Investigation on the adsorption of antibiotics from water by metal loaded sewage sludge biochar
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ABSTRACT

Application of sewage sludge biochar as an adsorbent for antibiotics treatment has obtained special attention owing to its low cost and surface functionality. Three metal ions were selected to modify sewage sludge biochar through the pyrolysis with the metal loaded method. Fe loaded sewage sludge biochar (BC-Fe), Al loaded sewage sludge biochar (BC-Al) and Mn loaded sewage sludge biochar (BC-Mn) were characterized and used to explore the performance of adsorbing tetracycline (TC), sulfamethoxazole (SMZ) and amoxicillin (AMC). BC-Fe, BC-Al and BC-Mn possessed rougher surfaces, larger specific surface area and better pore structure. Intra-particle diffusion and Langmuir models were more suitable to describe the adsorption process. The maximum adsorption amount of TC, SMZ and AMC could reach 123.35, 99.01 and 109.89 mg/g by BC-Fe. Furthermore, the main mechanism of antibiotics adsorption by metal loaded sewage sludge biochars might be pores filling, Van der Waals forces and H-bonding. The study can not only solve the problems associated with the pollution of antibiotics from wastewater, but also reduced the treatment pressure of sewage sludge effectively.

Key words | adsorption, antibiotic, metal ions, modification, sewage sludge biochar

HIGHLIGHTS

- Modification enhanced the microcellular structure and promoted the degree of carbonization.
- Compared with biochar, metal loaded sewage sludge biochar exhibited better adsorption capacity.
- Fe ion was demonstrated to be the optimal modified material.
- Metal loaded sewage sludge biochars avoided the risk of polluting the environment.

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INTRODUCTION

With the continuous development of urbanization and industrialization, all sewage plants in China produced 30 million tons of sewage sludge in 2013, expected to reach 60–90 million tons by 2020 (Lin et al. 2018). Sewage sludge is a mixture of fibers, animal and plant residues, microorganisms, pathogens and heavy metals. Traditional sewage sludge treatment techniques include use in agriculture, landfill and incineration (Rigby et al. 2016). Sewage sludge is applied to increase soil fertility and improve soil structure in agriculture commonly owing to its being rich in N, P and other nutrients. However, if untreated sewage sludge is applied to land, it will pose potential dangers to human health. Sewage sludge used for landfill easily to decays, goes off and produces smelly gas with water seeping into groundwater (Bondarczuk et al. 2016). If sewage sludge is used for incineration, dioxins and other highly toxic substances are produced with burning. It has become one of the most urgent environmental issues to dispose of sewage sludge safely and properly with up to 60% of the total cost spent on these processes for wastewater treatment (Yan et al. 2013). Therefore, it is desirable to explore an efficient and feasible method for sewage sludge treatment.

Biochar, a porous, stable and carbon-rich solid material, is produced by thermal decomposition or pyrolysis with little or no oxygen. It has been considered as compost additives and soil amendments due to its large specific surface area, porous structure and high ion exchange capacity. Also, these unique physicochemical properties make biochar attract increasing attention as a promising adsorbent and supporting matrix to remove organic contaminants, heavy metals and other inorganic contaminants from wastewater (Ahmad et al. 2014). The feedstocks of biochar production are a large number of low-cost organic wastes, such as agricultural wastes, garden residues, sewage sludge and algae. Compared with the direct incineration and other treatment methods, the cost and energy consumption of biochar preparation are lower and the treatment method is more environmentally friendly and hygienic. In the previous studies on adsorption of antibiotics by biochars, many scientists focused on the adsorption effect of lignocellulosic biochar. However, sewage sludge also can be carbonized to synthesize biochar because of its great content of biomass and organic matter. It can not only realize the resource utilization of sewage sludge, but also obtain good economic benefit and social benefit (Barry et al. 2019).

In the past few years, special attention has been paid to converting sewage sludge to biochar through a pyrolysis process. The ion exchange groups on the surface of the biochar, predominantly negatively charged, are decreased by the severe thermal treatment during the process of pyrolysis. Metal ions in sewage sludge mainly exist as cations, limiting the adsorption ability of biochar (Yu et al. 2017). To enhance the adsorption capacity of biochar, some efforts have been made to modify biochar, which has the favorable advantage of developing loading metal with more binding sites (Wang et al. 2017). Besides, metal loaded sewage sludge biochars could couple respective redox degradation with adsorption capability (Sun et al. 2019). It is common for a metal loaded method to require several procedures (synthesizing biochar and then impregnating metal). Iron (Fe), as one of the most abundant metals in the earth’s crust, is usually chosen for biochar modification. Wei et al. observed that one-step synthesized Fe loaded sludge biochar had excellent
ferromagnetic properties and a strong sorption ability towards tetracycline and doxycycline (Wei et al. 2019). Previous studies have shown that aluminum, iron and manganese can improve the anion exchange capacity of biochar (Lawrinenko et al. 2017), have higher zero net charge point, provide larger surface area and active hydroxyl group during the adsorption process (Shen et al. 2020), which can improve the adsorption capacity of biochar (Wang et al. 2015).

It is common to use antibiotic drugs widely for treating or preventing human and animal diseases. Annual production of antibiotics is estimated at 210,000 tons in China, most of which are poorly metabolized and directly excreted in feces (Liu et al. 2012). They eventually enter into the receiving environment following various wastewater treatments. At present, the concentration of antibiotics in some water bodies in China reaches μg/L, which may cause some potential harm in the water environment (Wei et al. 2019). Previous studies and relevant literature showed that the concentrations of ciprofloxacin, sulfamethoxazole and tetracycline in rivers and lakes ranged from 0.20 to 1.4 μg/L, 0.21 to 2.8 μg/L and 0.061 to 1.1 μg/L, respectively (Batt et al. 2007). The contamination of antibiotics is rapidly increasing in the natural environment due to the dissemination and development of antibiotic-resistant genes and bacteria. They will pose a potential impact on human health and ecosystems. From an environmental perspective, it is desirable to find an efficient and feasible method to remove antibiotics from wastewater.

There have been many technologies to deal with antibiotics from wastewater, such as membrane separation, oxidation, electrochemistry, photodegradation, biodegradation and adsorption (Aydin et al. 2016; Radjenovic & Petrovic 2007). Due to its high efficiency, simple operation and low energy consumption, the adsorption method has become the main method in practical application. Recently, biochar has been deemed as a promising adsorbent for pollutants removal by the International Bioconcentration Organization (Lega et al. 2018).

The preparation of metal loaded sewage sludge biochars can solve the problems associated with the treatment of sewage sludge effectively and realize the resource utilization of sewage sludge. In this research, BC, BC-Fe, BC-Al and BC-Mn were facilely prepared via high temperature pyrolysis and used to remove antibiotics. In this study, three kinds of antibiotics, tetracycline (TC), sulfamethoxazole (SMZ) and amoxicillin (AMC), were selected as target pollutants. The structure and surface properties of metal loaded sewage sludge biochars were explored via various characterized techniques. Moreover, the effects of initial antibiotic concentration and the adsorption time on the adsorption properties were carried out in detail. This study would lay the foundation for the follow-up basic research.

**MATERIALS AND METHODS**

**Materials**

Sewage sludge (moisture content is about 80%, pH = 8) taken from the Kuihe Sewage Treatment Plant in Xuzhou, China, was air-dried to constant weight (Yoh et al. 2020). TC, SMZ and AMC, purity ≥ 98%, were purchased from Aladdin Industrial Corporation, USA. The other chemicals, including FeSO4·4H2O, Al(NO3)3·9H2O and Mn(NO3)2·6H2O, were obtained from Sinopharm Chemical Reagent limited corporation.

**Preparation and modification**

Firstly, dried sewage sludge was pyrolyzed to produce biochar at 600 °C with a rate of 5 °C/min for 120 min in a nitrogen atmosphere. Following this, sewage sludge biochar was ground in a mortar and then passed through an 80 mesh nylon sieve. Then, the sewage sludge biochar sample was rinsed, oven-dried, collected and named BC. Subsequently, BC was soaked in the metal salts and metal ions were adsorbed to the pores and surface of biochar. Selected metal materials were FeSO4·4H2O, Al(NO3)3·9H2O and Mn(NO3)2·6H2O, respectively (Pan et al. 2014). Finally, metal ions were supported onto the surface of BC by secondary pyrolysis and the corresponding metal loaded sewage sludge biochars were represented by BC-Fe, BC-Al and BC-Mn.

**Characterization**

A series of physicochemical analyses were undertaken to characterize the prepared biochars. The surface morphology of biochars was analyzed by scanning electron microscopy (SEM, Model JSM-7401, Nippon Electronics). The specific surface area and pore volume of biochars were determined by a NOVA 2200 (Quantachrome, China) (the sample was degassed at 105 °C for 24 h and liquid nitrogen temperature was 77.15 K). Average pore size distribution was derived from the Brunauer-Emmett-Teller (BET) and Density Functional Theory (DFT) methods. The content percentages of carbon, hydrogen, oxygen, nitrogen and metal in biochars...
were determined for X-ray photoelectron spectroscopy (XPS) test by using Thermo ESCALAB250Xi (Thermo Scientific, USA) with a monochromatic Al-Ka source. The surface functional group information of biochars before adsorption was obtained by Fourier transform infrared spectroscopy (FTIR, Thermo, USA), scanning over the range of 400–4,000 cm⁻¹. The crystal phase structure of biochars was analyzed by X-ray diffraction (XRD, BRUKER, Germany).

**Batch experiments**

**Adsorption kinetics**

The preliminary experiment has proved that 1.440 min reaction time is sufficient to ensure contact between absorbate and absorbent. Adsorption kinetic experiment was conducted at 298 K by mixing the biochar and 50 mL antibiotics with an initial concentration of 40 mg/L in 100 mL centrifuge tubes (according to the preliminary experiment). The centrifuge tubes were shaken evenly, then put in the air bath constant temperature oscillator shaker (120 rpm) in the dark. The dosage of biochars for TC, SMZ and AMC was 10, 20 and 20 mg (according to the preliminary experiment), respectively. The pH values of the three antibiotic solutions were controlled at 7.0. The oscillation reaction time was 5–1,440 min. After the reaction, the solution was centrifuged (10,000 RPM, 10 min) and placed in a 10 mL aerosol tube through a 0.45 μm microporous membrane to determine the concentration of antibiotics in the filtrate. The concentration of antibiotics was measured with High Performance Liquid Chromatography. Before the test, the samples are generally stored in the refrigerator (4 °C) at low temperature for a maximum of 12 h.

**Statistical analysis of the adsorption experiment data**

The adsorption capacity Q (mg/g) of biochars was calculated according to the following equation:

\[
Q = \left(\frac{C_0 - C_e}{M}\right) \times V
\]

where \(C_0\) (mg/L) and \(C_e\) (mg/L) represent the antibiotic concentration at the initial and adsorption equilibrium, respectively, \(V\) (L) and \(M\) (g) represent the volume of antibiotic solution and the mass of biochar, respectively.

In this study, all tests were implemented in triplicate, and the results were expressed as the mean ± standard deviation. The above statistical analyses were performed using SigmaPlot14.

**RESULTS AND DISCUSSION**

**Characteristics of biochar samples**

**Surface morphology**

To investigate the differences in the morphology properties of sewage sludge biochars, SEM of BC, BC-Fe, BC-Al and BC-Mn was characterized. The SEM images (Figure 1) showed that all the sewage sludge biochars consisted of irregular blockbased particles with an average 30 nm size and presented aggregated morphology. This morphology was in line with that typically observed by Jia Wei (Wei et al. 2019). The surface of BC-Fe, BC-Al and BC-Mn was rougher than that of BC, with different degrees of holes, cracks and pits. It illustrated that metal ions had been attached to sewage sludge biochars successfully. The SEM images confirmed that the surfaces of biochars varied with the modification process and metal ions.

**Specific surface area**

The specific surface area and porous structure of biochars played an important role in the process of adsorption. The specific surface area, pore size and average pore size of sewage sludge biochars are shown in Table 1. The results of BC were 28.07 m²/g, 0.0154 cm³/g and 1.29 nm. The specific surface area, pore volume and average pore size increased for BC-Fe, BC-Al and BC-Mn along with the modification of metal ions. A larger specific surface area, larger pore volume, and smaller average pore size of sewage sludge
biochars formed, leading to improved adsorption performance (Ahmad et al. 2012). The increasing specific surface area might be explained by the enlarging average pore size. After partial element volatilization, less volatile and fixed carbon residue could use the remaining space in the matrix to form a better micro-pore structure (Chen et al. 2014).

### Chemical elements

XPS was used to characterize the elemental contents, and results are presented in Table 2. It is common for sludge biochars to present a low value of C because carbon would release in the form of small molecules (CO2, CH4, and others) during pyrolysis (Yin et al. 2018). Zielińska et al. (2015) recorded C values in the range of 18.1% to 27.8% in biochars produced from different sewage sludge samples, at temperatures ranging from 500 °C to 700 °C. The contents of C, H, O and N decreased with the modification of metal ions. It was caused by the increasing ash content of the pyrolysis substrate when the transition metal oxide modified materials were added to sewage sludge in the pyrolysis process (Chen et al. 2014). To explain the observed phenomenon, the contents of C, H, O and N decreasing, we might consider that volatiles and fixed carbon residues could use the remaining space from the matrix to form a better microscopic pore structure. Hence, BC-Fe, BC-Al and BC-Mn had well-developed pore structure on account of there being fewer volatiles and fixed carbon residues in them (Chen et al. 2014).

The atomic ratio based on element C could shield the influence of ash content change and reflect the variation of elements H, O and N. As illustrated in Table 2, the value (H/C) of BC was higher than that of BC-Fe, BC-Al
and BC-Mn, showing that the degree of aromatization and carbonization improved during the process of modification. The pyrolysis and dehydrogenation of carbon chains became more complete under the action of transition metal oxides during the rapid pyrolysis process (Chen et al. 2014). The value of O/C and (O + N)/C declined, indicating more O and N elements in the sludge released due to more thorough carbonization. Fe, Al and Mn ions had the highest content in the corresponding metal loaded sewage sludge biochars, indicating that metal ions had been successfully loaded onto BC. Also, transition metal oxides had a catalytic action on the gasification and reforming of C, H, O, and N to produce syngas.

**Surface functional groups**

FTIR analysis was further carried out to reflect the changes in the distribution of surface functional groups, and the results are shown in Figure 2. Abundance of adsorption peaks existed in the FTIR spectra of BC, BC-Fe, BC-Al and BC-Mn. Various functional groups, such as -OH at 3,420 cm⁻¹, -CO at 1,631 cm⁻¹, -CH₃ at 1,431 cm⁻¹, -C=O at 1,035 cm⁻¹ and the Fe-O bond at 508 cm⁻¹, were present on biochars (Fernandez et al. 2015; Khataee et al. 2017). There was the appearance of Fe-O bond on BC-Fe and no change of peak pattern on BC-Al and BC-Mn compared with BC. This was probably because Fe ions were good at surface modification of BC while Al and Mn ions may get into sewage sludge biochar particles under heating. The peak position of BC-Fe, BC-Al and BC-Mn had slight displacement due to the bonding of transition metal oxides to the surface of BC (Chen et al. 2014). During the modification, the weakness of the peak at 1,631 cm⁻¹ was explained by the conversion of -C=O to -C=O. The 3,420 cm⁻¹ and 1,431 cm⁻¹ peaks strengthened, indicating that long-chain hydrocarbon broke down into more -OH and -CH₃. A strong peak appearing at 1,035 cm⁻¹ confirmed that various oxygen elements could directly combine with adjacent carbon atoms during the pyrolysis reaction. Then it was integrated into the carbon chain in the form of -C=O (Chen et al. 2014).

**XRD**

XRD spectra of BC, BC-Fe, BC-Al and BC-Mn are shown in Fig. S1. The XRD pattern for BC-Fe exhibited peaks for FeOOH at angles of 26.725, 35.161 and 39.219 (Xiao et al. 2016; Zhang et al. 2016). The peaks corresponding to FeO were also observed at 2θ = 31.130 and 33.816 in the BC-Fe (Zhao et al. 2017). The XRD pattern of BC-Al identified the peak of the newly added aluminum containing material (AlPO₄), indicating that Al ions were loaded on BC. The characteristic peak of manganese ore appeared on BC-Mn, indicating that Mn mainly existed in the form of manganese oxide. It proved that manganese ion loading on biochar might combine with O atom to become oxide. The wide peak 19.887° and 26.624° in BC, BC-Fe, BC-Al and BC-Mn represented amorphous carbon and graphite crystal, acting as a π-donor during π-π electron donor-receptor interaction (Wang et al. 2010; Dante et al. 2017).

### Table 2 | Elementary compositions of sewage sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn)

| Biochar | C (%) | H (%) | O (%) | N (%) | C + H + O + N (%) | H/C | O/C | (O + N)/C | Fe (%) | Al (%) | Mn (%) |
|---------|-------|-------|-------|-------|------------------|-----|-----|----------|-------|-------|-------|
| BC      | 25    | 0.49  | 4.2   | 0.61  | 18.14            | 0.48| 0.25| 0.29     | 3.54  | 0.08  | 0.04  |
| BC-Fe   | 21    | 0.29  | 1.6   | 0.42  | 14.75            | 0.31| 0.13| 0.13     | 15.62 | 0.07  | 0.07  |
| BC-Al   | 22    | 0.28  | 1.5   | 0.44  | 13.73            | 0.26| 0.16| 0.19     | 3.18  | 2.37  | 0.02  |
| BC-Mn   | 20    | 0.21  | 1.2   | 0.33  | 8.86             | 0.27| 0.21| 0.01     | 3.23  | 0.07  | 3.16  |
Adsorption kinetics

To gain insight into the mechanisms of antibiotic adsorption by biochars, pseudo-first order, pseudo-second order and intra-particle diffusion models, widely selected to determine the relationship between the adsorbate amount and reaction time, were applied to fit the experimental data (Wang et al. 2010).

Pseudo-first order model: \[ \ln \left( \frac{Q_e}{Q_t} - 1 \right) = \ln Q_e - k_1 t \] (2)

Pseudo-second order model: \[ \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \] (3)

Here, \( Q_e \) (mg/g) and \( Q_t \) (mg/g) represented the amounts of TC, SMZ and AMC adsorbed at equilibrium and at time \( t \) (min), respectively. \( k_1 \) (1/min) represented the equilibrium rate constant of pseudo-first-order adsorption. \( k_2 \) (g/(mg·min)) was the rate constant of pseudo-second-order adsorption.

Table 3 summarized the parameters obtained from the two kinetic models for the adsorption of antibiotics by biochars. Fig. S2 shows the fitting curves. As compared to the pseudo-first-order model \( (R^2 = 0.7466–0.9582) \), the pseudo-second-order model better described the adsorption process with an extremely high value of \( R^2 \) (0.9974–0.9997). The results indicated that the adsorption mechanism depended on the adsorbate and adsorbent (Qian et al. 2011). The adsorption reaction was mainly chemical adsorption (Li et al. 2018a). Meanwhile, chemical sorption was possibly the rate-limiting step, which involved the valence forces by the sharing or exchanging of electrons (Wu et al. 2020).

As shown in Table 3, the addition of metal loaded sewage sludge biochars increased the adsorption amount of TC, SMZ and AMC, but decreased the \( k_2 \) value. The results indicated that loading by metal ions changed the adsorption kinetics. Concretely, the equilibrium adsorption amount of TC by BC and BC-Fe increased from 65.79 to 119.05 mg/g, and the \( k_2 \) value decreased from 0.00062 to 0.00031 g/(mg-min) (Table 3). The low \( k_2 \) value indicated the adsorption rate decreases with time, and the adsorption rate was proportional to the number of unoccupied sites (Gupta et al. 2010). For BC-Fe, BC-Al and BC-Mn, rougher surfaces (Figure 1(b)–1(d)) and larger specific surface area were observed (Table 1), which could provide increased adsorption sites for TC, SMZ and AMC.

It is proposed that the internal diffusion model could be used to determine the reaction process, and the model formula follows (Li et al. 2018)

\[ Q = k_{pi} t^{0.5} + C \] (4)

Here, \( Q \) (mg/g) represented adsorbing capacity, \( k_{pi} \) (mg/(g·min\(^{0.5}\))) represented the internal diffusion rate constant, and \( C \) represented the constant related to the boundary layer thickness.

The intra-particle diffusion modeling of the kinetics data (Fig. S3) showed that the plot of \( Q \) versus \( t^{0.5} \) was multi-linear, indicating that the adsorption process had multiple stages, and the order of the rate constants of three adsorbents was \( k_1 > k_2 > k_3 \) (Xu et al. 2012). Piecewise linear regression was applied to fit the data to the model, and correlation

| Antibiotic | Biochar | Pseudo-first-order model | Pseudo-second-order model |
|------------|---------|--------------------------|---------------------------|
|            |         | \( k_1 \) | \( Q_e^2 \) | \( R^2 \) | \( k_2 \) | \( Q_e^2 \) | \( R^2 \) |
| TC         | BC      | 0.0036 | 25.80 | 0.8417 | 0.00062 | 65.79 | 0.9994 |
|            | BC-Fe   | 0.0047 | 59.60 | 0.8522 | 0.00031 | 119.05 | 0.9986 |
|            | BC-Al   | 0.0043 | 45.56 | 0.8670 | 0.00033 | 103.09 | 0.9992 |
|            | BC-Mn   | 0.0039 | 37.10 | 0.8244 | 0.00036 | 92.590 | 0.9991 |
| SMZ        | BC      | 0.0021 | 5.79  | 0.7813 | 0.00046 | 22.62 | 0.9997 |
|            | BC-Fe   | 0.0034 | 18.21 | 0.7486 | 0.00036 | 58.48 | 0.9997 |
|            | BC-Al   | 0.0030 | 19.24 | 0.7466 | 0.00087 | 55.25 | 0.9996 |
|            | BC-Mn   | 0.0033 | 16.29 | 0.8491 | 0.00100 | 44.44 | 0.9993 |
| AMC        | BC      | 0.0029 | 14.13 | 0.8810 | 0.00075 | 24.45 | 0.9980 |
|            | BC-Fe   | 0.0035 | 24.73 | 0.8568 | 0.00043 | 59.88 | 0.9995 |
|            | BC-Al   | 0.0045 | 30.17 | 0.9582 | 0.00048 | 55.25 | 0.9982 |
|            | BC-Mn   | 0.0040 | 24.50 | 0.8479 | 0.00049 | 48.31 | 0.9974 |

\(^a(1/min), \ ^b(mg/g), \ ^c(g/(mg·min)).\)
coefficients are shown in Table 4. The linear segments were numbered I–III for indicating the three stages of adsorption, respectively.

Solid-liquid phase adsorption consisted of three basic processes. Stage I (external diffusion) was surface diffusion where antibiotics (TC, SMZ, AMC) migrated from the solution to the outer surface of BC, BC-Fe, BC-Al and BC-Mn, at a rapid adsorption rate (Fig. S3). Stage II (adsorption) was intra-particle diffusion where TC, SMZ and AMC diffused from the outer surface of biochars to the adsorption sites through the pores in the particle and were adsorbed to the active sites of the biochar. Stage III (the final equilibrium stage) was the adsorption equilibrium, which may have occurred due to the reduction of free adsorption sites of the biochar. It was also related to the increase of diffusion resistance (electrostatic repulsion) between the antibiotic molecules adsorbed on the surface of biochars and the antibiotic molecules in the solution (Zhang et al. 2019). It was reported that if the curve of the intra-particle diffusion model was linear and passed through the origin, the rate control of the adsorption process was caused by pore diffusion. If the linear curve did not pass through the origin, this indicated that intra-particle diffusion and other processes such as initial external mass transfer or chemical reactions were involved in determining the adsorption rate of TC, SMZ and AMC jointly (Zhu et al. 2014).

The $k_{p1}$ values of BC-Fe, BC-Al and BC-Mn were higher than that of BC (Table 4), indicating that the loading of Fe, Al and Mn ions could accelerate the adsorption rate of antibiotics on the surface of biochars. The conditions affecting the adsorption rate of antibiotics were not only surface diffusion, but also intra-particle diffusion. Since $k_{p1}$ significantly reflected the adsorption rate of the adsorbent surface, we speculated that metal ions mainly covered the external structure. It was consistent with the results of scanning electron microscopy that different degrees of holes, cracks and pits were attached to BC-Fe, BC-Al and BC-Mn. In addition, $k_{p2}$ and $k_{p3}$ specifically reflected the internal structure related to the adsorption rate of the adsorbent, which was consistent with the increase of the specific surface area and the enhancement of micropore development.

The intercept $C_i$ was an index to reflect the thickness of the boundary diffusion layer (Boparai et al. 2011). The $C$ values of BC-Fe, BC-Al and BC-Mn were higher than that of BC. This may be due to the reduced adsorption of antibiotics by BC, resulting in a decrease in the thickness of the boundary layer (Wei et al. 2019). The $C_i$ values of BC were larger than those of cow manure biochars (Table 4), indicating that the contribution of external surface adsorption for sludge biochars was larger than that of cow manure biochar (Zhang et al. 2019).

### Adsorption isotherms

Two typical isothermal models were used to fit the data in the adsorption isotherms. The Langmuir model showed that adsorbates were adsorbed on homogeneous surfaces and the distribution of adsorbate molecules was monolayer without interaction (Javanmardi & Bashiri 2017). The Freundlich model was an empirical model, which was

| Antibiotic | Biochar | $k_{p1}$ | $C_1$ | $R^2_1$ | $k_{p2}$ | $C_2$ | $R^2_2$ | $k_{p3}$ | $C_3$ | $R^2_3$ |
|------------|---------|----------|------|--------|----------|------|--------|----------|------|--------|
| TC         | BC      | 4.366    | 11.899 | 0.9978 | 1.318    | 35.521 | 0.9957 | 0.0383   | 63.168 | 0.9987 |
|            | BC-Fe  | 7.793    | 17.544 | 0.9971 | 3.361    | 114.434| 0.9948 | 0.0335   | 114.434| 0.9991 |
|            | BC-Al  | 7.823    | 18.524 | 0.9978 | 2.264    | 50.565 | 0.9968 | 0.0469   | 98.954 | 0.9953 |
|            | BC-Mn  | 6.675    | 19.534 | 0.9927 | 2.154    | 43.128 | 0.9954 | 0.0355   | 89.225 | 0.9999 |
| SMZ        | BC      | 0.678    | 11.197 | 0.9966 | 0.305    | 15.656 | 0.9917 | 0.0145   | 21.878 | 0.9975 |
|            | BC-Fe  | 4.396    | 11.515 | 0.9905 | 0.900    | 38.016 | 0.9949 | 0.0056   | 57.319 | 0.9991 |
|            | BC-Al  | 3.679    | 12.693 | 0.9968 | 0.986    | 32.906 | 0.9914 | 0.0089   | 54.879 | 0.9902 |
|            | BC-Mn  | 2.046    | 14.539 | 0.9978 | 0.909    | 23.644 | 0.9929 | 0.0503   | 42.523 | 0.9962 |
| AMC        | BC      | 1.752    | 2.523  | 0.9916 | 0.719    | 6.913  | 0.9971 | 0.0522   | 21.592 | 0.9997 |
|            | BC-Fe  | 4.699    | 5.813  | 0.9939 | 1.153    | 32.612 | 0.9947 | 0.0507   | 56.702 | 0.9985 |
|            | BC-Al  | 3.598    | 5.887  | 0.9975 | 1.070    | 51.252 | 0.9931 | 0.0702   | 51.252 | 0.9995 |
|            | BC-Mn  | 2.833    | 5.240  | 0.9975 | 1.379    | 15.712 | 0.9931 | 0.0239   | 45.868 | 0.9978 |

*a(mg/g·min$^{0.5}$).
usually used to explain chemisorption on heterogeneous surfaces (Engates & Shipley 2011).

**Langmuir model:**
\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m}
\]  

(5)

**Freundlich model:**
\[
\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e
\]  

(6)

Here, \( Q_m \) (mg/g) represented the adsorption saturation capacity, \( Q_e \) (mg/g) was the removal amount of antibiotics at equilibrium and \( C_e \) (mg/L) was the concentration of adsorbate in the solution at adsorption equilibrium. \( K_L \) was the constant corresponding to the isothermal model, \( K_f \) was the constant corresponding to the isothermal model, and \( n_f \) was the empirical constant for the adsorption process.

Table 5 lists the adsorption isotherm constants obtained from the adsorption of antibiotics on biochars. Fig. S4 shows the fitting curve. Higher \( R^2 \) were observed for the Langmuir isotherm model, indicating that this model was suitable for isotherm data and used to characterize the equilibrium adsorption.

As shown in Table 5, the \( Q_m \) of TC increased from 98.04 mg/g to 123.35 mg/g with the addition of metal ions. The \( Q_m \) of SMZ increased from 24.57 mg/g to 109.89 mg/g. These results were much better than different adsorbents reported in the literature. For instance, Zhang et al. (2013) had reported a capacity of 26.727 mg/g of the cow manure biochar prepared at different pyrolysis temperatures to adsorb TC. Also, Reguyal et al. (2017) had utilized magnetic biochar to remove SMZ and indicated an adsorption capacity of 17.49 mg/g. In comparison with the adsorbability of 92.87 mg/g by a functional activated fore-modified bio-hydrochar, metal loaded sewage sludge biochars exerted a stronger effect on the adsorption of AMC (Li et al. 2017b). The adsorption of antibiotics on the modified biochars was controlled by multiple mechanisms including pores filling, Van der Waals forces and H-bonding (Li et al. 2017b; Peizhen et al. 2019). \( K_L \) was related to the adsorption affinity or bond energy of adsorption between adsorbates and adsorbents (Sun et al. 2015). During the adsorption of TC and AMC, \( K_L \) on BC-Fe, BC-Al and BC-Mn was higher than that of BC, indicating that metal ions changed the adsorption affinity. However, the \( K_L \) values significantly decreased in the adsorption process of SMZ. The \( K_L \) values decreased from 0.2519 L/mg to 0.0664 L/mg in BC and BC-Al, respectively (Table 5). There was the phenomenon that SMZ was released into the wastewater. It indicated that BC-Fe, BC-Al, BC-Mn could be recycled in the removal of SMZ. And the economic advantages of modified biochar held out the prospect of large-scale production in the future.

**Implications of the study**

With the increase of sewage sludge production from the sewage plant, its reasonable treatment had become a big problem. At the same time, antibiotics used on a large scale inevitably entered the aquatic environment.

This study investigated the adsorption behavior of TC, SMZ and AMC on BC, BC-Fe, BC-Al and BC-Mn. The results showed that the modification made biochars posses

| Antibiotic | Biochar | Langmuir equation | Freundlich equation |
|------------|---------|-------------------|---------------------|
| TC         | BC      | \( K_L \)         | \( K_f \)            |
|            |         | \( Q_m \)         | \( n_f \)            |
|            |         | \( R^2 \)         | \( R^2 \)            |
|             | BC      | 0.0756            | 7.7835              |
|             | 98.04   | 1.4693            | 0.9736              |
|             | BC-Fe   | 0.7431            | 42.4489             |
|             | 123.35  | 2.4938            | 0.9462              |
|             | BC-Al   | 0.8174            | 40.5445             |
|             | 106.38  | 2.9231            | 0.9507              |
|             | BC-Mn   | 0.9596            | 40.7072             |
|             | 105.26  | 1.7150            | 0.9500              |
| SMZ        | BC      | 0.2519            | 1.5063              |
|            | 24.57   | 1.2261            | 0.9932              |
|            | BC-Fe   | 0.0801            | 7.2519              |
|            | 99.01   | 1.2925            | 0.9873              |
|            | BC-Al   | 0.0664            | 7.6737              |
|            | 98.04   | 1.4237            | 0.9814              |
|            | BC-Mn   | 0.1705            | 6.9608              |
|            | 56.18   | 1.5004            | 0.9765              |
| AMC        | BC      | 0.0251            | 6.0364              |
|            | 53.19   | 2.4981            | 0.9609              |
|            | BC-Fe   | 0.0686            | 7.6217              |
|            | 109.89  | 1.3631            | 0.9899              |
|            | BC-Al   | 0.0979            | 6.4592              |
|            | 83.33   | 1.3135            | 0.9800              |
|            | BC-Mn   | 0.1083            | 8.1899              |
|            | 68.03   | 1.6912            | 0.9561              |

\( a(L/mg), b(mg/g), c(mg/g/L/mg^{1/n}) \).
larger specific surface area, better microscopic pore structure and rougher surface with different degrees of holes and cracks. It was found that metal ions could significantly improve the adsorption capacity of BC, and BC-Fe had the best adsorptive property.

The investigation will be beneficial to better provide a potential adsorbent material for adsorbing antibiotics from wastewater and realize sewage sludge treatment and recycling, particularly considering the effect of metal ions modification.

It should be noted, however, that experimental conditions such as dosage, initial concentrations, pH and temperature may also play critical roles in exploring adsorption properties of sewage sludge biochars. Different metal/BC impregnation mass ratios may reduce the aggregation and oxidation of zero-valent iron, which needs further study. In addition, Fe, Al and Mn impregnation was used to modify biochar without discussing Fe, Al and Mn leaching in water. Further investigations are necessary in the future. And the effect of pH, temperature, salinity and other environmental factors on the adsorption capacity of biochar is not explored in the present study. It is also necessary to strengthen research in the future. The practical significance of this study is to prepare a biochar adsorption material that can effectively remove antibiotics from waste water and can be recycled. Further researches on recycling are necessary in the future.

**CONCLUSIONS**

The adsorption behavior of antibiotics (TC, SMZ and AMC) from wastewater on metal loaded sewage sludge biochars were investigated. The conclusions were as follows:

(1) Modification by metal ions had significant impacts on the physicochemical properties of sludge biochar. In this study, Fe ion was demonstrated to be the optimal modified material. Compared with the BC, BC-Fe possessed less volatile component, larger specific surface area and better microcellular structure. It was caused by the more thorough degree of aromatization and carbonization.

(2) In the intra-particle diffusion model, the $k_{pi}$ values of BC-Fe, BC-Al and BC-Mn were higher than that of BC, indicating that the loading of metal ions could accelerate the adsorption rate of antibiotics on the surface of modified biochars. The intercept $C_i$ was an index to reflect the thickness of the boundary diffusion layer. The $C_i$ values of BC, BC-Fe, BC-Al and BC-Mn were higher than that of BC. This may be due to the reduced adsorption of antibiotics by BC, resulting in a decrease in the thickness of the boundary layer.

(3) The adsorption isotherms experiment suggested that the Langmuir isotherm model best described the adsorption isotherm data. The $Q_{max}$ of TC, SMZ and AMC by BC-Fe was 123.35, 99.01 and 109.89 mg/g, respectively. It proved that the adsorption capacity of BC-Fe was greater than other biochars in this study. The $K_L$ values of TC and AMC adsorbed by BC-Fe, BC-Al and BC-Mn were higher than that of BC, while the $K_L$ value of SMZ adsorbed by modified biochars significantly decreased. This indicated that BC-Fe, BC-Al and BC-Mn could be better recycled during the removal of SMZ.

(4) In this study, the main mechanism in the adsorption process of antibiotics on the sewage sludge biochars mainly involved pore filling, Van der Waals forces and H-bonding.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**

Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J. K., Yang, J. E. & Ok, Y. S. 2022 Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresource Technology 118, 536–544.

Ahmad, M., Rajapaksha, A. U., Eun, L. J., Zhang, M., Nanthi, B., Dinesh, M., Meththika, V., Lee, S. S. & Ok, Y. S. 2014 Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.
Aydin, E., Sahin, M., Taskan, E., Hasar, H. & Erdem, M. 2016 Chlorotetracycline removal by using hydrogen based membrane biofilm reactor. *Journal of Hazardous Materials* **320**, 88–95.

Barry, D., Barbiero, C., Briens, C. & Bertrut, F. 2019 Pyrolysis as an economical and ecological treatment option for municipal sewage sludge. *Biomass & Bioenergy* **122**, 472–480.

Batt, A. L., Kim, S. & Aga, D. S. 2007 Comparison of the Occurrence of Antibiotics in Four Full-Scale Wastewater Treatment Plants with Varying Designs and Operations. Chemosphere, Oxford.

Bondarczuk, K., Markowicz, A. & Piotrowska, S. Z. *Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. Bioresource Technology* **164**, 47–54.

Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y. & Ren, L. 2014 Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource Technology* **164**, 47–54.

Dante, R. C., Chamorro, P. P., Cabo, J. V., López, O. R., Sánchez, Á. F. M., Huerta, L., Ramos, P. M., Rojas, L. L., Vega, C. F. A., Tapia, E. D. R, Pruna, C. A. F., Vega, A. Á. & Feria, O. S. 2017 Nitrogen-carbon graphite-like semiconductor synthesized from uric acid. *Carbon* **121**, 368–379.

Engates, K. E. & Shipley, H. J. 2011 Adsorption of Pb, Cd, Cu, Zn, and Ni to titanium dioxide nanoparticles: effect of particle size, solid concentration, and exhaustion. *Environmental Science and Pollution Research* **18**, 386–395.

Fernandez, M. E., Ledesma, B., Román, S., Bonelli, P. R. & Cukierman, A. L. 2015 Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants. *Bioresource Technology* **183C**, 221–228.

Gupta, V. K., Rastogi, A. & Nayak, A. 2010 Biosorption of nickel onto treated alga (Oedogonium hatiei): application of isotherm and kinetic models. *Journal of Colloid and Interface Science* **342**, 533–539.

Javanmardi, A. H. & Bashiri, H. 2017 Analytical solution of Langmuir behavior of statistical rate theory: adsorption at solid/solution interface. *Journal of Environmental Chemical Engineering* **5**, 4024–4030.

Khataee, A., Kayan, B., Kalderis, D., Karimi, A., Akay, S. & Konsolakis, M. 2017 Ultrasound-assisted removal of Acid Red 17 using nanosized Fe3O4-loaded coffee waste hydrochar. *Ultrasoicsonoechemistry* **35**, 72–80.

Lawrinenko, M., Jing, D., Banik, C. & Laird, D. A. 2017 Aluminum and iron biomass pretreatment impacts on biochar anion exchange capacity. *Carbon* **118**, 422–430.

Lega, F., Bouafif, H., Hamza, N., Neculita, C. M. & Koubaa, A. 2018 Production, characterization, and potential of activated biochar as adsorbent for phenolic compounds from leachates in a lumber industry site. *Environmental Science and Policy Research International* **25** (26), 26562–26575. doi: 10.1007/s11356-018-2712-9.

Li, B., Yang, H., Wei, L., Shao, J., Wang, X. & Chen, H. 2017a Absorption-enhanced steam gasification of biomass for hydrogen production: effects of calcium-based absorbents and NiO-based catalysts on corn stalk pyrolysis-gasification. *International Journal of Hydrogen Energy* **42**, 5840–5848.

Li, H., Hu, J., Cao, Y., Li, X. & Wang, X. 2017b Development and assessment of a functional activated fore-modified biohydrochar for amoxicillin removal. *Bioresource Technology* **246**, 168–175.

Li, D., Wang, P., Wang, C., Fan, X., Wang, X. & Hu, B. 2008 Combined toxicity of organophosphate flame retardants and cadmium to Corbicula fluminea in aquatic sediments. *Environmental Pollution* **243**, 645–653.

Lin, Y., Chen, Z., Dai, M., Fang, S., Liao, Y., Yu, Z. & Ma, X. 2018 Co-pyrolysis kinetics of sewage sludge and bagasse using multiple normal distributed activation energy model (M-DAEM). *Bioresource Technology* **259**, 173–180.

Liu, P., Liu, W., Jiang, H., Chen, J., Li, W. & Yu, H. 2012 Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. *Bioresource Technology* **121**, 235–240.

Pan, J. H., Jiang, J. & Xu, R. 2014 Removal of Cr(VI) from aqueous solutions by Na2SO3/FeSO4 combined with peanut straw biochar. *Chemosphere* **101**, 71–76.

Peizhen, Z., Yanfei, L., Yaoyao, C. & Lujia, H. 2013 Characteristics of tetracycline adsorption by cow manure biochar prepared at different pyrolysis temperatures. *Bioresource Technology* **285**, 121348.

Qian, J., Li, K., Wang, P., Wang, C., Shen, M., Liu, J., Tian, X. & Lu, B. 2017 Effects of carbon nanotubus on phosphorus adsorption behaviors on aquatic sediments. *Ecotoxicology and Environmental Safety* **142**, 230–236.

Radjenovic, J. & Petrovic, M. 2017 Removal of sulfamethoxazole by electrochemically activated sulfate: implications of chloride addition. *Journal of Hazardous Materials* **333**, 242.

Reguyl, F., Sarmah, A. K. & Gao, W. 2017 Synthesis of magnetic biochar from pine sawdust via oxidative hydrolysis of FeCl2 for the removal sulfamethoxazole from aqueous solution. *Journal of Hazardous Materials* **321**, 868–878.

Rigby, H., Clarke, B. O., Pritchard, D. L., Meehan, B., Beshah, F., Stephen, R. S. & Nichola, A. P. 2016 A critical review of nitrogen mineralization in biosolids-amended soil, the associated fertilizer value for crop production and potential for emissions to the environment. *Science of The Total Environment* **541**, 1310–1338.

Shen, Q., Wang, H., Yu, Q., Cheng, Y., Liu, Z., Zhang, T. & Zhou, S. 2020 Removal of tetracycline from an aqueous solution using manganese dioxide modified biochar derived from Chinese herbal medicine residues. *Environmental Research* **183**, 109195.

Sun, W., Jiang, B., Wang, F. & Xu, N. 2015 Effect of carbon nanotubus on Cd(II) adsorption by sediments. *Chemical Engineering Journal* **264**, 645–653.

Sun, Y., Yu, I. K. M., Tsang, D. C. W., Cao, X., Lin, D., Wang, L., Graham, N. J. D., Alessi, D. S., Komárek, M., Ok, Y. S., Feng,
Y. & Li, X. D. 2019 Multifunctional iron-biochar composites for the removal of potentially toxic elements, inherent cations, and hetero-chloride from hydraulic fracturing wastewater. *Environment International* **124**, 521–532.

Wang, Z. B., Xiang, B., Cheng, R. & Li, Y. 2010 Behaviors and mechanism of acid dyes sorption onto diethylenetriamine-modified native and enzymatic hydrolysis starch. *Journal of Hazardous Materials* **183**, 224–232.

Wang, M. C., Sheng, G. D. & Qiu, Y. P. 2015 A novel manganese-oxide/biochar composite for efficient removal of lead(II) from aqueous solutions. *International Journal of Environmental Science and Technology* **12**, 1719–1726.

Wang, P., Tang, L., Wei, X., Zeng, G., Zhou, Y., Deng, Y., Wang, J., Xie, Z. & Fang, W. 2017 Synthesis and application of iron and zinc doped biochar for removal of p-nitrophenol in wastewater and assessment of the influence of co-existing Pb(II). *Applied Surface Science* **392**, 391–401.

Wei, J., Liu, Y., Li, J., Zhu, Y., Yu, H. & Peng, Y. 2019 Adsorption and co-adsorption of tetracycline and doxycycline by one-step synthesized iron loaded sludge biochar. *Chemosphere* **236**, 124254.

Wu, H., Wei, W., Xu, C., Meng, Y., Bai, W., Yange, W. & Lin, A. 2020 Polyethylene glycol-stabilized nano zero-valent iron supported by biochar for highly efficient removal of Cr(VI). *Ecotoxicology and Environmental Safety* **188**, 109902.

Xiao, F., Li, W., Fang, L. & Wang, D. 2016 Synthesis of akageneite (beta-FeOOH)/reduced graphene oxide nanocomposites for oxidative decomposition of 2-chlorophenol by Fenton-like reaction. *Journal of Hazardous Materials* **308**, 11–20.

Xu, P., Zeng, G. M., Huang, D. L., Lai, C., Zhao, M. H., Wei, Z., Li, N. J., Huang, C. & Xie, G. X. 2012 Adsorption of Pb(II) by iron oxide nanoparticles immobilized *Phanerochaete chrysosporium*: equilibrium, kinetic, thermodynamic and mechanisms analysis. *Chemical Engineering Journal* **203**, 425–431.

Yan, L., Liu, Y., Zhang, Y., Liu, S., Wang, C., Chen, W., Liu, C., Chen, Z. & Zhang, Y. 2020 ZnCl₂ modified biochar derived from aerobic granular sludge for developed microporosity and enhanced adsorption to tetracycline. *Bioresource Technology* **297**, 122381.

Yin, Q., Wang, R. & Zhao, Z. 2018 Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. *Journal of Cleaner Production* **176**, 230–240.

Yoh, S., Sitepu, T. & Ambarita, H. 2020 Proximate, ultimate and calorific value analyses of paper industry sludge at different moisture content. *IOP Conference Series Materials Science and Engineering* **851**, 012052.

Yu, Z., Qiu, W., Wang, F., Lei, M., Wang, D. & Song, Z. 2017 Effects of manganese oxide-modified biochar composites on arsenic speciation and accumulation in an indica rice (*Oryza sativa L.*) cultivar. *Chemosphere* **168**, 341–349.

Zhang, X., Bai, B., Puma, G. L., Wang, H. & Suo, Y. 2016 Novel sea buckthorn biocarbon SBC@β-FeOOH composites: efficient removal of doxycycline in aqueous solution in a fixed-bed through synergistic adsorption and heterogeneous Fenton-like reaction. *Chemical Engineering Journal* **284**, 698–707.

Zhang, P., Li, Y., Cao, Y. & Han, L. 2019 Characteristics of tetracycline adsorption by cow manure biochar prepared at different pyrolysis temperatures. *Bioresource Technology* **285**, 121348.

Zhao, K., Niu, Q., Wang, L. & Zhang, H. 2017 Effect of water vapor and α-Fe₂O₃ on elemental mercury removal performance over cerium oxide modified semi coke. *Journal of Fuel Chemistry and Technology* **45**, 378–584.

Zhu, X., Liu, Y., Qian, F., Zhou, C., Zhang, S. & Chen, J. 2014 Preparation of magnetic porous carbon from waste hydrochar by simultaneous activation and magnetization for tetracycline removal. *Bioresource Technology* **154**, 209–214.

Zielinska, A., Oleszczuk, P., Charmas, B., Zieba, J. S. & Patkowska, S. P. 2015 Effect of sewage sludge properties on the biochar characteristic. *Journal of Analytical and Applied Pyrolysis* **112**, 201–213.

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