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Pb^{2+} adsorption properties of pine biochar and soybean straw biochar

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ABSTRACT

In recent years, due to its excellent performance in adsorbing heavy metals in sewage, biochar has attracted more and more attention. This paper studied the adsorption properties and mechanism of pine wood and soybean straw, which were produced under different pyrolysis temperature of 400, 600, and 800 °C. The biochar was characterized by scanning electron microscopy, elemental composition analysis and BET surface analyzer. Six types of biochar were used for adsorption experiments with solutions containing Pb^{2+}, respectively. The influences of pyrolysis temperature, solution pH on the adsorption performance of biochar Pb^{2+} were discussed. The results show that, the specific surface area of pine wood biochar is significantly higher than that of soybean straw biochar. The internal functional groups of soybean straw biochar are abundant. With the increase of pyrolysis temperature, the C content, specific surface area, and the amount of alkali metal all rise. Meanwhile, the adsorption capacity of biochar to Pb^{2+} in the solution all increase. Under the same pyrolysis temperature, the adsorption capacity of soybean straw biochar is stronger than that of pine biochar. As pH increases, the adsorption capacity of pine wood and soybean straw biochar would be stronger, especially for pine wood biochar.

Keywords: Biochar; Pyrolysis temperature; Cation exchange

1. INTRODUCTION

Heavy metal pollution is an inevitable problem that endangers human health and ecological environment. Lead gets introduced to the aquatic environment by means of industrial activities such as tool processing, plastic production, ceramics, lead flash and cable recycling [1][2]. In order to treat water polluted by heavy metals, researchers have conducted many studies. At present, several mature methods, including physical methods and chemical methods, have been proposed to remove metals from aqueous solutions, such as ion-exchange, precipitation, evaporation, membrane separation, solvent extraction and electrochemical methods [3]. Adsorption is considered as an efficient and environmentally friendly method to treat heavy metal pollution in aqueous solution. Up to now, most studies on biochar have focused on untreated agricultural wastes, such as corn straw, rubber leaf and peanut shell [4][5]. Agricultural wastes such as corn stalks and rice husks have high carbon content and can be obtained through cultivation in a short time, making them suitable materials for production of biochar. Treating agricultural waste into biochar can not only obtain activated biochar with adsorption capacity, but also avoid pollution in the process of agricultural waste incineration.

There are five main mechanisms of biochar adsorption of heavy metals from aqueous solution, including complexation, cation exchange, precipitation, electrostatic interaction and reduction. The specific mechanism of metal adsorption by biochar varies with different target metals [6]. There are three main mechanisms of lead adsorption from aqueous solution by biochar: cation exchange, complexation and precipitation. Unlike complexation and precipitation, cation exchange contributes greatly to the whole adsorption process. When biochar is mixed with solution, lead ions in the aqueous solution exchange with $Ca^{2+}$and Mg^{2+} in the biochar to achieve the effect of absorbing lead from the aqueous solution [7]. The changes of molecular structure and surface morphology formed by

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biochar adsorption of heavy metals can be used to indicate the adsorption mechanism. However, the microstructure analysis of biomass charcoal is still at the qualitative level [8]. The application of biochar to industrial production needs further research. It is beneficial to promote the development of the application of biochar to study the adsorption mechanism and performance of different kinds of biochar for heavy metals.

In this study, biochar is prepared by pine and soybean straw at pyrolysis temperatures of 400, 600 and 800 °C. It is mixed with aqueous solution containing Pb^{2+} for adsorption experiment, and then the change of Pb^{2+} concentration is detected in aqueous solution by ICP-AES. The effects of pyrolysis temperature and solution pH on biochar adsorption capacity is analyzed. The influence of each cation on the adsorption process is investigated. It is expected to serve as reference for the treatment of heavy metals in sewage.

2. MATERIAL AND METHODS

2.1 Biochar production

Two common biomass, pine and soybean straw are selected as materials for producing biochar. Before biomass pyrolysis, the biomass materials are processed into powder and dried. A crucible containing biomass materials is placed in a glass tube in the resistance furnace. The pyrolysis temperatures are set at 400, 600 and 800 °C, respectively. The temperature rise rate of the resistance furnace is 10 °C·min^{-1}. Pyrolysis process is under oxygen-limited condition for 1 h achieved by continuous N_2 intake (200 mL·min^{-1}). The 6 groups of experimental samples are respectively defined as P400(pine biochar produced at 400 °C), P600(pine biochar produced at 600 °C) and P800(pine biochar produced at 800 °C). The same naming method is also used for soybean straw biochar, namely SS400, SS600 and SS800.

2.2 Adsorption experiment

The adsorption experiment is used to study the adsorption performance of various biochar to Pb^{2+} in solution. Biochar (0.1 g) is mixed with Pb^{2+} solution (25 ml) in a centrifuge tube on an oscillator. After mixing for a certain time, the supernatant from the mixture is separated and the residual Pb^{2+} concentration in solution is detected by ICP. By controlling different experimental variables (time, solution concentration, solution pH), the influence of various factors on the adsorption capacity of each biochar on Pb^{2+} in solution is explored. According to previous studies, the adsorption capacity of pine biochar and soybean straw biochar is obviously different. The influencing factors of this experiment include adsorption time, pyrolysis temperature and solution pH. The specific settings are as follows:

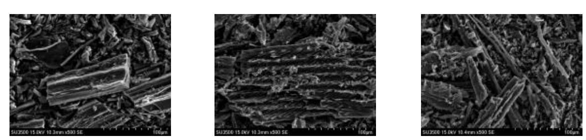
(1) Adsorption time. Different concentrations of Pb^{2+} solution is selected for different biochar. The concentration of Pb^{2+} solution mixed with pine biochar is 1 mmol·L^{-1}, and that of Pb^{2+} solution mixed with soybean straw biochar is 5 mmol·L-1. The concentration of Pb^{2+} is measured after 5min, 10min, 1 h, 2 h, 4 h, 6 h, 8 h, 12 h, 16 h and 24 h.

(2) Solution pH. P400 and SS400 are selected as research objects. The pH of PbNO3 solution is adjusted to about 2, 3, 5, 7 and 9 by using 0.1 mol·L^{-1} NaOH solution and 0.1 mol·L^{-1} HNO_3 solution. The adsorption capacity of Pb^{2+} by P400 and SS400 at different solution pH is measured.

3. RESULTS AND DISCUSSION

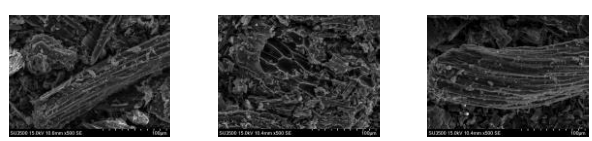
3.1 Physical and Chemical properties of Biochar

Table 1 shows that with the increase of pyrolysis temperature, the specific surface area and porosity of pine and soybean straw biochar increases in different degrees. Different from the trend of surface area and porosity, the average pore diameter decreased with the increase of pyrolysis temperature. Besides, the above six kinds of biochar are mesoporous (2~50 nm) materials. As pyrolysis temperature increases, the yield of pine and soybean straw biomass carbon decreases gradually. At the same temperature, the yield of pine is always less than that of soybean straw. Fig. 1 also illustrates that pine biochar has a larger specific surface area. The higher the specific surface area of biochar, the richer its pore structure, leading to the larger contact area between biochar and adsorbate in solution.



400 °C 600 °C 800 °

(a) SEM result of pine biochar(x500)



400 °C 600 °C 800 °C

(b) SEM results of soybean straw biochar(x500)

Fig. 1. SEM result of different biochar at different pyrolysis temperatures.

Table 2 indicates that the increase of temperature leading to the pH value of biochar increase. The pH value of biochar is alkaline, which is related to the content of K, Ca and other alkaline elements in biochar. The pH of biochar and the content of alkaline elements have the same trend with the pyrolysis temperature. At the same pyrolysis temperature, the pH of soybean straw biochar is higher than that of pine biochar.

Table 1 Specific surface area and yield of biochar at different pyrolysis temperatures

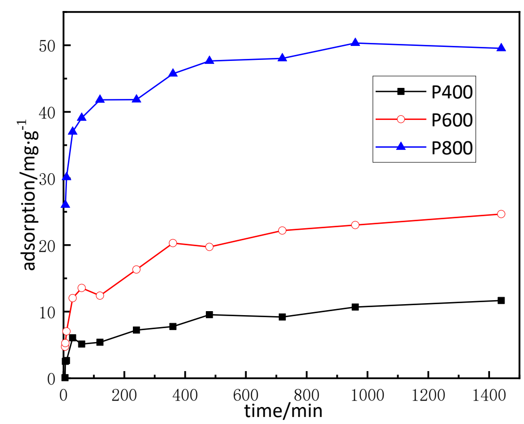
Biomass	Pyrolysis temperature/℃	Specific surface area/ $m^2 \cdot g^{-1}$	Porosity/ $cm^3 \cdot g^{-1}$	Average pore diameter/nm	Yield/%
Pine	400	53.84	0.035661	2.6493	23
	600	94.62	0.1807	1.755	18
	800	440.5	0.2003	1.8185	15
Soybean straw	400	5.59	0.009782	7.0057	27
	600	28.93	0.018413	2.5457	23
	800	86.33	0.049826	2.3085	21

Table 2 pH and elemental composition of 6 biochar

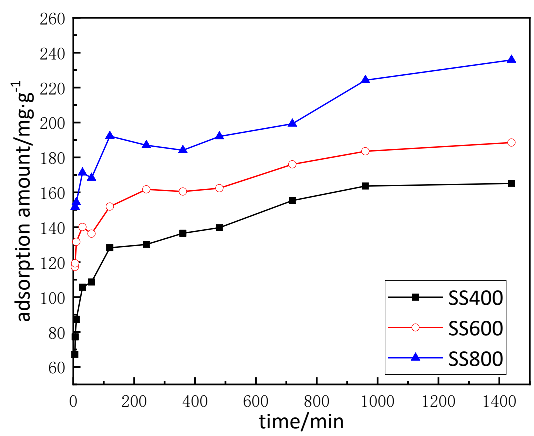
Biochar	Pyrolysis temperature/℃	pH	Na/%	K/%	Ca/%
Pine	400	7.45	-	0.046	0.039
	600	8.75	-	0.069	0.054
	800	10.02	0.0023	0.091	0.063
Soybean straw	400	10.40	0.0257	1.55	0.61
	600	10.50	0.0380	4.22	1.71
	800	10.62	0.0335	2.84	1.20

3.2 Factors affecting Adsorption capacity

The curves of adsorption amount of biochar produced by pine and soybean straws at different pyrolysis temperatures with time are plotted in Fig.2. The adsorption capacity of Pb^{2+} by biochar changes nonlinearly with the adsorption time. For example, after 24 hours of mixed adsorption, the adsorption capacity of P800 is close to 50 mg·g^{-1}, while that of P600 is nearly 25 mg·g^{-1}. Furthermore, the adsorption capacity of soybean straw biochar is obviously stronger than that of pine biochar, so the adsorption rate of Pb^{2+} by soybean straw biochar is higher than that of pine biochar at the same pyrolysis temperature. The adsorption rate of six kinds of biochar is fast in the early stage of mixing, and gradually slows down in the later stage. SS800 reach 60% of its adsorption limit after 5 minutes of mixed adsorption.



(a) Adsorption curve of pine biochar

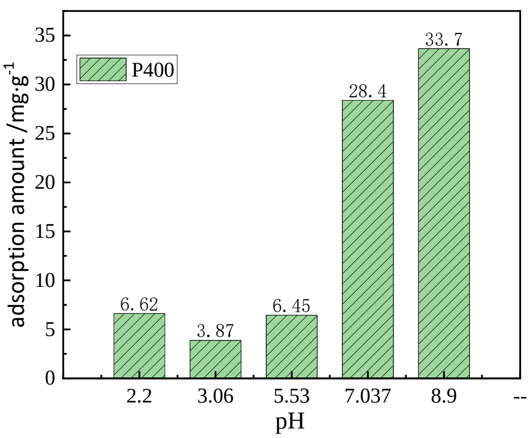


(b) Adsorption curve of soybean straw biochar

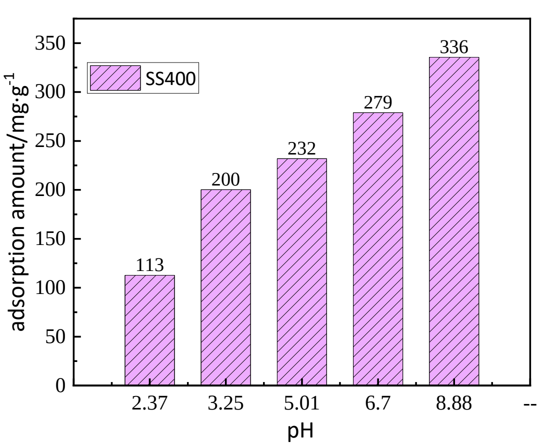
Fig. 2. The curve of adsorption capacity of biochar with time

The effect of high pyrolysis temperature on the adsorption performance of biochar is obvious, especially for pine biochar. Compared with P600, the Pb^{2+} adsorption capacity of P800 doubled. However, compared with P400, the adsorption capacity of P600 is not much improved, which has great guiding significance in practical application. The stronger the adsorption capacity, the later the biochar reaches the adsorption equilibrium.

Fig.3 represents that with the increase of solution pH, the adsorption capacity of Pb^{2+} in solution by P400 and SS400 shows an upward trend. Alkaline environment is beneficial to the adsorption of Pb^{2+} by pine biochar and Soybean straw biochar. In acidic environment, the adsorption capacity of P400 is always lower than 7 $mg \cdot g^{-1}$. When pH is 8.9, the adsorption capacity of P400 reaches 33.7 $mg \cdot g^{-1}$, which is about five times that of pH 5.53 (6.45 $mg \cdot g^{-1}$). When the solution pH is 3.06, the adsorption capacity of P400 is the weakest, which is about 1/10 of that when the solution Ph is 8.9. For SS400, when the solution pH is 2.73, the adsorption capacity is 113 $mg \cdot g^{-1}$. With the increased of pH, the adsorption capacity of SS400 increases steadily (336$mg \cdot g^{-1}$ pH=8.88). In addition, this phenomenon is more obvious in P400 adsorption experiments.



(a) Adsorption amount of P400



(b) Adsorption amount of SS400

Fig. 3. Biochar adsorption capacity of different solution pH

3.3 Cation exchange analysis

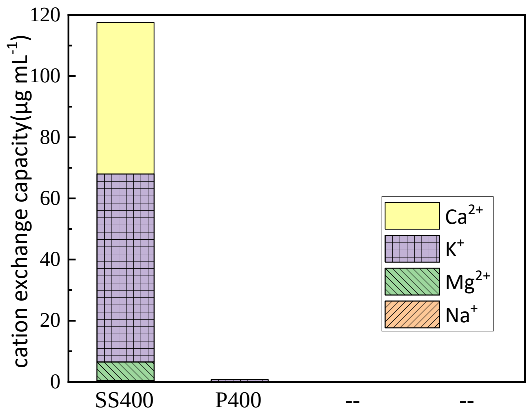


Fig. 4. The contribution of each cation to cation exchange in the adsorption process

The cation exchange capacity of SS400 is larger than that of P400. The adsorption amount of SS400 in 25 mL is 819.9 $\mu g \cdot mL^{-1}$, while that of P400 in 25 mL is 63.8 $\mu g \cdot mL^{-1}$. When SS400 adsorbs Pb^{2+} in solution, the order of contribution of ions in cation exchange is K^+> Ca^{2+}> Mg^{2+}> Na^+. Besides, the order for P400 is K^+> Na^+> Ca^{2+}> $Mg2^+$, in which the exchange amount of Mg^{2+} is almost zero. The contribution of cation exchange to Pb adsorption of pine wood is small.

4. CONCLUSIONS

(1) The increase of pyrolysis temperature result in the content of C and alkaline elements such as K and Ca in biochar increasing. Moreover, when the pyrolysis temperature increasing, the specific surface area and porosity of biochar increase. While the average pore diameter decreased (2.6493 nm at 400°C to 1.8185 nm at 800°C).

(2) At the same pyrolysis temperature, the adsorption capacity of soybean straw biochar to Pb^{2+} is stronger than pine biochar (50 $mg \cdot g^{-1}$ P800 vs. 231 $mg \cdot g^{-1}$). The adsorption capacity of Pb^{2+} in solution of biochar produced by the same biomass increases nonlinearly with the increase of pyrolysis temperature. In addition, alkaline environment is favorable for Pb^{2+} adsorption of biochar. This phenomenon is more obvious in the adsorption experiment of pine biochar (6.62 $mg \cdot g^{-1}$ at pH2.2 vs. 33.7 $mg \cdot g^{-1}$ at pH8.9).

(3) When biochar adsorbs Pb^{2+} in solution, cation exchange contributes a lot. The order of contribution of

ions in cation exchange is K^+> Ca^{2+}> Mg^{2+}> Na^+(Soybean straw), K^+> Na^+> Ca^{2+}> $Mg2^+$ (pine biochar).

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