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Study on Influencing Factors of Effect of Wheat Straw Biochar on Adsorption of Heavy Metal Pb^{2+}

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Abstract

Biochar made by a raw material of wheat straw was prepared by the method of limiting oxygen-heating cracking at 400, 500, and 600 ℃, respectively. The effects of different pyrolysis temperatures, different initial pH values, and different initial heavy metal concentrations on the adsorption of Pb^{2+} of biochar were investigated. The results show that the yield of biochar decreased with increasing pyrolysis temperature of biochar, indicating that dehydration occurred during the pyrolysis process under high temperature conditions. At high temperature, the carbonization of wheat straw was more complete, the aroma was higher, and the polarity was gradually reduced. At the same time, the adsorption amount of wheat straw on Pb^{2+} gradually increased. As the pH of the solution increases, the amount of Pb^{2+} adsorbed by the biochar gradually increased. The adsorption rate between pH 5-6 was greater than the adsorption rate between pH 7-8. Because when the pH is greater than 6, Pb^{2+} will precipitate with OH^- because of the initial appearance of OH, which affected the adsorption effect on Pb^{2+} consequently. With the increase of the initial heavy metal concentration, the adsorption amount of Pb^{2+} showed a significant increasing trend with a maximum of highest adsorption amount, reaching 180 mg/g. Finally, the linear parameter R^2 fitted by the two models of Freundlich and Langmuir were compared. The Freundlich model could well describe the biochar adsorption Pb^{2+} behavior. It also shows that the adsorption of heavy metal Pb^{2+} by biochar was accomplished through multilayer adsorption.

Keywords

Wheat straw; Biochar; Pb^{2+}; Adsorption.

1. INTRODUCTION

With the rapid development of urbanization and industrialization, due to the "three wastes" emitted by mining and smelting industries, the burning of fossil fuels such as coal and petroleum, and the excessive application of pesticides and fertilizers, heavy metals have entered the soil through various routes [1]. At present, the problem of soil pollution caused by different types of pollutants has become very serious. Among the existing $1 \times 10^8 hm^2$ arable land in China, nearly 1/5 is polluted to varying degrees, causing a reduction in grain output by 2.5×10^9 kg every year [2].

Biochar is a poorly soluble, stable, highly aromatic, carbon-rich solid that is produced by the use of biological residues under high-temperature pyrolysis (usually<700°C) [3, 4]. Its raw materials come from a wide range of sources. Agricultural wastes: chicken manure, pig manure, wood chips, straw, industrial organic waste, and urban sludge can be used as raw materials [5]. Biochar is mainly composed of aromatic hydrocarbons, elemental carbon, graphite, and ash. The

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main constituent elements are C, H, O, and N. The carbon content is above 60%. Other elements include N, P, Ca, Mg, K, and trace elements Mn, Zn, Cu, etc. [6]. Biochar has the characteristics of porosity, small bulk density, large specific surface area, and high negative charge, which makes biochar good in holding nutrients and moisture [7]. As an environmentally friendly improver, in the field of environmental protection, biochar is widely used in many aspects such as carbon sequestration, pollution control, and water purification [8]. The waste biomass in the agricultural and forestry production process is prepared into biochar through carbonization technology and used as a soil improver to return to the farmland. It can effectively improve soil physical and chemical properties and micro-ecological environment, repair contaminated soil, and improve soil production performance and crop yield and quality [9]. Of course, biomass energy conversion technology can also efficiently produce a variety of clean energy sources, replacing coal, oil, and natural gas. It is an important way to "open source and reduce expenditure" in the energy field [10].

Among them, Chang Xiliang et al. [11] used wheat straw as raw material to prepare biochar at different temperatures. According to the test, it was found that as the temperature increased, the pore size of biochar became larger and its aroma increased. Ding et al. [12] studied the adsorption effect of bagasse charcoal on Pb2 + prepared at different pyrolysis temperatures, and the results showed that the adsorption effect of Pb^{2+} on biochar prepared at 250 and 400°C was significantly better than 500 and 600°C. Made of biochar. Houben et al. [13] studied the repair effect of Pb^{2+} in soil by biochar with mass fraction of 1%, 5% and 10%, respectively, and compared it with lime. The experimental results show that the solidification effect of 10% biochar on heavy metals is similar to that of lime, and the bioavailability of Pb^{2+} is reduced by 92%.

In this paper, wheat straw biomass was selected as raw material, and biochar was prepared at 400, 500, and 600 °C. The effects of pyrolysis temperature, initial pH value, and initial heavy metal concentration on the adsorption of Pb^{2+} on biochar were investigated.

2. MATERIALS AND METHODS

2.1 Preparation of Biochar

Biochar was prepared from wheat straw, a typical crop in Xi'an, and the test soil was sampled from the surrounding suburbs of Xi'an, Shaanxi. The soil type was mainly loam, the average annual rainfall in this area was small, and the soil pH was alkaline. The organic matter content is low, the available nitrogen and phosphorus nutrients are relatively lacking. Collect 0~20 cm soil layer soil samples, air-dry the soil, pick out plant roots, stones and other debris, grind and mix through a 2 mm sieve, and measure the Pb2+ content in the soil to be 0.022 mg/L. The wheat straw was cleaned, cut into small pieces of about 3 cm, dried at 105 °C, and then spared.

The preparation of biochar adopted the method of limiting oxygen-heating cracking, and the standby wheat straws were controlled in a temperature-controlled muffle furnace (TSX-4-12) for the oxygen-limited pyrolysis preparation temperature at 400, 500, and 600 °C, respectively. The heating rate was set as 20 °C/min, rising from room temperature to the target temperature. It was held for 2 h after reaching the target temperature. The biochars were taken out and sieved when it was cooled down to room temperature naturally. Meanwhile the biochars were sealed with a sealed bag for future use. The biochars prepared at 400, 500, and 600 °C were labeled as W400, W500, and W600, respectively.

2.2 Adsorption Experiment

2.2.1 Effect of pyrolysis temperature of biochar on adsorption experiments

Weigh 0.1g of W400, W500, and W600 biochar and 5g of soil sample into 250ml Erlenmeyer flasks, and add 40ml of $Pb(NO_3)_2$ solutions with a concentration of 100 mg/L. The initial pH

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value of all solutions was 7.0, which contained an electrolyte $NaNO^3$ solution at a concentration of 0.01 mol/L. Place in a constant temperature shaking incubator at 25 °C and shake at 200 r/min for 12 h. Finally, the mixed sample was collected in a 50 ml centrifuge tube, centrifuged at 4000 r/min for 3 minutes, the filtrate was collected, and then filtered through a 0.45 μm cellulose acetate filter. After dilution and constant volume, the Pb^{2+} concentration of the sample was determined by atomic absorption spectrometer. Each sample was done 3 times in parallel. The adsorption amount and removal rate of heavy metal Pb^{2+} are calculated by the following formulas (1) and (2):

$$Q_t = \frac{(C_i - C_t)V}{m} \tag{1}$$

$$E = \frac{(C_i - C_t)}{C_i} \times 100\% \tag{2}$$

Where: Qt —the adsorption amount (mg/g) of Pb^{2+} by the biochar at time t;

Ci—Initial concentration of Pb^{2+} (mg/L);

Ct—Pb^{2+} concentration at time t (mg/L);

V—Add volume (L) of heavy metal Pb^{2+};

m—Mass of added biochar (g);

E—Removal rate of Pb^{2+}.

2.2.2 Effect of the amount of biochar added on the adsorption experiment

Weigh 5 g of soil sample, add 2, 5, 10% (0.1, 0.25, 0.5 g) of biochar, respectively, and add 40 ml of $Pb(NO_3)2$ solutions with a concentration of 100 mg/L. The initial pH value of all solutions was adjusted to 7.0. 50 ml of hydrochloric acid with a concentration of 0.01 mol/L was taken, which contained an electrolyte solution of $NaNO_3$ with a concentration of 0.01mol/L, and transferred into a 250 ml conical flask at 200 r/min at 25 °C Shake in a constant temperature shaking incubator for 12 h. The mixed sample was centrifuged in a 50 ml centrifuge tube at 4000 r/min for 3 minutes, and the filtrate was collected, and then filtered through a cellulose acetate filter having a pore diameter of 0.45 μm. After dilution and constant volume, the Pb^{2+} concentration of the sample was determined by atomic absorption spectrometer. Each sample was done 3 times in parallel. The adsorption amount and removal rate of heavy metal Pb^{2+} are calculated by the formulas, which are the same as the formulas (1) and (2).

2.2.3 Influence of initial pH value on adsorption experiment

Weigh 0.1 g of W500 biochar, 5 g of soil sample into 250 mL Erlenmeyer flask, and then add $Pb(NO_3)_2$ with pH values of 5.0, 6.0, and 7.0 concentration of 100 mg/L, respectively. The pH of the solution was adjusted with 1 mol/L NaOH and 1 mol/L HNO_3. After equilibrating at 25 °C and 200 r/min in a constant temperature shaking incubator for 12 h, the mixed sample was placed in a 50 ml centrifuge tube. Centrifuge at 4000 r/min for 3 minutes, collect the filtrate, and filter through a pore diameter of 0.45 μm cellulose acetate filter. After dilution and constant volume, the Pb^{2+} concentration of the sample was determined by atomic absorption spectrometer. Each sample was done 3 times in parallel. The adsorption amount and removal rate of heavy metal Pb^{2+} are calculated by the above formulas (1) and (2).

2.2.4 Effect of Initial Heavy Metal Concentration on Adsorption Experiment (Isothermal Adsorption Experiment)

Weigh 0.1 g of W400, W500, W600 biochar, 5 g of soil sample into a 250 ml Erlenmeyer flask, add 40 ml of $Pb(NO_3)_2$ solution with different concentrations of 100, 200, 300, 400, and 500

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mg/L. The initial pH value of all solutions is 7.0, and the solution contains an electrolyte NaNO3 solution with a concentration of 0.01 mol/L. In a constant temperature shaking incubator at 25 °C, shake at 200 r/min for 12 h. Finally, the mixed sample was centrifuged in a 50 ml centrifuge tube at 4000 r/min for 3 minutes, and the filtrate was collected and filtered through a 0.45 μm cellulose acetate filter. After dilution and constant volume, the Pb^{2+} concentration of the sample was determined by atomic absorption spectrometer. Each sample was done 3 times in parallel, and the isothermal adsorption curves of Pb^{2+} were made.

In this experiment, Freundlich model and Langmuir model were used to fit isothermal adsorption experiments. The calculation formulas (3) and (4) are as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_1} \quad (3)$$

$$InQ_e = \frac{1}{n} InC_e + InK_f \quad (4)$$

Where: C_e—equilibrium concentration (mg/L);

Q_e—equilibrium adsorption (mg/g);

Q_m—saturated adsorption of biochar (mg / g);

K_1—Langmuir model adsorption constant;

K_f, 1/n—Freundlich model adsorption constant.

3. RESULTS AND DISCUSSION

3.1 Influence of Pyrolysis Temperature on Adsorption

The picture shows the effect of biochar pyrolysis temperature on adsorption experiments. The initial lead concentration was 100 mg/L, and the pyrolysis temperatures were 400, 500, and 600 °C, respectively. In the adsorption experiment of Pb^{2+}, the adsorption amount of W400 was 36.82 mg/g, the adsorption amount of W500 was 37.30 mg/g, and the adsorption amount of W600 was 37.70 mg/g. Therefore, as the pyrolysis temperature of biochar increases, the adsorption amount of Pb^{2+} also increases, and the adsorption amount of Pb^{2+} is more than 30 mg/g. From the slope of the figure, it can be seen that the adsorption rates of Pb^{2+} are not much different, and the adsorption rate appears to increase slowly. This shows that with the increase of the pyrolysis temperature of biochar, the adsorption effect on Pb^{2+} will be enhanced.

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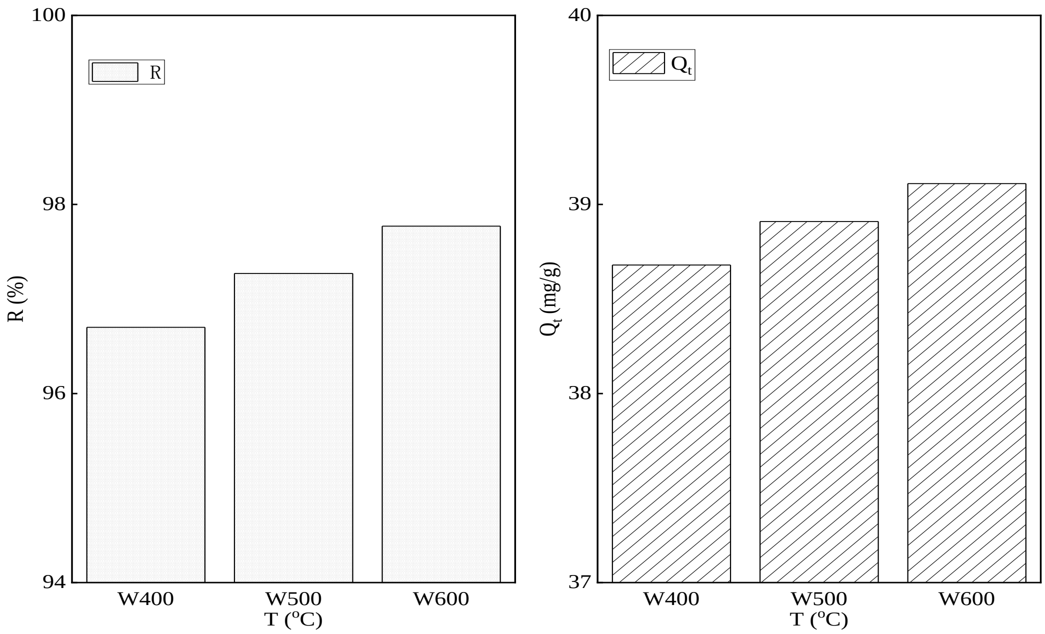

Figure 1. Effect of pyrolysis temperature on adsorption

3.2 Effect of Initial pH on Adsorption

The pH value of the initial solution will affect the existence of heavy metals, the degree of ionization, and changes in surface functional groups, which is one of the important factors affecting adsorption. Figure 2 shows the effect of initial solution pH on adsorption experiments. When the biochar adsorbs heavy metal Pb^{2+}, the initial pH values of 5, 6, 7, and 8 are 27.01, 34.63, 37.05, and 37.67 mg/g, respectively. It can be seen that the pH of Pb^{2+} is gradually increasing between 5-6, while the pH is between 6-8, and the adsorption rate is gradually increased. Because Pb^{2+} will precipitate with initial appearance of OH- when the pH value is greater than 6, which affects the adsorption effect on Pb^{2+}. Gradually decline. It shows that Pb^{2+} can be effectively adsorbed with the increase of pH value.

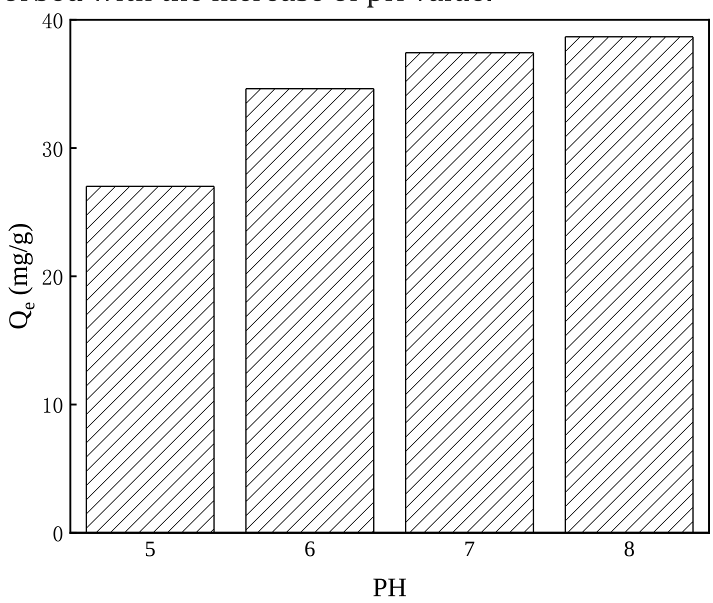

Figure 2. Effect of initial pH on adsorption

3.3 Adsorption Isotherm

Comparing the fitted linear parameters R^2 of the two models, the Freundlich model can well describe the behavior of biochar adsorption of Pb^{2+}. It shows that the adsorption of heavy metal

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Pb^{2+} by biochar is accomplished through multilayer adsorption. The Freundlich model is suitable for a multi-layer adsorption model under non-uniform surface conditions, and the adsorption amount will continue to increase at high concentrations. Figures 3, 4, and 5 show the fitting curves of biochar W400, W500, and W600 for heavy metals Pb^{2+} adsorption, respectively. Table 1 shows the fitting parameters of biochar for heavy metals Pb^{2+} adsorption. As can be seen from Table 1, in the Freundlich model, the Kf values of W400, W500, and W600 are 6.10, 9.33, and 1.49, respectively, and the n values are 5.26, 7.21, and 5.28, respectively. The Kf value and n value are greater than 1, indicating that the wheat straw biomass The adsorption capacity of carbon is strong. At the same time, the adsorption capacity of W400 and W500 for Pb^{2+} is greater than that of W600.

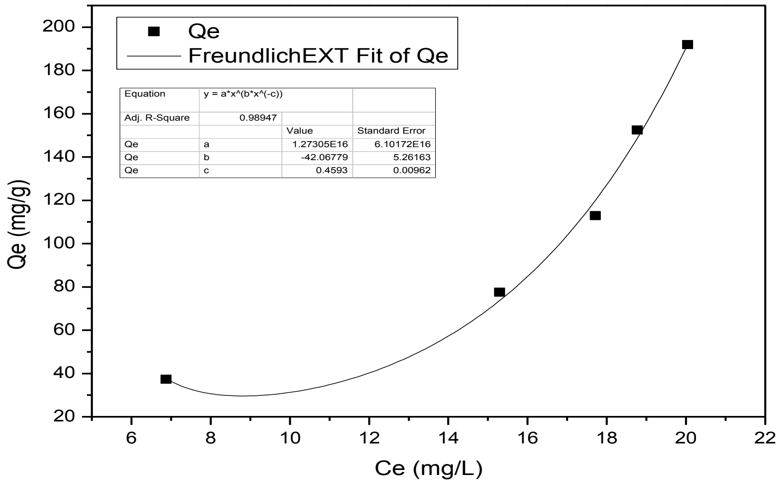

Figure 3. Fitting curve of W400 adsorbing Pb^{2+}

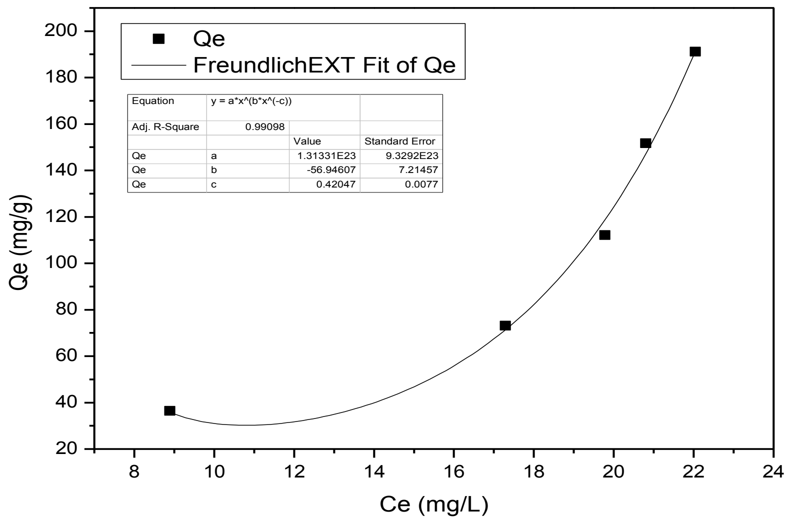

Figure 4. Fitting curve of W500 adsorption of Pb^{2+}

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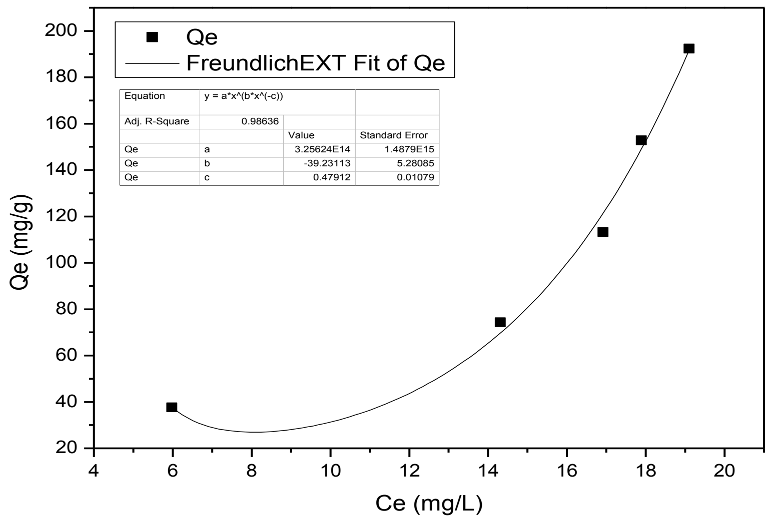

Figure 5. Fitting curve of W600 adsorption of Pb^{2+}

Table 1. Fitting parameters of Pb^{2+}

Adsorbent	Freundlich Isothermal model		
	Kf	n	R2
W400	6.10	5.26	0.9895
W500	9.33	7.21	0.9910
W600	1.49	5.28	0.9864

4. CONCLUSION

The prepared three kinds of biochar W400, W500, and W600 were used to adsorb heavy metals Pb^{2+} in the soil, and the mechanism of biochar adsorption of heavy metals Pb^{2+} was studied by changing the initial solution pH and initial concentration.

(1) As the pyrolysis temperature of biochar increases, the amount of Pb^{2+} adsorbed by biochar increases, and the highest value can reach 37.7 mg/g.

(2) As the initial pH of the solution increases, the amount of Pb^{2+} adsorbed by biochar increases. When the pH value is between 5-6, the adsorption rate is significantly higher than the pH between 6-8, and the maximum value reaches 37.67 mg/g. When the pH value is between 6-8, the adsorption rate gradually increases.

(3) With the increase of the initial concentration of heavy metal Pb^{2+}, the adsorption performance of biochar on Pb^{2+} is stronger; the adsorption of biochar on Pb^{2+} conforms to the Freundlich model, which indicates that the adsorption of heavy metal Pb^{2+} by biochar may be accomplished through multi-layer adsorption.

In summary, it can be seen that the adsorption of heavy metal Pb^{2+} by wheat straw biochar is accomplished through multi-layer adsorption; because the pH of biochar is alkaline, the pH in the solution is increased, and OH- is provided for the adsorption of heavy metal Pb^{2+}. It is effectively combined with OH- to form a precipitate of $Pb(OH)_2$, which adsorbs the heavy metal Pb^{2+}.

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