Removal and Adsorption Mechanism of Tetracycline Using Manganese-modified Cotton Straw Biochar in an Aqueous Solution

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Abstract

Farming in China's rural areas leads to antibiotic pollution in waterbodies making it a grave issue. Cotton straw biochar (CSBC) was prepared by oxygen-limited pyrolysis at 400 °C (CSBC400) and 600 °C (CSBC600); and Mn-modified CSBC (MCSBC) was produced by the KMnO_4 wrapping method for tetracycline (TC) removal from aqueous solutions. The effects of temperature, initial solution concentration, pH, ion type, and ionic strength on TC adsorption were investigated. The adsorption process of the biochars achieved an equilibrium state after 360 min, and the highest equilibrium adsorption amount (13.254 mg/g) was found for MCSBC. The kinetic adsorption process, which was dominated by chemisorption, was well-described by the pseudo-second-order kinetic model. The adsorption was a non-homogeneous heat absorption process, and the adsorption isotherm data fitting was compatible with the Freundlich model. A better adsorption effect of MCSBC was observed when the pH was < 4 . Monovalent cations (Na^+ , K^+ , NH_4^+ , and Ca^{2+}) had a facilitative effect on the adsorption process. The adsorption mechanisms of TC by MCSBC included pore diffusion, H bonding, electrostatic interactions, and π - π accumulation. Therefore, MCSBC has a good adsorption capacity for TC and can be used for the treatment of TC-based pollutants in aqueous environments.

Introduction

Antibiotics are chemical substances produced by microorganisms or higher plants and animals with anti-pathogen or other active cell development functions (Grenni et al. 2018). They not only inhibit the growth of bacteria in animals, but also promote animal feed utilization and growth rates. With the rapid development of large-scale breeding technologies, use of antibiotics have increased in the breeding industry. However, using antibiotics can have adverse impacts on humans and introduces new challenges to the treatment of emerging environmental pollutants. A Study by Wei et al. (2016) reported that only a small fraction of antibiotics can be absorbed after being used by humans and animals; the majority is discharged into water or soil via human and animal excrement, and may enter the human body via the food chain. Zhao et al. (2018) reported that many unabsorbed veterinary antibiotics are introduced by animal feces and retained in the farmland soil environment for a long time. Moreover, the order of magnitude of the concentration of antibiotics detected in soil has increased from ng/kg to mg/kg (Li et al. 2015). Therefore, attention should be paid to antibiotic pollution in the environment. Tetracycline (TC) is the second most common antibiotic produced and used worldwide; its production and consumption in China is one of the highest worldwide (Grenni et al. 2018). Similar to other antibiotics, TC is extremely harmful to human and animal health because of its low metabolic efficiency. Approximately 90 % of the ingested TC can be discharged into the environment via urine; TC ingested by pigs can be rapidly eliminated via urine and feces (Daughton and Ternes, 1999). A study analyzed the influence of poultry activities consuming TC; it concluded that the concentration of TC in the environment owing to animal activities was 30–497 ng/L (Winckler and Grafe, 2001). One study reported that the maximum total concentrations of three types of TC (i.e., TC, aureomycin, and oxytetracycline) in vegetable soils with manure application were 242.6 $\mu\text{g/kg}$ and 415.0 $\mu\text{g/kg}$ in southern and central China, respectively (Wei et

al. 2019). Therefore, it is important to explore effective TC removal technologies to control antibiotic pollution in soil and water environments.

Traditional methods for removing antibiotics from water include adsorption and fixation, biodegradation, membrane separation, coagulation, and advanced oxidation (Anthony et al. 2021). The adsorption and fixation method is widely used for the removal of TC from water because of its advantages, including simple operation, low price and adsorbent concentration, good removal performance, and non-toxic by-products. Among all the adsorbents, biochar (BC) a new material, is highly efficient and has been widely studied in recent years. It is a highly aromatic and refractory solid substance formed by the pyrolysis and carbonization of biomass materials in the absence of oxygen (Lehmann et al. 2006). BC application has advantageous effects in water environment remediation, C fixation, and waste reuse. BC is expected to become an appropriate alternative material for activated C adsorption. BC prepared with wheat straw, sawdust, plant residues, municipal sludge, and algae as precursor materials has been studied for the removal of TC in water environments (Hao et al. 2021; Liu et al. 2021; Luo et al. 2021). However, the limited specific surface area and undeveloped pore structure have led to a limited TC adsorption capacity of original BC. Modifying BC to improve its specific surface area, pore structure, surface functional groups, and other physical and chemical properties for improved adsorption of pollutants has become a research hotspot (Liu et al. 2021; Mei et al. 2021; Zhang et al. 2021). The BC modification process involves physical methods (steam and heating), acidification, alkaline activation, and physicochemical activation. Dai et al. (2020) studied the modification of rice straw BC using an alkali and acid composite magnetization method, and found that modification enhanced the TC removal performance with a maximum adsorption capacity of 98.33 mg/g. One study showed that BC loaded with Fe/Mn oxides could enhance the adsorption of TC (Zhang et al. 2021). Another study successfully synthesized MnO_2 -modified BC, which resulted in a much greater specific surface area, total pore volume, pore diameter, and adsorption capacity for TC removal (Shen et al. 2020). Thus, the improved adsorption capacity of antibiotics was attributed to the increased porosity, specific surface area, and effective functional groups of the modified BC.

MnO_x -modified BC is an excellent adsorbent for the removal of environmental pollutants, but it is easily agglomerated in the adsorption process (Song et al. 2014). Researchers have attempted to reduce the agglomeration performance by combining MnO_x with different substances, such as bentonite, zeolite, diatomite, sand, resin, tea residue and biochar. MnO_x -modified rice straw BC increased the specific surface area and pore volume of the original BC and increased the number of O-containing functional groups, thereby promoting the adsorption of Pb^{2+} (Tan et al. 2018). However, another study found that MnO_x and impurities may block the micropores at high temperatures, limiting their adsorption capacity (Song et al. 2014). Antibiotics contain hydroxyl and ketone groups, which can easily combine with the surface functional groups of BC to produce complexes (Hu et al. 2021; Saremi et al. 2020). It has been speculated that the dimethylamino in TC can be complexed with MnO_x (Song et al. 2014; Tan et al. 2018). Therefore, BC prepared from different precursor materials may have different mechanisms of

In this study, cotton straw (CS) BC (CSBC) was prepared by lower limit oxygen pyrolysis at 400 °C (CSBC400) and 600 °C (CSBC600) using CS as the precursor material. Mn-modified BC was prepared by the KMnO_4 coating method with CSBC600 as the precursor material, and its related structures were characterized. The kinetic adsorption and isothermal adsorption processes of TC by the three BCs were analyzed, and the effects of pH, ionic strength, and ambient temperature on TC removal were investigated. The adsorption of TC in wastewater by the three BCs was investigated using a kinetic adsorption model and thermodynamic adsorption models. The functional groups on the surface of the Mn-modified CSBC (MCSBC) before and after adsorption were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), and the adsorption mechanism was speculated. This study may provide new ideas for the development of BC materials and further promote the application of BC materials in water treatment.

Materials And Methods

CSBC and MCSBC preparation

CS was collected from a cotton field at the experimental station of Tarim University in Alar City, China (81°16'53"N, 40°36'28"E). The CS biomass materials were collected, washed with distilled water, dried at 60 °C, and pulverized using a small high-speed and multi-function pulverizer. The material was then loaded into a preheated quartz-tube furnace (KPX-9162 MBE, China) and incubated at 20 °C/min to 400 or 600 °C for 4 h. After air-cooling to 25 °C, the products were washed using deionized water and subsequently oven-dried at 80 °C for 12 h. The fine pulverized products were further separated by passing them through a 60 mesh sieve. The CSBC products (CSBC400 and CSBC600) were packed in a sealing bag and stored for further use.

KMnO_4 -loaded BC (MCSBC) was prepared using a chemical co-precipitation method, as described in previous studies (Song et al. 2014). Five grams of CSBC600 were mixed with 40 mL of 0.035 M, 0.070 M, 0.210 M, and 0.350 M KMnO_4 solution. The suspension was then mixed ultrasonically for 2 h at 25 °C to ensure close contact between CSBC600 and KMnO_4 . The samples were then dried in a water bath at 95 °C and pyrolyzed at 600 °C for 1 h in a vacuum tube furnace. The samples were cooled to 25 °C, ground, sieved through a 2 mm sieve, and stored in a vacuum desiccator before use. The BC modified with different concentrations of KMnO_4 are denoted as MCSBC, MCSBC1, MCSBC2, and MCSBC3, respectively.

Batch experiments

TC ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$; purity > 99.0%) was purchased from Macklin Biochemical Co., Shanghai, China. First, 0.05 g of CSBC400, CSBC600, MCSBC, MCSBC1, MCSBC2, and MCSBC3 were placed in 50 mL centrifuge tubes, and 50 mL TC solutions of different concentrations (5, 10, 20, 30, 40, 60, and 80 mg/L) were added. The centrifuge tube was then placed in a thermostatic oscillator with the temperature set to 25 °C.

The adsorption speed was set at 180 rpm and the centrifuge tube was oscillated in the dark at constant temperature for 6 h (the preliminary experiment showed that the adsorption reached equilibrium after 6 h). After reaching the equilibrium time, the samples were removed, left for 2 h, and centrifuged at 4000 rpm for 20 min. The supernatant was then filtered through a 0.45 μm membrane.

Adsorption kinetics was conducted by adding 50 mL of 25 mg/L TC solution to 0.05 g of adsorbent (CSBC400, CSBC600, and MCSBC) at 25 °C. The solution was oscillated in the dark at different time intervals (20, 30, 60, 90, 120, 180, 240, 270, 360, and 480 min). Then, the test tube was removed and centrifuged at 4000 rpm for 20 min. The supernatant was then filtered through a 0.45 μm membrane. Isothermal and thermodynamic experiments were conducted at initial TC concentrations of 5, 10, 20, 30, 40, 60, and 80 mg/L. Oscillation in the dark was conducted at temperatures of 25, 35, and 45 °C with a fixed adsorbent mass of 0.05 g (CSBC400, CSBC600, and MCSBC) and a contact time of 360 min (equilibrium time). The samples were removed and kept ideal for 2 h and then centrifuged at 4000 rpm for 20 min. The supernatant of all the samples was immediately filtered through a 0.45 μm nylon membrane. To ensure the accuracy and precision of the experimental data, three parallel experiments were performed for all experiments, and a blank was set as the control.

The influence of the ion type, ionic strength, and pH on TC adsorption by the adsorbents were further evaluated. First, 0.05 g of adsorbent (CSBC400, CSBC600, and MCSBC) was placed in a 50 mL centrifuge tube containing 50 mL of 25 mg/L TC solution. One set of tubes were mixed with different concentrations (0.00 M, 0.05 M, 0.10 M, 0.20 M) of Na^+ , K^+ , Ca^{2+} , and NH_4^+ to evaluate the influence of ion type and strength on TC adsorption. Another set of tubes were adjusted to pH values of 3–11 (3, 5, 7, 9, and 11) using 1 M NaOH and 1 M HCl solution, and the effect of pH on the adsorption of TC by the adsorbent was investigated. These tubes were placed on a mechanical oscillator (180 rpm) and left in the dark for 6 h at 25 °C. The samples were removed after equilibrium time, left for 2 h, and centrifuged at 4000 rpm for 20 min. The supernatants of all the samples were immediately filtered through a 0.45 μm nylon membrane filter. To ensure the accuracy and precision of the experimental data, three parallel experiments were performed for all experiments, and a blank was set as the control.

An ultraviolet-visible spectrophotometer (Shanghai Jinghua Company, China) was used to measure the TC concentration at 356 nm (Kang et al. 2011).

Adsorbent characterization

The C, N, H, and O contents of the BC were determined using an elemental analyzer (Elementar Micro Cube, Germany). The specific surface area, pore volume, and pore size of the BC were determined using a Brunauer–Emmett–Teller (BET) specific surface area analyzer (ASAP 2460, McInstruments, USA). The mineral composition of the functional groups was determined using FTIR (Perkin Elmer Spectrum 100, USA). The mineral composition of the BC was determined using XRD (Bruker D8 Advance, Germany).

Data analysis

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The TC adsorption capacity (q_e) and removal rate (R) were calculated as follows:

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

1

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

2

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 (mg/L) is the initial concentration of TC in the solution, and C_e (mg/L) is the equilibrium concentration of TC in the solution. V (L) is the volume of the solution, m (g) is the amount of BC added, and R (%) is the removal rate.

The pseudo-first-order kinetics model, pseudo-second-order kinetics model, and intra-particle diffusion model were used to fit the adsorption kinetics process of BC for TC, as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

3

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

4

$$q_t = k_d t^{0.5} + C$$

5

where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the adsorption capacity (t/min), k_1 (min^{-1}) is the pseudo-first-order kinetic rate constant, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order kinetic rate constant, k_d ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate constant of the diffusion model within the particles, and C (mg/g) represents the marginal layer effect.

Langmuir and Freundlich isothermal adsorption equations were used to fit the adsorption of TC by BC, as follows:

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e}$$

6

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

7

where q_e (mg/g) is the equilibrium adsorption capacity, $q_{\max}$ (mg/g) are constants and the maximum adsorption capacities related to the adsorption capacity and adsorption strength in the Langmuir model, respectively. k_F (L/mg) and k_L (L/mg) are the Freundlich constants, and the size of $1/n$ is related to the nonlinearity of the adsorption isotherm.

Results And Discussion

BC characterization

To accurately analyze the micro-morphology of the material and the distribution of MnO_x , the original BC and modified BC were observed by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) (Figure 1a, 1b, and 1c). The surface of the CSBC400 was smoother than CSBC600 and MCSBC, with uneven pleats, no significant pores, many particles deposited on the surface, and a non-porous structure, thereby indicating that the biomass was not completely cleaved and the pores were not completely opened. The surface of CSBC600 was rough, with irregular pleats, large protrusions, and some pores due to the escape of small molecules during pyrolysis (Liu et al. 2021). There were developed pores on the MCSBC surface, which was mainly a complex network structure with pores possibly provided by the MnO_x or embedded BC (Song et al. 2014; Tan et al. 2018). Therefore, providing more adsorption sites on MCSBC, thereby enhancing its adsorption capacity (Dai et al. 2020).

The surface of the adsorbent has a significant influence on its adsorption capacity for organic pollutants (Tong et al. 2019). Understanding the surface properties of adsorbents will help understand the adsorption kinetics and adsorption mechanism. The surface properties of BC largely depend on the feedstock and process used after pyrolysis (post-treatment) (Liu et al. 2018). Table 1 shows that the C content in the BC samples was in the order of CSBC600 (73.03 %) > CSBC400 (63.60 %) > MCSBC (60.40 %). MCSBC had a high O content, which was related to the introduction of MnO_x . The modification process resulted in an increase in the O/C ratio, thereby indicating the increased hydrophobicity of the BC samples modified by KMnO_4 (Jang et al. 2018). The BET method was used to analyze the structural characteristics of the BC samples, and the results showed that the BET specific surface area of MCSBC ($242.394 \text{ m}^2/\text{g}$) was larger than that of CSBC600 ($140.130 \text{ m}^2/\text{g}$) and CSBC400 ($8.619 \text{ m}^2/\text{g}$). The change in the BET specific surface area might have been due to the removal of impurities (Hao et al. 2018), which was also confirmed by the subsequent XRD analysis results. In addition, the attachment of MnO_x promoted the pyrolysis of CS, thereby resulting in the formation of many pores and roughening the surface of the modified BC, which led to an increase in the external specific surface area of the BC and an increase in the contact surface with TC, which was more conducive to the adsorption of TC (Song et al. 2014). Song et al. (2014) found that KMnO_4 has strong oxidizing properties that are capable of

Loading [MathJax]/jax/output/CommonHTML/jax.js inverting them into mesopores or macropores. The conversion

could have caused an increase in the pore diameter, thereby increasing the specific surface area and pore volume. Furthermore, an increase in the pore volume contributed to the entry of TC into the internal pore system (Shen et al. 2020).

Adsorption effect of BC

The adsorption effect of BC prepared under different conditions was evaluated so as to optimize the adsorption material for water treatment. The adsorption performance of CSBC600 at high pyrolysis temperatures was significantly better than that of CSBC400 at lower pyrolysis temperatures (Figure 2). Thus, CSBC600 was selected as the modified precursor material in subsequent experiments, and the adsorption mechanism was explored. The best adsorption performance was achieved with MCSBC modified with 0.035 M KMnO_4 solution, thereby indicating that the introduction of MnO_x significantly improved the surface structure of BC, and then led to an increase in the TC adsorption amount, which was confirmed by SEM-EDS analysis. However, modification with the high Mn concentration decreased the adsorption performance of BC (Figure 2), which might have occurred because many MnO_x particles agglomerated on the CSBC surface, thereby leading to partial blockage of the pore structure (Song et al. 2014).

Adsorption kinetics and effects of contact time

The kinetic adsorption of TC pollutants on porous materials is usually classified into rapid adsorption and slow adsorption (Li et al. 2021). In the initial stage of adsorption, the adsorption sites are quickly occupied by the adsorbent molecules. With time, all the surface adsorption sites become occupied and reach the adsorption equilibrium (Jiang et al. 2017). As shown in Figure 3, rapid adsorption of TC by CSBC400, CSBC600, and MCSBC occurred within 30 min, during which the accessible sites on the adsorbent surface were rapidly occupied. The hydroxyl group on TC and the O-containing functional group of BC combined with H bonds and π - π electron donors and acceptors (Song et al. 2014; Tan et al. 2018) resulting in a rapid adsorption capacity of more than 90 % of the equilibrium adsorption capacity. The slow adsorption stage lasted 360 min. The equilibrium adsorption capacity of CSBC400, CSBC600, and MCSBC was 9.834 mg/g, 10.875 mg/g, and 13.254 mg/g, respectively. The modified BC prepared by oxidizing sawdust and soaking FeCl_2 and KMnO_4 solution adsorbed TC, and the adsorption capacity after modification was approximately three times that before modification (Zhang et al. 2021). One study used the method of chemical co-precipitation to synthesize MnO_2 -supported BC for TC adsorption, and showed a good adsorption capacity compared with that of other adsorbents (Shen et al. 2020). In this study, the TC adsorption capacity of MCSBC was 1.7 times that of CSBC600. This might have been due to the modification of MnO_x , which increased the number of adsorption sites on the surface of the material (Tan et al. 2018; Wan et al. 2020). There was a large concentration difference between the BC and the solution interface at the initial adsorption stage, thereby resulting in a large mass transfer driving force (Iqbal et al. 2021; Liu et al. 2021), which led to the rapid occupation of the BC adsorption sites by TC. As the reaction time increased, the concentration difference of the solution decreased, which

weakened the driving force of adsorption, thereby resulting in a slow increase in the adsorption amount (Wang et al. 2018). The adsorption of TC by BC gradually stabilized after 360 min.

To better explain the adsorption mechanism, pseudo-first-order and pseudo-second-order adsorption models were used to fit the kinetic experimental data. The fitting results of the pseudo-first-order and pseudo-second-order adsorption models are listed in Table 2. The pseudo-second-order adsorption model accurately described the TC adsorption behavior of the original BC and modified BC ($R^2 > 0.93$). The TC adsorption amount obtained by fitting the pseudo-second-order kinetics equation was closer to the experimentally measured value, thereby indicating that chemisorption was predominant throughout the adsorption process (Shepherd et al. 2017). The adsorption mechanism and rate-limiting steps of TC on all the BCs were further examined using the intra-particle diffusion model (Jiang et al. 2017). Figure 4 shows the fitting curve of intra-particle diffusion is composed of two linear segments: the first stage is straight but not at the origin, thereby indicating that TC adsorption is a multi-step process and that intra-particle diffusion is not the only rate-limiting step (Xiong et al. 2018). In different diffusion stages, the linear relationship between the adsorption amount of TC and $t^{0.5}$ was mainly manifested by the difference in k_{di} . The large k_{d1} of the first stage indicated that external diffusion was the dominant process (Eltaweil et al. 2020; Ma et al. 2015), and the diffusion time at this stage was generally less than 90 min. TC adsorption may be controlled by molecular diffusion and membrane diffusion (Zeng et al. 2019), and the diffusion rate of MCSBC and CSBC600 was approximately three times that of CSBC400, which might have been due to the increased surface area of MCSBC and CSBC600, thereby providing more adsorption sites (Zhang et al. 2021). The slow slope of the second stage indicated that TC adsorption gradually transformed from the liquid film diffusion process to the particle internal diffusion stage, and TC was transferred through the liquid film to the pores of the BC matrix (Wang et al. 2018; Zhang et al. 2019a). The diffusion rate of MCSBC was approximately six times that of CSBC600 and CSBC400, thereby indicating that the diffusion rate in the particles decreased sharply with the complete adsorption and filling of the pores in MCSBC; however, TC molecules continued to migrate slowly on the surface until they entered the pores of the particles due to activation (Song et al. 2014). The intercept C represents the range of the boundary layer thickness, that is, the larger the intercept, the greater the boundary layer effect (Limousin et al. 2007). As shown in Table 3, the value of C_2 was greater than that of C_1 , and the diffusion boundary effect was more significant in the second layer, thereby indicating that the total adsorption rate was controlled by both liquid film diffusion and intra-particle diffusion (Limousin et al. 2007; Ma et al. 2015).

Adsorption isotherms

Adsorption isotherms are used to describe the distribution of adsorbate on adsorbents, thereby revealing their adsorption characteristics (Eltaweil et al. 2020; Grisales-Cifuentes et al. 2021; Limousin et al. 2007). With an increase in the adsorption equilibrium concentration, the adsorption amount of TC on the three materials increased significantly. The higher the concentration of TC, the larger the concentration gradient formed at the solid–liquid interface between TC and BC, thereby resulting in a greater driving force for

mass transfer and an increased adsorption amount of TC on the BC surface (Hao et al. 2021; Moussavi and Barikbin, 2010). The probability of TC capture by BC also increased as the TC concentration increased (Zhang et al. 2019). The Langmuir and Freundlich models were used to evaluate the isothermal adsorption characteristics of CSBC400, CSBC600, and MCSBC (Figure 5). The fitting results are listed in Table 4. The fitting coefficient of the Freundlich model ($R^2 > 0.98$) was better than that of the Langmuir model, thereby indicating that adsorption is a heterogeneous, multi-molecular layer adsorption process (Wang et al. 2018). The critical parameter $1/n$ is related to the degree of non-uniformity of the adsorption site (Pezoti Junior et al. 2014; Zhang et al. 2019). The minimum $1/n$ value of the modified BC sample was 0.456, indicating that the adsorption process of MCSBC can occur easily (Eniola et al. 2020; Moussavi and Barikbin, 2010). The specific surface area and pore volume of the BC were increased by Mn modification, and the surface adsorption capacity of the pore filling was improved (Song et al. 2014). In addition, the role of MnO_x and TC functional groups in the formation of complexes cannot be ignored (Shen et al. 2020; Song et al. 2014). k_F reflects the adsorption capacity of the adsorbent. A larger k_F value represents a stronger TC adsorption capacity of BC (Jang et al. 2018). The larger k_F of MCSBC indicated that the TC adsorption force of MCSBC was stronger than that of CSBC400 and CSBC600. One study (Liu et al. 2019) showed that the Langmuir model could better describe the TC adsorption process of BC, and the adsorption was mainly single-layer adsorption. However, another study (Jang et al. 2018) showed that the Freundlich model could better describe the adsorption of TC by loblolly pine BC, and the adsorption process was heterogeneous. The equilibrium adsorption capacity of the Mn-modified BC prepared in this study was 42.076 mg/g, which was higher than that of CSBC400 (26.936 mg/g) and CSBC600 (28.038 mg/g). Therefore, MCSBC can potentially be applied as a water treatment material for the adsorption and removal of TC.

Effect of temperature on TC adsorption

As shown in Figure 6, as the temperature increased from 25 to 45 °C, the TC adsorption capacity of the three BC materials gradually increased. The TC adsorption capacity of BC increased as the temperature and speed of molecular movement increased (Shen et al. 2020). In addition, the chemical processes in the adsorption process are intensified at high temperatures (Zhang et al. 2019). Chemisorption dominated the adsorption process of TC by modified BC, which led to a better adsorption performance of modified BC at high temperatures.

Effect of solution pH on TC adsorption

pH not only affects the solubility of the adsorbate, but also changes the surface charge characteristics of the adsorbent, thereby changing the interaction between the adsorbent and the adsorbate (Xiang et al. 2019). TC is an amphoteric molecule. TC species include H_4TC^+ , H_3TC , H_2TC^- , and HTC_2^- , respectively, with pH values of < 3.3 , $3.4-7.7$, $7.8-9.7$, and > 9.7 , respectively (Xiang et al. 2019).

The effect of solution pH on the removal of TC by different BCs is shown in Figure 7. As the pH of the solution increased from 3 to 9, the TC adsorption capacity of CSBC600 and MCSBC decreased gradually,

whereas the adsorption capacity of CSBC400 increased gradually, thereby indicating that the TC adsorption capacity of BC depends on both the pH and BC properties. Under different pH values, TC showed different species distributions. As the pH of the solution increased from 3 to 9, the TC adsorption capacity of CSBC600 and MCSBC decreased gradually because of the strong electrostatic repulsion between the TC molecules (H_4TC^+ and H_2TC^-) and the positive and negative charges on the surface of the adsorbent (Zhu et al. 2014). When the pH of the solution was lower than 3.3, the main type of TC was protonated TC (TC^+) and the BC surface was negatively charged. Therefore, the interaction between TC and BC is mainly electrostatic, and the adsorption effect is the best (Zhang et al. 2019a). When the pH was between 3.4 and 7.7, TC molecules (i.e., H_3TC) had no net charges, the electrostatic attraction was weak, and the adsorption efficiency decreased (Liu et al. 2021). In contrast, the TC adsorption capacity of CSBC400 showed an upward trend, which also verified that pH can affect the adsorption capacity of BC, thereby indicating that adsorption mechanisms such as surface complexation and cation bridging might have existed (Zhang et al. 2019). The study showed that ash affected the specific surface area and porosity of BC (Li et al. 2017), and thus affected its adsorption effect. The difference in ash content is a key factor affecting pH (Li et al. 2017). The ash content of the CSBC differed and was the key factor affecting the pH and zeta potential. Therefore, the difference in the adsorption effect at different pH values might have been caused by ash (Zhang et al. 2019). In conclusion, changes in pH affect the surface charge and TC type distribution on BC, which further shows that the electrostatic interaction between BC and TC is not the only influencing factor and mechanism.

Influence of ionic strength on adsorption capacity

The effects of salt ions (Na^+ , K^+ , Ca^{2+} , and NH_4^+) and the TC removal intensity using the various BCs are shown in Figure 8. As the concentration of monovalent cations in the solution increased, BC had a slight promoting effect on TC removal, which might have occurred because the low Na^+ concentration can improve the ionization level of TC molecules (Xiang et al. 2020), thereby resulting in a strong electrostatic interaction between the charged TC and the surface of the BC adsorbent. Related studies (Ersan et al. 2017; Gao et al. 2012) have reported that Na^+ and K^+ have a slight promoting effect on TC adsorption by BC; moreover, these studies speculate that the mechanism was attributed to salting-out. The studies also indicated that the non-electrostatic force could offset part of the electrostatic repulsion force, thereby increasing the adsorption capacity. Compared with the above salt ions, the bivalent cation Ca^{2+} also had a promoting effect on TC adsorption, which might have been due to the electrostatic interaction between Ca^{2+} and the BC adsorbent (Liu et al. 2017). However, the low TC concentration in the solution did not allow the formation of a complex between Ca^{2+} and TC, thereby affecting the adsorption of TC (Liang et al. 2019).

FTIR comparison before and after adsorption

Surface functional groups are important factors that affect the adsorption of pollutants by BC materials (Hao et al. 2018; Toles et al. 1999). As shown in Figure 9, the peak values of $3410\text{--}3660\text{ cm}^{-1}$,
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1585 cm^{-1} , 1400 cm^{-1} , and 1096–1131 cm^{-1} corresponded to the stretching vibrations of $-\text{OH}$, $\text{C}=\text{C}$, $-\text{CH}_2$, and $\text{C}-\text{O}-\text{C}$ groups, respectively, thereby indicating the existence of such functional groups on the surface of the BC. No organic functional groups ($\text{C}-\text{O}-\text{C}$) were found on the modified BC, thereby indicating that some O-containing functional groups were removed during BC modification. The peak value of the modified samples was 623 cm^{-1} , which corresponded to $\text{Mn}-\text{O}$. The peak value of MCSBC at 623 cm^{-1} was wide, which might have been due to $\text{Mn}-\text{O}$ vibrations in KMnO_4 . The $\text{Mn}-\text{O}$, $\text{C}=\text{C}$, and $\text{C}=\text{O}$ peaks confirmed the successful combination of KMnO_4 and BC (Dong et al. 2018). In addition, the total amount of functional groups on the surface of the modified BC decreased gradually and the vibration absorption peak in the scanning wavelength weakened gradually, thereby indicating that the functional groups were involved in the formation of MnO_x and the structural properties of BC were more stable. No difference was found between the functional groups on the surface of the MCSBC before and after adsorption, thereby indicating that the types of functional groups did not change during adsorption. After TC adsorption, the $-\text{OH}$ stretching of MCSBC at 3730 cm^{-1} decreased to 3740 cm^{-1} , which also revealed that the carboxyl functional group on MCSBC participated in the adsorption process and that the $-\text{OH}$ and $\text{Mn}-\text{OH}$ groups on the surface of MCSBC might have a complexing effect on TC (Liu and Fan, 2018). In addition, the $\text{C}=\text{O}$ functional group of MCSBC at 1605 cm^{-1} migrated after TC adsorption, which might have been related to the metal- π electron interaction between the part of BC not loaded with MnO_x and the metal cation in the adsorption process (Tan et al. 2018). The wave number of $\text{Mn}-\text{O}$ functional groups decreased after adsorption, which indicated that there was a chemical interaction between MnO_x and metal ions in the adsorption process (Song et al. 2014) and that MnO_x plays an important role in adsorption.

XRD comparison before and after adsorption

The crystal structure and phase composition characteristics of the BC samples were characterized using XRD, as shown in Figure 10. In the CSBC400, CSBC600, and MCSBC structures, the diffraction peaks at 28.0°, 41.0°, and 25.9° could be assigned to SiO_2 , which has also been reported in previous studies (Lin et al. 2017). After modification, sharp diffraction peaks were observed at 29.9°, 35.0°, and 43.0° in the MCSBC structure, thereby indicating the presence of Mn_3O_4 . However, Mn_3O_4 peaks were not found in the CSBC400 and CSBC600 structures, thereby indicating that Mn_3O_4 was successfully loaded into the MCSBC. After modification, the intensity of the C diffraction peak of CSBC600 was weakened, thereby indicating that there was a chemical effect between CSBC600 and KMnO_4 in the modification process. The sharp diffraction peak of Mn_3O_4 in the MCSBC structure was significantly weakened after adsorption, which proved that TC adsorption had an effect on the phase of the MCSBC material structure. However, MCSBC still had a diffraction peak similar to that of the original CSBC600 after adsorption, thereby indicating that MCSBC maintained a high degree of crystallinity after adsorption.

Adsorption mechanism

BC adsorption mechanisms include pore diffusion, Lewis acid-base action, electrostatic action, ion exchange, surface complexation, a cationic- π mechanism, H bonding, and π - π stacking (Hoslett et al. 2021; Peiris et al. 2017; Zhao et al. 2021). The specific mechanism depends on the physical and chemical properties of the BC and the properties of the solution.

The well-developed pore structure and large specific surface area of BC are conducive to the physical diffusion of TC molecules, which is also an important factor for the effective removal of TC by high-temperature BC (Liu and Fan, 2018). Electrostatic action can affect the removal of TC by BC, but it is clearer in strongly acidic or alkaline environments (Hao et al. 2018). The abundant carboxyl and hydroxyl functional groups on the surface of BC can form H bonds with the carboxyl, hydroxyl, and amino functional groups of TC (Shen et al. 2020; Tan et al. 2018). The protonated amino group of TC can also form a cationic- π mechanism with the aromatic structure of BC (He et al. 2018). BC rich in mineral ions can bind TC via an ion exchange mechanism (Ersan et al. 2017; Gao et al. 2012). In addition, the complete aromatic structure of high-temperature BC can form π - π stacking with the benzene ring structure of TC. In this study, the specific surface area of the CSBC was in the order of MCSBC > CSBC600 > CSBC400. The TC adsorption capacity of CSBC was in the order of MCSBC > CSBC600 > CSBC400. Therefore, pore action is an important mechanism for TC removal by BC.

The effect of solution pH on the adsorption of TC by BC indicates that the effect of electrostatic action is limited because pH changes the surface charge of BC and the presence of TC, thereby affecting the interaction between BC and TC (Liu et al. 2021).

FTIR analysis showed that -OH, C-O-C, the aromatic structure, and -CH₂ were involved in TC adsorption, and the mechanisms involved included H bonding and π - π stacking. The reaction mechanism can be inferred from the changes in the XRD binding energies and relative contents of the functional groups. The O-containing functional groups of MCSBC were different from those of CSBC600 and CSBC400. XRD analysis showed that the changes in the O-containing functional groups in MCSBC after TC adsorption were related to π - π stacking and H bonding (Wang et al. 2018). FTIR analysis and XRD showed that the aromatic structure and O-containing functional groups of BC played an important role in TC adsorption.

In conclusion, the main mechanisms of TC adsorption by MCSBC are pore diffusion, H bonding, electrostatic interactions, and π - π stacking.

Conclusion

In this study, a new type of MCSBC granular adsorbent with a porous and coarse structure was synthesized using the KMnO₄ coating method. The adsorption of TC by MCSBC was effective in the low pH range and was less affected by common coexisting cations (Na⁺, K⁺, Ca²⁺, and NH₄⁺) in aqueous solution. The kinetic results indicated that the TC adsorption process was chemisorption and that 360 min was an adequate time to reach equilibrium. The equilibrium data showed that the process represents

a mixture of monolayer and multilayer adsorption, and an increase in temperature is beneficial to the process. Although the MCSBC presented in this study showed its potential as a valid adsorbent for TC from aqueous solutions, additional factors (e.g., microorganisms, coexisting anions, and methods) should be considered before its application in future works.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors allow the publication of the paper.

Availability of data and materials

All data used to support the findings of this study are included with in the article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

Conceptualization and Methodology: Fayong Li; Formal analysis and investigation: Xiao Liu; Writing-original draft preparation: Xiao Liu; Writing-review and editing: Fayong Li and Xuefei Hu; Data curation: Shaoyang Shi; Detection: Tao Sun; Supervision: Juanxiang Zhang.

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Tables

Table 1. Basic properties of cotton straw biochars (CSBCs) pyrolyzed at 400 °C (CSBC400) and 600 °C (CSBC600) and cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

	CSBC400	CSBC600	MCSBC
C/%	63.600	73.0300	60.400
N/%	1.130	0.980	1.140
H/%	3.080	1.630	2.800
O/%	19.050	10.140	21.260
ash/%	13.140	14.220	14.400
H/C	0.050	0.020	0.046
O/C	0.300	0.140	0.350
(N+O)/C	0.320	0.150	0.370
Specific surface area (m ² /g)	8.619	140.130	242.394

Table 2. Fitting parameters of adsorption kinetics of cotton straw biochars (CSBCs) pyrolyzed at 400 °C (CSBC400) and 600 °C (CSBC600) and cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Adsorbent	Quasi-first -order kinetic equation			Quasi-second-order dynamics equation		
	$K_1(\text{min}^{-1})$	$q_e(\text{mg/g})$	R^2	$K_2(\text{g mg}^{-1} \text{ min}^{-1})$	$q_e(\text{mg/g})$	R^2
CSBC400	0.135	9.818	0.703	0.064	9.942	0.965
CSBC600	0.096	10.838	0.945	0.026	11.089	0.970
MCSBC	0.095	13.252	0.690	0.019	13.634	0.931

Notes: q_e is the amount of tetracycline adsorption; K_1 is the pseudo-first-order rate constant; K_2 is the pseudo-second-order rate constant.

Table 3. Fitting parameters of intra-particle diffusion equation of cotton straw biochars (CSBCs) pyrolyzed at 400 °C (CSBC400) and 600 °C (CSBC600) and cotton straw biochar modified with 0.035 M KMnO_4 (MCSBC).

Adsorbent	$K_{d1}(\text{mg g}^{-1} \text{ min}^{-0.5})$	$C_1(\text{mg/g})$	R^2	$K_{d2}(\text{mg g}^{-1} \text{ min}^{-0.5})$	$C_2(\text{mg/g})$	R^2
CSBC400	0.496	8.273	0.999	0.137	9.332	0.891
CSBC600	1.224	7.091	0.866	0.132	10.381	0.982
MCSBC	1.255	9.129	0.976	0.624	10.956	0.954

Notes: K_{d1} and K_{d2} are the intra-particle diffusion rate constant; C_1 and C_2 are a constant representing the thickness of boundary layer.

Table 4. Fitting parameters of adsorption isotherms of cotton straw biochars (CSBCs) pyrolyzed at 400 °C (CSBC400) and 600 °C (CSBC600) and cotton straw biochar modified with 0.035 M KMnO_4 (MCSBC).

Adsorbent	Langmuir model			Freundlich model		
	$q_{max}(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	$K_F(\text{L/mg})$	$1/n$	R^2
CSBC400	33.557	0.205	0.950	2.675	0.600	0.986
CSBC600	39.526	0.063	0.962	3.628	0.558	0.998
MCSBC	42.194	0.155	0.900	7.135	0.456	0.996

Notes: q_{max} is the Langmuir saturation adsorption capacity; K_L and K_F are the Langmuir and Freundlich constant, respectively; $1/n$ is the Freundlich exponent linked with adsorption intensity.

Figures

Figure 1

Scanning electron microscope images of biochars (BCs): (a) cotton straw biochar (CSBC) modified with 0.035 M KMnO₄ (MCSBC), (b) cotton straw biochar pyrolyzed at 600 °C (CSBC600), and (c) cotton straw biochar pyrolyzed at 400 °C (CSBC400).

Figure 2

Comparison of adsorption materials. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochars (CSBCs) modified with 0.035 M, 0.070 M, 0.210 M, and 0.350 M KMnO₄ are MCSBC, MCSBC1, MCSBC2, and MCSBC3, respectively.

Figure 3

Adsorption kinetics of tetracycline on biochar. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Figure 4

Fitting curves of intra-particle diffusion equation. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Figure 5

Adsorption isotherms of tetracycline on biochar. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Figure 6

Influence of temperature on tetracycline removal by MCSBC. Cotton straw biochar modified with 0.035 M KMnO_4 (MCSBC).

Figure 7

Effect of pH on tetracycline removal by biochar. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO_4 (MCSBC).

Figure 8

Effect of ion types on tetracycline removal by biochar. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Figure 9

Fourier transform infrared spectroscopy spectra of CSBC, MCSBC, and tetracycline adsorption onto MCSBC. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Figure 10

X-ray diffraction of CSBC, MCSBC, and tetracycline adsorption onto MCSBC. Cotton straw biochar pyrolyzed at 400 °C (CSBC400); cotton straw biochar pyrolyzed at 600 °C (CSBC600); cotton straw biochar modified with 0.035 M KMnO₄ (MCSBC).

Supplementary Files

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