Methanol-modified ultra-fine magnetic orange peel powder biochar as an effective adsorbent for removal of ibuprofen and sulfamethoxazole from water

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Abstract
The efficient capture of drug metabolites from aquatic environments has been recognized as an essential task for environmental protection. A methanol-modified ultra-fine magnetic biochar (CH$_3$OH-OP-char/Fe$_3$O$_4$) was prepared from orange peel powder using ball milling, and its
adsorption behaviors for ibuprofen and sulfamethoxazole were evaluated. The obtained materials were characterized by laser particle size analyzer, EA, ICP-OES, VSM, BET, TG-DTG, and FTIR. Furthermore, the experiments were conducted to study the vital operating parameters such as solution pH (2.0–11.0), contact time (0.5–240 min), initial drug concentration (0.5–100 mg/L), and temperatures (15–40°C) on the removal process. The results showed that the adsorption of IBP and sulfamethoxazole on CH₃OH-OP-char/Fe₃O₄ was highly pH-dependent. Kinetic studies indicated that physisorption was the dominant adsorption mechanism, and film diffusion played a vital role in adsorption onto CH₃OH-OP-char/Fe₃O₄. Equilibrium data were fitted well with the Langmuir isotherm model, implying monolayer adsorption. The adsorption process was spontaneous and endothermic due to the thermodynamic calculation, and high temperatures were favorable to the adsorption process.

**Keywords**
Magnetic ultra-fine biochar, ibuprofen, sulfamethoxazole, adsorption

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**Introduction**

Ibuprofen (IBP), belonging to the non-steroidal anti-inflammatory drugs (NSAIDs), induces analgesic, antipyretic, and anti-inflammatory effects (Álvarez-Torrelas et al., 2016). IBP, behaving as a weak acid with a value of 4.31, has moderate water solubility (21 mg/L) and hydrophobicity [log Kow (octanol–water partition coefficient) = 3.97], along with high mobility in the aquatic environment (Ueda et al., 1985). IBP metabolites are biochemically active and moderately toxic, especially on invertebrates and algae (Cleuvers, 2003).

Sulfamethoxazole (SMX) is a sulfonamide bacteriostatic antibiotic extensively used for the treatment of urinary tract infection, respiratory infection, intestinal infection, biliary tract infection, and local soft tissue or wounds infection caused by sensitive bacteria (Yang et al., 2012). SMX is reported to induce drug resistance in pathogens and can be toxic to aquatic organisms, even in small concentrations (Yao et al., 2012).

IBP and SMX are two best-selling drugs all over the world, and their metabolites are detected in wastewater and natural water bodies. Although the detected concentrations are usually at trace level (ng/L–µg/L), long-term exposure will generate bacterial resistance. Also, the spread of these bioactive compounds potentially damages aquatic organisms and affects human health through the food chain (Jing et al., 2014; Reguyal et al., 2017). Therefore, it is necessary to pay enough attention to this issue and to find effective methods to solve this problem.

Different treatment techniques have been reported for the removal of pharmaceuticals, including membrane separation (Prasertkulsak et al., 2019), ion exchange (Wang et al., 2017), electrochemical degradation (Antonin et al., 2019), adsorption (Liu et al., 2020), advanced oxidation (Alaton et al., 2019), and biodegradation to achieve such a goal (Cha and Carlson, 2019). Compared to other technologies, the adsorption with a high-binding adsorbent is considered to be a more practical and environmentally friendly approach because of its advantages such as smooth operation, simple design, and the possibility of regeneration.
The key to adsorption technology mainly depends on the choice of employed adsorbents. Wherein, pyrolytic biochar, as a waste management alternative, is considered as one of the most promising porous carbonaceous adsorbents due to its potential toward sustainability. Biochar, also known as agrichar, is analogous to black carbon and is the thermal degradation product of carbon-rich biomass under limited oxygen conditions.

Current research focuses on producing porous biochars from agricultural crop residues such as pine sawdust (Reguyal et al., 2017), rice straw (Khalil et al., 2018), Conocarpus wastes (Usman et al., 2013), cotton stalks (El-Hendaway et al., 2008), and nutshell (Tsielele et al., 2019) because of their large surface area and high hydrophobicity in water and wastewater purification (e.g. the removal of pharmaceuticals). For example, biochar derived from mung bean husk is used to reduce the risk posed by IBP (Mondal et al., 2016). Biochars from bamboo, Brazilian pepperwood, sugarcane bagasse, and hickory wood can remove SMX from aqueous solution (Yao et al., 2012).

Moreover, biochar surface contains hydroxyl, carboxylic acid, ketone, and ether functional groups produced during the thermochemical decomposition of biomass. Thus, the properties of biochar are improved through chemical modification—for example, Pezoti et al. (2016) studied the removal of amoxicillin from aqueous solutions using the treatment of guava seeds biochar with NaOH. Jing et al. (2014) reported that treating rice husk biochar with methanol enhances its adsorption of tetracycline antibiotics. However, one of the most significant disadvantages of using biochar adsorbent is the difficulty of recovering or separating the material after its use.

To improve the separation properties of biochar adsorbent, researchers developed an iron-reinforced composite material. Loading magnetic particles such as Fe, Fe$_2$O$_3$, and Fe$_3$O$_4$ on biochar surface can achieve solid–liquid separation in the aqueous phase under the surrounding magnetic field. Shan et al. (2016) discovered that magnetic biochar/Fe$_3$O$_4$ exhibits high adsorption of carbamazepine and is separated magnetically.

One of the valuable biomass wastes from the orange juice processing industry is orange peel (abbreviated as OP after that), which is cheap, abundant, and readily available. OP mainly consists of cellulose, hemicellulose, lignin, pectin, chlorophyll pigments, and other low molecular weight compounds (including limonene). Improper disposal of this biomass may cause serious environmental problems.

The work prepared methanol-modified magnetic biochar from OP, which was used to remove IBP and SMX from aqueous solutions via simple liquid-phase adsorption. Characterizations of the magnetic hybrid adsorbent have been explored through elemental analyzer (EA), inductively coupled plasma optical emission spectrometer (ICP-OES), surface area and porosity analyzer, thermogravimetric analyzer (TG-DTG), and Fourier transform infrared spectroscopy (FTIR). The adsorption performance of biochar adsorbent toward IBP sodium salt and SMX has been tested at different experimental conditions as solution pH, contact time, initial drug concentration, and temperature.

In order to clarify the adsorption mechanism, the equilibrium adsorption data of the adsorption system have been calculated using several isotherms and kinetic models. There are no previous studies on the removal of IBP sodium salt and SMX from aqueous solutions by OP-derived biochar. Consequently, this is innovative and provides a new idea for the development of efficient, economical, and environmentally friendly OP adsorbent.
Materials and methods

Chemicals

IBP sodium salt (IBP, 99.5% purity) and SMX (99.0% purity), used as adsorbates, were purchased from Guangzhou Jufeng Pharmaceutical Co., Ltd. (Guangzhou, China). Table S1 shows the molecular structure and the significant physicochemical properties of these two target pharmaceuticals. Methanol (CH$_3$OH, 99.9% HPLC grade) was obtained from Aladdin (Shanghai, China). Magnetite (Fe$_3$O$_4$, 99.5% analytical grade) powder was supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and milled for 3 h before use. All other chemicals were in the analytical grade or better and used without further purification. The stock solutions of IBP and SMX (concentration: 1 g/L) were prepared with ultrapure water in 1% methanol (insignificant co-solvent effect) and stored in brown volumetric flasks at low temperature in the refrigerator before use. Ultrapure water (18.2 MΩ/cm at 25°C) was used in the work.

Preparation of biochar

OP powder (with the particle size less than 0.047 mm) was obtained from Bozhou Lianrui Trade Co., Ltd (Bozhou, China). Initially, the biomass was washed several times with ultrapure water to take off impurities and then dried overnight in an oven at 110°C. Then it was stored away from light in the closed bottles for further procedures.

The biochar was prepared following a typical method reported earlier (Liao et al., 2013) with some modifications. OP powder was placed into a home-built tubular reactor (see Figure 1) and pre-carbonized at 200°C for 12 h and then carbonized at a heating rate of 20°C/min from 200 to 600°C for 6 h. After that, it was calcined at this temperature for 2 h. The above preparation was carried out in a furnace chamber under nitrogen atmosphere (N$_2$: 99.99%; flow rate of 200 cm$^3$/min). After cooling the reactor to room temperature, the obtained sample was washed with 500 mL of 1.5 M hydrochloric acid (HCl) for five times and repeatedly rinsed with ultrapure water to remove impurities (such as ash and metal residues) until the pH of the filtrate became neutral. Finally, the obtained biochar was dried at 80°C for 24 h and stored in an airtight desiccator and named as OP-char.

Modification and characterization of biochar

Modification of OP-char with acidic methanol was performed as follows. About 10 g of OP-char was added in the mixed solution (500 mL of CH$_3$OH and 5 mL of HCl) and stirred at 150 r/min for 24 h at room temperature (25°C). Then, about 3 g of Fe$_3$O$_4$ was added to the mixture, and the reaction continues again for another 6 h. The resulting black precipitate was collected by decantation and filtration and washed with 500 mL of cyclohexane for five times. Finally, the modified biochar was freeze-dried for 12 h and stored in an airtight plastic container at low temperature (6–8°C) for further use in the adsorption experiments. The biochar was hereafter abbreviated as CH$_3$OH-OP-char/Fe$_3$O$_4$.

Biochars’ particle size distributions were confirmed by a laser particle analyzer (BT-9300S, Bettersize, China). The pH values of biochars were measured in a suspension of 0.1 g biochar in 10 mL of ultrapure water using a digital pH meter (PHS-3C, Rex Electric Chemical, China). Ash contents of all samples were determined gravimetrically by drying in an oven after incineration in a muffle furnace at 800 ± 5°C for 4 h.
The carbon (C), hydrogen (H), and nitrogen (N) contents of biochars were determined using an EA (Vario MICRO cube, Elementar, Germany). The oxygen (O) content was estimated by mass difference (O% = 100% – C% – H% – N% – ash%). The iron (Fe) content was analyzed using the method of acid wet to digest the samples by an ICP-OES (PQ9000, Jena, Germany).

Thermal gravimetric analyses (TGA) of biochars were performed using a TG-DTG (Diamond 6300, Perkin Elmer, USA) with a heating rate of 10°C/min from 25 to 1000°C under nitrogen (N₂) atmosphere. The specific surface areas, cumulative pore volumes, and pore diameters of biochars were determined with the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods based on the nitrogen (N₂) adsorption–desorption isotherm data, respectively, which was obtained by the surface area and porosity analyzer (Autosorb iQ2, Quantachrome, USA) at 77 K. Moreover, the functional groups of biochars before and after adsorption were characterized using an FTIR spectrometer (FT/IR-410, JASCO, Japan) with the wavenumber ranging from 4000 to 400 cm⁻¹.

**Batch adsorption studies**

Batch adsorption was tested in 150 mL stopper conical flasks placed in a thermostatic orbital shaker (Orbitek, Scigenics Biotech, India) at 180 r/min. Each flask contained 50 mL of drug solution (IBP or SMX) and 0.025-g adsorbent (OP-char or CH₃OH-OP-char/Fe₃O₄). The above conditions remain unchanged in the work. The initial solution pH was adjusted to 2.0–11.0 at 25°C and drug (IBP or SMX) concentration of 25 mg/L using negligible volumes of 0.01 mol/L HCl or 0.01 mol/L NaOH solutions for 2 h to evaluate the effect of solution pH on IBP and SMX adsorption. The effect of contact time ranging from 30 s to 4 h on IBP or SMX performance was tested at 30°C, pH 6.0, and drug concentration of
In the adsorption isotherm experiments (under the conditions of pH 6.0, contact time of 2 h, and temperature of 25°C), biochars were added in drug solution at various concentrations (0.5–100 mg/L). Under similar conditions (under the conditions of pH 6.0, contact time of 2 h, and initial drug concentrations 25 mg/L), the adsorption thermodynamics was evaluated at 15, 20, 25, 30, 35, and 40°C. After adsorption, all samples were filtered through 0.22-μm nylon filter membranes, and the filtrate was analyzed for residual drug concentration. All experiments were performed in triplicate, and the results indicated that the adsorption of drugs on the bottles and filter membranes was negligible.

**Analytical method**

IBP and SMX concentration was measured in a UV–vis spectrophotometer (T6, Persee Co., Ltd, China). The maximum wavelength used in the detection was 220.5 and 266.0 nm, respectively. All the IBP and SMX samples were analyzed in triplicate. IBP and SMX detection limit was 50 and 75 μg/L, and the calibration curve was significantly linear in the concentration range of 0.25–20 mg/L ($R^2 = 0.9991$) and 0.50–15 mg/L ($R^2 = 0.9903$), respectively. The amount of adsorbed IBP and SMX as well as $q_e$ was calculated according to

$$q_e (mg/g) = \frac{(C_0 - C_i) \times V}{M} \quad (1)$$

where $R^2$ (mg/L) and $q_e$ (mg/L) are the initial and equilibrium concentrations of IBP and SMX, respectively; $k_2$ (L) is the volume of the solution; $R^2$ (g) the mass of the adsorbent.

**Data analysis**

Two kinetic models: pseudo-first-order model and the pseudo-second-order model were used to analyze the kinetic adsorption data of IBP and SMX. Additionally, the film diffusion model was evaluated as possible adsorption mechanisms. Text S1 shows the theories behind the above three models.

Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models were used to study the adsorption process, which determined the maximum adsorption capacities of IBP and SMX. The detailed equations for the calculation of adsorption results were explained in Text S2.

In order to study the thermodynamic behavior for the adsorption of IBP and SMX on biochar adsorbents, we calculated the thermodynamic parameters, including the standard Gibb’s free energy ($\Delta G^\circ$), the enthalpy change ($\Delta H^\circ$), and the entropy change ($\Delta S^\circ$). Thermodynamic equations used for these calculations were in Text S3.

**Results and discussion**

**Characterization of biochar adsorbents**

Figure 2 and Table S2 show the distribution of particle size of OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$, respectively. The mean particle size of CH$_3$OH-OP-char/Fe$_3$O$_4$ is 6.96 μm,
which is much lower than that of OP-char (42.19 μm). The particle size of biochar dramatically decreases by the ball-milling process.

Table 1 shows the information on elemental composition and surface properties of OP-char and CH₃OH-OP-char/Fe₃O₄. The analysis indicated that the two biochars were dominated by C (53.77% of OP-char and 39.12% of CH₃OH-OP-char/Fe₃O₄). The content of Fe detected by CH₃OH-OP-char/Fe₃O₄ was similar to that of adding Fe₃O₄ in preparation; however, only 0.04% of Fe was detected in OP-char. Fe₃O₄ could be the primary source of Fe in the modified adsorbent. Additionally, the H/C value of CH₃OH-OP-char/Fe₃O₄ was 0.0575, which was slightly lower than that of OP-char (0.0623). Therefore, a large number of organic components of herbaceous residue were retained in the preparation of biochar by ultra-fine ball milling. Meanwhile, the O/C value of CH₃OH-OP-char/Fe₃O₄ was 0.593, which was slightly higher than that of OP-char (0.487). It indicated that the hydrophobicity of the modified biochar was enhanced.

The surface area is a significant indicator for biochar adsorbent; therefore, the textural properties, e.g. BET surface area, BJH cumulative pore volume, and BJH average pore diameter of OP-char and CH₃OH-OP-char/Fe₃O₄ were examined by N₂-adsorption experiments (see Table 1). In the work, the surface area, the total pore volume, and the average pore size of OP-char were 664.92 m²/g, 0.09 cm³/g, and 3.42 nm, respectively. After modification, the surface area and the total pore volume of CH₃OH-OP-char/Fe₃O₄ increased to 857.42 and 0.12 cm³/g, respectively, and the average pore size of CH₃OH-OP-char/Fe₃O₄ decreased to 3.06 nm. Both methanol immersion and ball milling could develop the porous structures of biochar. Also, Fe₃O₄ in CH₃OH-OP-char/Fe₃O₄ reduced the BET surface area, which could crush biochar particles to produce more pores.

Figure 3 shows the magnetization curves of CH₃OH-OP-char/Fe₃O₄. CH₃OH-OP-char/Fe₃O₄ exhibited a saturation magnetization of 15.3 Am²/kg, which indicated good magnetism. Besides, CH₃OH-OP-char/Fe₃O₄ was easily separated from an aqueous solution with a permanent magnet after the adsorption process (see Figure 3, inset).
| Adsorbent                  | pH  | Ash (%) | C     | H     | O     | N     | Fe     | H/C  | O/C  | BJH cumulative pore volume (cm³/g) | BJH average pore diameter (nm) |
|---------------------------|-----|---------|-------|-------|-------|-------|--------|------|------|----------------------------------|-------------------------------|
| OP-char                   | 7.42| 15.11   | 53.77 | 3.35  | 26.18 | 1.59  | 1.04   | 0.0623| 0.487| 664.92                           | 3.42                          |
| CH₃OH-OP-char/Fe₃O₄       | 7.80| 34.22   | 39.12 | 2.25  | 23.21 | 1.20  | 1.916  | 0.0575| 0.593| 857.42                           | 0.12                          |
| CH₂OH-CH₃OH-OP-char/Fe₃O₄| 7.80| 34.22   | 39.12 | 2.25  | 23.21 | 1.20  | 1.916  | 0.0575| 0.593| 857.42                           | 0.12                          |

Table 1. The information of elemental composition and surface properties of the biochar adsorbents used in this study.
Pyrolytic characteristics of OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$ were examined by the TG-derivative thermogravimetric (TG-DTG) analysis, and Figure 4 shows its TG and DTG curves. The TG curves (see Figure 4(a)) showed that the thermal stability of CH$_3$OH-OP-char/Fe$_3$O$_4$ was slightly lower than that of OP-char. DTG curves (see Figure 4(b)) showed that two biochars lost free water between 40 and 60°C. The broad, robust peaks of two biochars around 460 and 470°C were the decompositions of carboxyl and carbonyl groups, which was associated with the pyrolysis of herb residue in OP biochar including hemicellulose, cellulose, lignin, and pectin. The narrow and weak peak of CH$_3$OH-OP-char/Fe$_3$O$_4$ at 188°C was related to the loss of hydroxyl groups introduced by methanol-modified biochar. The sharp, robust peak of CH$_3$OH-OP-char/Fe$_3$O$_4$ at 786°C was due to the reaction of Fe$_3$O$_4$ with C to form CO$_2$. 

Figure 3. Magnetic hysteresis cycles of CH$_3$OH-OP-char/Fe$_3$O$_4$ (inset plots showing the magnetic separation CH$_3$OH-OP-char/Fe$_3$O$_4$ after IBP and SMX adsorption).

Figure 4. TG and DTG profiles of OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$.
Effect of solution pH

Earlier studies indicate that the solution pH is a critical parameter in the processes of IBP and SMX adsorption because it might change the surface charge of the biochar absorbent and affect the speciation distribution of the IBP and SMX in the solution phase (Reguyal et al., 2017) (Mestre et al., 2007). Figure 5 illustrates the effect of initial solution pH (2–11) on the adsorption of both pharmaceuticals onto OP-char and CH₃OH-OP-char/Fe₃O₄. OP-char and CH₃OH-OP-char/Fe₃O₄ have similar overall trends regarding the impact of the solution pH on IBP and SMX adsorption, and CH₃OH-OP-char/Fe₃O₄ exhibits higher adsorption than OP-char. Under the acidic condition (at pH 2.0–6.0), the adsorption capacity of IBP and SMX increases slightly at first and then becomes stable. However, as the pH increases from 6.0 to 8.0, the adsorption capacity declines gradually. When the pH value adjusts to the extremely alkaline environments (at pH 10.0–11.0), adsorption significantly declines.

This pH-dependent phenomenon might be related to the molecular structure of the adsorbent and the functional groups presenting on the biochar surface. The point of zero charge (pHpzc) of OP-char and CH₃OH-OP-char/Fe₃O₄ found by reverse mass titration method was around 4.4. The surface of biochars was positively charged at the solution pH lower than 4.4 and negatively charged at the solution pH higher than 4.4 (Yang et al., 2012). Furthermore, depending on the solution pH, the IBP distributed in water as two species: molecular (IBP) and anionic (IBP⁻) forms. SMX, a typical amphoteric compound, could form three species, including cation (SMX⁺), zwitterion (SMX±), and anion (SMX⁻) forms, at different pH values (Li et al., 2017).

Therefore, at pH 4.0–6.0, the IBP⁻ and SMX± forms were predominant, which was beneficial to the adsorption of IBP and SMX due to attractive charge-assisted H-bond and hydrophobic interaction. Besides, electrostatic interaction and π–π electron donor–acceptor (EDA) interaction contributed to the adsorption to some extent (Wang et al., 2015).

In contrast, at pH < 4.0, the lower adsorption performance was caused by reduced hydrophobic interactions. However, the increased pH (pH > 6.0) gradually increased electrostatic repulsion between the adsorptive anion (IBP⁻ or SMX⁻) and the biochar surface, which decreased adsorption efficiency.

Figure 5. Effect of equilibrium pH on adsorption of IBP and SMX by OP-char and CH₃OH-OP-char/Fe₃O₄.
It is worth noting that the stability of Fe$_3$O$_4$ supporting materials was greatly affected by the pH value, and it was unstable in weakly acidic and weakly basic solutions (Ai et al., 2019). Considering that most hospital wastewaters were acidic, pH 4.0 was selected for use in the following adsorption experiment.

**Adsorption kinetics**

Equilibrium time is an essential parameter to study drug adsorption. Figure S1 shows the evolution of IBP and SMX adsorption versus time onto OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. For both drugs, the adsorption can be divided into two stages involving a rapid and slow adsorption process. Both adsorbents exhibited fast adsorption of IBP and SMX, and nearly 80% of the adsorption capacity was accomplished in the first 30 min, which was due to the adsorption occurred on the external surface rather than in the micropores. It was followed by the slower second phase in which the adsorption capacity slowly increased until reaching the equilibrium.

For CH$_3$OH-OP-char/Fe$_3$O$_4$, the adsorption of IBP and SMX nearly reached equilibrium in 90 min. While for OP-char, the adsorption equilibrium could be achieved in 120 min. The CH$_3$OH-OP-char/Fe$_3$O$_4$ showed better adsorption ability than OP-char, which indicated that CH$_3$OH-OP-char/Fe$_3$O$_4$ provided more abundant binding sites for adsorbates. Within 50 min, 70–80% of the equilibrium IBP and SMX uptakes were adsorbed. Their uptakes were faster at the initial stage due to the adsorption of the drug molecules on the adsorbent surface rather than in the micropores. Given this, the contact time of 120 min was adopted for the subsequent equilibrium experiments.

Adsorption kinetics reflects the reaction pathway and mechanism of adsorption, and it is a necessary index to evaluate the adsorption efficiency (Abbas et al., 2019). In order to evaluate the adsorption kinetics of IBP onto SMX, the experimental data were described by the widely used pseudo-first-order and pseudo-second-order non-linear kinetic models, and the fitting parameters were summarized in Table 2.

It could be observed that both models exhibited higher correlation coefficients. Except for IBP adsorbed by OP-char, the calculated $q_e$ values ($q_{e, cal}$) generated by the pseudo-first-order kinetic model was extremely close to the experimental values ($q_{e, exp}$). These indicated that the rate-limiting step of the adsorption process was controlled by physisorption. The similar results were obtained in the adsorption of tetracycline on human hair-derived high surface area porous carbon (Ahmed et al., 2017) and SMX on the magnetic biochar from pine sawdust (Reguyal et al., 2017).

**Adsorption isotherm**

The adsorption isotherm illustrated the interactions between the drug molecule and the biochar microparticles, which was of crucial importance to understand their specific relationship (Lonappan et al., 2018). Therefore, four widely used non-linear isotherm models, Langmuir, Freundlich, Temkin, and D–R, were employed to evaluate the adsorption process of IBP and SMX in the work, and the results were summarized in Table S3.

Table S3 shows that the considered adsorption isotherms matched the experimental data with $R^2$ values in the order of Langmuir > Freundlich and Temkin > D–R. This result confirmed that a uniform monolayer coverage of IBP and SMX adsorption on OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$ surface formed. According to the Langmuir fitting, the maximum
adsorption capacities for IBP and SMX over CH$_3$OH-OP-char/Fe$_3$O$_4$ were approximately two and three times that of OP-char, respectively. The adsorption capacity was significantly improved after CH$_3$OH modification and ball milling treatment.

Table 3 shows a comparison of the maximum adsorption capacity of two drugs with some other biochars reported in the literature. CH$_3$OH-OP-char/Fe$_3$O$_4$ is one of the most competitive adsorbents with the extensive application.

Except for IBP adsorbed by OP-char, the Temkin isotherm model provided higher $R^2$ values (0.8082–0.9284) and $\beta_T$ values (0.29–0.79) less than 1. It indicated that the adsorption reaction occurred endothermically, and the uniform distribution of binding energy characterized the adsorption process. The average adsorption energy ($E$) derived from the D–R isotherm model could transfer some of the information about the adsorption nature. The magnitudes of $E$ (1.71–4.31) were lower than 8 kJ/mol in the concentration range studied, which suggested that there was electrostatic interaction in the adsorption process of IBP and SMX, and the physical mechanism might dominate the adsorption process. Álvarez-Torrellas et al. (2016) observed similar behavior and result. Furthermore, Muthanna et al., who studied the adsorption of tetracycline by carbonaceous adsorbents and the removal of metronidazole by microporous, activated carbon from Siris seed pods, respectively.

**Adsorption thermodynamics**

The thermodynamic analysis was performed to investigate the adsorption characteristics of IBP and SMX on OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. Online Supplementary Table S4 shows the thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$) affecting the adsorption process.

The $\Delta G^\circ$ values were negative for both adsorbents at 293, 298, 303, 308, and 313 K, indicating that the adsorption of IBP and SMX was spontaneous and favorable thermodynamically (Liu et al., 2020). With the increased temperature, the absolute values of $\Delta G^\circ$ increased, which implied a greater driving force of adsorption at a higher temperature. All computed $\Delta G^\circ$ were less than 20 kJ/mol, which implied the physical nature of the adsorption. It was consistent with the physisorption deduced from the D–R isotherm analysis (Chao et al., 2014).

The positive value of $\Delta H^\circ$ confirmed the typical endothermic nature of IBP and SMX adsorption process onto OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. For CH$_3$OH-OP-char/Fe$_3$O$_4,$
Table 3. Comparison of adsorption capacities for IBP and SMX removal studies reported in the literature.

| Adsorbent                          | Abbreviation | Surface area (m²/g) | Adsorption conditions | C₀ (mg/L) | qₘ (mg/g) | IBP | SMX | References                      |
|------------------------------------|--------------|---------------------|-----------------------|-----------|-----------|-----|-----|---------------------------------|
| Activated bamboo waste             | ABW          | –                   | Temperature 25°C, contact time 40 min | ≤ 100     | 278.55    | –   | –   | Reza et al. (2014)              |
| Pinewood biochar                   | –            | 1.35                | pH 3.0, temperature 35°C | 25–100    | 10.74     | –   | –   | Essando et al. (2015)           |
| Cork waste activated carbon        | CAC          | 891                 | Temperature 30°C, contact time 4 h | 20–120    | 139.2     | –   | –   | Mestre et al. (2007)            |
| Cork waste activated carbon        | CPAC         | 1060                | Temperature 30°C, contact time 2 h | ≤ 100     | 393.4     | –   | –   | Mestre et al. (2007)            |
| Rice husk activated carbon         | AC-RH        | –                   | Temperature 30°C, contact time 72 h | 239.8     | –         | –   | –   | Álvarez-Torreles et al. (2016)  |
| Metal-organic framework-derived porous carbon | PCDM-1000  | 1855                | Temperature 25°C, contact time 12 h | 5–20      | 320       | –   | –   | Bhadra et al. (2017)           |
| Zeolitic-imidazolate framework-8   | ZIF-8        | 1073                | –                     | 29        | –         | –   | –   | –                               |
| Commercial activated carbon        | AC           | 1036                | –                     | 105       | –         | –   | –   | –                               |
| Rice straw biochar                 | RS           | 29.6                | pH 6.0, temperature 25°C, 2°C, ≤ 200 | –         | 3.65      | 1.963 | –   | Li et al. (2015)                |
| Alligator flag biochar             | AF           | 7.1                 | Contact time 48 h      | 4–40      | –         | 240 | –   | Chen et al. (2015)              |
| Graphene-oxide                     | GO           | 3.58                | –                     | 5–200     | –         | 1.828 | –   | Han et al. (2013)               |
| Pine sawdust biochar               | PSB          | 297.8               | pH 4.0, temperature 25°C, contact time 24 h | 1–66.2    | 17.49     | –   | –   | Reguyal et al. (2017)           |
| Burcucumber plants biochar         | BBC-700      | 2.31                | pH 3.0, temperature 25°C, contact time 72 h | 2.5–50    | –         | 20.56 | –   | Rajapaksha et al. (2015)        |
| Burcucumber plants biochar         | BBC-700S     | 7.10                | –                     | –         | 37.73     | –   | –   | –                               |
| OP biochar                         | OP-char      | 664.92              | pH 4.5, temperature 25°C, contact time 2 h | 0.5–100   | 28.67     | 23.14 | This study |                           |
| OP biochar                         | CH3OH-OP-char/Fe₃O₄ | 857.42              | –                     | –         | 58.12     | 60.90 | This study |                           |

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the values of 134.803 kJ/mol of IBP and 150.808 kJ/mol of SMX were much higher than 40 kJ/mol, and chemisorption was involved in the adsorption process. Meanwhile, the positive values of $\Delta S$ revealed the affinity between the IBP or SMX molecules and biochar particles with an increased degree of freedom (Lonappan et al., 2018).

**Mechanism of adsorption**

The kinetic results were analyzed by the film diffusion model to understand the adsorption behavior of IBP and SMX on OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. Figure S2 shows the plot for fitting the film diffusion model, and Table S5 shows the obtained parameters. The results indicated that the plots presented some linearity, but not wholly passed through the origin. Moreover, attesting the film diffusion was involved in the adsorption process, but it was not the only rate-limiting step.

The infrared spectra of CH$_3$OH-OP-char/Fe$_3$O$_4$ were detected before and after the adsorption of IBP and SMX (see Figure 6) to study the mechanism of adsorption further. The infrared absorption peak of CH$_3$OH-OP-char/Fe$_3$O$_4$ was not apparent. The IBP and SMX curves, which showed the broad and intense absorption peaks at 3417 and 3400 cm$^{-1}$, were attributed to the $\text{–OH}$ stretching vibration. The absorption bands at 1535 and 1600 cm$^{-1}$ were assigned to the skeleton stretching vibration of the C=C bond in the aromatic ring. The absorption bands at 1137 and 730 cm$^{-1}$ were attributed to the stretching vibration of the C–N bond and the deformation vibration of the C–H bond, respectively. After the adsorption of IBP, there were three new peaks in CH$_3$OH-OP-char/Fe$_3$O$_4$, namely the $\text{–OH}$ stretching vibration peak at 3334 cm$^{-1}$, the aromatic ring C=C skeleton stretching vibration peak at 1608 cm$^{-1}$, and the Fe characteristic peak at 584 cm$^{-1}$.

The above results indicated that CH$_3$OH-OP-char/Fe$_3$O$_4$ has successfully adsorbed IBP. Correspondingly, the adsorption of SMX by CH$_3$OH-OP-char/Fe$_3$O$_4$ exhibited similar characteristics and mechanisms.

According to all the above results, the charge-assisted H-bond, hydrophobic interaction, electrostatic interaction, and $\pi–\pi$ electron donor–acceptor (EDA) interaction existed in the IBP and SMX adsorption of OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. Figure 7 shows the possible reaction mechanism. Kinetic and equilibrium study revealed that the adsorption was a pH-dependent process, and hydrophobic interactions and electrostatic interaction were mostly responsible for the adsorption of IBP and SMX.

The adsorption performance of biochar was strongly related to its structure morphology and surface properties involving surface area, pore-volume, and surface chemical groups. It was the main reason that the adsorption performance of CH$_3$OH-OP-char/Fe$_3$O$_4$ was superior to that of OP-char (Zhou et al., 2019). Hence, the flexible application of the corresponding mechanisms controlled the IBP and SMX adsorption effect (Hu et al., 2019).

**Cost of adsorbents**

OP of the cheapest variety cost about CNY 17,000/ton. The modified materials used in the work were generally available at a relatively cheap rate, CNY 1800/ton for methanol, and CNY 1600/ton for magnetite.

The finished products would cost approximately CNY 22,000/ton for CH$_3$OH-OP-char/Fe$_3$O$_4$, including all expenses (transportation, handling, electrical, energy, and drying).
Conclusion

The work is the first study on the adsorption of IBP and SMX by methanol-modified magnetic OP powder biochar (CH$_3$OH-char/Fe$_3$O$_4$). This adsorption material CH$_3$OH-char/Fe$_3$O$_4$ exhibited excellent adsorption capacity for IBP and SMX and could be separated magnetically. The maximum adsorption capacity of IBP and SMX on CH$_3$OH-OP-char/Fe$_3$O$_4$ was 58.12 and 60.90 mg/g, respectively, which increased by about 102.72–163.18% compared to that on the untreated biochar (OP-char).

Figure 6. FTIR spectra of CH$_3$OH-OP-char/Fe$_3$O$_4$ before and after adsorption of IBP and SMX.

Figure 7. Plausible adsorption behaviour of IBP and SMX onto OP-char and CH$_3$OH-OP-char/Fe$_3$O$_4$. 
Declaration of Conflicting Interests

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Supplemental Material

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