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Study on the Adsorption Performance of Cu^{2+}, Cd^{2+} and Pb^{2+} in Water using Biochar from Black Fungus Bran

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Abstract: In order to investigate the adsorption performance of black fungus bran biochar on Cu^{2+}, Cd^{2+} and Pb^{2+} in water, waste black fungus bran was used as raw material to prepare black fungus bran biochar by oxygen-limited pyrolysis at 350℃, 550℃ and 750℃, then the adsorption experiments were conducted at different pH, reaction time and initial concentration. Thus, the adsorption performance of Cu^{2+}, Cd^{2+} and Pb^{2+} was investigated by different pH, reaction time and initial concentration.

Keywords: Black fungus bran; Biochar; Adsorption

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1. Introduction

Auricularia auricular also known as wood fungus, light fungus, fine fungus, wood moth, and wood mushroom, is a traditional bulk edible species and the second most grown edible fungus in China, resulting in a large amount of black fungus bran every year [1]. Black fungus bran is mainly composed of the remaining nutrient part of the planted sticks and the mycelium of black fungus, which contains more cellulose, hemicellulose, lignin and many other elements [2].

The current research on mushroom bran is mainly in crop-based fertilizers and animal feeds, while the research on the nature and utilization of biochar after making it, especially as an adsorbent, is still in its initial stage [3]. Using mushroom bran as a raw material, it can be prepared directly by high-temperature cracking into the desired biochar, which can be used to treat heavy metal polluted water bodies as one of the effective ways for its resource utilization, at the same time, it can reduce the impact on the environment, which has important practical significance [4,5].

In this study, black fungus bran biochar was prepared by oxygen-limited pyrolysis at 350℃, 550℃ and 750℃ using black fungus bran as raw material. Its adsorption performance on Cu^{2+}, Cd^{2+} and Pb^{2+} was investigated by adsorption experiments to provide some reference for the use of black fungus bran waste in the remediation of heavy metal pollution in wastewater and soil.

2. Materials and Methods

2.1. Preparation of black fungus bran biochar

The black fungus bran was provided by the center of food and medicinal mushroom of Shaanxi Province

Main Laboratory of Resource Biology, and the main components were miscellaneous wood chips, bran, soybean flour and etc. The bran was dried in an oven at 80℃, crushed and passed through 35 mesh sieve, and packed into a porcelain crucible for compaction, then placed in a muffle furnace and pyrolyzed at 350℃, 550℃ and 750℃ for 2.5 hours (h) using oxygen-limited pyrolysis method, respectively. Following that, taken out after the samples were naturally cooled to room temperature, dried in an oven at 80℃, ground and passed through 100 mesh sieve, and transferred into a plastic bag and kept in a desiccator for backup. The samples were named as HME350, HME550 and HME750 according to the production temperature.

2.2. Characterization of biochar

Weighed 1g of sample and add it in 10mL of water (solid-liquid ratio of 1:10) and shake it for 30min and then use a pH meter to determine the pH value of the sample; the yield of biochar was the mass ratio before and after preparation; the sample was heated in a muffle furnace at 800℃ for 2h and the ash content was calculated according to the mass ratio before and after heating.

2.3. Adsorption experiment

Cu^{2+}, Cd^{2+} and Pb^{2+} solutions were prepared with different concentrations of copper nitrate, cadmium nitrate and lead nitrate, 0.01 $mol \cdot L^{-1}$ $NaNO_3$ was used as the electrolyte, and the pH of the solution was adjusted with 0.1 $mol \cdot L^{-1}$ HNO_3 and 0.1 $mol \cdot L^{-1}$ NaOH. The solution was prepared at a solid-liquid ratio of 1 $g \cdot L^{-1}$ (30 mg biochar to 30 mL Cu^{2+}, Cd^{2+} and Pb^{2+} solution), a certain amount and concentration of Cu^{2+}, Cd^{2+} and Pb^{2+} solution was added into the pre-weighed polyethylene tube of biochar, and the batch adsorption experiments were carried out by shaking in a constant temperature shaker (200 r/min, 25℃). All samples were set up three times in parallel, and after the adsorption was completed, the supernatant was taken over a 0.22 μm filter membrane and the concentrations of Cu^{2+}, Cd^{2+} and Pb^{2+} in the filtrate were determined using inductively coupled plasma emission spectrometry (ICP-OES) to calculate the adsorption amounts of Cu^{2+}, Cd^{2+} and Pb^{2+} using biochar [6].

The adsorption amount Qt was used to measure the adsorption effect of black fungus bran biochar on Cu^{2+}, Cd^{2+} and Pb^{2+} with the formula: Qt=(Ci-Ct)V/m, Qt is the adsorption amount at moment t ($mg \cdot g^{-1}$); Ci is the initial concentration of heavy metal ions in the solution ($mg \cdot g^{-1}$), Ct is the concentration of heavy metal ions in the solution at moment t ($mol \cdot L^{-1}$); V is the volume of the heavy metal solution added (mL); m is the mass of the adsorbent added (mg).

2.3.1. Effect of pH on the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} using biochar

Dilute Cu^{2+}, Cd^{2+} and Pb^{2+} stock solutions to 40 $mol \cdot L^{-1}$, respectively, and adjust the pH of the solutions to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0; weigh 0.05 g of HME350, HME550 and HME750 in 50mL centrifuge tubes, respectively, and add 50mL of the adjusted solutions, shake well, put them into Shake the shaker and shake for 2h respectively.

2.3.2. The effect of reaction time on the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} using biochar

The Cu^{2+}, Cd^{2+} and Pb^{2+} stock solutions were diluted to 40 $mol \cdot L^{-1}$ and the pH value to 5.5, respectively; 0.05g of HME350, HME550 and HME750 were weighed and placed in 50mL centrifuge tubes, and 50mL of the adjusted solutions were added, shaken well, put into a shaker and shaken for 30min, 60min, 90min, 120min, 180min and 240min, respectively 120min, 180min, 240min, 360min.

2.3.3. The effect of initial concentration on the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} using biochar

The Cu^{2+}, Cd^{2+} and Pb^{2+} stock solutions were diluted to 20$mg \cdot L^{-1}$, 30$mg \cdot L^{-1}$, 40$mg \cdot L^{-1}$, 50$mg \cdot L^{-1}$ and 60$mg \cdot L^{-1}$, respectively. Then, the pH value of the solutions was adjusted to 5.5; 0.05g of HME350, HME550 and HME750 were weighed and placed in 50mL centrifuge tubes, and 50mL of the adjusted solutions were added, respectively. The adjusted solutions were shaken well, placed in a shaker, and shaken for 2h respectively.

3. Results and Discussion

3.1. Basic properties of black fungus bran biochar

Many studies have shown that the main reason for the alkaline appearance of biochar may be due to the highly conjugated aromatic structure on the surface. Besides that, some studies have also found that with the increase of pyrolysis temperature, the acidic substances in biochar will gradually volatilize and some weak acid salts will gradually fuse to form alkaline substances, which eventually cause the biochar to be alkaline [7]. As shown in **Table 1.**, with the increase of pyrolysis temperature, the yield of bacterium bran biochar gradually decreases, and the ash content as well as pH value increase significantly, also the high proportion of inorganic components in the ash composition, which volatilize little during the pyrolysis process, makes the ash content increase with the increase of pyrolysis temperature, thus the biochar at the pyrolysis temperature are all alkaline.

Table 1. Basic properties of spent mushroom substrate biochar

Samples	Yield (%)	pH	Ash (%)
HME350	50.16	8.99	20.44
HME350	43.82	9.26	24.48
HME350	29.42	10.96	26.33

3.2. Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different pH

Solution pH affects the surface charge of biochar, the morphology of the presence of metal ions, and consequently the ability of biochar to adsorb heavy metals [8]. To evaluate the effect of solution pH on the ability of biochar to adsorb Cu^{2+}, Cd^{2+} and Pb^{2+}, a pH range of 2.0-7.0 was selected for the experiments. The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different pHs is shown in **Table 2.**, and the results indicate that the adsorption of all three biochars gradually increased with the increase in solution pH, but the adsorption increased slowly with pH > 6.

Table 2. Effect of different initial pH on Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by three kinds of biochar

Heavy metal	Biochar	Effect of different initial pH on adsorption Q_t/(mg·g^{-1})						
		2	3	4	5	6	7	8
Cu^{2+}	HME350	0.12	2.24	10.25	18.24	22.38	23.58	23.62
	HME550	0.21	2.68	12.65	20.27	26.87	28.22	29.33
	HME750	0.25	3.22	16.33	26.89	32.55	33.25	34.21
Cd^{2+}	HME350	1.22	5.88	15.26	22.63	23.66	24.11	24.25
	HME550	1.26	6.78	18.32	24.68	26.33	27.22	28.11
	HME750	2.31	9.22	19.22	25.33	28.25	29.05	29.09
Pb^{2+}	HME350	2.52	5.63	12.62	14.88	15.96	16.96	19.22
	HME550	3.65	6.36	13.88	15.68	16.87	18.22	20.33
	HME750	0.26	10.25	19.26	25.63	26.33	27.65	29.22

3.3. Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different reaction times

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different reaction times is shown in **Table 3.**, and the results indicate that the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} presents rapid adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} within 120 min. Due to the large concentration of Cu^{2+}, Cd^{2+} and Pb^{2+} at the early stage of adsorption, the biochar can provide more surface adsorption sites, and the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by the biochar increases slowly at the later stage, and as the surface adsorption sites reach saturation, Cu^{2+}, Cd^{2+}

and Pb^{2+}

begin to gradually diffuse into the carbon pores and react with the active sites on the internal surface [9].

Table 3. Effect of different reaction time on Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by three kinds of biochar

Heavy metal	Biochar	Effect of different reaction time on adsorption $Q_{t/}(mg·g^{-1})$						
		30min	60min	90min	120min	180min	240min	360min
Cu^{2+}	HME350	2.51	4.68	15.26	24.22	25.22	26.22	26.32
	HME550	3.22	6.98	16.35	28.33	28.22	28.45	28.66
	HME750	4.25	8.36	18.22	33.21	33.65	33.88	34.05
Cd^{2+}	HME350	2.25	4.55	20.36	25.36	25.66	25.98	25.26
	HME550	3.66	6.63	19.63	26.33	26.98	26.58	26.88
	HME750	3.98	8.66	20.36	30.21	30.22	30.28	30.85
Pb^{2+}	HME350	3.25	6.35	14.65	18.32	18.66	18.98	19.06
	HME550	3.22	6.25	16.33	21.25	21.22	21.65	21.65
	HME750	1.25	8.55	22.36	29.65	29.88	30.22	30.65

3.4. Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different initial concentrations

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in solution at different initial concentrations is shown in **Table 4.**, and the results indicate that when the concentrations of Cu^{2+}, Cd^{2+} and Pb^{2+} are low, the adsorption increases rapidly with the increase of equilibrium mass concentration, and with the increase of the initial concentration of ions, Cu^{2+}, Cd^{2+} and Pb^{2+} are more easily contacted with the surface of biochar, which is beneficial to the active sites and surface functional groups on the adsorbent. Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+}, when reaching $50mg·L^{-1}$, the biochar remained basically unchanged for Cu^{2+}, Cd^{2+} and Pb^{2+}. Since the contact area and active sites provided by biochar are quantitative, the concentration increases to a certain level, the adsorption sites are fully utilized and the adsorption eventually reaches saturation [10].

Table 4. Effect of different Initial concentration on Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by three kinds of biochars

Heavy metal	**Biochar**	**Effect of different Initial concentration on adsorption $Q_{t/}(mg·g^{-1})$**						
		$10mg·L^{-1}$	**$20mg·L^{-1}$**	**$30mg·L^{-1}$**	**$40mg·L^{-1}$**	**$50mg·L^{-1}$**	**$60mg·L^{-1}$**	**$70mg·L^{-1}$**
Cu^{2+}	HME350	1.22	2.62	8.26	16.25	23.66	23.88	23.92
	HME550	1.25	2.99	10.26	17.88	28.96	28.99	29.05
	HME750	2.14	3.12	15.24	23.68	33.52	33.68	34.05
Cd^{2+}	HME350	1.08	5.88	14.29	22.66	25.36	25.88	25.98
	HME550	1.28	6.88	17.69	25.66	28.26	28.67	28.96
	HME750	2.55	8.96	20.33	26.99	28.63	29.15	29.85
	HME350	2.62	4.26	13.25	15.26	18.62	18.74	19.09
Pb^{2+}	HME550	3.66	7.09	14.26	16.04	19.88	20.06	20.33
	HME750	0.34	9.63	20.34	25.62	28.96	28.99	29.42

4. Conclusion

Pyrolysis temperature is an important factor affecting the physicochemical properties of biochar. With the increase of pyrolysis temperature, the yield of biochar decreased and the pH and ash content rose strongly.

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by the three black fungus bran biochars gradually increased with the increase of solution pH, but the adsorption amount increased slowly with pH>6. The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} showed rapid adsorption within 120 min, due to the concentration of Cu^{2+}, Cd^{2+} and Pb^{2+} at the early stage of adsorption The adsorption amount of Cu^{2+}, Cd^{2+} and Pb^{2+} increased slowly in the later stage; when the concentration of Cu^{2+}, Cd^{2+} and Pb^{2+} was low, the adsorption amount increased rapidly with the increase of equilibrium mass concentration, and with the increase of the initial concentration of ions, Cu^{2+}, Cd^{2+} and Pb^{2+} were more easily contacted with the surface of biochar, which was beneficial to the adsorbent on the active sites and surface functional groups of Cu^{2+}, Cd^{2+} and Pb^{2+} were adsorbed, and when it reached 50mg·L^{-1}, the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by biochar was basically unchanged.

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by using bacterium bran biochar can provide corresponding reference for the treatment of industrial wastewater and domestic wastewater.

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Disclosure statement

The author declares no conflict of interest.

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