ORIGINAL RESEARCH

High performance removal of sulfamethoxazole using large specific area of biochar derived from corncob xylose residue

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Abstract

To remove antibiotics from waste water, an alkali active porous biochar, 850BC, was prepared from corncob xylose residue. In preparation, NaOH dipping was used for silicon removal and KOH activation was operated at 850°C. Further characterization containing BET, SEM, and FTIR were confirmed. 850BC possessed a huge specific surface area of 3043 m²·g⁻¹, developed pore structure and abundant oxygen functional groups. The adsorption performance of sulfamethoxazole on 850BC was quick and efficient, and the adsorption capacity reached 1429 mg·g⁻¹, which was significantly higher than other adsorbents reported previously. While pseudo-second-order kinetic model and Langmuir model could better describe the adsorption, chemisorption dominated the SMX adsorption onto 850BC. In virtue of pore-filling and π - π interaction as major mechanism, a large surface area and rich oxygen-containing functional groups led to an excellent adsorption performance. Thus, this preparation method provided a biochar-based adsorbent with enhanced specific surface for efficient removal of antibiotic pollutants.

Graphical Abstract

Highlights

- Corncob xylose residue biochar was modified by KOH with huge surface area.
- Biochar product possessed excellent absorption quantity of SMX of 1429 mg·g⁻¹.
- The SMX on biochar adsorption was mainly attributed to pore filling effect, π - π interactions, and hydrogen bonding.

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Keywords Corncob xylose residue · Biochar · Sulfamethoxazole · Adsorption behavior · Adsorption mechanism

1 Introduction

Antibiotics, the most commonly used antibacterial drugs in the world, are ubiquitous and continuously discharged into environments due to extensive consumption (Grenni et al. 2017). The long half-lives lead to pseudo persistence, accumulation, high bioactivity, and biodegradation resistance of most antibiotics, once they enter the environment (Ben et al. 2020; Han et al. 2020). Thus, antibiotic residues are likely to pose a potential toxic threat to ecosystem from long-term exposure at low concentrations (Isidori et al. 2005), and may lead resistant pathogens to infect humans and animals (Ngigi et al. 2019). Antibiotic pollution has become an emerging concern and important class of pollutants in water environment, and residues of antibiotics have been detected in many different matrices accordingly (Chen et al. 2020). The antibiotic concentration had been measured up to $15 \mu\text{g}\cdot\text{L}^{-1}$ in the Americas, a higher concentration over $50 \mu\text{g}\cdot\text{L}^{-1}$ was reported from African, and the concentration over $450 \mu\text{g}\cdot\text{L}^{-1}$ had been detected in Asian-Pacific countries (Danner et al. 2019). Yang et al. (2013) detected $17\text{--}304 \text{ ng}\cdot\text{L}^{-1}$ ciprofloxacin, $6.9\text{--}65 \text{ ng}\cdot\text{L}^{-1}$ sulfamethoxazole (SMX), and $0.3\text{--}8.8 \text{ ng}\cdot\text{L}^{-1}$ erythromycin in the Pearl River Delta in China. De Souza (2006) found the microbial colonies with the resistance of both heavy metal and antibiotics were isolated in Antarctic waters due to long-term exposure to low antibiotic concentrations and heavy metals. The major source of antibiotic pollution in aquatic environment is the discharge from wastewater treatment plants (WWTPs), including pharmaceutical wastewater, hospital sewage, and domestic sewage (Carvalho and Santos 2016). After antibiotic effluent is treated by Anoxic/Oxic process in WWTPs, there are still some remaining antibiotics with concentrations of $\text{ng}\text{--}\text{mg}\cdot\text{L}^{-1}$ directly discharged into the environment, because conventional WWTPs are not specifically designed to remove these microbial toxicity pollutants (Cui et al. 2020). Li et al. (2018) reported the total antibiotic effluent concentration of $0.49\text{--}2.6 \mu\text{g}\cdot\text{L}^{-1}$ after acidification and anaerobic treatments in a typical pharmaceutical plant. Wang et al. (2016) detected $11 \text{ ng}\cdot\text{L}^{-1}$ of florfenicol and $7.6 \text{ ng}\cdot\text{L}^{-1}$ of thiamphenicol in tap water in Shanghai, China. Antibiotics are refractory to be biodegraded, meanwhile, the chronic toxicity of antibiotics can inhibit microbial activity, and cause the death of effective microorganisms in sewage treatment facilities, and further affect the decomposition efficiency of organic matter in wastewater (Tomlinson et al. 2010). In the meantime, the long-term domestication of antibiotics will inevitably induce various antibiotic resistance genes (ARGs) in sludge microorganisms (Zhang et al. 2020). Then, these microbes may be transformed into

drug-resistant pathogenic microorganisms, which will enter the water environment, attack advanced organisms, endanger the safety of human body, and cause secondary pollution (Elder et al. 2020). Jutkina et al. (2016) pointed out a very low concentration of tetracycline ($10 \mu\text{g}\cdot\text{L}^{-1}$) could promote the horizontal transfer of multiple antibiotic resistance. Therefore, the reduction of antibiotic concentration before entering the biological wastewater treatment process is of great importance.

Currently, sulfonamides (SAs) are some of the most commonly used broad-spectrum antibiotics for various bacterial infectious disease treatment and feed additives (Fei et al. 2016). Carvalho and Santos (2016) found SAs were the most frequently analyzed and detected antibiotics in water. Because of the hydrophilic nature of SAs, traditional WWTPs processes and the state-of-the-art post-treatment technologies, such as sand filtration, coagulation, flocculation, and flotation, are unable to remove SMX thoroughly (Nakada et al. 2007). Therefore, more studies now try to find advanced large capacity adsorbents to remedy ineffective antibiotic treatment in the traditional sewage treatment process. Generally, commercial activated carbon, graphene oxide, carbon nanotubes, and other porous materials are expensive and inefficient for antibiotic adsorption (Ndirangu et al. 2019). Therefore, biochar has gradually come into view because of its low cost and high adsorption ability (Dutta et al. 2019).

Biochar is a material with a large specific surface area, high hydrophobicity, and aromaticity (Jiao et al. 2021). It is a refractory, stable, environmentally friendly carbon-rich product produced in anaerobic or anoxic conditions from agricultural and forestry residues (Emma 2006; Hayes 2006). Many researchers used biochar to remove hydrophobic organic pollutants like SAs (Wu et al. 2020). The properties of biochar containing specific surface area, microporosity, and surface chemistry directly affect the adsorption efficiency of antibiotics (Yang et al. 2020). The unmodified biochar usually shows low adsorption quantity and weak anti-interference ability for its insufficient properties, and often fails to meet the requirements of antibiotic treatment in wastewater (Han et al. 2013). Usually, there are two main purposes of biochar modification for antibiotic removal: (1) to increase the surface area of biochar; (2) to increase the surface functional groups of biochar. The enhanced porosity and richer functional groups fatefully endow adsorbent with stronger adsorption ability (Tang et al. 2018). Generally, the introduction of micropores onto biochar can be achieved by physical or chemical activation (Li et al. 2020). But the high silica content in agricultural residues remains a barrier towards synthesizing biochar with large surface area.

Previous studies have reported NaOH or KOH solution at a high temperature are effective in removing silica from biomass (Muniandy et al. 2014). Furthermore, the KOH activation is a compelling method for creating highly microporous structure and functional groups on the surface of the carbon (Fu et al. 2018). For instance, Ling et al. (2016) mixed shrimp shell biochar with KOH at different mass ratios and further carbonized it at 700–850°C. The activated biochar presented a hierarchical porous structure with the maximum specific surface area of 3171 m²·g⁻¹, and the maximum sulfamethazine adsorption quantity of 699.3 mg·g⁻¹, which was far greater than that nonactivation.

Therefore, this study aimed to prepare alkali active porous biochar adsorbent to remove SAs SMX from waste water. The specific objective was to prepare biochar materials with large specific surface area, with the physical, chemical and structural information characterized in detail. The batch method was explored to evaluate the adsorption properties of biochar on SMX by adsorption kinetic model and, isothermal adsorption model. The adsorption mechanism was also inferred.

2 Materials and methods

2.1 Materials

SMX (98.0%) was purchased from Aladdin Industrial Co., China. All other chemicals used in this paper were of analytical grade. The corn cob xylose residue (CCR) was obtained from Shandong Longlive Bio-Technology Co., Ltd., China.

2.2 Preparation of biochar

After removing impurities, CCR was crushed with pulverizer, sifted through 40 meshes sieve, and dried overnight at 105°C. Then, CCR was impregnated in 1 mol·L⁻¹ NaOH solution at a ratio of 1:20 (*m*:*V*) at room temperature for 24 h, and the mixture was elutriated with deionized water until the washing liquid was close to neutral. The sample was pyrolyzed at 400°C under nitrogen protection for 1 h in a tube furnace. The obtained precursor biochar was named as AM400.

After the demineralization treatment, AM400 was evenly mixed with KOH particles at a mass ratio of 1:5 with a tiny bit of water and dried at 105 °C for 12 h in a vacuum oven. Then the sample was moved into the tube furnace and calcined by stages under the protection of nitrogen gas. After rising to 600 °C at the heating rate of 5 °C·min⁻¹, the pyrolysis temperature rose to 850 °C at the rate of 3°C·min⁻¹ and maintained for 1 h. Next, the biochar was soaked in 1 mol·L⁻¹ HCl solution, oscillated for 4 h to eliminate inorganic components after cooling to room temperature, and

washed with hot deionized water until the washing fluid became neutral. Finally, the biochar was oven-dried and named as 850BC.

2.3 Characterizations of the biochar

Biochar was characterized for specific surface area, total pore volume and average pore width by BET test (Brunauer–Emmett–Teller, Quantachrome Corp., Micromeritics Nove 2000e apparatus, USA), surface morphology by scanning electron microscopy (SEM, Zeiss, Supra55 Sapphire, Japan), elements content with SEM–EDS (Energy Dispersive X-ray spectrometer), and the change of surface groups by Fourier transform infrared spectroscopy (FTIR, PerkinElmer Inc., Spectrum One, USA). The groups on biochar surface were quantified by acid–base titration intermittent balance method. 50.00 mg biochar was accurately weighed in 250 mL of PTFE beaker with 50 mL ultrapure water. The biochar was titrated by a self-titrator at a fixed rate with 0.01 mol·L⁻¹ NaOH and HCl volumetric solution. The titration was protected in N₂ atmosphere to avoid the effect of CO₂ in air on pH. The pH meter was used to measure the change of pH while each acid/base drop was added.

2.4 Batch adsorption experiments

The adsorption kinetics was investigated with 5 mg 850BC and 50 mL SMX solution. Bottles were set in a shaker at the rate of 180 rpm at 30°C for 24 h in the dark. At each sampling time 1–3 mL solution was separated and filtrated through 0.22 µm filter membrane. For adsorption isotherms, different dosages of 850BC were added in 50 mL of 300 mg·L⁻¹ SMX solutions. The mixtures were shaken at 10–30°C. The control experiment was conducted in SMX solution without biochar. All adsorption data were run in triplicate and the average values were reported.

The concentrations of SMX in the sample were analyzed by high performance liquid chromatography (UPLC, Agilent Technologies 1290 Infinity II, USA) and ZORBAX RRHD Eclipse Plus C18 column (2.1 × 50 mm, 1.8 µm, Agilent) with a UV detector at 263 nm. The mobile phase conditions were acetonitrile:0.1% (*wt*) formic acid (50:50, *V*:*V*) at a flow rate of 0.05 mL·min⁻¹ by 10 µL injection.

2.5 Analytical models and data analysis

The adsorption quantity of biochar for SMX was calculated as follows:

$$q_e = (c_0 - c_e)V/m \quad (1)$$

$$R = c_e/c_0 \quad (2)$$

where q_e is the adsorption quantity of SMX on biochar at equilibrium, $\text{mg}\cdot\text{g}^{-1}$; R is the removal rate of SMX on biochar, %; c_0 is the initial concentration of SMX, $\text{mg}\cdot\text{L}^{-1}$; c_e is the remaining concentration of SMX at equilibrium, $\text{mg}\cdot\text{L}^{-1}$; V is the volume of system, mL ; m is the mass of adsorbent, g .

In order to investigate the main impetus of adsorption process of SMX onto 850BC, the adsorption kinetic data were fitted to the Pseudo-first order kinetic model, Pseudo-second order kinetic model, and Intraparticle diffusion model. These kinetic models can be represented as follows:

Pseudo-first order kinetic model:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (3)$$

Pseudo-second order kinetic model:

$$t/q_t = t/(k_2 q_e^2) + t/q_e \quad (4)$$

Intraparticle diffusion model:

$$q_t = k_i t^{1/2} + C \quad (5)$$

where q_t is the SMX adsorption quantity, $\text{mg}\cdot\text{g}^{-1}$; k_1 is the pseudo-first rate constant, min^{-1} ; k_2 is the pseudo-second rate constant, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$; k_i is the intraparticle diffusion model rate constant, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1/2}$; C is the intercept, $\text{mg}\cdot\text{g}^{-1}$. The pseudo-first-order and pseudo-second-order kinetic models describe the monolayer and multilayer adsorption, respectively, intraparticle diffusion model is used to determine the rate-limiting step of the adsorption process.

The isothermal adsorption data were fitted to the Langmuir and Freundlich isothermal adsorption models. These isotherm models can be represented as follows:

Langmuir model:

$$c_e/q_e = 1/(q_{\max} K_L) + c_e/q_{\max} \quad (6)$$

Freundlich model:

$$\ln q_e = \ln K_F + \ln c_e/n \quad (7)$$

where $q_{\max}$ is the maximum adsorption quantity, $\text{mg}\cdot\text{g}^{-1}$; K_L is Langmuir model adsorption capacity constant, $\text{L}\cdot\text{mg}^{-1}$; K_F is Freundlich adsorption capacity constant, $\text{mg}^{1-n}\cdot\text{g}^{-1}\cdot\text{L}^n$; $1/n$ is Freundlich adsorption intensity constant. The Langmuir model describes monolayer sorption on a homogenous surface and the Freundlich model explains a multi-layer adsorption process.

To determine the conformity degree of the Langmuir isothermal model to adsorption process, the isotherm was classified by the separation factor R_L , which was defined in Eq. (8):

$$R_L = 1/(1 + K_L c_0) \quad (8)$$

Table 1 Component content of corn cob residue

Material	Cellulose	Hemicellulose	Lignin	Ash
Corn cob	34.93%	30.90%	20.07%	2.32%
Corn cob residue	57.43%	3.47%	28.08%	10.75%

Table 2 Si content of samples (SEM-EDS)

CCR	Ash	AM400 without Si removal	AM400
18.99%	31.10%	0.37%	< 0.01%

where R_L is the parameter to measure the difficult degree of adsorption process, dimensionless parameter; c_0 is the initial concentration of SMX solution, $\text{mg}\cdot\text{L}^{-1}$; K_L is the Langmuir model adsorption capacity constant, $\text{L}\cdot\text{mg}^{-1}$.

3 Results and discussion

3.1 Preparation and characterization of 850

3.1.1 Silicon removal of corncob waste residue

To increase the solidity of the waste residue, sand was added into corncob residue after xylose production. Thus, CCR contained 10.75% ash (Table 1), which was approximately 5 times that of raw corncob, and one third of the ash content was SiO_2 (Table 2). It was believed that inorganic components could block pore entrance and inhibit pore evolution in the process of carbonization and activation (Chang et al. 2003). Therefore, removing minerals from precursor materials to minimize inorganic components was the prerequisite for producing porous biochar with high surface area. The pretreatment method of NaOH solution dipping and washing was employed to remove the mixed silicon impurities in the CCR to obtain porous biochar.

SiO_2 , which existed in internal structure of biomass, could be removed by NaOH solution dipping and repeatedly water cleaning after carbonization. Thus, as shown in Fig. 1, the presence of Si–O–Si in CCR could be identified by the appearance of peak at 1070 cm^{-1} (Tang et al. 2018; Yan et al. 2017), and the peak no longer appeared after pyrolysis at 400°C . Therefore, it justified the successful completion of the procedure of pre-carbonization for silicon removal. The presence of Si element was not detected in AM400 by SEM-EDS measurement, which also proved the success of pre-carbonization process for silicon removal (Table 2).

Fig. 1 FTIR spectra of raw material CCR and biochars

3.1.2 Characterization of biochars

The typical SEM micrographs of raw material CCR, pre-carbonation material AM400 and activated biochar 850BC were illustrated in Fig. 2. The CCR presented a flat and smooth surface with no clear porous structure (Fig. 2a). Then a small amount of pore began to present on the surface of AM400 after pre-carbonation at 400 °C (Fig. 2b). In contrast to CCR, the roughness degree of surface of 850BC increased, and the

apparent porous structure could be observed after KOH activation and carbonization at 850 °C (Fig. 2c). It demonstrated that KOH activation under high temperature could improve porosity and porous structure of biochar. This phenomenon was due to the reaction:

KOH produced flowing metals K and CO during activation at high temperature. Diffusion of K and CO into carbon interior contributed to well-developed micropores and macropores (Cheng et al. 2017; Shi et al. 2017). KOH had stronger activation and intercalation ability than NaOH and smaller ΔG when reacting with C at high temperature (Lillo-Ródenas et al. 2003), it's the reason for choosing KOH for pore formation.

The influence of KOH activation on the specific surface area (S_{BET}), pore volume (V_t) and pore diameter (D_{ap}) of biochar was compared as shown in Table 5. The S_{BET} of 850BC increased significantly from 14.8 m²·g⁻¹ for AM400 to 3043 m²·g⁻¹, which was approximately 200-fold and the V_t was approximately eightfold. The pore diameter distribution curves (Fig. 3a) showed the shift of mesopore to micropore after modification. The pore diameter of 850BC was mainly distributed in 1–4 nm. It proved that KOH treatment was especially suitable for development of micropore and obtainment of extremely high surface area.

Fig. 2 SEM images of raw material and biochars a) CCR, b) AM400, c) and d) 850BC

Fig. 3 **a** Pore size distribution curves of biochars; **b** N_2 adsorption-desorption curves of biochars

The N_2 adsorption-desorption isotherms also supported the conclusions above. As shown in Fig. 3b, the adsorption-desorption isotherm of AM400 belonged to the Type IV according to adsorption theory, AM400 contained few pores and even less micropore (Huang et al. 2020). Meanwhile, AM400 exhibited an apparent H2 hysteresis loop at $p/p_0 > 0.5$, which was associated with capillary condensation in mesopores. The type H2 hysteresis loop reflected the complex pore structure of AM400, which might include typical "ink bottle" pores, tube-shaped pores with uneven pore size distribution, and interstitial pores of close-packed spherical particles (Wang et al. 2017a, b). As to 850BC, a typical micropore material, it was confirmed by type II isotherms and an obvious type H4 hysteresis loop with the character of almost horizontal parallel adsorption-desorption isotherm. The type H4 loop was associated with narrow slit-like micropores and micropores embedded in the macropores, while the type H2 loop often occurred in pores with narrow necks and wide bodies. It indicated that the KOH activation at 850 °C changed the pore shape, caused the larger pores to collapse and developed smaller micropores of AM400

(Zhu et al. 2018). Compared with the detection of the concentrated micropore with BET, SEM graphs exhibited many macropores about 1 μm in diameter on 850BC surface (Fig. 2d). Accordingly, the internal micropores of 850BC were connected to the inner wall of the surface micropores so that the multi-level pore structure of 850BC was formed. Certainly, the increased SSA and pore volume could provide more favorable adsorption sites for antibiotics. According to the adsorption theory, the pore size of adsorbent should match the geometric size of adsorbate molecules or ions for effective utilization. When the pore size of adsorbent is 1.7–3 times larger than the adsorbate molecule, the adsorbent will show the best adsorption performance (Tang et al. 2018). The molecule dimension of SMX was approximately $1.49 \times 0.64 \times 0.56$ nm, and the pore diameter of 850BC was concentrated in 2–4 nm (Fig. 3a), which was 1.3–3 times molecular volume of SMX. It was reasonable to expect that the 850BC was suitable for effective and fast adsorption of SMX with sufficient pore size.

The FT-IR spectra in Fig. 1 indicated that biochar consisted of several functional groups, which could be mutually confirmed with results of acid-base titration in Table 5. The broad peaks appearing at approximately 3440 cm^{-1} were attributed to the presence of associative hydrogen bond of O–H. As can be seen, CCR exhibited the highest peak intensity of O–H, then O–H peaks were gradually weakened after pyrolysis because of the decomposition of cellulose and lignin (Yang et al. 2007). A series of peaks in the region of $1500\text{--}1700\text{ cm}^{-1}$, $1100\text{--}1460\text{ cm}^{-1}$ and $600\text{--}710\text{ cm}^{-1}$ of CCR could be associated to the frame vibration of aromatic C=C, the stretching vibration of carboxyl and anhydride, and the out-of-plane vibration of C–H, respectively (Tang et al. 2018). The above peaks also weakened or even faded away after carbonization for the same reason with hydroxyl, only skeleton vibration peaks of aromatic C=C and stretching vibration peaks of C–O remained in AM400 and 850BC.

3.2 Adsorption capacity of SMX on 850BC

3.2.1 Adsorption kinetics

The adsorption of SMX onto 850BC at different times was listed in Fig. 4. The adsorption of SMX showed two phases: (i) The adsorption quantity increased rapidly in the initial stage during the first 30 min. Because in the initial stage, there were a large number of exposed active sites on 850BC surface, SMX molecules rapidly diffused to 850BC surface for surface adsorption. (ii) The adsorption quantity slowly increased after 30 min until reaching the adsorption equilibrium, because the adsorption of SMX from the surface to the internal pore was hindered by intermolecular collision and the inter-channel extrusion, and the active sites were gradually occupied. As a result, the maximum

Fig. 4 Adsorption kinetics model fitting curves of SMX on 850BC with different concentrations of SMX. **a** pseudo-first order kinetic model; **b** pseudo-second order kinetic model; **c** intraparticle diffusion model

adsorption quantity was $1429 \text{ mg} \cdot \text{g}^{-1}$, and the maximum removal rate was up to 98.52%. This phenomenon became more pronounced with the increase of initial SMX concentration, with a growth of the adsorption quantity and the time required for adsorption to reach equilibrium.

The plots of the different kinetics models for SMX adsorption onto 850BC were described in Fig. 4. The calculated values of q_e and correlation coefficient (R^2) were listed in SI, Table S2. It could be observed that the pseudo-second-order (PSO) kinetics model, which showed the highest R^2 and q_e , provided a better fit for adsorption process and a good agreement with the experimental data. The PSO model assumed the adsorption of adsorbate on adsorbent was chemisorption, and that the rate-limiting step might be a chemical reaction or a chemisorption process via sharing or exchanging electrons between biochar and SMX molecules, since the aromatic skeleton structure in the molecular structure of SMX (SI, Fig. S1) is easily combined in the form of π - π conjugate with the aromatic structure and the surface oxygen-containing functional groups of biochar.

Figure 4c illustrated the intraparticle diffusion model. The intraparticle diffusion model was employed to analyze the adsorption kinetics further, and the calculated values were listed in SI, Table S3. As seen in Fig. 4c, none of the linear intercepts was positive, indicating that both surface sorption and intraparticle diffusion contributed to SMX sorption process onto 850BC. In the initial phase, SMX rapidly diffused through solution to the bare exterior surface sorption sites on 850BC as a boundary layer diffusion step. The initial concentration provided the driving force to overcome mass transfer resistance between solid and liquid phases. The adsorption rate was much higher than the desorption rate at that moment. The C-value helped determine the boundary thickness: the larger the C value, the greater the boundary layer diffusion effect (Wu 2007). The C-value increased with the initial SMX concentration, indicating an enhanced diffusion effect in the boundary layer. The secondary stage was the intraparticle diffusion across macropores on the surface of 850BC and with the gradual sorption, the adsorption rate gradually slowed down because of the hindrance of intermolecular collision and inter-porous-channel extrusion, and the active sites on biochar were occupied increasingly. In the third stage, SMX molecules moved through narrow pore channels to the micro-mesoporous of interior 850BC, the intraparticle diffusion rate was obviously lower than the former stage of surface diffusion. Finally, the adsorption rate was equivalent to the desorption rate, the surface adsorption tended to be balanced.

3.2.2 Adsorption isotherms

The isothermal model fitting curves for SMX adsorption onto 850BC were presented in Fig. 5. The calculated data were listed in Table 3. Although both isothermal models described the experimental data well, the Langmuir model obviously fitted the isotherms better at low temperature. It illustrated the monolayer adsorption of SMX on 850BC tended to be dominant at low temperature and gradually

Fig. 5 Adsorption isothermal model fitting curves of SMX on 850BC under different temperatures. **a** Langmuir isothermal model; **b** Freundlich isothermal model

Table 3 Adsorption kinetics model fitting data of SMX on 850BC

c_{SMX} (mg·L ⁻¹)	50	100	200	300	400	500
$q_{e,exp}$ (mg·g ⁻¹)	244.05	482.13	928.17	1223.64	1343.59	1429.09
Pseudo-first-order kinetic model						
q_e (mg·g ⁻¹)	235.82	457.17	858.91	1135.77	1234.70	1308.58
k_1 (min ⁻¹)	0.3331	0.3402	0.1478	0.1356	0.1778	0.4309
R^2	0.8206	0.7128	0.6443	0.7075	0.6191	0.4902
Pseudo-second-order kinetic model						
q_e (mg·g ⁻¹)	244.62	475.3494	902.5613	1190.609	1294.736	1363.052
k_2 (g·mg ⁻¹ ·min ⁻¹)	0.00234	0.00119	0.00028	0.00020	0.00023	0.00048
R^2	0.9914	0.9597	0.8898	0.9152	0.8860	0.8499

Table 4 Adsorption isotherms model fitting data of SMX on 850BC

T (°C)	Langmuir				Freundlich		
	q_{max} (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	R_L	K_F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	1/n	R^2
10	1294.77	0.0654	0.9803	0.0485	428.77	0.197	0.8586
20	1442.54	0.1038	0.9820	0.0311	562.87	0.172	0.9060
30	1501.20	0.1732	0.9592	0.0189	681.31	0.147	0.9218

shifted to multilayer adsorption at room temperature. The value of $1/n$ between 0–0.5 indicated the adsorption was a preferential process in the Freundlich isotherm. The values of R_L were listed in Table 3. When $R_L > 1$, the adsorption process was difficult to carry out, and the adsorption effect was poor; when $R_L = 0$, the adsorption process was irreversible; when $0 < R_L \leq 1$, the adsorption process was favorable (Zhu et al. 2014). In this work, the R_L values were found within the range of 0.01–0.05 for SMX adsorption onto 850BC, which suggested that the adsorption process was favorable and easily accessible.

The maximum adsorption capacities of 850BC in this study by comparison with other previously reported biochar for the antibiotic adsorption were listed in Table 4, and the SMX adsorption quantity onto 850BC was much higher than other records. Such contrast also exhibited that 850BC might be an effective adsorbent for SMX removal from polluted water.

3.3 Adsorption mechanisms of SMX on 850BC

The adsorptive and structural performance comparisons of raw material CCR, precursor AM400, biochar product 850BC and industrial activated carbon AC were listed in Table 5. The adsorption capacity of 850BC was much higher than unactivated biochar AM850 at the same pyrolysis temperature. Micropores dominated the pore size distribution of AM850 and the shape of adsorption–desorption curve was also the same as 850BC (Fig. 3). It showed that both biochars presented similar hole shapes at the same carbonization temperature, while the 850BC contained 7 times of

Table 5 Performance comparison of biochars

Biochar	CCR	AM400	AM850	850BC	AC
Adsorption quantity (mg·g ⁻¹)	15.29	18.35	256.94	1429.09	134.01
Pore structure					
S _{BET} (m ² ·g ⁻¹)	5.50	14.75	431.74	3043	2025
V _t (cm ³ ·g ⁻¹)	0.01	0.05	0.20	1.67	2.04
Dap (nm)	7.77	13.34	1.91	2.23	1.03
Surface functional groups (mmol·g ⁻¹)					
Carboxyl	-	41.05	38.98	11.34	6.02
Lactone base	-	0.07	0.35	0.18	-
Phenolic hydroxyl	-	3.08	1.92	8.20	0.51

the surface area and 8 times of the pore volume of AM850 as adsorptive sites for SMX, causing a massive difference in adsorption capacity. Through simple linear fitting (SI Fig. S2), it could be confirmed that the adsorption quantity of biochar derived from corncob residue was positively associated with surface area.

Simultaneously, compared with representative commercial microporous carbon–active carbon (AC), 850BC presented 1.5 times the specific surface area and 10 times the adsorption quantity (Table 5), and AM850 presented a fifth of the specific surface area and twice the adsorption quantity. It proved that the surface functional groups also participated in the adsorption process. In FTIR spectrogram Fig. 1, the O–H peaks at 3440 cm⁻¹ disappeared after adsorption, proving hydroxyl on the 850BC surface participated in the sorption process. Similarly, the stretching vibration peak of aldehyde group C–H at 2900 cm⁻¹ (Jia et al. 2013) vanished after sorption, which also demonstrated that aldehyde group was involved in the SMX adsorption. The peak of 1060 cm⁻¹ in the spectra was due to the disappearance of the stretching vibration of C–O (Wang et al. 2017a, b) after sorption. Although the number of acidic carboxy groups on the 850BC surface was greatly reduced compared to AM850, the phenolic hydroxyl was significantly increased due to the action of alkali. Likewise, Ling (Ling et al. 2016) prepared KOH activated shrimp shell biochar with the surface area of 3171 m²·g⁻¹ and a similar pore structure with 850BC, but the SMX adsorption quantity of 699.3 mg·g⁻¹ was much smaller than that of 850BC. Due to a higher polarity index (O+N)/C (SI. Table S4), 850BC possesses more functional groups. No matter –COOH on AM850 or –OH on 850BC, the π – π interaction and H–bond interaction dominated SMX to form chemical bond with multitudinous surface functional groups on biochar that participated in the adsorption process.

Consequently, the overall substantial adsorption property of 850BC could be attributed to multiple adsorption mechanisms, including the pore filling and π – π interaction. The pore filling effect matched SMX molecules with the appropriate pore structure, and the significantly enhanced porosity of 850BC could provide more adsorption sites for adsorption. Meanwhile, the π – π interaction and H–bond interaction bonded SMX and surface oxygen groups on biochar enhancing specific adsorption.

4 Conclusions

Biochar 850BC was successfully prepared by KOH activation derived from corncob xylose residue and applied for adsorption of SMX. 850BC presented an extremely high specific surface area of 3043 m²·g⁻¹, a total pore volume of 1.67 cm³·g⁻¹, and an average pore diameter of 2.23 nm. The pseudo-second-order kinetic and Langmuir models best fitted the kinetic and isotherm data representing SMX adsorption on 850BC. The maximum adsorption of SMX on 850BC was 1429 mg·g⁻¹, which was prominently effective, and the removal rate of SMX was up to 98.52%. The excellent adsorption performance of 850BC was attributed to the developed pore structure and abundant surface oxygen-containing functional groups, while pore filling, π – π interaction and some other chemisorption dominated the adsorbing mechanism. Thus, we developed an effective and economical way to prepare biochar adsorbent with huge surface area, developed pore structure and abundant surface functional groups. A feasible and superior adsorbent can be applied not only for antibiotic removal but also the potential removal of various water pollutants.

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Code availability Not applicable.

Declarations

Consent for publication Agreed to publish.

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Ethics approval and consent to participate Not applicable.

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