Adsorption Characteristics of Lead by Biochar from Mouth Rinse Residue

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Abstract. Biochars were prepared from mouth rinse residue between 200°C and 600°C. The effects of different pH, adsorbent dosage, adsorption time, and initial concentration of solution on Pb²⁺ adsorption were investigated. The results showed that the Pb²⁺ adsorption amount of the biochar increased with the increasing pH. At 200°C and 300°C, the optimum pH was 6.0, and the optimum pH was 7.0 between 400°C and 600°C. The optimal adsorbent dosage was 0.02 g. Pb²⁺ adsorption amount indicated that biochar prepared at lower temperature was better. The Pb²⁺ adsorption process of biochars could be well fitted by the quasi-second-order kinetic equation. Fitting five kinds of biochar with Langmuir and Freundlich model showed that the biochars fitted the Langmuir model whose maximum adsorption capacities were 188.68, 185.19, 135.14, 109.89 and 86.21 mg/g respectively. Accordingly, biochar can be an effective way to expand the resource utilization of residue.

1. Introduction

Due to the characteristics of high toxicity, extensive sources and non-biodegradable ability, heavy metals polluting water has become a serious environmental problem nowadays. As lead-containing water is discharged from mining-related industries in China every year[1], which can easily be accumulated in the environment and then be absorbed and deposited in biology. It has become a very important problem to remove heavy metals from polluted water environment to ensure the utilization of circulating water.

In recent years, biochar has been used as a suitable biosorbent to remove toxic metals, such as lead or cadmium[2-4]. These studies have shown that biochar has good adsorption and pollutant removal performance. Biochar is a pore structure-rich and carbon-rich biomass prepared by pyrolysis under anoxic or hypoxic conditions, which contains acids, acid derivatives, phenols, celluloses, carbonyls, alkanes, and complex organic carbon mixtures[5]. Biochar has a wide range of raw materials, such as wood, straw, sludge and so on. For example, the waste of nettles infusion was used as the raw material[6]. However, Biochar prepared from different raw materials have significant differences in adsorption properties because their surface structure, physical and chemical properties are obviously different[7]. Mouth rinse residue, as a gargle preparation from Turkish galls as medicinal materials, has the effect of strengthening teeth and gum, clearing blood and relieving pain. The increasing annual sales volume causes residue increasing with residue increasing year by year. And the residue of traditional...
Chinese medicine is a typical organic solid waste. Traditional treatment methods, such as landfill, incineration and biological treatment, not only waste resources, but also cause pollution. Previous studies on the utilization of mouth rinse residue mainly focus on the extraction of components\(^8\). There are few reports on the use of mouth rinse residue. Therefore, Mouth rinse residue was made as biochar by oxygen-limited pyrolysis at different temperatures between 200\(^\circ\)C and 600\(^\circ\)C in the study. The main ingredients of mouth rinse residue are gallic acid, ellagic acid, methyl gallate, etc. The adsorption characteristics and such these influence factors as adsorption time, initial concentration of solution, pH of solution and dosage of biochar in aqueous solution at different pyrolysis temperatures were investigated. The adsorption kinetics model and isothermal adsorption model were used to fit the experimental data in order to screen out the kinetic equation and isothermal adsorption model which can accurately reflect the adsorption of lead by biochar from mouth rinse residue. Thus, the method can provide a theoretical basis for the resource utilization of mouth rinse residue.

2. Materials and Methods

2.1. Materials and Instruments

The biochar was prepared from mouth rinse residue, collected from Xinjiang QiMu Medical Research Institute, Lead Nitrate and Sodium Nitrate were provided by Sheng’ao Chemical (Tianjing, China). Sodium hydroxide was purchased from Fuchen Chemical Reagent Factory (Tianjing, China). Small High Temperature Sintering Furnace (OTF-1200X-S) was purchased from Kejing Material Technology Company (Hefei, China). Entrifuge (TDL~5A) was from Philippines Analytical Instrument Company (Shanghai, China). Heavy metal ions in the biochar were determined by a flame atomic absorption spectrometer (FAAS) (Z-2000, Hitachi).

2.2. Biochar Preparation

Biochar was prepared by anaerobic pyrolysis from mouth rinse residue which was ventilated to dry, crushed and shifted with 200 mesh sieve. 0.2000 g residue was weighed and put into a magnetic boat, and pyrolyzed in a high-temperature sintering furnace. Carbonization was conducted at 200\(^\circ\)C, 300\(^\circ\)C, 400\(^\circ\)C, 500\(^\circ\)C, and 600\(^\circ\)C for 2 h under a nitrogen flow of 50 mL/min. The pyrolysis temperature was increased to the desired values at a rate of 10\(^\circ\)C/ min. The biochar samples were removed after cooling to room temperature and grinded, then sealed in a sealed bag and put into a vacuum dryer for reserve.

2.3. Batch Experiment

The effect of pH between 2 and 9 on the adsorption of 600 mg/L Pb\(^{2+}\) solution was studied in the experiment. 0.02 g biochar was added to 5 mL Pb\(^{2+}\) solution of 600 mg/L concentration. The pH of Pb\(^{2+}\) solution was adjusted by HNO\(_3\) (0.1 mol/L) or NaOH solution. The solution of Pb\(^{2+}\) contained NaNO\(_3\) (0.01 mol/L) as electrolyte solution, oscillated at 150 rpm at 25\(^\circ\)C for 24 h, centrifuged at 3800 rpm for 5 minutes, passed through 0.22 um microporous membrane, used FAAS to analyze the concentration of Pb\(^{2+}\) in the filtrate at 283.3 nm, and calculated the equilibrium adsorption capacity of biochar to Pb\(^{2+}\) at different pH. Each sample was measured three times in parallel. The adsorption capacity \(Q_e\) (mg/g) of biochar to Pb\(^{2+}\) was illustrated as follows:

\[
Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)
\]

In the equation (1), \(C_0\) (mg/L) is the initial Pb\(^{2+}\) concentration, \(C_e\) (mg/L) is the equilibrium Pb\(^{2+}\) concentration, \(V\) (mL) is the volume of the solution, and \(m\) is the weight (g) of the biochar.

In the experiment of adding amount of biochar, 5 ml Pb\(^{2+}\) solution (600 mg/L) was added to 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 g biochar at different pyrolysis temperatures. The pH of the solution was adjusted by HNO\(_3\) (0.1 mol/L) or NaOH solution. The solution of Pb\(^{2+}\) contained NaNO\(_3\) (0.01 mol/L) as electrolyte solution, and the equilibrium time was 24 h. Each sample was measured three times in parallel.

0.02g residue biochar was accurately weighed in 15mL centrifugal tube where 5mL lead solution with 600 mg/L concentration was added respectively. Drop a small amount of 0.1 mol/L HNO\(_3\) or NaOH
solution to adjust the pH of Pb²⁺ solution. The centrifugal tube was placed and oscillated in 25°C constant temperature oscillator and with the rate of 150 rpm. Sample was taken at 0, 1, 2, 4, 8, 12, 24, 36, 48 and 60 hours respectively, centrifuged for 5 min and passed through 0.22 um microporous membrane. The concentration of Pb²⁺ in the filtrate was analyzed by FAAS at 283.3 nm. The amount of Pb²⁺ adsorbed by biochar at different time was calculated. Each sample was measured three times in parallel.

Using Lagergren kinetic equation including Quasi-First-Order kinetic equation (2) and quasi-second-order kinetic equation (3) to describe the kinetic process equation of biochar adsorbing Pb²⁺ as follows[9]:

\[ Q_t = Q_e (1 - e^{-kt}) \]

\[ t/Q_e = 1/(k_2Q_e^2)1/(Q_e) \]

In the isothermal adsorption experiment, different initial concentration of Pb²⁺ ranged from 200 mg/L to 2200 mg/L, 0.02 g biochar was added to 5 mL Pb²⁺ solution. The adsorption isotherms of Pb²⁺ were obtained by gradient concentration of 200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000 and 2200 mg/L. Different biochar samples were taken at the adsorption equilibrium of 24 hours, and centrifuged and filtered. FAAS were used to analyze the concentration of Pb²⁺ in the filtrate. The amount of Pb²⁺ adsorbed by biochar at different initial concentration was calculated. Each sample was measured three times in parallel.

The adsorption isotherms are fitted by Langmuir model (4) and Freundlich model (5), respectively. The formulas are as follows:

\[ Q_e = \frac{Q_max K_L C_e}{1 + K_L C_e} \]

\[ Q_e = K_f C_e^n \]

In the equation (4) and equation (5), \( C_e \) is equilibrium concentration (mg/L), \( Q_e \) and \( Q_m \) are equilibrium adsorption capacity and maximum adsorption capacity (mg/g), \( K_L \) and \( K_f \) are Langmuir and Freundlich model parameters respectively, and \( n \) is Freundlich constant.

3. Results and Discussion

3.1. Effect of pH on Pb²⁺ Adsorption

The results of adsorption of Pb²⁺ by biochar from drug residue at different pH are shown in figure 1. The results show that the adsorption capacity of biochar to Pb²⁺ increases with the increasing pH, reached the maximum at 200°C and 300°C at pH=6, and then decreased. At pH=7, the adsorption capacity tended to be stable between 400°C and 600°C. Therefore, the optimum pH was 6.0 at 200°C and 300°C, and 7.0 between 400°C and 600°C. The order of the maximum adsorption capacity for Pb²⁺ by residue biochar was 200°C>300°C> 400°C> 500°C> 600°C. Under acidic and neutral conditions, residue biochar was more advantageous to adsorb lead.
3.2. **Influence of Dosage**

The amount of heavy metal ions adsorbed by residue biochar can be seen intuitively from figure 2. With the increasing dosage, the amount of Pb^{2+} adsorbed by residue biochar decreases gradually, which may be related to the solubility and exclusion of adsorbent\cite{10}. The figure 2 shows the optimum dosage of residue biochar is 0.02 g.

![Figure 2. Effect of dosage on biochars Pb^{2+} adsorption at different pyrolysis temperatures.](image)

3.3. **Adsorption Kinetics of Pb^{2+} by Residue Biochar**

In order to study the adsorption kinetics of Pb^{2+} by residue biochar, the effect of adsorption time was studied, and the kinetic model was determined in figure 3 and figure 4. The fitting curves obtained by Lagergren Quasi-first-order kinetic equation and Quasi-second-order kinetic equation were shown in figure 4, and the fitting parameters were listed in table 1. The fitting results are shown in figure 4 and table 1. Quasi-second-order kinetics model can better fit the whole adsorption stage. The correlation coefficient Quasi-second-order kinetics model is close to 1, and is larger than that of Quasi-first-order kinetics equation. The theoretical equilibrium adsorption quantity $Q_{e,cal}$ of Quasi-second-order kinetics equation are higher than that of Quasi-first-order kinetics equation. So Quasi-second-order kinetic equation is more accurate than Quasi-first-order kinetic equation in describing the adsorption of Pb^{2+} on biochar. Therefore, Quasi-second-order kinetic model is suitable for the whole dynamic process of Pb^{2+} adsorption, and the adsorption rate is mainly controlled by chemical adsorption.

![Figure 3. Different time on Pb^{2+} adsorption by residue biochars.](image)
Figure 4. Pb\textsuperscript{2+} adsorption kinetic curves of biochars at different pyrolysis temperatures: (a) Quasi-first-order; (b) Quasi-second-order.

Table 1. Pb\textsuperscript{2+} adsorption kinetics fitting data of biochars at different pyrolysis temperature.

| Biochars  | Q\textsubscript{e,exp} (mg/g) | Q\textsubscript{e,cal} (mg/g) | k\textsubscript{1} (h\textsuperscript{-1}) | R\textsuperscript{2} | Q\textsubscript{e,cal} (mg/g) | k\textsubscript{2} (g·mg\textsuperscript{-1}·h\textsuperscript{-1}) | R\textsuperscript{2} |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 200°C     | 168.3          | 11.13          | 0.0534         | 0.6983         | 166.7          | 0.040          | 1 |
| 300°C     | 109.9          | 66.02          | 0.0028         | 0.3438         | 109.9          | 0.069          | 0.9998 |
| 400°C     | 139.4          | 53.70          | 0.0124         | 0.5974         | 138.9          | 0.020          | 0.9992 |
| 500°C     | 92.67          | 92.96          | 0.0048         | 0.2932         | 92.59          | 0.069          | 0.9990 |
| 600°C     | 119.2          | 78.52          | 0.0104         | 0.4926         | 119.1          | 0.022          | 0.9983 |

3.4. Adsorption Isotherms of Pb\textsuperscript{2+} by Residue Biochar

Langmuir and Freundlich model were used to fit the adsorption isotherms of Pb\textsuperscript{2+} on biochars in figure 5 and figure 6, and the fitting parameters were listed in table 2.

Comparing the two models, the R\textsuperscript{2} of Langmuir and Freundlich adsorption isotherm models are 0.9927-0.9998 and 0.9221-0.5163, respectively. Therefore, Langmuir adsorption isotherm model can better describe the adsorption isotherm process of biochar for Pb\textsuperscript{2+}, indicating that the adsorption of lead by residue biochar seems to be monolayer\textsuperscript{11}. The adsorption capacity increases with the increase of solution concentration, but when the concentration increases to a certain extent, the adsorption of Pb\textsuperscript{2+} by residue biochar tends to be balanced. The separation factor R\textsubscript{L} in Langmuir adsorption isotherm equation can well describe the adsorption performance of adsorbents\textsuperscript{12}. R\textsubscript{L} is expressed as the affinity of adsorbent to adsorbate. It is not conducive to adsorption when R\textsubscript{L} is more than 1, or conducive when R\textsubscript{L} is between 0 and 1. When R\textsubscript{L} is 1, it is linear adsorption, and it is irreversible adsorption when R\textsubscript{L} is zero. From table 2, it can be seen that the R\textsubscript{L} values of the adsorption of Pb\textsuperscript{2+} by the residue biochar in Langmuir model are all between 0 and 1, indicating that the residue biochar has a good adsorption performance for Pb\textsuperscript{2+}.

Figure 5. Different concentration on Pb\textsuperscript{2+} adsorption by residue biochars.
Figure 6. Pb$^{2+}$ adsorption isotherm of biochars at different pyrolysis temperatures: (a) Langmuir model; (b) Freundlich model.

Table 2. Pb$^{2+}$ adsorption isothermy fitting data of biochars at different pyrolysis temperature.

| Biochars | Langmuir model | Freundlich model |
|----------|----------------|------------------|
|          | $Q_{\text{max}}$(mg/g) | $K_L$(L/mg) | $R^2$ | $R_L$ | $n$ | $K_F$(mg/(mg/L)$^n$) | $R^2$ |
| 200°C    | 188.68         | 0.0523      | 0.9998 | 0.0354-0.0044 | 6.8027  | 70.2102  | 0.5702 |
| 300°C    | 185.19         | 0.0559      | 0.9998 | 0.0387-0.0048 | 6.3012  | 64.2984  | 0.6237 |
| 400°C    | 135.14         | 0.0322      | 0.9989 | 0.0149-0.0020 | 7.1225  | 50.8042  | 0.6661 |
| 500°C    | 109.89         | 0.0237      | 0.9966 | 0.0096-0.0012 | 5.6433  | 31.5283  | 0.5163 |
| 600°C    | 86.21          | 0.0077      | 0.9927 | 0.0025-0.0003 | 3.0157  | 7.5509   | 0.9221 |

4. Conclusions
Biochar converted from mouth rinse residue can better adsorb heavy metals and realize the resource utilization of solid waste residue. The amount of Pb$^{2+}$ adsorbed by the residue biochar at different pyrolysis temperatures varies significantly, which provides a reference for the application of mouth rinse residue biochar in practical research.
Drug residue biochar can absorb Pb$^{2+}$ in water. Its equilibrium adsorption time is 24 hours. The adsorption process conforms to the quasi-second-order kinetic equation ($R^2=0.9983$). The adsorption rate is mainly chemical adsorption. The pH of solution will affect the adsorption of heavy metal ions by the residue biochar. With the increase of the pH of solution, the adsorption capacity increases continuously. In the adsorption capacity performance, the optimum pH of biochar is 6.0 at 200°C and 300°C, and 7.0 between 400°C and 600°C. The order of maximum adsorption capacity of biochar is at 200°C > 300°C > 400°C > 500°C > 600°C. Under acidic and neutral conditions, biochar from residue is more conducive to the adsorption of lead.
The adsorption isotherm of Pb$^{2+}$ by residue biochar is more in line with Langmuir isotherm model, which indicates that the adsorption process is similar to single molecular layer chemical adsorption. The $R_L$ values of Pb$^{2+}$ adsorption by residue biochar in Langmuir model are all between 0 and 1, Indicating that residue biochar has better adsorption performance for Pb$^{2+}$.

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