Article

Adsorptive Removal of Fluoroquinolone Antibiotics Using Bamboo Biochar

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Abstract: The occurrence of fluoroquinolone antibiotics in wastewater has drawn great attention. Adsorption of widely used fluoroquinolone antibiotics (enrofloxacin and ofloxacin) in wastewater using bamboo biochar was investigated. More than 99% of fluoroquinolone antibiotics were removed from the synthetic wastewater through adsorption. Adsorption capacities of bamboo biochar slightly changed when pH increased from 3.0 to 10.0. The adsorption capacity of bamboo biochar increased sharply when the initial concentration of enrofloxacin or ofloxacin increased from 1 to 200 mg L^{-1} and then began to plateau with further increases in initial concentration. The maximum adsorption capacity (45.88 ± 0.90 mg·g^{-1}) was observed when the ratio of bamboo biochar to fluoroquinolone antibiotics was 10. The enrofloxacin adsorption capacity of bamboo biochar decreased from 19.91 ± 0.21 mg·g^{-1} to 14.30 ± 0.51 mg·g^{-1} while that of ofloxacin decreased from 19.82 ± 0.22 mg·g^{-1} to 13.31 ± 0.56 mg·g^{-1} when the NaCl concentrations increased from 0 to 30 g·L^{-1}. The adsorptions of fluoroquinolone on bamboo biochar have isotherms that obeyed the Freundlich model (r^2 values were in the range of 0.990–0.991).

Keywords: fluoroquinolone; antibiotics; wastewater; bamboo biochar; adsorption

1. Introduction

The wide and frequent use of antibiotics in aquaculture has resulted in the development and spreading of antibiotic resistance [1]. Antibiotics kill or inhibit bacteria [2], which can subsequently lead to their persistence in biological wastewater treatment process [3]. An alternative method investigated for antibiotics removal from wastewater is the adsorption technique [4]. Activated carbon adsorption has been recognized as the most effective method, producing good-quality effluents that have low concentrations of dissolved organic compounds in wastewater from pharmaceutical manufacturing [4]. Due to the high operational cost of the traditional activated carbon adsorption techniques, many low cost adsorbents have been used to remove various pollutants [5–8]. Among these adsorbents, bamboo biochar has shown promising application for the removal of organic pollutants [5]. Bamboo biochar has approximately ten times more surface area and four times more sorption capacity than char [9].

Fluoroquinolone antibiotics have been widely useful in controlling many of the bacterial pathogens [1,10,11]. Studies have reported that fluoroquinolone antibiotics may be genotoxic [12]. The presence of fluoroquinolone antibiotics in the environment is potentially linked to their resistant bacteria in various environments, which may result in disturbed aquatic ecosystems and make humans and animals more susceptible to antibiotic resistant microbes [13]. The occurrence of fluoroquinolone antibiotics in various environments has drawn great attention [1,13].

Little information is available on the adsorption removal of fluoroquinolone antibiotics using bamboo biochar. In this study, removal of enrofloxacin and ofloxacin, which are widely used fluoroquinolone antibiotics, was investigated using bamboo biochar. The objective of this study was to evaluate the feasibility of using bamboo biochar as a cost-efficient adsorbent for removing fluoroquinolone antibiotics from wastewater. The impacts of pH, initial concentration, bamboo biochar dose, and ion strength on the adsorption were also investigated. The final goal was to obtain initial information on the treatment of wastewater containing fluoroquinolone antibiotics at low cost using bamboo biochar as the adsorbent.

2. Materials and Methods

2.1. Chemicals, Bamboo Biochar, and Synthetic Aquaculture Wastewater

Standards of enrofloxacin and ofloxacin (purity of 98.5%) were obtained from Sigma-Aldich. Deionized (DI) water was purified using a MilliQ Plus system (Millipore, Bedford, MA, USA). All other reagents used were of reagent grade. Bamboo biochar was prepared from bamboo sawdust by pyrolysis at 500 °C. Before the experiments, bamboo biochar was thoroughly washed with distilled water five times to remove the residual acids, Si, and soluble salts, and then oven-dried for 24 h at 105 °C. To make the synthetic wastewater containing fluoroquinolone antibiotics, pond water was filtered using Whatman GF/D glass fiber filters (pore size: 0.45 μm, Fisher Scientific, Pittsburgh, PA, USA) and spiked with enrofloxacin and ofloxacin, which are widely used fluoroquinolone antibiotics.

2.2. Adsorption Test

The initial concentration of enrofloxacin or ofloxacin was 100 mg·L^{-1}, except the study on the effect of initial concentration on adsorption. To estimate the applicability of bamboo biochar as an adsorbent

for fluoroquinolone antibiotics, 50 mg of bamboo biochar was placed in the sealed flasks those contained 10 mL of water with fluoroquinolone antibiotics. The flasks were shaken at a rolling speed of 170 rpm under a constant temperature of 25 ± 2 °C. After 96 h, the bamboo biochar was separated from solution by centrifugation (12000 rpm) for 5 min. The supernatant was collected for HPLC analysis. All experiments were performed in duplicate. The pH of the water was not adjusted using 1 N HCl or NaOH, except in the study on the effect of pH on fluoroquinolone antibiotics adsorption. The experiment has two controls. In the case of bamboo sawdust control, bamboo biochar was replaced by bamboo biochar. In the case of natural attenuation control, the unfiltered pond water without adsorbent was spiked with fluoroquinolone. To better understand the effect of pH on the adsorption process, the pH of the wastewater was adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, and 11.0 before mixing with the bamboo biochar. To understand the effect of initial concentration on adsorption, synthetic wastewater with different initial concentrations of enrofloxacin or ofloxacin ranging from 1 to 500 mg·L^{-1} was prepared and then mixed with bamboo biochar. To understand the effect of bamboo biochar dose on the adsorption, 10 mL of synthetic aquaculture wastewater was mixed with different bamboo biochar doses. The bamboo biochar addition amounts ranged from 10 to 100 mg, causing the related ratios of bamboo biochar to fluoroquinolone antibiotics to range from 10 to 100. To determine the effect of ion strength on the adsorption, NaCl (0, 0.3, and 3 g·L^{-1}) was added into the synthetic wastewater (original salinity was 0.09 g·L^{-1}) to achieve salinities of 0.09, 0.39, and 3.09 g·L^{-1}.

2.3. Adsorption Kinetics Experiment

To gain insight into the effect of contact time on fluoroquinolone antibiotics adsorption, samples were collected at 0, 0.5, 1, 2, 4, 8, 12, 24, 48, 72, and 96 h. Three typical kinetics models (including pseudo first-order, pseudo second-order, and Elovich models) were applied to understand the adsorption kinetics of fluoroquinolone antibiotics on bamboo biochar according to [14]. The equations are shown below:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \tag{2}$$

$$q_t = a + b \ln t \tag{3}$$

where t is the adsorption time; q_t is adsorption capacity at time t; q_e is the saturated adsorption capacity; k_1 is the rate constant of psuedo first-order adsorption; k_2 is the rate constant of psuedo second-order adsorption; and a and b are Elovich rate constants.

2.4. Adsorption Isotherm Experiment

The relationship between adsorption and aqueous concentration at a given temperature is described as adsorption isotherm [14]. For these isotherm experiments, the initial concentrations of enrofloxacin or ofloxacin were 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg L^{-1}. The experiment was conducted at 25 °C. The commonly used adsorption isotherm models are the Freundlich isotherm model and the Langmuir isotherm model [14]. The Langmuir equation (Equation (4)) and Freundlich equation (Equation (5)) are shown as follows [14]:

$$\frac{1}{q_{eq}} = \frac{1}{\beta Q_m C_{eq}} + \frac{1}{Q_m} \tag{4}$$

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq} \tag{5}$$

where q_{eq} is the adsorption capacity per unit mass adsorbent; C_{eq} is the adsorbate concentration in aqueous solution; K_f is the Freundlich coefficient; n is the Freundlich empirical constant; Q_m is the adsorption capacity under monolayer adsorption; and ß is the surface adsorption affinity constant.

2.5. Analysis Methods

Enrofloxacin and ofloxacin were analyzed using an Agilent 1200 high performance liquid chromatography (HPLC) with a DAD and a Hypersil BDS column (250 mm × 4.6 mm, 5 μm) following previous methods [15,16] with slight modification. The mobile phase was a 10:15:75 (in volume) mixture of methanol, acetonitrile and acidified water (1% formic acid) with a flow rate of 1.0 mL min^{-1}. UV detector wavelengths were set at 280 nm. The injection volume was 50 μL. The column temperature was 35 °C. The amount of adsorbed enrofloxacin or ofloxacin q_t at different time t, was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{6}$$

where C_0 and C_t are the initial concentration of enrofloxacin or ofloxacin and the concentration at time t, respectively; V stands for the volume of solution; and m is the mass of adsorbent. The maximum biodegradation rate of enrofloxacin or ofloxacin was determined from the time course of the removal, using points in the linear portion of graphs that released enrofloxacin or ofloxacin concentration to time. Specific surface area and pore structure were determined using a Brunauer-Emmet-Teller (BET)-N$_2$ surface area analyzer (ASAP 2000, Micromeritics, Norcross, GA, USA) using nitrogen adsorption/desorption isotherm at 77 K [17,18]. Surface areas of the samples were measured based on the BET method [19]. Barrett-Joyner-Halendar (BJH) theories were used for the analysis of pore size distributions [18].

3. Results and Discussion

3.1. Adsorptive Removal of Fluoroquinolone Antibiotics Using Bamboo Biochar

The rapid removal of enrofloxacin and ofloxacin was observed. The maximum removal rate for enrofloxacin and ofloxacin were 81.91 ± 0.41 and 88.17 ± 0.35 mg·L^{-1}·h^{-1}, respectively, which were much higher than those (<4.40 mg L^{-1}·h^{-1}) in the controls of bamboo sawdust and natural attenuation (Table 1). Most of the fluoroquinolone antibiotics were adsorbed within 1 h (Figure 1). In controls of bamboo sawdust and natural attenuation, less than 5% of fluoroquinolone antibiotics were removed at the end of the experiment. Compared with the controls of bamboo sawdust and natural attenuation, more than 99% of fluoroquinolone antibiotics were removed from the wastewater in the bamboo biochar treatment, indicating the efficient removal of these chemicals through adsorption. The adsorption kinetics of fluoroquinolone antibiotics on bamboo biochar fitted pseudo second-order model (r^2 values

are in the range 0.986 to 0.991). The rate constants, k_2, ranged from 1.23 to 1.26 $g \cdot h^{-1} \cdot mg^{-1}$. According to the prediction of pseudo second-order model, the saturation adsorption capacity for bamboo biochar was 20.00 $mg \cdot g^{-1}$ when the initial concentration of enrofloxacin or ofloxacin was 100 $mg \cdot L^{-1}$. The high adsorption capacity indicates that bamboo biochar is a promising low cost absorbent for the treatment of fluoroquinolone antibiotics-containing aquaculture wastewater.

Table 1. Maximum removal rate in different treatments.

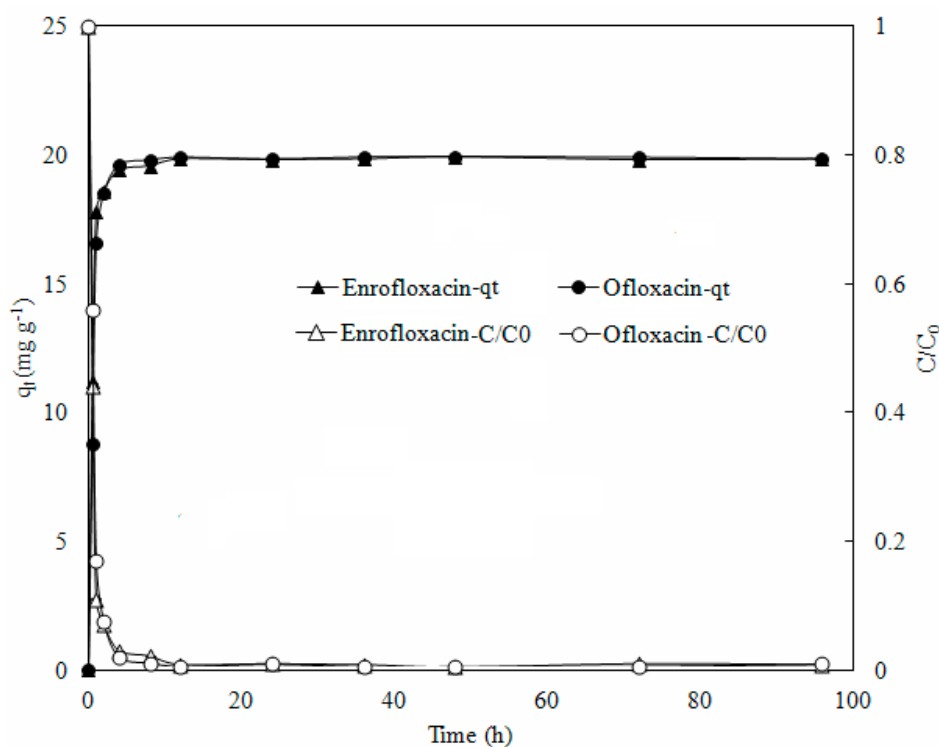| Treatment	Maximum Removal Rate ($mg \cdot L^{-1} \cdot h^{-1}$)	
	Enrofloxacin	Ofloxacin
Bamboo biochar	81.91 ± 0.41	88.17 ± 0.35
Bamboo sawdust (control)	4.16 ± 0.23	4.39 ± 0.12
Natural attenuation (control)	0.13± 0.04	0.16± 0.03

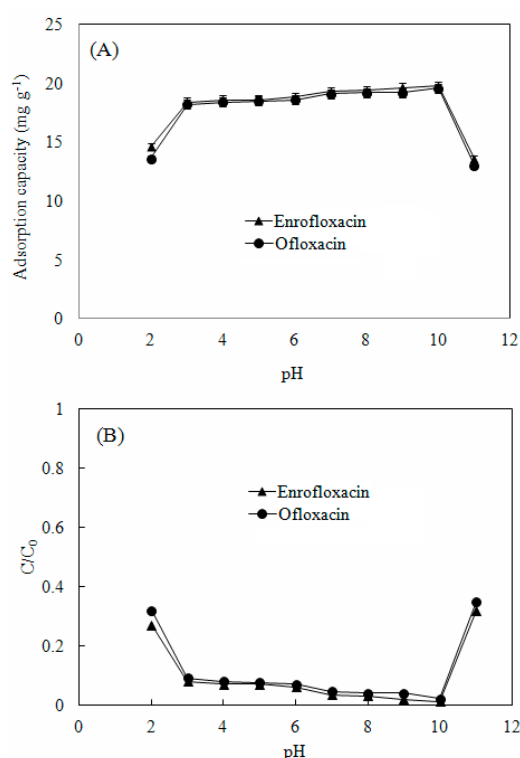**Figure 1.** Adsorptive removal of fluoroquinolone antibiotics as a function of adsorption time.

Bamboo biochar had a relatively large BET specific surface area and a high mesopore distribution (Table 2), which might lead to their efficient adsorption of fluoroquinolone antibiotics. The bamboo biochar had relatively large BET specific surface areas of 665.3 $m^2 \cdot g^{-1}$ and the average pore size of the bamboo biochar of 0.5 nm. The mesopore capacity was almost 90% of the total pore capacity of bamboo biochar based on the pore structure analysis. Most of the pores were mesopore with a smaller proportion of macropore and micropore, suggesting that the adsorption may mainly take place in mesopore of the bamboo biochar.

Table 2. Surface area and porosity of the produced bamboo biochar.

Parameter	Value
Size (μm)	100
Average pore size (nm)	0.5
Pore capacity ($cm^3 \cdot g^{-1}$)	0.236
Micropore capacity ($cm^3 \cdot g^{-1}$)	0.02
Mesopore capacity ($cm^3 \cdot g^{-1}$)	0.176
Macropore capacity ($cm^3 \cdot g^{-1}$)	0.02
Specific surface area ($m^2 \cdot g^{-1}$)	665.3

3.2. Effect of Aqueous pH

Fluoroquinolone antibiotics have carboxyl groups which may let the adsorption process be readily influenced by aquaculture wastewater pH. However, the result showed that the experimental adsorption capacities slightly increased from 18.10 ± 0.28 mg·g^{-1} to 19.89 ± 0.30 mg·g^{-1} when pH increased from 3.0 to 10.0 while the C/C_0 remained below 0.1 (Figure 2). The high adsorption capacity under alkaline conditions indicated that the molecular form was not the key factor in the case of fluoroquinolone antibiotics adsorption by bamboo biochar. Since the pH of wastewater usually ranged from 5.5 to 9.0 [20], the influence of wastewater pH on the adsorption of fluoroquinolone antibiotics by bamboo biochar can be neglected in most cases. Only extreme low or high pH has great influence on the adsorption of enrofloxacin or ofloxacin. The adsorption capacity dropped sharply when pH increased to 11.0 or decreased to 2.0. One reasonable explanation was that the extremely low or high pH changed the surface physical-chemical characteristics of the bamboo biochar, which subsequently led to the sharp decrease in adsorption capacity of the bamboo biochar.

Figure 2. Adsorptive removal of fluoroquinolone antibiotics under different aqueous pH.

3.3. Effect of Initial Concentration and Bamboo Biochar Dosage

The enrofloxacin adsorption capacity of bamboo biochar increased sharply from 0.21 ± 0.01 to 36.67 ± 0.76 mg·g^{-1} and that of ofloxacin increased from 0.20 ± 0.01 to 36.08 ± 0.60 mg·g^{-1} when the initial concentration of enrofloxacin or ofloxacin increased from 1 to 200 mg·L^{-1} and then began to plateau (Figure 3). The increase in adsorption capacity did not cease even when the initial concentration reached 400 mg·L^{-1}, suggesting a high fluoroquinolone antibiotics adsorption potential of bamboo biochar. The increase in adsorption capacity ceased when the initial concentration of fluoroquinolone antibiotics increased to 500 mg·L^{-1}. The effect of bamboo biochar dose on fluoroquinolone antibiotics was also investigated. The results showed that the adsorption capacity decreased as the dose of bamboo biochar increased. The adsorption capacity of *bamboo biochar* decreased sharply when the ratio of bamboo biochar/fluoroquinolone antibiotics increased from 10 to 50, and then reached a plateau, suggesting that the optimum ratio of bamboo biochar/fluoroquinolone antibiotics for adsorption efficiency was 50 where the bamboo biochar dose was 50 g·L^{-1}. The maximum adsorption capacity (45.88 ± 0.90 mg·g^{-1} enrofloxacin; 45.11 ± 0.66 mg·g^{-1} for ofloxacin) was observed when the ratio of bamboo biochar/fluoroquinolone antibiotics was 10.
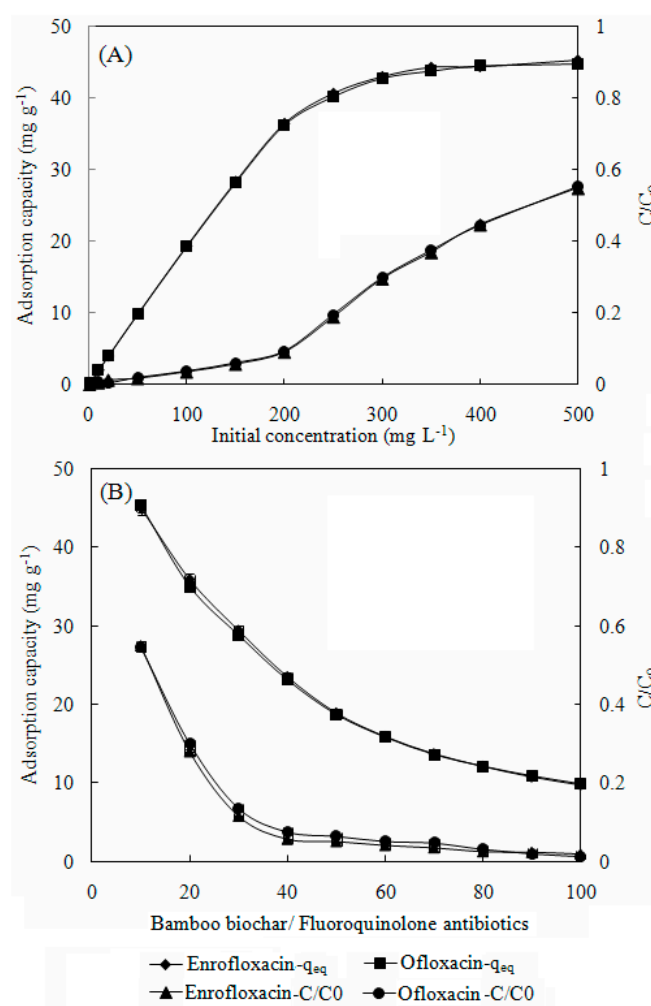

Figure 3. Effects of initial concentration (**A**) and bamboo biochar dose (**B**) on the adsorptive removal of fluoroquinolone antibiotics.

3.4. Effect of Ion Strength on the Adsorption

The effect of ionic strength on the adsorption of fluoroquinolone antibiotics was also investigated. High ionic strength led to the decrease in the adsorption of fluoroquinolone antibiotics (Figure 4). The enrofloxacin adsorption capacity of bamboo biochar decreased from 19.91 ± 0.21 mg·g^{-1} to 14.30 ± 0.51 mg·g^{-1} while that of ofloxacin decreased from 19.82 ± 0.22 mg·g^{-1} to 13.31 ± 0.56 mg·g^{-1} when the NaCl dose increased from 0 to 3 g·L^{-1}. The results indicated that the negative influence of salinity on the adsorption of fluoroquinone should not be neglected since the salinity of wastewater usually below 3 g·L^{-1}. Many researchers have found that increasing the ionic strength has a negative effect on the adsorption of various organic chemicals [21].

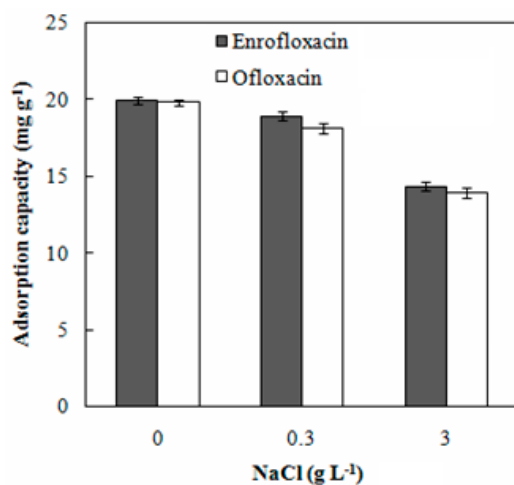**Figure 4.** Effect of ion strength on the adsorption of fluoroquinolone antibiotics.

3.5. Adsorption Isotherm

Based on the equilibrium adsorption data, Langmuir and Freundlich models were applied for the process simulation to better understand the adsorption isotherm of enrofloxacin and ofloxacin (Table 3). The Freundlich model (r^2 values were in the range of 0.990–0.991) yielded the best fit for the data. The Freundlich parameter K_f is relative to the adsorption capacity and n refers to the process intensity [6]. The adsorbate will be easily adsorbed when the constant n is greater than 1.00 [22]. The n values were beyond 2.00 in all treatments, suggesting that fluoroquinolone antibiotics were easily adsorbed onto bamboo biochar. The Freundlich isotherm assumes a heterogeneous surface with non-uniform distribution of heat of adsorption [23] while the Langmuir theory assumes that adsorption takes place at specific homogeneous adsorbent sites [24]. Since the equilibrium data agree well with the Freundlich model, but not the Langmuir model, it is likely that the adsorption did not take place at specific homogeneous bamboo biochar sites.

Table 3. Adsorption isotherm of enrofloxacin and ofloxacin.

	Freundlich Equation			**Langmuir Equation**		
	Kf	**n**	*R^2*	**Q**	**b**	*R^2*
Enrofloxacin	7.22	2.35	0.991	19.9	0.55	0.943
Ofloxacin	6.81	2.42	0.990	19.9	0.45	0.967

4. Conclusions

Efficient adsorptive removal of fluoroquinolone antibiotics using bamboo biochar was observed. The maximum adsorption capacity of 45.88 ± 0.90 mg$\cdot$g^{-1} observed in this study suggests great application potential of bamboo biochar for removing fluoroquinolone antibiotics. The influence of wastewater pH on the adsorption of fluoroquinolone antibiotics by bamboo biochar could be neglected in most cases since adsorption capacities were not greatly changed when the wastewater pH ranged from 3.0 to 10.0. High ionic strength led to the decrease in the adsorption of fluoroquinolone antibiotics. Freundlich isotherm fitted well with the adsorption data. These findings suggest that bamboo biochar is a promising low-cost absorbent for the treatment of wastewater containing fluoronquone antibiotics.

Author Contributions

Yanbin Wang prepared the bamboo biochar and performed adsorption experiments. Yanbin Wang and Jian Lu designed the experiments and prepared the manuscript. Jian Lu and Jun Wu interpreted the data and wrote the manuscript. Qing Liu analyzed the adsorption data, discussed the results, and prepared references. Hua Zhang discussed the results and analyzed the adsorption isotherm data. Song Jin discussed the results and analyzed the kinetics data.

Conflicts of Interest

The authors declare no conflict of interest.

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