Effect of sulfamethazine on surface characteristics of biochar colloids and its implications for transport in porous media

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ABSTRACT
Antibiotics are contaminants of emerging concern due to their potential effect on antibiotic resistance and human health. Antibiotics tend to sorb strongly to organic materials, and biochar, a high efficient agent for adsorbing and immobilizing pollutants, can thus be used for remediation of antibiotic-contaminated soil and water. The effect of ionizable antibiotics on surface characteristics and transport of biochar colloids (BC) in the environment is poorly studied. Column experiments of BC were conducted in 1 mM NaCl solution under three pH (5, 7, and 10) conditions in the presence of sulfamethazine (SMT). Additionally, the adsorption of SMT by BC and the zeta potential of BC were also studied. The experimental results showed that SMT sorption to BC was enhanced at pH 5 and 7, but reduced at pH 10. SMT sorption reduced the surface charge of BC at pH 5 and 7 due to charge shielding, but increased surface charge at pH 10 due to adsorption of the negatively charged SMT species. The mobility of BC was inhibited by SMT under acidic or neutral conditions, while enhanced by SMT under alkaline conditions, which can be well explained by the change of electrostatic repulsion between BC and sand grains. These findings imply that pH conditions played a crucial role in deciding whether the transport of BC would be promoted by SMT or not. Biochar for antibiotics remediation will be more effective under acidic and neutral soil conditions, and the mobility of BC will be less than in alkaline soils.

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1. Introduction
Antibiotics are widely applied in veterinary medicine, and play an important role as growth promoters in agriculture, aquaculture, beekeeping, and animal husbandry (Gothwal and Shashidhar, 2015). As antibiotics are often resistant to degradation, they make their way into soil and water systems (Kummerer, 2003). Antibiotics and their metabolites enter the environment through industrial wastewater, urban sewage, as well as manure or compost (Jjemba, 2006; Mutiyar and Mittal, 2014; Gothwal and Shashidhar, 2015; Rowe et al., 2017). Antibiotics in soil will not only affect the microbial population, but also enhance the resistance of bacteria to antibiotics (Finch and Smith, 1987; Hassani et al., 1992; Rowe et al., 2017). Antibiotics can further enter surface and groundwater, and contaminate drinking water supplies.

Sulfonamides are the second commonly used antibiotics in the world and have been detected frequently in the environment (Yang et al., 2017c). A typical antibiotic in the sulfonamide group is sulfamethazine (SMT), which is commonly used for prophylactic or therapeutic purposes in the swine industry (Larsbo et al., 2008). Because of the poor metabolism of SMT in organisms, the antibiotic is excreted in feces, and spread onto farmland by fertilizer application or animal excretions (Tzeng et al., 2016). The half-lifetime for SMT in pond water was 2.7 days (Carstens et al., 2013). The half-life of SMT in non-sterilized agricultural clay loam soil was 24.8 days under the aerobic condition and 34.7 days under anaerobic condition (Pan and Chu, 2016). Concentrations of SMT in the soils contaminated with SMT have been reported to be in the microgram per kilogram range (Shelver et al., 2010; Awad et al., 2014; An et al., 2015).

Sulfonamides are generally mobile and bioavailable in soil (Thiele-Bruhn and Aust, 2004). There is a concern that excessive antibiotics, such as SMT, in soil and groundwater tend to cause
antibiotic resistance of microorganisms and further pose potential risks to human health. It is therefore important to understand environmental fate and transport of SMT in soils and subsurface media. SMT contains aromatic amine and sulfonamide functional groups (pK_{a1}, 2.28; pK_{a2}, 7.42), and thus can occur as cation (SMT^+), neutral molecule (SMT^0), anion (SMT^-), or even zwitterion (SMT^z) (Lin et al., 1997). In a typical soil environment, SMT occurs as a neutral or negatively-charged molecule, and as such is relatively mobile. Experiments in soil columns have shown that SMT can migrate through soil (Chen et al., 2011; Vithanage et al., 2014; Dong et al., 2016; Su et al., 2016), and can be easily leached into deep soil or groundwater (Kemper, 2008).

Biochar has been proposed as a soil amendment to retain antibiotic in soils and biota. Antibiotics, such as SMT, tend to sorb strongly to biochar (Teixido et al., 2011; Teixido et al., 2013; Xie et al., 2014; Rajapaksha et al., 2016; Tzeng et al., 2016). The surface properties and physical structure of biochar make it a promising sorbent for antibiotics. Sorption can occur through a variety of mechanisms, including π-π electron-donor-acceptor interaction, nucleophilic addition, electrostatic attraction, pore filling, partitioning into uncarbonized fraction and formation of charge-assisted hydrogen bonding (CAHB) with surface oxygen groups (Ahmed et al., 2017). Both pH and type of biochar are controlling factors for SMT sorption. For instance, SMT sorption to high-temperature phosphoric acid-modified bamboo biochar was greatest at pH 4.5, where the sorption mechanism was mainly due to H-bonding and π-π electron-donor-acceptor interactions (Ahmed et al., 2017). High-temperature biochar, with its large surface area and aromatic surface properties, tends to effectively sorb SMT by π-π electron-donor-acceptor interactions (Tzeng et al., 2016).

Biochar has a fairly wide particle size distribution and contains a substantial fraction of colloids and nanoparticles. Nanoscale biochar can account for 1.6−2.6% of the total biochar mass (Wang et al., 2013a), although a large variation of these numbers can be expected due to wide differences in feedstock and processing of biochar. When applied to soils, biochar will further break down into smaller particles over time (Ameloot et al., 2013). Colloidal and nanoscale biochar particles have the potential to be transported through soil media by moving water (Chen et al., 2017; Chen et al., 2018). Because of the strong affinity of antibiotics to sorb to biochar, colloidal and nanoscale biochar likely will act as carriers of antibiotics during transport in porous media (Xing et al., 2016). The mobility of biochar colloids (BC) is influenced by solution chemistry (Zhang et al., 2010; Yang et al., 2017a; Liu et al., 2019; Yang et al., 2019), flow rate (Zhang et al., 2010), and surface properties of biochar and porous medium (Wang et al., 2013a; Wang et al., 2013b). A sorbed contaminant can change the surface properties of colloids, thus affecting their transport in porous media. Our previous research showed that naphthalene, a hydrophobic organic pollutant, can inhibit the mobility of BC by modifying the colloids’ surface properties (Yang et al., 2017b). We would expect that sorption of antibiotics will also change the surface properties of BC and thus will affect their transport characteristics.

Biochar colloid-facilitated transport of antibiotics can pose a potential environmental risk for groundwater. While adsorption of ionizable compounds by charcoal black carbon or biochar is well studied, little attention has been directed to the effect of these ionic contaminants on the transport of BC themselves and co-transport with BC in porous media. As biochar can be used as an amendment for remediation of antibiotic-contaminated soils, it is important to understand the effects of antibiotic sorption on the mobility of biochar colloids in soils. In this study, we systematically investigate the effect of SMT, a common antibiotic, on the surface properties and transport of BC under different pH conditions and SMT loadings. We use adsorption isotherms, surface characterizations of BC, and column transport experiments to determine the effects of SMT sorption on transport of BC. To date, no systematic study has been conducted to investigate the effect of antibiotics on biochar retention in saturated porous media. The co-transport of antibiotics and BC is of great environmental significance, because biochar is commonly used to immobilize antibiotics in soils, but colloidal biochar may facilitate transport of antibiotics.

2. Materials and methods

2.1. Chemicals and biochar characterization

We made biochars by pyrolyzing wheat straw under anaerobic condition at 300 or 600 °C, and grinded the biochar with a ball mill (JC2000D2, POWEREACH, China) to reduce the diameter to less than 1 μm. The obtained biochar colloids are denoted as WB300 and WB600. The morphology of the BC was characterized by scanning electron microscopy (SEM, FEI NanoSEM 430), the ash content was determined by gravimetric analysis (ASTM, 2013), and bulk elemental content (C, H, O, N) was quantified with an elemental analyzer (Flash 2000, Thermo Scientific, USA). BET-N2 surface area was measured with a Nova 2200e surface area analyzer (Quantachrome Instruments Corp., Boynton Beach, FL). Fourier-transform infrared (FTIR) spectra in the range of 4000−500 cm⁻1 were collected with a Nicolet iS50 spectrometer (Thermo-Fisher Scientific, USA).

Sulfamethazine (SMT) (purity 99%) was purchased from Shanghai Aladdin Chemistry Co. Ltd. (Shanghai, China). An SMT stock solution of 100 mg L⁻¹ was prepared (by dissolving 0.500 mg SMT in 5 mL 10% ethanol solution) and kept in amber glass vials at 4 °C prior to the experiments. The chemical structure of SMT is shown in Fig. S1.

2.2. Sorption experiments

Sorption isotherms of SMT to BC under different pH conditions (5, 7, and 10) were conducted. Batch sorption was performed in 10-mL amber glass vials with Teflon-lined screw-caps and wrapped with aluminum foil to avoid photodegradation. Preliminary experiments with no BC showed that the SMT concentration did not change after shaken, indicating that no photodegradation occurred during the 24 h of the isotherm tests. In each experiment, 10 mL of a 1 mM NaCl solution, spiked to contain different SMT concentrations (0, 0.5, 1, 1.5, 3 mg L⁻¹) were added into vials containing 1 mg BC. The solution pH was adjusted with 0.1 M HCl or NaOH to pH 5, 7, or 10. All the batch experiments were performed in duplicates. Then the glass vials were placed on a reciprocal shaker at room temperature for 24 h (Huang et al., 2017; Vithanage et al., 2014). After shaking, the suspensions were filtered through a 0.22 μm nylon membrane (JinLong, Tianjin, China) to remove biochar particles, and the SMT concentration of the eluent was determined by HPLC (UltiMate 3000, Thermo Fisher, US) (Huang et al., 2017; Rajapaksha et al., 2015). Details on the analysis procedure are provided in the SI (Section S1).

The adsorbed SMT amount on BC was calculated from the difference between total and measured aqueous SMT concentrations in the liquid phase. The Langmuir and Freundlich isotherm models were used to describe SMT sorption on BC.

2.3. Porous medium

Quartz sand (purity > 99.95%) was purchased from Jiangsu Kaida Silica Co. Ltd. The sand was sieved to a particle diameter between 425 and 600 μm. The sand was thoroughly washed with 2 M HCl at 90 °C for 24 h to remove impurities, including Fe oxides, organic
matter, and carbonates (Sharma et al., 2008). Finally, the sand was rinsed ten times with deionized water and dried in the oven at 105 °C for 24 h, and then stored in a plastic bottle.

2.4. Measurement of zeta potential and particle size

Suspensions of 50 mg L⁻¹ BC in 1 mM NaCl solutions containing different concentrations of SMT (0, 0.1, and 0.2 mg L⁻¹) were prepared with different pH (5, 7, and 10), and shaken in the dark for 24 h. The zeta potentials and hydrodynamic particle sizes of the biochar suspensions were measured by dynamic light scattering (Nano ZS90, Malvern Instruments Ltd., UK). We also measured the zeta potential of colloidal sand particles (obtained by milling the sand used for the column experiments to colloidal size). Measurements were made in triplicates with 15–20 cycles for each run. The results of these measurements were used for the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) calculations as described in SI (Section S2).

2.5. Transport experiments

The column experiment was used to investigate the effect of SMT on BC transport in 1 mM NaCl solution under three different pH conditions (5, 7, and 10). Before the transport experiment, a certain volume of SMT stock solution was added into the 250 mg L⁻¹ biochar suspension to obtain an SMT concentration of 0, 0.5, or 1 mg L⁻¹. The ionic strength of suspension was adjusted to 1 mM with 1 M NaCl, and the pH suspension was adjusted to 5, 7, or 10 with HCl or NaOH. The suspensions were placed in amber agent bottles and shaken for 24 h for equilibration.

The sand was wet packed into a column (12.5 cm long × 2.5 cm inner diameter) in increments of 1–2 cm layers, and the porosities of each packed column were about 0.47 cm³ cm⁻³. Two 80-mesh nylon nets were placed at each end of the column to retain the sand. The column experiment was conducted under saturated conditions at a constant pore water velocity of 0.43 cm min⁻¹ controlled by a peristaltic pump. The column was pre-equilibrated by injecting more than 5 pore volumes (PVs) of a 1 mM NaCl background solution at a given pH. Then, 5 PVs of biochar suspension were introduced into the column. After that, the column was eluted with 5 PVs of BC-free background solution. The effluent biochar suspensions were collected using an automatic fraction collector (BSZ-100, Huxi, China) at 5 min intervals, and the concentrations of BC were measured by UV−vis spectroscopy (TU-1900, Persee, China) at the wavelength of 790 nm (Yang et al., 2017b).

After elution, the sand was excavated with a spoon in about 1-cm increments and placed into 25-ml conical flasks. To release BC attached to the sand surface, 20 mL of deionized water was added and the vials were shaken for 4 h. The sand was then allowed to settle out, and the supernatant suspension was analyzed with UV−vis at a wavelength of 790 nm to quantify the amount of released BC (Yang et al., 2017b).

The breakthrough data were analyzed to obtain column transport parameters. The HYDRUS-1D code (Simunek et al., 2005) was used to fit the advection–dispersion equation, coupled with a two-site kinetic retardation model, to the experimental data. More details about the transport model are shown in SI (Section S3).

2.6. Statistical analysis

One-way analysis of variance (ANOVA) using Tukey’s honestly significant difference (HSD) test (p < 0.05) was performed to identify statistically significant differences of measured parameters. The statistical analyses were conducted by SPSS 25.0.

3. Results and discussion

3.1. Properties of biochar

The hydrodynamic particle diameters of WB300 and WB600 ranged from 190 to 1100 nm, and 160–1000 nm, respectively, and the size distribution followed a log-normal distribution (Fig. 1, Fig. S2). The mean and standard deviations of the particle diameters were 446 ± 148 nm and 382 ± 156 nm for WB300 and WB600, respectively, and the SEM images indicated the irregular surface morphology (Fig. 1). Under the same treatment, the particle size of WB600 was slightly smaller than that of WB300, which meant WB600 was more easily to be broken into small particles due to more carbon aromatic structure under high pyrolysis temperature. Claoston et al. (2014) also found that the high-temperature biochar was more brittle than the low-temperature biochar. The yield, ash content, chemical composition and specific surface area of the BCs are summarized in Table S1. The yield of biochar is consistent with what has been reported by other biochars derived from wheat straw, corn stalk, peanut shells, sweet potato vine, dry leaves of poplar tree, fresh leaves of apricot tree, and reed under the same pyrolysis temperature (Junna et al., 2016). With the increase of pyrolysis temperature from 300 °C to 600 °C, the yield of biochar significantly decreased from 63 to 29% (Table S1). This low yield is mainly due to the evaporation of volatile matter, and the degradation of cellulose and lignin between 265 and 500 °C (Troger et al., 2013). The elemental analysis showed that biochar mainly consisted of C (>57%) and O (>34%), and the surface area analysis indicated a fairly low surface area (Table S1). Because of the demethylation and decarboxylation reactions, both the H/C and O/C ratios decreased with increasing pyrolysis temperatures (Rosales et al., 2017). The lower molar ratios of WB600 indicated that the biochar was highly carbonized with aromatic structures, and less hydrophilicity of the biochar surface (Chen et al., 2015; Regual et al., 2017). The FTIR analysis showed the O−H stretching at 3380 cm⁻¹ (Kolodynska et al., 2017). C−H stretching vibrations of the CH₂ at 2925 cm⁻¹ (Zhang et al., 2019), −COOH at 1695 cm⁻¹ (Gamiz et al., 2019), aromatic C=C/C=O at 1580 cm⁻¹ (Lyu et al., 2018), and aromatic C−H bending at 877 cm⁻¹, 797 cm⁻¹, and 620 cm⁻¹ (Jia et al., 2018; Lyu et al., 2018) (Fig. S2).

3.2. Adsorption of SMT on biochar

The sorption isotherms are shown in Fig. 2, which exhibited a distinct effect of pH on SMT sorption on BC. At pH 5 and 7, the WB600 had a higher sorption capacity than WB300 (Fig. 2, Table S2), mainly due to the higher surface area of WB600. For both WB300 and WB600, the highest adsorption capacity of the biochar for SMT was observed at pH 5, and the lowest capacity at pH 10. These results were consistent with the previous findings (Rajapaksha et al., 2016; Jia et al., 2018). Surface charge is a dominant factor controlling sorption of SMT on biochar (Jia et al., 2018). At pH 5, SMT was mostly present as neutral molecule (SMT⁰), i.e., 99.3% of the total SMT species occurred as SMT⁰ (Teixido et al., 2011). Sorption of SMT⁰ is driven by H-bonding, electron-donor-acceptor, and Lewis acid-base electronic interactions (Teixido et al., 2011; Ahmed et al., 2017). With solution pH increasing, the proportion of dissociated SMT⁻ increased, leading to a decrease in sorption affinity to biochar. At pH 7, 80% of the total SMT was SMT⁻ (Teixido et al., 2011), and SMT sorption onto biochar was less than that at pH 5. At pH 10, most of SMT was dissociated and 99.9% of the SMT was SMT⁻ (Teixido et al., 2011). SMT sorption on biochar drastically decreased at pH 10. Although the SMT was anion, the slight sorption still occurred on the negatively charged BC, which was also reported by Teixido et al. (2011). They explained the sorption...
process by proton association of the sulfoamino group of SMT followed by H-bonding with a carboxylate group of biochar, i.e., a negative charge-assisted H-bond.

Both Freundlich and Langmuir models can fit the experimental data well (Fig. 2, Table S2). While the Langmuir adsorption isotherm is based on a finite and uniform sorption site with a monolayer adsorption assumption (Langmuir, 1932), the Freundlich model is mostly used for infinite and multilayer adsorption, which has been often used to describe isothermal sorption of organic pollutants to biochar (Cederlund et al., 2016; Liu et al., 2016; Zielinska and Oleszczuk, 2016; Guo et al., 2017; Han et al., 2017; Miao et al., 2017). When sorption is site-limited, the Langmuir model usually fits better than Freundlich, and our results indicated such a case at pH 10, where sorption of SMT at pH 10 was limited because of...
electrostatic repulsion.

### 3.3. Effect of SMT on zeta potential of biochar

The zeta potentials of the WB300 and WB600 in 1 mM NaCl solution was about −39 to −41 mV and −37 to −38 mV, respectively, and was not strongly affected by solution pH (Fig. 3, Table 1, Table S4). At pH 5 and 7, the zeta potentials of BC became less negative with increasing SMT concentration. The reason might be that 99.3% (at pH 5) and 80% (at pH 7) of SMT existed as SMT0 (Teixido et al., 2011; Chu et al., 2013), and large amounts of SMT0 sorbed to the BC (Fig. 2), thereby shielding some of its negative surface charges. Similar trends have been found in the zeta potentials of BC coated with naphthalene (Yang et al., 2017b), Wang et al. (2014) also found that polyvinylpyrrolidone (PVP) coatings reduced the negative charge of silver nanoparticles, and the reduction increased with increasing PVP concentration.

At pH 10, the opposite effect on zeta potential was observed, i.e., the zeta potentials became more negative with increasing SMT concentration. Although the decrease was not large in the absolute value of zeta potential (Table 1, Table S3), it was statistically significant for the higher SMT concentration (Fig. 3). Similar phenomenon were found in the sorption of other anionic species or substances, such as humic substances (Kanet et al., 2015; Wu and Cheng, 2016), rhamnolipid (Liu et al., 2017), and natural organic ligands (Jones and Su, 2014) onto bacteria and engineered metal nanoparticles.

### 3.4. Effect of SMT on transport of BC

The surface characteristics of these two biochar colloids, WB300 and WB600, were similar in terms of particle size, zeta potential, and sorption behavior with SMT. These also caused similar transport behavior for WB300 and WB600. Therefore, we only discuss WB600 transport behavior in detail in the text, and the transport data of WB300 are shown in Fig. S4.

The breakthrough curves and retention profiles of WB600 in the absence/presence of SMT in 1 mM NaCl solution under different pH conditions are shown in Fig. 4. The breakthrough curves show the normalized effluent concentration curves (C/C0) of WB600 as a function of pore volumes (PVs), whereas the retention profiles show the mass ratio (N/N0) of WB600 as a function of distance from the column inlet. The experimental conditions and mass balance information for these columns are presented in Table S4. The total mass balance of WB600 (Mtot) for all the column experiments was >85%, and for the experiments in the absence of SMT, the mass percentage recovered from the effluent (Mret) was >65%, indicating that a substantial amount of WB600 can be transported through the columns (Table S4). Transport of WB600 occurred under unfavorable attachment conditions, because both WB600 and sand surface showed negative charge (Table 1). Considering the high hydrophobicity of biochar surface, the Lewis acid-base (AB) interaction between biochar and sand grain was repulsive and cannot be neglected. The attachment of WB600 in the sand columns can be normally explained by attachment due to the secondary minima of the XDLVO interaction and surface roughness and heterogeneity (Yang et al., 2016; Chen et al., 2017; Yang et al., 2017a), and by straining (Bradford et al., 2006). The retention profiles of WB600 showed a hyper-exponential shape, and more than 50% of the retained WB600 were located at near the column inlet (within the top 0.3 dimensionless distance units of the column) (Fig. 4b,d,f). Hyper-exponential retention profiles have been reported for WB600 (Wang et al., 2013a; Chen et al., 2017; Yang et al., 2017a; Yang et al., 2017b), and can be likely attributed to the weak particle size distribution of WB600, which makes WB600 susceptible to straining. In our experiment, the ratio of maximum WB600 diameter to sand was 0.0023, which exceeded the critical ratio of 0.0020, meaning straining occurs (Bradford et al., 2003). The large fraction of the WB600 was likely retained by straining.

At pH 5, with increasing SMT concentration, the WB600 became less mobile (Fig. 4a and b). The plateau of WB600 breakthrough curves decreased from 0.75 to 0.60 as initial SMT concentrations increased from 0 to 1 mg L⁻¹. This might be that more than 65% of SMT was adsorbed onto the surface of WB600 (Table S4) and the zeta potential of WB600 was less negative after SMT sorption. According to XDLVO theory, after the initial SMT concentrations increased from 0 to 1 mg L⁻¹, the energy barrier between WB600 and sand surface decreased from 229 to 141 kT (Table 1, Fig. S4). The decrease of repulsive energy barrier allowed the WB600 to be more easily attached onto the sand surface. Other studies also showed that the decreased negative zeta potential of colloids caused by the adsorption of uncharged molecule (naphthalene, polyvinylpyrrolidone) decreased the mobility of these colloids in saturated porous media (Yang et al., 2014; Yang et al., 2017b).

At pH 7, the effect of SMT on WB600 transport was similar as at pH 5, but not as pronounced. This is again consistent with the zeta potential data, which show less negative zeta potentials for increasing SMT concentrations. The decrease of the plateau of the breakthrough curves also agreed with the calculated XDLVO profiles (Table 1, Fig. S4).

At pH 10. At pH 10, the mobility of WB600 was greater than at pH 5 and 7 for all SMT concentrations (Fig. 4, Table S4). This can be explained because both WB600 and sand surface — but especially the sand surface — had more negative zeta potentials at pH 10 as compared to those at pH 5 and 7, so the energy barrier between WB600 and sand surface increased considerably (Table 1). When SMT concentration in the solution increased, the amount of WB600 in the effluents also increased, an effect opposite to what was observed at pH 5 and 7 (Fig. 4). The main reason for the increased mobility of WB600 with increasing SMT concentrations was likely the change in the zeta potential of the sand surface rather than that of the WB600: SMT considerably increased the negative charge of the sand surface (Table 1). The more negative zeta potential led to the larger electrostatic repulsion between WB600 and sand surface.

For the WB300 biochar, the results in terms of transport...
behavior are shown in Fig. S3 and the XDLVO profiles are shown in Table S3, and Fig. S4. The effect of SMT sorption on WB300 transport was similar as discussed for WB600. However, the retention profiles of WB300 showed evidence of stronger straining; more than 60% of the retained WB300 were located near the column inlet (Figs. S3b,d,f). This is mainly caused by the larger particle size of WB300 (Fig. 1).

3.5. Mechanisms governing the effects of SMT on BC transport

The breakthrough curves and retention profiles of WB300 and WB600 for all experimental conditions were fitted well by using the two-site kinetic retention model (Table 2 and Table S5). Only when \( S_{\text{max}} \) was considered in the model, the modeling can simulate the breakthrough curves of BCs well, indicating that the blocking occurred on the attachment sites of sand surface. There were the nanoscale roughness and chemical heterogeneity on the sand surface (Yang et al., 2019), where colloid attachment is favored. When all of these attachment sites were occupied by BCs, the plateau of breakthrough curves started to increase.

Solution pH conditions largely affect transport behavior of BCs. The two-kinetic site model parameters \( k_1, k_2, \) and \( S_{\text{max}} \) decreased with increasing pH, while \( k_1d \) increased. Ma et al. (2016) also observed that the colloids were easily retained on the sand under acidic conditions. The same trend for parameters \( k_1, k_1d, k_2, \) and \( S_{\text{max}} \) with pH was observed in this study.

In the presence of SMT, transport of BC was more highly dependent on solution pH conditions. The solution pH controls the speciation of SMT, and also affects the surface charge of BC and sand. At pH 5 and pH 7, the values of \( k_1 \) and \( k_2 \) increased and the value of \( k_1d \) decreased with increasing SMT concentration, because the secondary energy minimum between BC and sand surfaces became deeper and the attachment was increased. Under acidic conditions (pH 5), more than 99% SMT exists as SMT\(^0\), which can be

![Fig. 4. Measured (symbols) and fitted (lines) breakthrough curves (top) and retention profiles (bottom) for WB600 in the presence of various concentrations of SMT in 1 mM NaCl solution at (a,b) pH 5, (c,d) pH 7, and (e,f) pH 10.](image-url)

### Table 1

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<th>pH</th>
<th>( C_{SMT} ) mg L(^{-1} )</th>
<th>( d_{WB600} ) nm</th>
<th>( \xi_{WB600} ) mV</th>
<th>( \xi_{sand} ) mV</th>
<th>( \Phi_{max} ) kT</th>
<th>( \Phi_{min} ) kT</th>
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\( a \) pH conditions of the injected suspensions. 
\( b \) Concentrations of SMT in the injected suspensions. 
\( c \) DLS size of WB600 in each solution condition. 
\( d \) Zeta potentials of WB600 and quartz sand, respectively. 
\( e \) Maximum primary energy barrier and secondary energy minimum for WB600-sand interaction, respectively.
was sorbed onto the BC. The sorption was via charge-assisted H-bonding, and increased the negative surface charge of both BC and sand surfaces. Acid-Base interactions, and H-bonding, Lewis acid-base interactions, and π-π electron-donor-acceptor interactions (Fig. 5), and similar phenomena were reported in the previous studies (Teixido et al., 2011; Xie et al., 2014). The adsorption of SMT onto BC decreased their absolute value of the zeta potential through charge shielding, and consequently reduced the mobility of BCs in the sand column. Under neutral conditions (pH 7), their effect on BC transport was less than that at pH 5 and 10, because around 80% SMT existed as SMT0 at pH 7 solution and less SMT was sorbed at pH 7. Similar mechanisms were existed, because around 80% SMT existed as SMT0 at pH 7 solution and less SMT was sorbed at pH 7. Under neutral conditions (pH 7), their effect on BC transport was less than that at pH 5 and 10, because around 80% SMT existed as SMT0 at pH 7 solution and less SMT was sorbed at pH 7. Similar mechanisms were existing, because around 80% SMT existed as SMT0 at pH 7 solution and less SMT was sorbed at pH 7.

At pH 10, the value of k1 and k2 decreased when SMT concentration increased. This meant the retention of BC on attachment sites 1 and 2 was weakened, which can be attributed to the increased electrostatic repulsive interactions of BC – BC and BC – sand surface. Under alkaline condition (pH 10), almost all of the SMT in solution existed as SMT0 (Jia et al., 2018), and thus less SMT was sorbed onto the BC. The sorption was via charge-assisted H-bonding (Fig. 5). Transport of BC was enhanced in the presence of SMT under alkaline conditions, because alkaline pH condition increased the negative surface charge of both BC and sand surfaces.

4. Conclusions

Sulfonamides have been widely applied in veterinary medicine for a long time. Biochar has attracted interest as a stabilizing agent of pollutants in contaminated soil, and has the capacity to sorb and immobilize sulfonamides. This study investigated the effect of sulfonamides on the surface properties and transport of biochar colloids under different pH conditions. Sulfonamides have a pH-dependent charge, so they occur in as different species under different pH conditions, and this affects their mobility in soil and their sorption to soil and biochar. Under acidic and neutral pH conditions (pH 5 and 7), biochar can effectively adsorb sulfonamides from solution, and the adsorption leads to the reduced mobility of biochar colloids. However, under alkaline condition (pH 10), we found that biochar had a weak adsorption capacity of sulfonamides, but the sorption of sulfonamides enhanced its transport. And as more sulfonamides were adsorbed onto the surface of biochar colloids, the impact of sulfonamides on their transport in porous media becomes more pronounced. This implied the different species of sulfonamides under different pH conditions not only changed their sorption to biochar, but also affected the co-

| Table 2 | Fitted parameters of the two-site kinetic retention model for WB600. |
|---|---|---|---|---|---|---|---|
| pH a | C_{SMT} b mg L^{-1} | k_1 ^{ c} min^{-1} | k_{1d} ^{ c} min^{-1} | k_2 ^{ c} min^{-1} | S_{max}/C_0 f \% | R^2 |
| 5 | 0 | 5.81 \times 10^{-2} | 1.24 \times 10^{-3} | 5.06 \times 10^{-2} | 0.190 | 0.985 |
| | 0.5 | 6.06 \times 10^{-2} | 1.01 \times 10^{-3} | 7.35 \times 10^{-2} | 0.190 | 0.972 |
| | 1 | 6.70 \times 10^{-2} | 8.32 \times 10^{-4} | 10.2 \times 10^{-2} | 0.190 | 0.948 |
| 7 | 0 | 5.19 \times 10^{-2} | 1.44 \times 10^{-3} | 5.89 \times 10^{-2} | 0.163 | 0.986 |
| | 0.5 | 5.55 \times 10^{-2} | 1.15 \times 10^{-3} | 6.64 \times 10^{-2} | 0.163 | 0.974 |
| | 1 | 6.17 \times 10^{-2} | 8.73 \times 10^{-4} | 8.51 \times 10^{-2} | 0.163 | 0.955 |
| 10 | 0 | 5.03 \times 10^{-2} | 3.02 \times 10^{-3} | 4.56 \times 10^{-2} | 0.149 | 0.989 |
| | 0.5 | 4.69 \times 10^{-2} | 3.08 \times 10^{-3} | 3.29 \times 10^{-2} | 0.149 | 0.985 |
| | 1 | 4.32 \times 10^{-2} | 3.39 \times 10^{-3} | 2.16 \times 10^{-2} | 0.149 | 0.977 |

a pH conditions of the injected suspensions.
b Concentrations of SMT in the injected suspensions.
c First-order attachment rate coefficient on site 1.
d First-order detachment rate coefficient on site 1.
e First-order attachment rate coefficient on site 2.
f Maximum capacity of attachment on site 1. This parameter was fitted for C_{SMT} 0 mg L^{-1}, and then fixed for the 0.5 and 1.0 mg L^{-1} model fits.

Fig. 5. Schematic of adsorption mechanisms for SMT sorption to biochar surfaces at pH 5 and 10.
transport of sulfonamides and biochar colloids in porous media. Therefore, when biochar is used to remediate sulfonamide contaminated soils by immobilizing the antibiotics, the remediation effect will be more effective in acidic and neutral soils than in alkaline soil. As most natural soils have acidic or neutral pH, the use of biochar to remediate ionizable antibiotics, like sulfonamides, seems to be a promising approach.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that could inappropriately influence our work, there is no professional or personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Effect of sulfamethazine on surface characteristics of biochar colloids and its implications for transport in porous media”.

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Appendix A. Supplementary data

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