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Alginate-modified biochar derived from Ca(II)-impregnated biomass: Excellent anti-interference ability for Pb(II) removal

Jiaqin Deng[a,b], Xiaodong Li[a,b,*], Yunguo Liu[a,b], Guangming Zeng[a,b], Jie Liang[a,b], Biao Song[a,b], Xue Wei[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, PR China

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ABSTRACT

A novel biochar modified with sodium alginate was prepared using Ca(II)-impregnated biomass, and used to remove metals from aqueous solutions. The maximum adsorption capacity for Pb(II) was estimated to be 1.225 mmol/g (253.6 mg/g), which is far more than that of most adsorbents. Moreover, the modified biochar had a great anti-interference ability for effective removal of Pb(II) from multi-metal system. The biochar still had strong ability to adsorb Pb(II) when the initial concentrations of interfering ions were 5 times higher than that of Pb(II). Functional groups and minerals of the biochar worked for Pb(II) removal and the anti-interference ability. On the one hand, carboxyl could complex with Pb(II) through monodentate and bidentate bridging; on the other hand, Pb(II) was easier to form a precipitate with minerals than other metals. This study suggested that the novel biochar had the potential for practical application in effective removal of Pb(II) from wastewater.

1. Introduction

Rice is widely planted in China. After harvest time, the rice straw is usually treated as agriculture waste. Open burning of crop residue is a common practice in rural areas for the elimination of waste, but it is harmful to the atmospheric environment and human health (Chen et al., 2017; Hong et al., 2016). Considering the sustainable use of resource and environmental protection, rice straw can be recycled as the raw biomass feedstock for biochar production.

Biochar is a carbonaceous material derived from biomass (Kołodyńska et al., 2017; Tan et al., 2015; Wu et al., 2017). Several studies have shown that metals including Pb(II) (Wang and Wang, 2017), Cd(II) (Li et al., 2017a), Cu(II) (Song et al., 2014), and Cr(VI) (Dong et al., 2017), could be adsorbed by biochar.

To further improve the removal ability of biochars, various modification methods have been established (Deng et al., 2017). For example, Wang et al. (2017) prepared a novel biochar by introducing nano-particles (magnetic and EDTA functionalized layered double hydroxides) on biochar surface, and this novel biochar had higher ability to adsorb Pb(II) from wastewater than that of the pristine biochar (Wang and Wang, 2017). Peng et al. (2017) reported a simple modification of biochar by phosphoric acid, and in this case, the Cd(II) and Cu(II) removal capacities of the modified biochar were significantly improved (Peng et al., 2017).

Several modified biochars have great ability to adsorb metals, but they have potential harm to environment during the preparation process. For instance, modification with strong acid or alkali solution can increase the surface area of biochar, enhance metal adsorption ability (Li et al., 2017b). But with the scale production of biochar, a great number of acid or alkali waste water need to be treated, otherwise, it will be discharged and cause environmental pollution (Park et al., 2008). As a result, the potential contamination problems in the process of production need to be considered.

In this study, a novel environment friendly biochar material was prepared through impregnation of rice straw with Ca(II) solution and modification of the biochar with sodium alginate. Alginate is an environment friendly biopolymer extracted from brown algal species. It is a linear acidic polysaccharide constituted by alternating blocks of 1–4 linked α-L-guluronic and β-D-mannuronic acid fragments. It is well known that carboxylic acid groups of alginate could react with divalent metal cations (Cataldo et al., 2016). The synthesis of the novel biochar material is mainly based on this specific reaction. Impregnation of biomass with $CaCl_2$ solution can improve the pore property of biochar and increase the number of functional groups (Liu et al., 2016). The calcium ion cross-link with sodium alginate, so that the functional groups of sodium alginate are loaded onto the surface of biochar. It is

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: lxdfox@163.com (X. Li).

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commonly believed that the improved pore property and increased functional groups could enhance the adsorption capacity of biochar. Moreover, alginate was used to modify the novel biochar. The substance had no harm to the environment. Compared with those biochar preparation with toxic and noxious agents, the potential contamination risk in this process of preparation is lower. The objectives of this work were (1) preparation and characterization of the studied biochars, (2) assessment of the adsorption properties of the modified biochar to metal, and (3) analysis of the metal removal mechanism of the modified biochar.

2. Materials and methods

2.1. Materials

All chemical reagents used in this experiment were analytical reagent grade, and the solutions were prepared using ultrapure water (18.25 MΩ/cm). Lead nitrate ($Pb(NO_3)_2$) were purchased from Sonopharm Chemical Reagent Co., Ltd. Biomass (rice straw) was collected from Yiyang, Hunan province, China.

2.2. Adsorbent preparation

The preparation of novel biochar was self-developed. The biomass (rice straw) was pretreated with Ca(II) solution before pyrolysis to produce biochar. Briefly, the rice straw was washed with ultrapure water and dried at 70 °C for 24 h. Then, the dried biomass was grinded and sieved to < 2 mm particles. After that, the biomass powder was immersed in 0.5 M Ca(II) solution ($CaCl_2$-$2H_2O$) and shaken for 4 h at room temperature. Subsequently, the biomass powder was collected and dried in an oven at 80 °C for 24 h. For biochar preparation, the pretreated biomass was pyrolyzed at 600 °C in a tube furnace (SK-1200 °C, Tianjin Zhonghuan Test Electrical Furnace Co., LTD, China) under N_2 atmosphere. The heating rate was 5 °C/min and the temperature was held at the peak for 2 h. The prepared biochar was referred to as CaRB.

For the preparation of biochar modified with sodium alginate (SA-CaRB), the CaRB suspension (3%, w/v) was added dropwise into sodium alginate (2%, w/v), and the mixed solution was kept for 30 min at room temperature. The resulting sample was then washed with deionized water and oven-dried for 24 h at 60 °C.

2.3. Adsorbent characterization

The morphologies of CaRB and SA-CaRB were observed via scanning electron microscopy (SEM) (JEOL JSM-6700, Japan). The surface area and the total pore volume were measured by the BET method with gas sorption analyzer (Quantachrome, USA). The crystal structures of the samples were determined by an X-ray diffractometer (Rigaku D/max-2500, Japan). Fourier transform infrared spectroscopy (FT-IR) of the samples were obtained by a spectrophotometer (Nicolet, Magna 550 spectrometer). XPS spectroscopy were carried out on ESCALAB 250 Xi X-ray Photoelectron Spectrometer (XPS, Thermo Fisher, USA).

2.4. Adsorption experiments

Standard stock solutions of Pb(II) were prepared by dissolving specific amounts of $Pb(NO_3)_2$ in ultrapure water. All batch adsorption experiments were performed in 150 mL Erlenmeyer flasks with 0.5 g/L biochar at 150 rpm. The Pb(II) ions could precipitate as hydroxides at pH ≥ 7 (Mishra et al., 2017). Thus, the initial pH of solutions were selected in the range of 2.0–6.0 for investigating the effects of pH on the adsorption of Pb(II) onto SA-CaRB. The effect of pH on adsorption were investigated at different pH values (2.0–6.0) of the Pb(II) solution via adjusting the initial solution pH using 0.1 M HNO_3 or 0.1 M NaOH as required. The effect of DOC on adsorption were investigated at varying pH conditions with 10 mg/L humic acid. Kinetic experiments were performed at different time intervals, ranging from 5 to 1440 min, with 0.5 mmol/L metal solutions. For adsorption isotherms, the initial metal concentrations varied from 0.05 to 2.5 mmol/L (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5, 2.0 and 2.5 mmol/L). Adsorption thermodynamic studies were conducted at 298, 303 and 308 K. To investigate the effect of interfering ions on the Pb(II) removal, K(I), Na(I), Mg(II), Ca(II), Cd(II), Cu(II), and Zn(II) with different ion concentrations were respectively added to the Pb(II) solution. The concentrations of residual metal ions were measured by a flame atomic absorption spectrometer (AAS, PEAA700, USA), and the blank solutions were below the instrument detection limits of 300 μg/L for Pb(II).

The adsorbed amount of Pb(II) by the adsorbent, q (mg/g) was calculated using the following equation (Jiang et al., 2017):

$$q = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where C_0 (mmol/L) and C_e (mmol/L) represent the initial and equilibrium concentration of the metal, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of adsorbents

The structures observed with the SEM showed that the CaRB has more pores with different shapes, compared with SA-CaRB (Fig. S1).

The ash contents of pristine biochar, CaRB and SA-CaRB were 32.3%, 51.3% and 39.6%, respectively (Table S1). The impregnation of the biomass with $CaCl_2$ solution increased the ash content due to the load of Ca(II). The modification of biochar with alginate decreased the ash content of the adsorbent, which indicated that the alginate was loaded onto the biochar composites when Ca(II) ion of CaRB crosslink with alginate.

The surface areas of pristine biochar, CaRB and SA-CaRB were 42.1, 110.8 and 91.6 m^2/g, respectively, and the pore volume were 0.049, 0.116 and 0.087 cm^3/g, respectively (Table S1). The results indicated that, compared with the pristine biochar, the surface area and porous structure of CaRB and SA-CaRB improved significantly after modification. Meanwhile, compared with CaRB, the modification with alginate, negatively changed the surface area and porous structure of SA-CaRB. It was corresponded with the analysis of surface morphology. The analysis of surface morphology and the surface area indicated that the CaRB has richer pore structure than SA-CaRB. The phenomenon can be explained by that alginate reacted with Ca(II) occupied the pores of biochar. Generally, adsorbent with greater structured porosity has better adsorption performance (Li et al., 2017c). Considering the relatively low structured porosity, SA-CaRB might not perform as well as CaRB. But there were more functional groups on SA-CaRB due to the load of the alginate, which improved the final adsorption performance (Benettayeb et al., 2017). The Pb(II) removal capacity of CaRB and SA-CaRB were 0.602 mmol/g and 1.009 mmol/g, respectively (Table 1). The results suggested that the functional groups on SA-CaRB may work for Pb(II) adsorption.

3.2. Effects of pH

The initial pH could influence the removal performance of SA-CaRB by (1) electrostatic affinity and repulsion between SA-CaRB and Pb(II), (2) the process of ion exchange between SA-CaRB and Pb(II), and (3) metal species distribution, such as solubility (soluble / insoluble) and charge (cation / anion) (Chen et al., 2015).

Fig. 1a shows the influence of pH on the adsorption efficiency for Pb (II) using SA-CaRB. At low pH (in the range 2.0–3.0) the adsorption capacity was negligible, while the adsorption capacity increases rapidly when the pH values was above 3.5. When the pH = 5.0, adsorption