

Journal Pre-proof

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PII: S0269-7491(20)32318-6

DOI: <https://doi.org/10.1016/j.envpol.2020.115001>

Reference: ENPO 115001

To appear in: *Environmental Pollution*

Received Date: 27 March 2020

Revised Date: 26 May 2020

Accepted Date: 7 June 2020

Please cite this article as: Teng, D., Zhang, B., Xu, G., Wang, B., Mao, K., Wang, J., Sun, J., Feng, X., Yang, Z., Zhang, H., Efficient removal of Cd(II) from aqueous solution by pinecone biochar: Sorption performance and governing mechanisms, *Environmental Pollution* (2020), doi: <https://doi.org/10.1016/j.envpol.2020.115001>.

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Efficient Removal of Cd(II) from Aqueous Solution by Pinecone

Biochar: Sorption Performance and Governing Mechanisms

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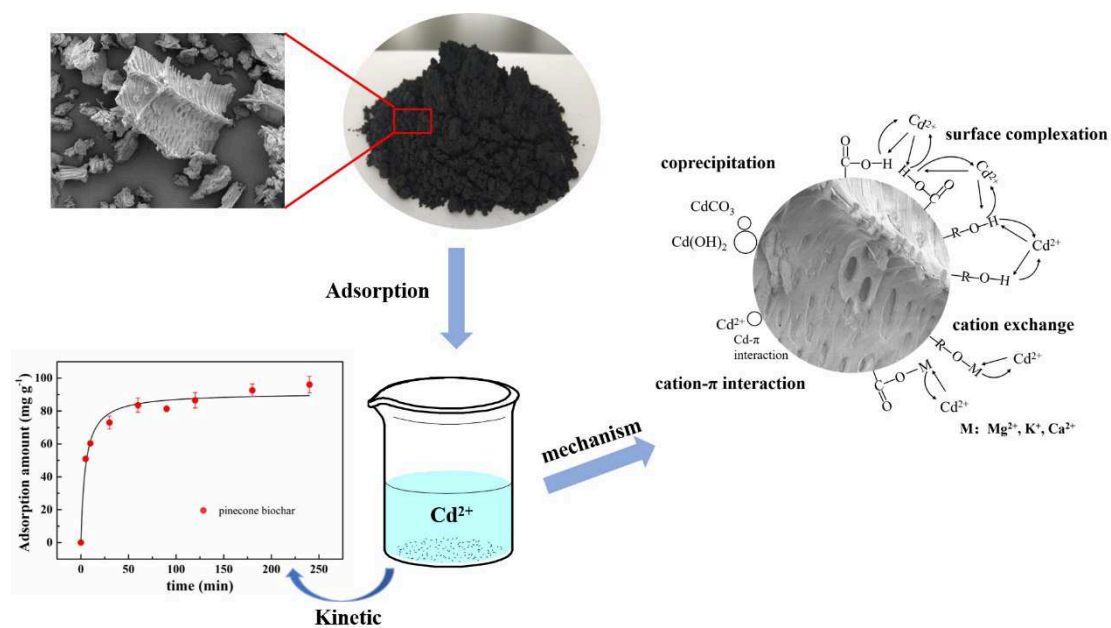
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Graphic Abstract

Abstract:

Cadmium (Cd) is one of the most harmful and widespread environmental pollutants. Despite decades-long research efforts, the remediation of water contaminated by Cd has remained a significant challenge. A novel carbon material, pinecone biochar, was previously hypothesized to be a promising adsorbent for Cd, while so far, it has received little attention. This study evaluated the sorption capacity of pinecone biochar through isotherm experiments. Based on Langmuir model, the adsorption maximum for Cd(II) was up to 92.7 mg g⁻¹. The mechanism of Cd(II) adsorption on pinecone biochar was also explored through both thermodynamic and kinetics adsorption experiments, as well as both solution and solid-phase microstructure characterization. The solid-solution partitioning behaviour of Cd(II) fitted best with the Tóth model while the adsorption process followed a pseudo-second-order rate, suggesting that the Cd(II) adsorption on the pinecone biochar was mainly a chemisorption process. Microstructure characteristics and mechanism analysis further suggested that coprecipitation and surface complexation were the main mechanisms of Cd adsorption by biochar. Coprecipitation occurred mainly through the forms of Cd(OH)₂ and CdCO₃. Our results demonstrated that pinecone biochar was an efficient adsorbent which holds a huge potential for Cd(II) removal from aqueous solution.

Keywords: Biochar; Cadmium; Adsorption; Heavy metals; Water treatment

1. Introduction

In recent years, the discharge of heavy-metal contaminated wastewater from industrial activities has caused serious contamination to soil and aqueous system, posing a great potential threat to human health and aquatic life (Zhang et al., 2019). Especially, due to the higher mobility, long persistence, solubility and biological accumulation of cadmium (Cd), the issue of Cd contamination has caused significant effects on environment and attracted significant concern (Bashir et al., 2018; Liu and Fan, 2018; Peng et al., 2017). Anthropogenic activities such as electroplating, the battery manufacturing industry, mining, smelting processes, alloy manufacturing, manufacturing of phosphate fertilisers, refining of non-ferrous metals and pigments lead to widespread Cd contamination (Ho and Ofomaja, 2006; Moyo et al., 2016; Purkayastha et al., 2014; Zhang et al., 2015), especially in aquatic ecosystems. Moreover, as a carcinogenic toxic heavy metal, Cd can cause a series of diseases including cumulative nephrotoxicity (Jain, 2020). Unlike organic pollutants, Cd is impossible to degrade and shows a half-life of 10-30 years in the kidney (Jarup and Akesson, 2009). Cd contamination has become a serious environmental problem and poses a great threat to human health. Therefore, controlling and removing Cd contamination has aroused widespread concern throughout society.

Many physicochemical techniques have been made to control Cd contamination in recent years, such as chemical oxidation, coagulation–precipitation, ion exchange, solvent extraction, electrochemical treatment, reverse osmosis, membrane treatment, and evaporation recovery (Moyo et al., 2016; Purkayastha et al., 2014). However, the traditional process has inherent limitations. For example, ion exchange and reverse osmosis are limited in practical application because of high operation cost (Muya et al., 2016). In comparison, chemical precipitation will create great quantities of Cd sludge (Lodeiro et al., 2006). Recently, biochar has been widely studied owing to its superior chemical stability, excellent adsorption properties, simple operation and low costs (Huang et al., 2019). Biochar is a carbon-rich material with an aromatic structure, high porosity, a large specific surface area and abundant oxygen-containing

functional groups (Tan et al., 2016). It is prepared by pyrolysis of biomass under the condition of O₂-limited supply and relatively low temperature (350-700 °C) (Komkiene and Baltrenaite, 2016; Manariotis et al., 2015). Because of its special physicochemical properties, biochar is regarded as a product that can effectively treat Cd contamination in water and soil (Jing et al., 2020). It has been found that biochars produced from different feedstock show diverse adsorption process and mechanisms (Gao et al., 2019; Wang et al., 2018). Numerous studies have investigated the adsorption of Cd by different biochars. For example, Kim et al. (2013) found that the maximum adsorption capacity of Cd by biochar produced from *Miscanthus sacchariflorus* at 500 °C was 13.2 mg g⁻¹. The study by Usman et al. (2016) indicates that date palm biochar obtained by pyrolysis at 700 °C shows an Cd adsorption capacity of approximately 43.6 mg g⁻¹. Han et al. (2013) found that the maximum adsorption capacity of Cd by rice straw biochar pyrolyzed at 400 °C was 34.1 mg g⁻¹. In contrast, Bashir et al. (2018) found that the maximum adsorption capacity of Cd by rice straw biochar (produced via pyrolysis at 500 °C) was only 12.2 mg g⁻¹. Based on the above analysis, it is noteworthy that biochars prepared from different raw materials or the same raw materials under different pyrolysis processes show significant differences in adsorption capacities. Indeed, the difference in feedstock and pyrolysis process can alter the surface functional groups, pore structure, elemental composition, and specific surface area of biochar (Wang et al., 2019), leading to dramatically diverse Cd removal efficiencies. Currently, many feedstocks, such as forestry and agricultural residues, domestic garbage, and sludge, can be used as biochar feedstocks. Therefore, experiments on the adsorption properties of biochar prepared from different feedstock are still needed. Moreover, it is urgently necessary to conduct a lot of research on the removal of Cd by biochar.

Elemental composition and the contents of cellulose, lignin, hemicellulose in the biochar are affected by the feedstocks, which could regulate the physicochemical properties and ultimately the adsorption characteristics of biochar (Alexis et al., 2007; Brewer et al., 2011; Mimmo et al., 2014). Pinecone, a common litter in the forest,

typically consists of 46.5% holocellulose, 37.4% lignin and 18.8% α -cellulose (Ofomaja and Naidoo, 2011). The cellulose, hemicellulose and lignin components provide various functional groups such as alcohols and aldehydes on the surface of pinecone (Van Vinh et al., 2015). According to the results of Igalavithana et al. (2017), the biochar prepared from pinecone at 500 °C has a high surface area of 193 m² g⁻¹. Generally, biochar with large surface area and pore volume can provide abundant adsorption sites for adsorbing pollutants (Park et al., 2016). Therefore, biochar produced from pinecone can potentially be an excellent adsorbent. Dawood et al. (2017) show that the adsorption capacity of pinecone biochar for nickel ions is up to 118 mg g⁻¹. Furthermore, pinecone is a cheap feedstock that allows for the sustainable production of economical and environmentally friendly biochar adsorbents (Dawood et al., 2017). There have been many studies on the removal of Cd by biochar prepared from different agricultural and forestry waste as well as animal manure, such as rice straw (Bashir et al., 2018), hickory wood (Wang et al., 2015a) and dairy manure (Xu et al., 2013). The feedstocks for preparing biochar are diverse, but not all of them have the potential to produce an excellent adsorbent. Based on literature (Dawood et al., 2017), we found that the pinecone biochar was an adsorbent worthy of further study. However, to date only sparse information is available on the removal of Cd by pinecone biochar. In this study, pinecone biochar was prepared and selected as an adsorbent to remove Cd from aqueous solution, and then the adsorption equilibrium isotherm and adsorption kinetics were studied. Furthermore, we explored the relationship between the structure and adsorption properties of the prepared pinecone biochar and the adsorption mechanism. In addition, we compared the adsorption capacity of the pinecone biochar used in this study with those of biochars in previous studies.

2. Materials and Methods

2.1 Materials

The pinecone biochar prepared by pyrolysis and carbonization at temperature (350-400 °C) under nitrogen environment was purchased from Shike Jinnian

Biotechnology of Guizhou Province (China) Co., Ltd. $\text{CdCl}_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$ (greater than 99% purity) was purchased from the Science and Technology Development of Tianjin Guangfu Co., Ltd. NaOH (analytical grade) and HNO_3 (ultrapure) were purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions used in this experiment were prepared by using ultrapure water.

2.2 Characterization of Pinecone biochar

The morphology and sizes of the pinecone biochar were characterized by scanning electron microscopy (SEM, QUANTA FEG 250, USA) and the element analysis was fulfilled by energy dispersive X-ray spectrometry (EDX).

The surface area, pore volume and pore size distribution of the pinecone biochar were detected using a NOVA-1000e automated gas adsorption system (QUANTA, USA) via N_2 adsorption isotherms analysis at 77 K.

The surface functional groups of the pinecone biochar were characterized by Fourier transform infrared (FT-IR) spectroscopy in the range of $4000\text{--}400 \text{ cm}^{-1}$. FT-IR were recorded using a NEXUS-670 spectrometer (Thermo Scientific, USA). The sample of pinecone biochar powder was prepared in KBr pressed pellets.

2.3 Adsorption Experiments

For adsorption experiments, stock heavy metal solution with a concentration of 800 mg L^{-1} was prepared from $\text{CdCl}_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$ using ultrapure water and stored in a reagent bottle prior to use.

The extent of Cd adsorption can change with pH and Cd concentration. Thermodynamic adsorption experiments as a function of Cd concentration at constant pH (adsorption isotherms) and as a function of pH at constant Cd concentration (adsorption envelopes), therefore, were both conducted. To perform adsorption isotherm experiments, pH=6.0 CdCl_2 solution with initial Cd^{2+} concentration of 10, 30, 50, 100, 200, 300, 400 and 600 mg L^{-1} was added into a series of centrifuge tubes, and 10 mg biochar was added to each sample. To perform adsorption envelopes, 10 mL of

CdCl₂ solution with Cd²⁺ concentration of 200 mg L⁻¹ was placed into a series of 15 mL centrifuge tubes, in which 10 mg of biochar was placed. Thereafter, the pH of the suspensions was adjusted to 1, 3, 5, 7, 9, respectively, by using 0.15-1.5M HNO₃ or 0.25-2.5M NaOH. Consistent with the procedures in Yang and Jiang (2014), the pH of suspension of each sample was adjusted after adding biochar.

To investigate the influence of adsorption time, 20 mg biochar was added to 20 mL CdCl₂ solution (the initial pH of solution was 6.0; the concentration of Cd²⁺ was 400 mg L⁻¹) in the centrifuge tubes of 50 ml, and then samples were taken at different time intervals (5, 10, 30, 60, 90, 120, 180, 240 min). All thermodynamic and kinetic adsorption experiments were performed in duplicate at room temperature.

Samples were oscillated in a horizontal oscillator at a speed of 250 r min⁻¹ for 300 min. After equilibrium, mixtures were centrifuged in a centrifuge at a speed of 3000 r min⁻¹ for 25 min. Then, the supernatant of the samples was filtered through a 0.45 µm filter and diluted for the determination of Cd. Standard deviations between duplicate experiments were about 5%. Flame atomic absorption spectrometry (AAS, Perkin Elmer, PinAAcle 900F) was used to measure the residual Cd ion content in the solution after adsorption experiments. X-ray photoelectron spectroscopy (XPS) was used to identify the metallic state of element of Cd on the surface of pinecone biochar before and after adsorption. XPS measurements were made with a spectrometer (Thermo Scientific Escalab 250Xi) equipped with a Kα-Al radiation (1486.6 eV, 6 mA, 12 kV) as the X-ray source.

Pseudo-first-order kinetic model and pseudo-second-order kinetic model (Eqs. (1)-(4) in supplementary data) were used to investigate the adsorption mechanisms. The Freundlich, Langmuir, Tóth and Langmuir-Freundlich (Sips) models (Eqs. (5)-(8) in supplementary data) were used to investigate the characteristics of adsorption process.

3. Results and Discussion

3.1 Characterization of pinecone biochar

Fig. 1 exhibits SEM micro-images of the pinecone biochar with different magnifications of 10^3 x, 3×10^3 x, and 5×10^3 x. The morphology of the pinecone biochar showed a “skeletal structure”, and the particle size was approximately 20-100 μm (as seen in Fig. 1 (a)(b)). Notably, there were many micropores with diameters of approximately 6-10 μm on the surface of the pinecone biochar (as seen in Fig. 1 (c)(d)). Moreover, energy dispersive X-ray spectrometer (EDX) analysis showed that carbon, oxygen and the metallic elements potassium, calcium and magnesium were found on the surface of the pinecone biochar, and the atomic ratio of O/C was approximately 0.36. The FT-IR results indicated that the functional groups of O-H at 3445 cm^{-1} ; C-H at 2925 cm^{-1} and 2854 cm^{-1} ; C=O and C=C at 1634 cm^{-1} ; COOH, CHO, phenolic-OH bending, and CO_3^{2-} at 1458 cm^{-1} ; and C-O at 1113 cm^{-1} were observed on the surface of the pinecone biochar (Fig. S1) (Liu and Fan, 2018; Moyo et al., 2016; Usman et al., 2016; Van Vinh et al., 2015; Yang and Jiang, 2014). From the results of gas adsorption-desorption, the calculated specific surface area, pore volume and pore diameter of the pinecone biochar were $165\text{ m}^2\text{ g}^{-1}$, $0.147\text{ cm}^3\text{ g}^{-1}$ and 15.5 nm, respectively. Amazingly, the specific surface area of the pinecone biochar used in this study was significantly greater than that of materials in previous studies (approximately $19.1\text{ m}^2\text{ g}^{-1}$ for rape straw biochar and $112\text{ m}^2\text{ g}^{-1}$ for wheat straw biochar (Li et al., 2017; Liu and Fan, 2018), which might be attributed to the large number of micropores, as confirmed by the SEM results.

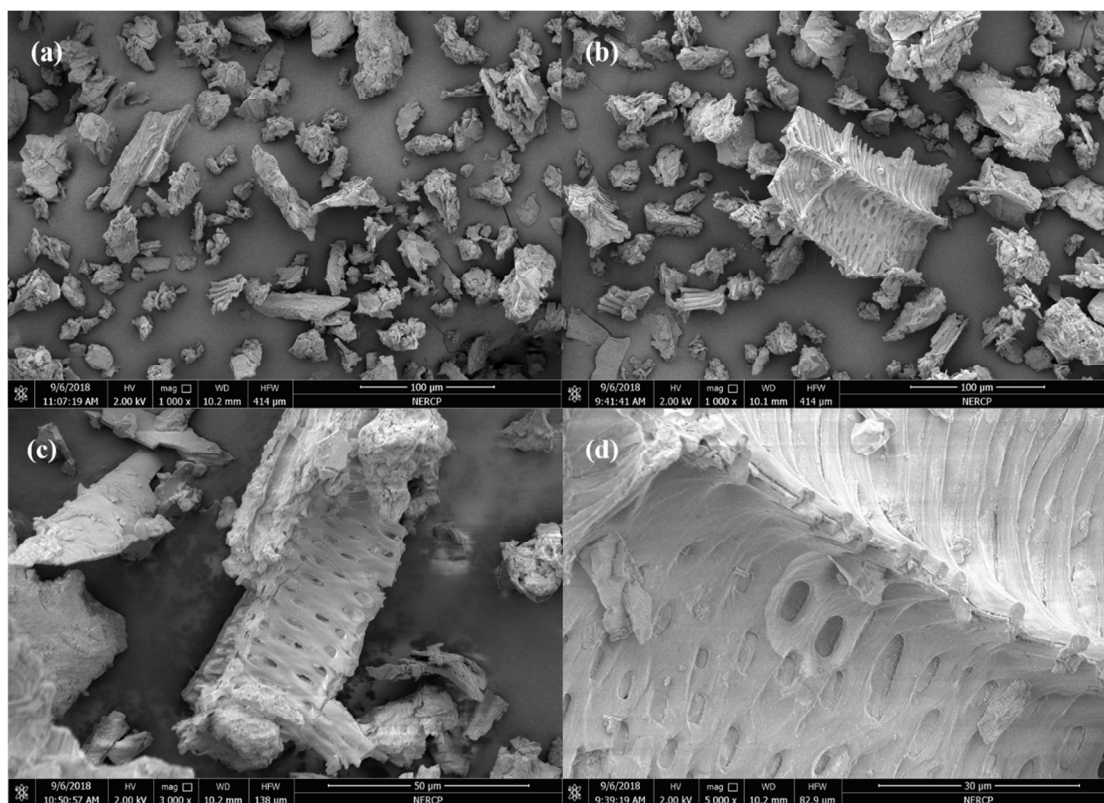


Fig. 1. SEM micro-images of the pinecone biochar with magnifications of $10^3 \times$, $10^3 \times$, $3 \times 10^3 \times$, and $5 \times 10^3 \times$.

3.2 Adsorption performance of Cd(II) by pinecone biochar

The effects of solution pH on the Cd^{2+} removal efficiency and adsorption capacity are shown in Fig. S2. With an increase in pH from 1 to 7, the removal efficiency of Cd^{2+} increased from 2.39% to 37.5%, and the adsorption capacity of Cd(II) increased from 5 mg g^{-1} to 74 mg g^{-1} . According to previous studies, the effect of pH on the removal efficiency and adsorption capacity of Cd(II) by pinecone biochar is ascribed to three reasons. First of all, under a low-pH environment, the large amount of H^+ in the system protonates the functional groups on the adsorbent surface, which results in the rejection of Cd^{2+} in the system (Cheng et al., 2016; Elaigwu et al., 2014; Liu and Zhang, 2011). Secondly, the adsorption sites on the adsorbent are limited, and the abundant H^+ in solution competes with Cd^{2+} at the adsorption sites (Cheng et al., 2016). The higher the H^+ content is, the higher the probability of adsorption, and the less Cd^{2+} will adsorbed by the adsorbent. Thirdly,

metal ions hydrolyse at high pH values, while heavy metals in the form of hydrolytic species have a higher adsorption density on the surface of biochar (Liao et al., 2016). Studies have shown that when the pH of solution system reaches 8, a large amount of OH^- will react with Cd to form several low solubility complexes such as $\text{Cd}(\text{OH})_2$ (Cheng et al., 2016). Therefore, precipitation could be seen at pH of 9 in this study.

3.3 Adsorption Kinetics

The curve of adsorption amount versus adsorption time and the plots of pseudo-first-order and pseudo-second-order kinetic model are shown in Fig. S3 and Fig. S4, respectively. Table 1 lists the related parameters obtained according to the adsorption time experiments and the equations. The adsorption of Cd on pinecone biochar showed to follow two distinct stages: a rapid adsorption stage during the first 60 min and a slower stage till achieving adsorption equilibrium in approximately 175 min, presumably because of diffusion (Zhang et al., 2018). The adsorption amount at equilibrium was approximately 96.1 mg g^{-1} (as seen in Fig. S3), and about 87% of the total adsorption of Cd by pinecone biochar occurred in the first 60 min. The adsorption process can be divided into bulk transfer, external mass transfer, internal diffusion and chemical adsorption (Zhang et al., 2019). In this study, the adjusted R^2 of the pseudo-second-order kinetic model (0.996) was higher than that of the pseudo-first-order kinetic model (0.932), indicating that the Cd^{2+} adsorption process was fitted by the pseudo-second-order kinetic model and that the adsorption process was mainly controlled by a chemisorption mechanism (Liu and Fan, 2018). It was calculated that the adsorption rate was approximately $1.05 \times 10^{-3} (\text{g mg}^{-1} \text{ min}^{-1})$ and the theoretical q_e of the pseudo-second-order kinetic model was 97.7 mg g^{-1} , which was close to the experimental value of 96.1 mg g^{-1} .

Table 1 Parameters of kinetic models.

Model	Parameters	
Pseudo-first-order model	$q_e(\text{mg g}^{-1})$	39.7

	$k_1(\times 10^{-3})$	13.2
	(min^{-1})	
	Adj. R^2	0.932
Pseudo-second-order model	$q_e(\text{mg g}^{-1})$	97.7
	$k_2(\times 10^{-3})$	1.05
	($\text{g mg}^{-1} \text{ min}^{-1}$)	
	Adj. R^2	0.996
Experiment	$q_e(\text{mg g}^{-1})$	96.1

3.4 Adsorption equilibrium isotherms

The adsorption isotherms of Freundlich, Langmuir, Tóth and Langmuir-Freundlich plotted against initial concentrations of Cd^{2+} solution from 10 to 600 mg L^{-1} are shown in Fig. S5, and the regression parameters are listed in Table 2. Fig. S5 shows that the equilibrium adsorption capacity of Cd^{2+} ions increased quickly with an increasing concentration of Cd^{2+} ions in the initial stage (lower concentration) and then slowed until reaching equilibrium. The adsorption capacity of pinecone biochar for Cd in this study was estimated by the Langmuir model to be 92.7 mg g^{-1} . The correlation coefficient (Adj. R^2) of the Tóth isotherm model (0.973) was higher than those of the Langmuir isotherm model (0.964) and Freundlich isotherm model (0.935). The non-linear regression coefficients (Adj. R^2) of the Tóth model (0.973) and Langmuir-Freundlich model (0.972) were similar, while the Tóth isotherm had a slightly higher Adj. R^2 than the Langmuir-Freundlich isotherm. Moreover, among the four models, the residual sum of squares (RSS) and Chi-squares (χ^2) of the Tóth isotherm were the lowest, which were 143 and 28.6, respectively (Table S1). All the goodness of fit indexes indicated that the Tóth model fitted the adsorption data better than the other isotherm models. The parameter m of Tóth model was 0.499, which deviated from unity. These results showed that the adsorption of Cd^{2+} by pinecone biochar was heterogeneous. In addition, the n_{LF} of the Langmuir-Freundlich model was 0.668, which was less than 1, further indicating that the surface of the adsorbent

was heterogeneous. This result was supported by SEM results, which also showed the surface to be heterogenous. The Langmuir-Freundlich isotherm model showed that the adsorption of Cd^{2+} by pinecone biochar was controlled by diffusion and saturated monolayer adsorption at low and high concentrations, respectively (Mohan et al., 2014; Mohan et al., 2011).

It is known that the separation factor R_L can be used to further describe the basic characteristics of the Langmuir model: when $R_L > 1$, adsorption is unfavourable; when $0 < R_L < 1$, adsorption is favourable; when $R_L = 1$, adsorption is linear; and when $R_L = 0$, adsorption is nonlinear (Hall et al., 1966; Reguyal et al., 2017). The R_L has a negative correlation with the initial concentration of Cd in solution, which is calculated by substituting the parameter K_L of the Langmuir model into the equation $R_L = 1/(1 + K_L C_0)$, where C_0 is the initial concentration of solution (Cheng et al., 2016; Reguyal et al., 2017). In this experiment, the calculated value of R_L was from 0.027 to 0.625, further signifying that there was great affinity between Cd and pinecone biochar and that the adsorption process was favourable. In addition, an adsorption system can be characterized by the exponent n of the Freundlich model (Zhou et al., 2018). A value of $1/n$ in the range of 0-1 indicates that adsorption is favourable. In this study, the value of $1/n$ for Cd was 0.264, further confirming that the adsorption process was favourable.

Table 2 Cd adsorption isotherm parameters determined using the Freundlich, Langmuir, Tóth and Langmuir-Freundlich models.

Model	Parameters	
Freundlich	$1/n$	0.264
	$K_F (\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n})$	19.8
	Adj. R^2	0.935
Langmuir	$q_{\max} (\text{mg g}^{-1})$	92.7
	$K_L (\text{L mg}^{-1})$	0.060

Tóth	Adj. R^2	0.964
	$q_{\max}$ (mg g ⁻¹)	117
	K_T (L mg ⁻¹)	0.158
	m	0.499
	Adj. R^2	0.973
Langmuir-Freundlich	a_{LF} (L mg ⁻¹)	0.107
	K_{LF} (L g ⁻¹)	11.6
	n_{LF}	0.668
	Adj. R^2	0.972

Recently, many studies have been carried out to explore the Cd removing efficiency of biochar prepared from different feedstocks. The theoretical maximum adsorption capacities ($q_{\max}$) of biochars prepared from different raw materials reported in previous studies were compared in Table S2. Excitingly, the $q_{\max}$ of the pinecone biochar used in this study (approximately 92.7 mg g⁻¹) was much higher than those common biochars reported in previous studies, such as straw, peanut husk and ipomoea biochar. The results of Cui et al. (2016b) show that the adsorption capacity of biochar prepared by wetland-plants reaches 119-126 mg g⁻¹, which is better than that of biochar produced from pinecone. However, pinecone biomass, as a low-cost and easily available biomass, was also an excellent feedstock of preparing biochars.

3.5 Cd adsorption mechanism

Based on the structural analysis results, it was apparent that the surface functional groups of the pinecone biochar used in this study were abundant, implying that many heavy metal chemisorption sites existed on the surface of the pinecone biochar and were responsible for the excellent adsorption performance of the pinecone biochar. Moreover, from the results of the isothermal adsorption model, diffusion was another means of Cd²⁺ adsorption; as a result, the specific surface area also contributed to the improvement of adsorption performance. Thus, it was inferred that

the synergistic effect of the abundant functional groups and the relatively large specific surface area led to the superior adsorption performance of Cd^{2+} by the pinecone biochar in this study.

To further explore the fixing mechanism of Cd ions onto the surface of the pinecone biochar at the micro level, XPS analysis was also carried out. Fig. 2 shows XPS spectra of the pinecone biochar before and after adsorption of Cd^{2+} . Cd3d peaks appeared in the XPS spectra after adsorption of Cd^{2+} (see Fig. 2 (a)), further indicating that Cd ions were adsorbed on the surface of the pinecone biochar. From the high-resolution XPS spectra of Cd3d, as shown in Fig. 2 (b), Cd ions were bound on the pinecone biochar by CdCO_3 bonds, as confirmed by the strong peaks at 405.5 eV, as well as $\text{Cd}(\text{OH})_2$ bonds, corresponding to peaks at 406.1 eV. The peak at 405.5 eV also suggested that Cd was adsorbed by biochar through complexation with hydroxyl ($-\text{OH}$) or deprotonated form (O^-) (Zhang et al., 2015). The high-resolution XPS spectrum of C1s of the biochar before the adsorption of Cd ions is shown in Fig. 2 (c). The peaks at 284.6 eV, 285.6 eV, 286.4 eV and 288.3 eV were attributed to C-C/C-H, C-O, C=O/C-O-C and O=C-O (bound to carboxyl and/or ester groups), respectively (Jing et al., 2014; Liu and Fan, 2018). As shown in Fig. 2 (d), the high-resolution XPS spectrum of C1s after Cd adsorption also exhibits four peaks similar to those before Cd adsorption, indicating that C atoms did not react with Cd ions (Li et al., 2016). Comparing the results of Fig. 2 (e) and (f) showed that the two major O1s peaks at 531.0 eV and 532.2 eV have a small shift to 531.8 eV and 533.0 eV, respectively. The change of O1s after Cd adsorption suggested that Cd was bound to the oxygen-containing functional groups of biochar (Liu and Fan, 2018).

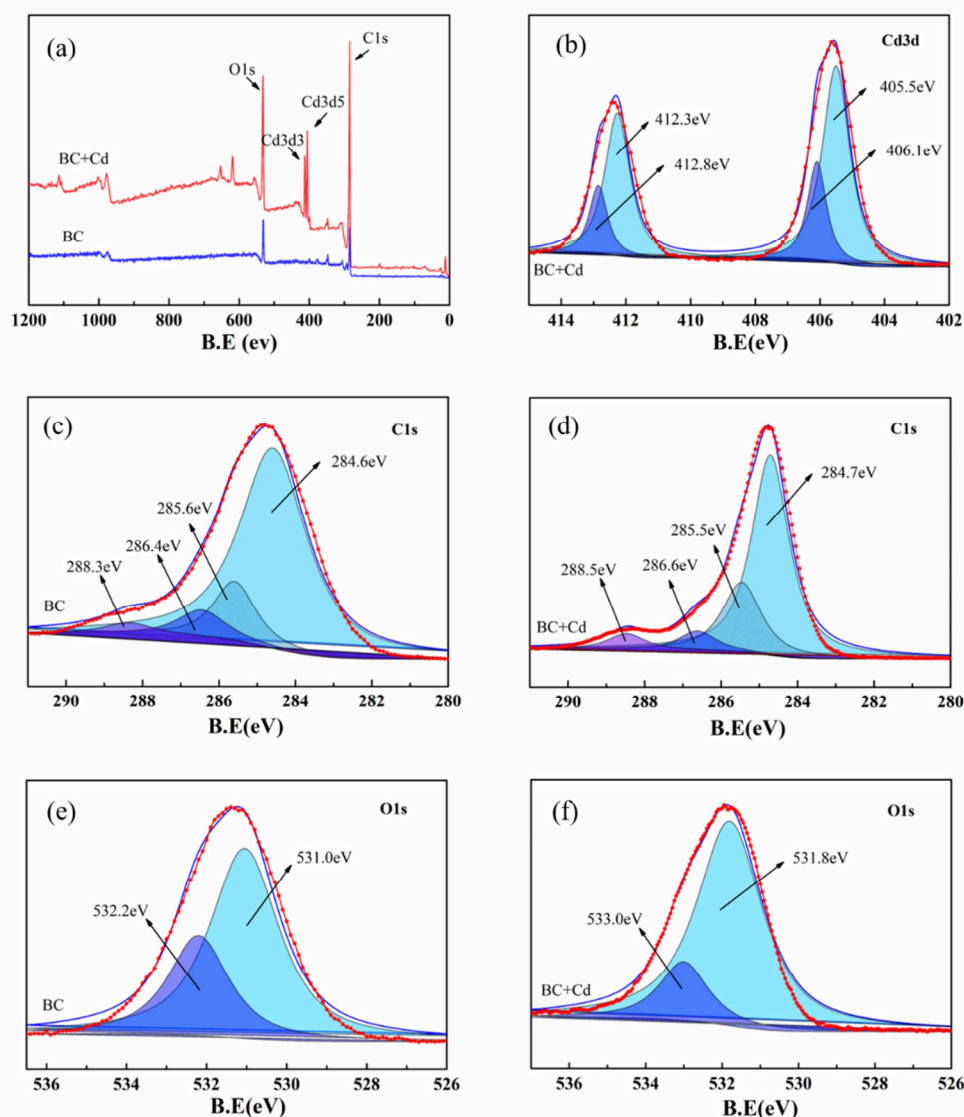


Fig. 2. XPS spectra of pinecone biochar loaded with Cd (a) and high-resolution XPS spectra of the related elements (b-f).

Previous studies show that there are four main mechanism for Cd adsorption by biochar: 1) coprecipitation; 2) metal ion exchange; 3) surface complexation; 4) Cd- π interaction (Cui et al., 2016a). The adsorption process and mechanism of Cd(II) on the pinecone biochar were revealed and were illustrated in the schematic drawing in Fig. 3. The high-resolution XPS spectra of Cd3d suggested some anions co-precipitated with Cd^{2+} and formed $\text{Cd}(\text{OH})_2$ and CdCO_3 minerals on the surface of the pinecone biochar. The complexation of oxygen-containing functional groups on the surface of biochar with metal ions is one of the main mechanisms for biochar to adsorb metals

(Cui et al., 2016a). From the results of FT-IR, it was known that the surface of the pinecone biochar contained oxygen-containing functional groups such as -OH and -COOH. And the XPS analysis of O1s further proved that the coordination between Cd^{2+} and oxygen-containing functional groups. Ion exchange is considered to be a common mechanism for the adsorption of metal ions on biochar (Gao et al., 2019; Li et al., 2013). Metal ions Mg^{2+} , K^+ , Ca^{2+} were detected on pinecone biochar by energy dispersive X-ray spectrometer (EDX). Therefore, we speculated that a weak ion exchange occurred during the adsorption of Cd by pinecone biochar. Cation- π interaction is a noncovalent interaction between a cation and a π -donor (Keiluweit and Kleber, 2009). The π -system serves as the π -donor and the ability of aromatic π -system to provide electrons increases with the number of corresponding rings (Wang et al., 2015b). FT-IR showed that the pinecone biochar contained aromatic C=C and C=O which could provide π -donor. Thus, we concluded that the Cd- π interaction occurs in pinecone biochar. By comprehensive comparison, we believed that coprecipitation and surface complexation were the main mechanisms for Cd adsorption by pinecone biochar. In contrast, cation- π interaction and ion exchange were relatively insignificant.

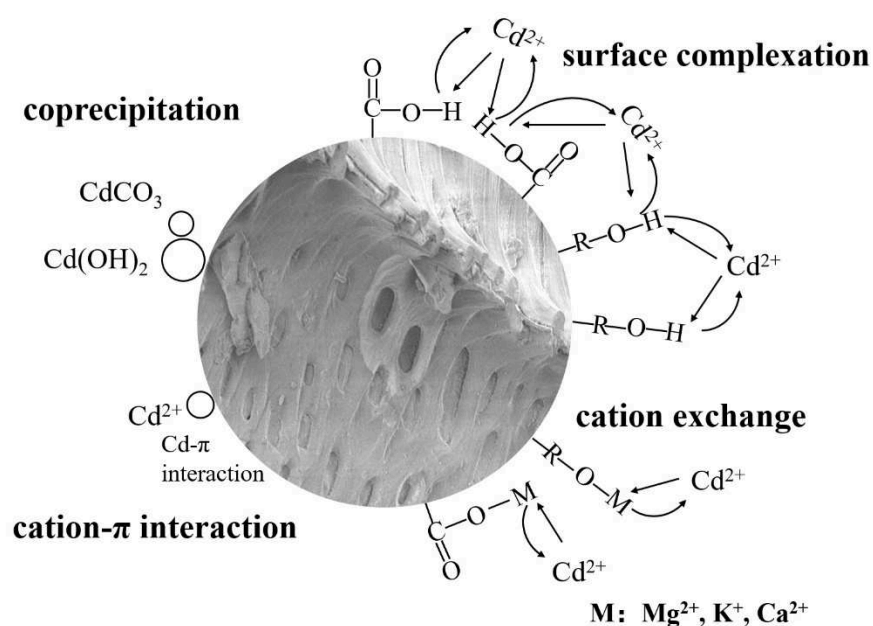


Fig. 3. Adsorption process and mechanism of Cd(II) on pinecone biochar.

4. Conclusions

In this study, we explored a novel pinecone biochar with a high Cd(II) adsorption capacity of 92.7 mg g^{-1} and studied the adsorption equilibrium isotherm and adsorption kinetics of the pinecone biochar. The experimental adsorption isotherm results indicated that the adsorption behaviour of Cd(II) onto the pinecone biochar fitted the Tóth model, signifying that there was great affinity between Cd(II) and pinecone biochar, the adsorption process was favourable, and the adsorption behaviour was highly heterogeneous. The adsorption kinetics showed that the adsorption process of Cd(II) by the pinecone biochar fitted the pseudo-second-order kinetic model and that the adsorption process was mainly controlled by a chemisorption. And the main mechanisms of Cd adsorption were coprecipitation and surface complexation. The detailed analysis demonstrated that coprecipitation occurred mainly through $\text{Cd}(\text{OH})_2$ and CdCO_3 . We believe that the prepared pinecone biochar was an economical and effective adsorbent for Cd and had a huge potential to remove heavy metal contamination in aqueous solution. We are exploring the potential for testing the real sample and scaling up in the field to evidence the impact for effective remediation.

Acknowledgements

The authors would like to acknowledge the financially supported from Financial support from National Key Research and Development Program of China (No. 2019 YFC1803600), the National Science Foundation of China-Project of Karst Science Research Center (U1612442), and Science and Technology Program of Guizhou Province [Grant No. (2019)5618, 2019(2963), (2019)2836, and (2019)4428]. ZY thanks UK NERC Fellowship grant (NE/R013349/2) and Royal Academy of Engineering Frontier Follow-up Grant (FF\1920\1\36).

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Highlights

- The amount of Cd^{2+} adsorbed by pinecone biochar increased with the increase of pH.
- The adsorption behavior of Cd(II) onto the pinecone biochar fitted the Tóth model.
- The adsorption process was mainly controlled by a chemisorption mechanism.
- The adsorption capacity of the pinecone biochar was excellent.
- Pinecone was a potential raw material for biochar preparation.

Dongye Teng: Conceptualization, Methodology, Software, Data curation, Writing- Original draft preparation. **Bingbing Zhang:** Conceptualization, Methodology. **Bing Wang:** Writing- Reviewing and Editing. **Kang Mao:** Writing- Reviewing and Editing. **Jianxu Wang:** Writing- Reviewing and Editing. **Jing Sun:** Writing- Reviewing and Editing. **Xinbin Feng:** Writing- Reviewing and Editing. **Zhugen Yang:** Writing- Reviewing and Editing. **Hua Zhang:** Supervision, Conceptualization, Methodology, Writing- Reviewing and Editing.

The authors declare no competing financial interest.

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Efficient removal of Cd(II) from aqueous solution by pinecone biochar: Sorption performance and governing mechanisms

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2020-06-12

Elsevier

<https://doi.org/10.1016/j.envpol.2020.115001>

Teng D, Zhang B, Xu G, et al., (2020) Efficient removal of Cd(II) from aqueous solution by pinecone biochar: Sorption performance and governing mechanisms. Environmental Pollution, 265, Part A, Article number 115001