

Kinetics of Cu(II) and fulvic acid adsorption on modified biochar derived from rice husk

Shuai Tang, Lujian Lin, Xuesong Wang*, Anxin Feng, Xue Feng, Jing Kong

Jiangsu Key Laboratory of Marine Bioresources and Environment, Jiangsu Ocean University, Lianyungang, Jiangsu, 222005, China, Tel. +86-518-8589-5408; Fax: +86-518-8589-5409; email: snowpine1969@126.com. (X.S. Wang), Tel. +86-15151196592; email: tangshuaiwudi@yeah.net (S. Tang), Tel. +86-15312134764; email: 317326034@qq.com (L. Lin), Tel. +86-18360577867; email: 1219263645@qq.com (A. Feng), Tel. +86-18451114297; email: 171547564@qq.com (X. Feng), Tel. +86-15801142129; email: shandongkongjing@163.com (J. Kong)

Received 29 July 2019; Accepted 25 January 2020

ABSTRACT

The kinetics of Cu(II) and fulvic acid (FA) adsorption onto biochar has been investigated. The modified biochar samples derived from rice husks were characterized by scanning electron microscopy equipped with the energy-dispersive X-ray spectroscope and Fourier transform-infrared spectroscopy. Some characteristic parameters, such as specific surface area and zeta potential, were also determined. The optimum condition of Cu(II) adsorption was temperature of 308 K, 2 g L⁻¹ of adsorbent dosage and 25 mg L⁻¹ of FA concentration. The maximum removal efficiencies of Cu(II) ions and FA were almost 81% and 94%, respectively. The experimental data for adsorption of Cu(II) and FA on modified biochar was fitted by various adsorption kinetic models. The results showed that the pseudo-second-order equation was the best-suited model. Elovich equation was consistent with the experimental data suggested chemical interactions between modified biochar and adsorbates. Also, the intraparticle diffusion model fitted the experimental data well, indicating that the process of Cu(II) and FA adsorption was diffusion-controlled. In addition, complexation reactions between FA and Cu(II) promoted the adsorption of adsorbates on modified biochar. The relatively high desorption efficiency proves the strong regeneration capacity of modified biochar.

Keywords: Biochar; Adsorption; Kinetic; Cu(II); Fulvic acid; Complexation

1. Introduction

Due to the health risk of humans and animals, heavy metals pollution has attracted increasing concern. Among heavy metals, copper is generally considered as one of the most harmful, hazardous, and toxic environmental pollutants [1]. Copper ingestion in humans may lead to some bad effects such as hair loss, headache, liver, and kidney damage [2]. Copper ions are discharged from various industries, including mining, metallurgy, chemical manufacturing, steel, printing circuit, electroplating, paints, fertilizers, etc. [3–5]. Some conventional methods are used to remove heavy

metals ions from aqueous solutions, such as chemical precipitation, ion-exchange, filtration, reverse osmosis, electrochemical treatment, membrane separation, adsorption [6–8].

Fulvic acid (FA), a kind of hydrophilic, multi-dispersed, black-brown organic matter, is one of the important components of humic substances, which widely exists in sediments, soil, and water [9]. FA has a strong binding affinity to heavy metals because it contains a variety of active functional groups [10,11]. Adsorption process was emerged as one of the promising techniques due to its low initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances [12]. Activated carbon, having large specific

* Corresponding author.

surface area, microporous structure, high adsorption capacity, is widely used to remove heavy metals. However, the use of activated carbon is limited due to its high cost and low selectivity, which has led many researchers to search for more economic substitutes [12–17].

Biochar, a vital extrinsic carbonaceous component produced by incomplete combustion of fossils and biomass, is considered as a potential adsorbent for pollutants in soils and sediments [18]. In our previous study, we prepared black carbon derived from wheat residue and studied the competitive adsorption of Pb(II), Cu(II) and Cd(II) ions [19]. Zhang et al. [20] highlighted the importance of surface oxygen-containing functional group of biochar derived from biomass wastes in controlling Cu(II) and Cr(III) adsorption. Zhou et al. [21] reported the adsorption of Pb, Cd, and Cu ions under different pyrolysis conditions using the tobacco stem biochar. The results showed that the main adsorption mechanism was surface complexation.

However, to our knowledge, in the presence of FA, the adsorption behavior of Cu(II) on modified biochar derived from rice husk has not been investigated. In this study, the adsorption kinetics of Cu(II) on modified biochar was studied, and the effects of reaction temperature, biochar dosage, and FA concentration on the adsorption kinetics were also discussed. The adsorption kinetic models of FA in binary solution by modified biochar were analyzed as well. In addition, the desorption behaviors of Cu(II) in single and binary (mixed FA with copper ions) solutions were explored using batch desorption experiments.

2. Materials and methods

2.1. Materials and reagents

Copper nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$], hydrochloric acid (HCl), potassium hydroxide (KOH), and FA were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD and are of A.R. grade. Biochar samples were prepared by the carbonization of rice husk for 12 h under 50°C and the presence of N_2 conditions. About 10 g of residues collected were treated in 500 mL of 0.1 mol L^{-1} HCl solution to remove carbonates and other impurities, stirred for 10 min and soaked for 24 h in a plastic container. The supernatant was discarded, and the residues were washed with ultra-pure water several times to pH neutral. Finally, the residues were dried at 100°C for 12 h in the oven and pass through 100-mesh sieve to obtain rice husk derived modified biochar.

2.2. Characterization

The functional groups of modified biochar samples used were analyzed using Fourier transform infrared spectroscopy (FTIR, Nicolet-iS10, America). The powders were blended with IR-grade KBr in an agate mortar and pressed into the table. The surface morphology and elemental composition of modified biochar before and after adsorption were determined using the scanning electron microscope with energy dispersive X-ray analysis (SEM-EDS, SUPRA-55, Germany) at 15 keV.

The Brunauer–Emmett–Teller (BET) specific surface area, total pore volume, and average pore diameter of biochar were determined from N_2 adsorption at 77 K using Specific

Surface and Pore Size Analyzer (3H-2000PM1, China). The zero point of charge (pH_{ZPC}) of modified biochar was measured by zeta potential analyzer (Anton Paar, Austria) [22].

2.3. Experimental

The concentration of 500 mg L^{-1} divalent Cu and FA stock solutions were prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and FA solid, respectively. The value of initial solution pH was adjusted with 0.1 mol L^{-1} HCl or 0.05 mol L^{-1} KOH solution. All experiments were conducted in duplicate.

The following variables on Cu(II) adsorption kinetics were studied:

- *Effect of reaction temperature:* The effect of reaction temperature on the adsorption rate by contacting a fixed dosage of biochar (2 g L^{-1}) with fixed initial Cu(II) ion concentration (10 mg L^{-1}) at initial pH 5.0 using a range of reaction temperature (288 K, 298 K, and 308 K). The experiments were performed in a water bath constant temperature oscillator and rotated shaken at 150 rpm for given time intervals (5, 10, 20, 40, 60, 90, 120, 210, 300, 390, and 480 min). Finally, solutions of 2 mL aliquots were passed through $0.22 \mu\text{m}$ filters to remove biochar particles, and Cu(II) ion concentration was determined by atomic absorption spectrometry (TAS-990, China).
- *Effect of adsorbent dosage:* The effect of adsorption dosage on the adsorption rate was studied at 298 K and a range of adsorbent dosages (2 and 4 g L^{-1}).
- *Effect of FA concentration:* The effect of FA concentration (0, 2, 5, and 10 mg L^{-1}) on the adsorption rate was also studied at 298 K. FA concentration was estimated using a UV-2000 UV-visible spectrophotometer (Unico Instrument Co., Ltd, Shanghai) at 254 nm [23]. In order to clarify the interaction effects between Cu(II) and FA, the other three FA concentrations (15, 20, and 25 mg L^{-1}) were added and the concentration of Cu(II) was determined by sampling at equilibrium time.

Desorption tests were conducted after Cu(II) adsorption equilibrium in single and binary solutions. The experiments were started with dried modified biochar (0.2 g) previously loaded with known amounts of Cu(II) or FA-Cu, and five different solutions (H_2O , 0.1 mol L^{-1} Na_2CO_3 , 0.1 mol L^{-1} HCl, 0.1 mol L^{-1} H_2SO_4 , and 0.1 mol L^{-1} HNO_3) were used as desorption medium. Each experiment was performed with 100 mL of solution for 12 h.

2.4. Calculation

The adsorption capacities of Cu(II) and FA by modified biochar adsorbent in aqueous solution was calculated based on the following Eq. (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}); V is the volume of adsorption solution (L); C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), respectively; and m is the mass of modified biochar (g).

3. Results and discussion

3.1. Characterization of biochar

The scanning electron microscopy equipped with the energy-dispersive X-ray spectroscopy (SEM–EDS) images of the modified biochar samples before and after contact with Cu(II) are showed in Fig. 1. The structure of modified biochar is obviously irregular and granular. There are some

small holes on the surface of modified biochar. The EDS spectrum of the modified biochar before contact with Cu(II) (Fig. 1e) exhibited distinct peaks of C, O, Ca, Mg, K, and Si, indicating the presence of these elements in the modified biochar. After contact with Cu(II), the spectrum showed peaks for Cu, which strongly proved that Cu(II) ions were adsorbed on the surface of modified biochar. The infrared spectra of the virgin modified biochar, the modified biochar

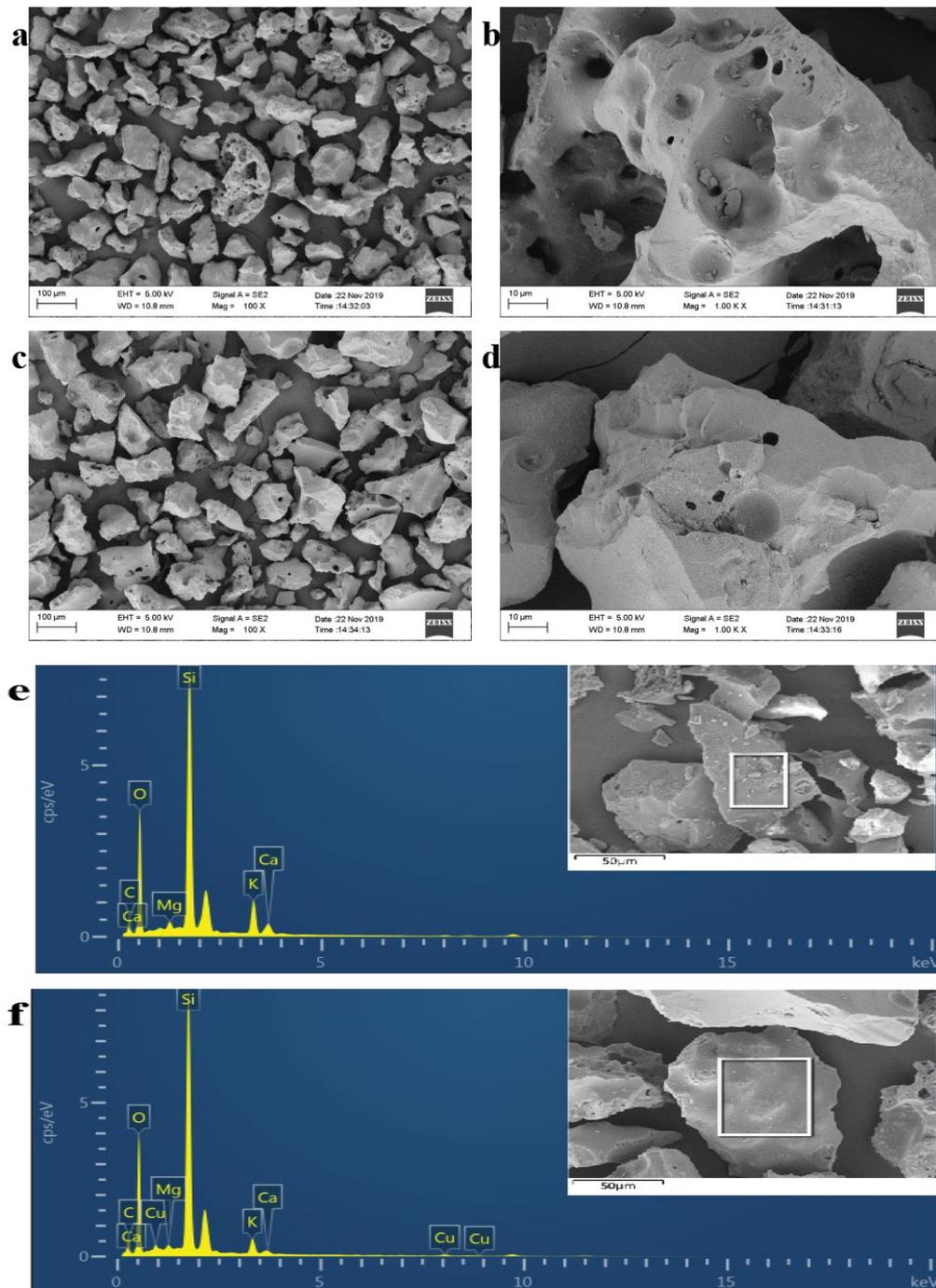


Fig. 1. SEM–EDS images [before reaction with Cu(II) ions: (a) magnification: 100×; (b) magnification: 1000×; after reaction with Cu(II) ions: (c) magnification: 100×; (d) magnification: 1000×; (e) EDS image of virgin modified biochar; and (f) EDS image of Cu(II)-loaded modified biochar].

loaded with Cu(II) and the modified biochar loaded with FA-Cu(II) are showed in Fig. 2. The most prominent peak at around $3,425\text{ cm}^{-1}$ was attributed to phenolic hydroxyl stretching vibration [24]. The band at $1,618$; $1,077$; and 669 cm^{-1} represented contribution from aromatic C=O stretching (quinines or conjugated ketone), aliphatic ether C–O stretching and aliphatic CH_2 deformation, respectively [24,25]. Some minor modifications of the IR spectrum were induced by the adsorption of Cu(II) (see Fig. 2b). A sharper absorption peak at 1395 cm^{-1} was assuredly assigned to the C–O⁻ stretching of carboxylate anion [26], indicating likely some interactions between the carboxylate anion ($-\text{COO}^-$) and Cu(II). As expected, a decrease of absorption intensities at $3,425$; $1,618$; and 1395 cm^{-1} were observed in modified biochar loaded with FA-Cu(II), which indicated that the O–H, C=O and C–O groups were involved in the reaction of FA with Cu(II) [27]. Also, Cu(II) binding with carboxylate groups on FAs has been demonstrated by NMR and FTIR analysis [28].

The BET specific surface area of the modified biochar used is $2.02\text{ m}^2\text{ g}^{-1}$, which is comparable to the pure biochar obtained from raw cornstalk ($2.29\text{ m}^2\text{ g}^{-1}$) [29]. The average hole diameter and total hole volume of modified biochar by BET are 15.22 nm and $0.0077\text{ cm}^3\text{ g}^{-1}$. The zeta potentials of modified biochar had been measured, and the value of pH_{ZPC} is around 2.0. Higher the pH value, more negative charges on the modified biochar surface, which suggests that electrostatic attraction may be one of the adsorption mechanisms.

3.2. Time profiles of Cu(II) and FA adsorption

Fig. 3 shows the time profiles of adsorption amounts of Cu(II) and FA at various conditions. As showed in Fig. 3a, at the contact time of 0–40 min, the capacities of Cu(II) adsorbed increased from 0 to 0.80, 1.40, 1.65 mg g^{-1} while at 40–300 min, the amounts of Cu(II) adsorbed only from 0.80

to 1.64, 1.40 to 1.92, and 1.65 to 2.57 mg g^{-1} . Similar trends were observed from Figs. 3b and c. Generally, the amounts of Cu(II) adsorbed increased rapidly in the 0–40 min period and slowly in the 40–300 min reaction period, indicating Cu(II) adsorption consisted of a multiple rate process. The multiple rate characteristics of Cu(II) adsorption may be related to the heterogeneity of the adsorption sites, which is believed to result from the different accessibilities of surface pores and sites with different adsorption affinity and binding strength [30]. While the adsorption of FA on modified biochar in binary solution can reach equilibrium in a short time (see Fig. 3d).

3.3. Interaction between Cu(II) and FA

The result showed that no adsorption of FA on modified biochar in a single solution. However, FA adsorption was found in the solution mixed FA with 10 mg L^{-1} Cu(II) ions, mainly due to that FA belongs to soluble compounds and some complexation reactions (hydroxyl complexation and carboxyl complexation) between FA and Cu(II) can lead to form soluble FA-Cu(II) complex [31]. The amounts of Cu(II) ions adsorbed increased with the rising of FA concentration because FA increases the total adsorption sites in modified biochar (see Fig. 4). This result is consistent with Wang et al. [32], who demonstrates FA can increase the adsorption amounts of Cu(II) and Zn (II) in soil. The adsorption amounts of Cu(II) were 3.43 mg g^{-1} in the mixed solution, therefore, modified biochar in this study possessed reasonable adsorption capacity in comparison with other sorbents (see Table 1) [33–37].

3.4. Kinetic models

In this study, four different kinetic models were described for Cu(II) and FA adsorption on modified biochar, including pseudo-first-order, pseudo-second-order, Elovich equation and intraparticle diffusion model. The goodness of conformity between experimental data the model-predicted values was expressed by the correlation coefficient (r^2). A relatively high r^2 value for the relationship between measured and predicted adsorbate adsorption data indicated that the model successfully described the kinetics. However, a high r^2 value for a special adsorption kinetic model does not mean that this equation is the best.

3.4.1. Pseudo-first-order equation

The pseudo-first-order Eq. (2) equation [38] can be written as:

$$\ln(q_{e,1} - q_t) = \ln q_{e,1} - k_1 t \quad (2)$$

where k_1 (min^{-1}) is the rate constant of pseudo-first-order equation, $q_{e,1}$ and q_t are amounts of Cu(II) or FA adsorbed at equilibrium (mg g^{-1}) and time t (mg g^{-1}), respectively.

If the adsorption of Cu(II) ions or FA onto modified biochar is one site binding mechanism, the pseudo-first-order equation will describe the adsorption process well. However, the result showed that the correlation between the

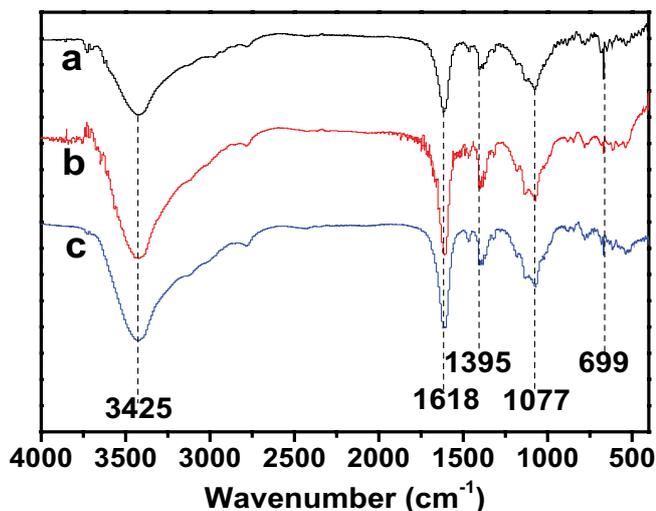


Fig. 2. Infrared spectra of (a) virgin modified biochar, (b) modified biochar loaded with Cu(II), and (c) modified biochar loaded with FA-Cu(II).

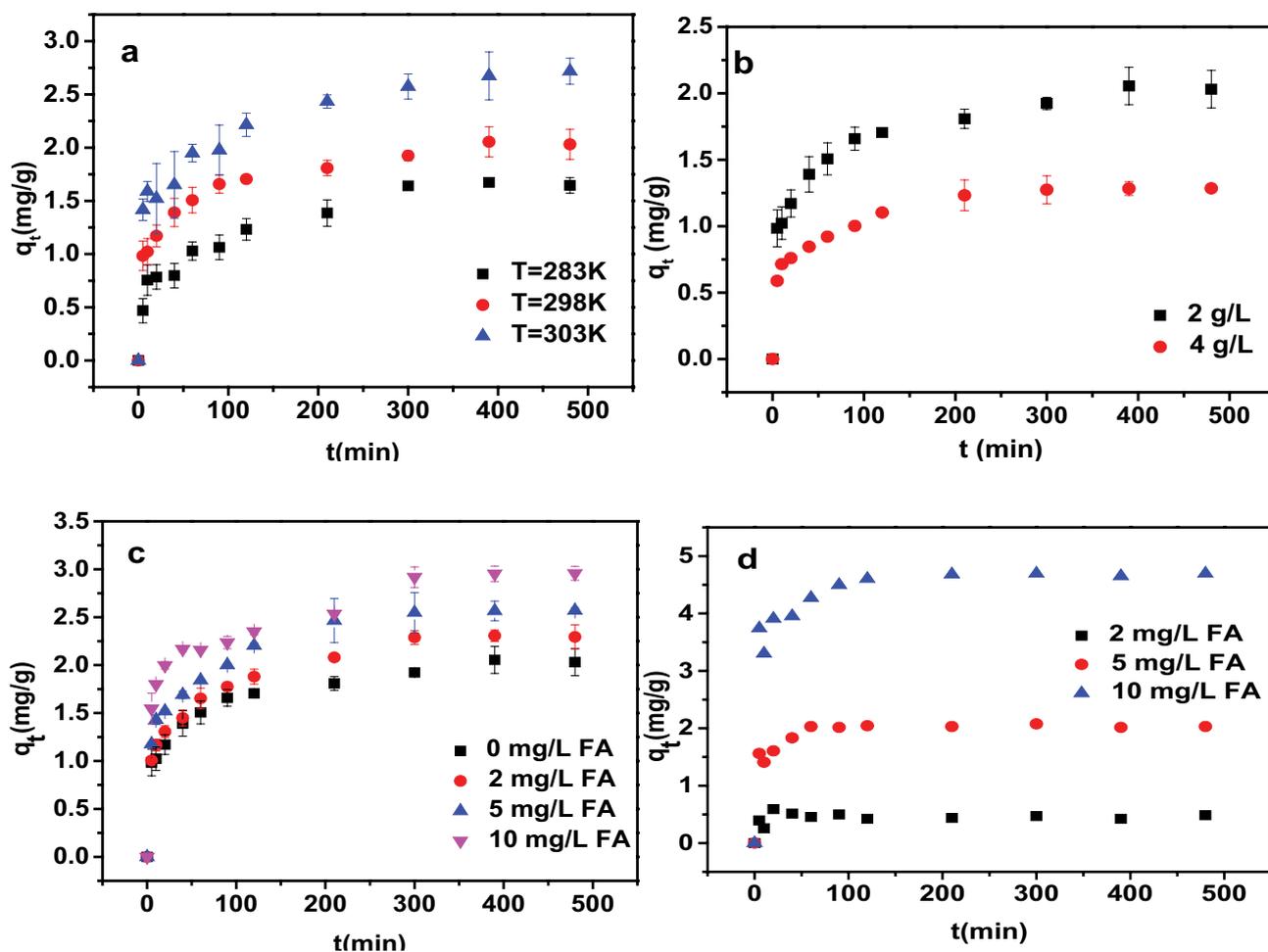


Fig. 3. Influence of various factors including (a) reaction temperature, (b) adsorbent dosage, (c) FA concentration on kinetics of Cu(II) adsorption onto modified biochar, and (d) influence of initial concentration on kinetics of FA adsorption onto modified biochar in binary solutions.

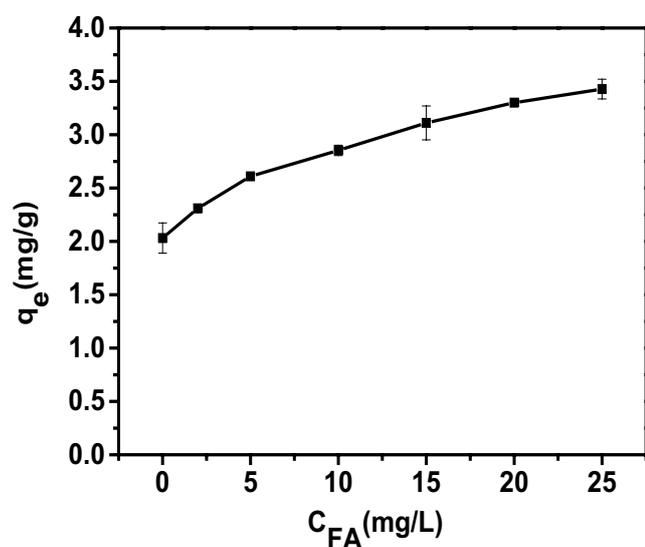


Fig. 4. Effect of different FA concentrations on Cu(II) adsorption in binary solution.

pseudo-first-order equation and experiment data points was very poor (data not shown).

3.4.2. Pseudo-second-order equation

The pseudo-second-order Eq. (3) by Ho and McKay [39] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}} \quad (3)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate of adsorption of pseudo-second-order equation, $q_{e,2}$ is amounts of Cu(II) or FA adsorbed at equilibrium (mg g^{-1}).

The results of fitting the experimental data by pseudo-second-order equation are shown in Fig. 5 and the related parameters acquired are summarized in Tables 2 and 3. The high values of r^2 were obtained for both Cu(II) and FA adsorption, evidencing chemical sorption as rate-limiting step of adsorption mechanism [40]. The q_e values by experiments are in agreement with the ones obtained from

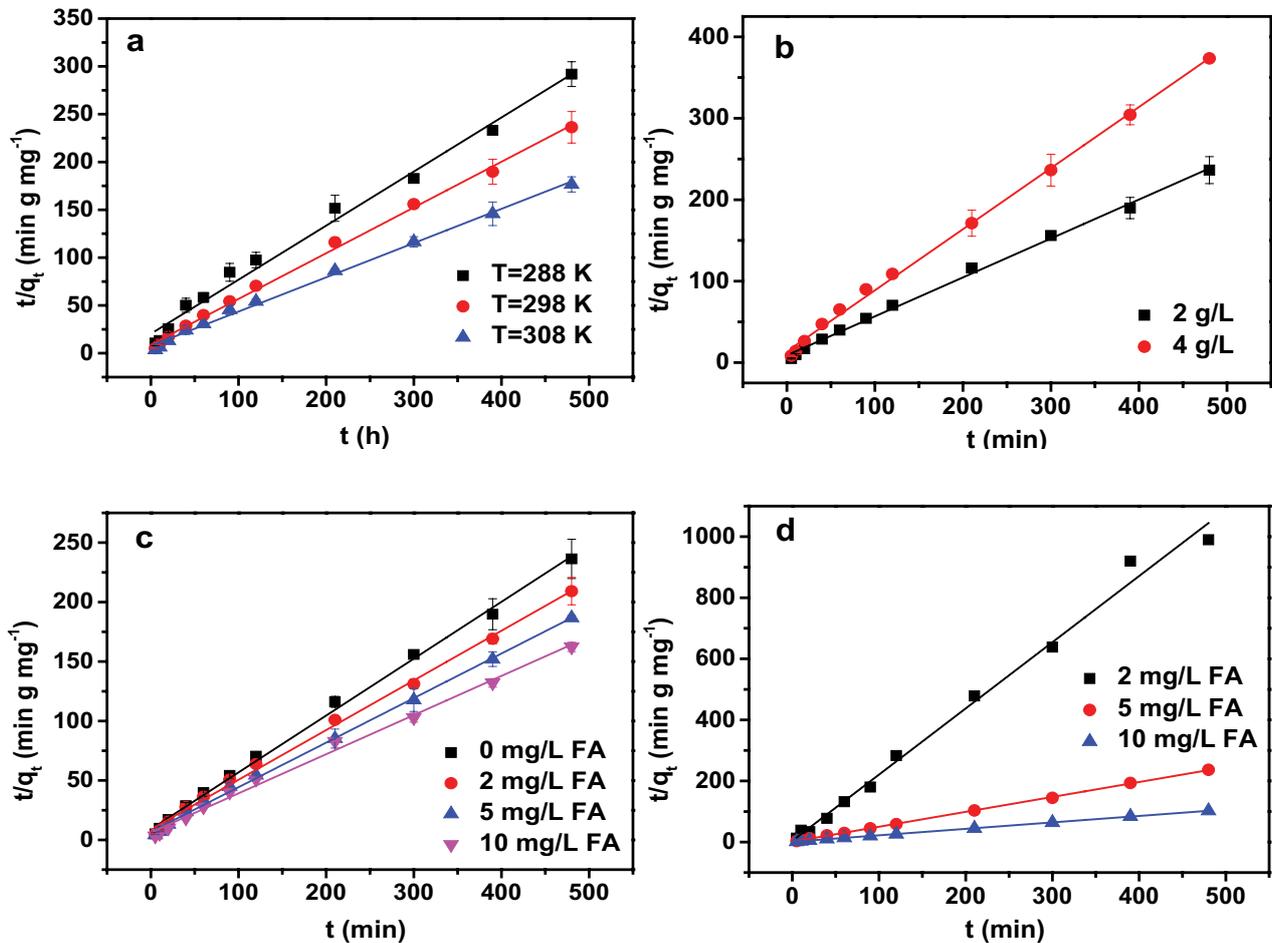


Fig. 5. (a,b,c) Adsorption of Cu(II) on biochar and (d) adsorption of FA on biochar in binary solution (the pseudo-second-order equation).

Table 1
Comparison of adsorption capacity for Cu(II) with various adsorbents

Adsorbent	q_{\max} (mg g ⁻¹)	References
Modified biochar	3.43	This study
Walnut hull	3.52	[33]
<i>P.yezoensis Ueda</i>	5.05	[33]
Wheat bran	6.85	[33]
Rice bran	12.41	[33]
Hydrochloric acid-doped PANi	1.28	[34]
Phytic acid-doped PANi	5.29	[34]
Jarrah biochar	4.39	[35]
Pine biochar	1.47	[35]
Dried marine green macroalga <i>Caulerpa lentillifera</i>	5.57	[36]
Raw carbon material	3.66	[37]

the fitting of pseudo-second-order equation. It can be seen from model-predicted $q_{e,2}$ values that the adsorption amounts of Cu(II) increased with the increase of reaction temperature and FA concentration. It may be that the high temperature is beneficial to promote the forward reaction [41]. The value

of $q_{e,2}$ becomes smaller when adsorbent dose changes from 2 to 4 g L⁻¹, but the removal efficiency of Cu(II) is increased, which seems as the adsorption sites of modified biochar increase with adding mass. During FA adsorption process in binary solution, the value of adsorption rate (k_2) decreases

Table 2
Calculated parameter values of Cu(II) adsorption on biochar in pseudo-second-order equation

Variables	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,2}$ (mg g ⁻¹)	r^2
Reaction temperature (K)			
288	0.0157	1.768	0.9892
298	0.0255	2.092	0.9972
308	0.0166	2.792	0.9961
Adsorbent dosage (g L ⁻¹)			
2	0.0255	2.092	0.9972
4	0.0410	1.333	0.9980
FA concentration (mg L ⁻¹)			
0	0.0255	2.092	0.9972
2	0.0198	2.394	0.9970
5	0.0205	2.669	0.9980
10	0.0173	3.038	0.9944

Table 4
Calculated parameter values of Cu(II) adsorption on biochar in Elovich equation

Variables	a (mg g ⁻¹)	b (g mg ⁻¹ min ⁻¹)	r^2
Reaction temperature (K)			
288	-0.003	0.265	0.961
298	0.483	0.253	0.993
308	0.745	0.308	0.970
Adsorbent dosage (g L ⁻¹)			
2	0.483	0.253	0.993
4	0.294	0.165	0.989
FA concentration (mg L ⁻¹)			
0	0.483	0.253	0.993
2	0.427	0.308	0.991
5	0.589	0.329	0.989
10	1.026	0.304	0.982

with the rising of initial concentration while adsorption amounts increase at equilibrium. This is because more soluble FA-Cu(II) complexes are formed at high concentration of FA.

3.4.3. Elovich equation

The Elovich equation mathematical expression as modified was given by Chien and Clayton [42] as follow:

$$q_t = a + b \ln(t) \quad (4)$$

where a (mg g⁻¹) and b (mg g⁻¹ min⁻¹) are the parameters of the Elovich equation (the chemical significance of a and b has not been resolved).

Generally, the interpretation to this equation is related to the energy of chemical adsorption varying with the

Table 3
Calculated parameter values of FA adsorption on biochar in various adsorption kinetic models

FA initial conc. (mg L ⁻¹)	2	5	10
Pseudo-second-order equation			
k_2 (g mg ⁻¹ min ⁻¹)	1.156	0.201	0.048
$q_{e,2}$ (mg g ⁻¹)	0.461	2.048	4.735
r^2	0.9924	0.9997	0.9998
Elovich equation			
a (mg g ⁻¹)	0.386	1.280	3.025
b (g mg ⁻¹ min ⁻¹)	0.015	0.139	0.291
r^2	0.722	0.964	0.980
Intraparticle diffusion equation			
k_3 (mg g ⁻¹ min ^{-0.5})	–	0.134	0.154
s (mg g ⁻¹)	–	0.994	3.010
r^2	–	0.998	0.894

Table 5
Calculated parameter values of Cu(II) adsorption on biochar in intraparticle diffusion equation

Variables	k_3 (mg g ⁻¹ min ^{-0.5})	s (mg g ⁻¹)	r^2
Reaction temperature (K)			
288	0.069	0.432	0.956
298	0.065	0.916	0.920
308	0.080	1.251	0.962
Adsorbent dosage (g L ⁻¹)			
2	0.065	0.916	0.920
4	0.077	1.088	0.927
FA concentration (mg L ⁻¹)			
0	0.065	0.916	0.920
2	0.083	0.924	0.975
5	0.091	1.109	0.967
10	0.076	1.548	0.929

surface coverage [43]. Fig. 6 illustrates the Elovich equation fitted the experiment points very well, which may clarify chemical interactions between adsorption sites on modified biochar surface and FA/Cu(II) in solution [33]. The parameter values fitted by the Elovich equation are listed in Tables 3 and 4.

3.4.4. Intraparticle diffusion model

The intraparticle diffusion model [44] can be described as:

$$q_t = k_3 t^{0.5} + s \quad (5)$$

where k_3 (mg g⁻¹ min^{-0.5}) and s (mg g⁻¹) are constants of the model. Plots of q_t vs. $t^{0.5}$ are often used to estimate a diffusion controlled reaction rate.

The intraparticle diffusion kinetics of Cu(II) and FA on biochar are presented in Fig. 7, and the regression parameters

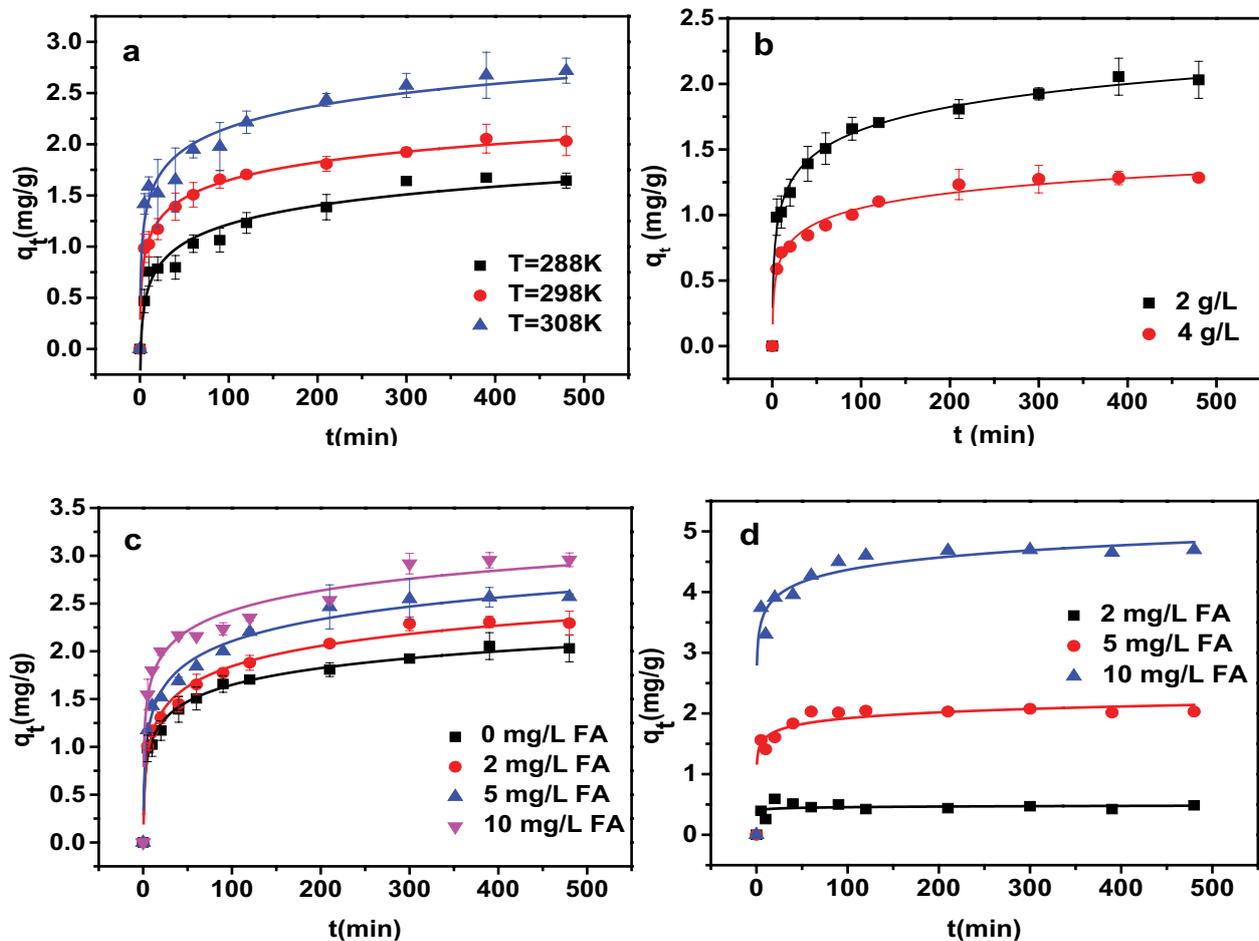


Fig. 6. (a,b,c) Adsorption of Cu(II) on biochar and (d) adsorption of FA on biochar in binary solution (the Elovich equation).

fitted in Tables 3 and 5. Several relatively high r^2 values indicate that the intraparticle diffusion model described the Cu(II) adsorption process well at the 5–300 min stage of adsorption. The fitting linear plots do not pass through the origin, meaning that intraparticle diffusion is not only the rate controlling step for adsorption process [45]. Values of s represent a conception about the thickness of boundary layer, that is to say, values of s are larger, the boundary layer effect is greater [46]. Clearly, the values of intercept rose with the increasing of contact temperature, adsorbent dose and concentration of FA, indicating that the thickness of boundary layer increased with the change of these influencing factors. Similarly, FA adsorption on modified biochar in binary solution has the same tendency.

3.5. Desorption study

The desorption efficiencies of Cu(II) ions are presented in Fig. 8 to validate the regeneration capacity of modified biochar. Fig. 8a shows that the desorption efficiencies of Cu(II) ions was found to increase obviously at the range of 0–5 min, and then began to slow down until reaching the desorption equilibrium. A higher desorption efficiency can be obtained from modified biochar loaded with single Cu(II) rather than FA-Cu(II), indicating that there is a stronger binding force

between FA-Cu(II) and modified biochar. The use of ultra-pure water either showed negligible desorption (<1%) for Cu(II) in modified biochar loaded with Cu(II) or FA-Cu(II). However, carbonate ($0.1 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$) and mineral acids ($0.1 \text{ mol L}^{-1} \text{ HCl}$, $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, and $0.1 \text{ mol L}^{-1} \text{ HNO}_3$) had resulted in high desorption efficiencies of Cu(II) about 27.83%, 47.36%, 47.72%, and 51.06% for modified biochar loaded with FA-Cu(II), 41.82%, 80.2%, 70.79%, and 74.85% for modified biochar loaded with Cu(II) (see Fig. 8b). The relatively high desorption efficiency proves the strong regeneration capacity of modified biochar.

4. Conclusions

Complexation reactions (hydroxyl complexation and carboxyl complexation) between FA and Cu(II) promote the adsorption of FA and Cu(II) onto biochar at the same time. The adsorption of Cu(II) followed a typical kinetic process with an initial rapid increase in capacities adsorbed followed by a slower increase to a quasi-equilibrium. While the adsorption of FA on modified biochar in mixed solution can reach equilibrium in a short time. The pseudo-second-order equation was the best suited model and Elovich equation fitted the experimental data very well, which suggested that the adsorption of adsorbates onto modified biochar is

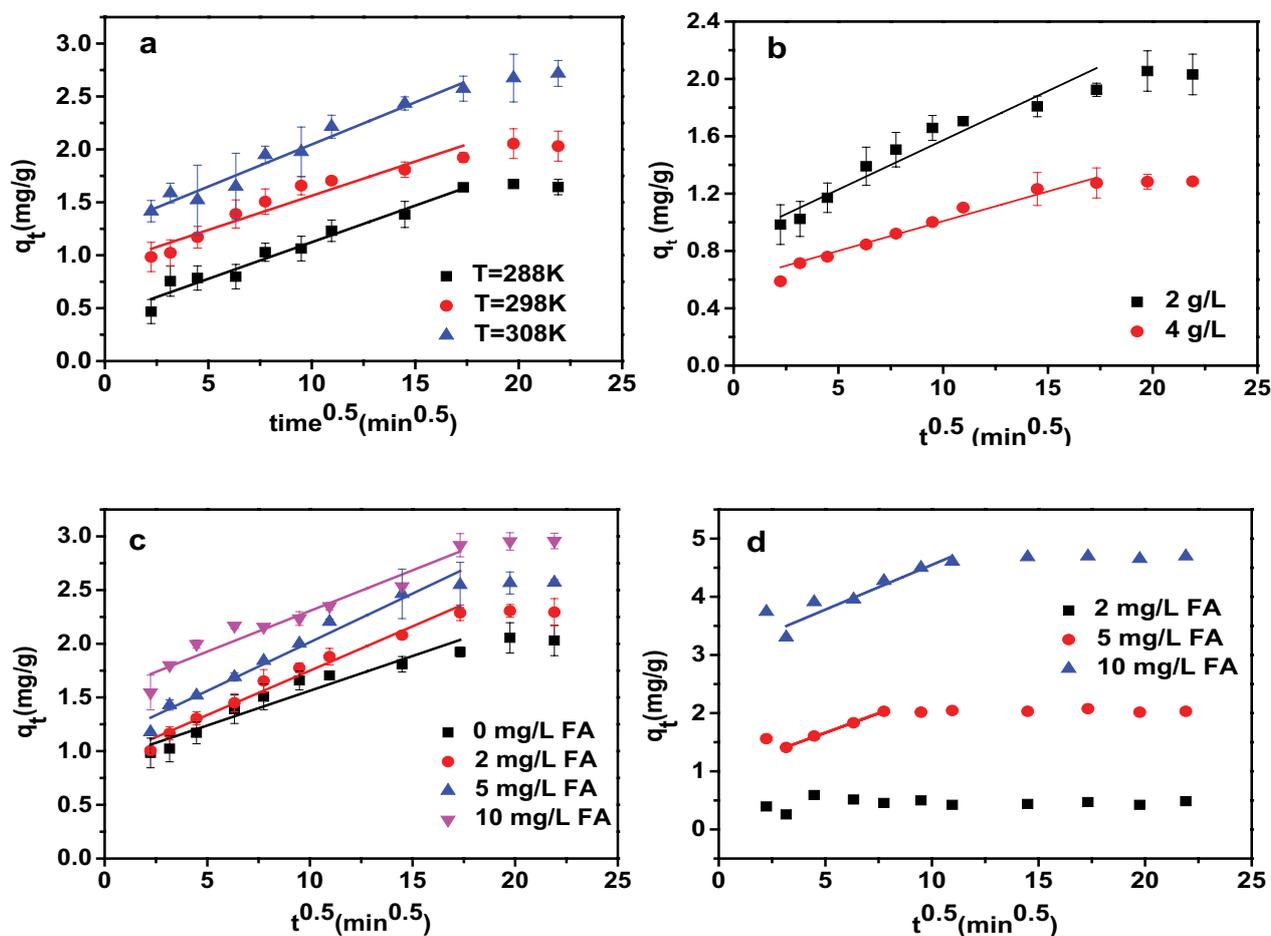


Fig. 7. (a,b,c) Adsorption of Cu(II) on biochar and (d) adsorption of FA on biochar in binary solution (the intraparticle diffusion equation).

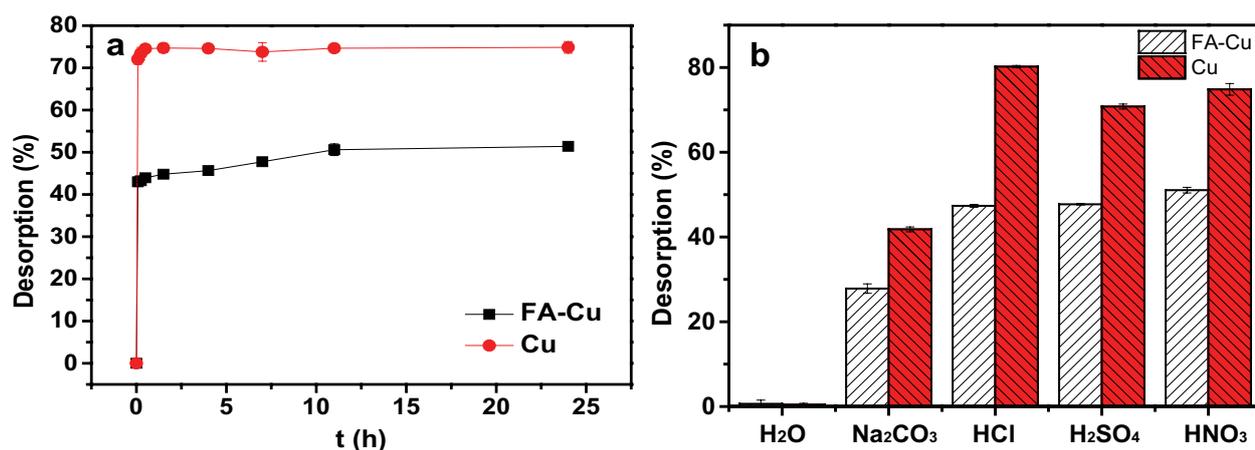


Fig. 8. Desorption efficiencies of Cu(II) (a) within the time range of 0–24 h in 1 mol L⁻¹ HNO₃; and (b) using different desorbing agents.

predominantly chemisorption. Also, the intraparticle diffusion model was successfully used to describe the adsorption of Cu(II) ions onto biochar at the 5–300 min stage of adsorption, indicating that the process of Cu(II) adsorption by biochar was diffusion-controlled. Similarly, FA adsorption on

biochar in binary solution has the same tendency. The optimum condition of Cu(II) ions adsorption was temperature of 308 K, 2 g L⁻¹ of adsorbent dosage and 25 mg L⁻¹ of FA concentration. In addition, the maximum removal efficiencies of Cu(II) ions and FA were almost 81% and 94%, respectively.

The relatively high desorption efficiency proves the strong regeneration capacity of modified biochar.

Symbols

a	—	Parameter of the Elovich equation (mg g^{-1})
b	—	Parameter of the Elovich equation ($\text{mg g}^{-1} \text{min}^{-1}$)
C_0	—	Initial concentration of solute in solution (mg L^{-1})
C_e	—	Concentration of solute in solution at equilibrium (mg L^{-1})
k_1	—	Rate constant of pseudo-first-order equation (min^{-1})
k_2	—	Rate constant of pseudo-second-order equation ($\text{g mg}^{-1} \text{min}^{-1}$)
k_3	—	Rate constant of intraparticle diffusion equation ($\text{mg g}^{-1} \text{min}^{-0.5}$)
m	—	Mass of biochar (g)
q_e	—	Adsorption capacity at equilibrium (mg g^{-1})
$q_{e,1}$	—	Equilibrium adsorption capacity of pseudo-first-order equation (mg g^{-1})
$q_{e,2}$	—	Equilibrium adsorption capacity of pseudo-second-order equation (mg g^{-1})
q_t	—	Adsorption capacity at time t (mg g^{-1})
r^2	—	Correlation coefficient (dimensionless)
s	—	Constant of intraparticle diffusion equation (mg g^{-1})
t	—	Time (min)
V	—	Volume of adsorption solution (L)

Acknowledgments

The authors would like to acknowledge four anonymous reviewers whose comments and advice greatly improved the quality of this article. This work is supported from the Natural Science Key Foundation of the Jiangsu Higher Education Institutions of China (19KJA430009) and Postgraduate Research and Practice Innovation Program of Jiangsu Province (KYCX19-2268).

References

- X. Yuan, S.I. Im, S.W. Choi, K.B. Lee, Removal of Cu(II) ions from aqueous solutions using petroleum coke-derived microporous carbon: investigation of adsorption equilibrium and kinetics, *Adsorption*, 25 (2019) 1205–1218.
- W.W. Tang, G.M. Zeng, J.L. Gong, J. Liang, P. Xu, C. Zhang, B. Bin Huang, Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: a review, *Sci. Total Environ.*, 468–469 (2014) 1014–1027.
- D. Mehta, S. Mazumdar, S.K. Singh, Magnetic adsorbents for the treatment of water/wastewater—a review, *J. Water Process Eng.*, 7 (2015) 244–265.
- J. Gao, F. Liu, P. Ling, J. Lei, L. Li, C. Li, A. Li, High efficient removal of Cu(II) by a chelating resin from strong acidic solutions: complex formation and DFT certification, *Chem. Eng. J.*, 222 (2013) 240–247.
- M.R. Awual, T. Yaita, S.A. El-Safty, H. Shiwaku, S. Suzuki, Y. Okamoto, Copper(II) ions capturing from water using ligand modified a new type mesoporous adsorbent, *Chem. Eng. J.*, 221 (2013) 322–330.
- M. Kobya, E. Demirbas, E. Senturk, M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, *Bioresour. Technol.*, 96 (2005) 1518–1521.
- M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, *J. Hazard. Mater.*, 129 (2006) 123–129.
- S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, *Biochem. Eng. J.*, 44 (2009) 19–41.
- J.F. Duval, K.J. Wilkinson, H.P. Van Leeuwen, J. Buffle, Humic substances are soft and permeable: evidence from their electrophoretic mobilities, *Environ. Sci. Technol.*, 39 (2005) 6435–6445.
- R.A. Saar, J.H. Weber, Comparison of spectrofluorometry and ion-selective electrode potentiometry for determination of complexes between fulvic acid and heavy-metal ions, *Anal. Chem.*, 52 (1980) 2095–2100.
- J.L. Xu, W.F. Tan, J. Xiong, M.X. Wang, L.C. Fang, L.K. Koopal, Copper binding to soil fulvic and humic acids: NICA-Donnan modeling and conditional affinity spectra, *J. Colloid Interface Sci.*, 473 (2016) 141–151.
- L. Dupont, E. Guillon, Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, *Environ. Sci. Technol.*, 37 (2003) 4235–4241.
- X.S. Wang, Z.Z. Li, C. Sun, Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: marine macroalgae and agricultural by-products, *J. Hazard. Mater.*, 153 (2008) 1176–1184.
- X.S. Wang, Z.Z. Li, S.R. Tao, Removal of chromium (VI) from aqueous solution using walnut hull, *J. Environ. Manage.*, 90 (2009) 721–729.
- X.S. Wang, Y.P. Tang, S.R. Tao, Kinetics, equilibrium and thermodynamic study on removal of Cr (VI) from aqueous solutions using low-cost adsorbent Alligator weed, *Chem. Eng. J.*, 148 (2009) 217–225.
- D. Park, Y.S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp., *Chemosphere*, 60 (2005) 1356–1364.
- X.S. Wang, Z.P. Lu, H.H. Miao, W. He, H.L. Shen, Kinetics of Pb (II) adsorption on black carbon derived from wheat residue, *Chem. Eng. J.*, 166 (2011) 986–993.
- J.J. Pignatello, S. Kwon, Y. Lu, Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids, *Environ. Sci. Technol.*, 40 (2006) 7757–7763.
- X.S. Wang, H.H. Miao, W. He, H.L. Shen, Competitive adsorption of Pb(II), Cu(II), and Cd(II) ions on wheat-residue derived black carbon, *J. Chem. Eng. Data*, 56 (2011) 444–449.
- Y.P. Zhang, V.S.K. Adi, H.L. Huang, H.P. Lin, Z.H. Huang, Adsorption of metal ions with biochars derived from biomass wastes in a fixed column: adsorption isotherm and process simulation, *J. Ind. Eng. Chem.*, 76 (2019) 240–244.
- Z. Zhou, Z.Z. Xu, Q.J. Feng, D.H. Yao, J.G. Yu, D.S. Wang, S.Q. Lv, Y.F. Liu, N. Zhou, M. Zhong, Effect of pyrolysis condition on the adsorption mechanism of lead, cadmium and copper on tobacco stem biochar, *J. Cleaner Prod.*, 187 (2018) 996–1005.
- D.M. Zhou, Y.J. Wang, H.W. Wang, S.Q. Wang, J.M. Cheng, Surface-modified nanoscale carbon black used as sorbents for Cu(II) and Cd(II), *J. Hazard. Mater.*, 174 (2010) 34–39.
- S.G. Wang, W.X. Gong, X.W. Liu, B.Y. Gao, Q.Y. Yue, Removal of fulvic acids using the surfactant modified zeolite in a fixed-bed reactor, *Sep. Purif. Technol.*, 51 (2006) 367–373.
- Y. Muñoz-González, R. Arriagada-Acuña, G. Sota-Garrido, R. García-Lovera, Activated carbons from peach stones and pine sawdust by phosphoric acid activation used in clarification and decolorization processes, *J. Chem. Technol. Biotechnol.*, 84 (2009) 39–47.
- Y. Qiu, H. Cheng, C. Xu, G.D. Sheng, Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption, *Water Res.*, 42 (2008) 567–574.
- S.C. Xu, *Organic Chemistry*, Higher Education Press, Beijing, China, 1983.
- X.H. Ding, W. Ma, X.M. Huang, W. Guo, R.Q. Wang, Y.C. Li, J.L. Dai, Characteristics of copper sorption by various agricultural soils in China and the effect of exogenic dissolved organic matter on the sorption, *Soil Sediment Contam.*, 27 (2018) 311–328.
- J.A. Leenheer, G.K. Brown, P. McCarthy, S.E. Cabaniss, Models of metal binding structures in fulvic acid from the Suwannee river, Georgia, *Environ. Sci. Technol.*, 32 (1998) 2410–2416.

- [29] J. Liu, W.Y. Cheng, X.Y. Yang, Y.C. Bao, Modification of biochar with silicon by one-step sintering and understanding of adsorption mechanism on copper ions, *Sci. Total Environ.*, 704 (2019), doi: 10.1016/j.scitotenv.2019.135252.
- [30] U.K. Saha, C. Liu, M. Kozak, P.M. Huang, Kinetics of selenite adsorption on hydroxyaluminum and hydroxyaluminosilicate-montmorillonite complexes, *Soil Sci. Soc. Am. J.*, 68 (2004) 1197–1209.
- [31] T.T. Li, F.H. Song, J. Zhang, S.J. Tian, N.N. Huang, B.S. Xing, Y.C. Bai, Experimental and modeling study of proton and copper binding properties onto fulvic acid fractions using spectroscopic techniques combined with two-dimensional correlation analysis, *Environ. Pollut.*, (2019), <https://doi.org/10.1016/j.envpol.2019.113465>.
- [32] Z.T. Wang, M.X. Cao, W.C. Cai, H.P. Zeng, The effect of humic acid and fulvic acid on adsorption-desorption behavior of copper and zinc in the yellow soil, *AIP Conf. Proc.*, 1820 (2017) 040027, <https://doi.org/10.1063/1.4977299>.
- [33] X.S. Wang, Z.Z. Li, C. Sun, A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by-products, *Desalination*, 235 (2009) 146–159.
- [34] H.J. Kim, S. Im, J.C. Kim, W.G. Hong, K. Shin, H.Y. Jeong, Y.J. Hong, Phytic acid doped polyaniline nanofibers for enhanced aqueous copper(II) adsorption capability, *ACS Sustainable Chem. Eng.*, 5 (2017) 6654–6664.
- [35] S. Jiang, L. Huang, T.A.H. Nguyen, Y.S. Ok, V. Rudolph, H. Yang, D. Zhang, Copper and zinc adsorption by softwood and hardwood biochars under elevated sulphate-induced salinity and acidic pH conditions, *Chemosphere*, 142 (2016) 64–71.
- [36] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, *Bioresour. Technol.*, 97 (2006) 2321–2329.
- [37] Y.J. Dai, K.X. Zhang, J.J. Li, Y. Jiang, Y.J. Chen, S. Tanaka, Adsorption of copper and zinc onto carbon material in an aqueous solution oxidized by ammonium peroxydisulphate, *Sep. Purif. Technol.*, 186 (2017) 255–263.
- [38] S. Lagergren, About theory of so-called adsorption of soluble substances, *K. Sven. Vetenskapsakad. Andl.*, 24 (1898) 1–39.
- [39] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.*, 34 (2000) 735–742.
- [40] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Sep. Purif. Rev.*, 29 (2000) 189–232.
- [41] M.M. Abdallah, M.N. Ahmad, G. Walker, J.J. Leahy, Batch and continuous systems for Zn, Cu, and Pb metal ions adsorption on spent mushroom compost biochar, *Ind. Eng. Chem. Res.*, 58 (2019) 7296–7307.
- [42] S.H. Chien, W.R. Clayton, Application of Elovich equation to the kinetics of phosphate release and sorption in soils, *Soil Sci. Soc. Am. J.*, 44 (1980) 265–268.
- [43] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, *Water Res.*, 35 (2001) 605–612.
- [44] W.J. Weber, J.C. Morris, *Advances in Water Pollution Research: Removal of Biologically Resistant Pollutants from Waste Waters by Adsorption*, Proceedings of International Conference on Water Pollution Symposium, Vol. 2, Pergamon Press, Oxford, 1962, pp. 231–266.
- [45] A.J. Kumar, R.P. Singh, D.F. Fu, C. Namasivayam, Comparison of physical-and chemical-activated *Jatropha curcas* husk carbon as an adsorbent for the adsorption of Reactive Red 2 from aqueous solution, *Desal. Water Treat.*, 95 (2017) 308–318.
- [46] A.H. Sulaymon, W.M. Abood, Equilibrium and kinetic study of the adsorption of reactive blue, red and yellow dyes onto activated carbon and barley husk, *Desal. Water Treat.*, 52 (2014) 5485–5493.