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Adsorption behaviors and mechanisms of florfenicol by magnetic functionalized biochar and reed biochar

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ABSTRACT

A magnetic reed biochar (MRBC) was synthesized through chemical co-precipitation firstly and subsequently pyrolysis. The MRBC and reed biochar (RBC) were characterized by SEM, XRD, FTIR and VSM and were used for the adsorption of florfenicol (FF). Batch experiment results showed that the FF adsorption on MRBC exhibited a pronounced pH-dependent pattern and presented a bell curve. However, the FF adsorption on RBC decreased gradually with the increasing pH values. Ionic strength initially inhibited and then promoted the FF adsorption and the multivalent co-existing anions significantly increased the FF adsorption on MRBC. The FF adsorption was non-spontaneous, exothermic and entropy-decreasing on MRBC and was of a non-spontaneous, endothermic and entropy-increasing nature on RBC. The pseudo second-order model presented better fittings for the FF adsorption kinetic data. Langmuir and Freundlich models can well describe FF adsorption on MRBC and RBC, respectively. The FF adsorption on RBC may be controlled by pore-filling effect and $\pi-\pi$ EDA interaction, while hydrogen bonding, pore-filling effect and $\pi-\pi$ EDA interaction contributed to the FF adsorption on MRBC. The adsorption–regeneration cycles confirmed that the MRBC was a highly efficient and reusable adsorbent for the removal of FF from aqueous solution.

1. Introduction

Florfenicol (FF), a fluorinated derivative of thiamphenicol, has been widely used in veterinary medicine for treating diverse infections in various countries. Many studies demonstrated that FF inhibits transpeptidation in the bacterial protein synthesis and is effective against many Gram-negative and Gram-positive bacteria [1,2]. Large amounts of FF have been inevitably released into the aquatic environments through urinary, branchial and fecal excretions due to its incomplete metabolism by domestic animals and fishes [3]. Furthermore, FF has been frequently detected in the animal farm effluents, pond waters and rivers [4–8]. The residues of FF affect the physical health of raised animals and pose serious threats to ecosystem balance and human health [9,10]. Therefore, it is highly urgent and imperative to eliminate FF from aquatic systems.

Over the past few years, much attention has been paid to develop efficient and inexpensive multifunctional materials for various industrial and biomedical applications [11–16]. Magnetic biochars are ideal adsorbents due to their chemical and physical stability, abundant and low-cost raw materials and versatility [16]. Particularly, the magnetization process is able to change the surface and porous structures of biochars along with creating additional adsorption sites, which could dramatically improve the adsorption capacity [17]. Furthermore, magnetic biochar particles can be easily separated by means of external magnetic field after treatment with no separation system fouling, allowing convenient adsorbent cleaning, recycle or replacement from contaminated water [18]. The rapid and effective separation of magnetic adsorbents from aqueous solution obviously shortens the duration of the whole decontamination process, accordingly reducing the costs, which is extremely significant in industrial scale application [19].

Magnetic biochars have been synthesized as adsorbents for the removal of various pollutants, including heavy metals [20], hydrophobic organic compounds [21], synthetic dyes [22], antibiotics [19] and nutrients [23–24]. For instance, magnetic oak wood biochar and magnetic oak bark biochar were employed to remove cadmium and lead [18], and magnetic Douglas fir biochar prepared by Fe_3O_4 precipitation was used to remove 4-nitroaniline, salicylic acid, benzoic acid and phthalic acid [25]. Magnetic biochars prepared by the pyrolysis of $FeCl_3$ impregnated biomass powder exhibited considerable adsorption capacities for norfloxacin elimination [26]. To date, few relevant studies have been performed with regard to the preparation of magnetic biochar using reed

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stalk as feedstock for the removal of FF from aqueous solution. Furthermore, the studies on the adsorption behaviors and mechanisms of FF on magnetic reed biochar (MRBC) and reed biochar (RBC) still remained obscure.

In the present study, a magnetic reed biochar was fabricated through chemical co-precipitation firstly and subsequently pyrolysis of Fe^{2+}/Fe^{3+} precipitated reed stalk powder. Batch experiments were carried out to comprehensively investigate the adsorption behaviors and mechanisms of FF on MRBC and RBC. The results demonstrated that the functionalized magnetic reed biochar was a highly effective and reusable adsorbent for the FF removal, which provided a promising and green route for biochars in wastewater treatment.

2. Materials and methods

2.1. Chemicals

Florfenicol (purity ≥ 98%) was purchased from Aladdin Reagent Corporation, Shanghai, China. Ferrous sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$), ferric sulfate ($Fe_2(SO_4)_3$), NaOH, HCl were used analytical grade. The chemical solutions were prepared using ultrapure water (18.2 MΩ).

2.2. Preparation of MRBC and RBC

The detailed manufactured approach for MRBC was described by Mohan et al. [18]. Briefly, a ferric sulfate solution (freshly prepared by adding 3.70 g of $Fe_2(SO_4)_3$ to 260 ml of ultrapure water) and a separate ferrous sulfate solution (prepared by dissolving 4.00 g $FeSO_4 \bullet 7H_2O$ in 30 ml of ultrapure water) were mixed and vigorously stirred. Then 10 g of the reed stalk powder was immersed into the prepared Fe^{2+}/Fe^{3+} solution, slowly stirred for 30 min. After that, 5 mol/L NaOH was added dropwise into the biomass/Fe^{2+}/Fe^{3+} suspension until the pH reached 11–12. After agitated for 30 min, the suspension was aged for 12 h, filtered and dried. The pre-treated dry biomass was pyrolyzed at the temperature of 873.15 K for 2 h under an oxygen-limited condition in a resistance furnace at a heating rate of 8 K/min. The carbonized material was rinsed with ultrapure water several times and oven dried overnight at 353.15 K. After milled and sieved to pass through a 100-mesh sieve, the obtained magnetic reed biochar was labeled as MRBC. The reed biochar was prepared with the similar pyrolysis procedures and was labeled as RBC.

2.3. Characteristics of MRBC and RBC

The elemental compositions (C, H, S, O and N) of the MRBC and RBC were measured using an elemental analyzer (vario EL III Element Analyzer, Germany). The weight percentage of Fe was calculated by the weight difference between the dry MRBC and sum of C, H, S, O and N. The BET surface area, micropore volume and pore size distribution were measured by N_2 adsorption/desorption method at liquid temperature (77 K) (ASAP2020-M+C, Micromeritics). The Boehm's titration method was employed to determine the amounts of the acidic oxygen-containing surface groups [27]. The point of zero charge (pH_{pzc}) was measured based on the reported method [21]. X-ray diffraction (XRD) analysis was conducted on a Shimadzu XRD-6100 diffractometer equipped with Cu Kα radiation ($\lambda = 1.54$ Å) over the 2θ range of 10–80°. The microscopic features of the MRBC and RBC were characterized by scanning electron microscopy (SEM) (JEOL JSM 840A, Japan). The FTIR spectra were applied to identify the surface functional groups of the MRBC and RBC in the 4000–400 cm^{-1} spectral range (Nicolet FTIR 6700, America). The magnetic properties of the MRBC were assessed by using a SQUID-VSM vibrating sample magnetometer (Quantum Design, San Diego, America). The stability measurement of MRBC was conducted using inductively coupled plasma optical emission spectrometry (ICP–OES) (Optima 5300 DV, America).

2.4. Adsorption experiments

Batch adsorption experiments were carried out in 150 ml Erlenmeyer flasks with 100 ml of FF solutions (pH7, 20 mg/L) and 50 mg of MRBC or RBC samples under the darkness condition in a reciprocating shaker at 190 r/min and 298.15 K for 24 h unless stated otherwise. The effect of pH was examined by adjusting the FF solutions in the range of 3–12 with HCl and NaOH. The influences of ionic strength (NaCl or $CaCl_2$ of 0–0.5 mol/L, respectively) and co-existing anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-} of 0.1 mol/L, respectively) on FF adsorption were carried out following the same procedures. The effect of temperature on the FF adsorption was explored at 288.15 K, 298.15 K and 308.15 K. For the adsorption kinetic study, 20 mg/L FF solutions were used with adsorption time ranging from 0.5 to 24 h. Adsorption isotherms were constructed using different initial FF concentrations ranged from 2 to 100 mg/L. All batch adsorption experiments were performed in duplicate. The FF concentrations were measured by a UV–visible spectrophotometer (Alpha-1860AS, China) at 223 nm.

2.5. Regeneration experiment

After the adsorption experiment with 50 mg of MRBC samples exposed to 100 mg/L FF solutions at pH 6 for 12 h, the exhausted MRBC samples were separated and directly regenerated by 100 ml of 0.5 mol/L NaOH solutions for 12 h. Before the next adsorption experiment, the MRBC samples were thoroughly washed with ultrapure water. Such adsorption–regeneration cycles were repeated for 5 times.

2.6. Data analysis

For the adsorption experiments, Eq. (1) was employed to calculate the equilibrium adsorption capacity, q_e (mg/g), of the MRBC or RBC:

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

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of FF solutions, respectively, V (L) is the solution volume, and m (g) is the mass of dry MRBC or RBC.

Pseudo first-order (PFO) model (Eq. (2)) and pseudo second-order (PSO) model (Eq. (3)) were used to analyze the kinetic data:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_t (mg/g) is the amount of FF adsorbed on the MRBC or RBC at any time t (h), k_1 (h^{-1}) and k_2 (g/(mg•h)) are the PFO and PSO rate constants, respectively.

The adsorption isotherm data was fitted in Langmuir and Freundlich models, which can be written as following equations:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F C_e^{1/n} \tag{5}$$

where q_m (mg/g) is the maximum monolayer adsorption capacity, K_L (L/mg) is the Langmuir isotherm constant, K_F ((mg/g)/(mg/L)^n) is the Freundlich affinity coefficient and n is a measure of adsorption linearity.

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