

# Microwave-assisted pyrolysis of phosphoric acid-activated Goldenberry peel powder biochar for enhancing the adsorption of trace beta-lactamase inhibitors

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**Abstract**—Novel efficient biochar of Goldenberry peels (GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>) was prepared through a microwave-assisted phosphoric acid activation method. It was characterized and used for removing two beta-lactamase inhibitors, sulbactam (SAM, first listed in Japan in 1986) and avibactam (AVI, first listed in the U.S. in 2015), from aqueous solution. Characterization confirmed that GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> displayed a high surface area (720.046 m<sup>2</sup> g<sup>-1</sup>), more abundant pore structure, smaller particle size, and higher thermal stability. The experimental results showed that the adsorption of the two antibiotics was a spontaneous, favorable, and endothermic process, highly dependent on solution pH. A contact time of 60 min assured equilibrium, and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> followed pseudo-first-order kinetics (R<sup>2</sup>=0.9950-0.9977). Furthermore, the adsorption capacities of GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> for SAM and AVI were 211.86 and 198.81 mg g<sup>-1</sup>, respectively, and the performance was better than that of unmodified biochar. Microscopically, the main mechanism could be explained by  $\pi$ - $\pi$  electron donor-acceptor interaction, hydrogen bonding interaction,  $\pi$ -hydrogen bonding, hydrophobic interaction, and electrostatic interaction. The study demonstrates that the microwave-assisted H<sub>3</sub>PO<sub>4</sub> activation method could produce biochar, and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> was confirmed to be a low-cost and high-efficiency adsorbent for removing beta-lactamase inhibitors from medical wastewater.

Keywords: Microwave-assisted, Biochar, Beta-lactamase Inhibitors, Adsorption, Goldenberry Peel

## INTRODUCTION

As one of the most important medical discoveries in early last century, antibiotics are widely used in medicine, modern aquaculture, and livestock production to prevent and treat bacterial infectious diseases [1,2]. Antibiotic residues are now regarded as emerging pharmaceutical contaminants in the water system [3]. In the past few decades, an increasing body of evidence has shown that antibiotics entering the various water environmental contexts, such as sewage or municipal wastewater, surface water, groundwater, and even drinking water, can threaten the ecological environment and even result in drug resistance of humans and animals [1,4]. Therefore, the World Health Organization (WHO) has categorized their spread as a serious public health problem, which has received extensive concern [5].

Beta-lactamase inhibitors, as a new class of beta-lactam antibiotic whose molecular structure contains a beta-lactam ring, are widely used to prevent and treat bacterial infections. Sulbactam sodium (SAM), invented by Barth at Pfizer in 1978, is a competitive, irre-

versible beta-lactamase inhibitor that acts as a synergist against Gram-positive bacteria and is effective for treating meningococcal and gonococcal diseases [6]. Avibactam sodium (AVI) is a novel synthetic beta-lactamase inhibitor without containing a beta-lactam core and has just come on the market for treating bacterial infections comprising Gram-negative organisms [7,8]. However, the presence of SAM and AVI in aquatic environments, even in low concentrations, can lead to the development of antibiotic-resistant bacteria, which significantly increases the potential risk to human health [9]. As a result, removing SAM and AVI from aquatic environments is particularly important at the societal level.

There are many methods for removing antibiotics from sewage water, such as physical treatment (e.g., filtration and flocculation), chemical treatment (e.g., photochemical degradation and ozonation), physico-chemical treatment (e.g., membrane separation and adsorption), and biological treatment (e.g., biodegradation and activated sludge) [10]. Adsorption, which is the transfer of a compound from the liquid phase to the solid phase, as been recognized as one of the most highly efficient techniques for removing low concentration antibiotics in practical applications, because of low expense, high efficiency, and easy operation [11].

In the research practice, the key to adsorption technology is to develop novel adsorbents. So far, biochar as an excellent adsorbent

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has come into notice due to its high cation exchange capacity, large porous structure, and abundant functional groups [12]. It is a thermal degradation product of various biomass, such as pine sawdust [13], rice straw [14], bamboo [15], and other crops, under an oxygen-limited atmosphere. Previous studies have shown that biochar is an effective adsorbent for antibiotics such as amoxicillin [16], tetracycline [16,17], chloramphenicol [17], cephalexin [18], sulfonamide [19], and oxytetracycline [20]. Note that some references have reported that biochar can adsorb beta-lactamase antibiotics in an aqueous solution, e.g., biochar from cornstalk can remove amoxicillin from aqueous solutions [21]. However, there are still few investigations in this area. It can be expected that biochar can significantly affect or even dominate the sorption of beta-lactamase inhibitors such as SAM and AVI [19].

At present, our research group has focused on the preparation of biochar from agricultural wastes with microwave-assisted chemical modification technology. It offers many unique superiorities, including quick start/stop, homogeneous non-contact heating, higher reaction rates, and better selectivity [22,23]. So far, various agricultural wastes such as sugarcane bagasse [24], pine sawdust [25], rice husk [26], and rapeseed shell [27] have been used as raw materials for preparing biochar using this technology.

Goldenberry, the common name of *Physalisalkengi L. var. franchetii* (Mast.) Makino, is an annual plant belonging to the Solanaceae family that is native to Heilongjiang, Jilin, Liaoning, and northeast Inner Mongolia in China. The peel of plant berries, considered a residue without a right destination, can cause blockages in waterways, especially during the rainy season. This high volume waste consists of appropriate lignocellulose. Thus, it can be potentially used as the source material of biochar.

New biochar from Goldenberry peels (GBP) was prepared by microwave-assisted chemical modification method for the first time in this work. It was characterized and tested for adsorption properties of beta-lactamase inhibitors, SAM and AVI (a class of emerging organic contaminants), from aqueous solutions. The specific objectives were to determine the effect of pH, contact time, initial antibiotic concentration, and temperature to understand SAM and AVI adsorption and mechanisms onto biochar. The corresponding adsorption kinetics, isotherms, and thermodynamics were also systematically evaluated. To the best of our knowledge, this is an innovative work, and its research findings will contribute to an improved understanding of the adsorption behavior of beta-lactamase inhibitors on biochar.

## EXPERIMENTAL

### 1. Chemicals

For two Beta-lactamase inhibitors, SAM (>99.0% purity, CAS 69388-84-7) was purchased from Zhejiang Shengtong Biotechnology Co., Ltd. (Jinhua, China), and AVI (>98.0% purity, CAS 1192491-61-4) was obtained from Enantiochem Corporation Ltd. (Zhongshan, China). Both compounds were used as received without any further purification. Their chemical structures and detailed physicochemical parameters are summarized in Table S1 (Supplementary Information). All other chemicals, including adjusted pH of sample solutions and analysis of SAM and AVI, were supplied by

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), with analytical or HPLC grade agents used. All work solutions were prepared in ultra-pure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ,  $25^\circ\text{C}$ ). Stock solutions of SAM ( $1,000 \text{ mg L}^{-1}$ ) and AVI ( $500 \text{ mg L}^{-1}$ ) were prepared in 1% methanol and kept in amber-colored bottles below  $4^\circ\text{C}$ . The desired SAM and AVI concentrations used in the adsorption experiment were obtained by successive dilution of the pre-made stock solutions.

### 2. Preparation of Biochar by Microwave-assisted Treatment

GBP was obtained from a farmer's market in Anshan, Liaoning, China. The fruits were isolated by hand, and the peels were repeatedly rinsed with ultra-pure water to remove impurities. Then, they were dried in the shade for 10 days and milled until obtaining a particle size of 60 mesh, and finally stored in a tightly closed bottle for further use.

Biochar was prepared using a full-automatic microwave (model MDS-6G, Shanghai Sineo Microwave Chemistry Technology Co., Ltd., China). The process details were as follows: 0.5-g raw material was put in a 100-mL Teflon PFA (Perfluoroalkoxy) vessel, and 10-mL  $\text{H}_3\text{PO}_4$  solution or ultra-pure water was added. The reaction tank containing the sample was placed into the microwave reactor by setting the temperature gradients of 150, 180, and  $210^\circ\text{C}$ , and the reaction time of 30 min in total. At the end of this process, the reactor was withdrawn and then cooled to room temperature. The mixture was filtered and the desired solid product was purified with ultra-pure water until the pH value reached neutral. Finally, modified and unmodified biochar was dried in vacuum at  $50^\circ\text{C}$  for 6 h, denoted as  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  and  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , respectively. After weighing, the yields of the two biochars were about 51.23 and 42.50 wt%, respectively.

### 3. Characterization of Biochar

The biochar particle size and size distribution were measured by a laser particle analyzer (Malvern model Mastersizer 3000, England). The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of two biochars was measured by a mass titration method using a digital pH meter (Rex Electric Chemical model PHS-3C, China). Ash content was determined by heating biochar in a muffle furnace (model GWL-XB, Luoyang Juxing Kiln Co., Ltd., China) at  $750^\circ\text{C}$  for 6 h. C, H, and N contents were performed using an elemental analyzer (Elementar Vario MICRO cube, Germany), and O content was calculated based on a mass balance. P content in biochar was analyzed using an inductively coupled plasma optical emission spectrometer (Jena model PQ9000, Germany). The thermal stability of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  and  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  was examined using a thermogravimetric analyzer (Netzsch model STA 449 F5 Jupiter, Germany) under  $\text{N}_2$  gas at  $25\text{-}1,000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . Textural characterization including the BET surface areas and pore structure analysis results of biochar samples was evaluated using  $\text{N}_2$  gas adsorption/desorption isotherms at 77 K on a surface area analyzer (Quantachrome Autosorb iQ2, USA). The surface morphologies and elemental composition of prepared adsorbents were investigated by scanning electron microscopy (Zeiss model Sigma 500, Germany) equipped with energy dispersive spectroscopy (Bruker model XFlash 6-100, Germany). Finally, the potential changes in surface functional groups of adsorbents before and after adsorption were recorded and studied by a Fourier transform infrared (FTIR) spectrometer (Thermo model Nicolet 380, USA) to explain the possible adsorp-

tion mechanism.

#### 4. Batch Adsorption Studies

In a typical adsorption experiment, a 25-mg biochar adsorbent was mixed with 50-mL beta-lactamase inhibitor aqueous solutions on a 150-mL stopper conical flask covered with tin foil paper. The flasks were shaken on a thermostatic orbital shaker (model SHZ-82B, Shanghai Jingaltar Instrument Manufacturing Co., Ltd., China) at 100 rpm, and kept constant throughout the work. The suspension pH values were adjusted by dilute HCl or dilute NaOH solution. After adsorption equilibrium, the suspensions were immediately filtered through a 0.45- $\mu\text{m}$  filter membrane, the remaining concentrations of SAM and AVI were monitored using a UV-vis spectrophotometer (Macy China Instruments Inc model UV-1300, China) at their maximum absorbance wavelength of 230 and 210 nm, respectively. Each experiment was performed in triplicate with relative standard deviations less than 5.0%. The equilibrium adsorption capacity of SAM and AVI,  $q_e$  ( $\text{mg g}^{-1}$ ), could be determined using the following formula:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium antibiotics concentrations ( $\text{mg L}^{-1}$ ), respectively;  $V$  is the solution volume (L);  $W$  the weight of prepared biochar (mg).

#### 5. Adsorption Kinetics, Isotherms, and Thermodynamics

Many studies have used methods with much higher concentrations ( $\text{mg L}^{-1}$ ) than that of actual environmental samples ( $\mu\text{g L}^{-1}$  or  $\text{ng L}^{-1}$ ) to prove the effectiveness of biochar [19,28,29]. Batch experiments were performed to compare the adsorption of SAM and AVI onto the obtained biochars. First, the effect of varying pH on the adsorption of SAM and AVI onto biochar was investigated at pH 1.0-13.0, using an initial antibiotic concentration of 25  $\text{mg L}^{-1}$  and a contact time of 180 min at 25 °C. The determined optimum pH was used in all the following experiments. For the kinetic study, the pre-determined time was controlled to be 0 to 300 min; initial antibiotics concentrations were maintained at 25  $\text{mg L}^{-1}$ ; the temperature was kept constant at 25 °C. In isotherm experiments, the initial antibiotics concentrations were in the range of 0.5 to 100  $\text{mg L}^{-1}$  for each biochar. Other operating conditions were the same as above (with a contact time of 180 min at 25 °C). Further-

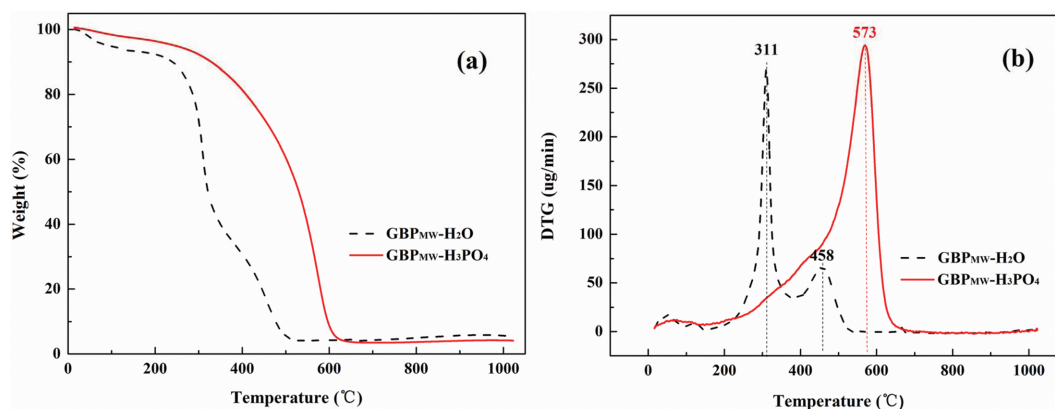
**Table 1. The kinetic, isotherm models, and thermodynamics equations used in this study**

Models	Expression
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Film diffusion	$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_f t + A$
Intra-particle diffusion	$q_t = k_s t^{1/2} + C$
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_L K_L} + \frac{C_e}{q_L}$
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$
Temkin	$q_e = \frac{RT}{\beta_T} \ln(K_T C_e)$
Dubinin-Radushkevich	$\ln q_e = \ln q_D - \left(\frac{RT}{\sqrt{2}E}\right)^2 \cdot \left(\ln\left(1 + \frac{1}{C_e}\right)\right)^2$
Van't Hoff	$K_C = q_e / C_e$ $\Delta G^\circ = -RT \ln K_C$ $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ $\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

more, the thermodynamics experiments were performed at controlled temperatures of 20, 25, 30, 35, and 40 °C (with a contact time of 180 min and an initial antibiotics concentration of 25  $\text{mg L}^{-1}$ ).

#### 6. Data Analysis

The experimental equilibrium data were analyzed to investigate the mechanisms of the SAM and AVI adsorption process using four adsorption kinetic models (pseudo-first-order, pseudo-second-order, intra-particle diffusion, and liquid film diffusion kinetic models), four most common adsorption isotherm models, (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models), and the three thermodynamic parameters (the standard Gibbs free energy ( $\Delta G^\circ$ ), the enthalpy change ( $\Delta H^\circ$ ), and the entropy change ( $\Delta S^\circ$ )). The expressions for the employed models and equations are summarized in Table 1.



**Fig. 1. (a) TG and (b) DTG profiles of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ .**

## RESULTS AND DISCUSSION

## 1. Characterization of Biochar Adsorbents

The pyrolytic characteristics of biochar before and after modification were monitored by thermal gravimetric-derivative thermogravimetric (TG-DTG) analysis at 1,000 °C (see Fig. 1 for the results). Fig. 1(a) shows that the final retention rates of 5.22 and 4.06% for  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  imply the continuous decomposition of hemicellulose and cellulose in biomass samples, respectively [22]. In the DTG curve of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , the first decomposition peak at 311 °C could be associated with the removal of hydroxyl groups of biomass (cellulose, hemicellulose, and lignin). The second broad peak at 458 °C was chiefly attributed to the decomposition of more heat-resistant components such as carboxyl or carbonyl groups during carbonization. After modification, only a new decomposition process (at 573 °C) emerged in the DTG curve of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  due to the cross-linking reaction between phosphoric acid and biomass. Thus, the stability of biochar was improved.

Table S2 and Fig. S1 show the particle size distribution of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . The mean particle sizes (D [3,2] and D

[4,3]) of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  are 35.4 and 72.4  $\mu\text{m}$  with 16.2, 62.3, and 140  $\mu\text{m}$  for Dx (10), Dx (50), and Dx (90), respectively, which are much smaller than those of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  (72.4, 244, 40.8, 202, and 495  $\mu\text{m}$  for D [3,2], D [4,3], Dx (10), Dx (50), and Dx (90), respectively). This indicates that the modification of phosphoric acid can significantly reduce the particle size of biochar.

Table 2 shows some of the physical and chemical properties of two types of biochars, including  $\text{pH}_{\text{pzc}}$  (with pH at the point of zero charge), elemental composition (%P, %C, %H, %O, and %N), and porous structure (BET surface area and pore volume). In Table 2, the  $\text{pH}_{\text{pzc}}$  of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  are 5.60 and 4.55, respectively, suggesting that the biochar surface is positively charged at solution pH below  $\text{pH}_{\text{pzc}}$  and negatively charged at pH above  $\text{pH}_{\text{pzc}}$ .

Elemental analysis indicated that  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  were dominated by C (55.07 and 63.27%, respectively), followed by O (31.32 and 25.76%) and contained very little N (less 3.0%). Meanwhile, the measured %P using acid digestion in  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  was negligible while  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  had 11.11% of %P. The above results showed that two types of biochar were carbon-rich materials,

Table 2. The information of elemental composition of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$

Adsorbent		$\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$	$\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$
Elemental compositions (%, mass based)	%C	55.07	63.27
	%H	6.37	5.53
	%N	2.80	1.10
	%S	0.30	0.34
	%O	31.32	25.76
	%P	N.D	0.58
Atom ratio	H/C	0.12	0.087
	O/C	0.57	0.41
Ash (%)		4.14	4.00
BET surface area ( $\text{m}^2 \text{g}^{-1}$ )		368.670	720.046
Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )		0.254	0.380
Micropore volume ( $\text{cm}^3 \text{g}^{-1}$ )		0.110	0.243
Mesopore volume ( $\text{cm}^3 \text{g}^{-1}$ )		0.144	0.137
Average of pore width (nm)		2.759	2.108
$\text{pH}_{\text{pzc}}$		5.60	4.55

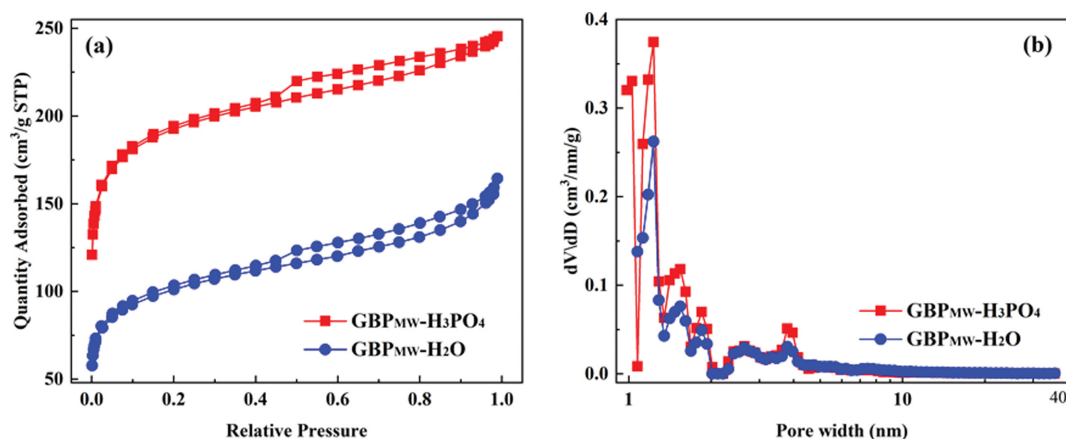


Fig. 2. (a) Nitrogen adsorption-desorption isotherms, (b) pore size distribution curves of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ .

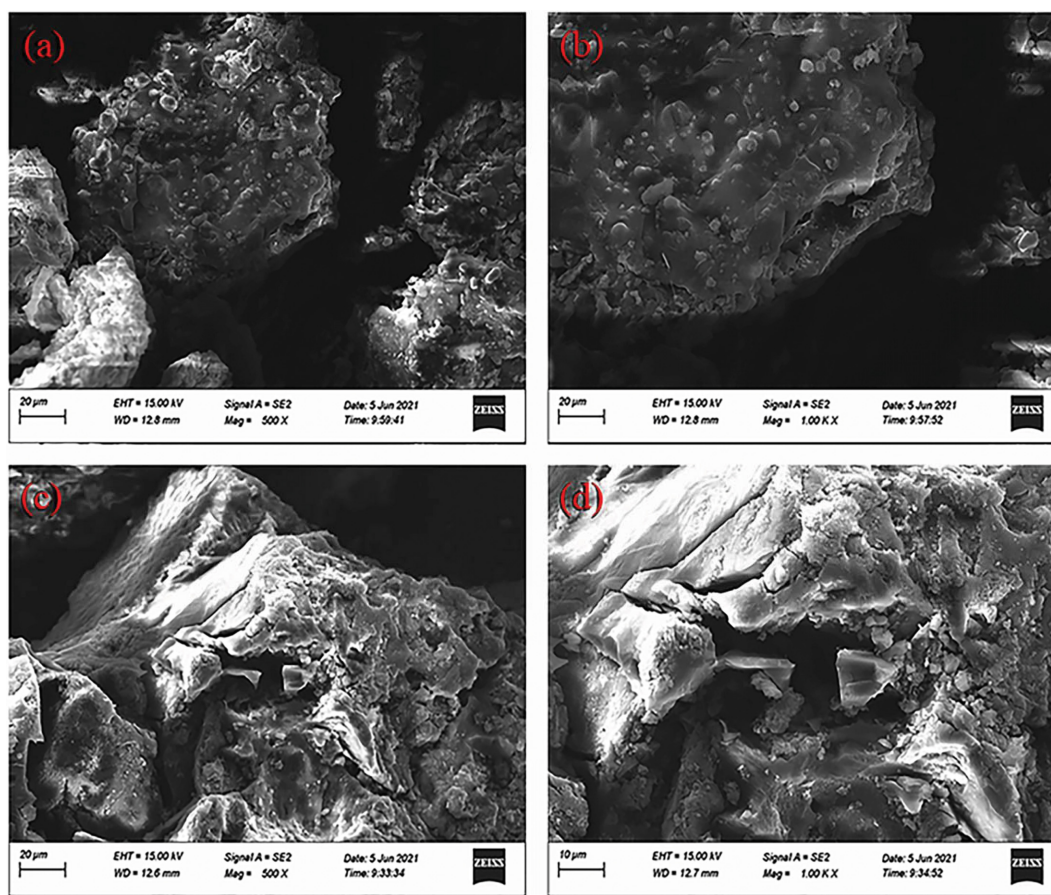


Fig. 3. SEM images of (a) and (b)  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , (c) and (d)  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ .

and P in  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  mainly came from the modifier, namely phosphoric acid. Besides, the r H/C and O/C values of 0.087 and 0.41 for  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  were relatively lower than those (0.12 and 0.57) of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , respectively, indicating that the biochar after microwave pyrolysis was highly carbonized and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  had a higher hydrophobicity than  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ . After  $\text{H}_3\text{PO}_4$  activation, the BET surface area, micropore volume, and mesopore volume of prepared biochar increased from  $368.670 \text{ m}^2 \text{ g}^{-1}$ ,  $0.110 \text{ cm}^3 \text{ g}^{-1}$ , and  $0.144 \text{ cm}^3 \text{ g}^{-1}$  to  $720.046 \text{ m}^2 \text{ g}^{-1}$ ,  $0.243 \text{ cm}^3 \text{ g}^{-1}$ , and  $0.137 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Thus, microwave radiation was favorable for the hydrolysis of GBP, and  $\text{H}_3\text{PO}_4$  activation could make biochar have a large number of pores and channels and convert a small fraction of mesopores into micropores, which provides a basis for the superior adsorption performance of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  [30].

Figs. 2(a) and (b) show the nitrogen adsorption-desorption isotherms and pore size distributions of two types of biochar, respectively. According to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the measured isotherms exhibit a type I pattern with the type H4 hysteresis loop, which is a typical feature of biochar adsorbent for micropore and mesopore filling [31]. The preparation of biochar-rich microporous structures in the work is particularly beneficial to the adsorption of low- to medium-sized pharmaceutical molecules, which has also been discussed in several previous studies [13,32,33].

The surface morphology and elemental composition of  $\text{GBP}_{\text{MW}}$

$\text{H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  were examined by SEM equipped with an EDX system. Fig. 3 illustrates two successive magnifications ( $\times 500$  and  $\times 1,000$ ) of the tested samples. The two types of biochar are porous, and  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  shows an irregularly smooth surface and chunked book-like layer structure with groove-like valleys on its side. Compared with  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , the surface texture of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  becomes rougher, and the pores develop into the interior with an abundant ravine. The pores can be partly attributed to phosphoric acid etching during microwave activation and can serve as an active adsorption site to enable beta-lactamase inhibitors molecules into biochar. Moreover, the element composition proportion (O and P) of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  is determined by EDS elemental mapping. Fig. S2 shows the content ratio of O to P is 10 : 1, indicating that P has significant residues in modified biochar as an activator.

## 2. Effect of pH on the Adsorption of SAM and AVI

Solution pH can significantly affect the adsorption process because it changes the ionization forms of adsorbates and the surface charge density of biochar [28,34]. Fig. 4 shows the effects of initial solution pH on the adsorption capacities of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  for SAM and AVI.  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  and  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  present a similar trend, but the adsorption capacity of the former is much higher than that of the latter. Their adsorption increases with initial solution pH from 1 to 4, and the maximum adsorption capacities of SAM and AVI ( $48.57$  and  $49.48 \text{ mg g}^{-1}$  for  $\text{GBP}_{\text{MW}}$

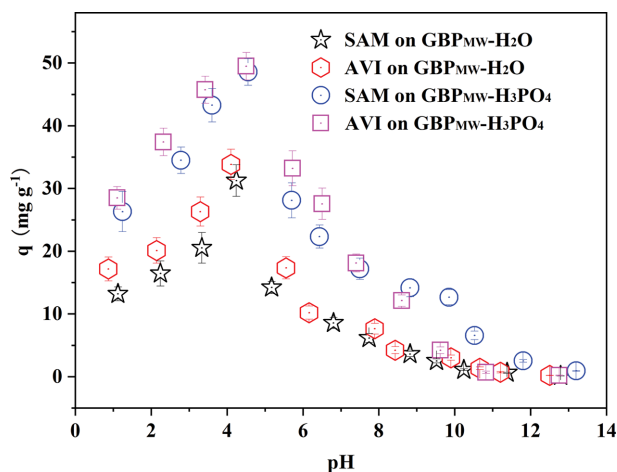


Fig. 4. Effect of equilibrium pH on adsorption of SAM and AVI by  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . Conditions: contact time 120 min, temperature 25 °C and initial drug concentrations 25 mg L<sup>-1</sup>.

$\text{H}_3\text{PO}_4$ , and 31.25 and 33.82 mg g<sup>-1</sup> for  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ ) occur at about pH 4.0. However, it decreases slightly as pH further increases, and the adsorption capacity sharply declines when pH exceeds 8.0. Combined with the zero-point potential analysis, electrostatic interaction may be one of the adsorption mechanisms.

The  $\text{pH}_{\text{PZC}}$  of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  and  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  was found around 4.0-5.0, suggesting that the surface of two biochars is electropositive when  $\text{pH} < 4.0$ , and then converted to the electronegative state as the pH value increases. SAM and AVI are negative ions in aqueous solutions according to their structural properties. When the pH value of the solution is lower than 4.0 ( $\text{pH}_{\text{PZC}}$ ), the electrostatic interaction between adsorbate and biochar is mainly electrostatic attraction, thus with remarkable adsorption. Interestingly, excellent adsorption near to  $\text{pH}_{\text{PZC}}$  indicates additional adsorption mechanisms, i.e., hydrogen bonding, electron donor-acceptor, and  $\pi$ - $\pi$  dispersion interaction [34]. It can be summarized as follows: (1) The presence of oxygen-containing groups on the biochar facilitates the adsorption through hydrogen bonding [35]; (2) carboxyl groups on the biochar can be used as electron acceptors, while -OH and P-O groups are used as electron donors [36]. After pH passes the optimal value, the negative charge on the surface of two types of biochar gradually increases, so adsorption is less favorable due to increased electrostatic repulsion [28]. It can be hypothesized that abundant hydroxide ions ( $\text{OH}^-$ ) have a competitive effect with pharmaceutical anions under alkaline conditions, resulting in a substantial decrease of adsorption capacity [11,37]. On the whole, the changes in pH have predominant effects on the adsorption of SAM and AVI, depending on the balance between attractive and repulsive forces. The adsorption mechanism will be discussed in detail in a separate chapter. Therefore, pH 4.0 is considered as the optimum and selected for the subsequent experiments.

### 3. Adsorption Kinetics

Fig. 5 shows the evolution of SAM and AVI adsorption versus time onto  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . All adsorption processes reach equilibrium in a really short time, and approximately

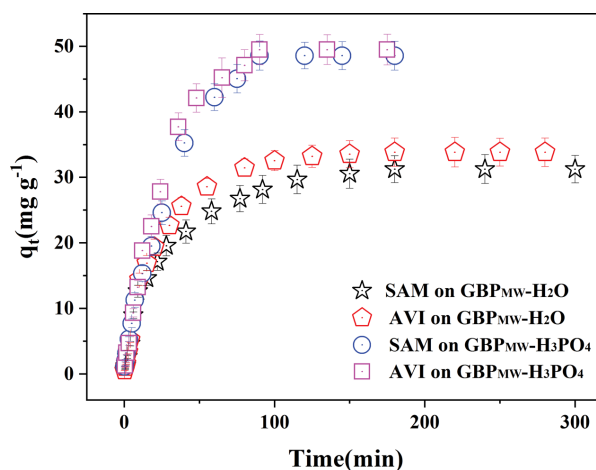


Fig. 5. Effect of contact time on adsorption of SAM and AVI by  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . Conditions: pH 4.0, temperature 25 °C and initial drug concentrations 25 mg L<sup>-1</sup>.

80-90% of equilibrium SAM and AVI uptake is adsorbed within the first 60 min. This excellent performance can be ascribed to the abundant availability of active sites and the high driving force in the mass transfer. Adsorption is presumed to occur on the external surface of biochar [13,38,39]. Afterward, adsorption gradually increases and finally reaches equilibrium within 180 and 90 min for  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ , respectively.

Adsorption kinetic models can evaluate the relationship between the structure of biochar and adsorption performance in terms of the order of rate constants [10,40]. Table S3 and Fig. S3 present the linearized fitting forms of pseudo-first-order and pseudo-second-order kinetic models as well as the kinetic parameters and the correlation coefficients ( $R^2$ ) of each model.

For  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ , the fitting of the pseudo-second-order model fails because of the low  $R^2$  ( $R^2=0.9285\text{-}0.9747$ ) and large  $\Delta q$  (%) ( $\Delta q=22.31\text{-}37.50\%$ ). Compared with the pseudo-second-order model, the pseudo-first-order model provides a more comprehensive reflection of the adsorption mechanism of SAM and AVI due to high  $R^2$  ( $R^2=0.9950\text{-}0.9977$ ) and low  $\Delta q$  (%) ( $\Delta q=1.43\text{-}1.77\%$ ). For  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$ , the experimental data fit well with pseudo-first-order and pseudo-second-order kinetic models, indicating both physisorption and chemisorption mechanisms occur for this adsorption system [41]. The above results prove that physisorption is the rate-controlling step, and hydrophobic interaction and  $\pi$ - $\pi$  dispersion interaction may act simultaneously in adsorbing SAM and AVI on biochar.

### 4. Adsorption Isotherm

Typical isotherm models, Langmuir, Freundlich, Temkin, and D-R models, were used to correlate the equilibrium isotherm data obtained from adsorbing SAM and AVI onto  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  for the initial concentrations of 0.5-100 mg L<sup>-1</sup>. Table S4 summarizes the fitting parameters ( $q_L$ ,  $K_L$ ,  $K_F$ ,  $n$ ,  $K_T$ ,  $\beta_T$ ,  $q_D$ , and  $E$ ) and correlation coefficients ( $R^2$ ) calculated from four equations of the model.

Langmuir and Freundlich equations provided the optimal fitting results, followed by Temkin and D-R models. However, the fitting

**Table 3. Comparison of the maximum adsorption capacities for beta-lactam antibiotics with various porous materials**

Adsorbent	Abbreviation	Beta-lactam antibiotics	$q_m$ (mg g <sup>-1</sup> )	References
Goldenberry peel powder	GBP <sub>MW</sub> -H <sub>2</sub> O	Sulbactam	42.50	This study
		Avibactam	49.83	
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	Sulbactam	211.86	
		Avibactam	198.81	
Ion exchange resin	A microparticles		962.07	[43]
	T1 microparticles	Cefotaxime	1,029.46	
	T2 microparticles		980.39	
Activated sludge	N/A		330	[44]
<i>R. arrhizus</i>	N/A	Penicillin G	459	
Activated carbon	N/A		375	
Giant reed-carbon	KAC		345.4	
Commercial carbon	CAC	Amoxicillin	250.7	[3]
Gain reed	N/A		75.8	[45]
Montmorillonite organoclay	DDAB-MT	Penicillin G	23.0	
		Nafcillin	25.4	
		Cefotaxime	26.2	
CdS-MWCNT nanocomposites	N/A	Cefotaxime	37.714	[46]
		Cefradine	40.525	
		Cefazolin	34.512	
NH <sub>4</sub> Cl-induced activated carbon	NAC	Amoxicillin	438.6	[47]
Standard activated carbon	SAC		261.8	

of the data using the Temkin ( $R^2=0.8063-0.9561$ ) and D-R ( $R^2=0.8297-0.9028$ ) isotherm models was not ideal; thus, it was not considered. For GBP<sub>MW</sub>-H<sub>2</sub>O, the Langmuir model ( $R^2=0.9983$  for SAM and 0.9967 for AVI) fit the data of adsorption isotherms better than the Freundlich model ( $R^2=0.9566$  for SAM and 0.9490 for AVI), implying the homogeneous and monolayer nature of SAM and AVI adsorption on the biochar surface. However, for GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>, the Freundlich model was more suitable for adsorption ( $R^2=0.9937$  for SAM and 0.9917 for AVI) than the Langmuir model ( $R^2=0.9623$  for SAM and 0.9555 for AVI), suggesting multiple adsorption processes and heterogeneous adsorption sites. Based on the Langmuir model, the maximum adsorption capacities of SAM and AVI on GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> were reported as 211.86 and 198.81 mg g<sup>-1</sup>, respectively. Biochar prepared by microwave activation could improve its adsorption capacity for SAM and AVI by 4 and 5 times, respectively. Overall, the adsorption of GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> was more diversified than GBP<sub>MW</sub>-H<sub>2</sub>O by comparing the parameters between the two types of biochar [42]. Table 3 compares the maximum adsorption capacity of beta-lactam antibiotics with some other adsorbents reported in the literature. According to the authors, GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> can be considered an efficient and promising adsorbent for removing beta-lactamase inhibitors.

### 5. Adsorption Thermodynamics

The thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) were used to explore the spontaneity and characteristics of the adsorption process. Table S5 summarizes the calculated values.

All  $\Delta G^\circ$  values were negative at 293, 298, 303, 308, and 313 K, indicating that the adsorption of SAM and AVI by GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> and GBP<sub>MW</sub>-H<sub>2</sub>O was spontaneous and favorable at the studied temperature. Meanwhile, as the adsorption temperature increased,

$\Delta G^\circ$  values became more negative, confirming that the adsorption of SAM and AVI was more likely to occur at higher temperature. Furthermore, the positive  $\Delta H^\circ$  values revealed the typical endothermicity of adsorbing SAM and AVI onto GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> and GBP<sub>MW</sub>-H<sub>2</sub>O [48]. Positive  $\Delta S^\circ$  values showed the increased randomness of beta-lactamase inhibitors' adsorbed state at the adsorbent-solution interface and the degree of freedom in the adsorption process [30].

### 6. Mechanism of Adsorption

The kinetic data were analyzed using the intra-particle diffusion model and liquid film diffusion model to determine the type of rate-controlling step. Table S6 and Table S7 list the plots obtained for models and all parameters ( $k_p$ ,  $A$ ,  $k_{s1}$ ,  $k_{s2}$ ,  $k_{s3}$ ,  $C_1$ ,  $C_2$ , and  $C_3$ ).

In Fig. S4, all intra-particle diffusion plots exhibit multilinearity, and these three linear segments do not pass through the origin, suggesting that diffusion within the channel is involved in the adsorption process, and the diffusion steps are controlled by other adsorption processes, such as boundary layer diffusion, surface adsorption, and external mass transfer.

Subsequently, the liquid film diffusion kinetic model is used to predict the possible diffusion mechanism. In all cases, the plots present good linearity ( $R^2>0.99$ ) and the intercept is almost zero ( $-0.150\sim+0.025$ ), indicating that the rate-limiting step is mainly the diffusion of antibiotic molecules on the biochar surface from the bulk liquid phase [10]. Similar results were obtained by Yan et al. [49] who used ZnCl<sub>2</sub> modified biochar derived from aerobic granular sludge to remove tetracycline.

Some literature has reported that the adsorption of antibiotic molecules onto the adsorbents is closely related to the active groups and chemical bonds on their surface [50-52]. The FTIR spectra of

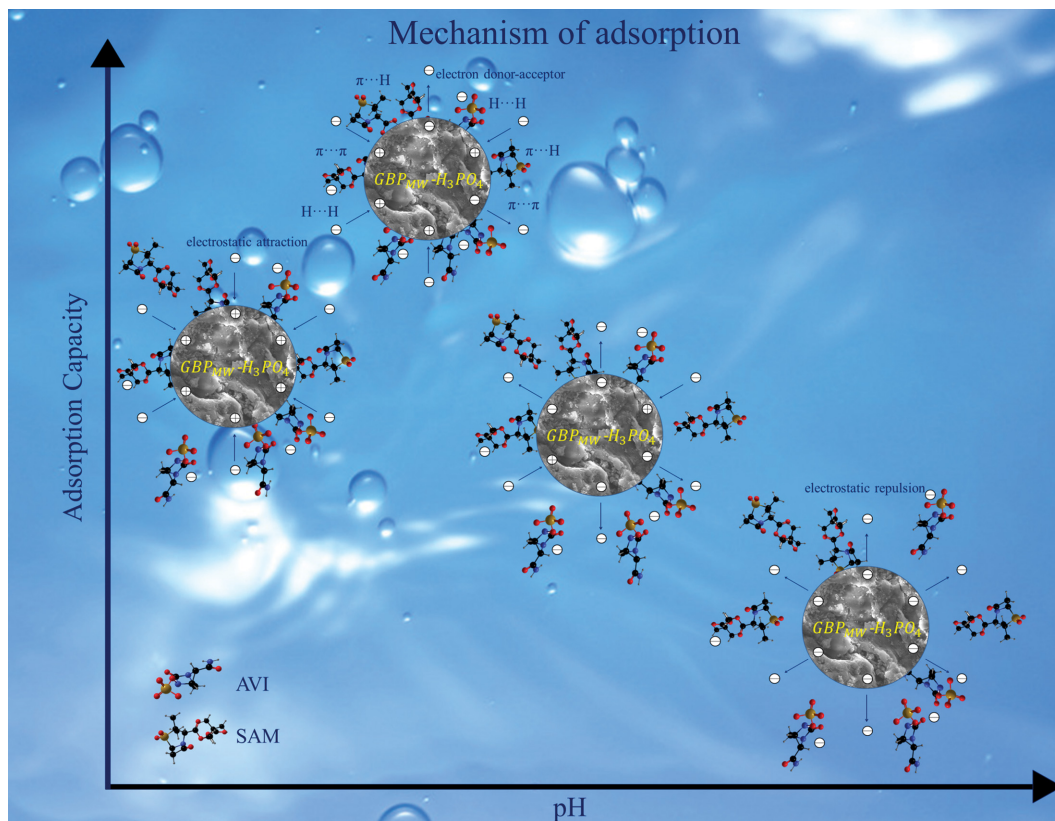


Fig. 6. The possible adsorption mechanism for SAM and AVI on GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>.

GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> before and after adsorption of SAM and AVI were analyzed in the wavelength of 4,000-400 cm<sup>-1</sup> to elucidate the adsorption mechanism of beta-lactamase inhibitors on the biochar (see Fig. S5 for results).

From the FTIR spectrum, the characteristic peaks of SAM were mainly located at 1,000-1,700 cm<sup>-1</sup>. Namely, the peak at 1,654 and 1,401 cm<sup>-1</sup> corresponded to the amino group and the sulfonyl group, respectively, and the peak near 1,152 cm<sup>-1</sup> correlated to the ether bond. The spectrum of AVI was characterized by three bands at 1,600-1,700, 1,200-1,300, and 1,000-1,100 cm<sup>-1</sup>. The peak at 1,754 and 1,678 cm<sup>-1</sup> was ascribed to the C=O stretching of ester and amide. The peak at 1,243 cm<sup>-1</sup> was ascribed to the C-O stretching, and the peak at 1,032 cm<sup>-1</sup> corresponded to C-N stretching. After adsorbing SAM or AVI by GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>, the main functional groups shifted at 3,143-3,461, 1,638-1,651 cm<sup>-1</sup>, and 1,402-1,407 cm<sup>-1</sup>, which represented O-H bond, C=C bond, and C-H bond stretching vibrations, respectively. Thus, the shifts of these peaks reflected the significant contribution on adsorption sites of these functional groups on the GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> surface [53]. From the above analysis and discussion,  $\pi$ - $\pi$  electron donor-acceptor (EDA) interaction, hydrogen bonding interaction, and  $\pi$ -hydrogen bonding could be the main adsorption mechanism.

In addition to the above mechanisms, the adsorption of SAM and AVI on GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> was regulated by hydrophobic interaction and electrostatic interaction. Both interactions played an important role because SAM and AVI adsorption was a pH-dependent process (see Section 3.2). Simultaneously, the proposed adsorp-

tion mechanism was consistent with the results of the kinetic and thermodynamic analysis. Fig. 6 shows a possible reaction mechanism of GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub> adsorbing SAM and AVI.

### 7. Desorption and Reuse of Biochar

From an economic perspective, the availability of reusable biochar is an important factor in reducing the costs of the process [54]. The adsorption/desorption (A/D) experiments were performed

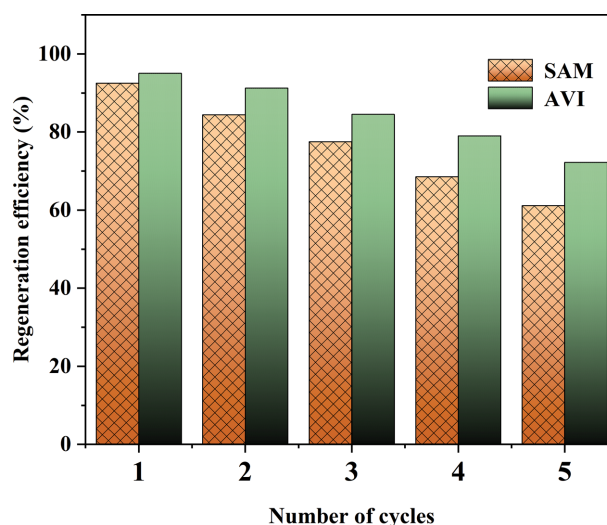


Fig. 7. Adsorption-desorption cycles of GBP<sub>MW</sub>-H<sub>2</sub>O and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>.

five times using the same biochar, and methanol was selected as a regeneration agent for each cycle experiment to explore the regeneration of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . Fig. 7 shows the variation curve of the adsorption capacities of SAM and AVI adsorbed on  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  through five sequential A/D cycles. The regeneration efficiency decreases slowly during five cycles, indicating the material is an efficient adsorbent with excellent stability and reusability.

### 8. Cost of Adsorbents

GBP of the cheapest variety costs about CNY 320/ton. The modified material used in the work was phosphoric acid at CNY 5,000/ton. The finished products cost approximately CNY 1,100/ton for  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  including all expenses (transportation, handling, electrical, energy, and drying). Compared with the traditional adsorption material activated carbon (at least CNY 3,000/ton), the cost of biochar prepared by microwave was much lower and the production process was more environmentally friendly.

### CONCLUSIONS

$\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  with high adsorption capacity for SAM and AVI was prepared by the microwave-assisted  $\text{H}_3\text{PO}_4$  activation method for the first time. A large amount of phosphorus-containing functional groups was introduced on the biochar surface, which promoted the adsorption affinity toward SAM and AVI. Moreover, the BET surface area increased from 368.670 to 720.046  $\text{m}^2 \text{g}^{-1}$ . Kinetics, isotherms, and thermodynamic studies exhibited that the adsorption process was spontaneous and endothermic, mainly affected by physisorption, and the rate of this process was controlled by multiple steps. Moreover, the adsorption mechanism, involving electrostatic interaction,  $\pi\text{-}\pi$  EDA interactions, hydrophobic force, and hydrogen bonds, depended on the changes in solution pH values. Most significantly,  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  could be regenerated and reused for removing SAM and AVI over five recycle steps. Based on all of these superior properties, the newly developed  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  as an effective adsorbent shows great potential application in removing emerging organic contaminants as beta-lactamase inhibitors from wastewater.

### ACKNOWLEDGEMENTS

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### DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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## Supporting Information

### Microwave-assisted pyrolysis of phosphoric acid-activated Goldenberry peel powder biochar for enhancing the adsorption of trace beta-lactamase inhibitors

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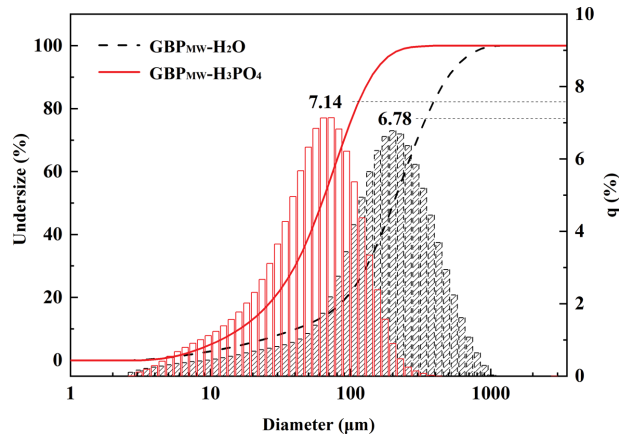


Fig. S1. Particle size distribution of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ .

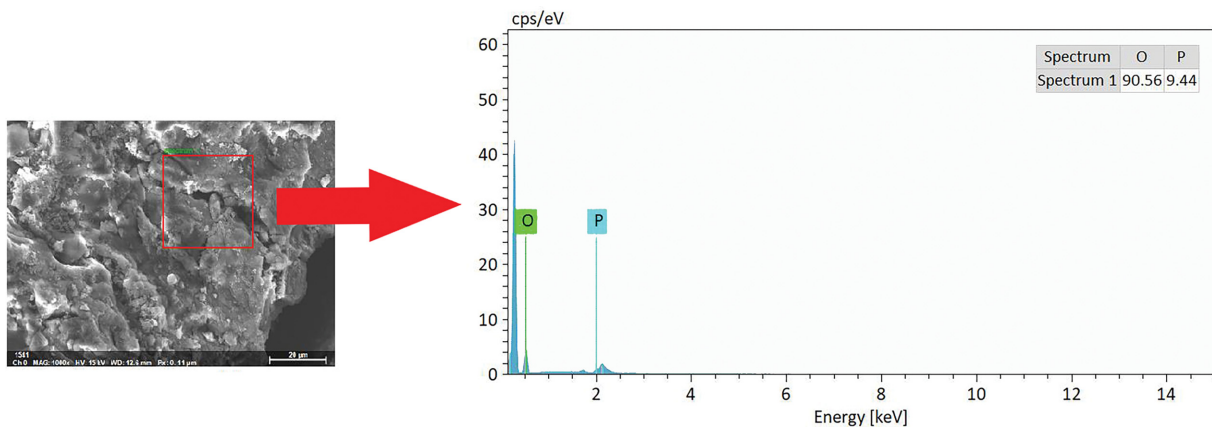


Fig. S2. Energy dispersive X-ray (EDX) spectrometry of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ .

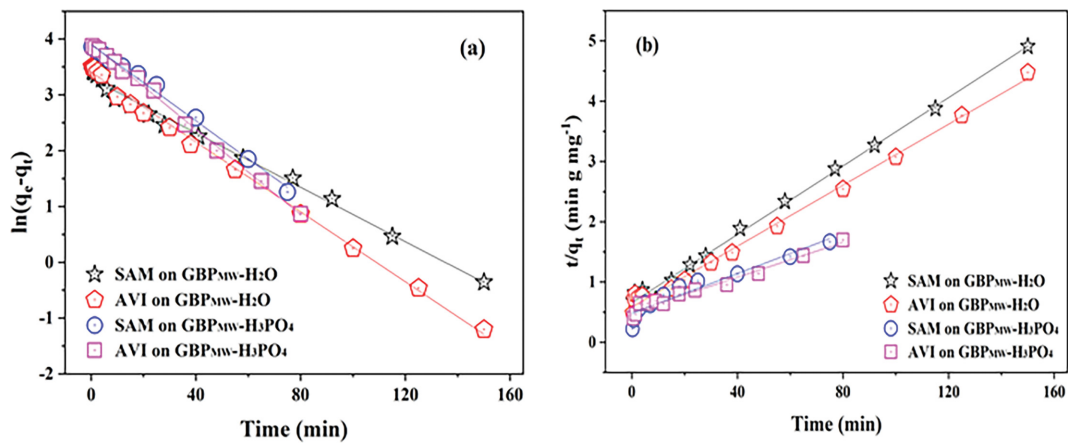


Fig. S3. (a) Pseudo-first-order and (b) pseudo-second-order kinetic plot.

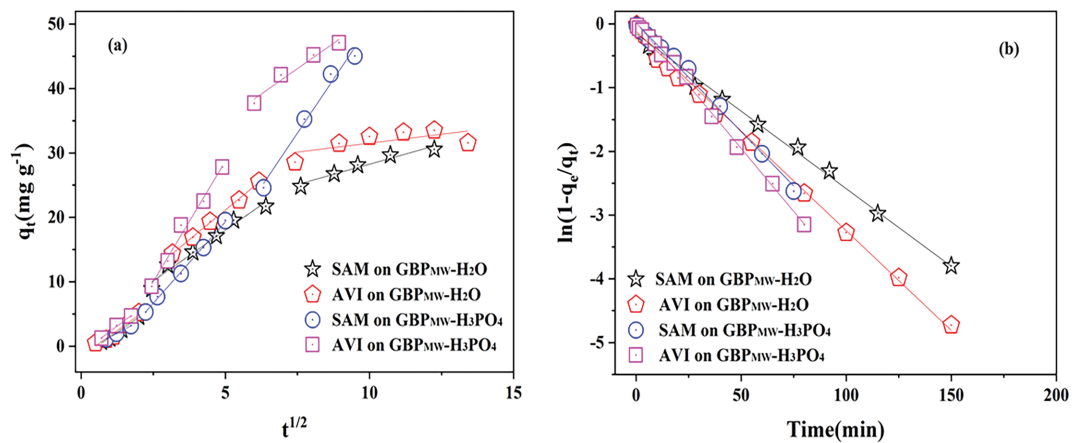


Fig. S4. Intra-particle diffusion (a) and film diffusion (b) kinetic plots.

Table S1. Main properties of SAM and AVI

Compound	Sulbactam sodium	Avibactam sodium
Molecular structure		
Chemical formula	$C_8H_{12}NNaO_5S$	$C_7H_{10}N_3NaO_6S$
Molecular weight	257.24	287.23
CAS number	69388-84-7	1192491-61-4

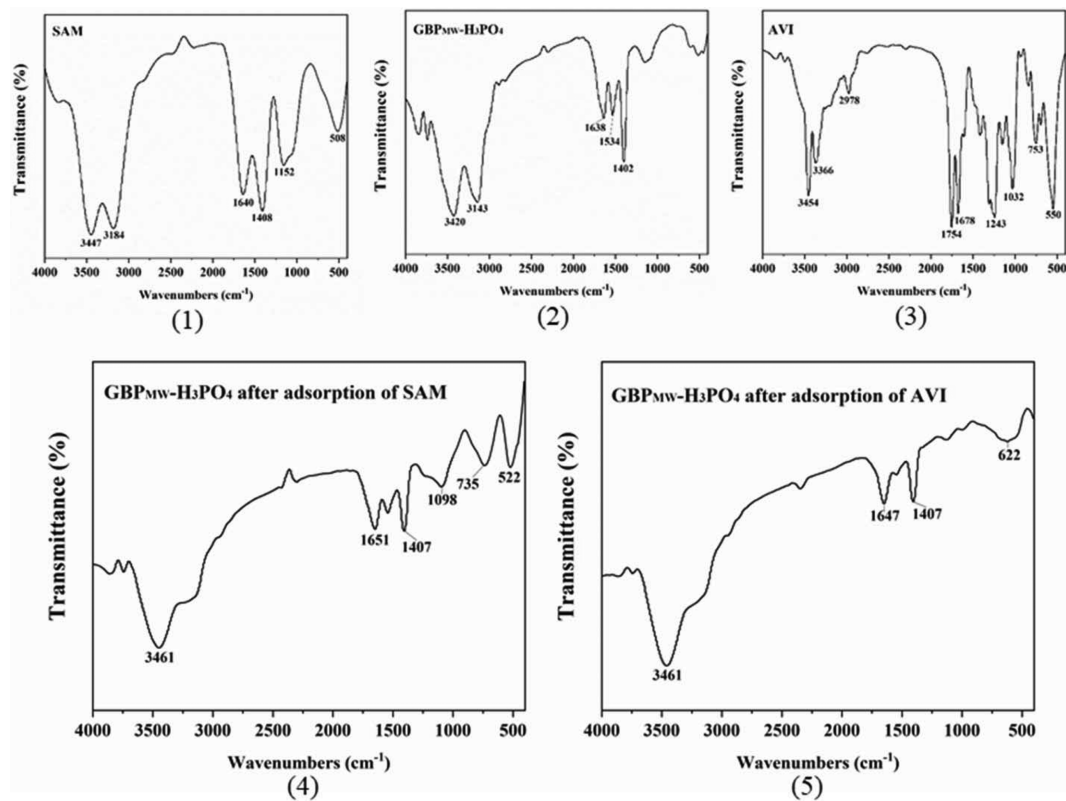


Fig. S5. FTIR spectra of  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$  before and after adsorption of SAM and AVI.

Table S2. Particle size distribution of  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$

Adsorbent	D [3,2] <sup>a</sup> ( $\mu\text{m}$ )	D [4,3] <sup>b</sup> ( $\mu\text{m}$ )	Dx (10) <sup>c</sup> ( $\mu\text{m}$ )	Dx (50) <sup>d</sup> ( $\mu\text{m}$ )	Dx (90) <sup>e</sup> ( $\mu\text{m}$ )
$\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$	72.4	244	40.8	202	495
$\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$	35.4	72.4	16.2	62.3	140

<sup>a</sup>Surface volume mean diameter

<sup>b</sup>Volume moment mean diameter

<sup>c</sup>Particle diameter corresponding to 10% cumulative (from 0 to 100%) undersize particle size distribution

<sup>d</sup>Particle diameter corresponding to 50% cumulative (from 0 to 100%) undersize particle size distribution

<sup>e</sup>Particle diameter corresponding to 90% cumulative (from 0 to 100%) undersize particle size distribution

Table S3. Parameters of pseudo-first-order and pseudo-second-order models for the adsorption of SAM and AVI on  $\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$  and  $\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$ . Conditions: pH 4.0, temperature 25 °C and initial drug concentrations 25  $\text{mg L}^{-1}$

Beta-lactamase inhibitors	Biochar	$q_{e, \text{exp}}$ ( $\text{mg g}^{-1}$ )	Pseudo-first-order model			Pseudo-second-order model		
			$k_1$ ( $1 \text{ min}^{-1}$ )	$R^2$	$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{ min}^{-1}$ )	$R^2$	$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )
SAM	$\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$	31.25	0.02435	0.9922	26.91	0.0012	0.9957	35.26
	$\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$	48.57	0.03413	0.9950	49.43	0.0006	0.9285	60.46
AVI	$\text{GBP}_{\text{MW}}\text{-H}_2\text{O}$	33.82	0.03129	0.9966	30.17	0.0011	0.9941	39.54
	$\text{GBP}_{\text{MW}}\text{-H}_3\text{PO}_4$	49.48	0.03832	0.9977	50.19	0.0004	0.9747	69.01

**Table S4. Parameters of isotherms for the adsorption of SAM and AVI on GBP<sub>MW</sub>-H<sub>2</sub>O and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>. Conditions: pH 4.0, contact time 120 min and temperature 25 °C**

Beta-lactamase inhibitors	Biochar	Langmuir			Freundlich		
		q <sub>L</sub> (mg g <sup>-1</sup> )	K <sub>L</sub> (L mg <sup>-1</sup> )	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>
SAM	GBP <sub>MW</sub> -H <sub>2</sub> O	42.50	0.4143	0.9983	8.02	2.1884	0.9566
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	211.86	0.4715	0.9623	46.09	1.4044	0.9937
AVI	GBP <sub>MW</sub> -H <sub>2</sub> O	49.83	0.4472	0.9967	8.84	2.0473	0.9490
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	198.81	1.7649	0.9555	89.37	1.5855	0.9917

Beta-lactamase inhibitors	Biochar	Temkin			D-R		
		K <sub>T</sub> (L g <sup>-1</sup> )	β <sub>T</sub> (kJ mol <sup>-1</sup> )	R <sup>2</sup>	q <sub>D</sub> (mg g <sup>-1</sup> )	E (kJ mol <sup>-1</sup> )	R <sup>2</sup>
SAM	GBP <sub>MW</sub> -H <sub>2</sub> O	19.42	0.4446	0.9561	23.42	3.4943	0.8300
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	42.66	0.1086	0.8063	62.74	4.2460	0.8297
AVI	GBP <sub>MW</sub> -H <sub>2</sub> O	16.67	0.3619	0.9543	27.26	3.2786	0.8357
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	184.23	0.1167	0.8196	82.56	5.3858	0.9028

**Table S5. Parameters of thermodynamic for the adsorption of SAM and AVI on GBP<sub>MW</sub>-H<sub>2</sub>O and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>. Conditions: pH 4.0, contact time 120 min and initial drug concentrations 25 mg L<sup>-1</sup>**

Beta-lactamase inhibitors	Biochar	ΔG° (KJ mol <sup>-1</sup> )					ΔH° (KJ mol <sup>-1</sup> )	ΔS° (KJ mol <sup>-1</sup> )	R <sup>2</sup>
		293 K	298 K	303 K	308 K	313 K			
SAM	GBP <sub>MW</sub> -H <sub>2</sub> O	-2.74	-2.99	-3.23	-3.48	-3.73	11.74	0.05	0.9906
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	-9.85	-10.58	-11.31	-12.05	-12.78	33.07	0.15	0.9906
AVI	GBP <sub>MW</sub> -H <sub>2</sub> O	-3.32	-3.59	-3.86	-4.13	-4.40	12.52	0.05	0.9928
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	-23.10	-23.93	-24.76	-25.58	-26.41	36.32	0.17	0.9921

**Table S6. Constants of Intra-particle diffusion model for SAM and AVI on GBP<sub>MW</sub>-H<sub>2</sub>O and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>**

Beta-lactamase inhibitors	Biochar	Intra-particle diffusion model								
		k <sub>S1</sub> (mg g min <sup>-1</sup> )	C <sub>1</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>	k <sub>S2</sub> (mg g min <sup>-1</sup> )	C <sub>2</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>	k <sub>S3</sub> (mg g min <sup>-1</sup> )	C <sub>3</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>
SAM	GBP <sub>MW</sub> -H <sub>2</sub> O	3.068	-1.650	0.9874	3.140	2.297	0.9743	1.260	15.641	0.9575
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	2.401	-0.956	0.9999	5.047	-5.941	0.9982	6.664	-16.891	0.9827
AVI	GBP <sub>MW</sub> -H <sub>2</sub> O	3.187	-1.536	0.9576	3.681	2.738	0.9986	0.553	25.973	0.4595
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	3.338	-1.034	0.9939	7.463	-8.625	0.9851	3.139	19.535	0.9702

**Table S7. Constants of film diffusion model for SAM and AVI on GBP<sub>MW</sub>-H<sub>2</sub>O and GBP<sub>MW</sub>-H<sub>3</sub>PO<sub>4</sub>**

Beta-lactamase inhibitors	Biochar	Film diffusion model		
		k <sub>F</sub> (min <sup>-1</sup> )	A	R <sup>2</sup>
SAM	GBP <sub>MW</sub> -H <sub>2</sub> O	0.0244	-0.1495	0.9922
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	0.0313	0.0175	0.9950
AVI	GBP <sub>MW</sub> -H <sub>2</sub> O	0.0341	-0.1142	0.9966
	GBP <sub>MW</sub> -H <sub>3</sub> PO <sub>4</sub>	0.0395	0.0247	0.9979