

Adsorption Characteristics of Norfloxacin by Biochar Prepared by Cassava Dreg: Kinetics, Isotherms, and Thermodynamic Analysis

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Biochars (BC) generated from biomass residues have been recognized as effective sorbents for organic compounds. In this study, biochars as adsorbents for the removal of norfloxacin (NOR) from aqueous solutions were evaluated. Biochars were prepared from cassava dregs at 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C, respectively (labeled as BC350, BC450, BC550, BC650, and BC750). The results showed that the kinetic data were best fitted to the pseudo second-order model, indicating that the sorption was governed by the availability of sorption sites on the biochar surfaces rather than the NOR concentration in the solution. Sorption isotherms of NOR were well described by the Freundlich model, and the Freundlich coefficients ($\lg k_F$) increased with the pyrolysis temperature of biochars. Thermodynamic analysis indicated the feasibility and spontaneity of the NOR adsorption process. The NOR adsorption on BC450, BC550, BC650, and BC750 was an endothermic process, while an exothermic process occurred for BC350. FTIR studies further suggested that the adsorption mechanism was possibly attributable to H-bond and π - π interactions between NOR and biochars. Overall, this work constitutes a basis for further research considering the bioavailability and toxicity of antibiotics in the presence of biochar.

Keywords: Biochar; Cassava dreg; Norfloxacin; Adsorption equilibrium; Kinetics; Thermodynamics

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INTRODUCTION

Norfloxacin (1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazine-2-yl)-3-carboxylic acid) (NOR), a fluoroquinolone antibiotic, is a synthetic, broad-spectrum antibacterial compound that has been widely used in human and veterinary medicine against both Gram-negative and Gram-positive bacteria; it works by inhibiting DNA gyrase (Hirsch 1999). It was reported that approximately 3300 metric tons of antibiotics were used for human medicine in the U.S. in 2011 (Mitchell *et al.* 2015). However, NOR and other fluoroquinolone antibiotics cannot be completely absorbed by animals or humans. NOR is often discharged into aquatic environments *via* domestic wastewater effluents, excretion, and disposal of expired pharmaceuticals in its original or metabolized form (Alcock *et al.* 1999). The presence of NOR in surface water and wastewater, even at low concentration, can lead to emergence and development of antibiotic-resistant bacteria (Carabineiro *et al.* 2011). Nevertheless, traditional water and wastewater treatment processes cannot completely remove NOR due to its stability, and it may cause a risk to

human health through contaminated drinking water (Zorita *et al.* 2009). Hence, finding a more effective way to remove NOR residue is important and has been a research hotspot.

Many techniques have been investigated for NOR decontamination, including adsorption (Lorphensri *et al.* 2006), photodegradation (Ahmad *et al.* 2015), and chlorine oxidation (Dodd *et al.* 2005), among which adsorption is considered to be a simple and effective method to remove NOR. Previous research on adsorption of fluoroquinolone antimicrobials by different environmental matrices has included silica, alumina (Lorphensri *et al.* 2006), soils (MacKay and Seremet 2008), clay minerals (Figueroa-Diva *et al.* 2010), natural aquifer material (Hari *et al.* 2005), oxide minerals (Gu and Karthikeyan 2005), carbon nanotubes (Wang *et al.* 2010), and activated carbon (Liu *et al.* 2011; Carabineiro *et al.* 2011; Ahmed and Theydan 2011), but few studies about its sorption by biochar have been done. Generally, the adsorption mechanisms of fluoroquinolone antimicrobials with model sorbent phases have been documented to be cation exchange, cation bridging, surface complexation, hydrophobic effect, electrostatic interaction, and electron-donor-acceptor interactions (Wang *et al.* 2010).

Biochar (BC) has been a research focus in recent years due to its potential roles in soil amendment, carbon sequestration, and heavy metal sorption (Lehmann and Joesph 2009; Manya 2012). Biochar is analogous to black carbon and is produced by pyrolysis of biomass under limited or absence of oxygen conditions. Various types of biomass have been used as feedstock for biochar production, such as agronomic crop residues, wood waste, forestry residues, organic portion of municipal solid waste, animal manures, activated sludge, *etc.* (Duku *et al.* 2011).

Biochar is usually applied to soil for both agricultural and environmental gains (Manya 2012). The addition of biochars to soils has been assessed to be an effective practice in sequestering carbon (Lehmann 2007), increasing soil fertility (Van Zwieten *et al.* 2010) and crop production (Major *et al.* 2010), reducing green house gas emissions (Lehmann *et al.* 2006), and also improving soil microbial activity (Steiner *et al.* 2008). Recently, biochar has been reported to be particularly effective in sorption and sequestration of organic contaminants, such as polycyclic aromatic hydrocarbons (Chen and Yuan 2011), diuron (Yu *et al.* 2006), atrazine and simazine (Zheng *et al.* 2010), pentachlorophenol (Devi and Saroha 2015), phenanthrene (Zhang *et al.* 2010), oxytetracycline (Jia *et al.* 2013), sulfamethoxazole (Yao *et al.* 2012; Lian *et al.* 2014), and sulfamethazine (Rajapaksha *et al.* 2014; Rajapaksha *et al.* 2015).

Pyrolysis temperature of biomass is an important factor that determines physicochemical properties of biochar, *e.g.*, structure, morphology, bulk, and surface properties (Harvey *et al.* 2012; Keiluweit *et al.* 2010). However, the adsorption behavior and mechanisms of NOR onto biochars prepared under different temperatures is largely unknown, which limits assessment of its adsorption capacity and exploration of possible applications.

The main objective of this study was to investigate the sorption behavior of NOR to biochar pyrolyzed from cassava dreg, a typical agricultural waste in tropical areas. The sorption kinetics, isotherms, and thermodynamics of NOR on biochars were investigated. The biochar, before and after sorption of NOR, was compared using Fourier transform infrared spectroscopy (FTIR) to elucidate the corresponding adsorption mechanisms. The results will provide some important information for potential NOR removal as well as its environmental risk assessment.

EXPERIMENTAL

Materials

NOR (99.5%) was purchased from Dr. Ehrenstorfer (Germany) and used as received. Fundamental physicochemical properties of NOR are molecular weight: 313.33 g·mol⁻¹; pKa: 6.22 and 8.51; and aqueous solubility: 161.00 mg·L⁻¹ at pH 5, 400 mg·L⁻¹ at pH 7 and 910 mg·L⁻¹ at pH 9 (Ross and Riley 1990). The stock solution of NOR (100 mg·L⁻¹) was prepared in methanol. Methanol and acetonitrile of HPLC grade were obtained from Sinopharm Chemical Reagent Co. Ltd. Other chemical agents were of analytical reagent grade. pH was adjusted using 0.1 mol·L⁻¹ NaOH and 0.1 mol·L⁻¹ HCl. All solutions were prepared with ultrapure water supplied by Spring-S60i+PALL system.

Methods

Biochar preparation and characterization

Cassava dregs, collected from Danzhou city, Hainan province of China, were used as feedstock of biochar under oxy-limited condition by a muffle furnace. The cassava dregs were air-dried at room temperature and ground to pass a 1 mm sieve. The ground cassava dregs were then placed in porcelain crucibles with lids and charred at 350 °C, 450 °C, 550 °C, 650 °C, 750 °C under limited oxygen in a muffle furnace. The prepared biochars were ground to pass through a 60-mm mesh sieve. Based on charring temperature, the biochars were labeled as BC350, BC450, BC550, BC650, and BC750.

The biochar yields were calculated through weighing the dry weight of cassava dregs before and after the carbonized. The ash was defined as remaining mass after subsequent heating at 750 °C for 4 h in an open crucible. The ash content was calculated according the following equation:

$$\text{Ash content (\%)} = (\text{weight of ash/dry weight of biochar}) \times 100 \quad (1)$$

The pH values of biochars were determined using glass electrode method with the biochar-to-water ratio (mass ratio) of 1:20. The contents of C, H, N, and S were measured by Varion EL analyzer, and the O content was estimated by mass difference. The biochar surface morphology was determined by scanning electron microscopy (EVO18 analyzer). Nitrogen adsorption and desorption experiment at 77 K was adopted to determine the specific surface area and porosity character of biochar samples.

Adsorption experiments

Sorption of NOR on manioc-dreg biochar was determined using a batch equilibrium method. A certain amount of biochar (0.5 g BC350, 0.2 g BC450, 0.1 g BC550, 0.1 g BC650, and 0.1 g BC750) was transferred to 50 mL centrifuge tubes containing 10 mL of 0.01 M CaCl₂ solutions (containing 200 mg·L⁻¹ NaN₃ to inhibit microbial activity) spiked at concentrations of 5 to 30 mg·L⁻¹ of NOR. All sealed tubes were shaken in the dark at 288, 298, and 308 K at 200 rpm for 24 h. The preliminary kinetic experiments showed adsorption of NOR on biochar reached an apparent equilibrium within 24 h. After shaking, the suspensions were centrifuged for 5 min at 8000 rpm and then immediately filtered through a 0.45 μm membrane of polyether sulfone using a syringe. The filtrate was analyzed for NOR concentrations using high pressure liquid chromatography (HPLC). The same concentration series of NOR solutions without biochars were run under the same condition as the controls, showing that loss was negligible and no interferences were found during the analysis. Sorption

kinetics of NOR was evaluated at an initial NOR concentration of $10 \text{ mg}\cdot\text{L}^{-1}$. To determine the contact time required to achieve sorption equilibrium, the suspensions were sampled at 0.5, 1, 1.5, 2, 4, 8, 12, 18, 24, 36, and 48 h. The initial concentration of NOR was $10 \text{ mg}\cdot\text{L}^{-1}$; this was shaken with biochars (0.5 g BC350, 0.2 g BC450, 0.1 g BC550, 0.1 g BC650, and 0.1 g BC750) and sampled at different time intervals at 298 K. The effect of solution pH on NOR removal by biochars was tested in pH range of 3-9. NOR sorbed by biochars was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e is the amount of NOR adsorbed ($\text{mg}\cdot\text{g}^{-1}$), C_0 is the initial NOR concentration ($\text{mg}\cdot\text{L}^{-1}$), C_e is NOR concentration at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), V is the solution volume and m is the mass of dry adsorbent (g).

Detection of NOR

The concentration of NOR in the supernatant filtrate was analyzed using a Waters 2695 Separations Module HPLC equipped with a 2487 UV detector at the maximum adsorption wavelength of 277 nm and a Gemini C18 reversed-phase column (150 mm \times 4.0 mm ID, 5 μm). The column temperature was at 30 $^{\circ}\text{C}$. The mobile phase consisted of formic acid (0.1%) and acetonitrile (80:20, v/v) at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$. The retention time for NOR was 2.8 min.

FTIR analysis

The biochar surface functional groups were measured with FTIR before and after adsorption of NOR according to Jia *et al.* (2013). After achieving sorption equilibrium, the suspensions were allowed to stand for 24 h, and then the suspensions were removed. Afterwards, the biochar residues were freeze-dried for FTIR analysis. The mixtures with 1.0 mg of biochar and 200 mg of oven-dried (105-115) KBr were pressed into a pellet. Fourier transform infrared spectroscopy (FTIR) studies were performed using a scanning from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Biochar Properties

The selected physicochemical properties of biochars are summarized in Table 1. As the pyrolysis temperature rose from 350 $^{\circ}\text{C}$ to 750 $^{\circ}\text{C}$, the percentage of biochar yield was reduced from 29.80% to 18.79%, which was similar to the observation reported by Mendez *et al.* (2013). The decline in biochar yield is mainly due to the destruction of cellulose and hemicellulose as well as combustion of organic materials with increased pyrolysis temperature (Demirbas 2004; Cao and Harris 2010). By contrast to biochar yield, the biochar ash content was increased significantly by increased pyrolysis temperature due to the concentrations of minerals and increased organic matter losses from the residues (Cao and Harris 2010). The biochar was acidic when prepared at the lower temperature of 350 $^{\circ}\text{C}$, shifting to alkaline at the high temperature. The pH values of biochars ranged from 6.08 to 9.55, which is in agreement with previous literature (Hossain *et al.* 2011), due to the minerals which ash content contained in the biochars, attributing to alkaline substances.

With increasing charring temperature, the carbon content of biochars increased, and the corresponding losses of H and N were recorded. Chen *et al.* (2008) and Al-Wabel *et al.* (2013) observed that the C content increased with temperature. However, the content of BC550 (68.93%) was higher than that of BC750 (62.38%), indicating that some amorphous carbon was decomposed into CO₂ at 750 °C. The ratios of molar H/C and O/C tended to decrease with increased pyrolytic temperature, which indicated an increase of the aromaticity and a decrease in polarity of biochars (Ahmad *et al.* 2012). The trend was attributed to the removal of polar surface functional groups and the formation of aromatic structures at high pyrolysis temperatures (Chen *et al.* 2008). The molar N/C ratio, with the same tendency of H/C and O/C, decreased with charring temperature, suggesting the surface functional groups of the biochars reducing. A similar observation is reported by Chen *et al.* (2014)

From Table 1, it can be seen that when increasing biochar production temperature, its specific surface area (SSA) increased. In addition, microporosity development was observed with the increase of pyrolysis temperature. These results were in accordance with previous studies (Mendez *et al.* 2013; Bagreev *et al.* 2001). Specific surface area is one of the most important factors that control biochar's ability to adsorb chemical compounds, as larger specific surface area indicates more porous structures within biochar (Yao *et al.* 2011; Kloss *et al.* 2012).

Table 1. Physico-chemical Properties of 5 Biochars

Property		BC350	BC450	BC550	BC650	BC750
Yield %		29.80	29.64	23.61	21.55	18.79
pH(1:20)		6.08	7.24	7.41	9.39	9.55
Ash content %		12.79	16.37	17.12	23.42	30.56
Elemental analysis %	C	58.52	63.56	68.93	70.36	62.38
	H	3.57	3.20	2.46	1.82	1.52
	O	23.62	15.54	10.23	3.15	4.31
	N	1.50	1.33	1.26	1.25	1.23
	S	0.15	0.14	0.13	0.15	0.15
Atomic ratio	H/C	0.061	0.050	0.036	0.026	0.021
	O/C	0.40	0.24	0.15	0.04	0.07
	N/C	0.026	0.021	0.018	0.018	0.017
SSA m ² ·g ⁻¹		48.19	80.56	167.55	219.76	430.37
TPV cm ³ ·g ⁻¹		0.080	0.135	0.183	0.155	0.169
Micropore volume cm ³ ·g ⁻¹		0.011	0.026	0.036	0.031	0.144

Adsorption Kinetics

Figure 1 showed the NOR adsorption kinetics onto the five biochars. The results demonstrated that the adsorption process of NOR on biochars was rapid at the start, then the adsorption increased slowly until the plateau of adsorption equilibrium was achieved. The fast adsorption rate at the initial stage could be attributed to the increase of driving force caused by the concentration gradient of NOR in aqueous solutions and the existence of large available active sites on the surface of biochars (Liu and Zhang 2015). Equilibrium was attained at about 8 h for all samples except for BC550, which took about 24 h, which was slower than other adsorbents (Sui *et al.* 2012). This is because surface

adsorption sites of biochar may be limited, and biochar combining with NOR active sites have been saturated, causing adsorption capacity to reach a balance. The equilibrium adsorption quantities of NOR adsorbed on biochars increased with production temperature, showing the same increase trend with specific surface area. As the surface of biochar prepared from high temperature may have more adsorption sites, it can provide more opportunities for the interaction between biochar and NOR (Huang *et al.* 1998).

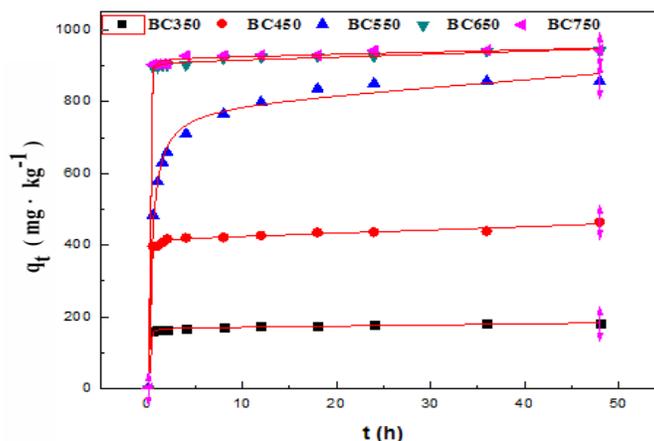


Fig. 1. Sorption kinetics of NOR onto 5 biochars

To compare the adsorption kinetics of NOR on biochars, several well-known kinetic models were applied to fit kinetic adsorption data. The pseudo-second-order kinetic (E), Elovich, and intraparticle diffusion models can be expressed as Eqs. (3), (4), and (5), respectively,

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

$$q_t = a + bt \quad (4)$$

$$q_t = k_p t^{1/2} + C \quad (5)$$

where q_t is the amount of NOR adsorbed at time t ($\text{mg}\cdot\text{kg}^{-1}$), q_e is the equilibrium adsorption amount of NOR ($\text{mg}\cdot\text{kg}^{-1}$), k_2 is the rate constant of pseudo-second-order kinetics adsorption ($\text{kg}\cdot(\text{mg}\cdot\text{h})^{-1}$), a is the rate constant about initial sorption, b is a constant about sorption activation energy, k_i is the intra-particle diffusion rate constant ($\text{kg}\cdot(\text{mg}\cdot\text{h}^{1/2})^{-1}$), and C is a constant providing the thickness of the boundary layer.

Adsorption kinetics parameters calculated from the pseudo-second-order kinetic, Elovich, and intraparticle diffusion models are listed in Table 2. As shown in Table 2, the pseudo-second-order model fit the kinetic data better than Elovich and intraparticle diffusion models with a coefficient of determination (R^2) above 0.997, which is consistent with the study by Sui *et al.* (2012). This indicated that the sorption was dominated by the availability of sorption sites on the biochar surfaces but not the NOR concentration in the solution (Liu 2008). It can be observed that the theoretical uptake, q_t , obtained from pseudo-second-order expression were in good agreement with the experimental data and increased with pyrolysis temperature of biochars. The change may be largely attributed to the increase of specific surface area with increasing pyrolytic temperature, which can provide more contacting area and specific sorption sites for NOR (Liu *et al.* 2011).

The Elovich equation has been widely applied to describe second-order kinetics when chemisorption of different analytes appeared on solids with energetically heterogeneous reactive sites (Arancibia-Miranda *et al.* 2015). The initial rate constants (a) increased with the increase of charring temperature, which was similar to the previously description by the pseudo-second-order model. The intraparticle diffusion model was used to analyze the rate controlling step in the adsorption process. In the present research, the slope of plot of q_t versus $t^{1/2}$ did not pass through the origin, indicating that intraparticle diffusion was not the only rate-controlling mechanism and the intraparticle diffusion and external film diffusion may also regulate adsorption (Li *et al.* 2015). The larger value of the intraparticle diffusion rate constant C revealed that film diffusion had a larger role as the rate-limiting step (Li *et al.* 2015). The value of C increased with the increasing of pyrolysis temperature, suggesting that the film diffusion became more important at high temperature biochar.

Table 2. Kinetic Parameters of the Pseudo-second-order, Elovich, and Intraparticle Diffusion Models for the NOR Sorption by Biochars

sample	Pseudo-second-order model			Elovich equation			Intraparticle diffusion model		
	q_e (mg·kg ⁻¹)	k_2 kg·(mg·h) ⁻¹	R^2	a	b	R^2	k_p kg·(mg·h ^{1/2}) ⁻¹	C	R^2
BC350	181.19	0.019	0.999	162.40	4.66	0.977	3.34	160.28	0.954
BC450	456.20	0.005	0.998	402.17	12.05	0.889	8.81	396.15	0.904
BC550	869.57	0.002	0.999	582.12	81.46	0.967	53.904	559.25	0.806
BC650	942.51	0.001	0.999	896.93	10.73	0.929	7.87	891.50	0.951
BC750	945.18	0.001	1.000	905.36	10.15	0.913	7.13	901.47	0.858

Adsorption Isotherms

Sorption isotherms are critical to evaluate the adsorption capacity of adsorbents and to understand the nature of sorbate-sorbent interactions. The sorption isotherms of NOR on the biochars are displayed in Fig. 2. It could be seen that adsorption isotherms of NOR on BC350, BC650, and BC750 were nonlinear, while the isotherms of NOR onto BC450 and BC550 were relatively linear. Usually, biochar is composed of carbonized and noncarbonized fractions, indicating that the surface of biochar is heterogeneous (Chen *et al.* 2008). Therefore, the adsorption of NOR on biochars have two principal types of sorption domains. One is a soft carbon domain similar to rubbery polymers, which is characterized by a partition mechanism to exhibit a linear; the other is a hard carbon domain analogous to glassy polymers, characterized by a pore-filling mechanism, which sorption isotherm is nonlinear (Xia and Pignatello 2001). Hence, for BC450 and BC550, partition was a dominant mechanism, while for BC350, BC650, and BC750, the major mechanism was a pore-filling.

Generally, the experimental adsorption data are fitted by the Freundlich and Langmuir models, which correspond to the heterogeneous and homogenous sorbent surfaces, respectively. Therefore, the Freundlich model (Eq. 6) was used to fit the adsorption data of NOR on the biochars,

$$\lg q_e = \lg k_F + \left(\frac{1}{n}\right) \lg c_e \quad (6)$$

where c_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentrations of NOR, $k_F [(\text{mg}\cdot\text{kg}^{-1})/(\text{mg}\cdot\text{L}^{-1})^n]$ is the Freundlich coefficient related to adsorption capacity, and n is Freundlich depicting the sorption intensity.

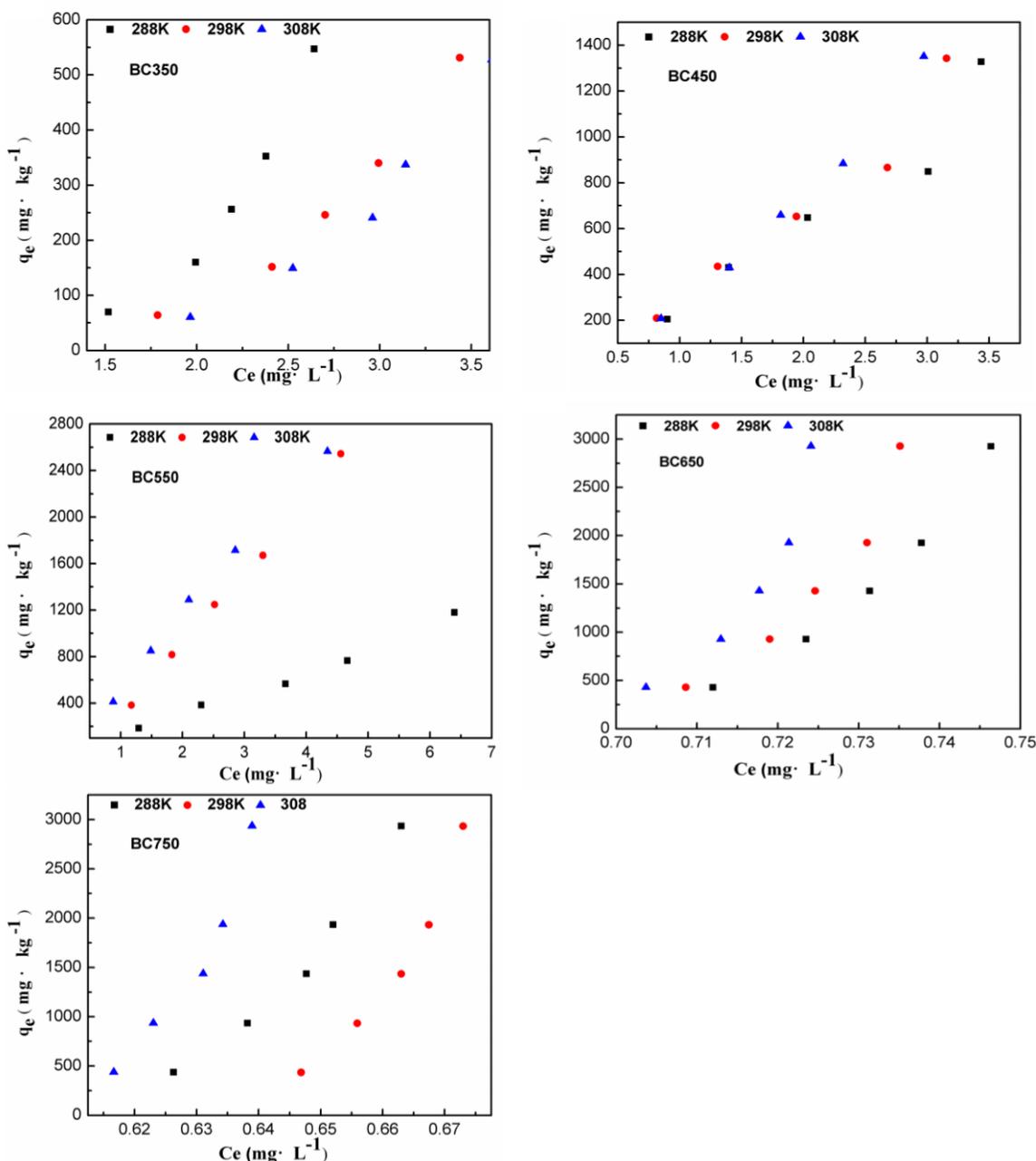


Fig. 2. Sorption isotherms of NOR onto biochars

All the fitting results of Freundlich parameters for the adsorption of NOR on biochars were listed in Table 3. The high R^2 values (0.969 to 0.998) suggested that the Freundlich model simulated the adsorption of NOR on the biochars well. As shown in Table 3, for BC350, BC650, and BC750, the sorption of NOR was highly nonlinear, with $1/n$ in the range of 3.26 to 64.93 (more than 1) at different temperatures, suggesting that the heterogeneous surfaces of biochars were bonded to NOR by weak free energies so that sorption is essentially dominated by adsorption rather than partitioning (Jia *et al.*

2013). On the other hand, the values of $1/n$ for BC450 and BC550 were relatively close to 1, indicating that the sorption was led by partitioning, which was consistent with the adsorption isotherms. The Freundlich coefficients ($\lg k_F$) followed the order of BC750 > BC650 > BC550 > BC450 > BC350, in accordance with the increased specific surface area, indicating that the surface area of biochars was an important factor for NOR sorption.

Table 3. Parameters from the Fitting of Freundlich Models for NOR Sorption on Biochars

Biochars	Temperature	Freundlich model		
		$\lg k_F$	$1/n$	R^2
BC350	288K	1.14	3.73	0.991
	298K	0.97	3.26	0.996
	308K	0.74	3.55	0.997
BC450	288K	2.40	1.26	0.969
	298K	2.45	1.27	0.981
	308K	2.42	1.48	0.998
BC550	288K	2.15	1.12	0.994
	298K	2.52	1.37	0.992
	308K	2.71	1.14	0.991
BC650	288K	8.63	40.48	0.994
	298K	10.23	50.72	0.994
	308K	12.53	64.93	0.991
BC750	288K	9.48	33.52	0.991
	298K	11.59	47.24	0.996
	308K	13.33	50.73	0.982

Effect of Temperature

The isotherms data of NOR adsorption by biochars (Fig. 2) at three temperatures (288K, 298K, and 308K) were also investigated as a function of temperature. As shown in Fig. 3, with the temperature ranging from 288K to 308K, the adsorption capacity of BC450, BC550, BC650, and BC750 increased, while BC350 decreased. Table 3 showed that for BC450, BC550, BC650, and BC750, the $\lg k_F$ values increased as the temperature increased, indicating heating promoted the adsorption of NOR, and the adsorption of NOR by biochars was exothermic in nature. However, for BC350, the $\lg k_F$ values diminished, suggesting that heating tended to reduce sorption, which was consistent with the adsorption isotherms.

The thermodynamic parameters, namely, Gibbs free energy (ΔG°), enthalpy change (ΔH°), and standard entropy changes (ΔS°) related to the feasibility and nature of the adsorption process was calculated with the following equations (7 and 8):

$$\Delta G^\circ = -RT \ln k_F \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

where R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is absolute temperature (K), and k_F is the Freundlich constant. The values of ΔH° and ΔS° were determined from the slope and intercept by the linear plot of ΔG° vs. T .

The obtained thermodynamic parameters for the sorption of NOR onto biochars are listed in Table 4. For all biochars, the negative values of ΔG° observed in the experimental temperature range indicated the spontaneity and feasibility of the NOR adsorption process onto the biochars. Negative values of ΔG° for BC450, BC550, BC650, and BC750 increased with the increase of the sorption temperature, namely, $\Delta G^\circ_{288\text{K}} > \Delta G^\circ_{298\text{K}} > \Delta G^\circ_{308\text{K}}$, suggesting that the spontaneous degree of the sorption was enhanced, as reported by previous studies (Lu *et al.* 2015). This may be because the high temperature can provide more energy to overcome the diffuse double layer and adsorb into the interior structure of biochars (Liu and Zhang 2009). While an opposite trend for BC350 was observed, it showed that the sorption was restrained under higher temperature, which may be related to the characteristic of BC350 and its mechanism requires further investigation. Moreover, negative values of ΔG° presented an increase trend with pyrolysis temperature of biochars, which suggested that a higher pyrolysis temperature for biochars led to a greater spontaneous degree. It has been reported that the values of ΔG° were in the range of 0 to $-20 \text{ kJ}\cdot\text{mol}^{-1}$ and -80 to $-400 \text{ kJ}\cdot\text{mol}^{-1}$ for physical and/or chemical sorption, respectively (Zhang *et al.* 2014). As presented in Table 4, it was found that the values of ΔG° were in the range from -4.36 to $-15.98 \text{ kJ}\cdot\text{mol}^{-1}$ for BC350, BC450, and BC550, which indicated that the sorption process of NOR onto BC350, BC450, and BC550 were mainly physical in nature. On the other hand, for BC650 and BC750, the values of ΔG° ranged from -47.59 to $-78.60 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting that the sorption process may be simultaneously controlled by physisorption and chemisorptions. The negative values of ΔH° imply that adsorption would be an exothermic process. In this study, the negative value of ΔH° for BC350 indicated that the NOR sorption on BC350 was an exothermic process, which is in agreement with the study of adsorption of NOR onto Mg-Al layered double hydroxides (Sui *et al.* 2012). Meanwhile, the positive values of ΔH° for BC450, BC550, BC650, and BC750 suggested the sorption was endothermic in nature. This was similar to the observation of NOR adsorption on Fe-MCM-41 molecular sieves (Chen *et al.* 2015). The variation of ΔH° may indicate the binding mechanisms including physisorption ($\Delta H^\circ < 40 \text{ kJ}\cdot\text{mol}^{-1}$), and chemisorption ($\Delta H^\circ > 40 \text{ kJ}\cdot\text{mol}^{-1}$). Thus the NOR adsorption onto BC350, BC450, and BC550 was primarily physisorption, while the NOR sorption on BC650 and BC750 was more likely to be a chemical sorption process. According to the studies by von Oepen *et al.* (1991), the sorption mechanism of NOR on BC350 and BC550 may be H-bonding and ion-exchange.

Table 4. Thermodynamic Parameters for the Adsorption of NOR onto 5 Biochars

Biochars	ΔG° ($\text{kJ}\cdot\text{mol}^{-1}$)			ΔH° $\text{kJ}\cdot\text{mol}^{-1}$	ΔS° $\text{kJ}\cdot(\text{mol}\cdot\text{k})^{-1}$
	288K	298K	308K		
BC350	-6.29	-5.54	-4.36	-34.14	-0.10
BC450	-13.24	-13.98	-14.27	1.45	0.05
BC550	-11.85	-14.37	-15.98	47.45	0.21
BC650	-47.59	-58.34	-73.85	331.41	1.31
BC750	-52.28	-66.12	-78.60	326.40	1.32

H-bonding and dipole bond force may exist between NOR and BC450, while the adsorption mechanism of NOR on BC650 and BC750 may be chemical bond. The positive ΔS° values for BC450, BC550, BC650, and BC750 suggested an increase in the randomness at the solid/liquid interface during the sorption process of NOR. On the contrary, the negative ΔS° values for BC350 suggested that the more ordered arrangement of NOR molecules are adsorbed on the surface of BC350.

Effect of pH

The pH is an important parameter affecting the NOR sorption performance, as it can alter the charge and species of NOR as well as the sorbent surface properties. NOR has two proton-binding sites, including carboxyl and piperazinyl group with pK_a values of 6.22 and 8.51. Therefore, NOR can exist in cationic form, zwitterionic form, or anionic form depending on the solution pH. The cationic form is the dominant species for NOR at pH below 6.2, the zwitterionic form is dominant in the pH range of 6.2 to 8.4, and the anionic form only exists at pH higher than 6.5 according to its acid-base equilibrium constant (Kong *et al.* 2014). To evaluate the influence of pH on NOR adsorption, adsorption of NOR by biochars was investigated at pH value ranging from 3.0 to 9.0 with initial NOR concentration of $10 \text{ mg}\cdot\text{L}^{-1}$, and the results are shown in Fig. 3. It was found that there was no significant difference between BC650 and BC750, which may be due to their approaching pH values. Figure 3 also shown that for BC550 adsorption process, the adsorbed amount of NOR first decreased with the pH range from 3 to 5, then increased with pH ranging from 5 to 7, finally decreased in the range of 7 to 9, which was contrary to a previous report (Hari *et al.* 2005). This may be because at low pH values ($\text{pH} < 5$), NOR existed in a cationic form in solution and the surfaces of BC550 were positively charged, producing an electrostatic repulsion that might weaken NOR adsorption. At a high pH value, an electrostatic repulsion might also occur between anionic form of NOR and the negatively charged BC450 and BC550, which weaken the adsorption process. As for BC350, BC450, BC650, and BC750, no significant changes were observed for NOR adsorption under the initial pH in the range of 3.0 to 9.0. This happened mainly because of the buffering ability of biochars.

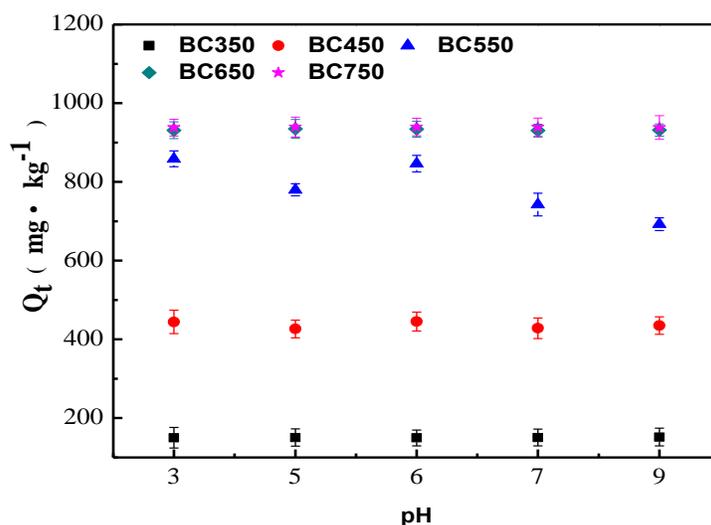


Fig. 3. The effect of pH on adsorption of NOR by biochars

FTIR analysis of biochars before and after adsorption

FTIR spectra of biochars before and after adsorption were presented in Fig. 4.

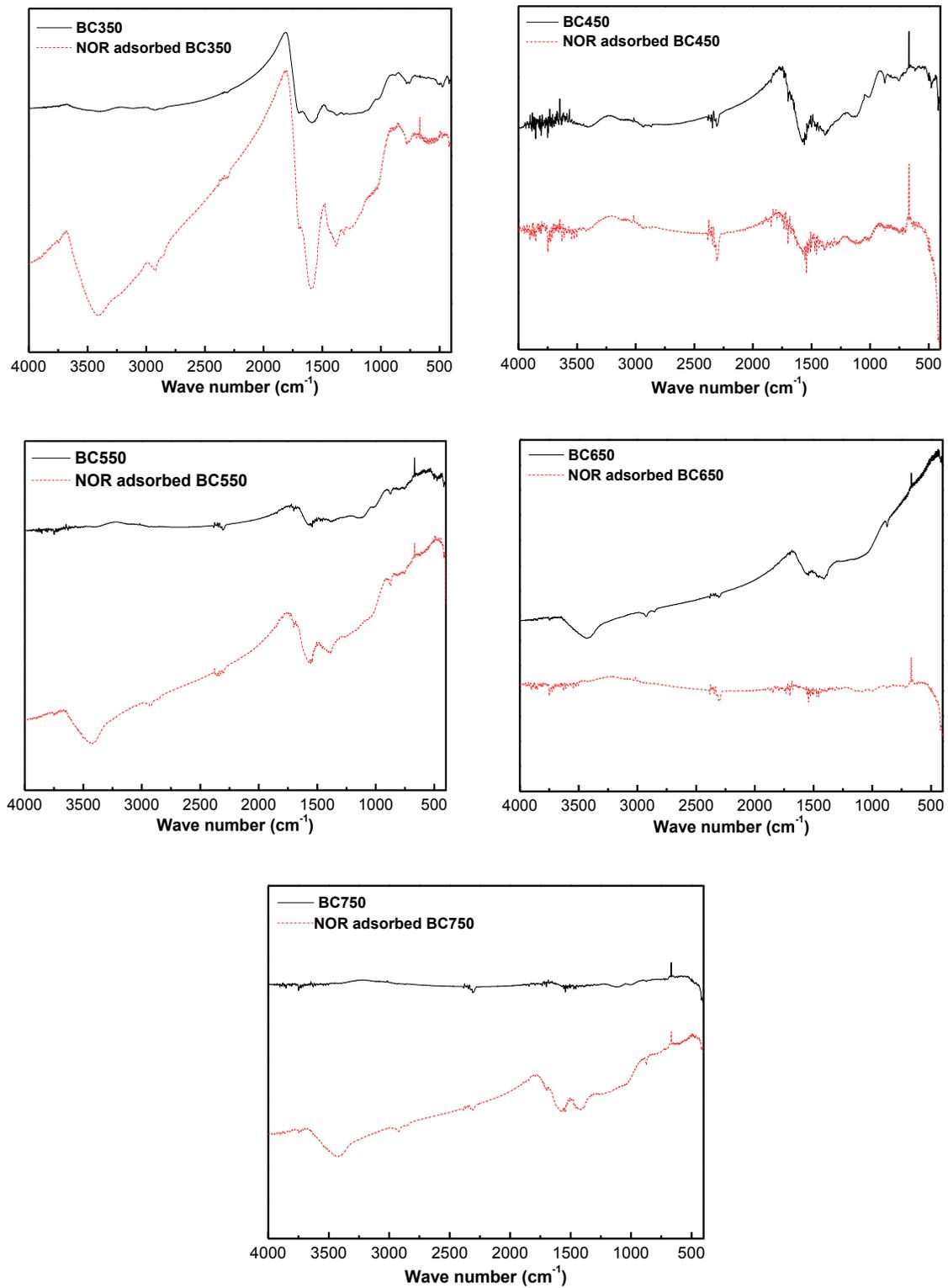


Fig. 4. FTIR spectra of biochars before and after NOR adsorption

An obvious and broad band was present at around 3400 cm^{-1} , which could be attributed to the stretching vibration of O-H groups of water or H-bonded hydroxyl groups (Keiluweit *et al.* 2010). The bands around 2930 and 2860 cm^{-1} were assigned to C-H stretching vibrations of aliphatic functional groups (Gao *et al.* 2005). The peaks at 1600 , 1514 , and 1440 cm^{-1} could be related to the C=O stretching vibration of aromatic compounds and C=C stretching of conjugated ketones and quinines and aromatic skeletal C, respectively (Cao *et al.* 2009). The peaks due to C-H bending for aromatic out-of plane deformation appeared at wave number 885 , 800 , and 695 cm^{-1} (Chen *et al.* 2008). A clear different band at around 3400 cm^{-1} appeared after the contact of NOR with biochars, which could be attributed to the presence of O-H groups. The asymmetric (1600 cm^{-1}) and symmetric (1370 cm^{-1}) stretching vibrations of COO^- were observed due to deprotonation of $-\text{COOH}$ group, which was similar to studies obtained for NOR sorption onto montmorillonite (Pei *et al.* 2012). This could be probably caused by electronic induced effects, indicating a possible sorption mechanism involving π - π interactions between the NOR and biochars (Jia *et al.* 2013).

CONCLUSIONS

1. Manioc wastes can be used as effective adsorbent for the removal of norfloxacin.
2. The kinetics of the adsorption were found to fit the pseudo-second-order model best and the equilibrium sorption amounts of NOR increased with pyrolysis temperature of biochars. Intraparticle diffusion was not the only rate-controlling mechanism, and the intraparticle diffusion and external film diffusion may also regulate adsorption.
3. The equilibrium data was well described by the Freundlich model within the temperature range 288K to 308K . The isotherms of BC450 and BC550 were relatively linear, suggesting partitioning was the dominant mechanism, whereas the main adsorption mechanism of NOR on BC350, BC650, and BC750 was pore-filling, which can be described by nonlinear isotherms.
4. Thermodynamic study showed that the adsorption of NOR onto biochars was spontaneous and NOR sorption on BC350 was an exothermic process, while on BC450, BC550, BC650, and BC750 it was endothermic in nature. Moreover, the NOR adsorption on BC350, BC450, and BC550 can be mainly attributed to physisorption, while the NOR sorption on BC650 and BC750 was more likely to be a chemical sorption process.
5. According to FTIR analysis, the main adsorption mechanisms of NOR to biochars may be H-bonding and π - π interactions.

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