$), sodium hydroxide (NaOH), and analytical grade $Pb(NO_3)_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. China and used without further purification. Ultrapure (Millipore Inc., USA) water (resistivity of 18.2 MΩ-cm) was used in the experiments.

1.2. Preparation of MLBB

MLBB was prepared from RS via a physical–chemical process of SO_3 micro-thermal explosion (Fig. 1a), which was described in detail elsewhere (Yao et al., 2011; Li et al., 2012a, 2012b). SO_3 plays a dual role of physical detachment between lignin and cellulose, and chemical modification of the lignin component. This in-situ physical detachment between lignin and cellulose can maintain the three-dimensional-structure of the lignin component. Chemical modification provides abundant sulfonic groups on the surface of lignin, which is propitious to the removal of heavy-metal-ion. A portion of RS sample at a weight of 1.0 kg was firstly treated with SO_3 gas (about 1.0 g, originated from the decomposition of oleum) for 2.5 hr in a home-made reactor (Fig. 1b). The pretreated RS sample was washed with ammonia solution (10 L, 0.3% $NH_3{\cdot}H_2O$). The solid residues were further washed with NaOH solution (10 L, 2% NaOH). High-value microcrystalline cellulose was further refined from the solid residue, and MLBB was separated from the liquid residue (~10 L, the black solution) through a pH-dependent flocculation process. The pH of the black solution was adjusted to around 7.0 with HCl solution (1.0 mol/L). Then, the solution was centrifuged at 5000 g for 1.0 min. The as-prepared MLBB sample was oven dried at

Table 1 – Elemental compositions of mesoporous lignin-based biosorbent (MLBB) and rice straw (RS) (wt.%).

Element	MLBB	RS
Carbon (C)	75.22 ± 0.07	32.62 ± 0.07
Hydrogen (H)	16.99 ± 0.09	10.62 ± 0.08
Oxygen (O)	5.23 ± 0.10	55.90 ± 0.12
Nitrogen (N)	0.05 ± 0.02	0.65 ± 0.04
Sulfur (S)	2.51 ± 0.01	0.21 ± 0.01

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