Research Article

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Enhanced adsorption of sulfonamide antibiotics in water by modified biochar derived from bagasse

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Abstract: In this study, biochars derived from bagasse were prepared and their ability for the adsorption of four kinds of sulfonamide antibiotics (sulfamethoxazol, thiazole, methylpyrimidine, dimethylpyrimidine) was investigated. Results showed that the modified biochar can efficiently adsorb sulfonamides in water. The biochar obtained at 500°C and modified with 30% hydrogen peroxide was chosen as the adsorbent. Under optimum conditions, pH 4 and 35°C, great adsorption performance was exhibited in the adsorption process of the four sulfonamide antibiotics. The productivity of the modified biochar was ~ 89% compared to un-modified biochar which is ~31%. The successful preparation of biochar from bagasse indicates that it is a good way to reuse the resources. Besides the adsorption of antibiotics, the obtained material also has a great prospect in the removal of other pollutants.

Keywords: adsorption; antibiotics; bagasse; biochar.

1 Introduction

Antibiotics, one of the pharmaceutical and personal care products (PPCPs), can remain in the environment for a long time due to their structural stability and environmental durability and can also cause great damage to water bodies [1-3]. At present, the removal of antibiotics in water mainly depends on conventional water treatment process [4]. The general municipal wastewater treatment plants both at home and abroad are designed and built for the removal of organic matter and some nutrients [5-7]. Therefore, the ability to remove antibiotics is limited. The traditional sewage treatment plant includes pre-treatment, primary stage treatment, two stages treatment system [8-9] and a conditional sewage treatment plant will also start a three stages treatment program, such as chemical oxidation, activated carbon adsorption or ultraviolet oxidation [10-12]. The pre-treatment and primary stage treatment processes are aimed at removing organic suspension which is large and easy to settle. Hence, the antibiotics removal performance is not good. Therefore, the degradation of PPCPs is mainly in secondary treatment and tertiary treatment which all have the problems of high cost and low removal rate.

Biochar adsorbents have demonstrated excellent sorption capacity for pollutants due to their complex pore structures and good surface characteristics [13-14]. At present, there are three widely used modification methods of biochar: physical, chemical and biological. Chemical modification can simultaneously improve the pore structure and surface chemical properties of adsorbent, thereby enhancing its adsorption capacity for the specific target[15-16].

Bagasse is a by-product in the production of sugarcane. The residue of sugar cane can reach tens of millions of tons every year with most of the bagasse only being used as cheap fuel or being disregarded, causing great waste of resources [17-20]. In theory, all organic matter with high content of carbon can be used in the preparation of biochar [21-22]. But the cost is much higher when some organic matter, such as starch, is used to produce biochar [23-24]. It is obviously not in accordance with the principle of best utilization of resources in present global resource scarcity. Therefore, the utilization of solid waste with high carbon content, such as straw, wood cutting waste branch, bagasse, sewage sludge, not only avoids environmental pollution, but can also generate new energy, forming a good strategy of waste recycling.

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Herein, the authors report a biochar-based method for antibiotics removal in water. Derived from bagasse, the biochar is modified and then used as adsorbent to remove antibiotics. Great adsorption performance is observed in the process. The effects of various parameters including pH, temperature and antibiotic species were evaluated. The adsorption process was also modelled by kinetics models and isotherm models.

2 Materials and Methods

2.1 The preparation of biochar

Bagasse was collected from a shop selling Sugar cane juice. The collected bagasse was washed with tap water, naturally dried for 2 days, then transferred into the oven at 70°C for 12 hours. After that, the particle size was crushed to less than 2 cm by a grinder. The weighed sugar cane shredding was placed in a porcelain crucible wrapped with foil paper and covered with a lid. The crucible was then placed in a tubular carbonization furnace and heated at a rate of 10°C/min to reach the target temperature (300, 500 or 700°C), then maintained for 2 hours. After cooling to room temperature naturally, the product was weighed. Then the product was ground over 50 mesh sieves and treated with 1200 mL of 1.00 mol/L hydrochloric acid for 2 hours to remove calcium carbonate and other ash substances. After being filtered and adjusted pH value to neutral with distilled water washing, the product was put into the oven at 80°C for 24 hours, then transferred into a sample storage bottle for further use.

2.2 The modification of biochar

After preparation, the biochar obtained under different temperatures (300, 500 and 700°C) was modified. The modification of biochar was carried out using four kinds of oxidizers (concentrated sulfuric acid, concentrated nitric acid, 30% hydrogen peroxide, and 0.4mol/L potassium permanganate). Two modification methods (dipping and ultrasonic dipping) were adopted.

The dipping method was as follows: 11.25 g of washed biochar was first put into a 1000 mL beaker. Then, 400 mL of 30% oxidizer was added to the beaker to get full contact with biochar for 24 hours. Then the solid was filtered and washed to the neutral repeatedly. Finally, the solid was placed in the oven at 60°C for 12 h until it reached a constant weight.

The ultrasonic dipping method was as follows: 11.25 g of washed biochar was first put into the 1000 mL beaker. Then 400 mL of 30% oxidizer was added to the beaker to get full contact with biochar. After 10 minutes in an ultrasonic bath, the beaker was placed for 24 hours. The following procedure is the same with that of dipping method.

2.3 Adsorption study

All of the antibiotics adsorption experiments were performed by biochar in batch conditions. The adsorption efficiency was tested by adsorption of sulfonamides, one of the most commonly used antibiotics. The effects of various parameters including pH, temperature, and antibiotic species were evaluated. The productivity of biochar is calculated according to equation (1):

$$productivity = \frac{m}{m_0} \tag{1}$$

where *m* is the obtained mass of modified biochar, *m0* is the starting mass of raw biochar (11.25g). The adsorption capacity (*qe*) is calculated according to equation (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where *C0* and *Ce* are the initial and final concentration of antibiotic in the solution (mg/L), respectively, *V* is the volume of antibiotic solution (mL), and *m* is the weight of the adsorbent (g). The removal efficiency of sulfonamides is calculated according to equation (3):

$$removal\ efficiency\ (\%) = \frac{C_0 - C_t}{C_0} \tag{3}$$

where *C0* and *Ct* represent the initial and final sulfonamide concentration (mg/L), respectively.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 The modification of biochar

According to Section 2.2, the biochar was modified with different oxidizers and two modification methods were

Table 1: The mass of modified biochar obtained and calculated productivity.

Modification method	Oxidizer	Burning temperature of carbon					
		300°C		500°C		700°C	
		m (g)	productivity	m (g)	productivity	m (g)	productivity
Dipping	concentrated sulfuric acid	7.0	62%	6.6	59%	8.0g	71%
	concentrated nitric acid	0.8	7%	12.0	106%	11.0	98%
	30% hydrogen peroxide	3.8	34%	7.0	62%	7.0	62%
	0.4 mol/L potassium permanganate	15.0	133%	15.0	133%	15.0	133%
Ultrasonic dipping	concentrated sulfuric acid	0.4	4%	11.0	98%	10.0	89%
	concentrated nitric acid	3.0	27%	14.0	124%	11.0	98%
	30 % hydrogen peroxide	6.7	60%	10.0	89%	9.0	80%
	0.4 mol/L potassium permanganate	17.0	151%	15.0	133%	17.0	151%

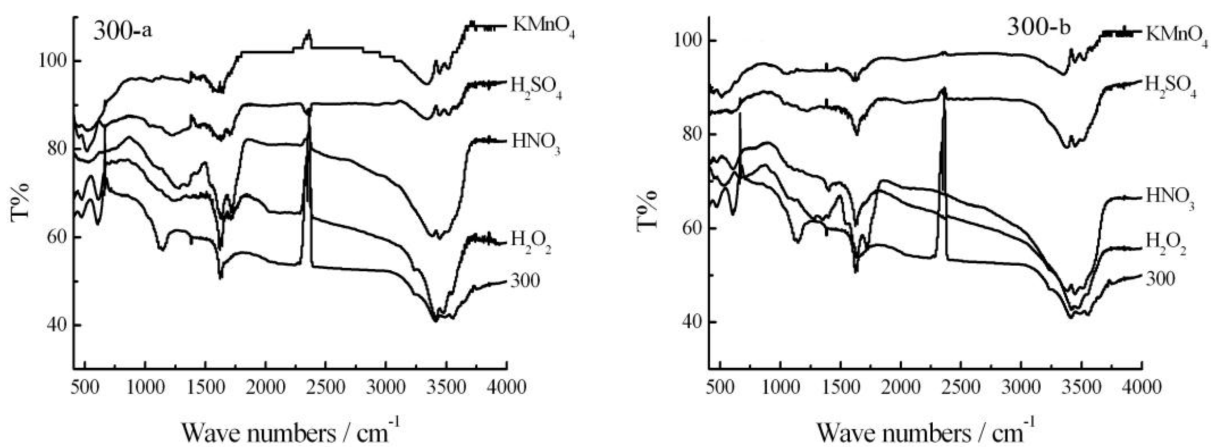

Figure 1: FTIR spectra of biochar obtained at 300°C before and after modification (a. Dipping, b. Ultrasonic dipping).

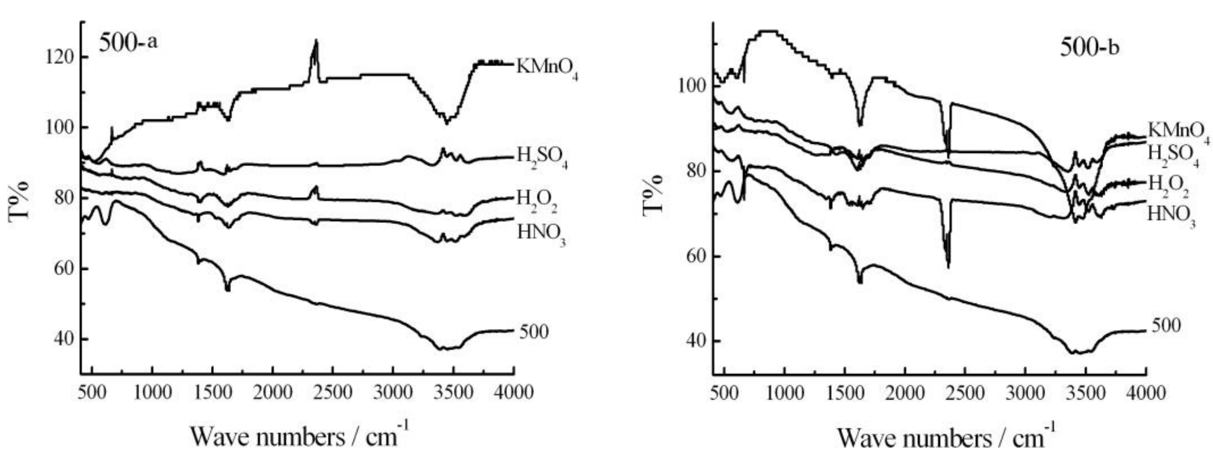

Figure 2: FTIR spectra of biochar obtained at 500°C before and after modification (a. Dipping, b. Ultrasonic dipping).

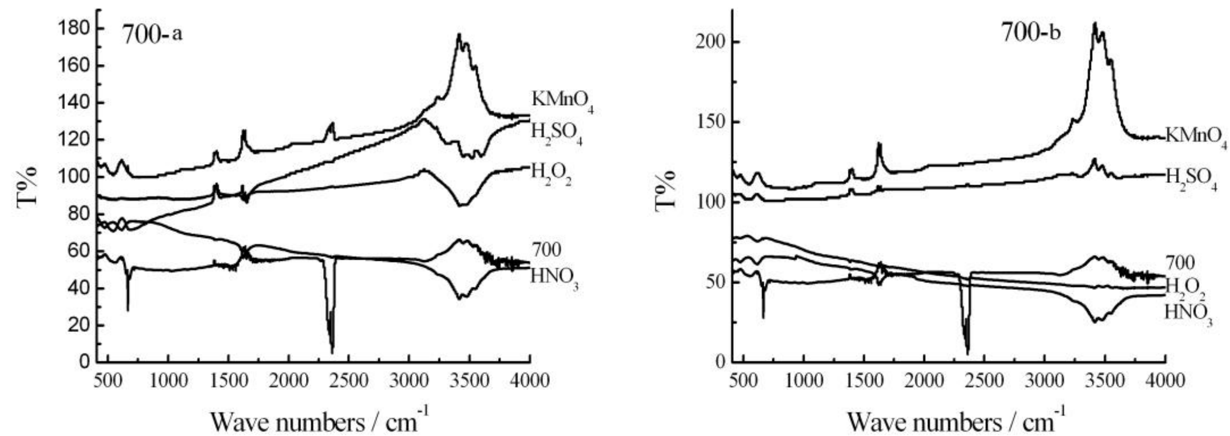

Figure 3: FTIR spectra of biochar obtained at 700°C before and after modification (a. Dipping, b. Ultrasonic dipping).

investigated. Table 1 shows the mass of modified biochar obtained and productivity for the investigated parameters. It is clear that the highest productivity was achieved by the modification with 0.4 mol/L potassium permanganate. When the other oxidizers were used, smoke was released, which may be the reason for the lower productivity compared to potassium permanganate.

The FTIR spectra of biochar obtained at 300°C before and after modification are shown in Figure 1. The absorption peak at around 3450 cm^{-1} belongs to the stretching vibration of O-H in the carboxyl group or the hydroxyl group on the surface of biochar. The absorption peak at around 3150 cm^{-1} belongs to the stretching vibration of C-H, indicating that both the modified biochar and the parent biochar both have active C-H bonds. The two absorption peaks at around 1650 cm^{-1} are produced by the modification of the carbon oxygen double bond of the carboxyl group on the biochar. Figure 2 shows the FT-IR spectra of biochar obtained at 500°C before and after modification. The absorption peaks have a slight red shift at around 3450 cm^{-1}, which belongs to the stretching vibration of O-H in the carboxyl group or the hydroxyl group, compared with that for biochar obtained at 300°C. The shift was ascribed to the increase of surface area, pore volume, surface carboxyl group, and phenol hydroxyl group of the biochar obtained at 500°C. The absorption peaks at around 3150 cm^{-1} nearly disappeared, indicating the decrease of the carboxyl group. Figure 3 shows the FT-IR spectra of biochar obtained at 700°C before and after modification. The observation was same with that of the biochar obtained at 500°C. All the results indicate that the modified biochar has larger specific surface area, well-developed pore structure and more functional groups. Many functional groups have aromatic electronic conjugated structure, which can act as a ligand to increase adsorption performance. Therefore, the biochar obtained at 500°C and modified with 30% hydrogen peroxide was chosen as the adsorbent in the following experiment.

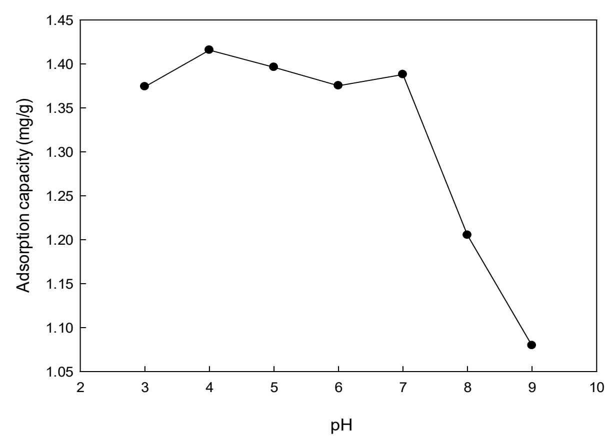

Figure 4: The total adsorption capacity of sulfonamides under different pH.

3.2 The effect of pH

In the experiment, seven colorimetric tubes with a working volume of 50 mL were prepared, and then 10 mL solution containing 20 mg/L sulfonamides was added to each tube. The pH value was adjusted to 3.00, 4.00, 5.00, 6.00, 7.00, 8.00 or 9.00 by a HCl or NaOH solution. Then, 0.50 g of modified biochar was added to the prepared solution. Each suspension was oscillated for 24 hours under constant temperature at 25°C. After these operations, the solution was taken out, and the content of antibiotics was analyzed by chromatograpy. Then the concentrations of

Table 2: The removal efficiency of different pollutants over biochar under different pH values.

pH	Sulfamethoxazol	Thiazole	Methylpyrimidine	dimethylpyrimidine	Total
3.00	99.66%	78.86%	60.14%	65.66%	85.88%
4.00	99.55%	79.56%	70.67%	73.50%	88.48%
5.00	99.48%	80.35%	66.50%	68.57%	87.26%
6.00	99.60%	78.15%	62.48%	65.35%	85.95%
7.00	99.66%	79.04%	65.80%	66.69%	86.75%
8.00	99.52%	52.71%	34.19%	47.31%	75.32%
9.00	99.81%	32.33%	19.46%	30.02%	67.47%

Table 3: The removal efficiency of different pollutants over biochar under different temperatures.

Temperature (°C)	Sulfamethoxazol	Thiazole	Methylpyrimidine	Dimethylpyrimidine
10	97.73%	61.94%	52.37%	78.85%
25	97.99%	83.55%	78.36%	93.27%
45	98.81%	91.55%	90.19%	95.83%
60	99.40%	95.25%	94.25%	98.52%
75	98.69%	99.12%	98.25%	98.39%

sulfonamides were analyzed to identify the effects of pH on the adsorption of pollutants over biochar.

Four kinds of sulfonamides (sulfamethoxazol, thiazole, methylpyrimidine, dimethylpyrimidine) were chosen to be the target pollutants. The removal efficiency of each pollutant over biochar under different pH values is shown in Table 2. It is clear that the effect of pH is minimal for the adsorption process of sulfamethoxazole, while other three substances were greatly affected. The removal efficiency increases slowly and then decrease rapidly with the increase of pH values. The experimental results are consistent with those previously reported in the literature [25-26]. The total adsorption amount is shown in Figure 4 which indicates that the best adsorption capacity is achieved when the pH value is 4.

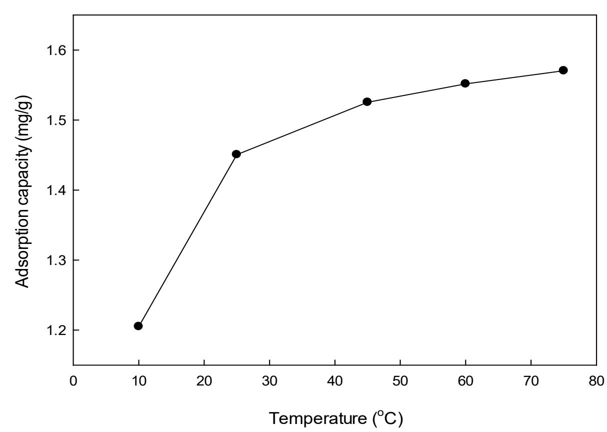

Figure 5: The total adsorption capacity of sulfonamides under different temperature.

3.3 The effect of temperature

In the experiment, the procedure was similar to that described in Section 3.2. Five colorimetric tubes with a working volume of 50 mL were prepared, and 10 mL solution containing 20 mg/L sulfonamides was added to each tube. Then, 0.5 g of modified biochar was added, respectively. According to the results of section 3.2, pH value of the reactors is optimized to be 4. Then the reaction temperature of each reactor was designed to be 25, 35, 45, 60, 75°C, respectively. All other parameters were as described in Section 3.2.

Table 3 shows the removal efficiency of different pollutants over biochar under different temperatures. It is clear that temperature has little effect on the adsorption of sulfamethoxazole. The other three substances showed similar removal tendency that the removal efficiency increases with the increase of temperature. The total adsorption amount can be observed in Figure 5. The adsorption capacity increased with temperature and seemed to plateau at around 45°C.

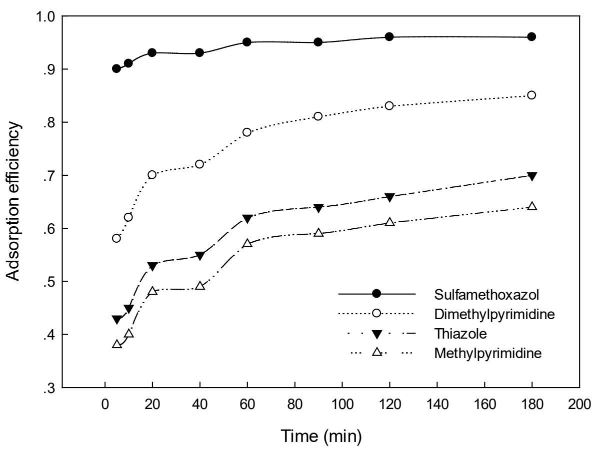

Figure 6: Adsorption kinetics of different antibiotics.

3.4 Equilibrium adsorption modeling (kinetics and isotherms)

Based on the results of Section 3.2 and 3.3, the following experiments were carried out at a pH of 4 and at 35°C.

3.5 The kinetic models

In the experiment, four colorimetric tubes with a working volume of 50 mL each were prepaerd, and 10 mL solution containing 20 mg/L sulfonamides was added to each tube. Then, 0.5 g of modified biochar was added respectively. Each suspension was oscillated for 24 hours under the condition of constant temperature. After these operations, the solution was taken out at given sampling times (0, 5, 10, 20, 40, 60, 90, 120 and 180 minutes), then filtered. The concentration of sulfonamides was analyzed later.

Figure 6 shows the adsorption kinetics of different antibiotics. It is clear that the adsorption efficiency of the biochar to the sulfamethoxazol was more than 90%, and

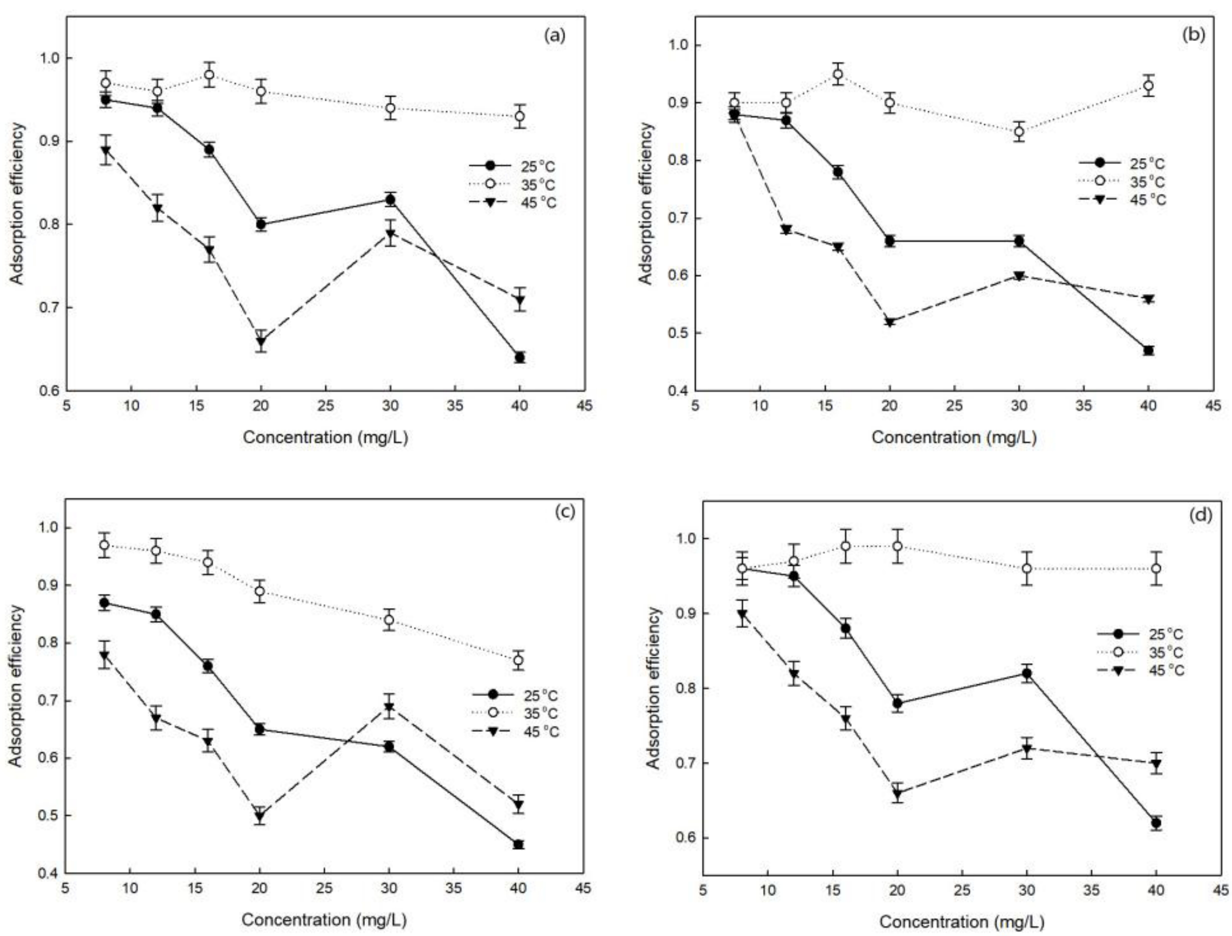

Figure 7: Adsorption isotherm of different antibiotics. (a) sulfamethoxazol; (b) thiazole; (c) methylpyrimidine; (d) dimethylpyrimidine.

the adsorption efficiency of dimethylpyrimidine, thiazole, and methylpyrimidine reached 84.96±0.15%, 69.71±0.33% and 64.24±0.28% after 180 minutes. These adsorption efficiency are much higher than the traditional sand filter method, which is less than 50%.

3.6 The isotherm models

In the experiment, six colorimetric tubes with a working volume of 50 mL were prepared, and 0.5 g of modified biochar was added to each tube.. Then, 10 mL solution containing 8, 12, 16, 20, 30, 40 mg/L sulfonamides was added respectively. The reactors were oscillated for 24 hours under the condition of constant temperature at 25, 35, and 45°C, respectively. Then the solution was removed to detect the concentration of sulfonamides. From Figure 7, it can be seen clearly that for the four sulfonamides (sulfamethoxazol, thiazole, methylpyrimidine, dimethylpyrimidine), the best removal efficiency was achieved when the temperature was 35°C.

4 Conclusion

In summary, a method for producing biochar from bagasse is reported in this paper. The biochar was first obtained, then modified via different oxidizers and used as an adsorbent to remove sulfonamide antibiotics. The biochar obtained at 500°C and modified with 30% hydrogen peroxide was chosen as the adsorbent. The productivity of biochar obtained from bagasse is ~31% and the productivity of modified biochar reached ~89%. The modified biochar showed great adsorption performance toward sulfonamides in water. Under the optimum conditions of pH 4 and 35°C, an enhanced adsorption performance is exhibited for four sulfonamide antibiotics (sulfamethoxazol, thiazole, methylpyrimidine, dimethylpyrimidine). Besides the adsorption of antibiotics, the obtained material also has a great prospect in the removal of other pollutants.

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Conflict of interest: Authors declare no conflict of interest.

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