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

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

2 **Biochar: Sorption Performance and Governing Mechanisms**

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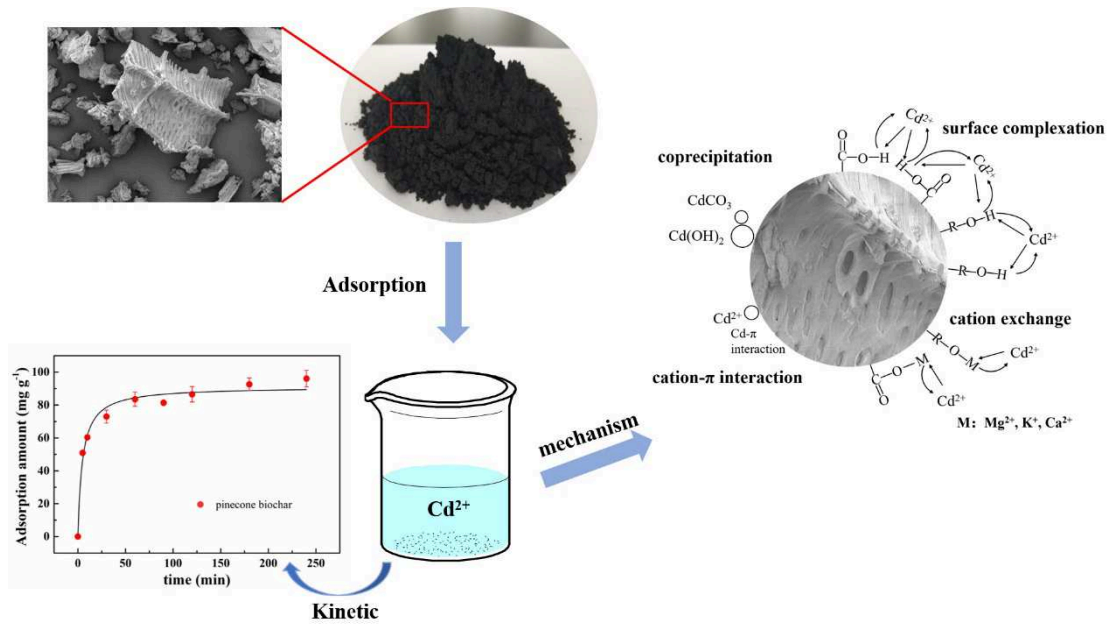
20   **Graphic Abstract**

21

22 **Abstract:**

23 Cadmium (Cd) is one of the most harmful and widespread environmental pollutants.

24 Despite decades-long research efforts, the remediation of water contaminated by Cd

25 has remained a significant challenge. A novel carbon material, pinecone biochar, was

26 previously hypothesized to be a promising adsorbent for Cd, while so far, it has

27 received little attention. This study evaluated the sorption capacity of pinecone

28 biochar through isotherm experiments. Based on Langmuir model, the adsorption

29 maximum for Cd(II) was up to 92.7 mg g^{-1}. The mechanism of Cd(II) adsorption on

30 pinecone biochar was also explored through both thermodynamic and kinetics

31 adsorption experiments, as well as both solution and solid-phase microstructure

32 characterization. The solid-solution partitioning behaviour of Cd(II) fitted best with

33 the Tóth model while the adsorption process followed a pseudo-second-order rate,

34 suggesting that the Cd(II) adsorption on the pinecone biochar was mainly a

35 chemisorption process. Microstructure characteristics and mechanism analysis further

36 suggested that coprecipitation and surface complexation were the main mechanisms

37 of Cd adsorption by biochar. Coprecipitation occurred mainly through the forms of

38 Cd(OH)$_2$ and CdCO$_3$. Our results demonstrated that pinecone biochar was an efficient

39 adsorbent which holds a huge potential for Cd(II) removal from aqueous solution.

40

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

42

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

72 functional groups (Tan et al., 2016). It is prepared by pyrolysis of biomass under the

73 condition of O_2-limited supply and relatively low temperature (350-700 □)

74 (Komkiene and Baltrenaite, 2016; Manariotis et al., 2015). Because of its special

75 physicochemical properties, biochar is regarded as a product that can effectively treat

76 Cd contamination in water and soil (Jing et al., 2020). It has been found that biochars

77 produced from different feedstock show diverse adsorption process and mechanisms

78 (Gao et al., 2019; Wang et al., 2018). Numerous studies have investigated the

79 adsorption of Cd by different biochars. For example, Kim et al. (2013) found that the

80 maximum adsorption capacity of Cd by biochar produced from *Miscanthus*

81 *sacchariflorus* at 500 □ was 13.2 mg g^{-1}. The study by Usman et al. (2016) indicates

82 that date palm biochar obtained by pyrolysis at 700 □ shows an Cd adsorption

83 capacity of approximately 43.6 mg g^{-1}. Han et al. (2013) found that the maximum

84 adsorption capacity of Cd by rice straw biochar pyrolyzed at 400 □ was 34.1 mg g^{-1}.

85 In contrast, Bashir et al. (2018) found that the maximum adsorption capacity of Cd by

86 rice straw biochar (produced via pyrolysis at 500 □) was only 12.2 mg g^{-1}. Based on

87 the above analysis, it is noteworthy that biochars prepared from different raw

88 materials or the same raw materials under different pyrolysis processes show

89 significant differences in adsorption capacities. Indeed, the difference in feedstock and

90 pyrolysis process can alter the surface functional groups, pore structure, elemental

91 composition, and specific surface area of biochar (Wang et al., 2019), leading to

92 dramatically diverse Cd removal efficiencies. Currently, many feedstocks, such as

93 forestry and agricultural residues, domestic garbage, and sludge, can be used as

94 biochar feedstocks. Therefore, experiments on the adsorption properties of biochar

95 prepared from different feedstock are still needed. Moreover, it is urgently necessary

96 to conduct a lot of research on the removal of Cd by biochar.

97   Elemental composition and the contents of cellulose, lignin, hemicellulose in the

98 biochar are affected by the feedstocks, which could regulate the physicochemical

99 properties and ultimately the adsorption characteristics of biochar (Alexis et al., 2007;

100 Brewer et al., 2011; Mimmo et al., 2014). Pinecone, a common litter in the forest,

101 typically consists of 46.5% holocellulose, 37.4% lignin and 18.8% α-cellulose

102 (Ofomaja and Naidoo, 2011). The cellulose, hemicellulose and lignin components

103 provide various functional groups such as alcohols and aldehydes on the surface of

104 pinecone (Van Vinh et al., 2015). According to the results of Igalavithana et al. (2017),

105 the biochar prepared from pinecone at 500 □ has a high surface area of 193 m^2 g^{-1}.

106 Generally, biochar with large surface area and pore volume can provide abundant

107 adsorption sites for adsorbing pollutants (Park et al., 2016). Therefore, biochar

108 produced from pinecone can potentially be an excellent adsorbent. Dawood et al.

109 (2017) show that the adsorption capacity of pinecone biochar for nickel ions is up to

110 118 mg g^{-1}. Furthermore, pinecone is a cheap feedstock that allows for the sustainable

111 production of economical and environmentally friendly biochar adsorbents (Dawood

112 et al., 2017). There have been many studies on the removal of Cd by biochar prepared

113 from different agricultural and forestry waste as well as animal manure, such as rice

114 straw (Bashir et al., 2018), hickory wood (Wang et al., 2015a) and dairy manure (Xu

115 et al., 2013). The feedstocks for preparing biochar are diverse, but not all of them

116 have the potential to produce an excellent absorbent. Based on literature (Dawood et

117 al., 2017), we found that the pinecone biochar was an adsorbent worthy of further

118 study. However, to date only sparse information is available on the removal of Cd by

119 pinecone biochar. In this study, pinecone biochar was prepared and selected as an

120 adsorbent to remove Cd from aqueous solution, and then the adsorption equilibrium

121 isotherm and adsorption kinetics were studied. Furthermore, we explored the

122 relationship between the structure and adsorption properties of the prepared pinecone

123 biochar and the adsorption mechanism. In addition, we compared the adsorption

124 capacity of the pinecone biochar used in this study with those of biochars in previous

125 studies.

126 ## 2. Materials and Methods

127 ### 2.1 Materials

128 The pinecone biochar prepared by pyrolysis and carbonization at temperature

129 (350-400 □) under nitrogen environment was purchased from Shike Jinnian

130   Biotechnology of Guizhou Province (China) Co., Ltd. $CdCl_2·2$ $1/2H_2O$ (greater than

131   99% purity) was purchased from the Science and Technology Development of Tianjin

132   Guangfu Co., Ltd. NaOH (analytical grade) and HNO_3 (ultrapure) were purchased

133   from Sinopharm Chemical Reagent Co., Ltd. All solutions used in this experiment

134   were prepared by using ultrapure water.

135

136   **2.2 Characterization of Pinecone biochar**

137   The morphology and sizes of the pinecone biochar were characterized by

138   scanning electron microscopy (SEM, QUANTA FEG 250, USA) and the element

139   analysis was fulfilled by energy dispersive X-ray spectrometry (EDX).

140   The surface area, pore volume and pore size distribution of the pinecone biochar

141   were detected using a NOVA-1000e automated gas adsorption system (QUANTA,

142   USA) via N_2 adsorption isotherms analysis at 77 K.

143   The surface functional groups of the pinecone biochar were characterized by

144   Fourier transform infrared (FT-IR) spectroscopy in the range of 4000-400 cm^{-1}. FT-IR

145   were recorded using a NEXUS-670 spectrometer (Thermo Scientific, USA). The

146   sample of pinecone biochar powder was prepared in KBr pressed pellets.

147

148   **2.3 Adsorption Experiments**

149   For adsorption experiments, stock heavy metal solution with a concentration of

150   800 mg L^{-1} was prepared from $CdCl_2·2$ $1/2H_2O$ using ultrapure water and stored in a

151   reagent bottle prior to use.

152   The extent of Cd adsorption can change with pH and Cd concentration.

153   Thermodynamic adsorption experiments as a function of Cd concentration at constant

154   pH (adsorption isotherms) and as a function of pH at constant Cd concentration

155   (adsorption envelopes), therefore, were both conducted. To perform adsorption

156   isotherm experiments, pH=6.0 $CdCl_2$ solution with initial Cd^{2+} concentration of 10, 30,

157   50, 100, 200, 300, 400 and 600 mg L^{-1} was added into a series of centrifuge tubes, and

158   10 mg biochar was added to each sample. To perform adsorption envelopes, 10 mL of

159 CdCl$_2$ solution with Cd^{2+} concentration of 200 mg L^{-1} was placed into a series of 15

160 mL centrifuge tubes, in which 10 mg of biochar was placed. Thereafter, the pH of the

161 suspensions was adjusted to 1, 3, 5, 7, 9, respectively, by using 0.15-1.5M HNO$_3$ or

162 0.25-2.5M NaOH. Consistent with the procedures in Yang and Jiang (2014) , the pH

163 of suspension of each sample was adjusted after adding biochar.

164 To investigate the influence of adsorption time, 20 mg biochar was added to 20

165 mL CdCl$_2$ solution (the initial pH of solution was 6.0; the concentration of Cd^{2+} was

166 400 mg L^{-1}) in the centrifuge tubes of 50 ml, and then samples were taken at different

167 time intervals (5, 10, 30, 60, 90, 120, 180, 240 min). All thermodynamic and kinetic

168 adsorption experiments were performed in duplicate at room temperature.

169 Samples were oscillated in a horizontal oscillator at a speed of 250 r min^{-1} for

170 300 min. After equilibrium, mixtures were centrifuged in a centrifuge at a speed of

171 3000 r min^{-1} for 25 min. Then, the supernatant of the samples was filtered through a

172 0.45 µm filter and diluted for the determination of Cd. Standard deviations between

173 duplicate experiments were about 5%. Flame atomic absorption spectrometry (AAS,

174 Perkin Elmer, PinAAcle 900F) was used to measure the residual Cd ion content in the

175 solution after adsorption experiments. X-ray photoelectron spectroscopy (XPS) was

176 used to identify the metallic state of element of Cd on the surface of pinecone biochar

177 before and after adsorption. XPS measurements were made with a spectrometer

178 (Thermo Scientific Escalab 250Xi) equipped with a Kα-Al radiation (1486.6 eV, 6

179 mA, 12 kV) as the X-ray source.

180 Pseudo-first-order kinetic model and pseudo-second-order kinetic model (Eqs.

181 (1)-(4) in supplementary data) were used to investigate the adsorption mechanisms.

182 The Freundlich, Langmuir, Tóth and Langmuir-Freundlich (Sips) models (Eqs. (5)-(8)

183 in supplementary data) were used to investigate the characteristics of adsorption

184 process.

185

186   ## 3. Results and Discussion

187   ### 3.1 Characterization of pinecone biochar

188   Fig. 1 exhibits SEM micro-images of the pinecone biochar with different

189   magnifications of 10^3 x, 3×10^3 x, and 5×10^3 x. The morphology of the pinecone

190   biochar showed a "skeletal structure", and the particle size was approximately 20-100

191   μm (as seen in Fig. 1 (a)(b)). Notably, there were many micropores with diameters of

192   approximately 6-10 μm on the surface of the pinecone biochar (as seen in Fig. 1

193   (c)(d)). Moreover, energy dispersive X-ray spectrometer (EDX) analysis showed that

194   carbon, oxygen and the metallic elements potassium, calcium and magnesium were

195   found on the surface of the pinecone biochar, and the atomic ratio of O/C was

196   approximately 0.36. The FT-IR results indicated that the functional groups of O-H at

197   3445 cm^{-1}; C-H at 2925 cm^{-1} and 2854 cm^{-1}; C=O and C=C at 1634 cm^{-1}; COOH,

198   CHO, phenolic-OH bending, and CO_3^{2-} at 1458 cm^{-1}; and C-O at 1113 cm^{-1} were

199   observed on the surface of the pinecone biochar (Fig. S1) (Liu and Fan, 2018; Moyo

200   et al., 2016; Usman et al., 2016; Van Vinh et al., 2015; Yang and Jiang, 2014). From

201   the results of gas adsorption-desorption, the calculated specific surface area, pore

202   volume and pore diameter of the pinecone biochar were 165 m^2 g^{-1}, 0.147 cm^3 g^{-1} and

203   15.5 nm, respectively. Amazingly, the specific surface area of the pinecone biochar

204   used in this study was significantly greater than that of materials in previous studies

205   (approximately 19.1 m^2 g^{-1} for rape straw biochar and 112 m^2 g^{-1} for wheat straw

206   biochar (Li et al., 2017; Liu and Fan, 2018), which might be attributed to the large

207   number of micropores, as confirmed by the SEM results.
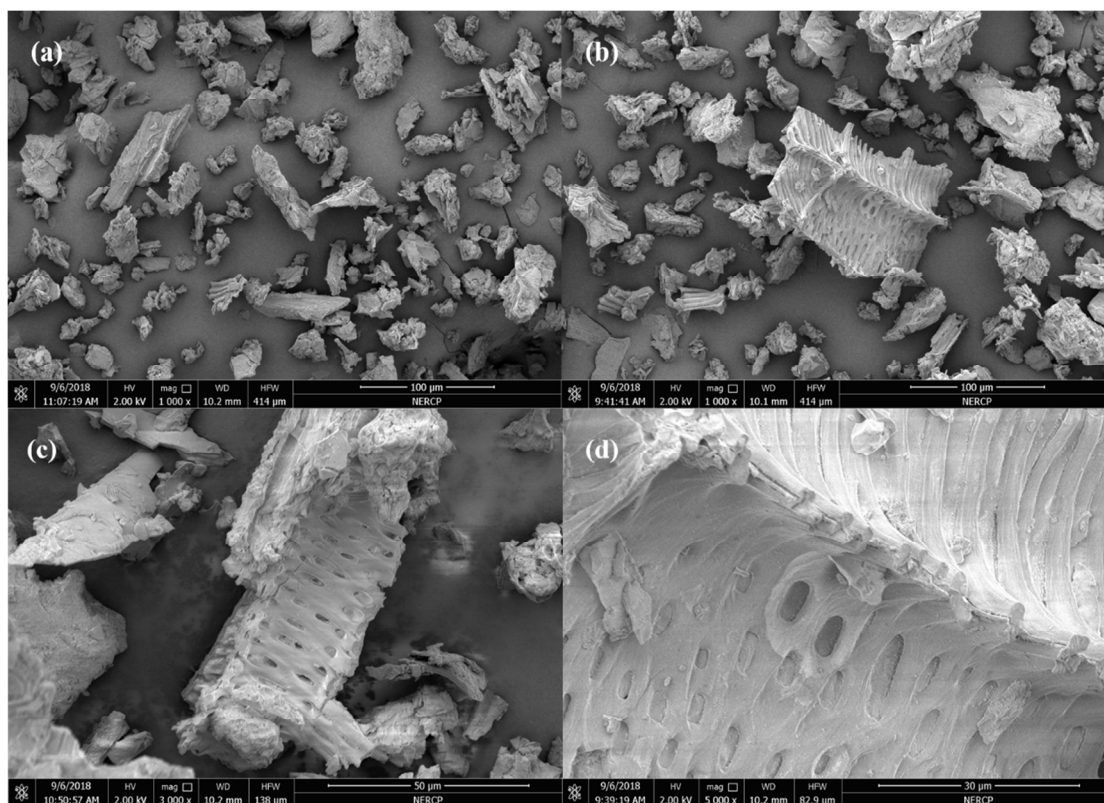
Fig. 1. SEM micro-images of the pinecone biochar with magnifications of 10^3 x, 10^3 x, 3×10^3 x, and 5×10^3 x.

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,

9

225   metal ions hydrolyse at high pH values, while heavy metals in the form of hydrolytic

226   species have a higher adsorption density on the surface of biochar (Liao et al., 2016).

227   Studies have shown that when the pH of solution system reaches 8, a large amount of

228   OH^- will react with Cd to form several low solubility complexes such as $Cd(OH)_2$

229   (Cheng et al., 2016). Therefore, precipitation could be seen at pH of 9 in this study.

230

231   **3.3 Adsorption Kinetics**

232   The curve of adsorption amount versus adsorption time and the plots of

233   pseudo-first-order and pseudo-second-order kinetic model are shown in Fig. S3 and

234   Fig. S4, respectively. Table 1 lists the related parameters obtained according to the

235   adsorption time experiments and the equations. The adsorption of Cd on pinecone

236   biochar showed to follow two distinct stages: a rapid adsorption stage during the first

237   60 min and a slower stage till achieving adsorption equilibrium in approximately 175

238   min, presumably because of diffusion (Zhang et al., 2018). The adsorption amount at

239   equilibrium was approximately 96.1 mg g^{-1} (as seen in Fig. S3), and about 87% of the

240   total adsorption of Cd by pinecone biochar occurred in the first 60 min. The

241   adsorption process can be divided into bulk transfer, external mass transfer, internal

242   diffusion and chemical adsorption (Zhang et al., 2019). In this study, the adjusted R^2

243   of the pseudo-second-order kinetic model (0.996) was higher than that of the

244   pseudo-first-order kinetic model (0.932), indicating that the Cd^{2+} adsorption process

245   was fitted by the pseudo-second-order kinetic model and that the adsorption process

246   was mainly controlled by a chemisorption mechanism (Liu and Fan, 2018). It was

247   calculated that the adsorption rate was approximately 1.05×10^{-3} (g mg^{-1} min^{-1}) and the

248   theoretical q_e of the pseudo-second-order kinetic model was 97.7 mg g^{-1}, which was

249   close to the experimental value of 96.1 mg g^{-1}.

250

Table 1 Parameters of kinetic models.

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

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

251

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

11

272 was heterogeneous. This result was supported by SEM results, which also showed the

273 surface to be heterogenous. The Langmuir-Freundlich isotherm model showed that the

274 adsorption of Cd^{2+} by pinecone biochar was controlled by diffusion and saturated

275 monolayer adsorption at low and high concentrations, respectively (Mohan et al.,

276 2014; Mohan et al., 2011).

277 It is known that the separation factor R_L can be used to further describe the basic

278 characteristics of the Langmuir model: when $R_L > 1$, adsorption is unfavourable; when

279 $0 < R_L < 1$, adsorption is favourable; when $R_L = 1$, adsorption is linear; and when R_L

280 $= 0$, adsorption is nonlinear (Hall et al., 1966; Reguyal et al., 2017). The R_L has a

281 negative correlation with the initial concentration of Cd in solution, which is

282 calculated by substituting the parameter K_L of the Langmuir model into the equation

283 $R_L = 1/(1 + K_L C_0)$, where C_0 is the initial concentration of solution (Cheng et al., 2016;

284 Reguyal et al., 2017). In this experiment, the calculated value of R_L was from 0.027 to

285 0.625, further signifying that there was great affinity between Cd and pinecone

286 biochar and that the adsorption process was favourable. In addition, an adsorption

287 system can be characterized by the exponent n of the Freundlich model (Zhou et al.,

288 2018). A value of $1/n$ in the range of 0-1 indicates that adsorption is favourable. In this

289 study, the value of $1/n$ for Cd was 0.264, further confirming that the adsorption

290 process was favourable.

291

Table 2 Cd adsorption isotherm parameters determined using the Freundlich,

Langmuir, Tóth and Langmuir-Freundlich models.

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

	Adj. R^2	0.964
Tóth	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

292

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

303

304   **3.5 Cd adsorption mechanism**

305   Based on the structural analysis results, it was apparent that the surface
306   functional groups of the pinecone biochar used in this study were abundant, implying
307   that many heavy metal chemisorption sites existed on the surface of the pinecone
308   biochar and were responsible for the excellent adsorption performance of the pinecone
309   biochar. Moreover, from the results of the isothermal adsorption model, diffusion was
310   another means of Cd^{2+} adsorption; as a result, the specific surface area also
311   contributed to the improvement of adsorption performance. Thus, it was inferred that

312   the synergistic effect of the abundant functional groups and the relatively large

313   specific surface area led to the superior adsorption performance of Cd^{2+} by the

314   pinecone biochar in this study.

315   To further explore the fixing mechanism of Cd ions onto the surface of the

316   pinecone biochar at the micro level, XPS analysis was also carried out. Fig. 2 shows

317   XPS spectra of the pinecone biochar before and after adsorption of Cd^{2+}. Cd3d peaks

318   appeared in the XPS spectra after adsorption of Cd^{2+} (see Fig. 2 (a)), further

319   indicating that Cd ions were adsorbed on the surface of the pinecone biochar. From

320   the high-resolution XPS spectra of Cd3d, as shown in Fig. 2 (b), Cd ions were bound

321   on the pinecone biochar by $CdCO_3$ bonds, as confirmed by the strong peaks at 405.5

322   eV, as well as $Cd(OH)_2$ bonds, corresponding to peaks at 406.1 eV. The peak at 405.5

323   eV also suggested that Cd was adsorbed by biochar through complexation with

324   hydroxyl (-OH) or deprotonated form (O^-) (Zhang et al., 2015). The high-resolution

325   XPS spectrum of C1s of the biochar before the adsorption of Cd ions is shown in Fig.

326   2 (c). The peaks at 284.6 eV, 285.6 eV, 286.4 eV and 288.3 eV were attributed to

327   C-C/C-H, C-O, C=O/C-O-C and O=C-O (bound to carboxyl and/or ester groups),

328   respectively (Jing et al., 2014; Liu and Fan, 2018). As shown in Fig. 2 (d), the

329   high-resolution XPS spectrum of C1s after Cd adsorption also exhibits four peaks

330   similar to those before Cd adsorption, indicating that C atoms did not react with Cd

331   ions (Li et al., 2016). Comparing the results of Fig. 2 (e) and (f) showed that the two

332   major O1s peaks at 531.0 eV and 532.2 eV have a small shift to 531.8 eV and 533.0

333   eV, respectively. The change of O1s after Cd adsorption suggested that Cd was bound

334   to the oxygen-containing functional groups of biochar (Liu and Fan, 2018).
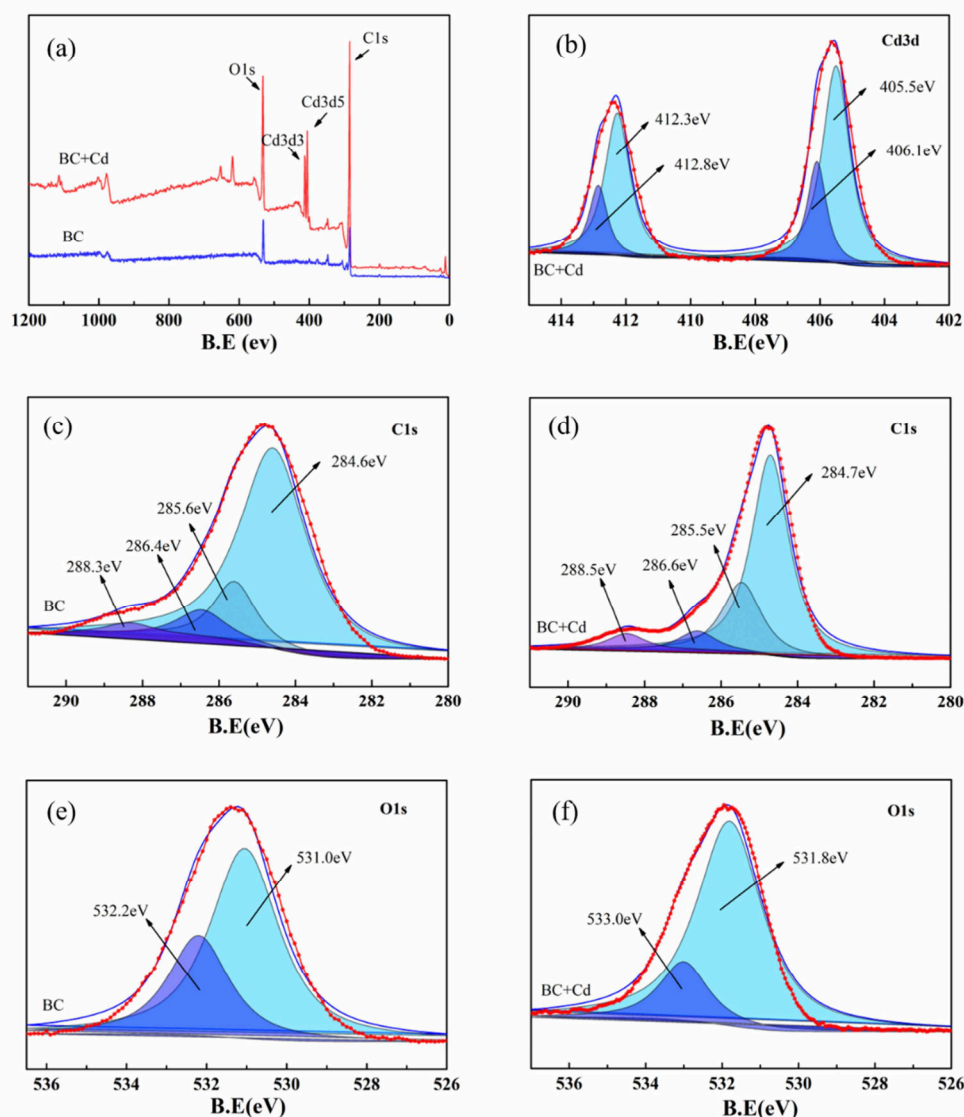
Fig. 2. XPS spectra of pinecone biochar loaded with Cd (a) and high-resolution XPS spectra of the related elements (b-f).

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 $Cd(OH)_2$ 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

15

346 (Cui et al., 2016a). From the results of FT-IR, it was known that the surface of the

347 pinecone biochar contained oxygen-containing functional groups such as -OH and

348 -COOH. And the XPS analysis of O1s further proved that the coordination between

349 Cd^{2+} and oxygen-containing functional groups. Ion exchange is considered to be a

350 common mechanism for the adsorption of metal ions on biochar (Gao et al., 2019; Li

351 et al., 2013). Metal ions Mg^{2+}, K^+, Ca^{2+} were detected on pinecone biochar by energy

352 dispersive X-ray spectrometer (EDX). Therefore, we speculated that a weak ion

353 exchange occurred during the adsorption of Cd by pinecone biochar. Cation-π

354 interaction is a noncovalent interaction between a cation and a π-donor (Keiluweit and

355 Kleber, 2009). The π-system serves as the π-donor and the ability of aromatic

356 π-system to provide electrons increases with the number of corresponding rings

357 (Wang et al., 2015b). FT-IR showed that the pinecone biochar contained aromatic

358 C=C and C=O which could provide π-donor. Thus, we concluded that the Cd-π

359 interaction occurs in pinecone biochar. By comprehensive comparison, we believed

360 that coprecipitation and surface complexation were the main mechanisms for Cd

361 adsorption by pinecone biochar. In contrast, cation-π interaction and ion exchange

362 were relatively insignificant.
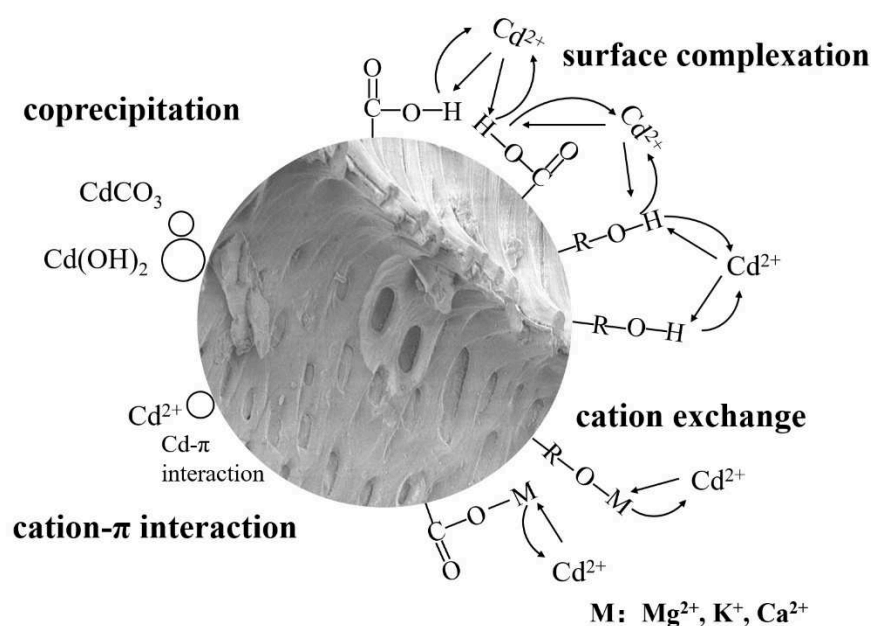
363

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

365 **4. Conclusions**

366   In this study, we explored a novel pinecone biochar with a high Cd(II) adsorption

367 capacity of 92.7 mg g^{-1} and studied the adsorption equilibrium isotherm and

368 adsorption kinetics of the pinecone biochar. The experimental adsorption isotherm

369 results indicated that the adsorption behaviour of Cd(II) onto the pinecone biochar

370 fitted the Tóth model, signifying that there was great affinity between Cd(II) and

371 pinecone biochar, the adsorption process was favourable, and the adsorption

372 behaviour was highly heterogeneous. The adsorption kinetics showed that the

373 adsorption process of Cd(II) by the pinecone biochar fitted the pseudo-second-order

374 kinetic model and that the adsorption process was mainly controlled by a

375 chemisorption. And the main mechanisms of Cd adsorption were coprecipitation and

376 surface complexation. The detailed analysis demonstrated that coprecipitation

377 occurred mainly through $Cd(OH)_2$ and $CdCO_3$. We believe that the prepared pinecone

378 biochar was an economical and effective adsorbent for Cd and had a huge potential to

379 remove heavy metal contamination in aqueous solution. We are exploring the

380 potential for testing the real sample and scaling up in the field to evidence the impact

381 for effective remediation.

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References:

Alexis, M.A., Rasse, D.P., Rumpel, C., Bardoux, G., Péchot, N., Schmalzer, P., Drake, B., Mariotti, A., 2007. Fire impact on C and N losses and charcoal production in a scrub oak ecosystem. Biogeochemistry 82, 201-216.

Bashir, S., Zhu, J., Fu, Q., Hu, H., 2018. Comparing the adsorption mechanism of Cd by rice straw pristine and KOH-modified biochar. Environ. Sci. Pollut. Res. 25, 11875-11883.

Brewer, C.E., Unger, R., Schmidt-Rohr, K., Brown, R.C., 2011. Criteria to Select Biochars for Field Studies based on Biochar Chemical Properties. BioEnergy Research 4, 312-323.

Cheng, Q., Huang, Q., Khan, S., Liu, Y., Liao, Z., Li, G., Ok, Y.S., 2016. Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions. Ecol. Eng. 87, 240-245.

Cui, X., Fang, S., Yao, Y., Li, T., Ni, Q., Yang, X., He, Z., 2016a. Potential mechanisms of cadmium removal from aqueous solution by Canna indica derived biochar. Sci. Total Environ. 562, 517-525.

Cui, X., Hao, H., Zhang, C., He, Z., Yang, X., 2016b. Capacity and mechanisms of ammonium and cadmium sorption on different wetland-plant derived biochars. Sci. Total Environ. 539, 566-575.

Dawood, S., Sen, T.K., Phan, C., 2017. Synthesis and characterization of slow pyrolysis pine cone bio-char in the removal of organic and inorganic pollutants from aqueous solution by adsorption: Kinetic, equilibrium, mechanism and thermodynamic. Bioresour. Technol. 246, 76-81.

Elaigwu, S.E., Rocher, V., Kyriakou, G., Greenway, G.M., 2014. Removal of Pb2+ and Cd2+ from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of Prosopis africana shell. J. Ind. Eng. Chem. 20, 3467-3473.

Gao, L.Y., Deng, J.H., Huang, G.F., Li, K., Cai, K.Z., Liu, Y., Huang, F., 2019. Relative distribution of Cd2+ adsorption mechanisms on biochars derived from rice straw and sewage sludge. Bioresour. Technol. 272, 114-122.

Hall, K.R., Eagleton, L.C., Acrivos, A., Vermeulen, T., 1966. PORE- AND SOLID-DIFFUSION KINETICS IN FIXED-BED ADSORPTION UNDER CONSTANT-PATTERN CONDITIONS. Ind. Eng. Chem. Fundam. 5, 212-+.

Han, X., Liang, C.F., Li, T.Q., Wang, K., Huang, H.G., Yang, X.E., 2013. Simultaneous removal of cadmium and sulfamethoxazole from aqueous solution by rice straw biochar. J. Zhejiang Univ.-Sci. B 14, 640-649.

Ho, Y.S., Ofomaja, A.E., 2006. Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. Biochem. Eng. J. 30, 117-123.

Huang, Y., Xia, S., Lyu, J., Tang, J., 2019. Highly efficient removal of aqueous Hg2+ and CH3Hg+ by selective modification of biochar with 3-mercaptopropyltrimethoxysilane. Chem. Eng. J. 360, 1646-1655.

Igalavithana, A.D., Lee, S.-E., Lee, Y.H., Tsang, D.C.W., Rinklebe, J.r., Kwon, E.E., Ok, Y.S., 2017. Heavy metal immobilization and microbial community abundance by vegetable waste and pine cone biochar of agricultural soils. Chemosphere 174, 593-603.

Jain, R.B., 2020. Cadmium and kidney function: Concentrations, variabilities, and associations across various stages of glomerular function. Environ. Pollut. 256.

Jarup, L., Akesson, A., 2009. Current status of cadmium as an environmental health problem. Toxicol. Appl. Pharmacol. 238, 201-208.

Jing, F., Chen, C., Chen, X., Liu, W., Wen, X., Hu, S., Yang, Z., Guo, B., Xu, Y., Yu, Q., 2020. Effects of wheat straw derived biochar on cadmium availability in a paddy soil and its accumulation in

435   rice. Environ. Pollut. 257.

436   Jing, X.R., Wang, Y.-Y., Liu, W.-J., Wang, Y.-K., Jiang, H., 2014. Enhanced adsorption performance of
437   tetracycline in aqueous solutions by methanol-modified biochar. Chem. Eng. J. 248, 168-174.

438   Keiluweit, M., Kleber, M., 2009. Molecular-Level Interactions in Soils and Sediments: The Role of
439   Aromatic π-Systems. Environ. Sci. Technol. 43, 3421-3429.

440   Kim, W.-K., Shim, T., Kim, Y.-S., Hyun, S., Ryu, C., Park, Y.-K., Jung, J., 2013. Characterization of
441   cadmium removal from aqueous solution by biochar produced from a giant Miscanthus at different
442   pyrolytic temperatures. Bioresour. Technol. 138, 266-270.

443   Komkiene, J., Baltrenaite, E., 2016. Biochar as adsorbent for removal of heavy metal ions Cadmium(II),
444   Copper(II), Lead(II), Zinc(II) from aqueous phase. Int. J. Environ. Sci. Technol. 13, 471-482.

445   Li, B., Yang, L., Wang, C.-q., Zhang, Q.-p., Liu, Q.-c., Li, Y.-d., Xiao, R., 2017. Adsorption of Cd(II)
446   from aqueous solutions by rape straw biochar derived from different modification processes.
447   Chemosphere 175, 332-340.

448   Li, M., Liu, Q., Guo, L., Zhang, Y., Lou, Z., Wang, Y., Qian, G., 2013. Cu(II) removal from aqueous
449   solution by Spartina alterniflora derived biochar. Bioresour. Technol. 141, 83-88.

450   Li, M., Zhang, Z., Li, R., Wang, J.J., Ali, A., 2016. Removal of Pb(II) and Cd(II) ions from aqueous
451   solution by thiosemicarbazide modified chitosan. Int. J. Biol. Macromol. 86, 876-884.

452   Liao, I.H., Huang, J.-H., Wang, S.-L., Cheng, M.-P., Liu, J.-C., 2016. Adsorptions of Cd(II) and Pb(II)
453   in aqueous solution by rice-straw char. Desalin. Water Treat. 57, 21619-21626.

454   Liu, L., Fan, S., 2018. Removal of cadmium in aqueous solution using wheat straw biochar: effect of
455   minerals and mechanism. Environ. Sci. Pollut. Res. 25, 8688-8700.

456   Liu, Z., Zhang, F.-S., 2011. Removal of copper (II) and phenol from aqueous solution using porous
457   carbons derived from hydrothermal chars. Desalination 267, 101-106.

458   Lodeiro, P., Herrero, R., Sastre de Vicente, M.E., 2006. Thermodynamic and kinetic aspects on the
459   biosorption of cadmium by low cost materials: A review. Environ. Chem. 3, 400-418.

460   Manariotis, I.D., Fotopoulou, K.N., Karapanagioti, H.K., 2015. Preparation and Characterization of
461   Biochar Sorbents Produced from Malt Spent Rootlets. Ind. Eng. Chem. Res. 54, 9577-9584.

462   Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C.A., Tonon, G., 2014. Effect of pyrolysis temperature
463   on miscanthus (Miscanthus × giganteus) biochar physical, chemical and functional properties.
464   Biomass Bioenergy 62, 149-157.

465   Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., Pittman, C.U., Jr., 2014. Cadmium and lead
466   remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. Chem. Eng. J. 236,
467   513-528.

468   Mohan, D., Rajput, S., Singh, V.K., Steele, P.H., Pittman, C.U., Jr., 2011. Modeling and evaluation of
469   chromium remediation from water using low cost bio-char, a green adsorbent. J. Hazard. Mater.
470   188, 319-333.

471   Moyo, M., Lindiwe, S.T., Sebata, E., Nyamunda, B.C., Guyo, U., 2016. Equilibrium, kinetic, and
472   thermodynamic studies on biosorption of Cd(II) from aqueous solution by biochar. Res.Chem.
473   Intermed. 42, 1349-1362.

474   Muya, F.N., Sunday, C.E., Baker, P., Iwuoha, E., 2016. Environmental remediation of heavy metal ions
475   from aqueous solution through hydrogel adsorption: a critical review. Water Sci. Technol. 73,
476   983-992.

477   Ofomaja, A.E., Naidoo, E.B., 2011. Biosorption of copper from aqueous solution by chemically
478   activated pine cone: A kinetic study. Chem. Eng. J. 175, 260-270.

20

479 Park, J.-H., Ok, Y.S., Kim, S.-H., Cho, J.-S., Heo, J.-S., Delaune, R.D., Seo, D.-C., 2016. Competitive
480   adsorption of heavy metals onto sesame straw biochar in aqueous solutions. Chemosphere 142,
481   77-83.
482 Peng, H., Gao, P., Chu, G., Pan, B., Peng, J., Xing, B., 2017. Enhanced adsorption of Cu(II) and Cd(II)
483   by phosphoric acid-modified biochars. Environ. Pollut. 229, 846-853.
484 Purkayastha, D., Mishra, U., Biswas, S., 2014. A comprehensive review on Cd(II) removal from
485   aqueous solution. J. Water Process Eng. 2, 105-128.
486 Reguyal, F., Sarmah, A.K., Gao, W., 2017. Synthesis of magnetic biochar from pine sawdust via
487   oxidative hydrolysis of FeCl2 for the removal sulfamethoxazole from aqueous solution. J. Hazard.
488   Mater. 321, 868-878.
489 Tan, G., Sun, W., Xu, Y., Wang, H., Xu, N., 2016. Sorption of mercury (II) and atrazine by biochar,
490   modified biochars and biochar based activated carbon in aqueous solution. Bioresour. Technol.
491   211, 727-735.
492 Usman, A., Sallam, A., Zhang, M., Vithanage, M., Ahmad, M., Al-Farraj, A., Ok, Y.S., Abduljabbar, A.,
493   Al-Wabel, M., 2016. Sorption Process of Date Palm Biochar for Aqueous Cd (II) Removal:
494   Efficiency and Mechanisms. Water, Air, Soil, Pollut. 227.
495 Van Vinh, N., Zafar, M., Behera, S.K., Park, H.S., 2015. Arsenic(III) removal from aqueous solution by
496   raw and zinc-loaded pine cone biochar: equilibrium, kinetics, and thermodynamics studies. Int. J.
497   Environ. Sci. Technol. 12, 1283-1294.
498 Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y., Yang, K., 2015a. Removal of Pb(II), Cu(II), and Cd(II)
499   from aqueous solutions by biochar derived from KMnO4 treated hickory wood. Bioresour.
500   Technol. 197, 356-362.
501 Wang, R.Z., Huang, D.L., Liu, Y.G., Zhang, C., Lai, C., Zeng, G.M., Cheng, M., Gong, X.M., Wan, J.,
502   Luo, H., 2018. Investigating the adsorption behavior and the relative distribution of Cd2+ sorption
503   mechanisms on biochars by different feedstock. Bioresour. Technol. 261, 265-271.
504 Wang, Y., Dong, H., Li, L., Tian, R., Chen, J., Ning, Q., Wang, B., Tang, L., Zeng, G., 2019. Influence
505   of feedstocks and modification methods on biochar's capacity to activate hydrogen peroxide for
506   tetracycline removal. Bioresour. Technol. 291.
507 Wang, Z., Liu, G., Zheng, H., Li, F., Ngo, H.H., Guo, W., Liu, C., Chen, L., Xing, B., 2015b.
508   Investigating the mechanisms of biochar's removal of lead from solution. Bioresour. Technol. 177,
509   308-317.
510 Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., Gao, B., 2013. Removal of Cu, Zn, and Cd from aqueous
511   solutions by the dairy manure-derived biochar. Environ. Sci. Pollut. Res. 20, 358-368.
512 Yang, G.X., Jiang, H., 2014. Amino modification of biochar for enhanced adsorption of copper ions
513   from synthetic wastewater. Water Res. 48, 396-405.
514 Zhang, F., Wang, X., Yin, D., Peng, B., Tan, C., Liu, Y., Tan, X., Wu, S., 2015. Efficiency and
515   mechanisms of Cd removal from aqueous solution by biochar derived from water hyacinth
516   (Eichornia crassipes). J. Environ. Manage. 153, 68-73.
517 Zhang, H., Yue, X., Li, F., Xiao, R., Zhang, Y., Gu, D., 2018. Preparation of rice straw-derived biochar
518   for efficient cadmium removal by modification of oxygen-containing functional groups. Sci. Total
519   Environ. 631-632, 795-802.
520 Zhang, Z., He, S., Zhang, Y., Zhang, K., Wang, J., Jing, R., Yang, X., Hu, Z., Lin, X., Li, Y., 2019.
521   Spectroscopic investigation of Cu2+, Pb2+ and Cd2+ adsorption behaviors by chitosan-coated
522   argillaceous limestone: Competition and mechanisms. Environ. Pollut. 254.

523   Zhou, Q., Liao, B., Lin, L., Qiu, W., Song, Z., 2018. Adsorption of Cu(II) and Cd(II) from aqueous

524   solutions by ferromanganese binary oxide-biochar composites. Sci. Total Environ. 615, 115-122.

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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.

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