Biochar produced from the co-pyrolysis of sewage sludge and waste tires for cadmium and tetracycline adsorption from water

Xiulei Fan, Jiajun Zhang, Ya Xie, Dezhi Xu, Yu Liu, Jiaqiang Liu and Jun Hou

ABSTRACT

Application of sewage sludge biochar as an adsorbent for pollutant removal has obtained special attention due to their low cost and surface functionality. In this research, sludge–tire composite biochar (STB) was successfully prepared through co-pyrolysis at 300, 500 and 700 °C, respectively. Cadmium (Cd) and tetracycline (TC) were selected as the target pollutant. The results indicated that STB has the highest surface area (49.71 m²/g), more inorganic minerals (Kaolinite) as well as relatively stable physicochemical properties with 10% tire particles (TP) at 700 °C. The adsorption results indicated that the pseudo-second-order equation and Langmuir isotherm model could better describe the adsorption of Cd²⁺ and TC by STB. The maximum adsorption capacity of Cd²⁺ and TC was 50.25 mg/g and 90.09 mg/g, respectively. The main mechanism of the adsorption process of STB for Cd mainly involves anion binding adsorption and ion exchange. The main mechanism of the adsorption process of STB for TC mainly involves complexation and cation exchange. The present study could set a scientific foundation for further research on the recycle of sewage sludge and tires.

Key words | adsorption, biochar, cadmium, sewage sludge, tetracycline, waste tires

HIGHLIGHTS

- 700 °C was demonstrated to be the best pyrolysis temperature, 10% is the optimal blending ratio of TP.
- The blending of TP can reduce the risk of adsorbate being discharged from biochar into the environment.
- Combining with anion and ion exchange are possible ways for STB to remove Cd²⁺.
- Complexation and the cation exchange are possible ways for STB to remove TC.
INTRODUCTION

As the pace of urbanization and industrialization is accelerating, more and more wastewater needs to be treated. The production of sewage sludge in wastewater treatment plants is increasing as a result (Fytiti & Zabaniotou 2008). The annual output of sewage sludge is about 30 million tons in 2013. Furthermore, this number is expected to reach 60–90 million tons (80% moisture content) in China by 2020 (Wang et al. 2018). Sewage sludge is a heterogeneous composite mixture mainly composed of fibers, animal and plant residues, microorganisms, pathogens, parasites and heavy metals (Xiao et al. 2018). Owing to the complicated composition, the treatment of sludge is one of the most troublesome tasks that wastewater treatment plants have to deal with. If discharged directly or treated unsuccessfully, sewage sludge would cause serious secondary environmental pollution. Nevertheless, good economic and social benefits can be achieved if sewage sludge can be effectively disposed for the numerous organic substances it contains (Bjrlund & Li 2017). Therefore, much attention has been paid on searching for an economic, efficient and safe way to dispose sludge.

Sewage sludge biochar is characterized by high density and easy formation, which are very important for storage, transportation and practical application. However, the pyrolysis of sewage sludge results in low specific surface area and underdeveloped pore structure of biochar due to the limitation of carbon content in sewage sludge (Rozada et al. 2008). Sun et al. (2019) found that the surface area of sewage sludge biochar was merely 24.72 m²/g when the pyrolysis temperature was 923 K. The sewage sludge also has a lower heat value due to its high ash content and low organic matter content, leading to a problem of insufficient energy supply provided in the process of sludge treatment. In actual applications, it is necessary to add supernumerary materials such as biomass to increase the heat value of pyrolysis system and achieve a balanced energy supply. As a polymer material, waste tires have high calorific value and low ash content compared to sludge (Gang et al. 2019). According to Zhou et al. (2009) research, the waste tire is a material with high calorific value, that is 69%/kg higher than wood, 10%/kg higher than bituminous coal and 4%/kg higher than coke (Zhou 2009). Li et al. (2016) used polymer materials and silica to form a soft and hard stencil to prepare layered porous forming carbon. The results showed that the soft frame formed by the polymer can maintain the complete morphology of the carbon particles (Li et al. 2016). Zhang et al. (1997) added organic polymers polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) particles during the carbon preparation process, and concluded that the addition of organic polymers could effectively increase the micro-porosity of the obtained carbon fibers. In summary, the co-pyrolysis of sewage sludge and waste tires may be beneficial to overcome the limitation of low calorific value of sludge and optimize the physical and chemical properties of sludge biochar. The co-pyrolyzed biochar may be a more suitable and effective adsorbent than sewage sludge biochar.

The continuous growth in the amount of waste tires disposed worldwide is currently a major environmental problem, as a sustainable recovery and recycling of this residue presents significant technical difficulties, primarily due to the complex structure and composition of tire materials.
(Sienkiewicz et al. 2017). One of the most promising alternatives to cope with this problem is to pyrolyze the scrap tires, as has been highlighted in several works (Martínez et al. 2015). Through pyrolysis, the feedstock is converted into light gases, liquids and carbonaceous solids or coke (Enagi et al. 2018). This process transforms waste tires into new products with added value.

Cadmium (Cd), one of the most toxic heavy metals, has become a focus of concern due to its solubility, fluidity and bioaccumulation, which is common around the world and can cause damage to bone and kidney after prolonged exposure (Muthusaravanan et al. 2018). Antibiotics are not easily biodegradable and can cause a variety of ecological impacts (Zhou et al. 2009). Tetracycline (TC) is one of the most widely used antibiotics for medical purposes and also used as a feed additive in some intensive farming operations (Martucci et al. 2014). However, the widespread use of TC has potential hazards to the environment and health (Shao et al. 2005).

In general, physical adsorption is more suitable than biological or chemical methods to remove pollutants from water because of its speed and no environmental risk and secondary pollution, especially at low concentrations (Balasubramani et al. 2020). In addition, adsorption techniques are low cost, have ease of implementation and operation, low energetic requirements and powerful performance (Kahlon et al. 2018). For example, biochar, cellulose based nanocomposites, clays, carbonaceous materials including activated carbon, graphene-based materials, polymers, metal oxides, polymer/metal oxide hybrids, biomaterials and silicate materials have been investigated for contaminants removal (Rathore et al. 2014; Abdi et al. 2019). Traditionally, fibrous-based biochar has been used as an adsorbent (Navya et al. 2020; Rambabu et al. 2020; Sivarajasekar et al. 2020), which is a main research direction, but there has been little research on the use of sludge-based biochar as an adsorbent to remove Cd\(^{2+}\) and TC from water. Moreover, the adsorption properties and mechanism of biochar prepared via sewage sludge mixed with tire particles (TP) to cadmium and tetracycline in water are still not clear.

In this research, biochar was prepared via the pyrolysis of mixed sewage sludge and TP and was used to remove cadmium and tetracycline in water. The objectives of this research were to: (1) explore the effect of blending ratio of sewage sludge and waste tires to the physical and chemical properties of STB and determine the best preparation conditions, and (2) investigate the adsorption mechanism of co-pyrolyzed biochar for cadmium and tetracycline from water. Compared to other methods to prepare biochar, using sewage sludge and waste tires as the feedstock is almost a whole new direction. This study is aimed to set a scientific foundation for further research on the recycle of sewage sludge and tires.

**MATERIALS AND METHODS**

**Materials**

The sewage sludge (SS) (moisture content is 83.7%, pH = 8) taken from the Xuzhou Guozhen Water Affairs Operation Co., Ltd, China, was air-dried to constant weight. The dried sewage sludge was crushed to 60 mesh for subsequent use. The TP in this study were obtained from a tire crushing plant and customized by providing new tires with 40–60 mesh TP. Analytical reagent (AR) grade chemicals and Milli-Q water (18 MΩ·cm) were used throughout this study. All the labware was soaked in dilute nitric acid at least overnight, thoroughly flushed with tap water, and washed three times with Milli-Q water.

**Preparation of biochar**

The SS and TP were fully mixed at different mass ratios and pyrolyzed at different temperatures to obtain the sludge–tire compound biochar. A certain amount of mixed sample was placed in a quartz boat and then in a tubular furnace. Then, N\(_2\) (99.99%, 300 mL/min) was injected into the tubular furnace to obtain a hypoxic pyrolysis environment. The tubular furnace was heated from room temperature to 300, 500 or 700 °C, at a rate of 10 °C/min, respectively. The tubular furnace naturally cooled to room temperature after maintaining the target temperature for 120 min. Following, the biochar sample was ground in a mortar and then passed through a 70 mesh nylon sieve. The biochar was rinsed several times with Milli-Q water to wipe off the surface residue. Finally, the biochar was oven-dried at 105 °C for 24 h and then collected and stored. The biochar samples produced from the co-pyrolysis of sewage sludge and waste tires were represented by STB. STB-300-0, STB-500-0.1, STB-700-0.3, etc. were used to represent the co-pyrolyzed biochar when the pyrolysis temperature was 300, 500, 700 °C and the mass ratios of TP in the SS was 0, 10, and 50%, respectively.

**Characterization**

Scanning electron microscopy (SEM) equipped with an Energy Dispersive Spectrometer (EDS) was used to
characterize the surface morphological and elemental maps of STB (Model JSM-7401, Nippon Electronics). X-ray powder diffraction (XRD) patterns were recorded using a D8 advance diffractometer (BRUKER, Germany), equipped with a Cu Ka radiation source (λ = 1.5418 nm) with an angle from 5B to 90B. The Fourier transform infrared (FTIR) spectrum of synthesized biochar was registered using a Nicolet 6700 (Thermo, USA) spectrometer, scanning over the range of 400–4,000 cm⁻¹. For X-ray photoelectron spectroscopy (XPS) test, Thermo ESCALAB250Xi (Thermo Scientific, USA) with a monochromatic Al-Ka source was used. The specific surface area and pore size of STB 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). Pore size distribution was derived from the Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods. The zeta potential of biochar was determined using a laser particle size meter (Zetasizer Nano ZS, UK) at pH 7.

Adsorption experiments

The adsorption ability of STB was examined for the exclusion of Cd²⁺ and TC from aqueous solution. For this, the major influencing parameters, such as STB dose or time was first determined. It is the concentration of Cd²⁺ and TC before and after the adsorption reaction time that played a crucial role (Sharma et al. 2020). In a typical procedure, for adsorption kinetics, 20 mg of STB was properly dispersed in 20 mg/L Cd²⁺ or 40 mg/L TC solution and placed in a thermostatic shaker at 120 rpm for 5 to 4,220 min. For the adsorption isotherm, 20 mg of STB was properly dispersed in 7 to 20 mg/L mg/L Cd²⁺ or 25 to 50 mg/L TC solution and placed in a thermostatic shaker at 120 rpm for 72 h. The sample was filtered through a 0.45 μm semipermeable membrane and stored in a 10 mL centrifuge tube for testing. In addition, various adsorption isotherm models (Langmuir, Freundlich) and kinetic models (pseudo-first order, pseudo-second order and intraparticle diffusion) were also used for examining the equilibrium data. Reusability studies were carried out for STB for a consecutive three cycles.

Analytical method

After filtration, the concentration of Cd²⁺ and TC in the filtrate was determined. The concentration of Cd²⁺ samples was determined by inductively coupled plasma mass spectrometry (ICPS-7510, Shimadzu) and TC residual concentration by liquid chromatography (ACQUITY UPLC I-Class, Waters). The adsorption capacity was determined as follows:

\[ q_t = \frac{(C_0 - C_t) \times V}{M} \]  

where \( C_0 \) (mg/L) and \( C_t \) (mg/L) denote the concentrations of Cd²⁺ and TC at the start and the time \( t \); \( V \) (L) is the volume of the solution; \( M \) (g) is the mass of the adsorbent; \( q_t \) (mg/g) is the amount of Cd²⁺ or TC adsorbed on the adsorbent at time \( t \).

Statistical analysis

All experiments were implemented in triplicate, and the results were expressed as the mean ± standard deviation. To improve the accuracy of experiments, all experiments in this study were blank experiments. In this study, the statistical charts of the data were drawn and analyzed with Sigmaplot v.14.0.

RESULTS AND DISCUSSION

Characteristics of biochar samples

Surface morphology

To investigate the differences in the morphology properties of particles, SEM of STB was characterized. As displayed in Figure 1(a), STB-300-0 presents a rough morphology, with a number of pores distributed around the surface. The STB with a higher the mass ratio of TP has a smoother surface, which can be seen from Figure 1(b) and 1(c). It is possibly the case that the TP blocked and padded the holes of STB in the pyrolysis process, thus leading to the smooth surface of biomass carbon materials. Figure 1(d) shows the surface characteristics of STB-700-0. It has more voids and gaps on the surface than that of STB-500-0. The SEM of STB-700-0.1 is shown in Figure 1(e). The blending TP promotes the larger cracks and collapses of biochar. With the further increase in the TP blending ratio at 700 °C, the TP would pad the crack of STB again, which can be confirmed from Figure 1(f). To conclude, the surface of STB-300-0.3 was the smoothest, and the surface of STB-700-0.1 has the most cracks and collapses.

In order to detect whether TP had been successfully loaded on the biochar, the EDS of STB was analyzed. As
displayed in Table 1, the Al content, Mg content and Fe content of STB-700-0 was 3.60%, 0.57% and 0.77%. After the blending, an obvious rise was seen on the content of substance listed above. The Al content, Mg content and Fe content of STB-700-0.1 increased to 10.54%, 1.55% and 3.42%. Lian et al. (2013) reported that the three substances were necessary additives in the tire manufacturing process (Lian et al. 2013). This phenomenon can be explained, as the existence of Al$^{3+}$, Mg and Fe may facilitate the exchange adsorption of heavy metals by STB.

### Specific surface area

To get the porosity properties of STB, BET was tested and the results are shown in Table 2. The BET surface area of STB, whose pyrolysis at a low temperature (300 °C) reduced dramatically by more than four times from 23.61 m$^2$/g to 5.77 m$^2$/g via blending ratio of TP, increased. Meanwhile, the BET surface areas of STB-700-0, STB-700-0.1 and STB-700-0.3 were 30.94 m$^2$/g, 49.71 m$^2$/g and 35.60 m$^2$/g, respectively. Superfluous TP causes an adverse impact.

On the whole, the temperature and the blending ratio of TP are the main factors affecting the micropore characteristics of the STB surface. To achieve better porosity properties, the appropriate temperature and blending ratio of TP are necessities. During the low-temperature (300 °C) pyrolysis process, TP was not pyrolyzed and

| Samples    | Al      | Mg  | Fe    |
|------------|---------|-----|-------|
| STB-700-0  | 3.60%   | 0.57%| 0.77% |
| STB-700-0.1| 10.54%  | 1.55%| 3.42% |
even blocked the pores on the surface of the biochar. These phenomena may occur due to flame retardants, which are added during the production process to prevent tires from spontaneously combusting (Muelas et al. 2019). Morphologically, TP wraps SS, which prevents SS from being completely pyrolyzed. When the pyrolysis temperature was increased to 700°C, TP was pyrolyzed. More cracks and holes appeared on the surface of the biochar and increased the BET surface area and total pore volume. As mentioned earlier, TP is a substance with a high heating value, which may make the pyrolysis reaction more sufficient. As shown in Table 2, the particles appear on the surface of STB-300-0.1 and STB-300-0.3, and the surface cracks of STB-700-0.3 are padded with particulate matter, which proves these assumptions. The BET surface area would increase when the appropriate amount of TP participated in the pyrolysis reaction. However, excess TP would block the pores on the surface of biochar, which can be seen from the SEM of STB.

| Samples   | BET surface area/(m²/g) | Total pore volume/(cm³/g) |
|-----------|-------------------------|----------------------------|
| STB-300-0 | 23.61                   | 0.013                      |
| STB-300-0.1 | 13.45               | 0.007                      |
| STB-300-0.3 | 5.77                | 0.003                      |
| STB-500-0 | 25.79                   | 0.014                      |
| STB-500-0.1 | 29.59               | 0.016                      |
| STB-500-0.3 | 33.40               | 0.017                      |
| STB-700-0 | 30.94                   | 0.016                      |
| STB-700-0.1 | 49.71               | 0.025                      |
| STB-700-0.3 | 35.60               | 0.017                      |

Figure 2 | FTIR spectra of STB pyrolyzes at 300 °C (a), STB pyrolyzes at 700 °C (b), and STB pyrolyzes at 700 °C (c).
Surface functional groups and inorganic minerals

The Fourier transform infrared (FTIR) image of each biochar sample is shown in Figure 2. The abundance of adsorption peaks existed in the FTIR spectra of the biochar. Various functional groups, such as –OH stretching vibration at 1,067 and 3,144 cm⁻¹, –C=O stretching at 1,410 cm⁻¹, and –C≡C bonds in aromatic compounds at 1,631 cm⁻¹ were present on the biochar surface (Titirici 2013; Fernandez et al. 2015; Khataee et al. 2017). As shown in Figure 2, for pyrolysis temperature only, with the increase in pyrolysis temperature, the peak value at 1,410 cm⁻¹ and 1,631 cm⁻¹ increased, and the degree of aromatization gradually increased as well, which is consistent with the research by Yoshida & Antal (2009b). For the blending of TP only, when the pyrolysis temperature was 700 °C (Figure 2(c)), the peak value at 1,067 cm⁻¹ and 3,144 cm⁻¹ reduced when the blending ratio of TP increases. This means that the intensity of the –OH stretching vibration and bending vibration decreased significantly in STB, indicating that TP could decrease the hydrophilicity of the biochar (Xiulei et al. 2018). It was suggested that the addition of TP contributed to the adsorption of hydrophobic organic contaminants, such as TC.

The crystalline phases of all types of biochar are shown in Figure 5. The peak of 2θ 26.64 in the XRD graph indicates that there is a large amount of SiO₂ on the surface of the biochar (Zhang et al. 2015). With the increase in the pyrolysis temperature, the peak value tends to decrease. Peak values appeared at 19.25 cm⁻¹ and 14.86 cm⁻¹ on the XRD pattern of STB-700-0.1, indicating the presence of black carbon and kaolinite on the surface of the biochar (Xiao et al. 2015). The presence of CO₃²⁻, PO₄³⁻ and SiO₄²⁻ in these inorganic minerals was conducive to the precipitation of cation on the surface of biochar (Zhang et al. 2019a).

Chemical element

The element composition and element ratio of STB-700-0 and STB-700-0.1 are shown in Table 3. Studies have shown that element ratios O/C and (O + N)/C can represent the hydrophilicity and polarity of samples, respectively. With the addition of TP, the O/C and (O + N)/C values of biochar decreased. The hydrophilicity and polarity of biochar decreased, and the number of oxygen-containing functional groups in biochar decreased. This is consistent with FTIR, the adsorption peak value of STB-700-0.1 at 1,067 cm⁻¹ and 3,144 cm⁻¹ reduced, and the hydrophilicity of the biochar has been decreased. The C/N value can reflect the stability of the substance. As can be seen from Table 3, with the increase of the blending radio of TP, the C/N value increases. The surface functional groups of biochar produced decreased and the properties are more stable and not easily decomposed by mineralization (Yoshida & Antal 2009a).

Electric charge

The zeta potential values of the primordial biochar and the biochar blended with TP at pH 7 are presented in Figure 4. It is indicated that the surface of STB-700-0 or STB-700-0.1 is negatively charged at pH 7, indicating that biochar has a certain ability to adsorb positively charged ions (Tan et al. 2015). This facilitates the adsorption of Cd²⁺ by biochar. Also, with blending of TP, the potential change on the surface of biochar is reduce from 12.8 eV to 14.2 eV. Therefore, there are more negative surface charges on the biochar produced from SS and TP than for the primordial biochar.

Adsorption kinetics

For gaining insight into the mechanisms by which Cd²⁺ and TC are adsorbed by STB, the pseudo-first-order and pseudo-second-order models were widely used to explain the kinetics data (Wang et al. 2016):

Pseudo-first-order model: \[ \ln (q_e - q_t) = \ln q_e - k_1 t \] \hspace{1cm} (2)

Pseudo-second-order model: \[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \] \hspace{1cm} (3)
where $q_e$ (mg/g) and $q_t$ (mg/g) represent the amounts of Cd$^{2+}$ or TC adsorbed at equilibrium and at time $t$ (min) respectively; $k_1$ (1/min) represents the equilibrium rate constant of pseudo-first-order adsorption; $k_2$ (g/ (mg·min)) is the rate constant of pseudo-second order adsorption.

The experimental results and the fitting curves are as shown in Figures 5 and 6. Table 4 summarizes the parameters for the two kinetic models for the adsorption of Cd$^{2+}$ and TC by the STB, respectively. Compared to the pseudo-first-order, the pseudo-second-order equation could better describe the adsorption of Cd$^{2+}$ and TC, with an extremely high $R^2$ (Cd$^{2+}$:0.9983–0.9999, TC:0.9993–1.0000). The results showed that the sorption systems to both Cd$^{2+}$ and TC of STB follow a pseudo-second-order reaction, indicating that the adsorption mechanism depends on the adsorbate and adsorbent. Meanwhile, chemisorption is possibly a rate-limiting step involving the sharing or exchange of electrons in valence forces (Ho & McKay 1999).

As shown in Table 4, the $k_2$ values of Cd$^{2+}$ and TC absorbed by STB-300-0 is 0.0013 and 0.0007 g/(mg min). The $k_2$ values of Cd$^{2+}$ and TC absorbed by STB-500-0 is 0.0009 and 0.0004 g/(mg min). The $k_2$ values of Cd$^{2+}$ and TC absorbed by STB-700-0 is 0.0006 and 0.0003 g/(mg min). To conclude, the $k_2$ values of biochar decreased with the increase in pyrolysis temperature which was without blending TP. $K_2$ (g/(mg·min)) denotes the rate constant for the pseudo-second-order adsorption (Tan et al. 2015). The lower is the $K_2$ value, the slower is the adsorption rate of Cd$^{2+}$ and TC by the biochar.

In the case of different pyrolysis temperatures, the effects of different TP blending ratios on adsorption rate constants showed a difference. When the pyrolysis temperature was 300 °C, with the increase of TP blending ratio, the $k_2$ values of Cd$^{2+}$ and TC adsorbed by biochar increased from 0.0013 and 0.0007 to 0.0016 and 0.0023 g/(mg min). When the pyrolysis temperature was 700 °C, the impact of the blending ratios of TP on the rate constant of adsorption was in stages. The $k_2$ values of Cd$^{2+}$ absorbed by biochar which was pyrolyzed at 700 °C are 0.0006, 0.0003 and 0.0005 g/(mg min), and the $k_2$ values of TC are 0.0003,
0.0002 and 0.0003 g/(mg min). The low \( k_2 \) value indicates that the adsorption rate decreases with time, and the adsorption rate is proportional to the number of unoccupied sites (Gupta et al. 2010). The adsorption sites of STB-700-0.1 were rapidly occupied by Cd\(^{2+}\) or TC, resulting in a lower \( k_2 \) (Goh et al. 2019). Goh and colleagues have also reported a similar effect of the kinetics of the adsorption of Cd\(^{2+}\) by sludge biochar (Goh et al. 2019).

An intraparticle diffusion model was proposed to determine whether intraparticle diffusion was the rate-limiting step. It can be expressed as follows (Wang et al. 2016):

\[
q_t = k_{pi} t^{0.5} + C_i.
\]

where \( k_{pi} \) (mg/(g min 0.5)) represents the intraparticle diffusion rate constant of stage \( i \); \( C_i \) represents the intercept of stage \( i \) and a constant related to the thickness of the boundary layer.

The intraparticle diffusion modeling of the kinetics data (Figures 7 and 8) showed that the plot of \( q_t \) versus \( t^{0.5} \) is non-linear, indicating that two or more stages are involved in adsorption (Wu et al. 2009). Piecewise linear regression was applied to fit the data to the model, and the model constants and correlation coefficients for Cd\(^{2+}\) and TC adsorption by STB are shown in Table 5. The linear segments were numbered I–III to indicate the three stages of adsorption. Stage I (rapid adsorption) is surface diffusion where Cd\(^{2+}\) or TC was adsorbed by the exterior surface of the STB, at a rapid adsorption rate. When the adsorption of the exterior surface reached saturation, stage II started. Stage II (gradual adsorption) is intraparticle diffusion where Cd\(^{2+}\) or TC entered into the STB through the pores within the particle and were adsorbed by the interior surface of the particles. When Cd\(^{2+}\) or TC diffused in the pores of particles, the diffusion resistance increased, resulting in a decrease in the diffusion rate. With the decrease of Cd\(^{2+}\) or TC concentration in solution, the diffusion rate kept on decreasing, and the diffusion processes attained stage III (the final equilibrium stage).

According to the intraparticle diffusion model, a plot of \( q_t \) versus \( t^{0.5} \) should be linear if intraparticle diffusion occurs in the adsorption process and if the plot passes through the origin, intraparticle diffusion would be the only rate-limiting process (Bhattacharyya & Sharma 2004). As the intraparticle diffusion plot did not pass through the origin in this study (Figures 7 and 8), this suggested that the adsorption in STB involved intraparticle diffusion but was not the only rate-limiting step (Ahmad et al. 2009). The increase of \( k_{pi} \) values for STB-700-0.1 indicated that TP can increase the rate of diffusion of Cd\(^{2+}\) and TC inside the biochar. The intercept \( C_i \) has been widely used as an index reflecting the thickness of the boundary diffusion layer (Boparai et al. 2011). The \( C_i \) values for STB-700-0.1 were larger than STB-700-0 (Table 5), indicating the contribution of external surface adsorption for STB-700-0.1 is larger than STB-700-0. The increase in \( k_{pi} \) and \( C_i \) values for STB-700-0.1 may be attributed to the strong adsorption ability, high surface mineral content (Figure 3) and more negative surface charges in the system (Figure 4).

**Adsorption isotherm**

Adsorption isotherms describe the mutual behavior between concentration of organic pollutant in solution and amount of pollutant adsorbed on an adsorbent (Sharma et al. 2017; Sharma & Naushad 2020). Here, Langmuir and Freundlich models were used to analyze the experimental data. Their
Figure 6  | Fitting curves for the adsorption of Cd\textsuperscript{2+} (a: the STB which the blending ratio is 0, c: the STB which the blending ratio is 10%, e: the STB which the blending ratio is 30%) and TC (b: the STB which the blending ratio is 0, d: the STB which the blending ratio is 10%, f: the STB which the blending ratio is 30%) by STB with the pseudo-second-order model.
Table 4 | Kinetic parameters of Cd\(^{2+}\) and TC adsorption by STB

| Adsorbate | Adsorbent | Pseudo-first-order | Pseudo-second-order |
|-----------|-----------|--------------------|---------------------|
|           |           | \(Q_e\) (mg/g) | \(K_1\) (1/min) | \(R^2\) | \(Q_e\) (mg/g) | \(K_2\) (g/(mg min)) | \(R^2\) |
| Cd\(^{2+}\) | STB-300-0 | 5.04 | -0.0006 | 0.9115 | 23.20 | 0.0013 | 0.9996 |
|           | STB-300-0.1 | 4.86 | -0.0007 | 0.9290 | 22.68 | 0.0014 | 0.9997 |
|           | STB-300-0.3 | 6.13 | -0.0008 | 0.9173 | 22.07 | 0.0016 | 0.9994 |
|           | STB-500-0 | 9.71 | -0.0010 | 0.9226 | 25.13 | 0.0009 | 0.9992 |
|           | STB-500-0.1 | 4.96 | -0.0009 | 0.8651 | 25.88 | 0.0009 | 0.9999 |
|           | STB-500-0.3 | 8.81 | -0.0009 | 0.9543 | 26.32 | 0.0008 | 0.9983 |
|           | STB-700-0 | 12.69 | -0.0008 | 0.8257 | 33.67 | 0.0006 | 0.9994 |
|           | STB-700-0.1 | 13.61 | -0.0006 | 0.8867 | 36.36 | 0.0003 | 0.9994 |
|           | STB-700-0.3 | 14.05 | -0.0008 | 0.8464 | 34.48 | 0.0005 | 0.9987 |
| TC        | STB-300-0 | 9.47 | -0.0011 | 0.9548 | 53.19 | 0.0007 | 0.9998 |
|           | STB-300-0.1 | 3.06 | -0.0010 | 0.8798 | 45.45 | 0.0029 | 1.0000 |
|           | STB-300-0.3 | 6.40 | -0.0031 | 0.9873 | 44.64 | 0.0023 | 1.0000 |
|           | STB-500-0 | 15.93 | -0.0010 | 0.9836 | 65.36 | 0.0004 | 0.9997 |
|           | STB-500-0.1 | 16.17 | -0.0012 | 0.9739 | 66.67 | 0.0004 | 0.9998 |
|           | STB-500-0.3 | 15.12 | -0.0011 | 0.9589 | 69.93 | 0.0003 | 0.9999 |
|           | STB-700-0 | 24.45 | -0.0014 | 0.9859 | 72.99 | 0.0003 | 0.9995 |
|           | STB-700-0.1 | 22.18 | -0.0012 | 0.9739 | 81.30 | 0.0002 | 0.9993 |
|           | STB-700-0.3 | 27.67 | -0.0013 | 0.9753 | 78.74 | 0.0003 | 0.9998 |

Figure 7 | Intraparticle diffusion model plots for Cd\(^{2+}\) adsorption by STB (a: STB pyrolyzes at 300 °C, b: STB pyrolyzes at 500 °C, c: STB pyrolyzes at 700 °C).
corresponding equations are typically expressed as follows (Reddad et al. 2002):

**Langmuir isotherm**:
\[
\frac{C_e}{q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}
\]  
(5)

where \(C_e\) (mg/L) represents the final concentration of \(\text{Cd}^{2+}\) or TC at equilibrium; \(q_e\) (mg/g) represents the amount of \(\text{Cd}^{2+}\) or TC adsorbed by STB; \(K_L\) (L/mg) represents the Langmuir isotherm coefficient related to the adsorption free energy; \(Q_{\text{max}}\) (mg/g) is the theoretical maximum monolayer adsorption capacity of the adsorbent for \(\text{Cd}^{2+}\) or TC.

**Freundlich isotherm**:
\[
\ln q_e = \ln K_F + \frac{\ln C_e}{n}
\]  
(6)

where \(K_F\) (mg/g(L/mg)^{1/n}) is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent, and \(1/n\) is the empirical Freundlich constant.

The experimental results and the fitting curve are shown Figures 9 and 10. Table 6 summarizes the adsorption isotherm constants obtained from the adsorption of \(\text{Cd}^{2+}\) or TC by STB. The \(R^2\) values (\(\text{Cd}^{2+}\): 0.9167–0.9810 and TC: 0.9966–0.9997) for the Langmuir isotherm model were higher than Freundlich isotherm model, indicating that the Langmuir isotherm model well fits the isotherm data and can be employed for characterizing equilibrium adsorption of \(\text{Cd}^{2+}\) and TC.

Table 6 shows the \(Q_{\text{max}}\) of \(\text{Cd}^{2+}\) and TC by STB-700-0 is 40.98 and 79.37 mg/g and that by STB-700-0.1 is 50.25 and 90.09 mg/g. For STB-700-0.5, the \(Q_{\text{max}}\) of \(\text{Cd}^{2+}\) and TC decreased to 41.32 and 81.30 mg/g. These results were also good compared with other different adsorbents reported in the literature. For instance, \(Q_{\text{max}}\) of \(\text{Cd}^{2+}\) was about 20 mg/g by biochar derived from municipal sewage sludge (Tan et al. 2015), and \(Q_{\text{max}}\) of TC by one-step synthesized iron loaded sludge biochar and cow manure biochar could reach 104.86 mg/g and 26.73 mg/g, respectively (Jia et al. 2019; Zhang et al. 2019b).
There were more cracks and bigger holes on the surface of STB-700-0.1 and STB-700-0.3 (Figure 1). The same conclusion (Table 2) could be drawn through the BET surface area of STB. EDS of STB shows that there were more metal ions on the surface of STB-700-0.1 such as Al$^{2+}$, Mg$^{2+}$ and Fe$^{2+}$ (Table 1). Tan et al. (2014) has reported that ion exchange for Cd$^{2+}$ with exchangeable cations in the biochar is an important removal pathway for cadmium. The surface of STB-700-0.1 presented some inorganic minerals which were rich in CO$_3^{2-}$/CO$_2$, PO$_4^{2-}$/CO$_2$ and SiO$_4^{2-}$/CO$_2$ (Figure 3), which may be conducive to the precipitation of cations on the surface of biochar (Kilic et al. 2013). The enhancement of the adsorption capacity of TC by STB-700-0.1 may result from surface complexation and cation exchange (Peiris et al. 2011). Surface complexation (SC) is defined as a ligand exchange process in which hydroxyl or water molecules bound to surface metal ions are replaced by ligands of organic adsorbents. Although SC is not common in biomass coke, it may occur in some synthetic raw materials (such as tire waste, sludge) (Lian et al. 2014). Cation exchange (CE) describes when positively charged organic molecules replace adsorption that naturally occurs on the surface during a negatively charged cationic phenomenon. Tetracycline’s easy protonation of amino acids may

| Adsorbate | Adsorbent | Stage I | Stage II | Stage III |
|-----------|-----------|---------|----------|-----------|
|           |           | $k_{p1}$ | $c_1$     | $R_1^2$   | $k_{p2}$ | $c_2$     | $R_2^2$   | $k_{p3}$ | $c_3$     | $R_3^2$   |
| Cd$^{2+}$ | STB-300-0 | 0.2738   | 15.05    | 0.9844   | 0.0044   | 22.15    | 0.9088   | —         | —         | —         |
|           | STB-300-0.1 | 0.2410  | 15.51    | 0.9646   | 0.0019   | 22.50    | 0.9682   | —         | —         | —         |
|           | STB-300-0.3 | 0.2930  | 15.12    | 0.9792   | 0.0021   | 23.57    | 0.9386   | —         | —         | —         |
|           | STB-500-0  | 1.0282   | 7.17     | 0.9985   | 0.3153   | 12.58    | 0.9934   | 0.0079    | 24.22     | 0.9934   |
|           | STB-500-0.1 | 0.4603  | 14.82    | 0.9473   | 0.1416   | 19.43    | 0.901    | 0.0101    | 24.14     | 0.993    |
|           | STB-500-0.3 | 0.3632  | 15.50    | 0.9074   | 0.264    | 16.39    | 0.9933   | 0.0066    | 26.04     | 0.9806   |
|           | STB-700-0  | 1.1219   | 10.32    | 0.953    | 0.5323   | 14.27    | 0.973    | 0.0098    | 32.53     | 0.9622   |
|           | STB-700-0.1 | 1.1544  | 11.11    | 0.923    | 0.5276   | 16.53    | 0.9741   | 0.012     | 35.02     | 0.9788   |
|           | STB-700-0.3 | 0.6437  | 13.38    | 0.9581   | 0.4978   | 14.75    | 0.9919   | 0.0132    | 33.04     | 0.944    |
| TC        | STB-300-0  | 0.5502   | 38.88    | 0.9706   | 0.2293   | 42.55    | 0.9664   | 0.0096    | 52.24     | 0.9764   |
|           | STB-300-0.1 | 0.3121  | 39.06    | 0.9959   | 0.0863   | 42.16    | 0.9739   | 0.0046    | 45.13     | 0.9904   |
|           | STB-300-0.3 | 0.3118  | 36.87    | 0.9551   | 0.0892   | 40.63    | 0.9005   | 0.0045    | 44.19     | 0.9675   |
|           | STB-500-0  | 0.6728   | 43.41    | 0.9869   | 0.247    | 52.49    | 0.9552   | 0.1235    | 57.25     | 0.9489   |
|           | STB-500-0.1 | 1.1835  | 39.99    | 0.9806   | 0.5087   | 48.09    | 0.9758   | 0.1167    | 59.28     | 0.9046   |
|           | STB-500-0.3 | 1.3937  | 40.69    | 0.9836   | 0.333    | 56.38    | 0.9641   | 0.0476    | 66.67     | 0.8037   |
|           | STB-700-0  | 1.0523   | 41.42    | 0.972    | 0.3968   | 52.06    | 0.9719   | 0.011     | 71.45     | 0.9992   |
|           | STB-700-0.1 | 1.4230  | 42.27    | 0.9708   | 0.4053   | 59.50    | 0.9133   | 0.0616    | 74.11     | 0.9838   |
|           | STB-700-0.3 | 1.4506  | 43.49    | 0.9887   | 0.4804   | 56.17    | 0.9748   | 0.0087    | 80.01     | 0.9634   

*mg/(g min$^{0.5}$)).

Figure 9 | Experimental results for the adsorption of Cd$^{2+}$ (a) and TC (b) by STB.
Figure 10 | Fitting curves for the adsorption of Cd\textsuperscript{2+} (a: the STB which the blending ratio is 0, c: the STB which the blending ratio is 10%, e: the STB which the blending ratio is 30%) and TC (b: the STB which the blending ratio is 0, d: the STB which the blending ratio is 10%, f: the STB which the blending ratio is 30%) by STB with the Langmuir isotherm model.
result in the interaction between cations, making CE another reason for the great adsorption capacity of tetracycline. Compared with STB-700-0.1, the reduced adsorption capacity of STB-700-0.3 may be ascribed to the excess unreacted TP, which would wrap the biochar, thus reducing the contact between biochar and the adsorbate.

$K_l$ is related to the adsorption affinity or bond energy of adsorption between adsorbates and adsorbents. In this study, the $K_l$ values of Cd$^{2+}$ and TC adsorbed by STB-700-0 is 5.4222 and 1.7746 L/mg, and 66.333 and 2.8102 L/mg for STB-700-0.1 (Table 6). This indicates that the Cd$^{2+}$ and TC adsorbed on STB-700-0.1 are more difficult to release into the environment than those on STB-700-0.

### Table 6 | Adsorption isotherm constants for Cd$^{2+}$ adsorption by STB

| Adsorbate | Adsorbent | Langmuir | Freundlich | | |
| --- | --- | --- | --- | --- | --- |
| | | $Q_{\text{max}}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $n_f$ | $K_f^a$ | $R^2$ |
| Cd$^{2+}$ | STB-300-0 | 24.57 | 0.2629 | 0.9371 | 1.97 | 5.9304 | 0.9423 |
| | STB-300-0.1 | 20.83 | 0.4752 | 0.9172 | 2.30 | 7.1442 | 0.8096 |
| | STB-300-0.3 | 21.19 | 0.6431 | 0.9323 | 3.02 | 9.0567 | 0.9104 |
| | STB-500-0 | 30.86 | 1.2000 | 0.9445 | 4.86 | 18.5005 | 0.8259 |
| | STB-500-0.1 | 32.26 | 1.2757 | 0.9167 | 14.86 | 23.4319 | 0.5561 |
| | STB-500-0.3 | 34.72 | 1.5652 | 0.9435 | 6.50 | 23.0254 | 0.8518 |
| | STB-700-0 | 40.98 | 5.4222 | 0.9810 | 7.82 | 32.5182 | 0.9542 |
| | STB-700-0.1 | 50.25 | 66.3333 | 0.9544 | 7.24 | 54.6309 | 0.8690 |
| | STB-700-0.3 | 41.32 | 11.0000 | 0.9227 | 6.43 | 36.3429 | 0.8772 |
| TC | STB-300-0 | 62.11 | 1.0255 | 0.9997 | 12.61 | 46.7213 | 0.9927 |
| | STB-300-0.1 | 60.24 | 1.0921 | 0.9966 | 18.66 | 48.5648 | 0.7792 |
| | STB-300-0.3 | 57.47 | 1.3385 | 0.9984 | 25.19 | 48.9549 | 0.7847 |
| | STB-500-0 | 72.46 | 1.7692 | 0.9992 | 14.14 | 57.4721 | 0.9956 |
| | STB-500-0.1 | 79.37 | 1.8366 | 0.9971 | 12.06 | 60.1535 | 0.9690 |
| | STB-500-0.3 | 75.19 | 2.1452 | 0.9977 | 19.49 | 62.8217 | 0.9238 |
| | STB-700-0 | 79.37 | 1.7746 | 0.9969 | 13.37 | 62.0847 | 0.9513 |
| | STB-700-0.1 | 90.09 | 2.8102 | 0.9987 | 5.54 | 52.1279 | 0.8499 |
| | STB-700-0.3 | 81.30 | 2.7955 | 0.9997 | 12.36 | 64.4636 | 0.9798 |

*a(mg/g)(L/mg)\(^{1/n}$."

Implications of the study

In this study, biochar was produced from the co-pyrolysis of sewage sludge and waste tires. The study aimed at solving the problems that are encountered by the nature of the sewage sludge, such as the low carbon content and heat value of sewage sludge. This research is anticipated to provide new ideas for the research of biochar and fill the research gap of sorption mechanisms and characteristics which is essential to develop more efficient methods for contaminant removal. The co-pyrolysis of biochar is a complicated process, many influence factors work in the biochar adsorption behavior. The study was only a preliminary exploration to investigate the preparation and adsorption behavior of STB. The influence of the pH and temperature of the adsorbate on the biochar adsorption was not considered. Meanwhile, only Cd$^{2+}$ and TC were selected as research objects, and the stability of the material was not be demonstrated fully in this study. Further studies on the influencing mechanisms, the material stability and possible ecological effects should be conducted.

CONCLUSIONS

The preparation, physicochemical property and adsorption behavior of STB were investigated. The conclusions are as follows.

1. In this research, 700 °C was demonstrated to be the best pyrolysis temperature, 10% is the optimal blending ratio of TP. The $Q_{\text{max}}$ of Cd$^{2+}$ and TC by STB-700-0.1 is 50.25 and 90.09 mg/g, respectively.
2. The main mechanism of the adsorption process of STB for Cd mainly involves anion binding adsorption and ion exchange. The main mechanism of the adsorption process of STB for TC mainly involves complexation and CE.
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DATA AVAILABILITY STATEMENT

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

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