Study on adsorption of lead by biochar prepared from sludge of municipal wastewater treatment plant

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Abstract. In general, with the increase of pyrolysis temperature, the adsorption effect of the prepared biochar to Pb²⁺ is better. Under the same experimental conditions at 25 °C, the adsorption capacity of biochar prepared by pyrolysis of sludge at 600 °C was highest which was 611.8 mg/g. The adsorption kinetics of Pb²⁺ in solution by BC600 is better fitted to the first order kinetic equation. With the increase of pH value of solution, the adsorption capacity of lead increased from 441.3 mg / g to 650.6 mg / g.

1. Introduction
Biochar is a highly aromatic black product produced by carbonization which is the heat of plant biomass under complete or partial hypoxia. Sludge biochar is a new type adsorbent which has good adsorption effect on heavy metal and organic matter. But on the two kinds of pollution the mechanism of action of compounds is different. Physical adsorption is the main mechanism for organic pollutants, while heavy metals are mainly adsorbed on organic pollutants.

In order to study the adsorption properties of municipal sludge based biochar for heavy metals and then to be used as adsorption material in pollution remediation, biochar was prepared by pyrolysis under anaerobic conditions. The adsorption effect of biochar on heavy metals was determined by static equilibrium method.

2. Experimental materials and methods
2.1. Preparation of sludge Biochar
Sludge for the preparation of biochar was collected from the dewatering workshop of a sewage treatment plant in Beijing and transported to the treatment plant. A sludge sample of 0.5g sewage treatment plant is weighed into a porcelain crucible and placed in a program muffle furnace. Nitrogen protection gas is introduced into the muffle furnace, and a sludge slow cracking method is utilized under the condition of oxygen-free. Simultaneously, the power supply is turned on to raise the temperature which is set to 100 °C for 30 minutes, then is raised to different pyrolysis temperatures (200, 300, 400, 500 and 600 °C respectively) at a temperature rising rate of 10 °C/min. At the respective temperature the samples were kept for 2 hours, cooled to room temperature, and the biochar...
is obtained after long-time cracking. The optimal pyrolysis time was found to be 2 h in previous experiments. There is a tail gas absorber at the end of the preparation device to collect tar produced during the pyrolysis of sludge. After natural cooling, biochar samples were taken out for weighing and related properties analysis.

2.2. Biochar characterization
SEM images of biochar pyrolyzed at different temperature were recorded by using Zeiss EVO 50 scanning electron microscope.

2.3. Adsorption of Pb²⁺ on sludge biochar prepared at different temperatures
In order to avoid interference and influence of additional ions (such as K⁺) on biochar ion exchange, 0.15g of biochar prepared at different temperatures was added to lead reserve solution with concentration of 1000mg L⁻¹, and placed in the solution of lead reserve of 100 mL. In order to avoid the interference and influence of applied ions (such as K⁺) on the exchange of biochar ions, no electrolytes were added in the experiment. Generally speaking, when the ionic strength of the solution increases, the electrostatic interaction between the adsorbent and the absorbate weakens, which will inhibit the adsorption of Pb²⁺. The solution to pH is adjusted to 5.0 (because when pH is greater than 5.0, Pb²⁺ will result in hydroxide precipitation). At constant temperature of 25 ± 1°C, the water bath oscillated at a speed of 120 rpm. Reaction solution centrifuged at 5000 rpm for 10 minutes, then filtered with 0.45 μm filter membrane. The concentration of Pb²⁺ in supernatant was determined by ICP and the adsorption capacity of biochar for heavy metals was calculated.

2.4. Adsorption of Pb²⁺ by sludge Biochar at different pH values
The adsorption effect of biochar by pyrolysis at 600 °C is the best. The biochar pyrolyzed at 600°C was selected. At 25 °C, 100ml Pb²⁺ solution of 1000 mg/L was added to a group of 250 ml conical bottles. According to 0.15g/100ml biochar, the pH was adjusted to a predetermined pH value by HCl or NaOH solution of 1 mol/L (2, 4, 5, 6, 8 and 10 mol/L respectively). The removal rate R(%) of Pb²⁺ and the adsorption capacity qₑ (mg/g) by biochar are calculated according to the formula below.

\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]  \hspace{1cm} (2-1)

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  \hspace{1cm} (2-2)

where R(%) is the removal rate of Pb²⁺, \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium adsorbate concentration in solution, respectively; \( q_e \) (mg/g) is the amount of adsorbate adsorbed at equilibrium; m (g) is the dried mass of used adsorbent; V (L) is the volume of the adsorbate solution; and m/V (g/L) is defined as a solid/liquid ratio.

2.5. Adsorption of Pb²⁺ on sludge Biochar at different time
Biochar prepared at the best adsorption temperature was added to 250ml conical bottle with 0.15g biochar and 1000 mg/L 100ml Pb²⁺ reserve solution. The sample was taken after shaking for a certain time and then centrifugated. The supernatant was filtered by 0.22 μm filter membrane, then the Pb²⁺ concentration in the filtrate was determined. All the above experiments were carried out with three parallel samples, and the average values were taken.

The influence of various factors on the adsorption reaction rate is studied. The adsorption kinetic characteristics are clarified and the adsorption mechanism is explored, by which the relationship between the macroscopical quantities of the chemical reaction system determined by experiments is correlated by empirical formula using the kinetic equation: the first order kinetic equation represented by the following formulas (2-3) and the second order kinetic equation represented by the following formulais (2-4) [1].
Pseudo-first-order (PFO) equation:

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

Pseudo-second-order (PSO) equation:

\[ q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \]

where \( q_e \) and \( q_t \) are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time \( t \) (h), respectively; \( k_1 \) (1/min) is the rate constant of the PFO equation; \( k_2 \) (g/mg • min) is the rate constant of the PSO equation.

3. Results and discussions

3.1. SEM

Figure 1. SEM images of biochar pyrolyzed at different temperature.
SEM images in Figure 1 illustrated the surface morphology of biochar derived in N$_2$ environments at temperatures of 200, 300, 400, 500 and 600. As depicted in Figure 1, Biochar pyrolyzed at higher temperature exhibited more rugged surface, but there was no impactful change in the surface of biochar. However, a few tiny holes were observed on surface of biochar pyrolyzed at 600 °C as shown in Figure 1e. These morphological modifications may attribute to the removal of heavy metal lead.

3.2. Adsorption of Pb$^{2+}$ on sludge Biochar prepared at different temperatures
In this study, six kinds of biochar at different temperatures were prepared from sludge at 200, 300, 400, 500 and 600 °C, respectively, as shown in Figure 2. Under the same conditions, biochar was put into lead ion solution. The results show that with the increase of pyrolysis temperature, the amount of lead adsorbed by biochar increases. The removal capacity of biochar by the prepared temperature is significant [2].

![Figure 2. Adsorption of Pb$^{2+}$ by biochar prepared at different temperatures.](image)

3.3. Adsorption characteristics under different pH conditions
The pH value of the solution is considered to be the most important factor for the adsorption of heavy metals by biochar [3]. The initial pH value affects the adsorption performance of biological carbon by: 1) electrostatic repulsive and affinity between adsorbent and adsorbate [4-6], 2) the ion exchange process between adsorbent and adsorbate [7-8], 3) the distribution of metal species, such as soluble or insoluble cations or anions. The results (Figure 3) show that pH value has a strong effect on the adsorption of Pb$^{2+}$ by biological carbon. In general, the removal efficiency increases with the increase of initial pH. In low pH environment, the surface of biological carbon has high positive charge and strong electrostatic resistance to heavy metal lead. When pH increased, the buffer capacity of biological carbon increased and lead changed to hydroxide. When pH increased from 1 to 10, the amount of lead adsorbed by biochar increased from 441.3 mg/g to 650.6 mg/g.
3.4. Adsorption of Pb$^{2+}$ by sludge Biochar at different time

In this study, the initial concentration of Pb$^{2+}$ was 1000 mg/L, and the adsorption of Pb$^{2+}$ on sludge biochar prepared at optimum temperature was studied (Figure 4). The adsorption process was fitted by the first-order kinetic model and the second-order kinetic model. The fitting parameters are shown in Table 1.

![Figure 3. Adsorption of Pb$^{2+}$ by BC600 under different pH value conditions.](image)

![Figure 4. PFO and PSO fitting of adsorption of Pb$^{2+}$ by BC600.](image)

| Table 1. PFO and PSO parameter fitting. |
|----------------------------------------|
| PFO | PSO |
| $K_1$ / min$^{-1}$ | $q_e$ / mg g$^{-1}$ | $R^2$ | $K_2$ / min$^{-1}$ | $q_e$ / mg g$^{-1}$ | $R^2$ |
| 0.56107 | 678.2 | 0.99 | 0.0007 | 850.33 | 0.98 |
The assumption of the first-order kinetic equation is that the unadsorbed sites on the solid phase are proportional to the adsorption rate [9]. The second-order adsorption kinetic model is based on the assumption that the adsorption rate is controlled by the chemisorption mechanism. This chemisorption involves electron sharing or electron transfer between adsorbents and adsorbates. It can be seen from Figure 3 that the adsorption of heavy metal Pb\textsuperscript{2+} by biochar is a typical kinetic process. The adsorption rate of Pb\textsuperscript{2+} is increased with the increase of time, but the adsorption rate is obviously decreased. When the time starts from 4 h, the adsorption basically reaches equilibrium.

4. Conclusions

In this paper, biochar was prepared from bio-physical dry sludge at different pyrolysis temperatures. The optimum preparation temperature was selected to study the adsorption characteristics of sludge based biochar on Pb\textsuperscript{2+} in solution.

1) under the same experimental conditions at 25°C, the adsorption capacity of biochar prepared by pyrolysis of sludge at 200, 300, 400, 500°C and 600°C was 545.5 mg / g, 553.8 mg/g, 563.2 mg / g, 588.9 mg / g and 611.8 mg / g, respectively. In general, with the increase of pyrolysis temperature, the adsorption effect of the prepared biochar to Pb\textsuperscript{2+} is better.

2) The adsorption kinetics of Pb\textsuperscript{2+} in solution by BC600 is better fitted to the first order kinetic equation.

3) With the increase of pH value of solution, the adsorption capacity of lead increased from 441.3 mg/g to 650.6 mg / g.

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