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Low-cost biochar derived from herbal residue: characterization and application for ciprofloxacin adsorption

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Abstract Thermally carbonization biochar produced from a traditional Chinese herbal medicine waste (*Astragalus mongholicus* residue) was investigated for its performance in ciprofloxacin adsorption. Batch sorption experiments were conducted, and scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and Brunauer–Emmett–Teller surface area analyses were employed to characterize the biochar. The results demonstrated that thermal activation process improves the adsorbent characteristics. Biochar produced at 800 °C had the best adsorption capacity, a better pore structure and the largest surface areas. The adsorption process fit well to a pseudo-second-order kinetics model. The adsorption isothermal model results revealed that the adsorption process of ciprofloxacin is described better by the Freundlich isotherm and the type of adsorption is a chemical process. The maximum adsorption of ciprofloxacin occurred at pH 7. The present research demonstrated that *A. mongholicus* biochar might be an attractive and cost-effective adsorbent with good adsorption performance for removing ciprofloxacin from water solution.

Introduction

In recent years, antibiotics, including sulfonamides (SAs), quinolones (QNs), macrolides (MCs), tetracyclines (TCs) and β-lactams, have been used extensively to prevent or treat infective diseases in human or animals (Thiele-Bruhn 2003). However, many antibiotics cannot be absorbed completely or metabolized. The by-products are released into the ground or drinking water and adversely affect human health as well as the environment, becoming pseudo-persistent in the environment (Wang et al. 2014; Zhou and Broodbank 2014).

Previous researchers have reported the presence of antibiotics in water bodies, such as rivers, lakes and oceans at concentrations ranging from ng/L to µg/L. Sulfonamides were the dominant antibiotics found in surface water (Wang et al. 2014). Zhang et al. (2015) used market survey, data analysis and modeling methods to estimate that approximately 53,800 tons of 36 antibiotic chemicals entered the environment in China following various types of wastewater treatment. Various treatment methods, including physical adsorption (Carabineiro et al. 2012), bio-sorption, chemical degradation methods, such as advanced oxidation and ozonation (Gao et al. 2014) and biological degradation (Qiu et al. 2013), have been used for the treatment of antibiotics.

Several degradation products of antibiotics were shown to be more toxic to organisms than their parent antibiotics. For example, N4-acetyl sulfamethazine, which is one of the metabolites of sulfamethazine, proved to be more hazardous than its parent compound (Le-Minh et al. 2012).

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Therefore, the treatment techniques for antibiotic pollutants must be highly effective and prevent secondary contamination. Compared with other treatment techniques, adsorption is more effective because of its simplicity in design, ease of handling and ability to overcome secondary pollutants. Commercial activated carbon (AC) is considered as an excellent adsorbent with a higher adsorption capacity for a large Brunauer–Emmett–Teller (BET) surface area (Ali et al. 2012). However, the cost of AC is high and prevents its wide application, especially in developing countries. As a consequence, developing a highly effective and low-cost adsorbent is necessary.

Biochar, which is a porous, carbon residue derived from the thermal conversion of waste biomass under limited oxygen or anaerobic conditions, is one of the most promising materials because it is more highly effective, environmentally friendly and cost-effective than other materials (Ahmad et al. 2014; Mohan et al. 2014). Biochar can be derived from a variety of materials, such as plant residue, animal waste and sludge. A large number of studies on pollutant removal focus on the use of biochar. Examples of recent research papers include the adsorption of heavy metals from wastewater (e.g., Cd, Cu, Pb, As) using sewage sludge waste or biomass biochar (Dubey et al. 2014; Chen et al. 2015; Wang et al. 2015; Komkiene and Baltrenaite 2016), the adsorption of tetracycline and fluoroquinolone using rice husk biochar, wastewater sludge biochar or cow manure biochar (Yao et al. 2013; Jing et al. 2014; Tzeng et al. 2016), the adsorption of pesticides by agricultural biomass biochar (Inyang and Dickenson 2015) and the adsorption of dye using plant waste biochar (Sun et al. 2013). Using plant waste in biochar synthesis is preferable and sustainable because plant wastes such as agricultural residues are still underutilized, and a large portion of this biomass is discarded as waste (Loow et al. 2015).

The biochar investigated in the present research is *Astragalus mongholicus* residue (Huangqi in China), which is a commonly used traditional Chinese herbal medicine. Several million tons of herb residue are produced in China every year, which means that the residue can easily cause a serious environmental problem. These herb residue wastes have a high lignin, cellulose and hemicellulose contents, so they are suitable for biochar production. Another advantage of this herb–biochar production is that it is an environmentally friendly and cost-effective way to treat wastewater from the medicine factory.

The aim of this study was to investigate the possibility of using *A. mongholicus* biochar (AMBC) as a cost-effective adsorbent for ciprofloxacin (CIP) removal from water solutions. The adsorption characteristics of CIP onto AMBC were investigated under varying conditions, which included the contact times, dosages, pH and initial CIP concentrations. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses were carried out. The adsorption experiments were carried out from June to September 2015 on the laboratory scale at China Pharmaceutical University, Nanjing, China.

Materials and methods

AMBC preparation and characterization

The residue of one of the commonly used traditional Chinese herbal medicines, *A. mongholicus*, was washed with distilled water and dried at 105 °C for 24 h. The dry herb residue was ground and passed through a 100-mesh sieve. The ground herb residue was then treated via a thermal carbonization procedure as described Shang et al. (2015). The herbal residue was subjected to thermal activation for 5 h under oxygen-limited conditions (200, 400, 500, 600, 700 and 800 °C). After thermal activation, the residues were washed with 0.1 mol/L HCl overnight to remove the suspended ash. Then, the biochar was washed with DI water until the pH was stable and dried at 105 °C overnight.

The S_{BET} (BET surface area) was measured by the nitrogen sorption method at 77 K with a surface area and porosity analyzer (ASAP2020, Micromeritics Instrument Corp., Norcross, GA, USA). Surface functional groups were investigated by FTIR spectroscopy using a Nicolet FTIR spectrophotometer (Thermoscientific Nicolet iS10, USA), scanning from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}. The microstructure analysis of the biochar was performed with an SEM (JEOL JSM-7500F, JEOL Ltd., Tokyo, Japan). The surface chemistry of biochar was determined using an XPS spectrometer (Thermo Fisher Scientific, K-Alpha, USA) with a monochromated Al Kα source and a spot size 400 μm in diameter.

Preparation of ciprofloxacin solution and HPLC Conditions

Ciprofloxacin (CAS: 85721-33-1) with purity greater than 99 % was obtained from Aladdin Chemical Reagent Co. (Shanghai, China). CIP stock solution was prepared (500 mg/L) by dissolving the ciprofloxacin in DI water and storing at 4 °C. The basic properties of compound are given as follows: molecular formula, $C_{17}H_{18}FN_3O_3$, and molecular weight, 331.34.

The concentration of CIP was analyzed using high-performance liquid chromatography (HPLC) with a UV detector. Chromatographic separation was performed at 30 °C on a Waters Symmetry C18 Column (4.6 mm × 150 mm,

5 µm particle size). The mobile phase was composed of 0.05 mol/L of citric acid solution [acetonitrile (82:18 v/v)]. The pH was adjusted to 3.5 with triethylamine. The flow rate was 1.0 mL/min, and the injection volume was 10 µL. UV measurement was taken at a wavelength of 278 nm.

Adsorption studies

A series of adsorption experiments was performed using a Teflon tube (Nalgene, Thermol, USA). The mixture was shaken under 25 °C on a shaker at 200 rpm and then filtered through a 0.45-µm filter. In the first set of experiments, 25 mL CIP solution (100 mg/L) and 0.05 g of AMBC (produced at 200, 400, 500, 600, 700 and 800 °C) were mixed into tubes and stirred for 12 h to investigate the influence of the activation temperature. Natural *A. mongholicus* residue (BC100) was set as the control. The AMBC results that showed the highest adsorption capacity were chosen to be used in the following experiments.

The effect of the adsorbent dosage on the removal of CIP was demonstrated in the second experiment. AMBC with the highest adsorption capacity was added to the tube containing the solution (25 mL, 100 mg/L of CIP) and stirred for 12 h (dosage: 25, 50, 100, 500 mg). To understand the influence of pH on CIP adsorption by AMBC, experiments were performed by adding 25 ml of CIP working solution (100 mg/L) and 50 mg AMBC to the tube and equilibrating for 12 h. The pH was adjusted from 3 to 10 with NaOH and HCl (1 mol/L). The adsorption isotherm experiments were conducted with 50 mg of biochar and 25 mL of CIP solution, with the CIP concentration ranging from 10 to 300 mg/L (10, 25, 50, 100, 150, 200 and 300 mg/L). The effect of equilibration time on the adsorption was studied in the fifth set of experiments. AMBC (50 mg) and CIP solution (25 mL, 25, 50, 100, 150, 200 mg/L) were mixed in the tube and stirred from 0 h to 12 h.

Adsorption isothermal and kinetics models

Langmuir (Eq. 1), Freundlich (Eq. 2), Temkin (Eq. 3) isotherm and D–R isotherm (Eq. 4) models were used to analyze the adsorption equilibrium data in the present study.

$$\frac{C_e}{q_e} = \frac{1}{k_a q_m} + \frac{C_e}{q_m} \tag{1}$$

$$\log q_e = \log k_f + \frac{\log C_e}{n} \tag{2}$$

$$q_e = A \log k_T + A \log C_e \tag{3}$$

$$\ln q_e = \ln q_m - \beta \left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2 \tag{4}$$

where C_e is the equilibrium concentration after adsorption (mg/L), q_e is the amount of CIP adsorbed per gram of AMBC (mg/g), k_a (L/mg) is the Langmuir constant, q_m (mg/g) is the maximum adsorption capacity of the Langmuir isotherm model, k_f is the constant indicative of the relative adsorption capacity of AMBC (mg/g), 1/n is the constant, A is the constant related to the heat of the adsorption process (J/mol), k_T is the constant of the Temkin isotherm equilibrium, the parameter β is the constant of the sorption energy (mol²/J²), T is the temperature (K) and R is the gas constant (8.314 J/(mol K)).

The value of the sorption energy, E (kJ/mol), can be calculated as follows:

$$E = \frac{1}{\sqrt{2 \times \beta}} \tag{5}$$

The value of E gives information about the adsorption processes. The value ranges from 1 to 8 kJ/mol for physical sorption and from 8 to 16 kJ/mol for chemical sorption (Ma et al. 2015).

Linear forms of the pseudo-first-order (Eq. 6) and pseudo-second-order model (Eq. 7) were used to investigate the adsorption kinetics of CIP onto biochar:

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where q_t and q_e (mg/g) correspond to the adsorption capacity of the biochar at time t and equilibrium. The parameters k_1 and k_2 (min⁻¹) are the rate constants of the adsorption models 6 and 7, respectively.

Results and discussion

Effect of carbonization temperature

Temperature is one of the most important factors in controlling the physicochemical properties of biochar (Ahmad et al. 2014). The carbon content rose when the pyrolysis temperature increased, whereas the H and O contents decreased; further, the surface area increased with an increase in temperature (Tzeng et al. 2016). Mui et al. (2010) concluded that the bamboo biochar produced under the higher temperature had a better adsorption capacity for dye. The present research also yielded the same conclusion as described in former studies. The removal efficiency and adsorption capacity of CIP using natural *A. mongholicus* residue, AMBC, were compared (Fig. 1). According to the results, the natural *A. mongholicus* residue and BC200 had the lowest removal performance, whereas thermal treatment at higher temperature provided a significant
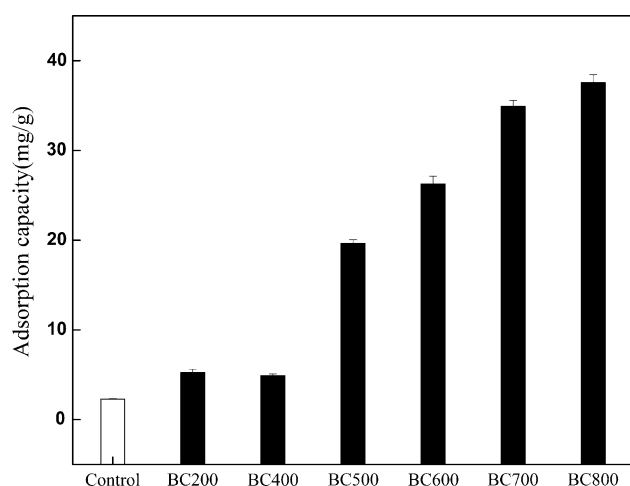
Fig. 1 Adsorption capacity of AMBC

enhancement in the adsorption capacity, with a significant increase in the removal efficiency when carbonization at 500 °C (19.65 ± 0.41 mg/g). BC800 had the highest adsorption capacity ($q_e = 37.6 \pm 0.87$ mg/g, CIP concentration 100 mg/L) compared with the other pyrolysis temperatures. In the following study, BC800 with the highest

q_e was selected as the adsorbent because of its excellent performance for CIP adsorption in the present study.

Characterization of AMBC

Biochar has proved to be effective for the adsorption of organic pollutants because of its high surface area and micropore structure (Inyang and Dickenson 2015). Previous studies showed that biochar produced at temperatures higher than 400 °C had better adsorption capacity (Ahmad et al. 2014). In this research, the S_{BET} and SEM images also proved that pyrolysis temperature produces a significant enhancement of AMBC characteristics. For example, the BET surface area ranged from 0.42 m^2/g (natural residue) to 176.33 m^2/g (BC800). This significant increase in S_{BET} (approximately 420-fold) could be attributed to the pores in the biochar as shown in Fig. 2. The results demonstrated that a large BET surface area can offer more active adsorption sites for CIP by increasing the adsorption capacity (BC800 had the highest q_e).

The surface area characteristics, proximate analysis and carbon, hydrogen, oxygen and nitrogen content of biochar are given in Table 1. The proximate analysis gives the ash,
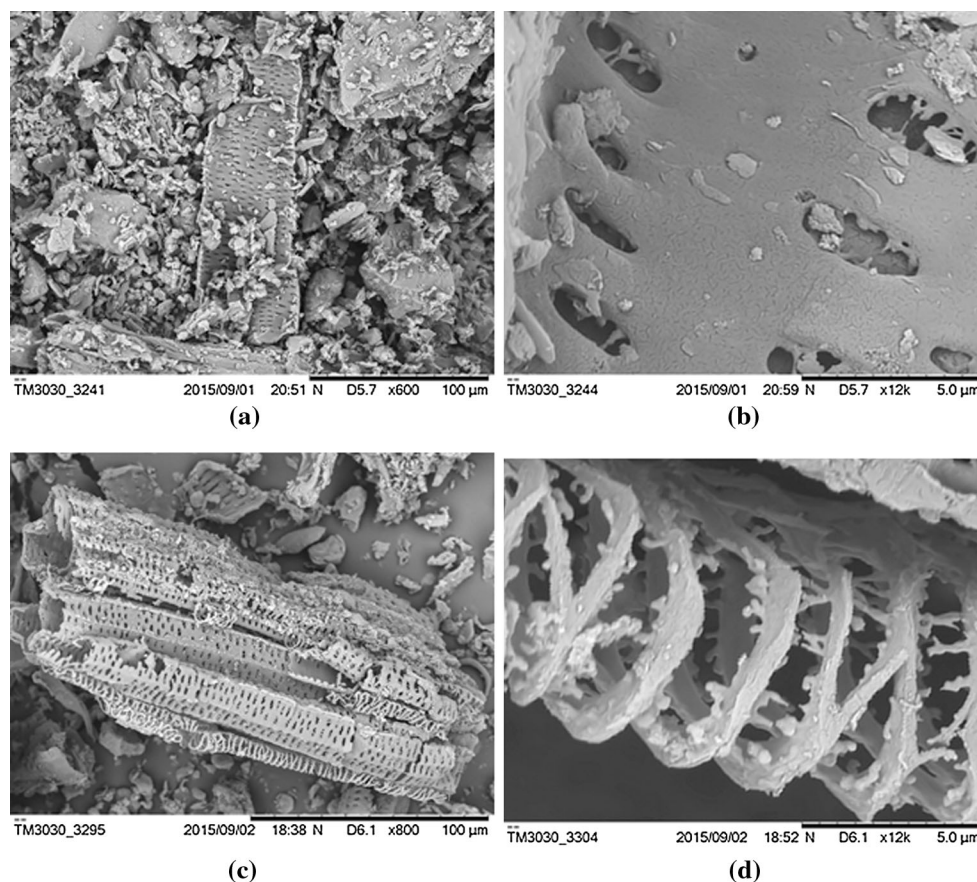

Fig. 2 SEM images of *A. mongholicus* residue (**a**, **b**) and BC800 (**c**, **d**)

Table 1 Properties of biochar derived from *A. mongholicus* at 800 °C

Properties of BC800 and *Astragalus mongholicus*[a]	
Surface area characteristics	
S_{BET} (m²/g)[b]	176 .33 (0.42)
S_{mic} (m²/g)[c]	100.76 (ND)[d]
S_{min}/S_{BET} (%)	57.14
V_T (cm³/g)[e]	0.1399 (0.0077)
V_{mic} (cm³/g)[f]	0.044 (ND)
V_{mic}/V_T (%)	31.53
Elemental analysis	
C (%)	57.76 (41.74)
H (%)	0.975 (4.994)
O (%)	15.13 (44.13)
N (%)	1.66 (1.5)
Proximate analysis	
Moisture (%)	2.5 (6.84)
Ash (%)	32.2 (9.76)
Volatile (%)	10.21 (71.11)
Fixed carbon (%)	55.09 (12.29)

[a] Values in the parenthesis are for natural *A. mongholicus* residue

[b] Surface area measured using N_2 adsorption with the BET method

[c] Micropore surface area calculated using the *t*-plot method

[d] The value was too small to measure

[e] Total pore volume

[f] Micropore volume calculated with the *t*-plot method
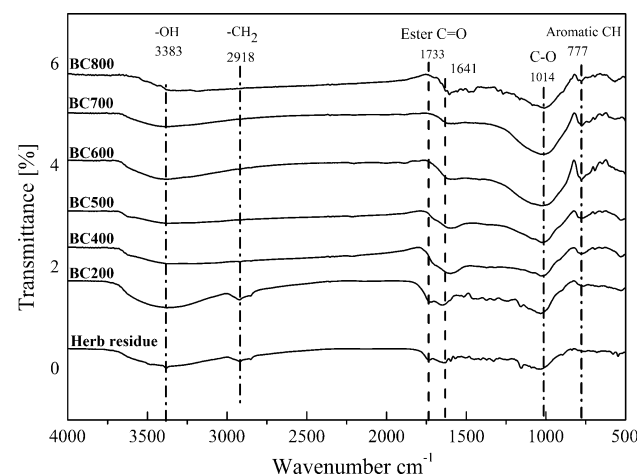
**Fig. 3** FTIR spectra of the nature *A. mongholicus* residues and biochar

volatile and fixed carbon contents of biochar. Elemental C, H and N content was determined by combustion. Oxygen was determined by difference. FTIR spectra for natural *A.*

mongholicus residues and Biochar were measured in the 4000–500 cm⁻¹ region (Fig. 3). The results were consistent with the previous research (Zheng et al. 2013). Various bands in the FTIR spectra represent band vibrations in the biochars: O–H (3000–3690 cm⁻¹), aliphatic C–H (2918 cm⁻¹), ester C=O (1733 cm⁻¹), polymeric CH_2 (1641 cm⁻¹), C–O (1014 cm⁻¹) and aromatic C–H (777 cm⁻¹). The FTIR spectra indicated that carbonization temperature has a significant influence on the functional groups of biochars.

The XPS spectra of the C1s electrons are shown in Fig. 4. The C1s functional groups were characterized according to previously published studies, and the present results closely matched those of previous studies (Azargohar et al. 2014; Singh et al. 2014; Liu et al. 2015). The peak at 284.8 eV was assigned to carbon components, such as C–C, C=C, aromatic and aliphatic carbon, the 286.4 eV peak was assigned to C–O–C, and 288.9 Ev was assigned to COO. The functional groups that contain the oxygen mentioned above may react with CIP by various mechanisms, such as hydrophobic, H-bond and π–π interactions, thereby increasing the adsorption capacity of AMBC (Inyang and Dickenson 2015).

Effect of adsorbent dosage and solution pH

The impact of adsorbent dosage on CIP removal efficiency and adsorption capacity (q_e) was investigated at an initial concentration of 100 mg/L. An increase in the adsorbent dosage from 25 to 500 mg significantly increased the CIP removal efficiency from 36 to 100 %. This improvement can be attributed to the great number of adsorption sites and the larger surface area caused by the increased biochar
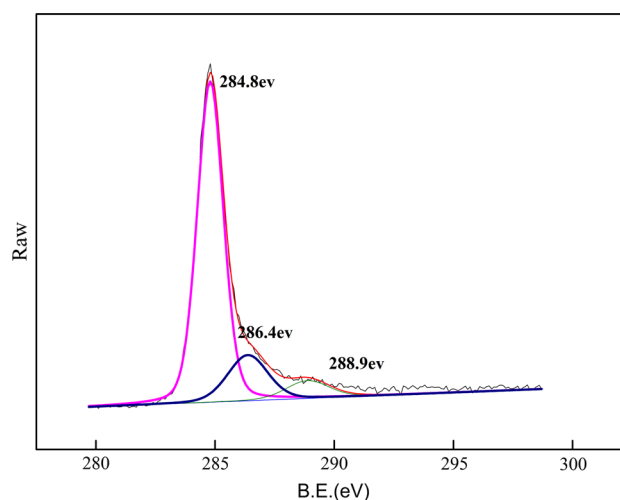
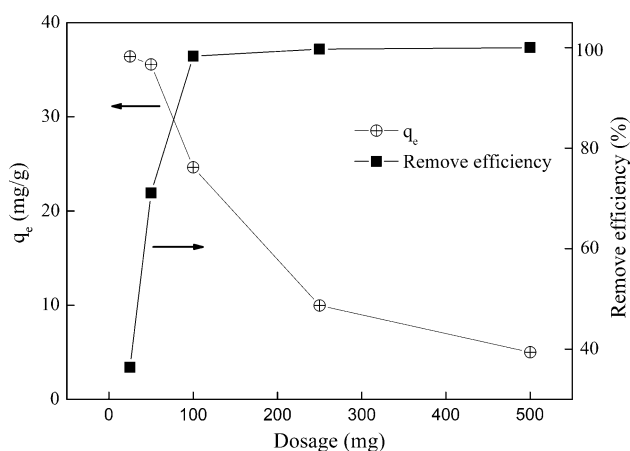**Fig. 4** XPS spectra of C1s of AMBC (800)

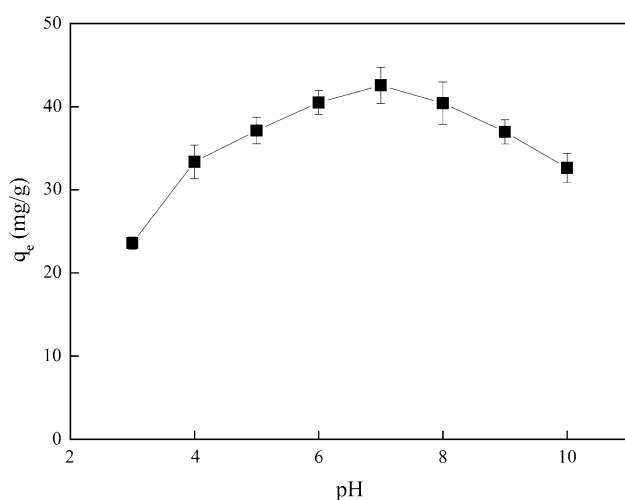**Fig. 5** Effect of biochar dosage on removal efficiency and q_e

Fig. 6 Effect of solution pH on biochar adsorption capacity (q_e)

dosage (Adamczuk and Kołodyńska 2015). However, q_e decreased with the increase in biochar dosage because of the increase in unsaturated adsorption sites on the BC surface. Based on these results (Fig. 5), the following batch experiments were conducted at an adsorbent dosage of 50 mg with 25 mL CIP solution ($m/v = 1:500$).

The pH of the solution is one of the most important control parameters in the adsorption process. The effects of pH were investigated, and the results are shown in Fig. 6. The results demonstrated that with a pH increase from 3 to 7, the adsorption capacity of biochar increased, whereas the adsorption capacity of biochar decreased with the change from pH 7 to 10. Previous studies have proven that the

effects of pH were dependent on both the biochar surface properties and the adsorbate pollutant characteristics. For example, the functional groups on the surface of biochar change with the pH; published studies have also demonstrated that there are different ionizations and degrees of ionization of CIP under different pH conditions (Li et al. 2014). Because CIP molecules contain several moieties, such as NH_2 and $COOH$ groups, hydrophilic CIP exists as the cation (CIP^+), anion (CIP^-), uncharged molecule (CIP^0) and zwitterion ($CIP^\pm$) in water (CIP: p$Ka1 = 6.2$ and p$Ka2 = 8.8$). Thus, the removal of CIP can be attributed to the formation of H-bonding between CIP and biochar, depending on the pH of the solution (Jing et al. 2014), thus possibly presenting another reason for the importance of pH as one of the most important control factors in the present study.

Adsorption isotherms

Four isotherm models (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms) were tested in the present research to evaluate the maximum q_e and understand the mechanism of adsorption of CIP onto AMBC (Fig. 7). The results presented in Fig. 7 and Table 2 demonstrate that the adsorption data can be described better by the Langmuir isotherm (R^2, 0.999) than by the Freundlich isotherm (R^2, 0.983), Temkin isotherm (R^2, 0.983) or D–R isotherm (R^2, 0.878). Similar results were reported for adsorption of persistent organic pollutants, antibiotics and other organic pollutants with carbonaceous materials, such as active carbon, biochar or carbon nanotubes (Carabineiro et al. 2012; Zheng et al. 2013; Essandoh et al. 2015; Ma et al. 2015; Mita et al. 2015).

The essential features of the Langmuir equation can be expressed in terms of a dimensionless constant separation factor (R_L) as defined by McKay (1982):

$$R_L = \frac{1}{1 + k_a C_0}$$

where C_0 is the highest initial CIP concentration (mg/L). The value of R_L indicates whether the shape of the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

R_L was 0.009 in this study, showing that the adsorption behavior of CIP was favorable. According to the Freundlich isotherm model, the value of n was 6.821 and that

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Fig. 7 Adsorption isotherms of CIP on BC800
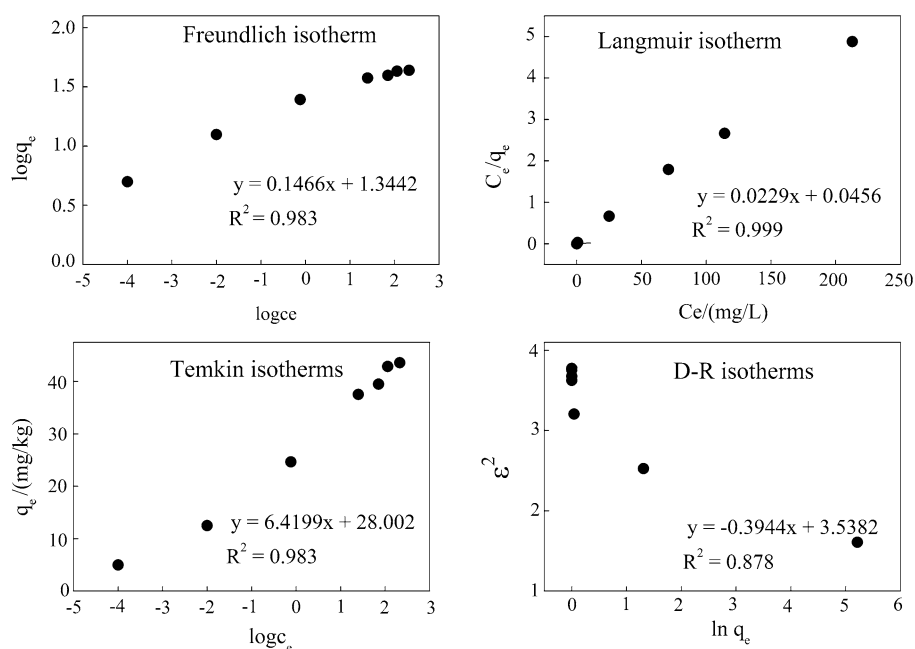
Table 2 Isotherm model parameters for the adsorption of CIP by BC

Freundlich		Langmuir		Temkin		D–R	
K_f	3.835	q_m (mg/g)	43.668	B_1 (J/mol)	7.363	q_m (mg/g)	36.551
n	6.821	K_a (L/mg)	0.502	k_t	44.834	E (kJ/mol)	11.259
R^2	0.983	R^2	0.999	R^2	0.983	R^2	0.878

Table 3 Adsorption capacities of different carbonaceous adsorbents for adsorption of antibiotics

Type of biochar	Pollutants[a]	q_e (mg/g)[b]	References
Plant biochar	SMT	37.7	Rajapaksha et al. (2015)
Agricultural soil biochar	SMX	4.99 ± 0.74	Zheng et al. (2013)
Cow manure biochar	SMT	10.87	Tzeng et al. (2016)
Wastewater sludge biochar	GAT	19.80	Yao et al. (2013)
Herb biochar	CIP	42.9	This study[c]
Activated carbon	CIP	231	Carabineiro et al. (2012)
Carbon nanotubes	CIP	209.6	Yu et al. (2016)
Graphene	CIP	235.6	Ma et al. (2015)
Graphene	CIP	194.6	Yu et al. (2015)

[a] *SMT* sulfamethazine, *SMX* sulfamethoxazole, *GAT* gatifloxacin, *CIP* ciprofloxacin

[b] q_e is the maximum adsorption capacity

[c] CIP concentration 200 mg/L

of K_f was 3.835, also indicating that the adsorption conditions for BC were favorable for CIP. The E value (11.259 kJ/mol) was found to be in the range of 8–16 kJ/mol, which further indicates that the type of

adsorption of CIP on biochar is a chemical process (Ma et al. 2015). The result is consistent with the report of sulfamethazine chemical sorption on plant-derived biochar (Rajapaksha et al. 2015), the removal of ciprofloxacin with
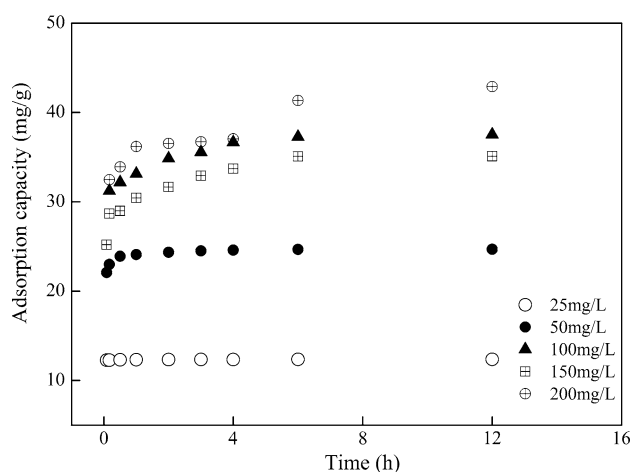
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Fig. 8 Influence of contact time on q_e

activated carbon (Huang et al. 2014) and the removal of sulfamethoxazole with biochar prepared from agricultural soil (Zheng et al. 2013), as briefly summarized in Table 3.

Various mechanisms, such as hydrophobic, electrostatic, hydrogen bond and π–π interactions, may simultaneously participate in the antibiotic adsorption processes (Mohan et al. 2014). CIP may interact with adsorbent via π–π EDA (electron donor–acceptor) interactions because the benzene rings have a fluorine group and an N-heteroaromatic ring. The π–π interaction has previously been verified as one of the most important driving forces for the sorption of organic pollutants onto biochar (Ahmad et al. 2014) and carbon nanomaterials adsorbent (Li et al. 2014; Yu et al. 2016).

Adsorption kinetics

Kinetics experiments that were conducted with different initial concentrations with the time ranging from 1 h to 12 h are presented in Fig. 8. The adsorption capacity increased with time, and 12 h was considered the equilibrium time (Fig. 8).

The pseudo-first-order and pseudo-second-order models were used to test for the adsorption of CIP onto BC800 to evaluate the adsorption kinetics parameters. These parameters are important for predicting the adsorption capacity and estimating the adsorption rates when designing adsorption columns. Table 4 presents the kinetic parameters of the pseudo-first-order and pseudo-second-order models, including the constants k_1, k_2, calculated adsorption capacities $q_{e,cal}$ and R^2. The value of R^2 proved that the pseudo-second-order kinetic model (>0.999) is a better fitting model for the adsorption of CIP onto BC800. The calculated q_e in the pseudo-second-order model is also in agreement with the experimental adsorption capacity, indicating that adsorption of CIP with biochar is a chemical process (Ho and McKay 1999; Yu et al. 2015).

Conclusion

In the present research, a batch adsorption study for the adsorption of CIP with *A. mongholicus* residue biochar was conducted. The characteristics of AMBC were examined at different initial CIP concentrations, contact times and pH values. The results demonstrated that the *A. mongholicus* biochar can be used as an effective low-cost adsorbent for removal of CIP. The adsorption capacity of AMBC was found to increase with an increase in temperature. BC800 was observed to have the maximum adsorption capacity, whereas natural *A. mongholicus* had the lowest adsorption capacity. The adsorption was pH dependent, and the maximum q_e was found to occur at pH 7. The adsorption of CIP on AMBC is a chemical process and was found to follow the pseudo-second-order model. The Langmuir adsorption model was a better fit for the adsorption process than the Freundlich isotherms was.

Table 4 Kinetic parameters of adsorption kinetics

C_0 (mg/L)	q_e (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
		$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (min^{-1})	R^2
25	12.38	0.33	0.15	0.758	12.38	32.64	0.999
50	24.68	1.70	0.79	0.941	24.75	2.04	0.999
100	37.54	9.31	0.64	0.980	37.74	0.23	0.999
200	42.90	10.96	0.12	0.816	43.29	0.08	0.999

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