International Journal of Environmental Protection and Policy
2022; 10(3): 67-72
http://www.sciencepublishinggroup.com/j/ijepp
doi: 10.11648/j.ijepp.20221003.14
ISSN: 2330-7528 (Print); ISSN: 2330-7536 (Online)

Adsorption Performance of Two Kinds of Biochar for Cd^{2+} in Water

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To cite this article:

Ye Jinsha, Luo Xin, Liu Ruisen. Adsorption Performance of Two Kinds of Biochar for Cd^{2+} in Water. *International Journal of Environmental Protection and Policy*. Vol. 10, No. 3, 2022, pp. 67-72. doi: 10.11648/j.ijepp.20221003.14

Received: May 4, 2022; **Accepted**: May 31, 2022; **Published**: June 1, 2022

Abstract: Cadmium is one of the most widely distributed and toxic pollutants in nature, and the remediation of Cd pollution is still a difficult and serious task. In this paper, the biochar derived from walnut shells and sunflower seed shells were prepared at 700°C. The two kinds of biochar were characterized by SEM and FTIR, and the effects of pH, adsorption time, initial concentration on the adsorption of Cd^{2+} in aqueous solution were investigated. The adsorption kinetics were studied and the experimental data was also fitted with the isotherm equilibrium models. The results showed that the adsorption amount of Cd^{2+} increased with the pH when the solution pH was between 2 and 7. The maximum adsorption amount of Cd in water was up to 12.94 $mg \cdot g^{-1}$ and 21.11 $mg \cdot g^{-1}$ for BWS and BSS. The adsorption kinetics of Cd^{2+} on the BWS and BSS followed pseudo-second-order kinetics. The Langmuir adsorption isotherm was used to describe the adsorption equilibrium process isotherms. Thermodynamic studies showed that the adsorption reaction was spontaneous, endothermic and entropy increasing. The analysis of microstructural characteristics indicated that complexation and ion exchange are the main mechanisms of cadmium adsorption on the two kinds of biochar. And the surface of the BSS contained a large number of functional groups. Compared with the BSS exhibited better Cd^{2+} adsorption capacity. The results of this research are important for the resourceful use of waste and the purification of heavy metals in water.

Keywords: Biochar, Walnut Shell, Sunflower Seed Shell, Cd^{2+}, Adsorption

1. Introduction

Cd^{2+} is a toxic ion produced by battery manufacturing, metallurgy, mining and metal plating industries, which is highly soluble and persistent in water and easily enriched in the food chain [1]. According to the 2014 China Soil Survey Bulletin, the exceedance rate of soil cadmium contamination reached 7.00% [2]. Long-term exposure to Cd^{2+} can cause acute or chronic diseases of the liver, kidneys, nervous and cardiovascular systems, and contaminated water sources used for drinking and irrigating food crops pose a serious threat to the general public, so cadmium is considered one of the most toxic heavy metal ions [3]. There are several methods to remove Cd^{2+} from water, such as ion exchange, chemical precipitation, membrane filtration, solvent extraction, electrochemical treatment, and adsorption. Among them, the adsorption method has received much attention for its high efficiency, low cost and simple operation, while the selection and preparation of energy-efficient adsorption materials has been one of the research hotspots in the field of environmental remediation.

Commonly used adsorbent materials include activated carbon, lignin, diatomaceous earth, zeolite chitosan, and fly ash [4]. In recent years, the application of biomass materials in pollution remediation has received increasing attention. Biochar is a non-homogeneous carbon-containing material produced by pyrolysis of biomass under oxygen-limited conditions. Due to its good physical and chemical surface properties, it can be used as an adsorbent to remove pollutants from water [5]. The biochar has high porosity and larger specific surface area, and the surface contains carboxyl groups, hydroxyl groups and other oxygen-containing functional groups, which helps the adsorption of heavy metal

ions in water [6]. At the same time, its unique properties such as low cost and high stability make biochar a great potential absorbent in the field of removing pollutants from wastewater. Biochar can be produced from a variety of organic raw materials such as agricultural waste, livestock manure, and urban sludge. The biomass feedstock type is an important factor that affect the physicochemical properties and adsorption performance of biochar [7]. Shen X C compared the rice straw biochar with the wheat straw biochar, and found that the raw material had a large influence on the properties of biochar and the adsorption performance on Cd [8].

In 2017, the production of sunflower seeds in China was about 3.2 million tons, and walnut production is expected to reach 3 million tons in 2020 [9, 10]. Most walnut shells and sunflower seeds shells are discarded or burned, resulting in waste of resources and environmental pollution. Therefore, in this study, two kinds of biochar were prepared from walnut shells and sunflower seed shells. The two kinds of biochar were used for adsorption of Cd^{2+} in water to study the adsorption performance and the adsorption mechanism on Cd^{2+}.

2. Materials and Methods

2.1. Materials

The walnut shells and sunflower seed shells were produced from Chifeng, Inner Mongolia, China. All the chemical reagents in this work are analytically pure and purchased from Tianjin Yongda Chemical Reagent Co, including cadmium nitrate, nitric acid, sodium hydroxide.

2.2. Preparation of Samples

The walnut shells and sunflower seed shells were washed with deionized water, air-dried and crushed through 40 mesh sieve. The sieved biomass material was put into a quartz tube, placed in a tube furnace and heated up to 700°C at a rate of 8°C·min^{-1} in a nitrogen atmosphere, pyrolyzed at a constant temperature for 2 h. After cooling, the material was removed, ground and passed through 80 mesh sieve to produce walnut shell biochar and sunflower seed shells biochar, which were recorded as BWS and BSS.

2.3. Analysis Methods

Biochar was prepared in a muffle furnace (MFL-3664, Changchun Protactinium Technology Co) and tube type high temperature electric furnace (DC-R5/11, Beijing Ducron Technology Co). Cadmium ion concentration was determined by an atomic absorption spectrophotometer (GGX-600, Beijing Haiguang Instruments Co) and pH was measured by an acidity meter (PHS-3C, Shanghai Magnetics Instruments Co). The apparent morphologies of biochar were characterized by a scanning electron microscope (JSM-7500F, Nippon Electron Co), and the types and amounts of functional groups of biochar materials were analyzed by a Fourier infrared spectrometer (Nicolet IS5, Shanghai Thermo Fisher Scientific (China) Co).

2.4. Adsorption Studies

Cd^{2+} solution was prepared by dissolving cadmium nitrate in deionized water. The pH of the solution was adjusted by adding 0.1 mol·L^{-1} HNO_3 or 0.1 mol·L^{-1} NaOH. The 100 mL of Cd^{2+} solution was placed in a conical flask and 1 g·L^{-1} of biochar was added, shaken at 160 r·min^{-1} for a period of time and filtered through a 0.45 μm filter membrane, and the mass concentration of Cd^{2+} in the filtrate was determined by atomic absorption spectrophotometer (analytical wavelength of 228.8 nm).

3. Results and Discussions

3.1. Biochar Characterization

3.1.1. SEM Analysis

The scanning electron microscopy of BWS and BSS are shown in Figure 1. As can be seen from Figure 1, BSS has a laminar structure with a smooth and dense surface and an undeveloped pore structure. BWS has a massive structure with more fine particles scattered on the surface and pores of varying sizes. The formation of pores in biochar is related to the decomposition of cellulose in the raw material [11]. Sunflower seed shells have a high crystallinity of cellulose [12], which is not easily decomposed during pyrolysis. Walnut shells have more volatile components [13], and the overflow of volatile components in the pyrolysis process will form more pores, thus BWS has a larger specific surface area.

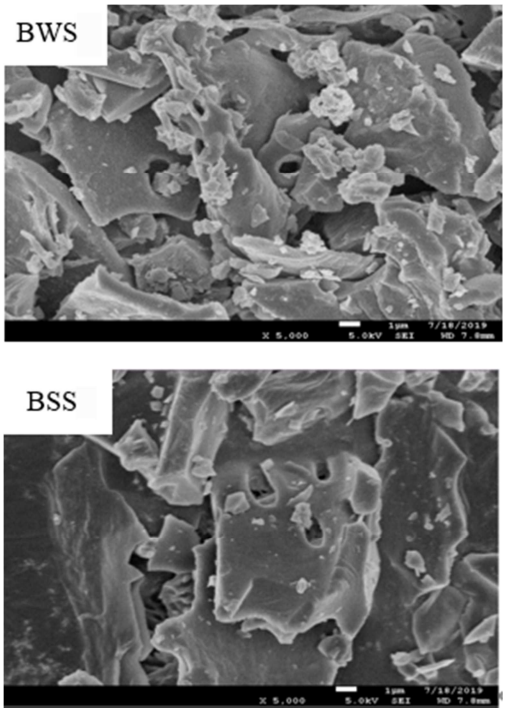

Figure 1. *Scanning electron micrograph of BWS and BSS.*

3.1.2. FTIR Analysis

The FTIR spectra of BWS and BSS is shown in Figure 2. O-H stretching vibration peaks at 3552 cm^{-1}, 3476 cm^{-1}, 3411 cm^{-1}; C=O stretching vibration peak at 1633 cm^{-1}; Aromatic ring C=C stretching vibration peak at 1617 cm^{-1}; C-OH

out-of-plane bending vibration absorption peak at 620 cm^{-1}. The corresponding absorption peak at 550 cm^{-1} is generated by the vibration of pyridine, furan and other heterocycles;

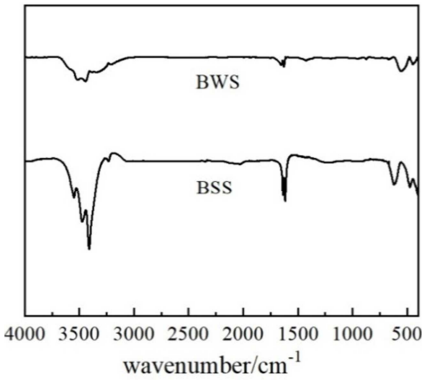

Figure 2. *FTIR plot of BWS and BSS.*

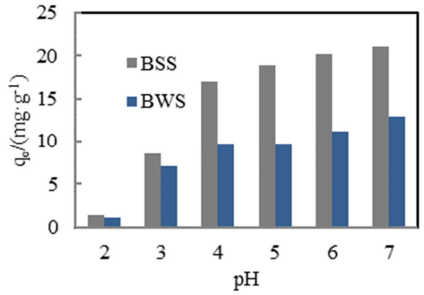

Figure 3. *Effect of solution pH on the adsorption of Cd^{2+} by BWS and BSS.*

And the stretching vibration peak of Si-O-Si at 470 cm^{-1}. The heavy metal ions can complex with functional groups such as carboxyl, hydroxyl and Si-O-Si [14], and ligand with π-bonds (C=C) [15]. As seen in Figure 2, the vibrational intensity of the BSS absorption peak is significantly higher than that of BWS, indicating that BSS contains more reactive groups, enhancing the complexation and cation-π interaction of BSS with Cd^{2+}.

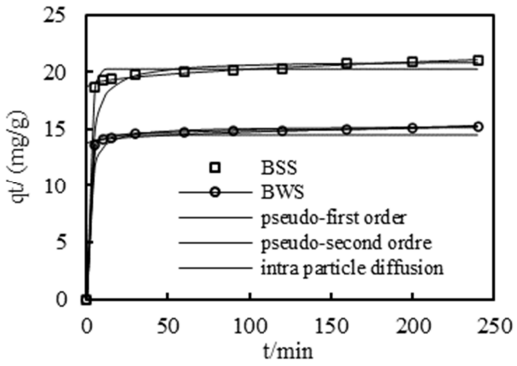

Figure 4. *Fitting of kinetic model for Cd^{2+} adsorption.*

3.2. Adsorption of Cd^{2+} by Biochar at Different pH

pH affects the morphology of heavy metal ions present in the solution, the degree of protonation and deprotonation of the adsorbent, and thus the adsorption effect of biochar. Experimental conditions: Cd^{2+} 50 mg·L^{-1}, 303 K, 4 h, 1 g·L^{-1}. The adsorption amounts of Cd^{2+} in aqueous solution by BWS and BSS at different pH conditions are shown in Figure 3. From Figure 3, it can be seen that the adsorption amount of Cd^{2+} is low when the pH value is in the range of 2 to 3. Under the low pH conditions, more H^+ existed in the solution, which would compete for the adsorption sites on the surface of biochar, resulting in the low adsorption of Cd^{2+}. As the pH increased, the competing adsorption capacity of H^+ gradually weakened and the adsorption capacity of biochar for Cd^{2+} increased. When the solution pH was 7, the adsorption capacities of BWS and BSS for Cd^{2+} were 12.94 mg·g^{-1} and 21.11 mg·g^{-1}. Compared with BWS, the specific surface area of BSS was smaller, but because BSS contained more functional groups, it could provide more active sites and its adsorption capacity for Cd^{2+} was higher than that of BWS. This indicated that the adsorption performance of biochar did not depend entirely on its specific surface area, a phenomenon also found by Bing Li [5] in their experiments.

Table 1. *Parameters fitted to the adsorption kinetic model.*

Biochar	$q_{e,exp}$ (mg·g^{-1})	Pseudo-first-order			pseudo-second-order			intra-particle diffusion		
		k_1 min^{-1}	$q_{e,c}$ (mg·g^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	$q_{e,c}$ (mg·g^{-1})	R^2	k_{dif} (mg·g^{-1}·$min^{-1/2}$)	c (g·mg^{-1})	R^2
BWS	14.98	0.461	14.47	0.884	0.0465	15.22	0.999	0.098	13.81	0.839
BSS	20.98	0.499	20.23	0.924	0.0239	21.05	0.999	0.155	18.71	0.951

Table 2. *Isothermal adsorption model fitting parameters.*

Biochar	T/K	Langmuir			Freundlich			D-R		
		q_m (mg•g^{-1})	k_L (L•mg^{-1})	R^2	k_F	n	R^2	q_m (mmol·g^{-1})	β_{DR}	R^2
BWS	303	24.94	0.040	0.998	2.094	2.028	0.950	0.77	0.0047	0.972
	313	29.94	0.034	0.998	2.068	1.887	0.944	1.04	0.0048	0.967
	323	37.45	0.027	0.995	1.828	1.681	0.946	1.50	0.0050	0.969
BSS	303	32.89	0.031	0.999	2.152	1.869	0.967	1.10	0.0051	0.985
	313	38.76	0.027	0.998	2.143	1.767	0.971	1.38	0.0054	0.987
	323	44.25	0.026	0.999	2.163	1.686	0.960	1.71	0.0056	0.979

3.3. Adsorption Kinetics

Experimental conditions: Cd^{2+} 50 mg·L^{-1}, 303 K, pH 5.3, 1 g·L^{-1}. The variation of the adsorption amount of Cd^{2+} by BWS and BSS with the adsorption time are shown in Figure 4. During the first 5 min, the adsorption amount of Cd^{2+} by both biochar increased rapidly. And then the adsorption amount of Cd^{2+} increased slowly with the increase of

adsorption time. When the adsorption time was 30 min, the adsorption basically reached the equilibrium. At the early stage of adsorption, Cd^{2+} rapidly occupied the adsorption sites of biochar, which inhibited the diffusion of metal ions in solution to the residual adsorption sites. Meanwhile, the higher Cd^{2+} mass concentration gradient at the early stage of adsorption led to a larger adsorption mass transfer rate. As the gradient of Cd^{2+} mass concentration in the solution decreased, the adsorption mass transfer rate of Cd^{2+} by biochar gradually decreased.

The adsorption process of Cd^{2+} was further fitted via the pseudo-first-order, pseudo-second-order and intra-particle diffusion models. (See in Figure 4), and the corresponding fitted parameters are shown in Table 1. As can be seen from Table 1, the correlation coefficients (R^2) of the pseudo-second-order models were both higher than the R2 values of the other two kinetic models, indicating that the adsorption of Cd^{2+} by BWS and BSS was dominated by chemisorption. None of the fitted curves for intraparticle diffusion passed through the origin, implying that intraparticle diffusion was not the only rate control step in the adsorption of Cd^{2+}. The k_2 value of BSS was smaller than that of BWS at the same initial Cd^{2+} concentration, indicating that BSS has a stronger affinity for Cd^{2+} adsorption [15].

3.4. Adsorption Isotherms

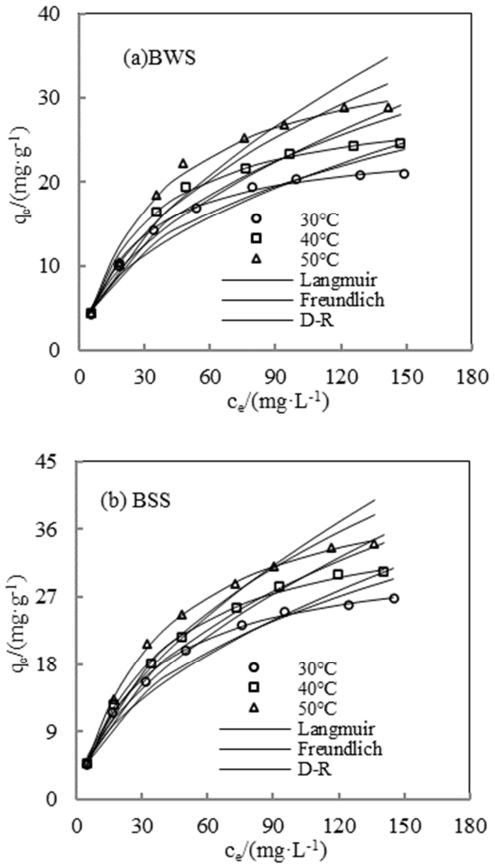

Figure 5. *Fitting of Cd^{2+} isothermal sorption model.*

The adsorption isotherms can reflect the adsorption capacity of the adsorbent. Experimental conditions: pH 5.3, 4 h, 1 g·L^{-1}. Figure 5 shows the adsorption isotherms of Cd^{2+} on BWS and BSS at different temperatures. The adsorption isotherms gradually increased with increasing Cd^{2+} concentration and then leveled off. The higher initial concentration increased the mass transfer driving force, which prompted the reaction between Cd^{2+} and the active sites present on the surface of biochar. However, the adsorption sites provided by a certain amount of biochar are limited, and when the Cd^{2+} concentration increases to a certain level, the adsorption sites are gradually occupied and the adsorption reaches saturation.

The commonly used models to describe the adsorption isotherms are the Langmuir model, Freundlich model and D-R model. The experimental data on the adsorption of Cd^{2+} by BWS and BSS are more consistent with the Langmuir model (R^2>0.99), as shown in Table 2. This indicates that the adsorption mechanism of BWS and BSS on Cd^{2+} is monolayer chemisorption. Denoting the separation factor by R_L, this defining equation is shown in Eq. (1).

$$R_L = \frac{1}{1+k_L c_0} \tag{1}$$

The R_L of BWS and BSS were calculated to be between 0.159 and 0.802, which is between 0 and 1, indicating that all the processes of Cd^{2+} adsorption by BWS and BSS are favorable [16]. The average free energy of adsorption (E, kJ·mol^{-1}) can be calculated from the parameter β_{DR} in the D-R model and the formula is as follows in Eq. (2).

$$E = \frac{1}{\sqrt{2\beta_{DR}}} \tag{2}$$

The calculated values of E in the experiments ranged from 10 to 10.31 kJ·mol^{-1}, indicating that the adsorption of Cd^{2+} on both two kinds of biochar were ion-exchange [17]. Based on the assumptions of the Langmuir model, the adsorption capacities of BWS and BSS were 24.94-37.45 mg·L^{-1} and 32.89-44.25 mg·L^{-1} at 30-50 °C, respectively. The adsorption capacities of the two biochar were greater than those of activated carbon (8.00 mg·g^{-1}), sludge-based biochar (15.29 mg·g^{-1}) and rice husk biochar (15.65 mg·g^{-1}), corn straw biochar (24.43 mg·g^{-1}), wheat straw biochar (17.38 mg·g^{-1}), peanut shell biochar (15.52 mg·g^{-1}), and many other agricultural waste-based biochar [18-21].

3.5. Thermodynamic Analysis

The intrinsic energy changes of the adsorption process at different temperatures were investigated by the adsorption thermodynamics. The thermodynamic parameters were calculated using Eqs. (3) and (4). The thermodynamic parameters of Cd^{2+} adsorption by BWS and BSS are listed in Table 3.

$$\Delta G = -RT \ln K_D \tag{3}$$

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{4}$$

Table 3. *Thermodynamic parameters of adsorption.*

adsorbent	T (K)	Cd^{2+}		
		ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
BWS	303	-14.49	16.13	101.17
	313	-15.56		
	323	-16.51		
BSS	303	-15.07	10.50	84.37
	313	-15.89		
	323	-16.76		

According to Table 3, the negative value of ΔG indicates that the adsorption is spontaneous. The gradual decrease of ΔG with increasing temperature implies that the adsorption is easier and more efficient at high temperatures. This is because high temperature facilitates Cd^{2+} to overcome the spatial site resistance, thus accelerating the adsorption process [10]. At the same temperature, the ΔG value for BSS is smaller than the corresponding value for BWS, indicating that BSS has a stronger adsorption capacity for Cd^{2+}. In addition, a positive value of ΔH indicates heat absorption adsorption, which is consistent with the effect of temperature on the amount of Cd^{2+} adsorption (Figure 5). a positive value of ΔS indicates an increase in the disorder at the solid/liquid interface.

4. Conclusion

In this work, two kinds of biochar were prepared by pyrolysis of walnut shells and sunflower seed shells as raw material at 700°C. The results indicate that the adsorption of Cd^{2+} by both walnut shell biochar and sunflower seed shell biochar increased gradually with increasing pH when the solution pH was from 2 to 7. Under different pH conditions, the adsorption effect of BSS on Cd^{2+} was better than that of BWS. Besides, the adsorption of Cd^{2+} by BWS and BSS were in accordance with the proposed secondary kinetic equation and Langmuir equation, and the average free energy of adsorption was between 10 and 10.31 kJ·mol^{-1}, and the adsorption process was mainly controlled by the ion exchange mechanism. Moreover, from the thermodynamic analysis of adsorption, it is clear that the adsorption of BWS and BSS on Cd^{2+} in solution is a spontaneous, entropy-increasing, heat-absorbing process. Therefore, both sunflower seed shell biochar and walnut shell biochar have the potential to adsorb the heavy metal Cd from water, especially sunflower seed shell biochar (BSS). In the future, the effect of biochar adsorption of cadmium in actual wastewater will be studied.

Acknowledgements

This research was supported by the Fundamental Research Funds for the Central Universities of China (3142014017).

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