Adsorption of chlortetracycline onto biochar derived from corn cob and sugarcane bagasse

Lin Zhang, Lei Tong, Pengguang Zhu, Peng Huang, Zhengyu Tan, Fangling Qin, Wen Shi, Mengyun Wang, Han Nie, Guicheng Yan and Hongtao Huang

ABSTRACT

Biochar was prepared from two different types of biological waste materials, corn cob (CC) and sugarcane bagasse (SB). The adsorption capacity of each class of adsorbent was determined by chlortetracycline (CTC) adsorption tests. The adsorption kinetics and isotherms of chlortetracycline onto sugarcane bagasse biochar (SBB) and corn cob biochar (CCB) were studied. Experimental results indicated that pseudo-second-order adsorption kinetics of CTC onto SBB and CCB were more reasonable than pseudo-first-order kinetics, and the adsorption kinetic model of CTC onto SBB was slightly better than that onto CCB. The maximum adsorption capacity of CTC onto SBB was 16.96 mg/g at pH 4, while the highest adsorption efficiency of CTC onto CCB was achieved at pH 5 with a maximum adsorption of 12.39 mg/g. The Freundlich isotherm model was better than the Langmuir model at illustrating the adsorption process of CTC onto SBB and CCB. These results provide a way to understand the value of specific biochars, which can be used as efficient and effective adsorbents for CTC removal from waste-water. Compared with raw pinewood, SBB and CBB were considered as alternative materials to remove antibiotics from aqueous environments.

Key words | adsorption isotherm, adsorption kinetics, chlortetracycline, corn cob biochar, sugarcane bagasse biochar

INTRODUCTION

Since antibiotics were first discovered in the mid-twentieth century, they have been widely used for health protection and animal husbandry and as animal growth promoters (Li et al. 2013; Alavi et al. 2015). However, extensive use of antibiotics has resulted in serious environmental problems (Zheng et al. 2013; Liu et al. 2017). The appearance of antibiotics in the environment will induce antibiotic resistance genes (Zheng et al. 2013; Zhou et al. 2014). Long-term exposure to low levels of antibiotics has improved the drug resistance of pathogenic microbes, and they have a potentially toxic effect on aquatic organisms and cause potential threats to humans through the food chain (Tong et al. 2009, 2014; Pinheiro et al. 2015). Among current antibiotics, chlortetracycline (CTC) is a broad-spectrum antibiotic from the tetracycline family, which is commonly used in farming at large dosages (Taheran et al. 2016). Furthermore, it has been frequently detected in the animal and aquaculture industry, as well as the aquatic environment (Wang et al. 2017). Therefore, finding an efficient and simple method to prevent and minimize the risks related to antibiotics has become a big challenge.

Several methods have been used to remove antibiotics from aqueous environments, including conventional techniques (biological process, filtration, coagulation, flocculation and sedimentation), advanced oxidation processes (AOPs), membrane treatment, adsorption, and combined methods (Babaei et al. 2016). Adsorption treatments for antibiotics removal are considered efficient and have been widely applied in previous studies (Wang et al. 2015). For example, biochar has become a useful adsorbent for many types of antibiotics. The adsorption mechanism of biochar is similar to that of activated
carbon (Jia et al. 2015). Biochar is obtained from the pyrolysis of organic material. It is rich in C, N, H, O and other chemical elements and exhibits relatively high surface area (Zheng et al. 2013). Using agricultural wastes such as peels as biomass for the production of low-cost sorbents for water treatment applications removes an ecological burden (Bhatnagar et al. 2015). In the process of solid waste recycling, biochar is derived from burning biological waste materials of municipal or agricultural origin, and its excellent adsorption performance for different contaminants has been well acknowledged (Lonappan et al. 2016). An enormous amount of biological materials has already been tested (Chowdhury et al. 2019). In most cases, efficient biosorbents are based on plant materials, microbial biomass or different types of polysaccharides (Šafarík et al. 2016). For example, biochars from corn straw (Zhang et al. 2012, 2015), pinewood (Taheran et al. 2016), rice-husk (Liu et al. 2012) and bamboo (Wang et al. 2015) were tested for antibiotics removal, and more than 99% of fluoroquinolone antibiotics were removed from synthetic wastewater through adsorption (Wang et al. 2015).

In developing countries such as China, corn is one of the main cereals, and sugar cane is the largest national source of sugar. The output of corn is 132.9 million tons in China and is increasing year by year (National Bureau of Statistics of China (NBSC) 2008). Southern China as the major sugarcane producing region, with approximately 1.7 million hectares of sugarcane cultivated (Zu et al. 2018). In recent years, sugarcane and corn production in China has increased due to effective management, leaving behind significant amounts of solid waste. However, less than one-third of corn cob (CC) are used as a fuel, while sugarcane bagasse (SB) is basically not reused. Biochar derived from SB and CC not only avoids the environmental pollution caused by incineration disposal but can also be used as fertilizer to enhance soil fertility. Therefore, the excellent adsorption ability of biochar gives it potential application prospects.

The purpose of this study was to detect the adsorption capability of CTC onto sugarcane bagasse biochar (SBB) and corn cob biochar (CCB). The effects of conditions such as pH, reaction time, and initial concentration on the adsorption of CTC were determined. Meanwhile, the adsorption kinetics and isotherms of CTC onto SBB and CCB were also investigated. The significance of this study is that it makes full use of natural resources and reveals a high adsorption efficiency of CTC.

MATERIALS AND METHODS

Preparation and characterization of biochar

Biochars were prepared from fresh CC and SB. CC was produced from farmland near Pu Yang City, Henan Province, China, and SB was produced in Yang Shuo, Guangxi Province, China. The CC and SB were cleaned with deionized water and naturally air-dried for 2 days, then oven dried for 24 h at 100 °C (Zhang & Wu 2017). Next, the materials were smashed by a pulverizer, passed through a 60-mesh sieve, and then were transferred to the biochar reactor (muffle furnace, Shanghai Laboratory Equipment Company Limited, China) under an O2-limited atmosphere. The reaction temperature and time were set at 500 °C and 24 h. After cooling to room temperature, the final biochar samples were collected in sealed bags.

The yield of biochar (SBB and CCB) and ash content were calculated by the following equation (Ma et al. 2016), respectively:

$$\omega_1(\%) = \frac{W_b}{W_r} \times 100\%$$

$$\omega_2(\%) = \frac{W_a}{W_b} \times 100\%$$

where \(\omega_1(\%)\) and \(\omega_2(\%)\) are the yield of biochar and ash content, respectively. \(W_b(\text{g})\) is the mass of the biochar produced via smashing and pyrolysis processes, \(W_r(\text{g})\) is the mass of raw material for biochars, and \(W_a(\text{g})\) is the mass of the ash content from the biochars.

Scanning electron microscope (SEM) (FEI-Quanta 200, The Netherlands) images were utilized to reveal the micro-structure and surface characteristics of the SBB and CCB samples (Zhang & Wu 2017). The pH value of SBB and CCB were measured with a pH metre (HQ40D, HACH, USA) in deionized water at the solid-liquid ratio of 1:100 biochar (SBB and CCB)/water (Ma et al. 2016). The specific surface area of biochars (SBB and CCB) were determined using the ASAP 2460 Surface Area and Porosity Analyzer (ASAP 2460, Micromeritics Instrument Corporation, USA).

Chemical and stock solution preparation

Chlortetracycline (C₂₂H₂₃ClN₂O₈, purity >95%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The...
chemical structure and some main characteristics of CTC are presented in Table 1. High performance liquid chromatography (HPLC)-grade water (deionized water) was prepared in the laboratory using a Millipore system (USA). Methanol, sodium hydroxide and hydrochloric acid were used in the study. All chemicals and solvents were of analytical reagent grade and were used without further purification. CTC was diluted with methanol solution, and the solid-liquid ratio was 1:1000. The standard stock solution concentration was 200 mg/L, and the solution was kept in the dark below 4 °C. For each experiment, the target solution concentration used was obtained by dilution of the standard stock solution.

**CTC determination**

The concentration of CTC in the supernatant filtrate was analysed directly by a UV spectrophotometer at 365 nm. The standard curve drawing steps were as follows. Precisely nine initial volumes (2.5, 5, 10, 12.5, 15, 17.5, 20, 22.5, 25 mL) of standard stock solution were measured, respectively, into nine identical volumetric flasks (100 mL), and then water was added to the standard line, finally resulting in nine prepared initial concentrations (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/L). The nine initial concentrations of CTC in the supernatant filtrate above were analysed directly by a UV-spectrophotometer at 365 nm, then a blank control experiment was run, and a standard curve was drawn for the regression equation of the straight line.

**Batch adsorption experiments**

Batch adsorption experiments were carried out to study the adsorption efficiency of CTC onto SBB and CCB. For the adsorption kinetics, experiments were run in a series of 50 mL, brown centrifugal tubes (to prevent possible light degradation of CTC) containing 20 mL CTC at 200 mg/L concentrations. The SBB and CCB were weighed at 0.2 g and then added into the CTC solution, respectively. The centrifugal tubes were then transferred into an incubator shaker and agitated at 250 rpm at 25 ± 0.5 °C in the dark. The control experiment was conducted under the same conditions. The suspension liquid was collected at time intervals of 0, 1/6, 1/3, 1/2, 1, 1.5, 2, 3, 5, 8, 12, 20, 28, 36 and 48 h. Then, the mixtures were separated by filtration for CTC determination. In addition, a series of adsorption experiments were performed to evaluate the effects of the solution pH on the adsorption kinetics of CTC. The pH values were adjusted to 3.0, 4.0, 5.0, 6.0, and 7.0 using 0.1 M NaOH and 0.1 M HNO₃. The impact of pH on the experiments was studied with the initial CTC concentration at 200 mg/L.

The adsorption isotherm explores the relationship between adsorption and the aqueous concentration at a certain temperature. Sorption isotherms of CTC onto SBB and CCB were studied by measuring the variation of the CTC concentrations in the aqueous phase at room temperature during the equilibration time. The initial concentrations of CTC in eight brown glass tubes were 0, 20, 50, 100, 200, 300, 400 and 500 mg/L, and 0.2 g biochars (SBB or CCB) and 20 mL CTC solution with the required concentration were added to the 50 mL brown centrifugal tubes for batch experiments. CTC solution without biochar was used for the control experiment following the same procedure. Then, the mixtures were separated by filtration to determine the CTC concentration in the solution.

The amount of CTC adsorbed from the solution was expressed as (Ma et al. 2016; Alahabadi et al. 2017):

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (3)
\]

\[
q_t = \frac{(C_0 - C_t)V}{m} \quad (4)
\]

where \(q_e\) (mg/g) is the amount of CTC antibiotic adsorbed onto biochar at the equilibrium, \(q_t\) (mg/g) is the amount of CTC antibiotic adsorbed onto biochar at time \(t\), \(C_0\) (mg/L) is the initial CTC concentration in the solution, \(C_e\) (mg/L) is the equilibrium concentration of CTC in the aqueous solution at time \(t\), \(V\) (L) is the batch volume and \(m\) is the mass of biochar (SBB or CCB, g). The percent removal efficiency of CTC (R, %) from the solution was determined using (Ma et al. 2016; Alahabadi et al. 2017):

\[
R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (5)
\]
Adsorption models

The adsorption data of CTC onto SBB and CCB, respectively, were fitted using two typical kinetic models (pseudo-first-order and pseudo-second-order). The nonlinear equations are listed as (Shirmardi et al. 2016; Takdastan et al. 2016):

\[
q_t = q_e \cdot [1 - \exp(-K_1t)] \quad (6)
\]

\[
q_t = \frac{K_2 \times q_e^2 \times t}{1 + q_e \times K_2 \times t} \quad (7)
\]

where \(K_1\) (min\(^{-1}\)) and \(K_2\) (g/(mg-min)) are the rate constants corresponding to the pseudo-first-order and pseudo-second-order kinetic models, respectively, and \(q_t\) (mg/g) and \(q_e\) (mg/g) are the adsorption amounts of the adsorbent for CTC at contact time ‘t’ and equilibrium state, respectively.

The commonly used adsorption isotherm models are the Freundlich and Langmuir isotherm models. The Langmuir and Freundlich equations are shown as (Wang et al. 2017):

\[
q_e = \frac{K_1Q_mC_e}{(1 + K_1C_e)} \quad \text{Langmuir equation} \quad (8)
\]

\[
q_e = K_fC_e^{1/n} \quad \text{Freundlich equation} \quad (9)
\]

where \(q_e\) is the adsorption capacity per unit mass adsorbent at the equilibrium, \(C_e\) is the adsorbate concentration in aqueous solution at the equilibrium, \(K_f\) is the Freundlich coefficient, \(n\) is the Freundlich empirical constant, \(Q_m\) is the adsorption capacity under monolayer adsorption, and \(K_f\) is the surface adsorption affinity constant.

RESULTS AND DISCUSSION

Characterization of biochar

The pH\(_i\), specific surface area, ash content and yield of SBB and CCB are shown in Table 2. SBB and CCB were prepared via smashing and pyrolysis processes. The yield was calculated as a percentage of the amount of ash produced by the biomass. The results showed that the yield of CC (34.66%) was higher than that of bagasse (23.32%). Normally, biochar molecules show hydrophobic characteristics, but in some cases, they are hygroscopic in nature and exhibit significant adsorption capacity for water vapor (Ahmad et al. 2012). The hygroscopic nature of biochar may be due to the water of hydration within the ash or water molecules associated with the organic portions of the biochar, including adsorbed water vapor (Jia et al. 2013; Inyang & Dickenson 2015). In this study, SBB and CCB originating from plant sources exhibited medium ash contents, at 20.15% and 30.87%, respectively. The specific surface area of SBB (248.05 m\(^2\)/g) was higher than that of CCB (2.86 m\(^2\)/g) (see the supplementary material, available with the online version of this paper).

The scanning electron microscopy images of raw materials and biochar are shown in Figure 1, and the surface characteristics of the SB and SBB are shown in Figure 1(a) and 1(b), respectively. The results show that freshly produced bagasse exhibited heterogeneity in the surface morphology with few pores, but the derived biochar had many large pores and a high specific surface area. The SB took the shape of long strips, while the CC took the shape of blocks. Moreover, the pore structure of CCB, which exhibited an uneven and rough surface texture, was not very developed compared with that of SBB. The irregular cracks and short fibres mixed with aggregates of CCB (Figure 1(d)) were typical structures from cellulose biochar (Méndez et al. 2009).

Characteristics of adsorption kinetics

To better understand the sorption behaviour and mechanism, the adsorption kinetics of CTC onto SBB and CCB were evaluated. The adsorption kinetics provided useful information on the reaction pathways (Cardoso et al. 2011). It can be seen from Figure 2(c) and 2(d) that the pseudo-second-order kinetic model had a more significant effect than did the pseudo-first-order kinetic model for CTC onto SBB and CCB. The two-stage kinetic model was fitted with the model parameters, which are shown in Table 3. The correlation coefficient (R\(^2\)) of the pseudo-second-order kinetic equation for SBB was 0.8202, and the rate constant \((K_2)\) was 0.1173 g/(mg-h). For CCB, the pseudo-second-order kinetic model was more effective than the pseudo-first-order kinetic model, and the correlation coefficient was 0.9801 for the pseudo-second-order kinetic equation, with the rate constant of 0.0264 g/(mg-h). Therefore, the pseudo-second-order is more suitable for predicting the adsorption process.

| Table 2 | The basic physical and chemical properties of biochars |
|---|---|
| Properties | pH | Specific surface area (m\(^2\)/g) | Ash content (%) | The yield of biochar (%) |
| SBB | 7.76 | 248.05 | 30.87 | 23.32 |
| CCB | 8.53 | 2.86 | 20.15 | 34.66 |
Figure 2(a) and 2(b) show that the concentration of CTC decreased rapidly in the first 4 h due to the large available surface area of SBB, and then rate of decrease slowed. After 28 h, the curve became gentle, and the concentration of CTC showed slight fluctuations. Similarly, Figure 2(b) also shows that the concentration of CTC on CCB changed rapidly at the beginning of the adsorption, and then decreased slowly. After 28 h, the curve was stable, and the concentration of CTC slightly fluctuated. Compared with Figure 2(b), the adsorption process of CTC onto SBB was faster than that onto CCB, while the equilibrium adsorption capacities were similar. The different adsorption performances of SBB and CCB could be due to variation of the specific surface area and porosity ratio of the materials.

Effect of pH value

The adsorption kinetics of CTC at different pH conditions were studied. The pH of the initial solutions was adjusted to between 3 and 7, with the original concentration of CTC at 200 mg/L. Figure 3 shows that the condition of pH had an obvious impact on the adsorption capacities of CTC. The highest adsorption capacity of CTC onto SBB was observed at pH 4 with 16.96 mg/g, and the equilibrium time was 20 h. The adsorption capacity of SBB increased considerably when the solution pH increased from 3 to 4; however, it decreased slowly when the pH of the solution increased from 4 to 7. As shown in Figure 3(b), both the equilibrium adsorption capacity (12.39 mg/g) of CTC onto CCB and the removal rate were the highest at pH 5.

Figure 3 also shows that the removal efficiencies of CTC onto SBB and CBB were strongly dependent on the initial pH, and the optimum pH was observed between 4 and 5. In addition, removal percentage of CTC onto biochars (SBB and CCB) at different pH values are illustrated in Figure 4. CTC is an amphoteric molecule with multiple ionizable functional groups, and has three values of pKa (3.3, 7.44, and 9.27), thus the pH could be an important factor influencing the CTC adsorption by electrostatic attraction (Liu et al. 2012). Lü et al. (2012) found that the structure
of CTC was changed at different pH values. When the solution pH was below 3.30, the dimethyl group was protonated, and CTC was present as a cation, while phenolic-pentanedione lost protons and CTC existed as a zwitterion at pH values between 3.30 and 7.44. If the pH was higher than 7.44, both carbonyls and phenolic-pentanedione lost protons, and CTC presented as a monovalent anion or a divalent anion (Figure 5, Lü et al. 2012). Therefore, the effect of pH on the adsorption efficiencies of CTC onto biomass charcoal cannot be ignored.

The adsorption kinetics of CTC onto biochar were studied by using the pseudo-first-order and pseudo-second-order
kinetics equations at different pH levels (pH = 3–7). The fitting models of CTC onto SBB are shown in Figure 6(a)–6(e), while Figure 6(f)–6(j) reveal the fitting models of CTC onto CCB at pH from 3 to 7.

The parameters of the correlation coefficient ($R^2$), $K_1$, $K_2$, equilibrium adsorption capacity ($q_e$), and equilibrium adsorption time ($t_e$) of the adsorption kinetic models are shown in Table 4. As shown in Table 4, the $R^2$ values of the pseudo-second-order equation were higher than those of the pseudo-first-order equation for both SBB and CCB. This result suggested that the pseudo-second-order kinetic model could better describe the adsorption processes of CTC onto SBB and CCB.

Regardless of whether the pH value changed, the pseudo-second-order kinetic equation was highly significantly fitted to the adsorption data. However, the equilibrium adsorption capacity ($q_e$) and the equilibrium time ($t_e$) were different when the adsorption of CTC was
observed at different pH values (Table 4). For SBB, the largest value of $q_e$ was found at pH = 4 during the adsorption process. When the pH value decreased or increased from pH 4, the equilibrium adsorption capacity decreased accordingly. Therefore, the buffering capacity of SBB in the acid solution was weak, and the adsorption amount of SBB onto the CTC increased first and then decreased with the trend turning at pH 6. For CCB, the largest value of $q_e$ was found at pH 5, and it decreased when the pH decreased or increased. Therefore, the experimental

Figure 6  |  Adsorption kinetic models of CTC onto biochar under different pH conditions at 298 K: (a)–(e) SBB under pH = 3–7; (f)–(j) CCB under pH = 3–7. (Continued.)
results show that the effect of pH on the adsorption of derived biochar is significant, and the adsorption amount of CTC onto biochars increased first and then decreased with increasing pH value.
Characteristics of sorption isotherms

Adsorption isotherms describe how adsorbate molecules distribute between the solid phase and liquid phase when the adsorption process reaches an equilibrium state (Takdastan et al. 2016). According to previous studies, the most widely used isotherms for modelling equilibrium are the Langmuir and Freundlich isotherm equations (Wang et al. 2019). The relationship between the CTC adsorbed onto biochars (SBB and CCB) and CTC concentrations under equilibrium conditions are described in Figure 7. The parameters of the two adsorption isotherm models are presented in Table 5.

The correlation coefficients ($R^2$) of the Langmuir adsorption isotherm equation for CTC adsorption onto SBB and CCB are 0.9314 and 0.7552, respectively. These parameters were slightly higher in the Freundlich adsorption isotherm model, at 0.9525 and 0.9930, respectively, for CTC onto SBB and CCB. Thus, the Freundlich adsorption isotherm model fitted better than did the Langmuir adsorption isotherm model (Figure 7). The adsorption intensities $(1/n)$ of CTC onto SBB and CCB were 0.3091 and 0.8357, respectively. Here, $(1/n) < 1$ indicated that the adsorption performances of CTC onto both SBB and CCB were good. In addition, $K_f$ could also be considered an indicator of the adsorption capacity (Qin et al. 2017). In other words, a higher $K_f$ suggested a higher adsorption capacity, and vice versa (Xu & Li 2010). Comparing the parameters of $K_l$ (in the Langmuir isotherm model) and $K_f$ (in the Freundlich isotherm model), they appear to have slight differences, but both are far less than 1. In addition, in the Langmuir isotherm model, the maximum adsorption capacities of CTC onto SBB and CCB were 25.7400 and 36.1184, respectively.

Comparison with other adsorbents

Table 6 indicates that the maximum adsorption capacities of CTC onto the biochar (SBB and CCB) were compared with other materials reported in the literature. SB and CC are regarded as renewable, sustainable energy sources, and the preparation costs are relatively low. Therefore, SBB and CCB are a promising effective adsorbent for aqueous solutions. This material eases economic issues and environment problems to a certain degree.

The biggest difference between this study and previous works is that the predecessors used inorganic materials or
The adsorption mechanism of CTC was studied in detail, especially the adsorption rate of CTC onto SBB under different pH conditions. The results showed that the adsorption trend of CTC at different pH conditions is similar on both materials. In addition, the adsorption isotherm models of CTC onto the two kinds of biochar were well fitted with Freundlich adsorption isotherm equation. In short, SBB and CCB could play important roles in antibiotics removal (in particular, CTC). SBB and CCB will be recognized as a cost-effective and efficient absorbent in environmental management in the near future.

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CONCLUSIONS

The results showed that pseudo-second-order adsorption kinetics of CTC onto both SBB and CCB were more reasonable than pseudo-first-order adsorption kinetics for CTC. The maximum adsorption capacities of CTC onto SBB and CCB were 25.7400 mg/g and 36.0084 mg/g, respectively. The adsorption mechanism of CTC was studied in detail, especially the adsorption rate of CTC onto SBB under different pH conditions. The results showed that the adsorption trend of CTC at different pH conditions is similar on both nanomaterials instead of organic absorbent materials, which are used in this study. It is well-known that China is a large producer of corn and sugarcane, and a large amount of SB and CC is turned to farmland solid waste. The vast majority of farmers addressed the materials through on-site incineration, which not only wastes resources and pollutes the environment but also causes a safety hazard. In the present study, SB and CC were carbonized and decomposed to obtain biomass with a high carbon content. It changed SB and CC from agricultural solid waste into adsorption materials which can be used to treat different kinds of pollutants in the environment. This not only explores the recycling of waste materials but also provides a new research direction for the study of pollutants removal in wastewater.
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