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

Xiulei Fan, Zheng Qian, Jiaqiang Liu, Nan Geng, Jun Hou and Dandan Li

ABSTRACT

Application of sewage sludge biochar as an adsorbent for antibiotics treatment has obtained special attention owning 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

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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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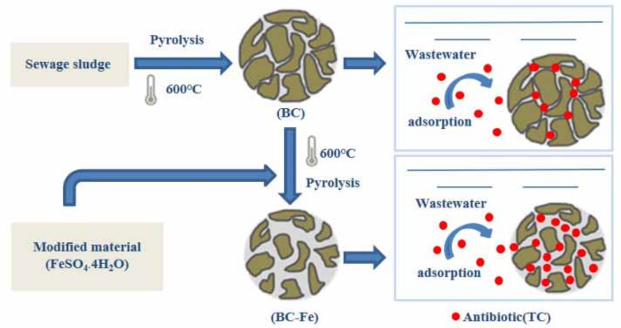
GRAPHICAL ABSTRACT



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.* 2020). 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 μ/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 2017). 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 $FeSO_4{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$, 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 $FeSO_4{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$, 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 m microporous membrane to determine the concentration of antibiotics in the filtrate. The concentration of antibiotics was measured with High Performance Liquid Chromatography.

Adsorption isotherms

Adsorption isotherm experiments were conducted in a series of 100 mL centrifuge tubes. First, the biochar and 50 mL antibiotic solution were added into a 100 mL centrifuge tube, with initial antibiotic concentrations ranging from 2 to 45 mg/L (2, 5, 10, 15, 20, 25, 30, 35, 40, 45 mg/L). The dosage of biochar for TC, SMZ and AMC was 10, 20 and 20 mg, respectively (according to the preliminary experiment). The pH value in the experiment (neutral reagents) was adjusted to about 7 Then, the centrifuge tubes were subjected to shaking at 120 rpm for 24 h in the air bath constant temperature oscillator shaker in the dark at 298 K. The sample was filtered through a 0.45 μm membrane filter and stored in a 10 mL centrifugal tube for testing. 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:

$$Q = [(C_0 - C_e)/M] \times V \quad (1)$$

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 m^2/g, 0.0154 cm^3/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

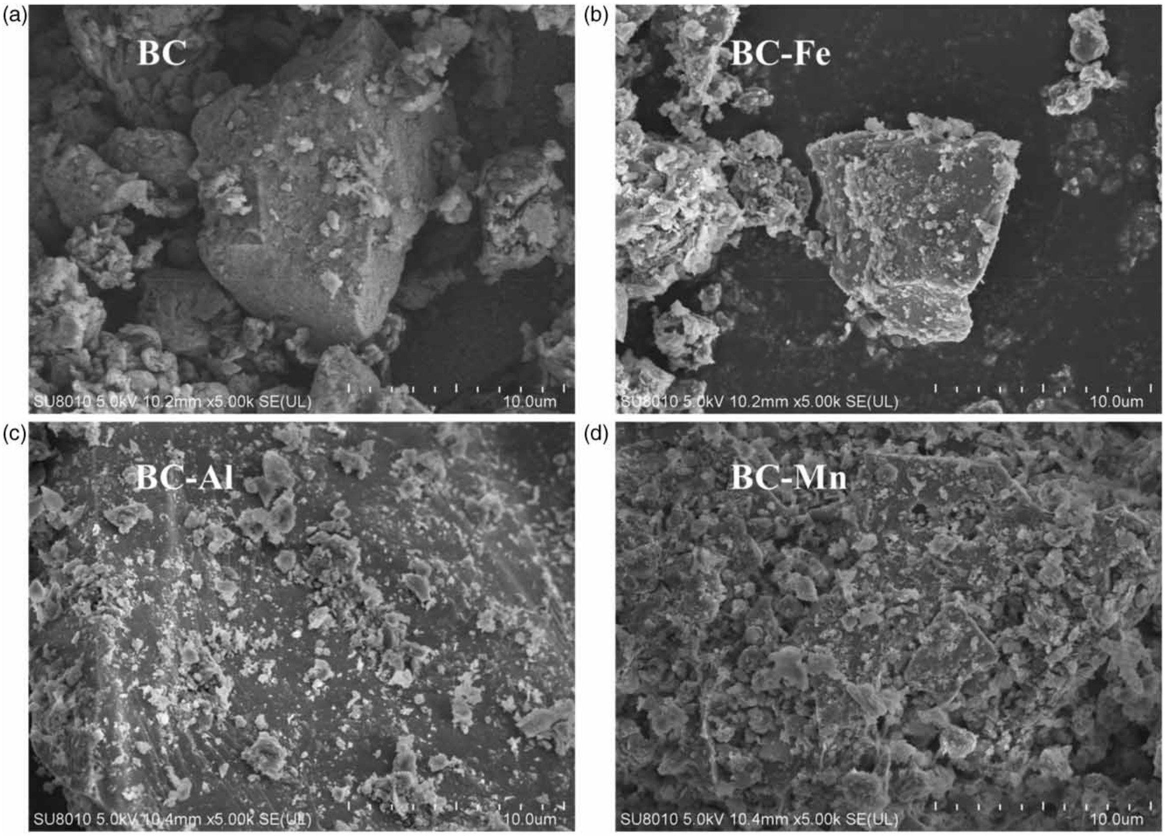


Figure 1 | SEM micrograph of sewage sludge biochar (a) and metal loaded sewage sludge biochars (b, c and d).

Table 1 | Specific surface area, pore volume and average pore size of sewage sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn)

Biochar	Specific surface area/(m^2/g)	Pore volume/(cm^3/g)	Average pore size/(nm)
BC	28.07	0.0154	1.29
BC-Fe	38.08	0.0197	1.11
BC-Al	35.43	0.0186	1.19
BC-Mn	33.58	0.0183	1.21

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 (CO_2, CH_4, 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

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

	Basic element content (%)					Atomic ratio			Metal element content (%)		
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

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}, -C = O at 1,631 cm^{-1}, -CH_3 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 -CH_3. 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).

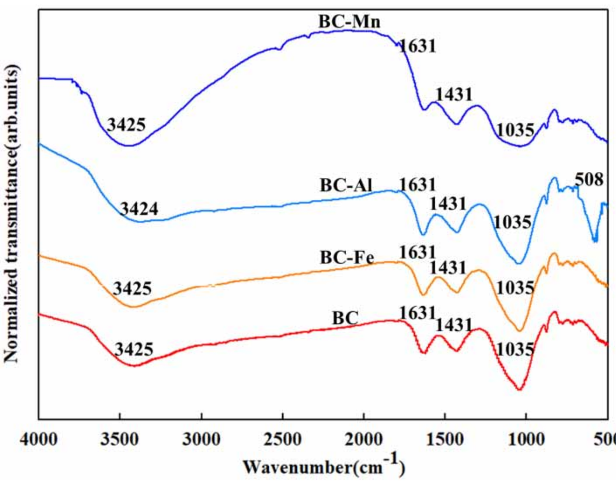


Figure 2 | FTIR spectra of sewage sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn).

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 $2\theta = 31.130$ 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 ($AlPO_4$), 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).

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).

$$\text{Pseudo-first order model: } \ln(Q_e - Q_t) = \ln Q_t - k_1 t \quad (2)$$

$$\text{Pseudo-second order model:} \frac{t}{Q_t} = \left(\frac{1}{k_2 Q_e^2}\right) + \frac{t}{Q_e} \quad (3)$$

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.* 2017). The adsorption reaction was mainly chemical adsorption (Li *et al.* 2017a). 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)

$$Q = k_{p_i} t^{0.5} + C \quad (4)$$

Here, Q (mg/g) represented adsorbing capacity, k_{p_i} (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

Table 3 | Kinetic parameters for the adsorption of TC, SMZ and AMC to sewage sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn)

		Pseudo-first-order model			Pseudo-second-order model		
Antibiotic	**Biochar**	k_1^a	Q_e^b	R^2	k_2^c	Q_e^b	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	0.00346	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_{pi} 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} specifically 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

Table 4 | Intra-particle diffusion model constants and correlation coefficients for the adsorption of antibiotics TC (a), SMZ (b), AMC (c) to sewage sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn)

		Stage I			Stage II			Stage III		
Antibiotic	Biochar	k_{p1}^a	C_1	R_1^2	k_{p2}^a	C_2	R_2^2	k_{p3}^a	C_3	R_3^2
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	0.0353	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	0.0303	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	2.853	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).

$$\text{Langmuir model:} \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (5)$$

$$\text{Freundlich model:} \ln Q_e = \ln K_f + 1/n_f \ln C_e \quad (6)$$

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 99.01 mg/g, while the Q_m of AMC increased from 53.19 mg/g to 109.89 mg/g. These results were much better than different adsorbents reported in the literature. For instance, Zhang et al. (2019) 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 comparision 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

Table 5 | Adsorption isotherm constants for the adsorption of antibiotics TC (a), SMZ (b) and AMC (c) to sludge biochar (BC) and metal loaded sewage sludge biochars (BC-Fe, BC-Al and BC-Mn)

		Langmuir equation			Freundlich equation		
Antibiotic	**Biochar**	K_L[a]	Q_m[b]	R^2	K_f[c]	n_f	R^2
TC	BC	0.0756	98.04	0.9972	7.7835	1.4693	0.9736
	BC-Fe	0.7431	123.35	0.9964	42.4489	2.4938	0.9462
	BC-Al	0.8174	106.38	0.9968	40.5445	2.9231	0.9507
	BC-Mn	0.9596	105.26	0.9942	40.7072	1.7150	0.9500
SMZ	BC	0.2519	24.57	0.9946	1.5063	1.2261	0.9932
	BC-Fe	0.0801	99.01	0.9926	7.2319	1.2925	0.9873
	BC-Al	0.0664	98.04	0.9966	7.6737	1.4237	0.9814
	BC-Mn	0.1705	56.18	0.9987	6.9608	1.5004	0.9765
AMC	BC	0.0251	53.19	0.9954	6.0364	2.4981	0.9609
	BC-Fe	0.0686	109.89	0.9984	7.6217	1.3631	0.9899
	BC-Al	0.0979	83.33	0.9993	6.4592	1.3135	0.9800
	BC-Mn	0.1083	68.03	0.9978	8.1899	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.

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