Enhanced adsorption of ciprofloxacin by KOH modified biochar derived from potato stems and leaves
Ruining Li, Zhaowei Wang, Jialei Guo, Yan Li, Hanyu Zhang, Junmin Zhu and Xiaoyun Xie

ABSTRACT
Potato stems and leaves biochar (PB) was prepared by pyrolysis at a temperature of 500 °C under anoxic conditions. In order to strengthen the adsorption capacity, biochar was modified with alkaline solution (alkali modified biochar, APB). Two kinds of biochars were adopted as adsorbents to remove ciprofloxacin (CIP) from aqueous solution. The adsorption behavior of CIP onto biochar before and after alkali modified including adsorption kinetics and isotherms were investigated. The effects of different factors (equilibrium time, pH, temperature and initial concentration) during the adsorption process were also investigated. Biochar samples were characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and nitrogen adsorption–desorption isotherm. The results showed that the alkali treated biochar possessed more mesopores than raw biochar, and accordingly exhibited a more excellent adsorption performance (23.36 mg·g⁻¹) than raw biochar. Hydrophobic interaction, hydrogen-bonding interaction, electrostatic interaction, and π – π interaction were the adsorption mechanisms for CIP uptake onto the two adsorbents.

Key words | biochar, modification, characterization, ciprofloxacin, adsorption mechanisms

INTRODUCTION
Ciprofloxacin (CIP), a common human and veterinary fluoroquinolone antibiotic (Liu et al. 2013), has been used worldwide for the prevention or treatment of serious infections in humans and animals for several decades (Genç et al. 2013). CIP can enter into the water environment by incomplete metabolism in the body and the discharging of effluents from drug manufacturers (Daughton & Ternes 1999). Concentration of CIP can be detected in wastewater and surface water at several hundred ng/L–μg/L (Witte et al. 2013). The presence of CIP in wastewater and surface water, even at low concentrations, can lead to serious damages to the ecosystem and human health (Ghosh et al. 2009). Therefore, the exploration of CIP removal from water sources has attracted considerable interest. Biochar, a biomass-derived carbonaceous adsorbent, is used to remove antibiotics because of its porous structure and surface aromaticity and functionality (Srinivasan & Sarman 2015). Compared with other traditional carbon material adsorbents, like activated carbon, and carbon nanomaterials, biochar is less expensive due to the abundance of biomass materials including agricultural wastes (Jin et al. 2016). Potatoes (Solanum tuberosum L.) is an important crop in China, particularly in the southwest, northwest and northeast of China. However, the potato stems and leaves are normally treated as solid wastes. Burning them in the field is common practice, and it will lead to serious environmental problems. Herein, we try to re-utilize potato stems and leaves as a precursor to obtain a potato stems and leaves based biochar for adsorption of CIP, which is proved to be an eco-friendly and economically viable process. Although the potato stems and leaves based biochar has some merits, its adsorption capacity for pollutants is not very high because of its limited functionalities (Tan et al. 2016). In addition, the surface functional groups are still not sufficient to remove pollutants (Ma et al. 2014) and the irregular small micropore sizes (<2 nm) of the pore structure would lead to a size-exclusion effect (Jung et al. 2013). It is possible for biochar to be engineered for enhanced adsorption. Modification of biochar with alkali may change the physical/chemical properties (surface area, pore size, types of functional groups) of biochar, which can be used as a favorable adsorbent. Several studies have proved that the acid or...
alkali modified biochar removals of antibiotics are effective and show potential (Carabineiro et al. 2011; Sun et al. 2016). Liu et al. (2012) found that the adsorption of tetracycline was increased by 3.47 times when they used modified biochar, using a KOH solution to improve its ability to adsorb tetracycline from aqueous solution.

This study focused on the adsorption characteristics of CIP on raw and KOH modified biochar derived from potato stems and leaves. The specific objectives of this work were to: (1) activate biochar to improve its porous structure and functional groups and compare CIP removal efficiencies with raw biochar (2) evaluate the adsorption behavior as a function of condition variables (effect of equilibrium time, pH, initial concentration and temperature) and (3) gain a fundamental understanding of the interaction mechanisms of two biochar materials by characterizing the two materials utilizing BET surface area, Fourier transform infra-red spectroscopy (FTIR) and scanning electron microscopy (SEM).

**MATERIALS AND METHODS**

**Chemical reagents**

CIP was purchased from J&K Scientific Ltd (China). Its typical physicochemical properties are shown in Table 1. The chemicals employed in this study were of analytical grade. A stock solution of CIP (10 mg·L$^{-1}$) was prepared in ultrapure water.

**Biochar preparation and modification**

Two biochar materials were used in this work: raw biochar and alkali modified biochar. Raw biochar was obtained from potato stems and leaves which were collected from Haiyuan county, Ningxia, China. The stems and leaves of the potato were washed in order to remove surface impurities, and then crushed and pyrolyzed at 500 °C with a heating rate of 20 °C min$^{-1}$ for 6 h under limited O$_2$. The product was collected and sieved to obtain an average particle size of 0.15 mm.

The modified biochar method was based on the previous study (Liu et al. 2012). The raw biochar was processed by specifying an alkali; details of the processes are as follows: 10 g raw biochar was placed in a beaker, 100 mL 3 M KOH solution was added, and these were stirred by a magnetic stirrer for 1 h at temperature of 333 K. The suspension was then filtered and the biochar was recovered. After that, it was washed with deionized water and the biochar was stirred several times until the pH of the filtrate remained stable. The biochar samples were weighed and then stored in an air-tight container for further analysis. Raw and alkali treated biochars that were obtained from potato stems and leaves were abbreviated as PB, and APB, respectively.

**Characterization of adsorbents**

SEM (JSM-5600LV, JEOL, Japan) was used to investigate the surface morphology of PB and APB. The surface area, pore volume and pore size distribution were determined using a Trustar II 3020, Micromeritics instrument (USA). FTIR spectroscopy was also employed using a FTIR spectrometer (NEXUS 670, Thermo Fisher Nicolet, USA) in the wavelength range of 4,000–500 cm$^{-1}$ with background subtraction. The pHZC values of two adsorbents were determined using the pH drift method that was proposed in the literature (Carabineiro et al. 2011).

**Experimental**

All adsorption experiments were carried out in 50 mL conical flasks by adding 0.01 g of biochar with 25 mL of CIP solution in a thermostatic shaker. The background solution for adsorption contained 0.1 M CaCl$_2$. The same adsorption experiments were repeatedly carried out two times under identical conditions. Control experiments without adsorbents were carried out in order to determine the adsorption of CIP onto the surfaces of the conical flask.

### Table 1 | Physicochemical properties of CIP

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Molecular weight (g·mol$^{-1}$)</th>
<th>pK$_{a1}$</th>
<th>pK$_{a2}$</th>
<th>Solubility (mg·L$^{-1}$)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{17}$H$</em>{18}$FN$_3$O$_3$</td>
<td>331.4</td>
<td>5.9 ± 0.1</td>
<td>8.8 ± 0.1</td>
<td>150 mg·L$^{-1}$ (pH = 7.0)</td>
<td><img src="https://example.com/structure.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
Results showed that the removal of CIP in the control experiments could be negligible. The CIP concentrations were measured by a UV-vis spectrophotometer (UNICAM UV300, Thermo Spectronic, USA) at 272 nm.

**Adsorption kinetics**

The kinetics of adsorption experiments were carried out by adding 0.01 g of adsorbents into a conical flask containing 25 mL of the aqueous solution with a CIP concentration of 10 mg·L\(^{-1}\). All the conical flasks were agitated and sealed in the dark on a shaker for 24 h and a rate of 200 rpm at 25 °C.

**Adsorption isotherms and thermodynamics**

Adsorption isotherms of CIP to PB and APB were determined by adding 0.01 g adsorbents with 25 mL CIP solutions of different concentrations ranging from 2–16 mg·L\(^{-1}\) in conical flasks, respectively. The other experimental conditions were the same as the kinetics of adsorption experiment. The temperature effect was assessed by equilibrating 0.01 g biochar with 25 mL aqueous solutions with CIP on a shaker at 15, 25 and 35 °C.

**Effect of solution pH**

The effect of pH on CIP adsorption (10 mg·L\(^{-1}\)) onto PB and APB was examined at different pH values (pH 3–10) for 24 h. The pH of the CIP solution was adjusted to a certain value using 1.0 M HCl and 1.0 M NaOH solution by pH meter.

**RESULTS AND DISCUSSION**

**Characteristics of two biochar materials**

The SEM micrographs of the biochars are shown in Figure 1. It was shown that the surface morphology of PB and APB
were different. The structures of PB (Figure 1(a), Figure 1(b)) were smooth and porous on the surface (Liu et al. 2012). The APB (Figure 1(c) and (d)) showed a rougher surface than the PB. The structures of the modified biochar were not homogeneous. Stacked particles with a sheet shape were observed on the surface of the APB (Figure 1(c)). And APB exhibits a cracked morphology (Figure 1(d)), which might be due to alkali modification corroding its surface.

Adsorption study

Effect of time and adsorption kinetics

Adsorption capacities of the biochars toward CIP were measured as a function of time as shown in Figure 2. The adsorption of CIP increased rapidly within the first 10 min, followed by a gradual increase up to 12 h, and remained almost constant thereafter for both biochars. Therefore, 12 h was taken as the equilibrium time for adsorption in this study. Two kinetic models, pseudo-first-order and pseudo-second-order equations, Equation (1) and Equation (2), were used to fit the experimental data.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(1)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(2)

where \(q_e\) and \(q_t\) are the amount of CIP adsorbed per unit mass of the adsorbent (mg·g\(^{-1}\)) at equilibrium and time \(t\) respectively. \(k_1\) (min\(^{-1}\)), and \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) are the pseudo-first-order, and pseudo-second-order rate constant respectively. The calculated values of \(q_e(\text{cal})\), \(k_1\), \(k_2\), correlation coefficient \(R^2\), and experimental values of \(q_e(\text{exp})\) are listed in Table 2.

As the results showed, the \(R^2\) values of the pseudo-second-order model were higher than those of the pseudo-first-order model, and the values of \((q_e - \text{exp})\) were closer to the theoretical values, suggesting that the pseudo-second-order model can preferably describe the adsorption process. The kinetic processes that are fitted by the pseudo second-order kinetic model has chemiadsorption as the rate-determining step and involve the chemical bonding between CIP molecule and polar functional groups on the adsorbent.

To further analyze the diffusion process of CIP from aqueous solution to adsorption, the intra-particle diffusion model was used in the adsorption of the CIP, and its equation is calculated as follows:

\[
q_t = K_d t^{1/2} + L
\]

(3)

where \(K_d\) is the intraparticle diffusion rate constant (mg (g h\(^{1/2}\))\(^{-1}\)), and the values of \(L\) (mg·g\(^{-1}\)) depict the thickness of the boundary layer. The parameters \(K_d\) and \(L\) are determined from the linear plot of \(q_t\) versus \(t^{1/2}\).

The values of the intercept \(L\) and the intra-particle diffusion coefficient \(K_d\) are shown in Table 3. The \(L\) value of the third stage is greater than that of the first two stages, which reflects an increase in the thickness of the boundary layer (Liu et al. 2016). The intercept \(L\) should cross the origin if the diffusion mechanism is controlled by intraparticle diffusion. As shown in Table 3, all the \(L\) values are non-zero, suggesting that intraparticle diffusion is not the unique rate-controlling step.

As shown in Figure 3, the plots were multi-linear, indicating the existence of two or more steps during the adsorption process. The first stage was from 0 h to 1 h, which represent the transport of the CIP molecule from the adsorbent’s external surface to the pores of the adsorbent internal structure. The second stage is the transport of the CIP molecule from the adsorbent external surface to the pores of the adsorbent internal structure. The second linear portion included the adsorption period from 1 h–8 h, which represents intraparticle diffusion. The third stage is the adsorption of the CIP molecule on the interior surface of the adsorbent, which includes the adsorption period from 8 h–36 h. The line of the third stage reflected a significantly low slope ascribed to the decrease of CIP concentration and available active sites, indicating that the adsorption equilibrium state is nearly reached. The ratio of...
portion 1 duration to the portion 2 was about 1:8, indicating that intraparticle diffusion prevailed over the external mass transfer diffusion. (Luo et al. 2013; Harogoppad et al. 2013).

### Adsorption isotherms

Adsorption isotherm models can be used to describe the adsorption processes and investigate the adsorption mechanism. The classic equations of Langmuir (Equation (4)) and Freundlich (Equation (5)) were used to fit the experimental equilibrium adsorption data. All the parameters are listed in Table 4, while the fitting curves of before and after the modification of PB and APB for CIP were shown in Figure 4. The equations of the Langmuir and Freundlich adsorption models are expressed by

$$q_e = \frac{Q_{max}bC_e}{1 + bC_e}$$  

(4)

$$q_e = \frac{k_L}{(mg·g^{-1}·h^{-1/2})}$$

(5)

where $q_e$ (mg·g⁻¹) and $C_e$ (mg·L⁻¹) are the solid-phase and aqueous-phase concentrations at adsorption equilibrium, respectively. $Q_{max}$ is the maximum adsorption capacity (mg·g⁻¹) and $b$ the constant related to the affinity. $K_f$ and $n$ are indicators of adsorption capacity and intensity, respectively.

From Table 4 can be seen, $R^2$ suggested that the Langmuir model fits the data better than the Freundlich model for PB and APB, which indicated the monolayer coverage of CIP onto the adsorbents (Peng et al. 2015). The maximum adsorption capacity of CIP by APB was 23.36 mg·g⁻¹ at 308.15 K. This was higher than those of PB. The results showed that the adsorption capacities of APB exceeded PB.

The parameter $b$ is related to the affinity of the binding sites, which allows comparisons of the affinity of biochar towards the CIP molecule. APB had a higher affinity for CIP (0.57, 0.47 and 0.15 L mg⁻¹, respectively) than did PB (0.058, 0.15 and 0.127 respectively), revealing that formation of functional groups on the surface of APB, resulting in having the highly adsorption ability.

### Thermodynamic study

The thermodynamic parameters of the adsorption process, including Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$) are commonly used to describe the spontaneity and heat of system. The thermodynamics of the adsorption processes were presented using the following equations.
\[
\Delta G^0 = -RT \ln K_e
\]  
(Equations (6)–(7)):

\[
\ln K_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

where \( R \) (kJ mol\(^{-1}\)·K\(^{-1}\)) is the gas constant \(8.314 \times 10^{-3}\), \( T \) (K) is the absolute temperature, and \( K_e \) (L·g\(^{-1}\)) is the adsorption equilibrium constant. By plotting \( \ln K_e \) against \( 1/T \), the values of \( \Delta H^0 \) and \( \Delta S^0 \) can be estimated from the slope. The values of these parameters are presented in Table 5.

The Gibbs free energy change (\( \Delta G \)) of adsorption (Table 5), was useful in defining whether adsorption was endothermic or exothermic. The negative values of \( \Delta G \) indicate that the adsorption of CIP onto APB was spontaneous and thus thermodynamically favorable (Elaigwu et al. 2014). When the biochar was modified by KOH, the magnitude of \( \Delta G \) decreased in the CIP solution, which suggested that the adsorption was more spontaneous after alkali modification. In addition, the decreasing \( \Delta G \) values with increasing temperature for the adsorption of CIP onto adsorbents indicated that the adsorption processes were favorable at high...
temperatures (Jin et al. 2016). The positive values of $\Delta H$ indicate the endothermic nature of the adsorption of CIP onto the two adsorbents in the temperature range of 288.15–308.15 K (Elaigwu et al. 2014). While the positive values of $\Delta S$ suggest an increase in randomness at the solid/solution surface during the adsorption.

### Adsorption mechanism analysis

#### The effect of physical properties

Table 6 summarizes the BET specific surface area, total pore volume, pore volume and average pore size of the adsorbents. The physical changes including pore volume and surface area that occurred in biochar. They may change the adsorption efficiency, and would likely be one of the mechanisms involved in the improved CIP adsorption by APB. The surface area was evaluated with the BET method. The Barret–Joyner–Halender method was used to determine the pore size distribution. The BET surface area ($S_{BET}$) of APB was 38.75 m$^2$·g$^{-1}$, which was almost 2.6 times lower than that of PB. The decreased surface area possibly resulted from reduction of the microporous structure (Ho et al. 2014). Total pore volume slightly decreases after alkali modification. The meso-/macropore volume of APB increased, probably due to the destruction of some micropore structures and deformation into meso-/macropores by alkali treatment. In addition, this may explain that alkali modification cleans up blocked pores and removes inorganic materials (Peng et al. 2013). The increase of meso-/macropores on the material was favorable for the substance diffusing into the inner pore system of the adsorbent (Jin et al. 2016). The average pore size of the two adsorbents mainly centered at around 3.12 nm and 6.72 nm, indicating a development of mesoporosity of APB.

The $N_2$ adsorption isotherms at 77 K (Figure 5) displayed different shapes for PB and APB. The $N_2$ adsorption isotherm of PB showed that the exhibited characteristics are representative of a Type I isotherm based on the International Union of Pure and Applied Chemistry (IUPAC) system of classification. It is a typical type of isotherm for microporous material (Elaigwu et al. 2014). The major adsorption occurred at low relative pressure and reached a plateau at high relative pressure, while the $N_2$ adsorption isotherm of APB resembled Type IV. In the low-pressure region, the amount adsorbed is small and the knee is not well defined. At higher pressures to $p/p_0 \approx 1.0$, the adsorption process first increases slightly and then very markedly. These isotherm features indicate $N_2$ adsorption occurs mostly in the mesopores (Mohan et al. 2014). This result also indicated that APB evolved two types, I and IV, which suggests that APB has both microporous and mesoporous structures.

It is evident from Table 6 that PB was predominated by micropores, while APB was predominated by meso-/macropores. PB has a higher surface area and larger total volume in comparison with APB. However, the meso-/macropores in APB have lower diffusion resistance, therefore it is easier for the CIP molecule to diffuse inside APB than PB, and this might be one of the reasons that APB had a higher adsorption capacity for CIP than PB.

#### The effect of functional groups

FTIR spectra for PB and APB are presented in Figure 6. The spectra were significantly shifted after alkali treatment of PB, including some interactions between KOH and biochar.
It is obvious that the strong bands region at 3,400–3,700 cm\(^{-1}\) could correspond to –OH stretching vibrations due to alcoholic or phenolic functions (Jin et al. 2016). The peak at 3,697 cm\(^{-1}\) was strengthened after modification. The region 1,400–1,800 cm\(^{-1}\) is assigned to C=O stretching vibrations due to esters and carboxylic acids (Mohan et al. 2014). The disappearance of the peak at 2,924 cm\(^{-1}\) (asymmetric and symmetric stretch of alkyl C–H) occurs, in comparison to that in unmodified biochar material (Li et al. 2015). Peaks of 1,100–1,165 cm\(^{-1}\) were for C–O stretching vibration of carboxylic acid and alcohols, and the peaks at wavenumber lower than 1,100 cm\(^{-1}\), were deemed to be the Si–O–Si vibrating (Liu et al. 2012). Noticeably, the peaks of 1,430 cm\(^{-1}\) and 3,418 cm\(^{-1}\) weakened for APB. This indicates that the content of O-containing groups was reduced compared with PB, making the surface more hydrophobic, resulting in improved adsorption capacities (Peiris et al. 2017).

FTIR spectra of PB, APB after CIP adsorption (Figure 7 and Figure 8) were also collected to identify the functional groups responsible for adsorbing CIP. It is obvious that they were both slightly changed after adsorption. The bands shifted from 1,421 cm\(^{-1}\) to 1,437 cm\(^{-1}\) in Figure 7, and shifted from 1,430 cm\(^{-1}\) to 1,438 cm\(^{-1}\) in Figure 8, revealing the change of C=O after adsorption. The shift of these bands indicated the important role of π–π interactions between CIP and the adsorbents in the adsorption processes (Zhu et al. 2015). For APB after CIP adsorption in Figure 8, the peak at 3,419 cm\(^{-1}\) intensified, which indicates significant hydrogen-bonding interactions.

**Effect of solution pH**

The effect of solution pH on CIP adsorption is presented in Figure 9(a). The adsorption capacity of CIP was barely influenced by initial pH. This could be explained by the biochar derived from potato stems and leaves having a strong buffer effect (Liu et al. 2012). The equivalent pH values of alkali biochar are illustrated in Figure 9(b).

Equivalent pH values during adsorption were a more important factor affecting the adsorption performance of PB and APB (Liu et al. 2012). It not only influenced the properties of the adsorbent surface, but also affected the ionization forms of CIP solutes in solution. CIP has two values of pK\(_a\): pK\(_{a1}\) 5.9 ± 0.1 (for the carboxylic acid group) and pK\(_{a2}\) 8.8 ± 0.1 (for the amine group on the
piperazine moiety). When solution pH < 5.9 ± 0.1, the cationic form of CIP is dominant, and when solution pH is between 5.9–8.8, CIP loses a hydrogen atom off the nitrogen in the piperazine moiety, thus establishing a balance of charges on the molecule. This balance is characteristic of the zwitterionic form for CIP. At solution pH > 8.8 ± 0.1, after passing the pKa2, a proton is lost from the carboxylic group and the anionic form of CIP is dominant in solution (Wu et al. 2010). As shown in Figure 9(b), both APB and PB were having equilibrium values of 8.3–8.7 and 8.6–9.2 respectively, and the main species of CIP were zwitterionic and anionic forms. The two adsorbents, PB and APB, exhibited pH_{PZC} values of about 10.1 and 9.87, respectively. At the solution equilibrium pH < pH_{PZC} (PB and APB), the surface of PB and APB will be positively charged and some attractive electrostatic forces will be involved. At equilibrium pH, part of the CIP is still in the zwitterionic form, which indicates that a hydrophobic effect may be involved in the adsorption of CIP on the carbon sorbents (Peng et al. 2015). In addition, adsorption of CIP is also ascribed to π–π EDA interactions occurring between zwitterionic CIP and arene rings of the adsorbent surface (Peiris et al. 2017).

**CONCLUSION**

A novel and bio-based adsorbent, KOH modified potato stems and leaves-based biochar, was prepared. The modified biochar presented better performance for CIP removal than the raw biochar. The maximum adsorption ability of APB for CIP was 2.3 times higher than BC, attributed to the different functional groups and large meso-/macropore volume of APB for the CIP removal. FTIR analysis indicates that hydrogen-bonding interactions also play an important role in adsorption process. The main species of CIP were zwitterionic and anionic forms at equilibrium pH; therefore, assisted hydrophobic interaction and electrostatic force can occur, which assist adsorption of CIP onto APB. In addition, the specific structure on the modified biochar surface facilitates the formation of π–π EDA interaction between the ring structure of biochars and the CIP molecule. These results suggest that the adsorption mechanisms of CIP onto APB may be ascribed to a combination effect of hydrophobic interaction, π–π EDA interaction, hydrogen-bonding interaction and electrostatic interaction.

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