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Removal of Pb(II) ions from aqueous solution by manganese oxide coated rice straw biochar – A low-cost and highly effective sorbent

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ABSTRACT

MnO_x-coated rice straw biochar was simply synthesized through the reaction of rice straw biochar with $KMnO_4$ in aqueous solution. SEM-EDS analysis confirmed the successful coating of Mn on the surface of the biochar. XPS and FTIR analyses were carried out to study the possible mechanism of Pb(II) binding onto *rice straw (RS)* biochar and MnO_x-coated RS biochar. The work focused mainly on the evaluation of the sorbents for Pb(II) binding. Effect of solution pH, agitating time, Pb(II) initial concentration and co-existing Ca(II) ions on Pb(II) binding were examined. Both for RS biochar and MnO_x-coated RS biochar, sorption kinetic data closely follow the pseudo-second-order model. Langmuir isotherm fits well with the experimental data, and the maximum sorption capacity for Pb(II) calculated from Langmuir model were 0.5782 and 1.4732 mmol g^{-1} for RS biochar and MnO_x-coated RS biochar, respectively. This study suggested that $KMnO_4$ modification is a simple and effective method to increase the sorption capacity of RS biochar.

1. Introduction

Heavy metals contamination is a worldwide environmental concern with respect to environmental and human health. Many countries have set-up more and more stringent standards to control heavy metal concentrations in discharged water [1]. Numerous methods including chemical precipitation, ion exchange, coagulation, sorption, and membrane technologies are used to remove heavy metals from aqueous solutions. Compared to conventional technologies, sorption separation method has many advantages and numerous kinds of sorbents are evaluated. Recently, biochar has gained much concern in heavy metal ions removal from wastewaters system [2–4]. However, the sorption capacity of the original biochars is not satisfying, so modification processes were needed to enhance the sorption performance, *e.g.* oxidation, acid or base treatment, introduction of some functional groups and magnetically modification [4–8].

Coating of biochar with minerals oxides has been recently used to improve the properties of biochar and subsequently enhance its sorption capacity. Modification process involved the treatments of carbon precursors or resulted biochar after pyrolysis [9–11]. Zhang and Gao produced biochar/AlOOH composite through pyrolysis of $AlCl_3$ pretreated biomass for arsenic removal [9]. Porous MgO-biochar nanocomposites were synthesized through pyrolysis of $MgCl_2$ incorporated biomass [10]. Also, Fe-impregnated biochar was prepared through direct hydrolysis of iron salt onto hickory biochar [11].

Manganese oxides (MnO_x) have proven to be an excellent adsorbent for heavy metal removal [12,13]. However, there are still some limitation of applying MnO_x in sorption system, such as agglomeration of MnO_x particles. Therefore, researchers have attempted different materials as supporters to stabilize MnO_x for decreasing the agglomeration, such as zeolite, bentonite, diatomite, sand, resin, activated carbon and tea-waste [14–21], and these composites have shown outstanding sorption capacity for metal ions. Similarly, biochar was employed as supporters to synthesize biochar/MnO_x composites with enhanced sorption functions. For example, Song et al. synthesized MnO_x-loaded biochar through pyrolysis $KMnO_4$ modified corn straw biochar under high temperature and the synthesized sample showed high sorption capacity for Cu(II) [22]. However, the synthesized biochar/MnO_x composite showed much lower surface area compared with the original biochar because manganese oxides and impurities from the decomposition of $KMnO_4$ under high temperature may block the micropores, which is disadvantages to the metal ions binding. So, manganese oxide coating process may be carried out in lower temperature.

The chemical and physical properties of biochar depend on feedstock type and modification process. Rice straw (RS) is a

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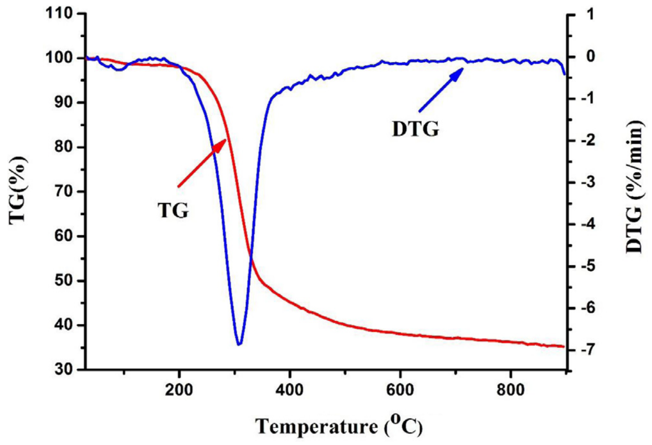

Fig. 1. TG and DTG curves of rice straw biomass (heating rate: 10 °C min^{-1}; Ar flow).

common and abundant agriculture by-product, which contains large amounts of cellulose, hemi-cellulose, lignin and silica. These compounds provide binding sites for metals [23]. Native or modified rice straws were widely used in various sorption system [24–26]. In this study, rice straw was chosen as feedstock to prepare manganese oxide coated RS biochar. That is, rice straw was first pyrolyzated under certain temperature to produce RS biochar. Further, MnO_x-coated RS biochar were synthesized through the reaction of original RS biochar and $KMnO_4$ in an incubator shaker equipped with a water bath at 30 °C for 8 h. Several characterization analyses were carried out to evaluate the synthesized composite and the sorption properties of the samples were examined through Pb(II) binding in aqueous solution.

2. Materials and methods

2.1. Materials

Rice straws used in this study were collected from Shuangliu County near Sichuan University, Chengdu, China. RS samples were washed with tap water and deionized water carefully to remove the impurities, and then oven-dried at 80 °C overnight. Subsequently, the RS was ground in a grinder and passed through a 100-mesh (0.154 mm) sieve. Lead stock solution (10 mmol L^{-1}) and calcium stock solution (1.0 mol L^{-1}) were prepared by dissolving analytical grade $Pb(NO_3)_2$ and $Ca(NO_3)_2$ (Chengdu Kelong Chemical Reagent Corporation) with double deionized water, which were further diluted to certain concentration prior to use.

2.2. Preparation of RS biochar from rice straws

Yang et al. reported that the pyrolysis of hemicellulose and cellulose mainly happened at 220–315 °C and 315–400 °C. While lignin was more difficult to decompose, and the pyrolysis happened in a wide temperature range from 160 to 900 °C [27]. Nevertheless, high temperature biochar (>500 °C) always contained more aromatic matter and less aliphatic matter, and showed higher aromaticity and lower polarity [28,29], which is disadvantageous to metal ions binding. Based on the TG and DTG curves of the rice straw biomass (as shown in Fig. 1), 420 °C was chosen as the pyrolysis temperature.

The preparation of RS biochar was as following: about 10 g of the rice straw powder was tightly packed in a ceramic pot with a cover, which was then put in a controlled-temperature furnace (SX2-4-13, Shanghai Yuejin Medical Instrument Corporation, China). The furnace was programmed to 420 °C with a heating rate of 10 °C min^{-1} and held for 4 h at this temperature, and then allowed to cool down to room temperature naturally. The RS biochar (RSB) produced were soaked in 200 mL deionized water and stirred mildly for 2 h. After that, the samples were washed with multiple double deionized water, filtered and oven-dried at 80 °C. The final products were stored in sealed glass bottles for further use.

2.3. Preparation of manganese oxide coated RS biochar

MnO_x-coated RS biochar was prepared through the reaction of $KMnO_4$ and RS biochar and the specific procedure was as following: 2 g RS biochar and 100 mL aqueous solution containing 0.632 g $KMnO_4$ was added into a stoppered conical flask. The mixed solution was vibrating continuously in an incubator shaker equipped with a water bath at 30 °C for 8 h and then placed overnight. The obtained manganese oxide coated biochar (RSB/MnO_x) were rinsed thoroughly with multiple double deionized water and then oven-dried at 80 °C for 24 h.

2.4. Batch sorption experiments

Heavy metal ion Pb(II) were chosen as the target pollution to test the sorption capacity of the above synthesized samples. Sorption process were carried out using common bottle-point method in conical flasks. The incubator shaker was used to vibrate the stoppered flasks at 150 rpm and room temperature (about 20 °C). To investigate the effects of reaction time and solution pH on Pb(II) binding, 50 mg sorbent was dispersed in 50 mL, 1.0 mmol L^{-1} Pb(II) aqueous solution. The effects of solution pH on Pb(II) sorption was carried out with pH ranging from 2.6 to 6.3, which was adjusted using 0.10 mol L^{-1} HCl or NaOH. The equilibrated solutions were filtered and analyzed for lead concentration using a SOLAAR M6 MK2 atomic absorption spectrometer (Thermo Electron Corporation). The wavelength used was 217.0 nm. The effects of reaction time on Pb(II) sorption was also conducted with 1.0 mmol L^{-1} Pb(II) solution at regular intervals of time up to 480 min.

In order to calculate the maximum sorption capacity and evaluate the possibility of RSB/MnO_x as Pb (II) sorbent, the equilibrium sorption isotherm experiment was conducted by varying the initial lead concentration from 0.2–2.5 mmol L^{-1}. The amount of bound lead per gram of the sorbents q_e (mmol g^{-1}) was calculated as follows: $q_e = V \times (c_0 - c_e)/w \times 1000$. Also, removal efficiency (%) was calculated as the following equation: $R\,(\%) = (c_0 - c_e) \times 100/c_0$. Where c_0 and c_e are the initial and final lead concentration (mmol L^{-1}) in solution, respectively, and V is the volume of solution in mL and w the mass of sorbent in g.

Ca(II) was chosen as the co-existing cation ions to evaluate the sorption selectivity of RSB and RSB/MnO_x to Pb(II). Pb(II) initial concentration was set as 0.5 mmol L^{-1}, and Ca(II) concentration ranged from 10 to 50 times higher than that of Pb(II). The mixed solution (pH 5.0) was vibrated for 8 h and filtered for Pb(II) analysis. Evaluation of the regenerability of RSB/MnO_x was carried out as following: 500 mg RSB/MnO_x was reacted with 500 mL 0.5 mmol L^{-1} Pb(II) solution (pH5.0) for 8 h. The equilibrated solutions were filtered and the sorbents loaded with Pb(II) were collected. 0.3 mol L^{-1} HCl was used as the desorption agent to recovery the sorption capacity of the sorbent. The recycling experiment was conducted for four times.

2.5. Characterization of the samples

Several characterization analyses were carried out to evaluate the synthesized composite. Thermogravimetric analysis (TG) was conducted by Netzsch STA 449F5 Jupiter (heating rate: 10 °C min^{-1}

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