Sorption of tetracycline on H$_2$O$_2$-modified biochar derived from rape stalk

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ABSTRACT
To determine the sorption potential and mechanisms of tetracycline (TC) on pristine and H$_2$O$_2$-modified biochars, rape stalk biochars were produced and modified by H$_2$O$_2$. The specific surface area and pore volume of biochars increased with improving pyrolysis temperature, while the acidic groups decreased. Moreover, modified by H$_2$O$_2$, much more oxygen-containing functional groups were introduced. The results of sorption dynamics and isothermals tests showed that RB300 had the largest TC sorption capacity of 35.90 mg/g, which was ascribed to a plenty of non-carbonized organic matter and surface functional groups were retained. Modified by H$_2$O$_2$, the sorption of TC on biochars was enhanced which indicated the dominated sorption mechanisms were H-bonding and π–π electron donor acceptor interaction. The pH value would impact on sorption, and the maximum sorption capacity was obtained at pH = 9.0. Both cation concentration and type would affect the TC sorption.

1. Introduction
Various pharmaceutical antibiotics such as tetracyclines (TCs), sulfonamides, macrolides and quinolones have been used extensively to prevent and control infections in animal and human medicine [1]. Among the common used antibiotics, TCs are one of the most frequently used in the agriculture and livestock industry because of their relative effectiveness and low costs [2]. However, about 70–90% of the ingested TCs can not be metabolized by humans and animals, thus the undigested antibiotic would be excreted and accumulated in the environment [3]. Luo et al. [4] reported that the average concentrations of TCs in the water and sediment of Haihe River were around 26 ng/L and 600 ng/kg, respectively. The bioaccumulation of TCs which passed along the food chain would induce the proliferation of antibiotic-resistant genes (ARGs) [5], and might pose potential hazards to human health and ecosystems [2,6]. Thus, removal of TCs from wastewater has received increasing attention in recent years, and it is necessary to develop effective and low-cost technology for antibiotic removal.

Numerous antibiotics elimination techniques have been proposed and widely used, such as electrochemical treatments [7], membrane filtration [8], photocatalytic degradation [9] and sorption onto porous materials. Specifically, the sorption technology was considered to be one of the most convenient and economical methods for its low cost, easy operation and no toxicities generated. However, the selection of adsorbents was the key factor on the application of this technology. Up to now, various adsorbents such as clay minerals [10], graphene-based materials [6], aluminum oxide [11], functionalized carbon nanotubes [12], and activated carbons had been used for the antibiotic sorption. Besides, the biochar had been considered as the most potential adsorbent candidate [13,14].

Biochar is a porous carbonaceous material with a high degree of aromatization and strong anti-decomposition ability. It is produced by the decomposition of carbon-rich biomass in an oxygen-limited environment [15,16]. Because of its high specific surface area, rich pore structure and surface functional groups, biochar has been widely used in environmental remediation, such as wastewater treatment, soil remediation [17], waste management and greenhouse gas reduction [18]. Biochar can adsorb both organic and inorganic pollutants in water and soils systems, such as heavy metals, dyes, ammonium, hydrophobic organic contaminants and antibiotics [15,16,19].

For the feedstock of biochar, all most any carbon containing biomass can be used as precursor of biochar [20,21]. Therefore, the biochar can be produced from a wide range of raw materials, including plant residues [22], sewage sludge [23], animal manures [24] and even waste tires [25]. Among the above mentioned materials, plant residues were the most widely used due to their abundance and low cost. In addition, the plant residues were used as feedstock to...
produce biochar can mitigate greenhouse effect by reducing the CO₂ emitting. Therefore, in the present study, the plant residue of rape stalk, which had a large yield in China, was chosen as feedstock. Additionally, previous studies found that the sorption ability of biochar was mainly determined by both the feedstock type and preparation methods, such as pyrolysis temperature [26]. Therefore, three different pyrolysis temperatures of 300°C, 450°C and 600°C were used to produce the rape stalk biochars.

Although biochar was a potential candidate sorbent, low sorption capacity limited their commercial application. To improve the sorption ability of biochar, various modification methods, such as physical and chemical activation methods [27] had been applied on biochars. Most of the modification methods could effectively change the surface physico-chemical characteristics of biochar, such as increase surface area and functional groups [28], change porous structures, O/C and H/C ratios [29]. H₂O₂ is a kind of strong oxidant that can generate much of hydroxyl radical. Besides, it is green chemical for it will become water after being used, no secondary pollution would be produced. Therefore, H₂O₂ was introduced in the present work to modify the biochar aim to improve their TC sorption ability.

In this study, three rape stalk biochars (RB300, RB450 and RB600) were produced by pyrolysis at 300°C, 450°C and 600°C, respectively. Then H₂O₂ was used to modify the obtained biochars. The sorption property of TC on both the pristine and H₂O₂-modified biochars was investigated. The overarching goals of this work were (1) evaluate the sorption capacity of TC on pristine and H₂O₂-modified rape stalk biochars, (2) elucidate their sorption mechanism and (3) investigate the effects of pH value and cation concentration on TC sorption by biochars.

2. Material and methods

2.1. Raw materials

TC (C₂₂H₂₄N₂O₆; purity > 99.0%; CAS Number: 60-54-8) was purchased from Beijing Tai Ze Jia Ye Technology Development Co., Beijing, China. All other reagents used in this work were purchased from Sinopharm Chemical Reagent Co. Ltd (China) and were all analytical grade (purity > 99%). All of the solutions were prepared with ultra-pure water (18.2 MΩ, Millipore USA). Rape stalk was collected from the farmland of Xuzhou in China. Before pyrolysis, the feedstock was cleaned, air-dried and cut to 1 cm in length.

2.2. Production of biochars and modified biochars

Pyrolysis of rape stalk was carried out in a tube furnace for 4 h at 300°C, 450°C and 600°C, respectively. The heating rate was 10°C/min with 50 ml/min N₂ as shielding gas. According to the pyrolysis temperature, the produced biochars were labeled as RB300, RB450 and RB600, respectively. H₂O₂-modified biochars were produced in a 50-ml centrifuge tube where 1 g pristine biochar and 50 ml 30% H₂O₂ (w/w) were added. The centrifuge tube was placed in the thermostatic shaker and shaken at 25°C for 24 h. The obtained H₂O₂-modified biochars were named as RB300-H, RB450-H and RB600-H, respectively. All of the biochars were continuously washed with ultra-pure water until the filtrate reached stable pH, and then they were dried at 105°C overnight. At last, the biochars were ground and sieved to a uniform size fraction of 0.15–0.45 mm before being used.

2.3. Characteristics of biochars

Specific surface areas, pore volume of biochars were measured by aperture and specific surface area analyzer (Kubo X1000, Beijing bio Electronic Technology Co., Beijing, China) through multipoint N₂ adsorption. The specific surface areas and pore volume were calculated by Brunauer-Emmett-Teller (BET). The structure and surface morphology of biochars were characterized by scanning electron microscopy (SEM, Inspet S50, FEI USA). The surface functional groups on the biochars were determined by a Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Nicolet Corporation USA) in the range of 4000–400 cm⁻¹ using the potassium bromide (KBr) disc technique.

2.3. Sorption experiments

2.4.1. Sorption kinetics

The sorption kinetics of TC on biochars was carried out by mixing 50 mg biochar with 1 L TC solution (20 mg/L) in brown bottle. At different time intervals, about 10 ml solution was taken out and then filtered by 0.22-μm millipore membranes. Thereafter, the filtrate was determined by UV-Vis spectrophotometer (L65, INESA instrument China) at wavelength of 356 nm, which was the maximum absorption of TC by scanning within the range of 200–700 nm. In addition, the blank tests with only TC solution and biochar were carried out to eliminate the effect of TC decomposition and the distractions release from biochar. All of the experiments were carried out in triplicates, and the average value was calculated.

2.4.2. Sorption isotherms

About 5 mg of each biochar was placed in a 50-ml centrifuge tube. A series of TC solutions with different initial concentrations of 1, 3, 5, 8, 10 and 15 mg/L were added to the centrifuge tube and shaken at 25°C for 48 h. Afterward, the following procedures such as filtration, measurement and blank tests were the same as Section 2.4.1.
2.4.3. Effect of pH value and cation concentration
The initial TC aqueous concentration was 15 mg/L. The initial pH value was adjusted to 3, 5, 7, 9, and 11 by using 0.01 mol/L HCl and 0.01 mol/L NaOH solution. The cation concentration was adjusted to 0.01–0.1 mol/L by adding NaCl, MgCl₂, and CaCl₂. The other procedures were the same way as described in Section 2.4.2.

2.5. Sorption data analysis
Pseudo-first-order and pseudo-second-order were used to fit the sorption kinetics data. The equations were presented as follows:
   
   \[ q_t = q_e \left(1 - e^{-k_1 t}\right), \]
   
   \[ q_t = \frac{q_e}{1 + \frac{k_2 q_e}{k_1}}. \]

Where \( q_t \) and \( q_e \) are the amount of sorbate removed at time \( t \) and at equilibrium, respectively (mg/g); \( k_1 \) and \( k_2 \) are the first-order and second-order sorption rate constants (h⁻¹), respectively.

The Langmuir and Freundlich models were used to fit the sorption isotherms. The equations were presented as follows:

   \[ \text{Langmuir: } q_t = b q_{\text{max}} C_e / (1 + b C_e), \]
   
   \[ \text{Freundlich: } q_t = K_c C_e^{1/n}. \]

Where \( b \) and \( K_c \) are the solute surface interaction energy-related parameter and the affinity coefficient of the Freundlich model (mg⁻¹·Lⁿ/g), respectively, \( K_c \) is Freundlich affinity coefficient indicating sorption strength, and considered as a relative indicator of sorption capacity. \( q_{\text{max}} \) is the Langmuir maximal sorption capacity (mg/kg); \( C_e \) is the equilibrium solution concentration (mg/L) of the sorbate; and \( n \) is the Freundlich linearity index. The Langmuir model assumes monolayer sorption onto a homogeneous surface with no interactions between the adsorbed molecules. The Freundlich model is an empirical equation commonly used for heterogeneous surfaces.

3. Results and discussion
3.1. Characterization of biochars
The specific surface area and pore volume of pristine biochars ranged from 3.9 to 112.4 m²/g, and from 0.023 to 0.076 cm³/g (Table 1). Generally, both the specific area and pore volume increased with elevating the pyrolysis temperature, which was in coincident with previous observation [26]. This suggested that temperature plays an important role in biochar production by controlling the creation of pores in the biochars basal-structural sheets. Modified by H₂O₂, the specific surface area of biochars did not improve significantly, the surface area of RB600 increased from 112.36 to 117.05 m²/g. On the contrary, there were a slightly decrease on RB300 and RB450, which decreased from 3.87 to 1.17 m²/g, and from 6.80 to 4.16 m²/g, respectively. Obviously, H₂O₂ modification did not enlarge the specific surface area of biochar effectively, which was consistent with the previous literature [30]. The SEM images of pristine biochars (Figure 1) exhibit the layered structure and some rudimentary pores on rape stalk biochars. Additionally, with the increase of pyrolysis temperature, the cellulose, hemicellulose, and lignin in the feedstock decomposed gradually and much more pores emerged, which induced to the increase of internal surface area. Furthermore, the surface of RB300 was smooth while it became rough and irregular when the pyrolysis temperature increased to 600°C.

With the increase of pyrolysis temperature, the C-H bending vibration peaks of methyl (-CH₃) and methylene (-CH₂) in alkanes on biochars decreased gradually (Figure 2), which was attributed to the decomposition of cellulose, hemicellulose and other organic matter in the rape stalk. As reported the alkyl groups on the surface of the biochar would decompose at higher temperature and might form gaseous hydrocarbons, such as CH₄, C₂H₄ and C₃H₆ [26]. In addition, the absorption peak caused by bending vibration of aromatic ring C-H (around 875 cm⁻¹) increased significantly, which indicated the aromatization degree of biochar increased with elevating the pyrolysis temperature. Lian et al. [31] reported the similar findings that intense deoxygenation and dehydrogenation reactions occurred during the pyrolysis process, and the decreasing H/C and O/C ratios as well as polarity index ([O + N]/C) suggested the biochars become more hydrophobic and aromatic during pyrolysis at high temperatures.

As for H₂O₂-modified biochars, the bending vibration of carboxyl C = O (around 1710–1690 cm⁻¹) were enhanced, which indicated H₂O₂ modification increased the carboxyl groups on the biochars. In addition, a new peak appeared near 1300 cm⁻¹ in RB300-H, was assigned to the bending vibration of phenolic hydroxyl groups. Nevertheless, it was not found on RB450-H and RB600-H, which could be suggested that the formation of phenolic hydroxyl groups was related to the reaction between H₂O₂ and uncarbonated organic matter in RB300.

### Table 1. Basic morphology characteristics of pristine and H₂O₂-modified rape stalk biochars.

| Sample   | BET-SA (m²·g⁻¹) | BJH-PV (cm³·g⁻¹) | BJH most probable diameter (nm) |
|----------|-----------------|------------------|-------------------------------|
| RB300    | 3.87            | 0.0247           | 3.0500                        |
| RB450    | 6.80            | 0.0230           | 2.3200                        |
| RB600    | 112.36          | 0.0764           | 2.4700                        |
| RB300-H  | 1.77            | 0.0193           | 2.7600                        |
| RB450-H  | 4.16            | 0.0250           | 3.8200                        |
| RB600-H  | 117.05          | 0.0969           | 2.1600                        |

SA = specific surface area, and PV = pore volume.
3.2. Sorption kinetics

The result of sorption kinetics experiments (Figure 3) showed that the sorption rate of TC on biochar was faster in the first 400 min. Then the sorption rate gradually reduced to zero until the sorption reached equilibrium at about 33 h for pristine biochars and 22 h for H_2O_2-modified biochars. The sorption equilibrium can be reached quickly on the H_2O_2 modified biochars indicated that the H_2O_2 modification could effectively enhance the sorption performance of biochar for TC.

![Figure 1. Scanning electron micrographs (SEM) images of biochars: (a) and (d) RB300, (b) and (e) RB450, (c) and (f) RB600.](image)

![Figure 2. FTIR spectra of RBx and RBx-H (x = 300, 450, 600).](image)
The sorption process was analyzed by two kinetic models of pseudo-first-order and pseudo-second-order equation. The $R^2$ (0.898–0.999) values of the pseudo-second-order model were higher than those of the pseudo-first-order model (0.765–0.988). Besides, the theoretical $q_e$ values calculated by the pseudo-second-order kinetics model were more closer to experimental sorption capacity (Table 2). Therefore, the pseudo-second-order model could describe the experimental data better, which implied the TC sorption on biochar was dominated by the binuclear surface adsorption mechanism [32]. The equilibrium sorption capacities of TC on RB300, RB450 and RB600 were 35.90, 26.33 and 32.00 mg/g, respectively. However, the order of biochars sorption capacity was not in agreement with the order of their specific surface area. It was different from some previous research, such as Inyang et al. [13], who reported that the sorption capacity of TC on biochar increased with the increase of preparation temperature and specific surface area of carbon materials. In this study, RB600 with the high-surface area and pore volume had higher TC sorption capacity of 32.0 mg/g than RB450 (26.33 mg/g), which indicated high-surface area was conducive to the sorption. However, RB300 with the lowest surface area had the largest TC sorption capacity of 35.90 mg/g. Therefore, other mechanism would govern the TC sorption besides the adsorption dominated by high-surface area, e.g., partition. As Chen et al. reported [33], the non-carbonized organic matter retained in biochar could effectively absorb contaminants in the manner of partition. Such as the sorption of naphthalene, nitrobenzene and m-dinitrobenzene on pine needle biochar [33]. The similar observation was reported by Zhang et al. who studied the sorption of cyclohexane, acetone and toluene on 15 biochars [34]. Likewise, the partition mechanism might dominate the TC sorption on RB300.

Comparing the sorption ability of pristine and $\text{H}_2\text{O}_2$-modified biochars, the pristine RB300 had slightly higher TC sorption amount of 35.90 mg/g than RB300-H (34.0 mg/g), which might be related with the loss of non-carbonized organic matter on $\text{H}_2\text{O}_2$ modified biochar. As for the higher pyrolysis temperature biochars, both RB600-H (42.45 mg/g) and RB450-H (32.83 mg/g) had higher sorption capacity than the pristine RB600 (32.0 mg/g) and RB450 (26.33 mg/g). Given that both the surface area and pore volume of RB600-H and RB450-H did not change obviously, thus it was reasonable to attributed the enhancement of sorption capacity on the increase of oxygen functional groups, such as carboxyl C = O, etc. Generally, $\text{H}_2\text{O}_2$ can be used as an oxidation reagent to modify/activate the high-temperature pyrolysis biochar by creating more oxygen functional groups on the biochars, while it has adverse effect on the low-temperature biochar by removal the non-carbonized organic matter.

### 3.3. Sorption isotherm

The most commonly used two-parameter isotherms models of Langmuir and Freundlich were used to fit the test data (Figure 4), and the fitting parameters

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Sorption kinetics of TC on RBx and RBx-H (x = 300, 450, 600) at 25°C.

**Table 2.** Sorption parameters of TC on rape stalk biochars at 25 °C.

| Model kinetcs | Pseudo-first-order | Pseudo-second-order | Experiment sorption capacity |
|---------------|--------------------|---------------------|------------------------------|
| Equations     | $q_t = q_e (1 - e^{-kt})$ | $q_t = \frac{q_e}{1 + \frac{C_0}{K_C}}$ | $q_t = \frac{1}{k_d q_e}$ |
| Parameter     | $q_e$ (mg·g$^{-1}$) | $k_d$ (min$^{-1}$) | $R^2$ | $q_e$ (mg·g$^{-1}$) | $K_C$ (g·mg$^{-1}$·min$^{-1}$) | $R^2$ | $Q$ (mg·g$^{-1}$) |
| RB300         | 33.58              | 0.9923              | 0.9632 | 36.11          | 0.0002              | 0.9917 | 35.90          |
| RB450         | 23.73              | 0.9906              | 0.9371 | 25.32          | 0.0005              | 0.9828 | 26.33          |
| RB600         | 30.78              | 0.9950              | 0.9881 | 33.59          | 0.0001              | 0.9990 | 32.00          |
| RB300-H       | 28.45              | 0.9771              | 0.7646 | 30.69          | 0.0009              | 0.8982 | 34.00          |
| RB450-H       | 28.14              | 0.9844              | 0.7972 | 30.21          | 0.0007              | 0.9131 | 32.83          |
| RB600-H       | 37.64              | 0.9879              | 0.8559 | 40.23          | 0.0004              | 0.9470 | 42.45          |
were listed in Table 3. The Langmuir sorption isotherm model assumes that a large number of adsorbed active sites are present on the adsorbent surface, and the sorption equilibrium is reached when all of the adsorbent active sites are occupied. Thus, Langmuir model is suitable for describing the monolayer sorption. While the Freundlich model is usually used to describe the multi-molecular layers sorption. In this study, both Freundlich and Langmuir model could fit the TC sorption on all of the six biochars well with the correlation coefficients $R^2 > 0.9047$. Comparatively, the Langmuir model fitted most of the data a little better than the Freundlich model.

Antibiotics have certain polarity and hydrophobicity. Therefore, $\pi-\pi$ electron donor acceptor (EDA) interaction, cation exchange, hydrogen bonding and surface complexation were possible sorption mechanisms for the TC sorption on biochar [35]. There would be a $\pi-\pi$ interactions between graphite-like structure (act as a $\pi$-electron-donor) and aromatic ring structure (act as a $\pi$-electron-acceptor) [36]. Thus, the polarized electron-rich graphite surface of biochar can act as a $\pi$-electron-donor, while TC molecules act as the effective $\pi$-electron-acceptor for their strong electron-withdrawing ability on ketone group and aromatic ring structure [31]. Additionally, High temperature carbonization would promote the formation of graphene structures in biochar, which would further enhance the $\pi-\pi$ EDA interaction between biochar and TC [37]. This may be an important reason why the sorption capacity of TC on RB600 was larger than RB450. In addition, the hydrogen bonding would be formed between TC and biochar for a plenty of oxygen-containing functional groups was present on the biochar. After modification by $\text{H}_2\text{O}_2$, the amount of oxygen-containing functional groups increased significantly, which would contribute to the increase of TC sorption capacity on biochar.

### 3.4. Effect of pH

TC is an amphoteric molecule with multiple ionizable functional groups, such as tricarbonylamide.

#### Table 3. Sorption isotherm parameters of TC on rape stalk biochars at 25°C.

| Sample    | $q_e$ | $b$ | $R^2$ | $K_L$ | $n$ | $R^2$ |
|-----------|-------|-----|-------|-------|-----|-------|
| RB300     | 45.71 | 0.1612 | 0.9927 | 7.5145 | 1.7277 | 0.9775 |
| RB450     | 33.94 | 0.1759 | 0.9575 | 5.9804 | 1.7897 | 0.9047 |
| RB600     | 41.61 | 0.1810 | 0.9863 | 7.4587 | 1.7879 | 0.9575 |
| RB300-H   | 40.11 | 0.1988 | 0.9941 | 7.9024 | 1.8788 | 0.9692 |
| RB450-H   | 40.82 | 0.1745 | 0.9895 | 7.2471 | 1.7988 | 0.9616 |
| RB600-H   | 55.11 | 0.2444 | 0.9914 | 12.151 | 1.9181 | 0.9533 |

Figure 4. Sorption isotherms of TC on RBx and RBx-H (x = 300, 450, 600) at 25°C.
(C-1:C-2:C-3), phenolic diketone (C-10:C-11:C-12) and dimethylamine (C-4) groups [36]. Moreover, the TC has three values of pKa (3.3, 7.7 and 9.7), which make it exist as a cation (TC\(\text{H}_3^+\)), zwitterion (TC\(\text{H}_2^\circ\)) or anion (TC\(\text{H}^-\) and TC\(\text{S}_2^-\)) based on different pH values [38]. In this study, the impact of pH value on the TC sorption by biochar was explored, and the results were illustrated in Figure 5. The sorption capacity decreased slightly when the initial pH increased from 3.0 to 5.0, and then it increased significantly with the pH increasing from 5.0 to 9.0. The maximum TC sorption amount on biochar was achieved at pH = 9.0.

TC was mainly present in the form of TC\(\text{H}_3^+\) and TC\(\text{H}_2^\circ\) during 3.0 < pH <5.0, while the biochar was overwhelmingly positive. Therefore, the sorption of TC on biochar would be inhibited by the electrostatic repulsion between cationic TC and positively charged biochar. With the increase of pH, TC was gradually deprotonated and the fractions of zwitterion and anionic species increased, which resulted in higher sorption capacity due to the enhanced electrostatic interaction between TC and biochar. In addition, excess \(\pi\)-electrons on the surface of biochar would strengthen the \(\pi\)--\(\pi\) EDA interaction between TC and biochar [31], which would greatly promote TC sorption on biochar. When the pH was further increased to higher than the isoelectric point of biochar, the biochar would become negatively charged. Thus the electrostatic repulsion between anionic TC and biochar would result in the decrease of sorption capacity. In conclusion, the sorption of TC on biochar was mainly attributed to \(\pi\)--\(\pi\) EDA interaction and the electrostatic interaction.

### 3.5 Effect of initial cation concentration

The effect of cation concentration on the TC sorption by RBx and RBx-H (x = 300, 450, 600°C) at 25°C were illustrated in Figure 6. The sorption capacity of TC on biochars tend to decrease when the Na\(^+\) and Mg\(^{2+}\) concentration increased from 0.01 to 0.1 mol/L (Figure 6(a,b)), on the contrary, the sorption would be enhanced with the increase of Ca\(^{2+}\) concentration (Figure 6(c)). The Na\(^+\) and Mg\(^{2+}\) would suppress the TC sorption on biochars for they would occupy the
sorption sites on biochar. Moreover, the competition between TC and cation increases with improving the valence of cation, thus, Mg$^{2+}$ presents greater adverse effect than the Na$^+$. However, the Ca$^{2+}$ facilitated the sorption significantly, and for example, the adsorption capacity increased from 45.45 mg/g to 63.64 mg/g on RB600-H. To further explore the effect of Ca$^{2+}$ on the TC sorption, a blank experiment on the reaction between Ca$^{2+}$ and TC was carried out without adding biochar. The result (Figure 6(d)) showed that the TC concentration decreased gradually with the increase of Ca$^{2+}$ concentration. Thus, the promotion of Ca$^{2+}$ on TC removal was related with the complexation between Ca$^{2+}$ and TC. The TC has multiple ionizable

Figure 6. Effect of cationic concentrations on the TC sorption by biochars at 25°C, (a) Na$^+$ (b) Mg$^{2+}$ (c) Ca$^{2+}$ (d) Blank.
functional groups and various species in solution, thus exhibits strong complexing capability with Ca$^{2+}$. Therefore, Ca$^{2+}$ would facilitate the removal of TC by the formation of TC-Ca$^{2+}$ complexes.

4. Conclusions
Rape stalk biochar can effectively adsorb the TC in aqueous solution with the sorption capacity ranged from 26.33 to 35.90 mg/g. The RB300 with low surface area had the largest TC sorption capacity, which may be related with the partition mechanism. After modification by H$_2$O$_2$, the sorption ability was enhanced and the highest sorption capacity of 42.45 mg/g was observed on RB600-H, which was caused by the introduction of quantity of oxygen functional groups. The pseudo-second-order model and Langmuir model described the experimental data better. The sorption amount of TC on biochars was significantly increased along with pH increasing from 5.0 to 9.0. Both the cation concentration and type would affect the TC sorption on biochar by the competitive sorption, specially, the Ca$^{2+}$ would facilitate the removal of TC by the formation of TC-Ca$^{2+}$ complexes. Generally, both the pristine and H$_2$O$_2$-modified rape stalk biochars are potential adsorbent for TC removal.

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Disclosure statement
No potential conflict of interest was reported by the authors.

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