Adsorption of Tetracycline by Ammonium Molybdate Modified Chinese Fir Biochars

Caimei Lu[1], *Hanbing* Zhang[1,*], *Rui* Tang[2], *Sishan* Yu[1] and *Zehua* Li[1]

[1]College of Resources, Environment and Materials, Guangxi University, Nanning 530004, Guangxi, China;
[2]Guangxi Colleges and Universities Key Laboratory of New Technology and Application in Resource Chemical Engineering, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, Guangxi, China

Abstract. Tetracycline (TC) adsorption amount on original wood biochar was finitely, so modification is imperative to improve its adsorption capacity. This study mixed chinese fir sawdust with ammonium molybdate to prepare a modified chinese fir biochar (MCB) via pyrolysis at 800 ℃. Meanwhile, pristine chinese fir biochar (CB) was produced as control. The effects of pH, adsorption time, initial concentration and adsorbent dosage on the adsorption process were also studied. Langmuir model and quasi second-order kinetic model were used describe the characteristics of adsorption process. The optimally capacity of TC adsorption on MCB reached 36 mg/g, which was 6 − fold increase to CB. Therefore, modification by ammonium molybdate can be used as a potential way of chinese fir sawdust biochar for increasing adsorption capacity of TC from antibiotic sewage water.

1 Introduction

Till now, antibiotics have been diffusely used worldwide, especially in China. Antibiotics are generally used in not only for human therapies as an important class pharmaceuticals, but also for aquaculture and animal husbandry as the feed additive to enhance the growth efficiency of animals. But in the meanwhile, it is inevitable to discharge into aquatic environments for the overuse as well as the slow metabolism of antibiotics, resulting in refractory pollution sources and potential harm to human health. Among all of the antibiotics, tetracycline (TC) is one of the most widely used antibiotics in both animal and human treatment. However, what is noteworthy is that human beings and animals could not break down tetracycline basically by normal metabolism, and a great deal of tetracycline was released into the environment with the discharge of sewage. Misuse of TC will increased antimicrobial resistance of microorganism lead to increase potential threats to ecosystem's food chain, and consequently to human health. Therefore, it is necessary to not only avoid the abuse of antibiotics but also to effectively remove them from water [1].

Up to now, many technologies have been served for removing TC from the aquatic environment, such as biodegradation, advanced oxidation, photolysis and adsorption [2]. Among them, adsorption treatment is considered as one of the most effective methods and is expected to be widely used in practical applications, because of its relatively cheap, easy operation and environmental friendliness. The selection of adsorbent is the key of adsorption technology. In recent years, carbon-based materials have been discovered by researchers to exhibit good performance in adsorbing antibiotics from aqueous solution. However, the high cost and complex preparation process of most carbon materials limit their wide application [3].

Of carbon-based adsorption materials, biochar is obtained by pyrolysis of waste or inexpensive biomass under an inert atmosphere. As an environmentally friendly adsorbent, biochar has gained importance due to wide raw material sources, low-cost preparation, having diverse functional groups and a large surface area. There have been some scholar used biochar as a sorbent to treat antibiotic wastewater [4]. However, the surface area, pore size and surface active group of the original biochar are limited, so further activations or modification are required to increase their adsorptive property [5]. Acid and alkali activation are common methods for the production of porous biochar, but it is easy to corrode the equipment during the preparation. Therefore, looking for eco-friendly raw material and modifier or activator is the mainstream of the present study.

Chinese fir is a unique tree species in China and is widely used in papermaking, construction, furniture and shipbuilding. At the same time, in a large number of chinese fir sawdust was generated during production. To be environmentally friendly, chinese fir sawdust can be used as raw materials for biochar preparation instead of discard. In addition to their large output, chinese fir sawdust are rich in lignin, cellulose and hemicellulose, which make it a promising raw material of biochar adsorbent [6]. Currently, few reports have investigated the pyrolysis treatment and modification of chinese fir sawdust. Daniela et al[7] prepared zinc chloride-activated

* Corresponding author: coldicezhang0771@163.com

chinese fir carbon as an adsorbent for p-nitrophenol removal from wastewater. However, there is no report on the preparation of chinese fir biochar for antibiotic wastewater treatment. Hence, it is important to investigate how to produce high value-added chinese fir biochar adsorbent by modification and realize low-cost treatment for antibiotic removal from wastewater.

In this study, choosing eco-friendly inorganic ammonium molybdate as a modifier, chinese fir sawdust was mixed with ammonium molybdate to prepare an ammonium molybdate modified chinese fir sawdust biochar (MCB) at 800 ◦C. Meanwhile, chinese fir biochar (CB) was also prepared as control. The adsorption performance of TC on the MCB is studied. The effects of adsorption time, pollutant concentration, adsorbent dosage and pH on the adsorption performance are then discussed. The adsorption kinetics, isotherms of TC on biochars were further studied, and the adsorption mechanism of TC on MCB was also revealed. This research can provide reference for the exploitation of chinese fir sawdust resources and the removal of TC from antibiotic sewage water.

2 Materials and methods

2.1 Raw materials

The chinese fir sawdust were collected from Guangxi, China. Chinese fir sawdust was washed 3 times by water and then dried in oven at 60℃ for 24 h, stored in the desiccator. Ammonium molybdate was procured from Guangdong Guanghua Sci-Tech Co., Ltd. Tetracycline (>95% purity) was obtained from Shanghai Macklin Biochemical Co., Ltd. HCl (36%) was purchased from Xilong chemical Co., Ltd. The solutions were prepared using ultrapure water (Milli-Q, Germany).

2.2 Preparation of biochar

Initially, 5 g chinese fir sawdust was mixed with 5 g ammonium molybdate in 100 mL ultrapure water stirred for 4 h, and then the product was rinsed with ultrapure water 3 times and dried at 80℃ for 12 h. Secondly, the solid materials were pyrolyzed in the pipe furnace at 800℃ for 2 h (under nitrogen atmosphere and heating rate was 10 ◦C/min). The obtained carbonaceous material was washed by 2 M HCl in order to eliminate inorganic components and then washed with ultrapure water until neutral pH. Finally, the obtained biochar products were dried at 80 °C for 12 h, ground, sieved through a 200-mesh sieve. The resulting samples were named MCB, where M stands for modification. By contrast, biochar without modification was prepared by Chinese fir sawdust pyrolysis in the pipe furnace at 800℃ for 2 h. Thereafter, the biochar was washed, dried, ground followed the above method, and noted CB.

2.3 Batch adsorption studies

Stock solutions of TC (100 mg/L) was prepared, from which working solutions were prepared in sequence during follow-up experiment.

Batch adsorption experiments were performed in conical flasks with wobbling (140 rpm) in a water bath shaker at room temperature (25±1°C). Experimental parameters including contact time (0 ~ 240 min), initial TC concentration (10 ~ 50mg/L), adsorbent dosage (0.6 ~ 1.4 g/L) and solution pH (3 ~ 11) were studied in details. The initial pH of the TC solution was transformed with 0.2 M HCl and NaOH solution. Each batch test was carried out triplicates to ensure repeatability. After adsorption, the solid-liquid mixtures were filtered by 0.45 μm membrane and then measured with UV-2550 at a wavelength of 356 nm [8].

2.4 Adsorption isotherms

The amount of TC sorbed onto adsorbents was calculated by the mass balance equation as below:

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

$$R=\frac{(C_0-C_t)}{C_0\times 100\%} \quad (2)$$

C_0 is the initial concentration of TC (mg/L). C_t is the concentration of the supernatant of TC (mg/L) was adsorbed at t (min). m is the dosage of biochar (g/L). q_e is the adsorption capacity of biochar for TC (mg/L). R is the removal efficiency (%) of TC on biochar.

To understand the characteristics of the adsorption process, adsorption kinetics included quasi first-order kinetic model (Eq. (3)) and quasi second-order kinetic model (Eq. (4) were performed with an initial TC concentration of 30 mg/L and a biochar dosage of 1 g/L.

$$\ln(q_e-q_t)=\ln q_e-k_1 t \quad (3)$$

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \quad (4)$$

q_e and q_t are the adsorption capacity of TC (mg/L) at equilibrium and t (min) respectively; k_1 (min^{-1})and k_2 (g/mg/min)are the degradation rate constant of quasi -first-order and quasi second-order kinetic model respectively.

Besides, the isotherm models studies of TC adsorption was performed by stirring 50 mL TC (10–50 mg/L) in 100 mL conical flasks for 180 min until reaching equilibrium, and the adsorption date was fitted via adsorption Freundlich (Eq. (5)) and Langmuir (Eq.(6)) equations.

$$\ln q_e=\ln K_f+\frac{1}{n}\ln C_e \quad (5)$$

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{K_L q_m} \quad (6)$$

q_e is the adsorption capacity of TC (mg/L) at equilibrium; C_e is the concentration of TC (mg/L) at equilibrium; K_f (mg/L) is the Freundlich model adsorption capacity (mg/g); n is the heterogeneity factor; q_m is the maximum adsorption capacity of biochar (mg/g); and K_L (L/mg) is the Langmuir constant.

3 Results and discussion

3.1 Characteristics of the adsorbent

The XRD patterns of the samples after TC adsorption was showed in Fig. 1. Two broad peaks at 22.63 and 43.54 which corresponding to amorphous carbon (002) and graphite structure (100) planes, respectively [9]. Comparing the XRD patterns of CB, MCB give distinct crystal peaks corresponding to Mo_2C (JCPDS card No. 71–0242). This result indicated that the Mo ion was successfully loaded in the MCB as Mo_2C. While after TC adsorption, the typical peaks of MoO_2 could be observed in the XRD spectra of spent MCB that may be due to the reaction between Mo_2C and TC in the adsorption process or oxidation during the spent MCB recovery.

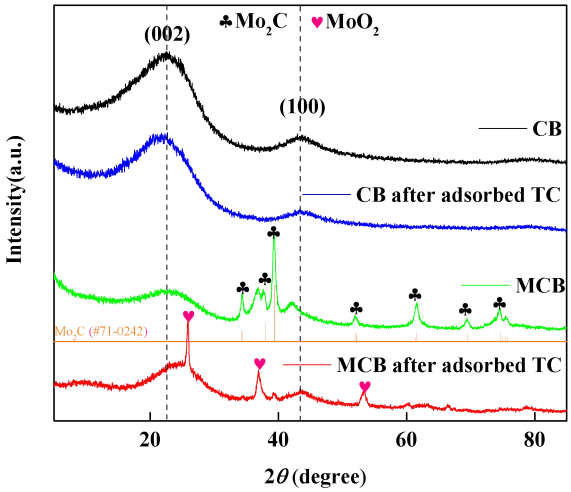

Fig. 1. XRD spectra of various biochar samples before and after TC adsorption

The surface functional groups in CB and MCB before and after TC adsorption were showed by FTIR spectroscopy (Fig. 2), which confirmed the existence of characteristic peaks of sawdust biochar including 1648 cm^{-1} assigned to the stretching vibration of C=O for carbonyl and carboxyl groups, the band at 1426 cm^{-1} ascribed as the aromatic rings of C=C of the unsaturated carbon structure, and 1133 cm^{-1} ascribed to C-O [10]. A broad band at about 3200-3600 cm^{-1} in samples was observed and corresponded to the stretching vibration of the -OH from hydroxyl. Upon treatment with ammonium molybdate, the intensity of the peaks at 2370 cm^{-1} ($-CH_3$) was increased and the new peaks at 680 cm^{-1} was observed and corresponded to the Mo-C, that is result of the generation of Mo_2C. After the adsorption of TC on MCB, the intensity of the peaks at 2370 cm^{-1} ($-CH_3$) was decreased may be due to Mo_2C was oxidized to MoO_2 during the adsorption process. This result from FTIR spectra coincide with the XRD.

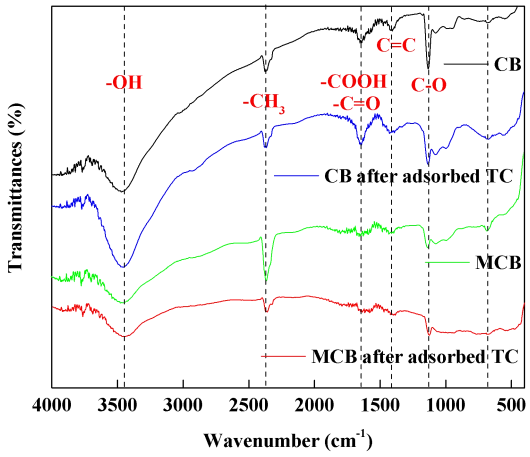

Fig. 2. FTIR spectra of various biochar samples before and after TC adsorption

3.2 Effect of contact time

From Fig. 3, it is observed that the effect of contact time on TC (30 mg/L) removal by MCB and CB. TC adsorption on MCB and CB were rapid initially and then relatively slowed down, finally attains equilibrium. For MCB, the TC adsorption efficiency reached approximately 35% within 5 min, equilibrium was achieved in 180min and the maximum adsorption efficiency attained more than 85%. Unlike MCB, the maximum TC adsorption efficiency of CB is only about 20%. The possible reason is that higher surface area and more available binding sites existed in biochar after modification [11].

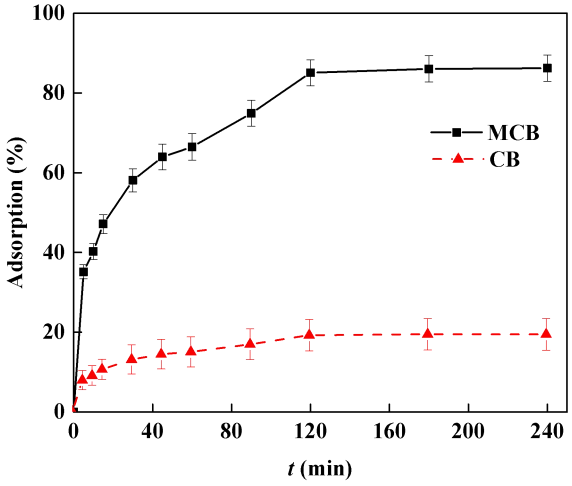

Fig. 3. Effect of contact time on TC adsorption by MCB and CB.

3.3 Effect of initial concentration

The influence of initial concentration of TC was studied by increasing the amounts of TC concentration from 10 to 50 mg/L. As we can see from Fig. 4, the TC adsorption efficiency decreased as the initial concentration increased. That is result of a limited amount of adsorption sites on the surface of biochar. In the concentration extent of 10 to 50 mg/L, the adsorption efficiency of MCB reached 70 to 100 %, while that of CB only reached about 10 to

20 %, which indicates the modification can effectively improve the adsorption capacity of biochar for TC.

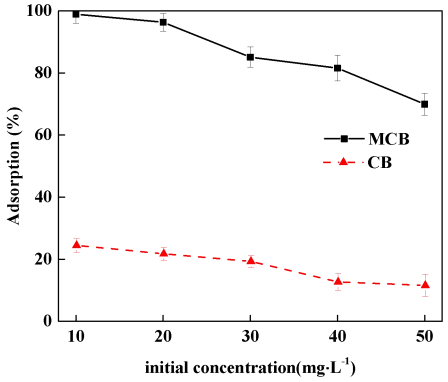

Fig. 4. Effect of initial concentration on TC adsorption by MCB and CB.

3.4 Effect of adsorbent dosage

Fig. 5 shows a similar regularity of MCB and CB adsorbed TC about the effect of adsorbent dosage. With increasing the biochar dosage, the adsorption efficiency of biochar improved to a certain extent. However, excessive dosage could decrease the adsorption capacity due to the aggregation effect of biochar [12]. Suitable dosages that can be used in TC removal is 1.0 g/L.

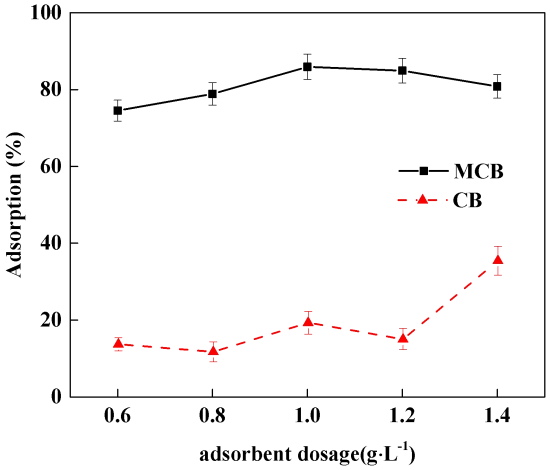

Fig. 5. Effect of adsorbent dosage on TC adsorption by MCB and CB.

3.5 Effect of pH

The TC solution initial pH obviously influences the adsorption consequence by changing surface characteristics of both adsorbent and adsorbate, because of solution pH not only affects surface charge of biochar but also change the existence form of TC. The adsorption efficiency of TC as a function of pH was presented in Fig. 6. The TC initial pH is 6.5, and TC adsorption quantity increased at initially in the pH range of 3.0 to 5.0, then significant drop with the pH increased from 7.0 to 11.0. As a result of TC is an amphipathic molecule and exists as TC^{+} at a pH value of less than 8.0, TC^{-} and TC^{2-} at pH higher than 8.0, that resulting in electrostatic attraction between TC and biochar, and an increase in the adsorption capacity of biochar [13]. On the contrary, significantly decreased adsorption ability due to electrostatic repulsion between adsorbent and adsorbate under pH 9.0 to11.0.

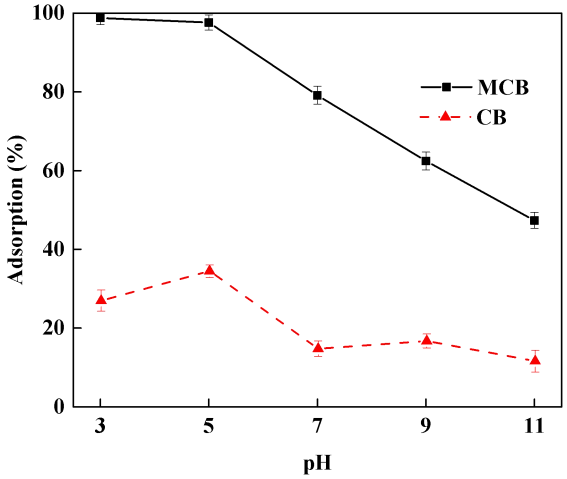

Fig. 6. Effect of pH on TC adsorption by MCB and CB.

3.6 Adsorption isotherms

The constants of isothermal adsorption for TC is shown in Table 1. TC adsorption on MCB and CB fit Langmuir model well with R^2 0.996 and 0.979, and the Langmuir adsorption capacities of MCB and CB for TC were 36.0 mg/g and 7.5 mg/g, respectively. The theoretical q_m of MCB is very close to the experimental value and it demonstates that this adsorption process probably was monolayer adsorption that related to chemisorption [14]. The K_L values of TC adsorbed by MCB was much higher than those on CB, indicating that MCB had higher affinity and stronger adsorption capacity of TC.

Table 1. Fitting parameters of TC adsorption isotherm models of MCB and CB.

	Langmuir model			Freundlich model			
	K_L/L·mg^{-1}	$q_{m,cal}$/mg·g^{-1}	R^2	K_f/mg·g^{-1}	1/n	R^2	$q_{m,exp}$/mg·g^{-1}
MCB	1.19	36.0	0.996	18.37	0.46	0.958	35.02
CB	0.07	7.5	0.979	1.07	0.23	0.915	6.01

The parameters of kinetic models for adsorption of TC on the biochar are shown in Table 2. The data for the TC showed a better adjustment to the quasi second-order kinetic model as supported by the higher R^2. Hence, the adsorption of TC on MCB and CB occurs through chemisorption mainly and is a process of fast initially, slowed down then and finally reached equilibrium [15]. For MCB, adsorption of TC is

enhanced as the chemical interactions are further improved because of the high surface area and more functional groups imparted on the biochar by modifier. Table 3 shows that MCB has been compared with other reported adsorbents for TC adsorption.

Table 2. Fitting parameters of TC adsorption kinetic models of MCB and CB.

	quasi first-order kinetic model			quasi second-order kinetic model			
	$k_1\times0.01$/ min^{-1}	$q_{e,cal}$/ $mg\cdot g^{-1}$	R^2	$k_2\times0.01$/ $g\cdot mg^{-1}\cdot min^{-1}$	$q_{e,cal}$/ $mg\cdot g^{-1}$	R^2	$q_{e,exp}$/ $mg\cdot g^{-1}$
MCB	0.68	23.2	0.903	8.19	37	0.992	35.02
CB	0.55	4.6	0.912	1.39	6.12	0.984	6.01

Table 3. Comparison of adsorption performance of various adsorbents for TC removal.

Targeted pollutant	Adsorbent	Adsorption conditions	q_{max} (mg/g)	Ref
TC	Zinc (II) modified hydroxyapatites	20 °C, pH 5, dosage 25 g/L, concentration 0.6 mmol/L	16.5	[16]
	Magnetic sludge bio char	25 °C, pH 5, dosage 0.2 g/L, concentration 200–500 mg/L	145	[17]
	Shell powder that was coated with ZnO nanoparticles	30 °C, pH 5, dosage 1 g/L, concentration 100 mg/L	99	[18]
	Grapefruit peel biochar	25 °C, pH 7, dosage 1 g/L, concentration 50 mg/L	32.5	[19]
	Cow manure biochar		11.7	[20]
	MCB	25 °C, pH 5, dosage 1 g/L, concentration 10−50 mg/L	36	This study

4 Conclusions

MCB was prepared via a one-pot pyrolysis method at 800 ℃. Modification increased the hydrophilicity and surface area of biochar. The optimal adsorption capacity of TC on MCB is 36 mg/g, which was attributed to pore filling and electrostatic interaction occurred on surface of MCB. Acidic conditions benefited TC adsorption on MCB and the adsorption process fit Langmuir model and quasi second-order kinetic model well. Furthermore, the practical application of MCB should be performed in the future studies.

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