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Study on Adsorption of Cd(II) in Water by Biochar Prepared from Coconut Shell

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ABSTRACT

In this paper, biochar was prepared from coconut shell. Adsorpton performance of biochar for Cd(II) was studied by the adsorption experiment under static state. Effect of biochar mass, Cd(II) inital concentration, adsorption time and pH on adsorption performance of biochar were investigated in detail. The results showed that the biochar had good adsorption performance for Cd(II). The optimal operation conditions were as follows: pyrolysis temperature was 600 ℃, biochar mass was 8 g/L, adsorption time was 9 h, initial concentration of Cd(II) was 80 mg/L, and pH values of the solution was 5, respectively. Under the above mentioned conditions, the adsorption capacity of biochar for Cd(II) in water reached the maximum value of 9.886 mg/g.

Keywords Biochar, Coconut Shell, Cd(II), Adsorption

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I. INTRODUCTION

In recent years, the large quantities discharge of heavy metal ion Cd(II) is mainly caused by the development of electroplating, mining and battery manufacturing industries[1]. Cd(II) is one of the most toxic heavy metal ions according to the World Health Organization, which can cause bone and kidney damage with excessive exposure[2-4]. Therefore, it is urgent to explore effective methods to treat Cd(II) in wastewater to prevent its harm to environment and human body. To date, the main treatment methods of cadmium wastewater include adsorption, membrane separation, ion exchange, iron oxide precipitation and biological removal technology, which display their own advantages and disadvantages in terms of operation cost, treatment cost and removal efficiency[5, 6].

Biochar is a carbon rich material produced by high-temperature pyrolysis of biomass in anoxic or anaerobic environment, which can reduce the biological effect of heavy metals through electrostatic adsorption, ion exchange, surface complexation and precipitation due to the characteristics of rich oxygen-containing functional groups, large specific surface area and well-developed pore structure. In view of the above advantages, biochar has been widely used in environmental remediation, industrial production, agricultural production and other fields[7]. To date, many scholars have used agricultural wastes such as wheat straw, rice straw, corn straw, peanut shell, bagasse, tea residue and orange peel to adsorb Cd(II) in water [8], which are a wide range of sources for the preparation of biochar.

Coconut peel, as one of the common by-products of coconut food processing industry, has been an ideal candidate of agricultural and forestry waste biomass resource in that low cost and rich quantity. However, only few examples of utilizing coconut shell as raw material for biochar preparation and studying adsorpton performance for heavy metals have been reported[9]. Therefore, in this paper, biochar was prepared derived from coconut shell and then adsorption performance of biochar to Cd(II) in water was further explored.

II. MATERIALS AND METHODS

2.1 Reagents and instruments

Doubly distilled water was used throughout the experiments. All the materials for synthesis were purchased from commercial suppliers and used without further purification. Coconut shell was collected from Wenchang city in Hainan Province of China. The amount of Cd(II) was obtained using inductively coupled plasma mass spectrometry (ICP-MS). The preparation of coconut shell biochar was obtained by Muffle Furnace and Program Temperature Controller.

2.1 Biochar preparation

After coconut shell was crushed and dried, it was wrapped with tin foil paper and added in a 100 mL crucible, and then placed in a Muffle Furnace.

The biochar was prepared by oxygen-limited temperature -programmed carbonization method. First, it was heated to 330 ^{o}C in a 30 min and kept at this temperature for 60 min, then continuously heated to 500 ^{o}C, 600 ^{o}C and 700 ^{o}C at a rate of 10 ^{o}C/min, and kept at every constant temperature for 150 min, respectively. After the thermolysis was completed, it was cooled to room temperature, and then was ground with a mortar and mixed. The samples were stored in dry flasks through a 100 mesh standard inspection sieve, labeled as B500, B600 and B700, respectively. The biochar yield can be obtained by Eq. (1).

$$R(\%) = \frac{M}{M_0} \times 100\% \quad (1)$$

where M represents the mass of coconut shell after pyrolysis (g) and M_0 represents the mass of coconut shell dried before pyrolysis (g).

2.3 Adsorption experiments

2.3.1 Effect of biochar amount on adsorption

The biochar B500, B600 and B700 in the proportion of 0.05, 0.1, 0.2, 0.3, 0.4 g were added to a 25 mL Cd(II) solution with an initial concentration of 80 mg/L, respectively. pH value was adjusted to 4 ± 0.1 using HCl or NaOH. Each centrifugal tube was vibrated at 30 ^{o}C in 300 r/min for 3 h, and then the mixed solution was filtered with 0.45 μm microporous filter membrane. The concentration of Cd(II) in filtrate was determined by ICP-MS for 3 times to obtain average value. The adsorption capacity and removal rate of the biochar for Cd(II) can be obtained by Eq.(2) and (3), respectively.

$$q = \frac{(C_0 - C_t)V}{1000W} \quad (2)$$

$$E = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (3)$$

where C_0 and C_t represent the starting and equilibrium consistence of Cd(II) (mg/L) in aqueous solution, V is the volume of Cd(II) solution, and W represents the amount of the biochar sample (mg).

2.3.2 Effect of differernt initial pH on adsorption

0.2 g of biochar B500, B600 and B700 were placed in centrifugal tube, and then added to a 25 mL Cd(II) solution with an initial concentration of 80 mg/L, respectively. pH value was adjusted to 3.0, 4.0, 5.0, 6.0, and 7.0 using HCl or NaOH. The other conditions were as same as experiment 2.3.1. Average value was obtained by three repeated experiments.

2.3.3 Effect of initial concentration of Cd(II) on adsorption

0.2 g of biochar B500, B600 and B700 were added to a 25 mL Cd(II) solution with a different initial concentrations of 20, 40, 60, 80, 100, and 120 mg/L, respectively. The other conditions were as same as experiment 2.3.1. Average value was obtained by three repeated experiments.

2.3.4 Effect of different time on adsorption

0.2 g of biochar B500, B600 and B700 was respectively added to a 25 mL Cd(II) solution with an initial concentration of 80 mg/L. The oscillation time was set as 0.5, 1, 2, 3, 5, 7, 9 and 11 h, respectively. The other conditions were as same as experiment 2.3.1. Average value was obtained by three repeated experiments.

III. RESULTS AND DISCUSSION

3.1 Influence of pyrolysis temperature on biochar yield

As shown in Table 1, the biochar yield of coconut shell droped with the increasing pyrolysis temperature. When the pyrolysis temperature increased from 500 ℃ to 700 ℃, the yield decreased from 36.38% to 30.62%. One reason may be that cellulose and lignin in coconut shell gradually decomposed to form ash due to temperature changes, which led to the decrease of biochar yield. These results displayed that the biochar yield of coconut shell was affected by pyrolysis temperature.

Table 1 Biochar yield of coconut shell

Temperature (℃)	500	600	700
Biochar yield (%)	36.38	32.10	30.62

3.2 Influence of the initial concentration of Cd(II) on adsorption capacity

The influence of biochar (B500, B600 and B700) on the adsorption capacity with different initial Cd(II) concentrations was displayed as Fig. 1. The adsorption capacity of biochar (B500, B600 and B700) for Cd(II) enhanced with the increase of the initial concentration of Cd(II) solution, and eventually tended to equilibrium when Cd(II) concentration was in the range of 80 mg/L.

The number of adsorption sites provided by biochar was certain under the condition of fixed biochar amount. In the low concentration range of Cd(II), most could interact with the adsorption sites on the surface of adsorbent. Therefore, along with the increase of Cd(II) concentration, the adsorption capacity of biochar enhanced gradually until it reached saturation, which would not change with the increasing Cd(II) concentration. As shown in Fig. 1, when the initial concentration of Cd(II) solution was 80 mg/L, the maximum adsorption capacity of biochar (B500, B600 and B700) for Cd(II) were 8.423 mg/g, 9.886 mg/g and 9.793 mg/g, respectively. Therefore, the adsorption capacity of biochar B600 on Cd(II) in water was optimal when the initial concentration of Cd(II) solution was 80 mg/L under the same conditions.

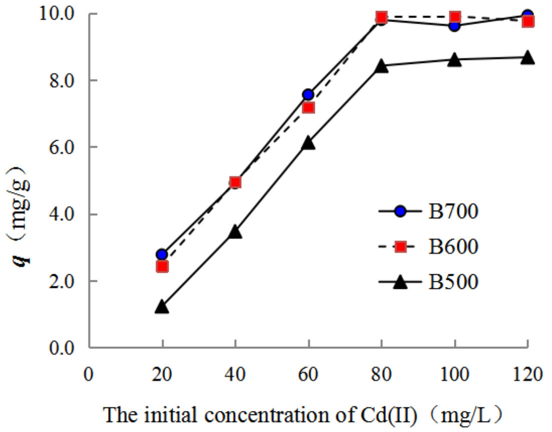

Fig. 1. Influence of the initial concentration of Cd(II) on adsorption capacity

3.3 Effect of time on adsorption capacity

Effect of time on the adsorption of Cd(II) onto biochar was measured as displayed in Fig. 2. It could be seen that the adsorption capacity (*q*) increased with the extension of adsorption time. All the adsorption process could be divided into two distinctive phases (t > 9 h and t < 9 h). Adsorption rate of Cd(II) was relatively fast for the first 9 h; then the amount of adsorbed Cd(II) onto biochar continued to increase slightly and reached their maximum values and adsorption equilibrium onto bitchar after 9 h.

At the beginning of adsorption, Cd(II) preferred to be adsorbed on the outer surface due to many free sites on the surface of biochar, and then entered the internal sites through the micropores of biochar. When the adsorption sites gradually reached saturation, the adsorption capacity tended to balance. From the Fig. 2, it could be seen that the order of biochar adsorption capacity for Cd(II) was B600 > B500 > B700 with increasing adsorption time, which depended on the speed of Cd(II) entering the internal point from the outside of biochar[10]. Therefore, under the same condations, the biochar B600 showed the best adsorption effect on Cd(II) within 9 h of adsorption time.

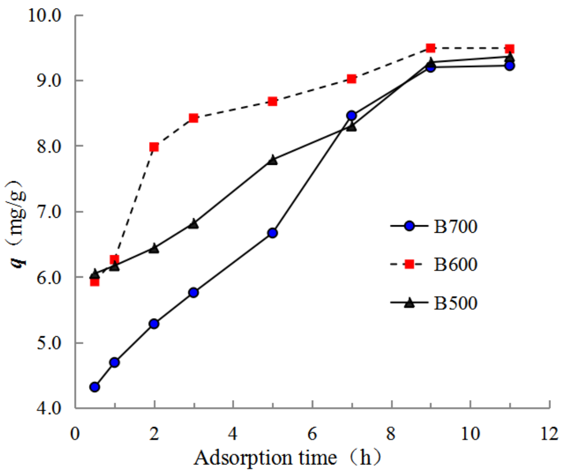

Fig. 2. Effect of adsorption time on removal of Cd(II) at different temperatures.

3.4 Influence of biochar amount on adsorption capacity and removal effect

Fig. 3 showed the effect of different biochar amount on the adsorption capacity of Cd(II). When the concentration of Cd(II) was itendical, the adsorption capacity increased in the range of biochar amount 2-8 g/L, which was optimal at 8 g/L of biochar amount. While biochar amount > 8 g/L, the adsorption capacity decreased remarkably. The reason was that the biochar amount was much enough to block the migration of Cd(II) to biochar, resulting in the decrease of adsorption capacity. Meanwhile, along to the increase of pyrolysis temperature, the biochar was more fully pyrolyzed and the specific surface area was expanded, which was conducive to the adsorption of Cd(II) in water, which was also supported by the removal rate of Cd(II) as depicted as Fig. 4. When the amount of biochar was 8 g/L, the corresponding removal rates were up to 96.1%, 98.2% and 97.1%, respectively. These results suggested that biochar B600 had the best adsorption effect on Cd(II).

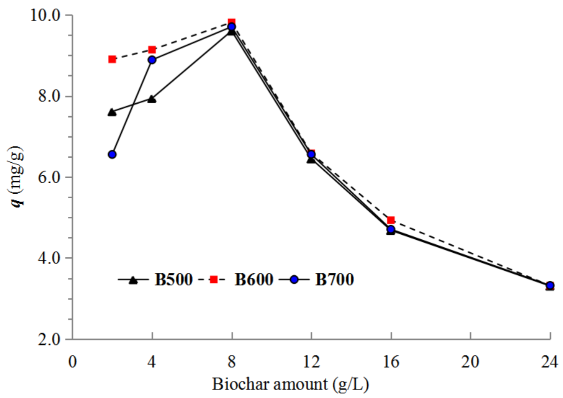

Fig. 3. Effect of biochar amount on the adsorption capacity of Cd(II)

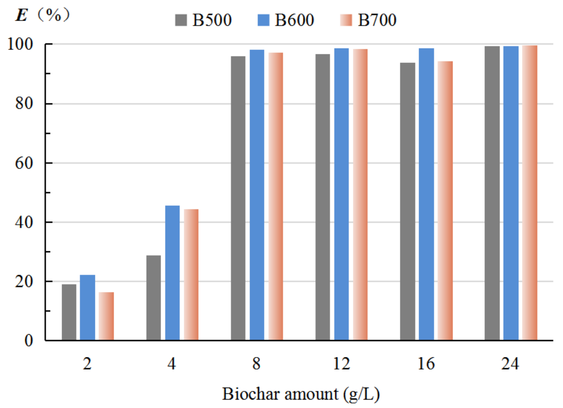

Fig. 4. Effect of biochar amount on the removal rate of Cd(II)

3.4 Influence of initial pH on adsorption capacity

The solution's pH was considered to be an important parameter in heavy metal adsorption, as the pH values can affect the speciation of metal ions and the surface properties of adsorbents. The adsorption capacities of Cd(II) increased with pH (pH 3–5), which reached a maximum at pH 5 as shown in Fig. 5, and then decreased while pH > 5.

In the case of low pH value, the biochar was surrounded by H^+, and the electrostatic repulsion limited the adsorption of Cd(II) onto the biochar surface. With the increase of pH, the oxygen-containing functional groups were gradually deprotonated, resulting in the weakening of the competitive adsorption capacity of H^+, and the adsorption capacity of biochar for Cd(II) was enhanced. When pH>5, the adsorption capacity of Cd(II) increased significantly and tended to be stable[11]. Therefore, pH=5 was selected as the best pHcondition for Cd(II) adsorption.

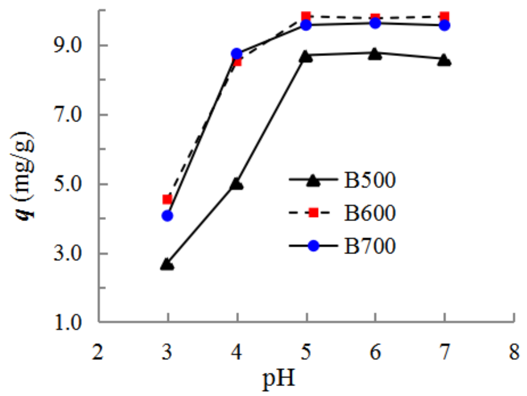

Fig .5. Effect of pH on the adsorption capacity of Cd(II)

IV. CONCLUSION

This study demonstrated that the adsorption behaviors of Cd(II) onto biochar under the different conditions were remarkably different. Further studies needed to focus on the influence of different coexisting metal ions, anions and mechanisms on biochar adsorption behaviors of these heavy metals. This study will provide a reference for the recycling and utilization of coconut shell for the treatment of heavy metals in wastewater.

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