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Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar



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ABSTRACT

In this work, a novel engineered biochar prepared through modification with chitosan and pyromellitic dianhydride (PMDA) was investigated as an adsorbent for the removal of heavy metal ions from single metal and mixed-metal solutions (Cd, Cu and Pb). Characterization experiments with FTIR and XPS suggested that the novel modified biochar had more surface functional groups compare to the pristine biochar. Adsorption experiments indicated that the initial pH of the solution influenced the ability of biochars to adsorb heavy metals in single- and multi-metal systems. Moreover, the chitosan-PMDA modified biochar had strong selective adsorption of Cu(II). Mechanism studies showed that chemisorption was the major mechanism for heavy metal removal by the chitosan-PMDA modified biochar. Furthermore, the types of effective functional group for these heavy metal removal were different. The N–C=O group played a dominant role in the process of Pb(II) removal, while several N-containing functional groups and C=C groups participated in the adsorption of Cd(II). The novel engineered biochar had selective adsorption capacity for copper due to the N-containing functional groups, meanwhile abundant carbonyl groups also participated in the removal of copper, and may reduce Cu(II) to Cu(I).

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1. Introduction

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http://dx.doi.org/10.1016/j.jcis.2017.07.069 0021-9797/© 2017 Elsevier Inc. All rights reserved. Water pollution by heavy metals poses a severe threat to the environment and human beings due to the metals' toxicity and non-biodegradability [1]. Heavy metals could be accumulated in living organisms by the food chain, which have become a worldwide environmental problem [2]. To solve this issue, numerous treatment technologies, such as adsorption, chemical oxidation, ion exchange, precipitation, and membrane separation have been developed [3,4]. Most of these methods require a high operational energy and relevant cost; meanwhile, they also bring environmental consequences related to energy consumption [5]. Adsorption has been considered a universal choice for heavy metal removal from wastewater due to its low cost and high efficiency.

Among various sorbents, carbon materials such as biochar and activated carbon (AC) have been widely developed to remove contaminants. Compared with activated carbon, biochar is easier to prepare and is less expensive [6]. The typical price for commercial AC is around US \$ 3000/ton [7]. Although a stable market for biochar has not been established to date, recent reviews have estimated production costs at US \$ 246/ton [8] and US \$ 51–386/ton [9]. Given that finding, biochar is far less expensive than AC. Biochar, a carbonaceous material obtained by heating biomass, has several excellent properties, such as high specific surface area, porous structure and abundant surface functional groups [10]. Many studies have compared the adsorption abilities of biochar and activated carbon (Table S1). Biochar has received increasing attention as a result of its low cost, convenient preparation and high removal capacity [11,12].

With the purpose of further improving the adsorption capacity of biochars, numerous modification approaches have been established. These modified biochars are also referred to as engineered biochars [13–15]. These methods may dramatically change the physicochemical properties of biochars and significantly improve their ability to adsorb contaminants. Trakal et al. prepared an engineered biochar by impregnating with magnetic particles, which exhibited better adsorption capacity for Cd(II) from aqueous solutions than that of the original biochar [16]. Zuo et al. reported a modification using H_2O_2 , by which the Cu(II) adsorption capacity of hydrothermal biochar was significantly enhanced [17].

In this study, a novel modified biochar for the removal of heavy metals from aqueous solution was prepared through modification with chitosan and pyromellitic dianhydride (PMDA). Chitosan, a surface modification agent, has been used to modify surfaces of adsorbents due to the ability of amine and hydroxyl functional groups to bind to various heavy metal ions [18]. The anhydride of PMDA may react with amino groups to form acid amides (-CO-NH-) and carboxyl groups. The remainder of the anhydride group, which is not involved in the reaction, may be hydrolyzed to carboxyl groups [19]. This reaction is illustrated in Fig. S1. It is commonly believed that these functional groups show strong interactions with heavy metals such as ion-exchange, electrostatic attraction and surface complexation [10,20]. The objectives of this work were (1) preparation and characterization of the studied biochars; (2) assessment of the adsorption capability of the biochars to lead, cadmium and copper; and (3) analysis of the adsorption mechanism of the modified biochar.

2. Materials and methods

2.1. Materials

All chemicals and reagents utilized in these experiments were of analytical grade. Solutions were prepared using Milli-Q water. Chitosan (95% acetylation degree) was purchased from Hefei Bomei Biotechnology Co., Ltd. Cadmium nitrate tetrahydrate (Cd $(NO_3)_2-4H_2O)$, copper nitrate trihydrate (Cu $(NO_3)_2-3H_2O)$ and lead nitrate (Pb $(NO_3)_2$) were purchased from Sonopharm Chemical Reagent Co., Ltd. Rice straw was obtained from Changsha, Hunan province, China. The biomass was air-dried, milled and sieved (<1 mm).

2.2. Preparation of adsorbents

The biomass was converted into biochar by pyrolysis in a tube furnace at 450 °C with a heating rate of 5 °C /min under an N_2 atmosphere for 2 h. The pristine biochar is referred to as BC.

The method to synthesize chitosan-modified biochar was based on a previous study by Zhou et al. (2013) [21], and it was amended and optimized in this study. The procedure is as follows: 1.0 g of chitosan was first dissolved in 50 mL acetic acid (2%), and 1.0 g of BC was later added to the solution. The mixtures were stirred for 30 min in a water bath at 50 °C. Then, the biochar-chitosan homogenous suspension was added dropwise into a 300 mL NaOH (1%) solution and kept in the solution for 18 h at room temperature. The chitosan-modified biochar was subsequently washed with Milli-Q water to remove the excess NaOH, oven-dried for 24 h at 60 °C, and later milled and sieved (<1 mm).

Next, 1.5 g PMDA was dissolved in 50 mL dimethyl formamide (DMF), and 0.5 g of the chitosan-modified biochar was added into the solution and stirred constantly for 4.5 h in a water bath at 50 °C. After naturally cooling to room temperature, the materials were washed with DMF, Milli-Q water and NaOH successively, and washed with Milli-Q water to be neutral, and, finally, ovendried for 24 h at 60 °C. The resulting biochar sample is referred to as CPMB.

2.3. Characterization of adsorbents

The morphologies of BC and CPMB were characterized by scanning electron microscopy (SEM) (JEOL JSM-6700. Japan). The Brunauer-Emmett-Teller (BET) surface area and the total pore volume were calculated based on the N₂ adsorption-desorption isotherms measured by a gas sorption analyzer (Quantachrome Quadrasorb SI, USA). Ash content was determined by heating the biochars to 750 °C in air. The X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Rigaku D/max-2500, Japan). The Fourier transform infrared spectroscopy (FTIR) of the samples were measured on a spectrophotometer (Nicolet, Magna 550 spectrometer). Surface chemical composition was confirmed by an ESCALAB 250 Xi X-ray Photoelectron Spectrometer (XPS) (Thermo Fisher, USA).

2.4. Adsorption experiments

In this experiment, 1 g/L standard stock solutions of Cd(II), Cu (II) and Pb(II) were prepared by dissolving specific amounts of Cd (NO₃)₂-4H₂O, Cu(NO₃)₂-3H₂O, and Pb(NO₃)₂ in Milli-Q water. All batch adsorption experiments were performed in 150 mL Erlenmeyer flasks by mixing 1.0 g/L biochar with metal solutions of varying initial concentrations (5-500 mg/L) on a shaker at 150 rpm. The pH values of the solutions were adjusted by adding 0.01 M HNO₃ or 0.01 M NaOH until the desired pH was reached. The concentrations of residual metals were determined by an atomic absorption spectrometer (AAS, PEAA700, USA). The effect of pH on the adsorption of heavy metals was determined by adjusting the pH of the initial metal solution (100 mg/L) to values in the range of 2.0-6.0. The flasks were shaken for 24 h at room temperature. The competitive adsorption tests were conducted with multi-metal aqueous solutions, which contained Cd(II), Cu(II) and Pb(II), by adjusting the pH values from 2.0 to 6.0, with constant metal ion concentrations of 100 mg/L. Kinetic experiments were performed at different time intervals, ranging from 5 to 1440 min, with 100 mg/L metal solutions at pH 5.0. Adsorption isotherms were determined by shaking suspensions at pH 5.0 for 24 h,

with initial metal concentrations varying between 5 and 500 mg/L. Adsorption thermodynamic studies were conducted by holding experimental temperatures at 298, 303 and 308 K.

The amount of adsorbate removed by the adsorbent, q (mg/g) was calculated using the following equation:

$$q = \frac{C_0 - C_e}{m} \times V \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) represent the initial and equilibrium concentration of the heavy metal, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characteristics of the studied biochars

SEM images of the sorbents are shown in Fig. 1. The particle morphologies of BC and CPMB were different. It was observed that the external morphology of CPMB was rougher than that of BC. A number of tiny and fine pores were observed in the SEM image of CPMB. These differences demonstrated that these modifications changed the structure of BC.

An analysis of the XRD spectrum (Fig. S2) provided information about the crystalline structure and the phase composition of the biochars. Several peaks were detected in the XRD spectrum, suggesting that there were a quantity of mineral crystals presented in the biochars. After modification, KCl and CaCO₃ disappeared, which indicated that the modification changed the phase composition of BC.

The surface area of BC/CPMB was $32.1/62.6 \text{ m}^2/\text{g}$ and the pore volume was $0.038/0.096 \text{ cm}^3/\text{g}$ (Table S2), which indicated that the surface area and porous structure of the biochar improved significantly after modification. Generally, relatively greater structured porosity of the adsorbents could achieve a better adsorption performance [22]. The ash content of BC was 32.1%, and that of CPMB was 22.6%. The modification decreased the ash content significantly, which was due to the disappearance of KCl and CaCO₃.

The functional groups of biochars are connected with their physicochemical properties, which impact their adsorption abilities [15,20]. In this study, FTIR analysis was used for detecting the functional groups. The functional groups of CPMB were different from those of BC (Fig. S3). Typically, the broad and strong band of approximately 3430 cm^{-1} might be assigned to be overlapping N-H and O-H stretching bands, whereas the peak at 2925 cm⁻¹ might be assigned to the aliphatic C–H group [23,24]. The peak at 1597 cm⁻¹ might be explained by the blueshift of the peak at \sim 1720 cm⁻¹ which was characteristic for C=O stretches of carboxyl groups and carbonyl groups [25-29]. This peak might be shifted by a change in protonation, the proximity to other atoms, steric hindrances, hydrogen bonding strengths, local dielectric strength, or a change in polarity [26]. For BC, the peaks at 1420 cm⁻¹ and 875 cm⁻¹ demonstrated the presence of carbonate [23,29], which was consistent with the result of the XRD spectrum analysis. The peak at 1385 cm⁻¹ might be assigned to an -OH



Fig. 1. Scanning electron microscopic images of BC (a, c) and CPMB (b, d).

bending vibration or a COO— stretching vibration [26,27,30]. These two peaks indicated the presence of carboxyl groups at the surface of CPMB. The peaks at 534 cm⁻¹ and 460 cm⁻¹ may be attributed to the presence of aluminum salts [29]. The peaks at about 1093 cm⁻¹ were attributed to the stretching vibration of C—O and C—C [29]. The peak at 797 cm⁻¹ was assigned to —CH twisting [31].

The elemental composition of BC and CMPB was shown in the XPS survey spectra (Fig. S4). The atomic percentages of C, N and O were obtained from XPS characterization analysis (Table S3). The N content of BC and CPMB was 2.49% and 9.35%, respectively, and the O content of BC and CPMB was 22.57% and 27.92%, respectively. This result indicated that large quantities of amino groups and O-containing functional groups were introduced onto the biochar surface by modification. Furthermore, the XPS spectra of C1s and N1s for the biochars (Fig. S5) indicated that the surface of the CPMB was modified with N-containing and O-containing functional groups. The peak approximately 400 eV could be attributed to N1s, which was comprised of N-H (399.3 eV), N-C=O (399.9 eV) and N-C (400.6 eV) [20,24,32]. The C1s peak of BC was deconvoluted into five peaks, and deconvolution of the C1s peak for CPMB showed the presence of six peaks. Those signals could be fitted well to five components: C--C bonds near 284.2 eV and 285.4 eV, C=C bonds near 284.7 eV, hydroxyl groups (C-OH) near 286.5 eV, carbonyl groups (C=O) near 288.0 eV, and carboxyl groups (COOH) near 289 eV [1,24,33,34]. The peaks for carboxyl groups were only observed in CPMB, which indicated that anhydride modification played a significant role in the amount of carboxyl groups on the CPMB surface.

3.2. Effects of pH

Changes in the initial pH of the solution considerably influenced Pb(II), Cd(II) and Cu(II) removal by these adsorbents (Fig. 2). In this study, the adsorption capacities for heavy metals was very low at pH below 3.0, and increased gradually with increasing pH. The influence of pH on heavy metal adsorption can be attributed to the surface charge of the biochars. At lower pH, H⁺ binds with the surface functional groups, making these groups unavailable for metal ion bindings. When increasing the pH value, deprotonation makes the functional groups available to co-ordinate with metal ions, leading to greater adsorption ability [35]. When the pH was higher than 5.0, it had little effect on the removal capacity of these heavy metals, which was similar to the findings of Yao et al. [36]. In these researchers' study, copper adsorption capacity increased when the pH of the solution increased from 2.0 to 5.0. and no more significant change occurred above pH 5.0 [36]. This finding may be explained by other theories; for instance, precipitation might influence the metal adsorption [1]. In addition, the Pb(II) removal capacities of BC, chitosan-modified biochar and CPMB were 10.33 mg/g, 10.48 mg/g and 11.43 mg/g respectively. There was only a slight increase in the lead adsorption due to the modifications. However, the Cd(II)/Cu(II) removal abilities for BC and chitosan-modified biochar were 23.29/36.07 mg/g and 26.35/46.96 mg/g, respectively. There were different degrees of improvement for Cd(II) and Cu(II) uptakes, which indicated that the biochar modification with chitosan was successful. The Cu(II) adsorption capacity of CPMB was 70.28 mg/g. Comparing the adsorption capacities for Cu(II), there was a significant improve-



Fig. 2. Effect of initial solution pH value on single metal adsorption for BC (a), forchitosan-modified biochar (b), for CPMB (c) and competitive adsorption for CPMB (d).

ment due to modification with PMDA, which suggested that the biochar modification to enhance adsorption capacity was successful.

3.3. Competitive adsorption

The influence of pH on competitive adsorption was similar to that of the respective single metal adsorption, but the removal abilities of these heavy metals declined with different degrees (Fig. 2d). In general, the Cu uptake by CPMB decreased approximately 13.78%, and the decrease in adsorption capacities for Pb and Cd was 48.20% and 68.05%, respectively, which indicated that more pronounced pH effects occurred for Pb and Cd removal in the multi-metal system.

The distribution coefficient (K_d) was used to analyze the selectivity of CPMB for heavy metals. The equation is stated as [37]:

$$K_{\rm d} = \frac{V \cdot (C_0 - C_{\rm e})}{m \cdot C_{\rm e}} \tag{2}$$

where C_0 and C_e (mg/L) represent the initial and equilibrium concentrations of metal ions, respectively; V(L) is the volume of solution; and m (mg) is the mass of the adsorbent.

A selectivity coefficient (α) for the binding of a particular adsorbate in the presence of interfering ions is defined in Eq. (3) as [37]:

$$\alpha = K_{\rm d}({\rm T})/K_{\rm d}({\rm I}) \tag{3}$$

where K_d (T) is the K_d value of the targeted metal (Cu in this case) and K_d (I) is the K_d value of the other metal in the multi-metal solutions (Pb or Cd here). Larger value of α indicates greater selectivity toward Cu than Pb or Cd. The calculated K_d and α values of CPMB at various pH values are listed in Table 1.

Evidently, K_d values (except K_d (Pb)) increased at low pH, and with increasing pH no further notable changes were observed. This finding corresponds to the effect of pH on the removal capacity, such that the increase in K_d can be explained by deprotonation effects. With increasing pH, more adsorption sites were activated, and more metal ions were available to migrate from the solution to the surface of the biochar [37].

In addition, CPMB showed more prominent selectivity for Cu over Cd than for Cu over Pb at each pH value. According to α values and single metal adsorption onto CPMB, Cu presented great affinity for CPMB, but Pb and Cd showed strong adsorption inhibition in the multi-metal system. These results showed better adsorption capacities for Cu than Cd or Pb, indicating that CPMB had selective adsorption for Cu.

3.4. Adsorption kinetics

рН 2 3

4

5

6

Adsorption kinetic model is commonly used to estimate the rate of adsorption and offers valuable insights for the adsorption mechanism [38]. Fig. 3 presents the effects of contact time on heavy metal adsorption onto CPMB. The results showed that rapid adsorption rates occurred in the first several hours, and later decreased. The adsorption equilibriums were reached within 24 h. That finding indicated that the adsorption occurred in two step, consisting of rapid adsorption of metal ions that had migrated

 Table 1

 Distribution and selectivity coefficient of competitive adsorption

1.4242

1.7412

1.7809

ectivity coefficient of competitive adsorption.							
<i>K</i> _d (Cu)	$K_{\rm d}({\rm Cd})$	$K_{\rm d}({\rm Pb})$	α_{Cd}^{Cu}	α_{Pb}^{Cu}			
0.1021	0.0134	0.0074	7.6157	13.7905			
0.6551	0.0459	0.0139	14.2719	47.1281			

0.0328

0.0506

0.0530

0.0653

0.1033

0.0991

80 60 qt (mg/g) 40 20 Pesudo-first-order 0 Pesudo-second-orde 200 400 600 800 1000 1200 1400 1600 0 t (min)

Fig. 3. Adsorption kinetics of lead (■), cadmium (●) and copper (▲) onto CPMB.

to the adsorbent surface, and slow diffusion in the biochar interior. In addition, the first step occurred within 1 h, 2 h and 4 h for Pb(II), Cd(II) and Cu(II), respectively, which could be attributed to the surface properties of CPMB [39]. There may be more effective surface adsorption sites for Cu than for Cd or Pb on CPMB, meaning that the biochar could uptake more copper ions onto the surface in the first step, which required more time.

Pseudo first-order (Eq. (4)) and pseudo second-order (Eq. (5)) kinetic models were used to explicate the adsorption mechanism of CPMB for heavy metal removal [40].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{5}$$

where q_t and q_e (mg/g) represent adsorption capacities at time t (min) and at equilibrium, and k_1 (1/min) and k_2 (g/ (mg/min)) are the rate constants for the pseudo first-order and pseudo second-order adsorption kinetics, respectively. The results of the adsorption kinetics experiment are presented in Table 2.

The correlation coefficients (R^2) for the pseudo first-order kinetic model were 0.9631, 0.9511 and 0.9808 for Pb(II), Cd(II) and Cu(II), respectively. The model worked well only for the first several hours of the adsorption process (Fig. 3). This result suggested that the pseudo first-order model did not fit well with the experimental data, and may not be sufficient to elucidate the mechanism of heavy metal adsorption.

For the pseudo second-order model, the values of R^2 for Pb(II), Cd(II) and Cu(II) were 0.9914, 0.9970 and 0.9968, respectively. These values were higher than the results of pseudo first-order model. Compared to the pseudo first-order model, the pseudo second-order model simulated the experimental kinetic data more closely. Accordingly, the adsorption mechanism of Pb(II), Cd(II) and Cu(II) onto CPMB might depend on the adsorbent and metal ions.

21.8108

16.8560

17.9704

43.4220

34.4116

33.6013

2	G	n
J	υ	υ

Table 2						
Kinetic parameters for adsorption	of Pb(II)	Cd(II) and Cu	(II)	onto	CPMB.

Metal	Pseudo-First-Orde	r		Pseudo-Second-Order		
	<i>k</i> ₁ (1/min)	$q_{\rm e}({ m mg/g})$	R^2	$k_2(g/(mg min))$	$q_{\rm e}({ m mg/g})$	R^2
Pb	0.0627	8.2625	0.9631	0.0116	8.6161	0.9914
Cd	0.0560	24.6767	0.9511	0.0035	25.7800	0.9970
Cu	0.0273	66.7432	0.9808	0.0005	71.4019	0.9968

The adsorption process might involve chemisorption related to valence forces through electron exchange or sharing [41].

In this study, the values of k_2 were 0.0116, 0.0035 and 0.0005 for Pb(II), Cd(II) and Cu(II), respectively. Fig. 3 shows that Cu(II) adsorption required more time to reach equilibrium, compared to Cd(II) or Pb(II) adsorption. This finding indicated that the lower the value of k_2 is, the longer the time required to reach equilibrium in the adsorption. The differences between the k_2 values were primarily due to the differences in the adsorption rates, which were dependent on the properties of the biochar [42].

3.5. Adsorption isotherms

In this study, the Freundlich isotherm (Eq. (6)) and the Langmuir isotherm (Eq. (7)) were used to model the adsorption behavior [43].

$$q_e = K_F C_e^{1/n} \tag{6}$$

$$q_{\rm e} = \frac{K_{\rm L} q_{\rm m} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{7}$$

where $K_{\rm F}$ is the adsorption coefficient, and 1/n represents the surface heterogeneity or adsorption intensity, a value of 1/n < 1 is an indicative of a normal Freundlich isotherm, while a value of 1/n > 1 indicates cooperative adsorption [44]. $C_{\rm e}$ is the equilibrium concentration of metal ions (mg/L), $q_{\rm m}$ is the maximum adsorption capacity (mg/g), and $K_{\rm L}$ denotes the Langmuir constant (L/mg).

Analysis of Fig. 4 demonstrated that the Langmuir model fit better than the Freundlich model, implying that the monolayer adsorption played a significant role in the metal removal mechanism. According to the values of q_m (Table 3), CPMB had higher affinity and adsorption ability for Cu than for Cd(II) or Pb(II).

The dimensionless separation parameter, R_L (Eq. (8)), may be applied for describing the adsorption characteristics of the Langmuir isotherm model.

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_0} \tag{8}$$

where K_L is the Langmuir constant, and C_0 is the initial metal ion concentration (mg/L). The calculated R_L value refers to the isotherm type, either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The lowest and highest concentrations were used for C_0 in the calculations [45]. In this study, the R_L values remained in the range of 0-1 (Table 3), indicating that the adsorption of metal ions was favorable for all studied temperatures.

3.6. Thermodynamic analysis

Temperature is commonly considered an important factor for adsorption. Usually, entropy and energy changes should be considered in adsorption procedures. The change in free energy ΔG^{o} , enthalpy ΔH^{o} and entropy ΔS^{o} associated with the adsorption process were calculated by the following equations [22]:

$$\Delta G^{\rm o} = -RT \ln K_{\rm L} \tag{9}$$



Fig. 4. Adsorption isotherms of lead (a), cadmium (b) and copper (c) onto CPMB.

Table 3	
Langmuir and Freundlich isotherm parameters for adsorption of Pb(II) Cd(II) and Cu(II) onto	CPMB

Metal	Т	Freundlich model				Langmuir model		
	K _F		1/n	1/n R ²		RL	$q_{ m m}$	R^2
Pb	298	5.0407	0.1181	0.9147	0.5221	0.2770-0.0038	9.24	0.9343
	303	5.4022	0.1498	0.9091	0.2730	0.4228-0.0073	11.91	0.9262
	308	5.8881	0.1608	0.8926	0.2126	0.4847-0.0093	13.93	0.9423
Cd	298	9.9117	0.2011	0.8587	0.1205	0.6240-0.0163	30.12	0.9901
	303	9.9606	0.2207	0.9022	0.0978	0.6716-0.0200	33.89	0.9797
	308	10.3926	0.2324	0.9205	0.0808	0.7123-0.0242	38.24	0.9854
Cu	298	24.61	0.2326	0.8611	0.0956	0.6766-0.0205	89.69	0.9947
	303	28.61	0.2167	0.8652	0.1487	0.5736-0.0132	92.19	0.9959
	308	34.95	0.1916	0.8561	0.2193	0.4770-0.0090	96.11	0.9933

$$\ln K_{\rm L} = -\frac{\Delta G^{\rm o}}{RT} = -\frac{\Delta H^{\rm o}}{RT} + \frac{\Delta S^{\rm o}}{R} \tag{10}$$

where *R* is the gas constant (8.314 J/(mol K)), *T* is the absolute temperature (K), K_L is the Langmuir constant (L/mol), ΔH° is the enthalpy change (J/mol), and ΔS° is the entropy change (J/ (mol K)). ΔH° and ΔS° can be calculated from the plot of ΔG° versus *T*. The thermodynamic parameters are presented in Table 4.

It was apparent that the adsorption abilities of Pb(II), Cd(II) and Cu(II) were enhanced with increasing temperature. The negative values of ΔG° for Pb(II), Cd(II) and Cu(II) at all temperatures indicated that the adsorption processes were spontaneous under the experimental conditions. In addition, ΔG° became more negative at higher temperature, which suggested that the degree of spontaneity increased with rising temperature, which is primarily due to chemisorption rather than physisorption [46,47]. The positive values of ΔH° for Pb(II), Cd(II) and Cu(II) indicated that the adsorption processes were endothermic. A potential reason for the positive ΔH^{o} values was that the hydration sheaths were deprived to a certain degree when metal ions were dissolved in the aqueous solution prior to adsorption, and the endothermicity of metal ion desolvation was greater than the exothermicity of metal ion adhesion to the surface of CPMB [48]. The positive values for ΔS° indicated that randomness of the solid/liquid interface improved during the process of adsorption, and also suggested that the interaction of functional groups with metals might change the structure of CPMB [38].

3.7. Adsorption mechanisms

Table 4

The adsorption mechanisms for heavy metals on modified biochar usually involve the comprehensive influence of several types of interactions, including complexation, ion exchange, physical adsorption, and micro-precipitation [20,49]. According to the results of the kinetic and isotherm experiments, chemisorption on the monolayer surface played a dominating role in Pb(II), Cd (II) and Cu(II) removal. It is widely believed that the major factor influencing metal ion adsorption is the chemical interaction

between metal	l ions and	the	surface	functional	groups	of	biochar	1
[15,49].								

Fig. 5d–f shows the N1s spectra of the modified biochar after metal adsorption. The peak for N—C=O significantly changed after Pb(II) adsorption. This finding suggested that N—C=O might be an important and effective functional group for lead removal. Furthermore, these specific peaks shifted to higher binding energy after Cd (II) and Cu(II) adsorption. The shift in these peaks was likely attributed to the formation of XN- metal complexes (XN is the abbreviation for N-containing functional groups). That was, the shared bond between the N atom and metal obtained a lone pair of electrons from the N atom, which decreased the electron cloud density on the N atom, and increased the binding energy [24].

Similar result was obtained for the C1s spectrum of the CPMB after cadmium adsorption (Fig. 5b). The specific peaks for C=C shifted to higher binding energy after adsorption. It was attributed to the π -complexation, which involved the formation of Cd- π binding between Cd and C=C. That was to say, the metal could form the usual σ bonds with its s-orbitals and its d-orbitals could back-donate electron density to the antibonding π -orbitals of the C=C double bond [50–53]. This finding indicated that C=C might play an important role in the cadmium adsorption. In comparison to the C1s spectrum of the CPMB before adsorption (Fig. S3c), the peaks did not change significantly after Pb(II) adsorption, which indicated that these C-containing functional groups might not have a remarkable effect on lead removal. Conversely, the C1s spectrum of the CPMB after copper adsorption (Fig. 5c) appeared different from the spectrum prior to adsorption. The peaks for C=O (N-C=O and -COOH) were distinctly shifted, but there was no obvious change in the C=C peaks. It demonstrated that C=O (N-C=O and -COOH) functional groups were the major factor for copper adsorption.

The XPS spectra of Cu2p in the CPMB after the adsorption of copper is shown in Fig. S4. Cu peaks are detected at binding energies of approximately 933 eV for Cu(I), and 953 eV for Cu(II) [54,55]. This reduction process might be explained by the existence of large quantities of carbonyl groups and the positive potential of Cu(II) [42].

Thermodynamic parameters of Pb(II), Cd(II) and Cu(II) adsorption onto CPMB.							
Metal	<i>T</i> (K)	$\Delta G^{\rm o}$ (kJ/mol)	$\Delta H^{\rm o}$ (kJ/mol)	ΔS^{o} (J/(mol K))			
Pb	298 303 308	-5.5082 -6.2451 -6.7450	31.39	123.93			
Cd	298 303 308	8.4364 8.8750 9.3311	18.22	89.45			
Cu	298 303 308	-4.4876 -5.6758 -6.7643	63.37	227.78			



Fig. 5. XPS spectra of the element scan of C 1s in the CPMB after the adsorption of lead (a), cadmium (b) and copper (c) and N 1s in the CPMB after the adsorption of lead (d), cadmium (e) and copper (f).

Mineral components, including potassium (K), calcium (Ca), carbonate, and phosphate, in biochar were also responsible for metal sorption from water. These mineral components could exchange or precipitate with heavy metals [56]. From the XRD results, it was observed that KCl and CaCO₃ disappeared after modification. This effect resulted in a decline of ions participating in the reactions of exchange or precipitation, which might influence the ability of biochar to remove heavy metals. Considering that there might only be one functional group of CPMB (N–C=O) playing a

significant role in the Pb adsorption, the decline of ions could explain why there was only a slight increase in the lead adsorption after the modification.

In general, mechanism analysis showed that chemisorption was the major mechanism for Pb(II), Cd(II) and Cu(II) removal by CPMB, and that the mineral components of CPMB were also responsible for metal removal. Furthermore, the types of effective functional groups for heavy metal removal were different. In the process of lead adsorption, only N—C=O played a significant role, while other functional groups did not present an obvious effect. This finding was likely the reason why the removal capacity for Pb(II) was lower than that of Cd(II) or Cu(II). Several N-containing functional groups and C=C groups worked for the cadmium removal. The CPMB had better adsorption capacity for Cu(II) due to the N-containing functional groups. Meanwhile, abundant carbonyl groups also participated in the copper removal, and might reduce Cu(II) to Cu(I). The adsorption mechanism was schematically illustrated in the Graphical Abstract.

4. Conclusions

In this work, a novel engineering biochar was successfully synthesized through modification with chitosan and PMDA and was developed for the removal of heavy metals from aqueous solutions. The optimum pH for the adsorption of heavy metals was 5.0. Compared to BC, the Pb and Cd removal abilities of CPMB were improved by approximately 10%, and the Cu removal ability of CPMB (70.28 mg/L) was 2.5 times higher than that of BC (26.35 mg/L). Adsorption experiments showed that CPMB had strong selective adsorption ability to Cu in multi-metal systems. The pseudo second order model and the Langmuir model were better for describing the kinetics and isotherms for heavy metal adsorption onto CPMB, respectively. Accordingly, chemisorption on the monolayer surface played a dominant role in Pb(II), Cd(II) and Cu(II) removal. Moreover, this study showed that different functional groups worked for the removal of different metals. Adsorption of Pb(II) was influenced by N–C=O, while N-containing functional groups and C=C groups complexed with cadmium for removal of this metal. The CPMB had better adsorption capacity for Cu(II) due to its abundant carbonyl groups and N-containing functional groups. The results obtained in this study suggested that CPMB was a high-efficiency adsorbent for heavy metal removal from aqueous solutions, specifically for Cu. Compared to the maximum adsorption capacities of other adsorbents [3,42,57], CPMB had a greater capacity for Cu removal. Previous studies have shown that the modified biochar could be used for the removal of heavy metals [1,13,39,42]. The current work improves our understanding of the interaction between heavy metals and the functional groups on biochar, and demonstrates that the groups are important for the control of environmental pollution. Future research could be focused on the mechanism for the selectivity of these functional groups for specific heavy metals, and the practical application of CMPB to treat actual industrial wastewater.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2017.07.069.

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