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Effect of Pyrolysis Temperature on Adsorption Characteristics of Biochar Derived from Corn Straw

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ABSTRACT

With the growth of population and the rapid development of industry, a large amount of wastewater containing heavy metals has been produced. How to treat wastewater containing heavy metals effectively is an important problem. In this study, biochar derived from corn straw is prepared at different carbonization temperatures by oxygen-limited carbonization, and finally, biochar derived from the corn straw at different temperatures is obtained. Then, the adsorption characteristics of ionic heavy metal copper in aqueous solution were studied by biochar prepared at different temperatures. Adsorption kinetics of copper in aqueous solution by biochar from corn straw is discussed in detail. Experimental results show that the adsorption capacity of Cu^{2+} ions in solution by biochar prepared at different temperatures is significantly different. The prepared biochar derived from corn straw is a fragmentary and porous structure. A lot of functional groups appear on the prepared biochar. The pseudo second order kinetic equation can better describe the entire adsorption of Cu^{2+} ions in solution by biochar prepared under different temperatures. The adsorption process of Cu^{2+} ions by biochar is controlled by liquid diffusion and intraparticle diffusion.

INTRODUCTION

With the growth of population and the rapid development of industry, a large amount of wastewater containing heavy metal pollution has been produced (Chiron et al. 2003, Jeon et al. 2003). These wastewater containing heavy metal can flow into water, soil and air through various means, which eventually are harmful to the environment (Arthur et al. 1993, Shukla 2000, Ömer et al. 2003). Once people drink sewage water or eat vegetables and food that have been irrigated by sewage, heavy metals in the water can enter the human body (Jung et al. 1998). These heavy metals will gradually accumulate in the human body, which eventually causes human pathological changes, abnormal fetal development, reproductive disorders, and physical fitness decline (Shen & Duvnjak 2005, Veli & Alyüz 2007). At present, the following two methods are mainly used to repair and control heavy metal pollution in water bodies. One approach is to reduce the migration and bioavailability of heavy metals in water. Another method is to completely remove heavy metals from the polluted water body (Bailey et al. 1999, Swami & Buddhi 2006, Sud et al. 2008, David et al. 2010).

Biochar is a highly aromatic refractory solid substance produced by slow pyrolysis and carbonization of biomass under complete or partial anoxic conditions (Chen et al. 2007). They are mainly mixtures of complex organic carbons, such as acid and acid derivatives, phenol, cellulose, carbonyl, alkanes and olefin derivatives (Beck et al. 2011, Ahmad et al. 2014, Yasser et al. 2017). They have the characteristics of large specific surface area, good porosity and strong adsorption capacity (Ok et al. 2015). Therefore, biochar is widely used in agriculture and the environment. Biochar has good adsorption capacity for heavy metal pollutants and organic pollutants (Kaudal et al. 2016, Rehman et al. 2016). Researching on the adsorption mechanism of biochar on pollutants will be a benefit to understand the adsorption pathway of biochar, to better carry out the purification effect of biochar on pollutants (Ma et al. 1994).

Related studies have shown that different biomass feedstocks and biochars prepared at different pyrolysis temperatures have different properties, such as pore structure, surface functional groups and so on (Singh et al. 2012). Therefore, these characteristics determine the significant difference in the adsorption of heavy metals on biochar prepared under different conditions (Alkan & Dogan 2001, Altundogan et al. 2007).

In this study, biochar derived from corn straw is prepared at different carbonization temperatures by oxygen-limited carbonization, and finally, biochar derived from corn straw at different temperatures is obtained. Then, the adsorption characteristics of ionic heavy metal copper in aqueous

solution are studied by biochar prepared at different temperatures. Adsorption kinetics of copper in aqueous solution by biochar from corn straw is discussed in details. The above research results will provide a theoretical basis for the treatment of heavy metal pollution by biochar.

MATERIALS AND METHODS

Materials: Copper nitrate was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Corn straw came from a farm in the suburbs of Jinan City, Shandong Province.

Preparation of biochar: Biochar was prepared according to the following method. Weigh a certain amount of corn straw and wash it with deionized water three times. Dry in an oven at 80°C for 12 h. After being crushed, it is placed in a crucible. The lid was capped and transferred to a muffle furnace for pyrolysis at 300°C, 500°C and 700°C respectively for 6 h. After cooling to room temperature, the sample is taken out, ground and sieved through 100 meshes. The biochar derived from corn straw at 300°C, 500°C and 700°C respectively are obtained for adsorption experiments.

Adsorption experiments: 0.1 g of biochar powder was weighed into a 250 mL Erlenmeyer flask, and 100 mL of a copper nitrate solution containing a concentration of 20 mg/L was added. Then, the Erlenmeyer flask was placed in a constant temperature shaking box, and the adsorption experiment was carried out at the speed of 200 rpm at 25°C. The sample was determined with atomic absorption spectrophotometry.

Effect of contact time on the removal rate: Added 0.1 g of biochar powder into a 250 mL Erlenmeyer flask containing 100 mL of 10mg/L copper concentration, and placed in the incubator at 25 ℃ and 200 rpm. The contact time was 5, 10, 20, 40, 60, 90, 120, 180, 240 and 360 min, respectively. The sample was taken from the supernatant, placed in a centrifuge tube and centrifuged at 8000 r/min for 5 min. Then, it was measured with atomic absorption spectrophotometry.

Analytical methods: The particle microstructure of biochar was determined by Scanning Electron Microscopy (JEOL 6500F, Japan). The functional groups on the surface of biochar were determined by Fourier Transform Infrared Spectroscopy (Varian Scimitar 2000). The wavenumber was ranged from 400 to 4000 cm^{-1}. The concentration of Cu^{2+} ion in solution was analysed by atomic absorption spectrophotometry.

The removal rate of Cu^{2+} ions was calculated as following:

$$Q = \frac{C_0 - C_t}{C_0} \times 100\% \quad \ldots(1)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium concentrations of Cu^{2+} ions in solution respectively. Q (%) is the removal rate of Cu^{2+} ions.

The amount of adsorbed Cu^{2+} ion q_t (mg/g) at different time was calculated as following:

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad \ldots(2)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cu^{2+} ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Adsorption kinetics of copper in aqueous solution by biochar: To study the adsorption kinetics of copper in aqueous solution by biochar, pseudo first order kinetic equation (Lagergren 1898), pseudo second order kinetic equation (Ho & McKay 1999), Elovich model (McLintock 1967) and Weber-Morris intraparticle diffusion model (Jeon et al. 2003) are adopted in this research. Their fitting equations are Eqns.3 to Eqns. 6, respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \ldots(3)$$

Where, Q_t (mg/g) represents the amount of adsorption at time t. Q_e (mg/g) represents the amount of adsorption at the time of adsorption equilibrium. k_1 (min^{-1}) is the constant of pseudo first order kinetic equation.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad \ldots(4)$$

Where, Q_t (mg/g) represents the amount of adsorption at time t. Q_e (mg/g) represents the amount of adsorption at the time of adsorption equilibrium. k_2 (min^{-1}) is a constant of pseudo second order kinetic equation.

$$Q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t \quad \ldots(5)$$

Where, Q_t (mg/g) represents the amount of adsorption at time t. α (g/mg/min) and β (g/mg) are constant of Elovich model. They represent the initial adsorption rate constant and the desorption constant, respectively.

$$Q_t = k_{ip} t^{1/2} + C \quad \ldots(6)$$

Where, Q_t (mg/g) represents the amount of adsorption at time t. k_{ip} ($mg/g/min^{-0.5}$) and C is constant of Weber-Morris intraparticle diffusion model. C represents a biochar boundary layer.

RESULTS AND DISCUSSION

The characteristic of biochar: SEM images of biochar under a different carbonization temperature were determined by Scanning Electron Microscopy. The results are shown in Fig.1. It indicates that biochar derived from corn straw is a

fragmentary and porous structure. This structure is a benefit for adsorption of heavy metals by biochar. However, it also can be seen that this porous structure is destroyed as the carbonization temperature increases (Fig.1c). This change will affect its adsorption capacity of heavy metals.

The functional groups on the surface of biochar under a different carbonization temperature are determined by Fourier Transform Infrared Spectroscopy (Varian Scimitar 2000). The wavenumber is ranged from 400 to 4000 cm^{-1}. The results are shown in Fig. 2.

Fig. 2 suggests that a lot of functional groups appear on the prepared biochar under different carbonization temperatures. The numbers and intensity of functional groups increase as the carbonization temperature increases at the first stage. When carbonization temperature reaches 700°C, the numbers and intensity of functional groups decrease. The carbonization temperature of 500°C is optimum temperature. For biochar under 500°C, there is a strong adsorption peak in the range of 3398 cm^{-1}, which may be referred to the stretching vibration of a hydroxyl radical group. It indicates that a large number of oxygen-containing functional groups appear on the surface of biochar, such as carboxyl groups, hydroxyl groups, carbonyl groups and so on. The peak at 2015 cm^{-1} may correspond to stretching vibration of a carboxyl group. The peak at 1608 cm^{-1} may correspond to stretching vibration of the N-H group. The peaks at 1378 cm^{-1} and 1079 cm^{-1} may correspond to an aromatic group and C-O-C group respectively. The peaks at 620 cm^{-1}, 582 cm^{-1} and 428 cm^{-1} may correspond to C-H stretching functional group, -COO- bending vibration functional group and Si-O-Si functional group.

Adsorption capacity of Cu^{2+} ions by prepared biochar under different pyrolysis temperatures: 0.1 g of prepared biochar derived from corn straw under different pyrolysis temperatures is weighed into a 250 mL Erlenmeyer flask respectively, and 100 mL of a copper nitrate solution containing a concentration of 20 mg/L was added. Then, the Erlenmeyer flask was placed in a constant temperature shaking box, and the adsorption experiment was carried out at the speed of 200 rpm at 25°C. Samples were taken after 360 min for analysis. The adsorption rate of copper ions in solution by biochar under different temperatures is shown in Fig. 3.

It can be seen from the figure that when the pyrolysis temperature is between 300°C and 500°C, the adsorps tion capacity of copper ion in solution by biochar under different pyrolysis temperatures gradually increases as the pyrolysis temperature increases. It may be related to the adsorption mechanism of Cu^{2+} ions in solution by biochar under different pyrolysis temperature. With the increase of carbonization temperature, the adsorption mechanism of

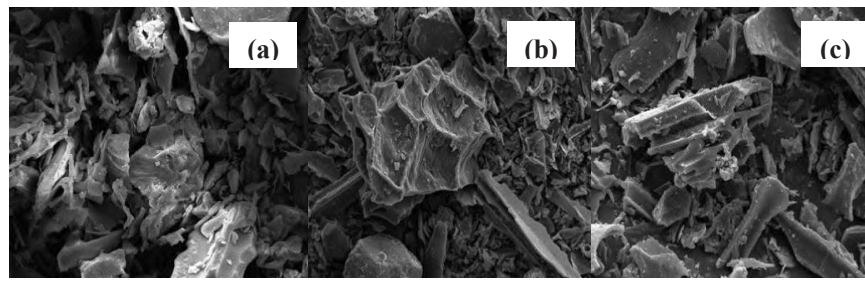

Fig.1: SEM images of biochar [300°C (a), 500°C (b) and 700°C (c)].

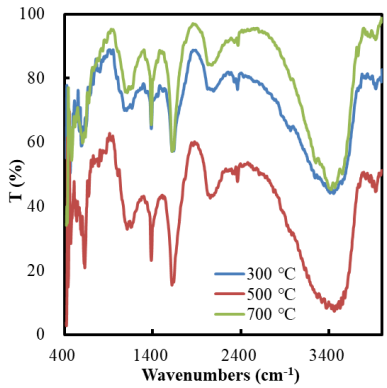

Fig. 2: FT-IR spectrum of biochars.

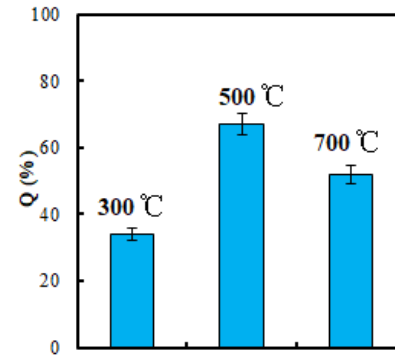

Fig. 3: Adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures.

Cu^{2+} ions in solution by biochar is from the distribution in the non-carbonized organic carbon component to the surface adsorption on the carbonized component. The types and density of surface functional groups of biochar prepared at different temperatures are different (Chen et al. 2008). For the biochar prepared at 700°C, the adsorption rate of Cu^{2+} ions in solution becomes low. It may be due to the effect of pore filling.

Effect of contact time on the removal rate: Effect of contact time on the removal rate of copper ions by biochar is shown in Fig. 4.

As shown in Fig. 4, it can be seen that the removal rate of copper ions by biochar increases quickly at the first stage of contact time. When contact time reaches 60 min, the removal rate of copper ions by biochar increases slowly. When contact time reaches 360 min, the removal rate of copper ions by biochar reaches equilibrium.

Adsorption kinetics of Cu^{2+} ion in aqueous solution by biochar: ***Pseudo first order kinetic equation*****:** According to the adsorption data and Eqn. 3, curves fitting by pseudo first order kinetic equation for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperature are shown in Fig. 5. The parameters of kinetic adsorption by biochar under different pyrolysis temperatures are listed in Table 1.

It can be seen from Fig. 5 and Table 1 that pseudo first order kinetic can well fit the adsorption process in the initial stage of adsorption. However, in the following stage of adsorption, it gradually deviates from the fitted pseudo first order kinetic equation. Therefore, this equation does not describe the entire adsorption process well of Cu^{2+} ion by biochar under different pyrolysis temperatures. It can be concluded that the adsorption process of Cu^{2+} ion by biochar under different pyrolysis temperatures is affected by many influencing factors.

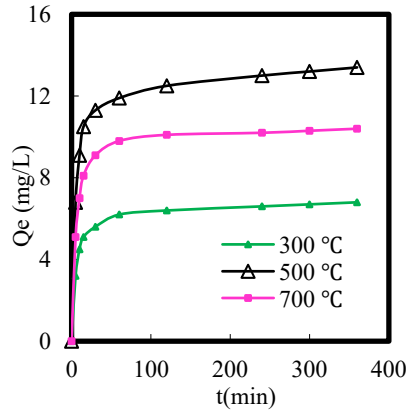

Fig. 4: Effect of contact time on the removal rate of copper ions by biochar.

Pseudo second order kinetic equation**:** According to the adsorption data and Eqn. 4, curves fitting by pseudo second order kinetic equation for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures are shown in Fig. 6 and Table 2.

It can be seen from Fig. 6 and Table 2 that the pseudo second order kinetic equation can better fit the entire stage of adsorption by biochar prepared under different temperatures. Comparing Table 1 and Table 2, it can be seen that the R^2 value of the pseudo first order kinetic equation is significantly higher than the R^2 value of the pseudo second order

Table 1: The parameters of pseudo first order kinetic adsorption by biochar under different pyrolysis temperatures.

Pyrolysis temperature (°C)	Q_e(mg/g)	k_1(min^{-1})	R^2
300	14.256	0.0115	0.8539
500	26.459	0.0112	0.8625
700	22.784	0.0128	0.8122

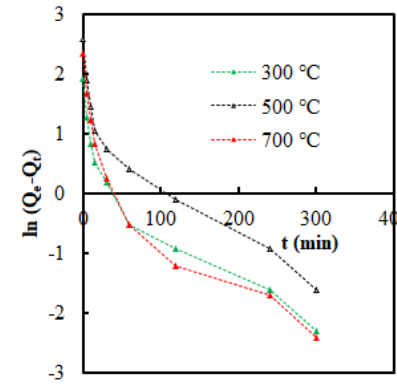

Fig. 5: Curves fitting by pseudo first order kinetic equation for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures.

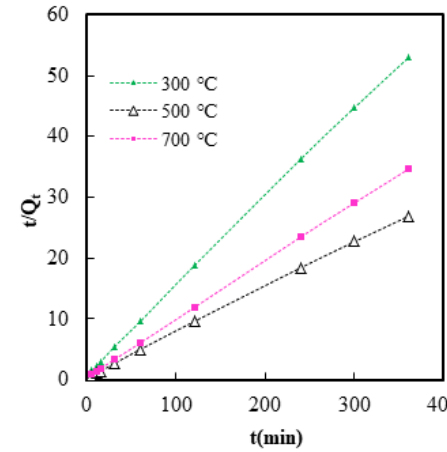

Fig. 6: Curves fitting by pseudo second order kinetic equation for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures.

Table 2: The parameters of pseudo second order kinetic adsorption by biochar under different pyrolysis temperatures.

Pyrolysis temperature (°C)	Q_e (mg/g)	k_2 (min^{-1})	R^2
300	14.912	0.00341	0.9998
500	27.681	0.00313	0.9997
700	23.124	0.00116	0.9998

kinetic equation. Therefore, the pseudo second order kinetic equation can better describe the whole process of adsorption by biochar prepared under different temperatures. The entire adsorption process includes a composite adsorption reaction of external liquid film diffusion, surface adsorption and intraparticle diffusion.

***Elovich model*:** Elovich model is a description of the heterogeneous diffusion process that is controlled by the reaction rate and diffusion factor. The process includes the diffusion of the solute at the bulk or interface of the solution, activation and deactivation of the surface, and so on. Curves fitting by Elovich model for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures are shown in Fig. 7. It can be seen that the adsorption process of Cu^{2+} ions in solution by biochar prepared under different temperature deviates from the equation.

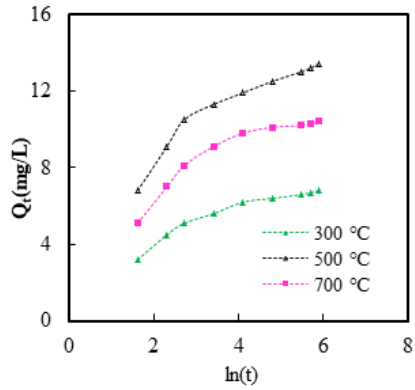

Fig. 7: Curves fitting by Elovich model for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperature.

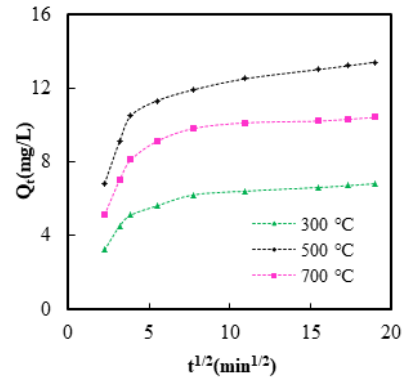

Fig. 8: Curves fitting by Weber-Morris intraparticle diffusion model for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperatures.

***Weber-Morris intraparticle diffusion model*:** Curves fitting by Weber-Morris intraparticle diffusion model for the adsorption of Cu^{2+} ions by biochar under different pyrolysis temperature are shown in Fig. 8. It can be seen from the figure that the initial stage of the adsorption curve shows an upward trend and then gradually goes to a horizontal state. It may be the reason that when the heavy metal ions diffuse into the interior of the adsorbent, the diffusion resistance gradually increases and leads to a decrease in the diffusion speed. It can be seen from the model that the diffusion in the particle during the control phase of removal rate is not the only influencing factor, but is controlled by both liquid diffusion and intraparticle diffusion.

CONCLUSIONS

According to the above experiment, it can be concluded that the adsorption capacity of Cu^{2+} ions in solution by biochar prepared at different temperatures is significantly different. The carbonization temperature of 500°C is optimum temperature. A lot of functional groups appear on the prepared biochar. It will affect its adsorption capacity of heavy metals. The contact time and the initial copper concentration both affect the adsorption capacity of Cu^{2+} ions by biochar. The pseudo second order kinetic equation can better describe the entire adsorption of Cu^{2+} ions in solution by biochar prepared under different temperatures. The adsorption process of Cu^{2+} ions by biochar is controlled by liquid diffusion and intraparticle diffusion.

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