



Effect of pyrolysis condition on the adsorption mechanism of heavy metals on tobacco stem biochar in competitive mode

Nan Zhou¹ · Junning Zu¹ · Qiuju Feng² · Huanli Chen¹ · Juan Li¹ · Mei-e Zhong¹ · Shuxin Zhuang³

Received: 5 March 2019 / Accepted: 3 July 2019 / Published online: 15 July 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

To clarify the adsorption mechanism of multi-ions on biochars in competitive environment is very important for the decontamination of co-existed heavy metals. Herein, tobacco stem was pyrolyzed in different temperatures with selected residences to obtain biochars with various surface chemistry. Then the adsorption of co-existed typical heavy-metal ions like lead, cadmium, and copper was studied, followed with systematic analysis of surface properties of the post-adsorption biochars. After carefully examining the adsorption performance and surface property alteration of the demineralized biochars, the adsorption mechanism of multi-ions in competitive environment was discovered. Lead showed the most competitive nature with co-existence of cadmium and copper, but the adsorption capacity reduced significantly with the removal of minerals. Combined with the observation of large amount of lead containing crystals on the post-adsorption biochars, the main adsorption mechanism of lead should be precipitation. The adsorb capability of copper barely changed for biochars with and without minerals, which suggests the best affinity of copper on surface functional groups even with large content of competitors. Biochar that pyrolyzed in 700 °C for 6 h that contained more aromatic structures showed the highest sorbing capability of cadmium, which suggested the dominant position of cation- π interaction in cadmium removal.

Keywords Biochar · Pyrolysis condition · Surface property · Tobacco stem · Adsorption mechanism

Introduction

With the fast development of modern industry and rapid increase of human activities, heavy-metal contamination, both in water and in soil environments, has caused enormous concerns (Shen et al. 2018). Heavy metals such as lead (Pb), cadmium

(Cd), and copper (Cu) can be easily accumulated in the environment due to their non-biodegradable character, stimulating serious threat for the living of plants, animals, and especially human beings (Yin et al. 2016). More dangerous is that kinds of heavy metals usually co-existed, with various combinations and concentrations, making the contaminated environment too complex to administrate. Although adsorption is considered to be one of the most effective ways to remove heavy metals (He and Chen 2014; Teng et al. 2018; Xu et al. 2018), the decontamination of multi-metals in combined pollutions is still a great challenge, even with the development of new adsorbents with high efficiency and low cost such as biochars (Kılıç et al. 2013).

Biochar is a carbon-based material derived from biomass, especially organic wastes in anaerobic environments. Quantity of the attractive characteristics, including abundant resources, simple conversion procedures, environmental benign nature, and developed physicochemical properties, ensures the same adsorption capacity for hazardous ions as activated carbon, making biochar a best replacement of the present commercial adsorbents for environment cleaning and protection (Peng et al. 2017; Vithanage et al. 2015; Wang et al. 2017). To develop the adsorption performance of biochars, the key point is to reveal the adsorption mechanisms between the

Responsible editor: Tito Roberto Cadaval

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11356-019-05917-1>) contains supplementary material, which is available to authorized users.

✉ Zhi Zhou
zhouzhi@hunau.edu.cn

✉ Shuxin Zhuang
zsxtony@xmut.edu

¹ College of Science, Hunan Agricultural University, Changsha 410128, China

² College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, China

³ Key Laboratory of Functional Materials and Applications of Fujian Province, School of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, China

adsorbates and the adsorbents (Wang et al. 2015; Zhang et al. 2017a; Zhou et al. 2016). However, current works were mainly focused on single-metal system and adsorption mechanism investigation on multi-metal system was barely reported. Park group investigated the competitive adsorptions of Pb, Cd, Cu, Cr, and Zn on pepper stem biochar, chicken-bone biochar, and sesame straw biochar respectively. The selecting sequence of those heavy metals was detected by studying the distribution efficiency and the adsorption isotherms (Park et al. 2016a; Park et al. 2015; Park et al. 2016b). But their works were based on the heavy-metal characteristics like electro-negativities, hydrated radius, and ionization potentials, rather than the properties of biochars, which should be a dominant factor of the adsorption performance and metal preference. Recently, competitive adsorption of lead, cadmium, and copper onto biochar modified by chitosan-pyromellitic dianhydride had been examined by Deng et al. (2017). They found out that different heavy metals had selected affiliation to different functional groups and confirmed the importance of biochar's properties in the adsorption preference of multi-metal systems. Thus, it is indispensable to elaborate the exact mechanisms underlying multi-metal ion sorption in competition environment by biochars produced with various pyrolysis parameters, especially with the fact of significant impact of conversion conditions on the physicochemical properties of biochars.

It is reported that the component of the feedstock also has important effect on the properties of biochars (Mandal et al. 2017; Zhang et al. 2017b). Our previous work found out that biochars derived from tobacco stem (TS) had excellent adsorption behavior toward lead, cadmium, and copper (Zhou et al. 2018). Tobacco stem is a main solid waste of the tobacco production during the harvest season. The output tobacco stems every year is as large as 2.43 Mt due to the wide planting of tobacco. However, most of those solid wastes were currently disposed casually and wrongly, causing serious environmental problems like air pollution and soil disease. Transferring it into carbon-rich material is a promising way and several studies had been performed to carbonize tobacco stem into carbon-based energy fuels and pollutant adsorbents (Li et al. 2008; Meng et al. 2015). Nevertheless, study on tobacco stem biochar was still in its infancy and previous reports were mainly focused on the fuel application (Lin et al. 2016; Qin et al. 2016). Although our previous work had carefully investigated the adsorption properties and revealed the adsorption mechanism of single metal ion on tobacco stem biochars (Zhou et al. 2018), their performance as well as the mechanism in multi-ion system remains unclear, which needs further and systematic investigations.

Herein, tobacco stem was used as the feedstock to produce biochars under various pyrolysis temperature range of 300–700 °C with gradient duration time of 2, 4, and 6 h. The as-prepared biochars were mixed with multi-ion solution including lead, cadmium, and copper with same concentration to

study the adsorption performances. After systematically investigating the alteration of surface functional groups and crystal structures, the relationships between sorption mechanisms of various metal ions in competition environment and biochar properties based on different pyrolysis conditions were established.

Materials and methods

Production of biochars from TS feedstock

The raw material of this work, tobacco stem, was collected during the harvest season by selecting matured leaves, which were planted in Liuyang, Hunan, P. R. China. The raw materials were washed with distilled water (DW) for a couple of times to thoroughly eliminate the soluble species and dust and then dried at 100 °C until constant weight was achieved. The cleaned TS was cut into small powder. After that, a 40-mesh sifter was used to further regularize the size of the feedstock. Then the raw biomass was put into a tube furnace and converted into biochars with settled pyrolysis temperature ranging in 300–700 °C for 2–6 h respectively. The whole reaction was protected by nitrogen atmosphere and the heating rate was set to be 10 °C·min⁻¹. After this process, the furnace was cooled down naturally and the production of black solid biochars was finished. For convenience, the as-prepared biochars were named according to the pyrolysis conditions that were utilized. Take B700-6 for example; this is the sample obtained under 700 °C with 6 h.

Characterization of the TS biochars

The morphology of the TS biochars was detected by a field emission scanning electron microscope (SEM) (JSM-6380LV). The element composition and atomic ratios of the samples were determined via an elemental analyzer (Vario Micro cube, Elementar, Germany). The pH value of the as-prepared biochars was collected by a pH meter (Lei-ci PHS-3C, Shanghai, China) by testing the mixture of 1-g sample and 20 mL DW, after shaken in a mechanical shaker for 24 h. The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) equation based on the nitrogen adsorption/desorption data that was recorded through a Gemini VII 2390 Surface Area Analyzer. The surface functional groups of the biochars, with and without heavy-metal loading, were analyzed via Fourier-transform infrared (FTIR) (Spectrum 65 Instrument PE, America) with KBr pellets between 400 and 4000 cm⁻¹. The crystal structure of the biochars, before and after adsorption process, was characterized by powder X-ray diffraction (XRD) (XRD-6000, SHIMADZU, Japan) in the 2 θ range of 10–80° with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The surface binding state and

elemental speciation of post adsorption biochars were determined by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Escalab 250Xi) taking Mg Ka irradiation (1486.71 eV of photons) as X-ray source. The sorbed contents of heavy-metal ions were determined by examining the filtrate via a flame atomic absorption spectrophotometer (FAAS) (Z-2000 HITACHI, Japan). The quantities of replaced cationic ions (K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700, USA). The pH at the point of zero charge (pH_{PZC}) of nZVI/ATP₃ was ascertained using a zeta potential analyzer (Malvern Nano-ZS90, UK).

Batch adsorption analysis

The resource of heavy metals was obtained by resolving $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, and $CuSO_4 \cdot 5H_2O$, which were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China), with DW into settled concentrations. All agents had an analytical purity and were used directly without any further purification. Typically, 0.1 g biochar was mixed with 25 ml mixture consisted of equal amount of Pb^{2+} , Cd^{2+} , and Cu^{2+} ions with a total concentration of $1000 \text{ mg} \cdot \text{L}^{-1}$. The mixture was then shaken with a speed of 150 rpm for 12 h. After the total adsorption, the mixture was vacuum filtered. The as-obtained filtrates were examined without any further treatment to calculate the quantity of sorbed heavy metals by FAAS and the substituted cationic ions including Ca^{2+} , Mg^{2+} , Na^+ , and K^+ via ICP-MS, while the metal-loaded samples were washed by DW for several times and used for further XRD, FTIR, and XPS analysis after being dried at $80 \text{ }^\circ\text{C}$ for 24 h. All batch adsorption investigations were carried out at room temperature for three times, and average results were used with blank solution measurement to minimize the errors. For convenience, the metal-loaded biochars were named as ML-B x - y , where x presents the pyrolysis temperature and y stands for the time.

B400 and B700 biochars were chosen to be the typical samples for further investigation of the detailed adsorption performance of as-obtained tobacco stem biochars in competitive environment. Specifically, the impacts of adsorbent quantity, the initial pH, the heavy-metal content, and the reaction time on the adsorption behavior were systematically studied. The exact experimental processes, as well as the acid dipping procedure for demineralized biochar preparation and the following adsorption performance of Pb^{2+} , Cd^{2+} , and Cu^{2+} in competitive mode, are illustrated in the supplementary information. The contents of oxygenated acidic groups on the demineralized biochars were clarified through Boehm titration route (Goertzen et al. 2010; Oickle et al. 2010), which is also specifically illustrated in the supplementary information.

Statistical analysis equations of the experimental data

The absorbing capacities Q ($\text{mg} \cdot \text{g}^{-1}$) of pollution cations on biochars were numerated based on the following equation respectively:

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

where C_0 is the starting metal concentrations ($\text{mg} \cdot \text{L}^{-1}$) and C_e is the metal concentrations after equilibrium ($\text{mg} \cdot \text{L}^{-1}$). m is the content of biochar (g) applied to the adsorption experiments. V is the volume of mixture (mL).

$E\%$ is the adsorption efficiency of heavy-metal ions, which can be obtained according to the equation below:

$$E\% = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

To statistically analyze the isotherm and kinetics data, typical models for isotherm such as Langmuir and Freundlich and classical models for kinetic like Pseudo-first-order (PF order) and Pseudo-second-order (PS order) were applied. The equations used to treat the data according to those models are listed in the supplementary data. The fittings were carried out through the software of Origin Pro 8.0 (OriginLab, USA).

Results and discussion

Characterization of the TS biochars

The basic characteristics such as micromorphology, element composition, pH value, and surface area of the produced tobacco stem biochars were first analyzed (Fig. S1 and Table S1). Biochars derived from tobacco stem had block- and strip-like morphologies, which were quite like the starting materials (Fig. S1). The size of particles continuously decreased with the augment of conversion temperature and retention time, which indicated the higher degree of decomposition of the lignocellulose feedstock and the collapse of the original structures due to the extreme pyrolysis environment. This was further confirmed by the elemental analysis results, since the relative percentage of the carbon content in the biochars had been enlarged constantly while that of elements including oxygen and hydrogen reduced continuously. Accordingly, the atomic ratio of O/C and H/C decreased dramatically, as well as the quantity of surface functional groups (SFGs). SFGs, especially oxygenic functional groups (OFGs) like hydroxyl and carboxyl, are largely involved in the coordination of heavy metals, then further effect the adsorption performance and mechanism of biochars (Tan et al. 2015; Zhou et al. 2017). On the contrary, surface area increased with

Table 1 S_{BET} and pH of the biochars

Sample	300 °C			400 °C			500 °C			600 °C			700 °C		
	2 h	4 h	6 h	2 h	4 h	6 h	2 h	4 h	6 h	2 h	4 h	6 h	2 h	4 h	6 h
S_{BET} (m^2/g)	71.140	49.801	45.356	108.293	74.485	68.449	153.697	130.233	108.275	248.349	124.964	115.348	362.271	166.425	140.042

temperature but decreased with residence time (Table 1). It has been confirmed that large surface area can enhance the surface energy and improve the porous structure, which may strengthen the physical adsorption attractions. However, the physical attractions are mainly dependent on the intermolecular forces, which are not strong and stable enough, especially when compared to chemical adsorptions including surface complexes, precipitation, and cation- π interactions (Tan et al. 2015). Obviously, the physicochemical properties of the tobacco stem biochars largely depended on the conversion temperature and retention time, leading to the significant alteration of adsorption mechanisms towards heavy-metal ions.

Adsorption performance of the TS biochars

Adsorption behavior of biochars in competitive mode

The adsorption property of Pb^{2+} , Cd^{2+} , and Cu^{2+} on those 15 TS biochars in competitive mode was determined firstly. The sorbed contents of Pb^{2+} , Cd^{2+} , and Cu^{2+} during the adsorption procedure by tobacco stem biochars were around 100, 50, and 70 mg g^{-1} , indicating that the best competitive characteristics of lead among all three ions and giving a selective order of $\text{Pb} > \text{Cu} > \text{Cd}$, as displayed in Fig. 1(a–c), respectively. Our previous study investigated the adsorption property of these three ions on tobacco stem-pyrolyzed biochars in single solute and the results turned out to be around 302, 120, and 160 mg g^{-1} , respectively (for sample B400-2), with the same initial metal ion concentration and same quantity of biochar adsorbent, following the same selecting adsorption sequence of $\text{Pb} > \text{Cu} > \text{Cd}$ (Zhou et al. 2018). Although the adsorption capability of each metal became much lower in competitive mode than that in single solute, the total adsorbed amount of metal ions (the sum of adsorbed lead, cadmium, and copper) was greater than that of single system except lead adsorption. It is reported that there is no stationary relationship between the adsorption capacity in single solute and competitive mode, since the value of the capacity in multi-ion environment can be more, less, or equal with the one in single system (Bayramoğlu and Arica 2008). The sum value of around 200 mg g^{-1} given by our samples, which was much greater than other adsorbents reported before (Table S2), indicated that biochar pyrolyzed from tobacco stem is a potential adsorbent candidate for heavy-metal removal in competitive environment.

The variety of surface properties of the 15 biochars confirmed that the pyrolysis temperature was a dominant factor that determined the adsorption properties of biochars. As illustrated in Fig. 1, adsorption capacity could be enhanced by increasing the pyrolysis temperature with an exception of 500 °C, which might be higher enough to remove the OFGs sharply but not enough to obtain abundant aromatic carbon and mineral pieces, leading to sorrowful adsorption performance

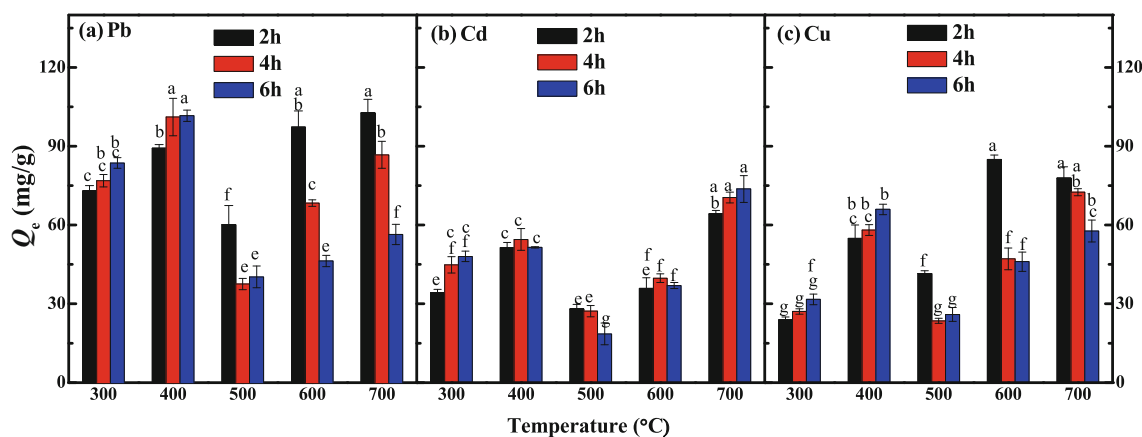


Fig. 1 Adsorption capacities of (a) lead, (b) cadmium, and (c) copper on tobacco stem biochars in competitive mode

(Table 2). According to the LaMer model (Sevilla and Fuertes 2009; Sun and Li 2004), several reactions such as decomposition, dissociation, and polymerization would take place during the conversion of biomass into biochars. During this process, OFGs would be formed, which would be significantly impacted by the conversion temperature. However, the reactions during the conversion procedure were quite complicated so that the exact reason of lower content of OFGs in B500 biochars remains unclear, where further and deeper investigation is needed. The removal ability of those tobacco stem-derived biochars was also impacted by the residence time greatly. Longer time exposure would introduce decomposition of OFGs and carbonates but formation of aromatic carbons then affected the adsorption capability of different heavy metals accordingly due to various mechanisms.

Influence of adsorbent dosage, pH, isotherm, and kinetics

Our previous study indicated that B400-2 and B700-2 showed great variability in surface properties (Zhou et al. 2018). To take an insight view of the adsorption capability of TS biochars, these two products were chosen to be typical samples to carefully analyze the influence from sorbent dosage, original metal ion concentration, contact time, and initial pH value. Figure 2a shows the adsorption data of adsorbent content experiments. Similar phenomenon of reducing capacity with increasing efficiency was found for all three metals with the adding of adsorbent, which was a normal situation that had been reported frequently in literatures (Cheng et al. 2016; Li et al. 2013). A storage capacity order of Pb > Cu > Cd that was in well agreement with that of single-metal system could be summarized (Zhou et al. 2018), which should be contributed to the adsorption mechanism as well as biochar surface properties. B700-2 showed better attraction to heavy-metal ions than B400-2, giving another evidence that pyrolysis condition could greatly affect the properties of biochars and then impact the adsorption behavior. As listed in Table 2, the maximum adsorption capacities of all 15 biochars were calculated based

on Langmuir model, which show the same trend with the adsorption results that were discussed above, further confirming that the adsorption performance of tobacco stem biochars was significantly impacted by the pyrolysis conditions.

Then, the impact of the initial pH of the metal solution on the competitive adsorption was investigated (Fig. 2b). The experiment region was set within pH 1–7, since the heavy-metals ions would start to form sediments with hydroxyl ions in environment with higher pH. Apparently, the initial pH had a significant influence on the heavy-metal removal capacity. Nearly no appreciable absorption had been observed for all three metal ions when pH value was below 2. This is a normal situation since the active binding sites on the surface of biochars are mainly occupied by high quantity of protons at lower

Table 2 Contents of oxygen-containing acidic functional groups of the demineralized biochars

Sample	Contents of OFGs (mmol·g ⁻¹)		
	Carboxyl	Lactone	Phenol hydroxyl
B300-2	2.46 ± 0.01	2.18 ± 0.01	0.00 ± 0.00
B300-4	2.41 ± 0.03	2.91 ± 0.00	0.00 ± 0.00
B300-6	1.50 ± 0.02	2.79 ± 0.01	0.00 ± 0.00
B400-2	2.13 ± 0.03	2.78 ± 0.02	0.47 ± 0.01
B400-4	1.43 ± 0.02	2.35 ± 0.03	1.20 ± 0.01
B400-6	1.94 ± 0.03	2.20 ± 0.02	0.42 ± 0.02
B500-2	0.63 ± 0.02	0.84 ± 0.03	0.00 ± 0.00
B500-4	0.51 ± 0.01	0.91 ± 0.01	0.00 ± 0.00
B500-6	0.49 ± 0.01	0.99 ± 0.02	0.00 ± 0.00
B600-2	0.74 ± 0.02	1.13 ± 0.00	0.00 ± 0.00
B600-4	0.51 ± 0.02	1.18 ± 0.02	0.00 ± 0.00
B600-6	0.50 ± 0.01	0.64 ± 0.01	0.00 ± 0.00
B700-2	1.33 ± 0.00	1.45 ± 0.02	0.00 ± 0.00
B700-4	0.48 ± 0.01	0.87 ± 0.01	0.00 ± 0.00
B700-6	0.41 ± 0.01	0.44 ± 0.01	0.00 ± 0.00

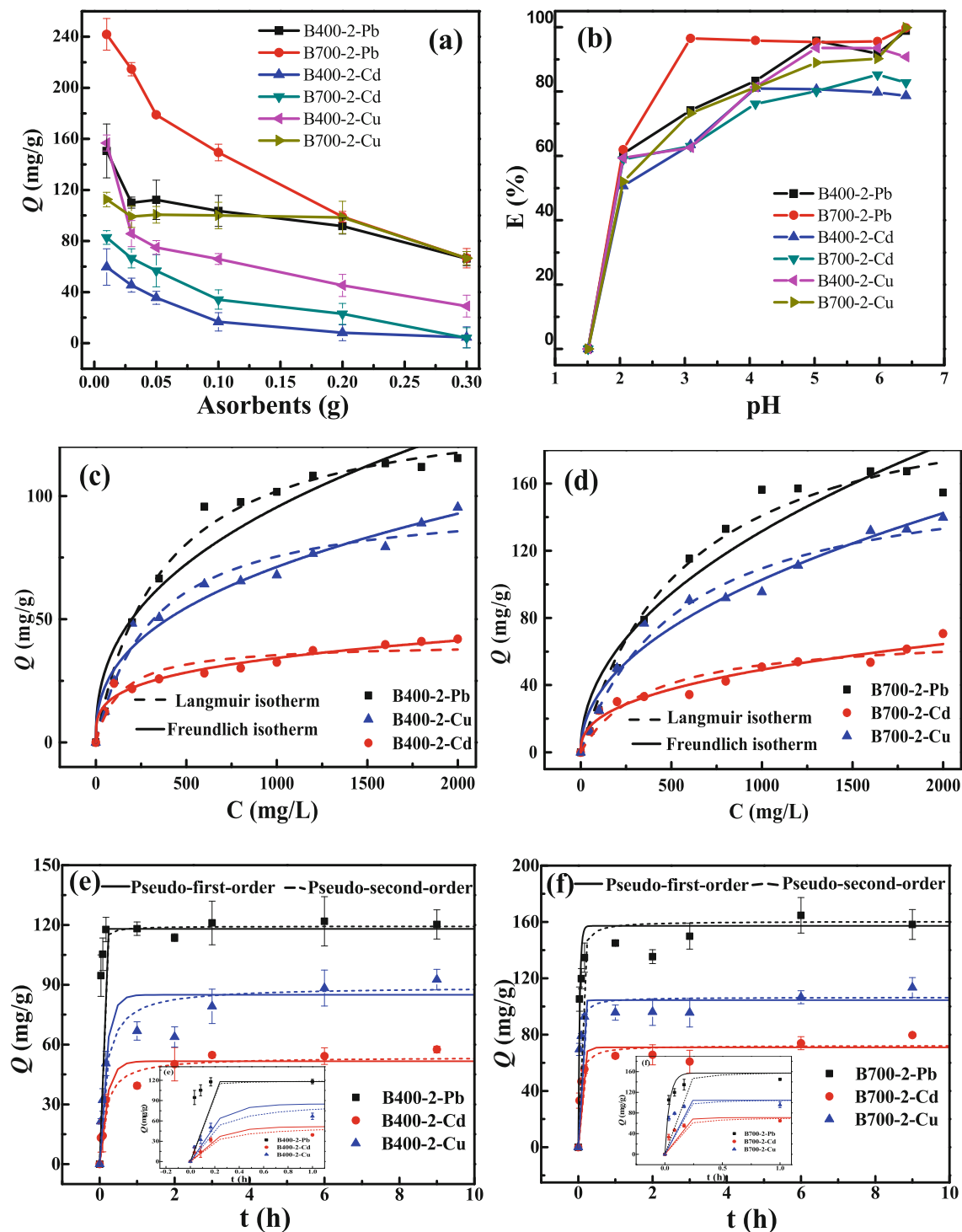


Fig. 2 Effect of biochar dosage (a), pH (b), initial concentration of metal ions (c, d), and contact time (e, f) on adsorption, and corresponding fitting according to different models

pH (Elwakeel et al. 2014). But the storage capacity enlarged rapidly with the increase of pH and the adsorption efficiency of a couple of the samples got the equilibrium above 80% immediately when the pH got 4. It can be concluded that the suitable pH range for Pb^{2+} , Cu^{2+} , and Cd^{2+} removal by TS biochars in mix-component system should be 4–7, which was

one order smaller than that in single-component system (Zhou et al. 2018). The reason may be contributed to the occupation of active bonding sites by protons and other metal competitors in competitive environment, due to which much lower sorbing content of single metal ion was exhibited. Nevertheless, the poor adsorption capability at lower pH implies that the

adsorption of Pb^{2+} , Cu^{2+} , and Cd^{2+} on the TS biochars was chemical reaction rather than physical attraction; thus, the adsorption mechanism should be surface complexation, ion exchange, p - π electron coordination, and precipitation.

The influence of the starting metal ion concentration on the sorbing performance was also conducted (Fig. 2c, d). The experimental results demonstrated that the uptakes of all three metal ions increased progressively with the increasing of initial concentration, despite the co-existed competitors, which indicates the continuous saturation of metal ions onto the adsorbents. For typical biochars B400-2 and B700-2, the Pb^{2+} , Cu^{2+} , and Cd^{2+} storage capacity achieved the equilibrium at around 110, 80, and 40 mg g^{-1} and 160, 120, and 50 mg g^{-1} , respectively. The value of the adsorption capacities was much lower when compared with the uptakes in single-metal systems, but the sum value was greater. This indicates that the TS-derived biochars are outstanding removing agents for heavy metals. Langmuir and Freundlich isotherm models were employed to analyze the isotherm data, based on which the fitting parameters could be obtained (Table S3). According to the value of coefficient of determination (R^2), the model of Langmuir fits the isotherm data of lead better than that of the Freundlich dose, suggesting that the immobilization of Pb^{2+} was single-layer adsorption. On the opposite, the Freundlich model fits the isotherm result of cadmium and copper adsorption more than the Langmuir model dose, implying the attraction of these two ions were double-layer adsorption.

The impact of reaction time on the adsorption property was studied lastly (Fig. 2e, f). The storage capability of all three metal ions boosted quickly during the initial stage, and the equilibrium could be gotten within 3 h. This phenomenon claims the speeded adsorption behavior of those as-obtained biochars, which is a necessity for modern adsorbents. Classical kinetic models of PF order and PS order were employed to study the kinetics statistically, based on which the kinetic parameters were calculated (Table S3). According to the obtained R^2 , the latter fits all the adsorption data better than the former dose. This phenomenon suggests that chemisorption should be the limit step of the adsorption velocity. That further confirms the immobilization of lead, cadmium, and copper on TS-derived biochars in competitive system which were chemical reactions.

Adsorption mechanism

Surface complexation

FTIR analysis was performed to determine the alteration of the possible functional groups presented on the surface of those tobacco stem biochars after the adsorption of lead, cadmium, and copper in mix-component solutions (Fig. 3). Typical peaks indexed to hydroxyl and carboxyl groups were detected in original B300 and B400 biochars and drastically

diminished or even disappeared after the sorbing process, which indicates the participation of those groups into the coordination of heavy-metal ions. The existence of sharp peak indexed to the stretching vibration belongs to C–OH in phenols at 1300 cm^{-1} (Puziy et al. 2002), and aliphatic C–O–C structures of cellulose at 1057 cm^{-1} (Uchimiya et al. 2010) indicated that the decomposition and carbonization of the raw biomass was not completely in B300 biochars, which explained the less adsorption capacity due to the lockage of part of OFGs. Peaks indexed to hydroxyl or carboxyl groups disappeared when the pyrolysis temperature increased to $500 \text{ }^\circ\text{C}$, implying the elimination of OFGs with the augment of temperature. The drastic decrease of OFGs would largely cut off the surface coordination, causing a negative influence on the adsorption capacity.

To further specify the exact functionality between OFGs and different heavy-metal ions, the TS biochars were demineralized via acid dipping to eliminate the effect of mineral species (for details, see the supplementary information), followed with the examination of surface functional groups through Boehm titration method and adsorption investigation under the constant conditions. The acid dipping process had been confirmed that could thoroughly eliminate the mineral species while not impacting the acidic functional groups (Wang et al. 2015; Zheng et al. 2013). As listed in Table 1, the contents of the OFGs were closely affiliated with the pyrolysis conditions. The quantities of OFGs kept reducing with the adding of reaction temperature and retention time, which possibly resulted from the loss of hydrogen and oxygen due to the high decomposition of polymers (Sun et al. 2017). One exception has been detected in B700-2 biochar, which exhibited relatively higher content of OFGs with a total amount of 2.78 mmol g^{-1} (the sum of the content of carboxyl, lactone, and phenol hydroxyl). The zeta potential analysis of the B700-2 sample (Fig. S2) also confirmed the negatively charged surface of this sample, which was responsible for the existence of oxygen-containing functional groups (Suliman et al. 2016). The reason resulted in this phenomenon remains unclear and further investigation is needed. However, those functional groups could be largely involved into the surface coordination with heavy-metal ions such as Cu^{2+} , since high adsorption capacitance of copper ions on B700-2 biochars was observed, as displayed in Fig. 4.

Figure 4 displays the adsorption performance of 15 demineralized biochar samples in multi-metal system. Since the mineral species had been totally removed after the acid dipping process, the adsorption performance of demineralized biochars might be attributed to the aromatic structure and functional OFGs. As shown in Fig. 4, the storage capability of copper on demineralized biochars was obviously higher than that of lead and cadmium, and an adsorption order of $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ was detected for all 15 samples. This result suggests that Cu had the best affinity onto surface

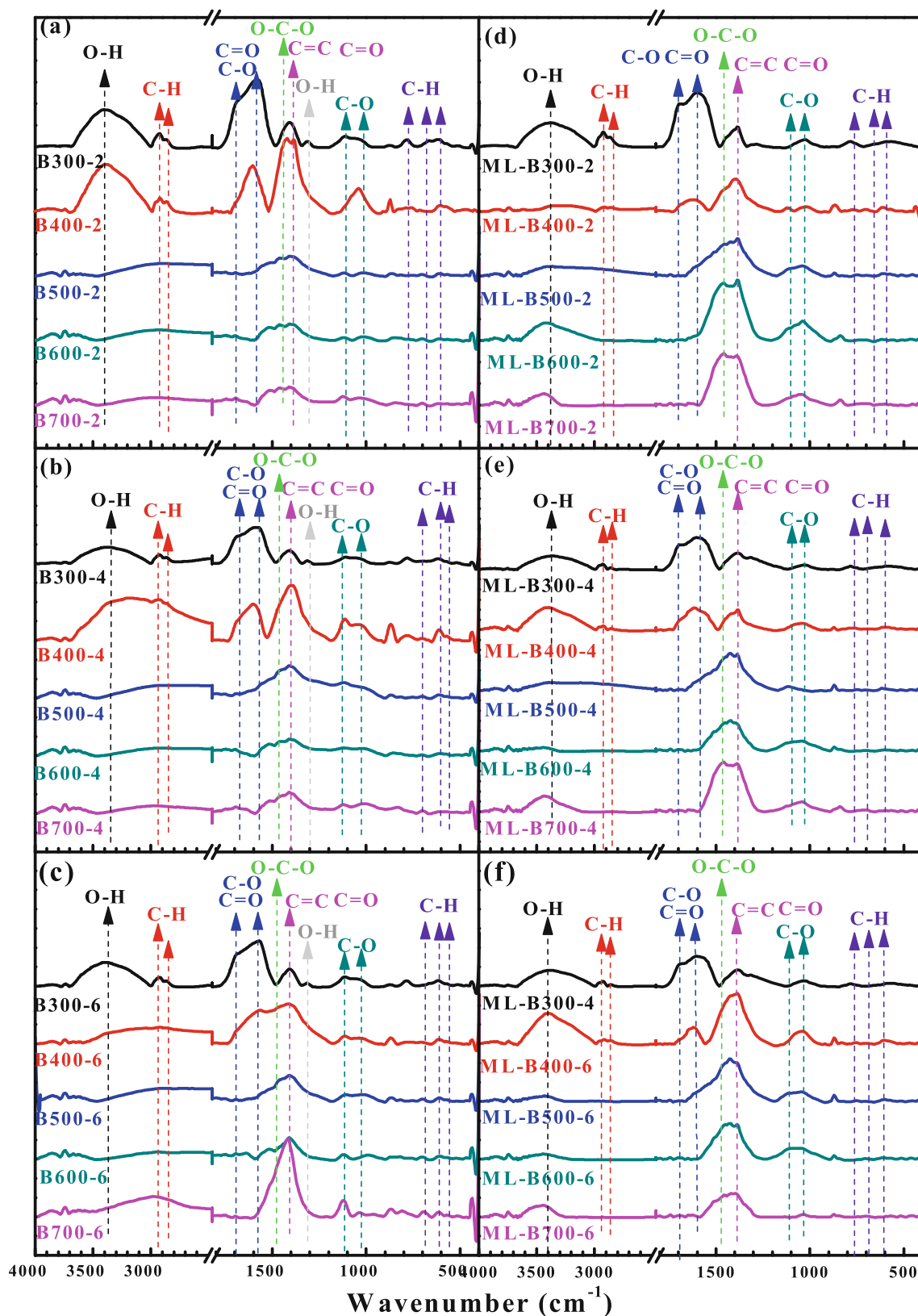


Fig. 3 FTIR spectra of tobacco stem biochars before and after adsorption of lead, cadmium, and copper in competitive mode

functional groups when compared to the other two heavy-metal ions. This result is in accordance with that of single-

metal system (Zhou et al. 2018), except two varieties. For single-metal system, B700-4 and B700-6 had better

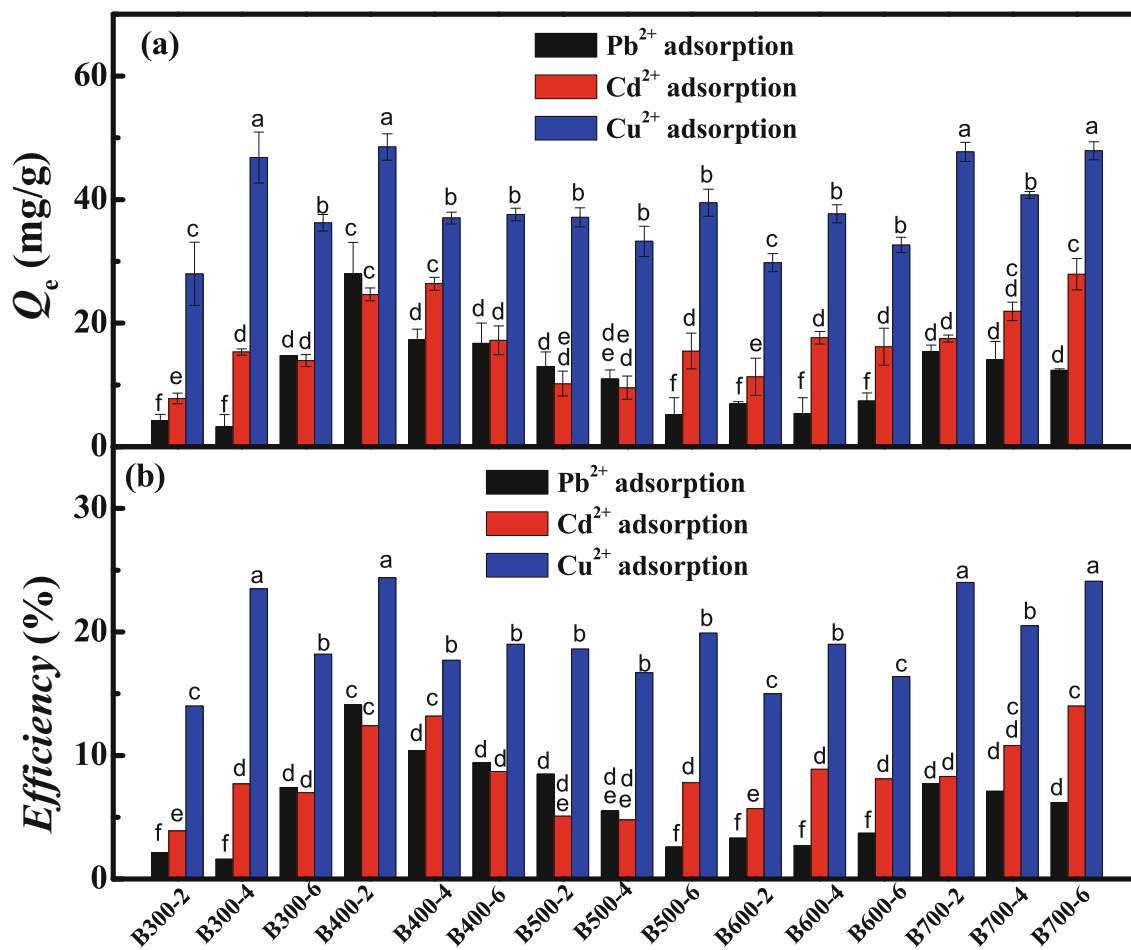


Fig. 4 Adsorption capacities (a) and efficiencies (b) of lead, cadmium, and copper on demineralized biochars

adsorption performance to cadmium than that to copper, which should result from the preference of cadmium to aromatic carbon due to π -interactions. However, faster dispersion of copper than cadmium due to the smaller ion radii may guarantee better interaction with active sites in competitive mode, and then impact the storing sequence. In addition,

poorest sorbing content of Pb²⁺ among three metals was detected, implying that precipitation should possibly be the primary adsorption mechanism of lead.

This conclusion was evidenced again by the XPS result of the typical demineralized biochars (B400 and B700 series) after adsorption of three heavy-metal ions in

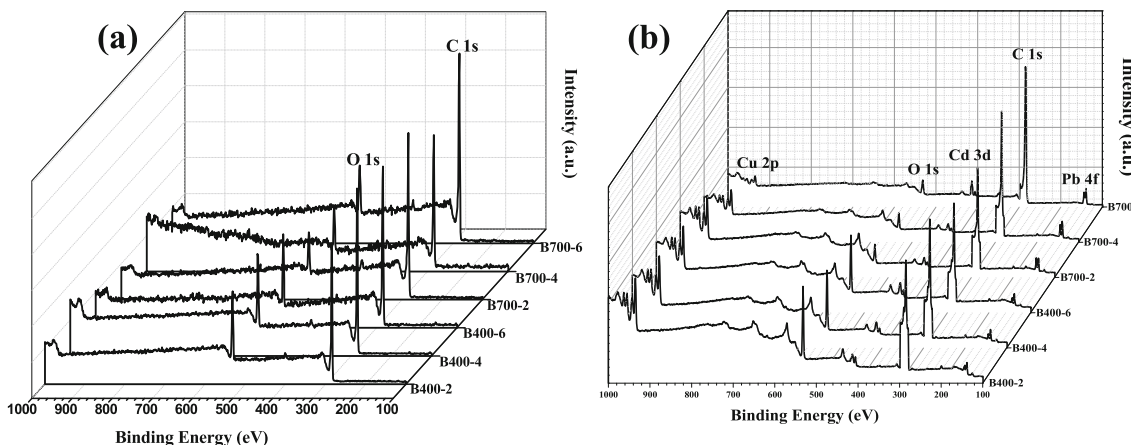


Fig. 5 XPS spectra of tobacco stem biochars before (a) and after (b) adsorption

competitive mode (Fig. 5b), and the high-resolution C 1s, Pb4f, Cd3d, and Cu2p peak is shown in Fig. 6. As compared to the XPS survey of tobacco stem biochars (Fig. 5a), peaks corresponding to Pb^{2+} , Cd^{2+} , and Cu^{2+} were detected in XPS data of post adsorption biochars, respectively, which confirms the immobilization of those pollutant cations on the demineralized biochars. Apparently, the peaks indexed to copper had higher intensity and wider width. This detection clarifies the best affinity property of copper on OFGs, and surface coordination should be the primary adsorption mechanism of Cu, both in single and in competitive systems.

π -electron interaction

Since the first report of cation- π -electron interaction in 1997 (Ma and Dougherty 1997), aromatic π -system had been confirmed to be a functional π -donor to attract covalence cations. According to the FTIR patterns shown in Fig. 3, bands assigned to aromatic C–H positioned at 612, 649, and 781 cm^{-1} existed in low-temperature products and then disappeared with the increase temperature above 400 °C. However, those peaks showed up again when the pyrolysis temperature increased to 700 °C, and became larger with the adding of residence time. The presence of those peaks in low-temperature samples might be attributed to the organic residence of the tobacco stem raw materials, which would be further decomposed with the augment of temperature. For high-temperature biochars, the reappearance of those peaks should represent the formation and enrichment of aromatic structures due to the application of extreme pyrolysis, which would greatly enhance the electron-donating ability (Keiluweit and Kleber 2009), and then facilitate the heavy-metal ion affiliation by providing more π -electron interaction. After adsorption, the intensity of those peaks assigned to aromatic structures shorted and the width broadened (Fig. 3), which indicates the participation of π -electron donors during the adsorption process. Thus, it is reasonable to report that the cation- π interaction between the biochars and heavy-metal ions had occurred, especially in samples pyrolyzed in high temperatures.

As depicted in Fig. 4, demineralized biochars had better storing capability toward cadmium than lead, especially for samples pyrolyzed under higher temperature with longer residence time. This implies that cadmium had better affinity to aromatic carbons than lead dose. Besides, extending the reaction time could promote the adsorption of cadmium, suggesting that cadmium had a better preference to cation- π reactions. It is in well agreement with the results of single-metal system (Zhou et al. 2018) as well as previous reports (Zhang et al. 2017a).

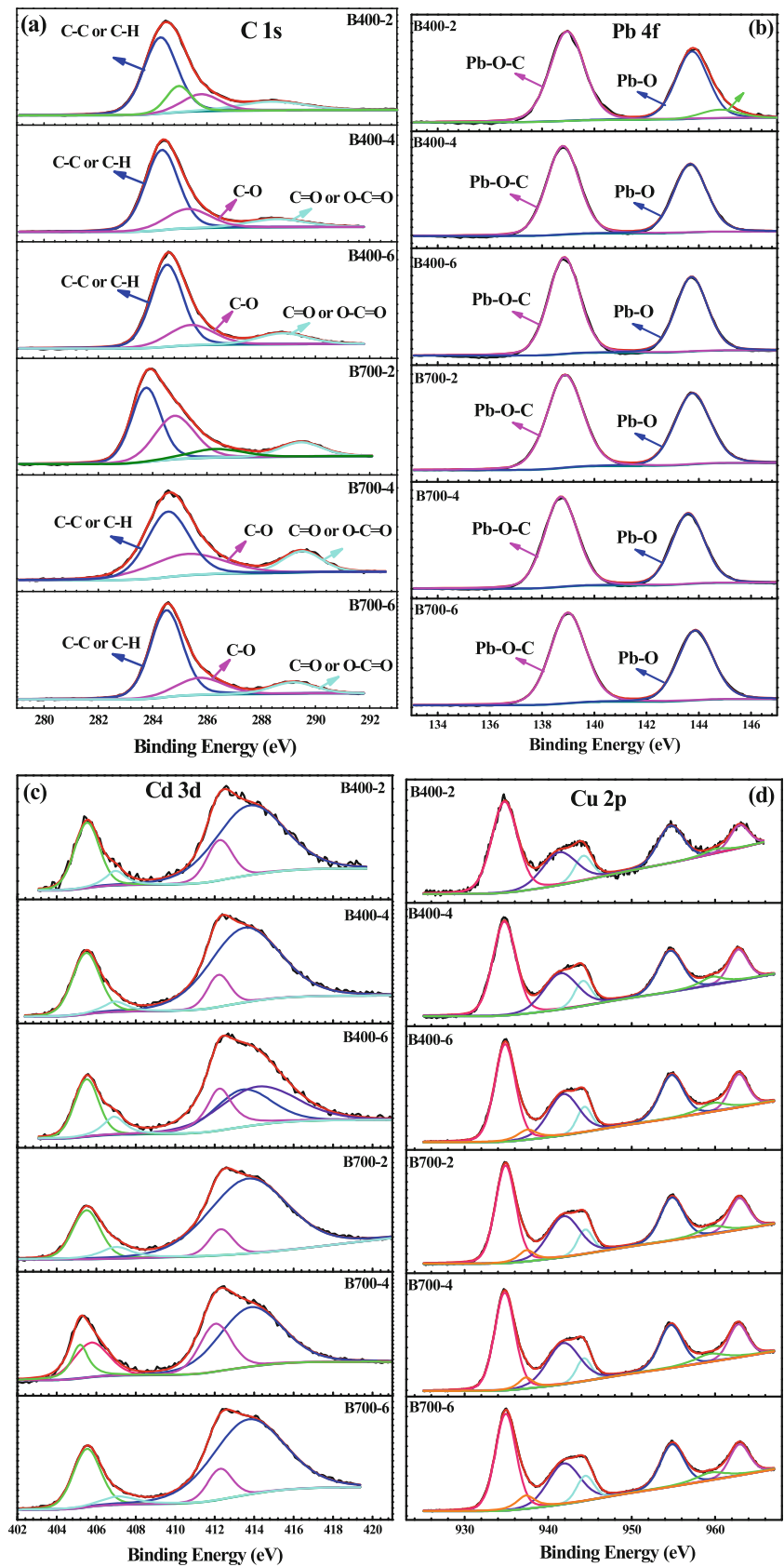
Precipitation

Another thing strengthened with the augment of pyrolysis temperature was the content of minerals, as peaks corresponding to C–O/C=O in CO_3^{2-} located at around 1760 and 1450 cm^{-1} emerged in the FTIR spectra of biochar samples pyrolyzed above 500 °C (Fig. 4) (Andersen et al. 1991). Previous studies confirmed the enhancement of both concentration and crystallinity of mineral materials in biochars with elevated temperature, especially higher than 500 °C (Cao and Harris 2010; Yuan et al. 2011), which should be a great promotion for the precipitation reaction between the biochars and pollutant cations. This was verified by the enlarged intensity of the peaks indexed to C–O/C=O groups in post-adsorption FTIR patterns.

XRD analysis was then carried out to analyze the crystal differences between the original and cation-loaded biochars, results shown in Fig. 7. For the original biochars, no obvious peaks indexed to crystal graphite was observed, demonstrating that the as-obtained carbon-rich char products were mostly amorphous or disordered, even after pyrolyzed in elevated temperature of 700 °C for 6 h. However, typical peaks with high intensity corresponding to calcium carbonates were detected, suggesting the formation of large content of mineral components, which were significantly involved in the storage of cadmium due to the precipitation affiliation. The quantity of those minerals was impacted by the pyrolysis conditions significantly, since the intensity of those peaks enhanced with the increase of pyrolysis temperature for short-time products while most of the peaks diminished or disappeared after 4-h exposure in high temperature like 700 °C. It has been confirmed that the contents of mineral fragments in biochars could be enriched by increasing the pyrolysis temperature (Cao and Harris 2010; Yuan et al. 2011), which was in accordance with the above-discussed results. However, it was also reported that exposure in elevated temperature for longer time would cause decomposition of carbonates, and the reaction could be accelerated by organic material (Beruto et al. 2010; Kasselouri et al. 1995). In this case, the organic species could work as a catalyst, and then the temperature for reaction stimulation could be decreased. Thus, it was highly feasible that the carbonates scattered in the tobacco stem biochars were negatively impacted by the residence time, especially for higher pyrolysis temperature products. Accordingly, the decomposition of those carbonates would greatly reduce the amount of anions that could precipitate with heavy-metal ions, resulting in irreversible loss of adsorption capacity.

For biochars after adsorption, those sharp peaks assigned to calcium carbonates disappeared, substituted by typical peaks indexed to lead carbonates like cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and cadmium carbonates like otavite (CdCO_3). However, the intensity of those peaks was lower than that of single-metal

Fig. 6 XPS spectra of the post-adsorption biochars **a** C1s, **b** Pb4f, **c** Cd3d, and **d** Cu2p



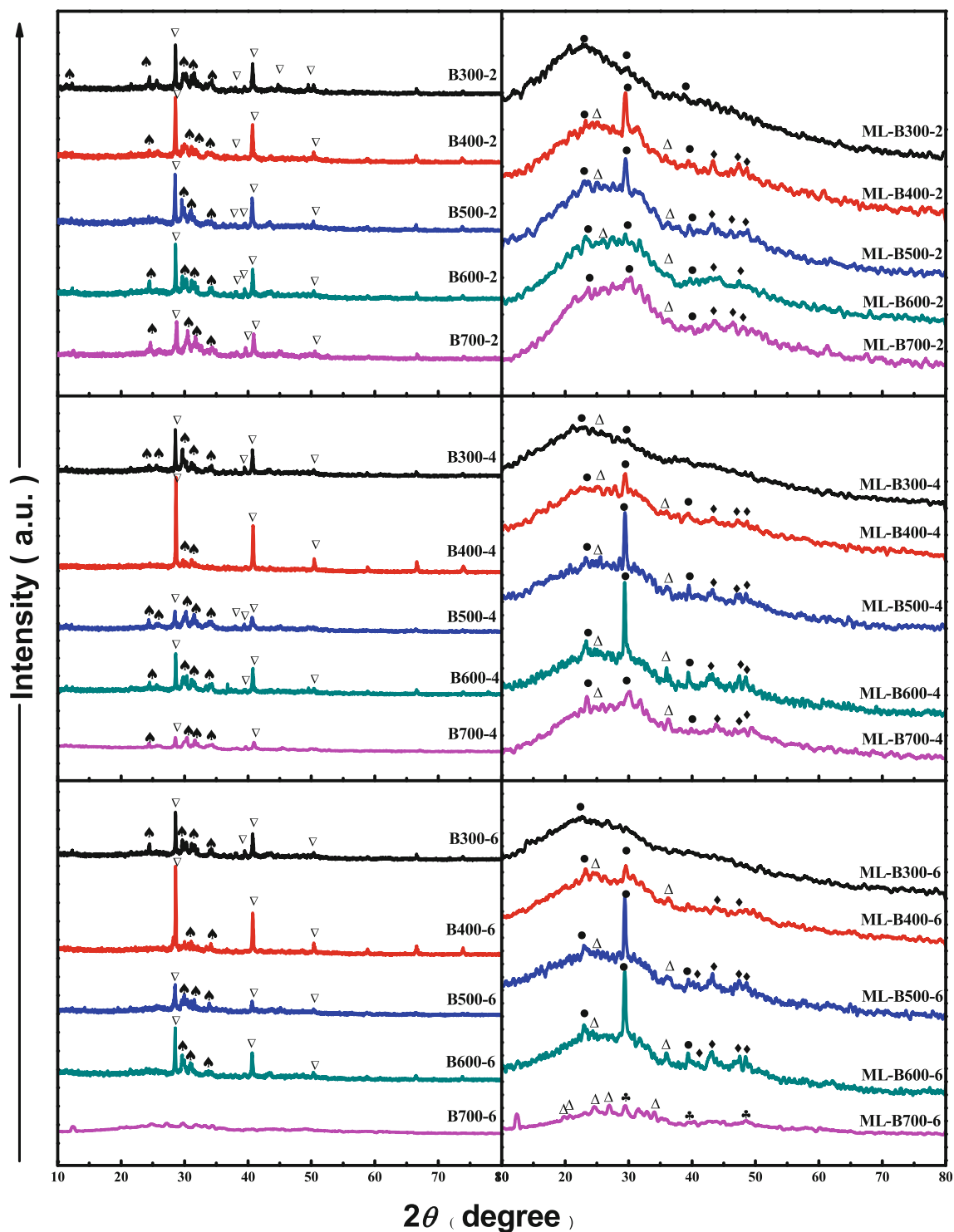


Fig. 7 XRD patterns of the tobacco stem biochars and metal-loaded TS biochar. \blacktriangle , calcite, CaCO_3 ; ∇ , aragonite, CaCO_3 ; \blacklozenge , cerussite, PbCO_3 ; \bullet , otavite, CdCO_3 ; \blacktriangle , hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; \bullet , otavite, CdCO_3 ; \blacktriangle , aragonite, CaCO_3 ; \blacklozenge , copper carbonate, CuCO_3

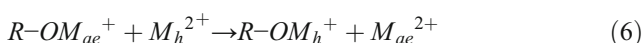
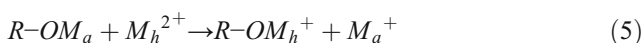
system (Zhou et al. 2018), suggesting the reduction of stored metal ions in competitive mode, which was in well agreement with the adsorption performance results. There was no detection of peaks indexed to copper sediments, representing no or few precipitation had been formed,

indicating that precipitation was not the main storing mechanism of copper ions. The Solubility-Product Constants (K_{sp}) of CaCO_3 , CuCO_3 , PbCO_3 , and CdCO_3 are 2.9×10^{-9} , 1.4×10^{-10} , 7.4×10^{-14} , and 5.2×10^{-12} , respectively. Obviously, the K_{sp} value of CaCO_3 is very

close to that of CuCO_3 , but it is about five and three orders larger than that of PbCO_3 and CdCO_3 respectively. Consequently, calcium ions in the mineral salts can be replaced by Pb^{2+} and Cd^{2+} effortlessly rather than Cu^{2+} . Combined with the former results, it is clarified that precipitation should be the main adsorption mechanism of lead on TS biochars, in both single and multi-metal systems (Zhou et al. 2018). Since the amount of the corresponding peaks as well as the degree of the intensity was positively related to the reaction temperature while negatively related to the retention time, biochar pyrolyzed under higher temperature with short retention time shall be a better adsorbent for lead.

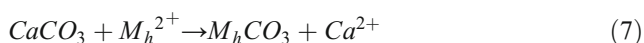
Ion exchange

The result of the pH determination of the as-obtained biochars turns out that all biochars derived from tobacco stem via pyrolysis had alkaline characteristics (Table S1). Thus, it was highly feasible than the oxygen-containing functional groups like carboxyl and hydroxyl attached on the surface of biochars would coordinate with alkaline (earth) metals to form phenolates and carboxylates instead of maintaining the original acidic structures. Consequently, the bonded cations would be replaced by the adsorbed heavy-metal ions after the adsorption process and then released into the solution (Vithanage et al. 2015). The possible equations are as follows:



where M_a is the alkaline metal ions, M_{ae} is the alkaline earth metal ions, and M_h is the heavy-metal ions, and R represents the carbon skeleton.

Besides, the amount of Ca^{2+} in the solution shall also be increased after the adsorption procedure if precipitation reactions between the minerals and heavy-metal ions occurred. The corresponding equation is as follows:



Obviously, with the occurrence of the surface complexation and precipitation, large amount of cations including K^+ , Na^+ , Ca^{2+} , and Mg^{2+} would be replaced by the heavy-metal ions and then released into the solution. In this case, increased amounts of K^+ , Na^+ , Mg^{2+} , and Ca^{2+} were detected (Table S4). Besides, the contents changed with the pyrolysis conditions and the type of cations. For K^+ , Na^+ , and Mg^{2+} , the amount of the substitution firstly increased with the increasing

temperature, which confirms the enrichment of free surface functional groups with the further decomposition of biomass. After reaching the maximum in B400 biochars, this value began to decline with the continuously increasing temperature, which should be attributed to the elimination of surface OFGs due to the full deoxygenation and dehydrogenation. Besides, extending the pyrolysis duration could also lead to the reduction of exchanged cations, possibly because of the negative effect from longer reaction time on the OFGs. Those results were in well accordance with the obtained FTIR patterns, giving another evidence of the as-concluded influence on the surface properties of tobacco stem biochars from the pyrolysis conditions and the involvement of those cations in the surface complexations during the adsorption process. Unlike K^+ , Na^+ , and Mg^{2+} , the released content of Ca^{2+} showed opposite regularity. It slided with the augment of temperature, reached the bottom at 500 °C and then boosted with the increase of temperature. The variety of the substitution concentration of calcium should be mainly contributed to the occurrence of precipitation between the calcium carbonates and heavy-metal ions, which was also impacted by the pyrolysis conditions.

To better illustrate the functionality of OFGs during the adsorption process, the pH values of the demineralized biochars before and after the adsorption procedure were also determined. Similar with the results obtained in single-metal system (Zhou et al. 2018), lower pH values of the post-adsorption solutions were detected, suggesting the release of protons during the adsorption, from which it could be concluded that a large part of OFGs participated into the storing of heavy-metal ions. Apparently, the amount of released protons is closely related to the conversion conditions of those TS biochars as well as the kind of heavy metals.

Figure 8 schematically illustrates the adsorption mechanism of heavy metals in competitive environment on the tobacco stem-derived biochars obtained with different pyrolysis conditions. The adsorption mechanisms of Pb^{2+} , Cu^{2+} , and Cd^{2+} on TS-pyrolyzed biochars in multi-metal systems were mainly surface complexation, cation- π interaction, and precipitation reactions. The reaction temperature and retention time also impacted the adsorption mechanism significantly. To sum up, (1) biochar produced in lower temperature containing large amount of OFGs can store higher content of copper; (2) biochar prepared in higher temperature with short residence time containing enriched minerals can immobilize higher quantity of lead; and (3) biochar obtained in higher temperature with longer residence time containing abundant aromatic carbon structures can adsorb cadmium ions. As a conclusion, biochars converted from tobacco stem are promising removal agents for heavy-metal amendment, even in competitive environment with multi-metal pollutions.

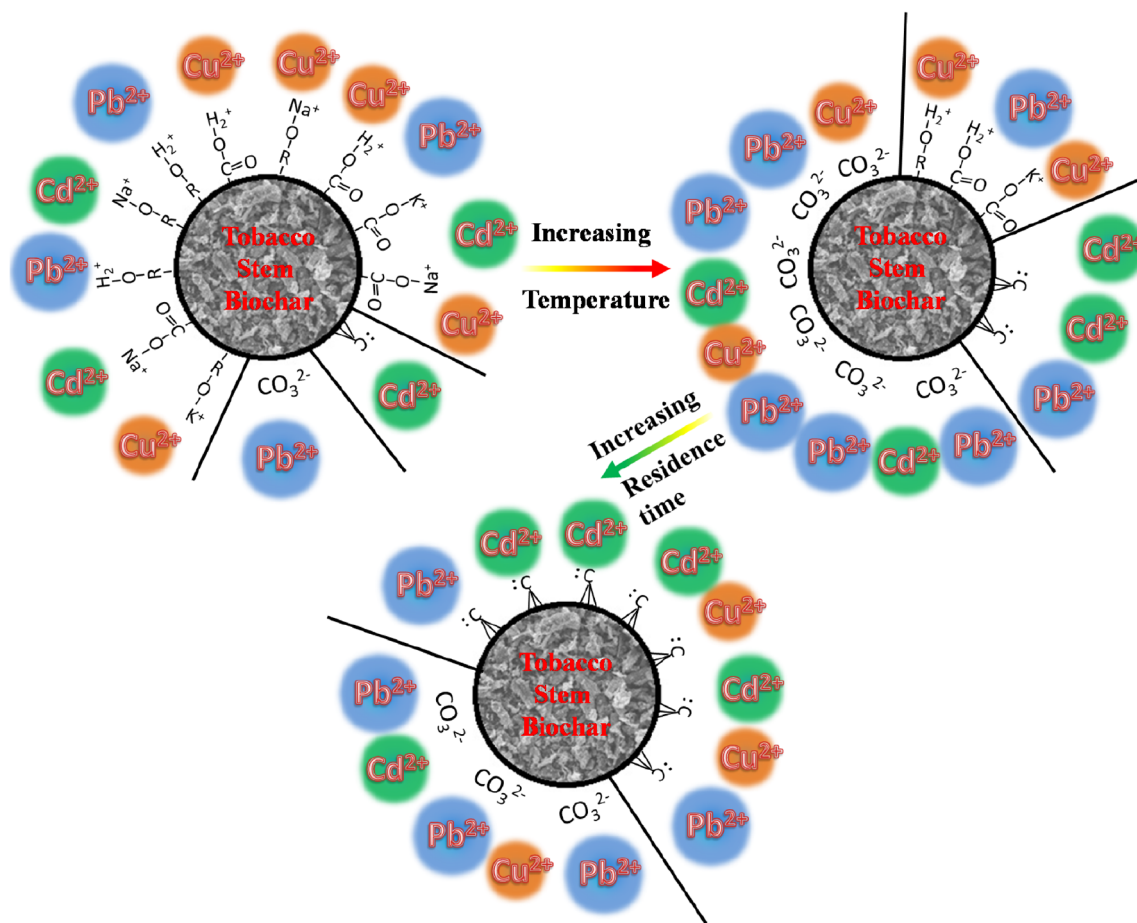


Fig. 8 Schematic illustration of the adsorption mechanism of different metal ions related to the pyrolysis conditions of biochars in competitive environment

Conclusion

The relationship of the immobilization mechanism and the pyrolysis parameters like temperature and time of biochar in competitive environment was carefully investigated by analysis of the adsorption behavior in multi-metal system and the alteration of the surface properties of biochar adsorbents. The surface complexation, cation- π interaction, precipitation, and ion exchange are the crucial factors that attribute to the adsorption behavior of TS biochars in multi-metal system. Those reactions work together during the immobilization processes, but still follow a sequential order that is largely determined by the species of heavy-metal ions and the pyrolysis parameters of biochars. The exact adsorption mechanism for Pb^{2+} , Cu^{2+} , and Cd^{2+} in multi-metal system is precipitation, cation- π interaction, and surface coordination respectively. Biochars pyrolyzed under lower temperature with short time, higher temperature with short time, and higher temperature with longer time can adsorb higher content of copper, lead, and cadmium, respectively, since biochars prepared under those conditions contain abundant OFGs, enhanced minerals, and increased aromatic structures respectively.

Acknowledgments The authors also would like to thank Mr. Deming Liu (Analysis Center, Hunan Agricultural University) for his help in performing the ICP-MS analysis.

Funding information The work was financial supported by the National Natural Science Foundation of China (Nos. 51703061, 21706060, 51504212), the Natural Science Foundation of Hunan Province (No. 2018JJ3214), the Research Foundation of Education Department of Hunan Province (No. 18A103), and the Fujian Provincial Key Laboratory of Functional Materials and Applications (Xiamen University of Technology, No. fma2017202).

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interest.

References

- Andersen FA, Brečević L, Beuter G, Dell'Amico DB, Calderazzo F, Bjerrum NJ, Underhill AE (1991) Infrared spectra of amorphous and crystalline calcium carbonate. *Acta Chem Scand* 45:1018–1024

- Bayramoğlu G, Arica MY (2008) Removal of heavy mercury(II), cadmium(II) and zinc(II) metal ions by live and heat inactivated *Lentinus edodes* pellets. *Chem Eng J* 143:133–140
- Beruto D, Barco L, Searcy AW, Spinolo G (2010) Characterization of the porous CaO particles formed by decomposition of CaCO₃ and Ca(OH)₂ in vacuum. *J Am Ceram Soc* 63:439–443
- Cao X, Harris W (2010) Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour Technol* 101:5222–5228
- Cheng Q, Huang Q, Khan S, Liu Y, Liao Z, Li G, Ok YS (2016) Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions. *Ecol Eng* 87:240–245
- Deng J, Liu Y, Liu S, Zeng G, Tan X, Huang B, Tang X, Wang S, Hua Q, Yan Z (2017) Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. *J Colloid Interface Sci* 506:355–364
- Elwakeel KZ, Atia AA, Guibal E (2014) Fast removal of uranium from aqueous solutions using tetraethylenepentamine modified magnetic chitosan resin. *Bioresour Technol* 160:107–114
- Goertzen SL, Thériault KD, Oickle AM, Tarasuk AC, Andreas HA (2010) Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination. *Carbon* 48:1252–1261
- He J, Chen JP (2014) A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools. *Bioresour Technol* 160:67–78
- Kasselouri V, Dimopoulos G, Parissakis G (1995) Decomposition of CaCO₃ in the presence of organic acids. *Cem Concr Res* 25:955–960
- Keilueit M, Kleber M (2009) Molecular-level interactions in soils and sediments: the role of aromatic π -systems. *Environ Sci Technol* 43:3421–3429
- Kılıç M, Kırbıyık Ç, Çepelioğullar Ö, Pütün AE (2013) Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis. *Appl Surf Sci* 283:856–862
- Li M, Liu Q, Guo L, Zhang Y, Lou Z, Wang Y, Qian G (2013) Cu(II) removal from aqueous solution by *Spartina alterniflora* derived biochar. *Bioresour Technol* 141:83–88
- Li W, Zhang L-B, Peng J-H, Li N, Zhu X-y (2008) Preparation of high surface area activated carbons from tobacco stems with K₂CO₃ activation using microwave radiation. *Ind Crop Prod* 27:341–347
- Lin Y, Yan W, Sheng K (2016) Effect of pyrolysis conditions on the characteristics of biochar produced from a tobacco stem. *Waste Manag Res* 34:793–801
- Ma JC, Dougherty DA (1997) The cation- π interaction. *Chem Rev* 97:1303–1324
- Mandal S, Sarkar B, Igalavithana AD, Ok YS, Yang X, Lombi E, Bolan N (2017) Mechanistic insights of 2,4-D sorption onto biochar: influence of feedstock materials and biochar properties. *Bioresour Technol* 246:160–167
- Meng A, Zhang Y, Zhuo J, Li Q, Qin L (2015) Investigation on pyrolysis and carbonization of *Eupatorium adenophorum* Spreng and tobacco stem. *J Energy Inst* 88:480–489
- Oickle AM, Goertzen SL, Hopper KR, Abdalla YO, Andreas HA (2010) Standardization of the Boehm titration: part II. Method of agitation, effect of filtering and dilute titrant. *Carbon* 48:3313–3322
- Park J-H, Cho J-S, Ok YS, Kim S-H, Kang S-W, Choi I-W, Heo J-S, DeLaune RD, Seo D-C (2015) Competitive adsorption and selectivity sequence of heavy metals by chicken bone-derived biochar: batch and column experiment. *J Environ Sci Health A* 50:1194–1204
- Park J-H, Cho J-S, Ok YS, Kim S-H, Heo J-S, Delaune RD, Seo D-C (2016a) Comparison of single and competitive metal adsorption by pepper stem biochar. *Arch Agron Soil Sci* 62:617–632
- Park J-H, Ok YS, Kim S-H, Cho J-S, Heo J-S, Delaune RD, Seo D-C (2016b) Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere* 142:77–83
- Peng H, Gao P, Chu G, Pan B, Peng J, Xing B (2017) Enhanced adsorption of Cu(II) and Cd(II) by phosphoric acid-modified biochars. *Environ Pollut* 229:846–853
- Puziy AM, Poddubnaya OI, Martínez-Alonso A, Suárez-García F, Tascón JMD (2002) Synthetic carbons activated with phosphoric acid: I. Surface Chem Ion Bind Properties Carbon 40:1493–1505
- Qin Z, Luo X, Rong N, Wang M, Wang J, Wu J, Li Z, Duns GJ, He F, Chen H, Yang L (2016) Preparation and analysis of physicochemical properties of tobacco stem biochar. *J Nanosci Nanotechnol* 16:12237–12243
- Sevilla M, Fuertes AB (2009) Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chem Eur J* 15:4195–4203
- Shen Z, Hou D, Zhao B, Xu W, Ok YS, Bolan NS, Alessi DS (2018) Stability of heavy metals in soil washing residue with and without biochar addition under accelerated ageing. *Sci Total Environ* 619:620:185–193
- Suliman W, Harsh JB, Abu-Lail NI, Fortuna AM, Dallmeyer I, Garcia-Perez M (2016) Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. *Biomass Bioenergy* 84:37–48
- Sun J, He F, Pan Y, Zhang Z (2017) Effects of pyrolysis temperature and residence time on physicochemical properties of different biochar types. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science* 67:12–22
- Sun XM, Li YD (2004) Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angewandte Chemie-International Edition* 43:597–601
- Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, Yang Z (2015) Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125:70–85
- Teng J, Zeng X, Xu X, Yu J-G (2018) Assembly of a novel porous 3D graphene oxide-starch architecture by a facile hydrothermal method and its adsorption properties toward metal ions. *Mater Lett* 214:31–33
- Uchimiya M, Lima IM, Thomas Klasson K, Chang S, Wartelle LH, Rodgers JE (2010) Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *J Agric Food Chem* 58:5538–5544
- Vithanage M, Rajapaksha AU, Ahmad M, Uchimiya M, Dou X, Alessi DS, Ok YS (2015) Mechanisms of antimony adsorption onto soybean stover-derived biochar in aqueous solutions. *J Environ Manag* 151:443–449
- Wang F, Sun H, Ren X, Liu Y, Zhu H, Zhang P, Ren C (2017) Effects of humic acid and heavy metals on the sorption of polar and apolar organic pollutants onto biochars. *Environ Pollut* 231:229–236
- Wang Z, Liu G, Zheng H, Li F, Ngo HH, Guo W, Liu C, Chen L, Xing B (2015) Investigating the mechanisms of biochar's removal of lead from solution. *Bioresour Technol* 177:308–317
- Xu X, Jiang X-Y, Jiao F-P, Chen X-Q, Yu J-G (2018) Tunable assembly of porous three-dimensional graphene oxide-corn zein composites with strong mechanical properties for adsorption of rare earth elements. *J Taiwan Inst Chem Eng* 85:106–114
- Yin S, Wu Y, Xu W, Li Y, Shen Z, Feng C (2016) Contribution of the upper river, the estuarine region, and the adjacent sea to the heavy metal pollution in the Yangtze Estuary. *Chemosphere* 155:564–572
- Yuan J-H, Xu R-K, Zhang H (2011) The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour Technol* 102:3488–3497
- Zhang C, Shan B, Tang W, Zhu Y (2017a) Comparison of cadmium and lead sorption by *Phyllostachys pubescens* biochar produced under a low-oxygen pyrolysis atmosphere. *Bioresour Technol* 238:352–360
- Zhang H, Chen C, Gray EM, Boyd SE (2017b) Effect of feedstock and pyrolysis temperature on properties of biochar governing end use efficacy. *Biomass Bioenergy* 105:136–146

- Zheng H, Wang Z, Zhao J, Herbert S, Xing B (2013) Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. *Environ Pollut* 181:60–67
- Zhou L, Liu Y, Liu S, Yin Y, Zeng G, Tan X, Hu X, Hu X, Jiang L, Ding Y, Liu S, Huang X (2016) Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures. *Bioresour Technol* 218:351–359
- Zhou N, Chen H, Xi J, Yao D, Zhou Z, Tian Y, Lu X (2017) Biochars with excellent Pb(II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization. *Bioresour Technol* 232:204–210
- Zhou Z, Xu Z, Feng Q, Yao D, Yu J, Wang D, Lv S, Liu Y, Zhou N, M-e Z (2018) Effect of pyrolysis condition on the adsorption mechanism of lead, cadmium and copper on tobacco stem biochar. *J Clean Prod* 187:996–1005

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.