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Analyses of tetracycline adsorption on alkali-acid modified magnetic biochar: Site energy distribution consideration

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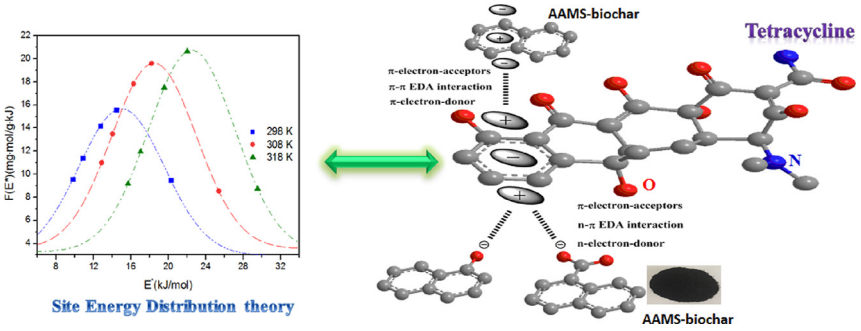
HIGHLIGHTS

- Site energy and its distribution of the adsorption system were determined.
- Strength of adsorption affinity was evaluated by the weighted mean of distribution.
- Percentage of adsorption sites was estimated.
- Electron-donor-acceptor interactions dominated the adsorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

As a widely used antibiotic, tetracycline has a huge hidden danger to human health. Municipal sludge rich in organic substances has the potential to produce biochar. In this work, the municipal sludge biochar from solid waste was modified by the alkali-acid binding method, and tetracycline was efficiently removed from the aqueous solution, the adsorption removal efficiency reached to 86% at initial concentration of 200 mg/L. The activation energy was determined by analyzing the adsorption kinetics at different temperatures and tetracycline concentrations. The results showed that tetracycline adsorption on modified biochar was endothermic reaction. Presenting the *Langmuir-Freundlich* model, adsorption site energy distributions was reckoned. The average adsorption site energy and corresponding standard deviation of the adsorption site energy distribution were deduced emphatically to inquiry the strength of tetracycline adsorption on modified biochar and the adsorption site heterogeneity. The method proposed of research further proves that modified biochar from sewage sludge remove tetracycline from contaminated water has great potential, and exploration of tetracycline adsorption mechanisms by quantifying average site energy. The results and methods of this work can be transferred to study water treatment systems.

1. Introduction

Antibiotics are emerging pollutants widely applied in animal husbandry and human medicine, receive much emphasis of research (Chen et al., 2017; Liu et al., 2017; Norvill et al., 2017). Tetracycline

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(TC) is a commonly used antibiotic in cultivation and livestock husbandry. Due to soil infiltration and incomplete animal metabolism, most parent compounds are released into the aquatic environment in their original and metabolic form (Conde-Cid et al., 2018; Zhu et al., 2014). Researchers analyzed the concentration of TC in rivers affected by livestock life in Chengmen Rivers, Kam Tin and in Yuen Long Hong Kong, and found that TC concentrations ranged from 30 to 497 ng/L (Selvam et al., 2017). In addition, antibiotics such as TC will induce to the produce antibiotic resistance genes (ARG) in the microorganisms (Li et al., 2017; Wang et al., 2016). It can be widely spread in the ecological environment and poses a major risk to human health (Huang et al., 2016).

At present, there are various technologies for eliminating TC such as adsorption, chemical, photolysis, biodegradation and electrochemical oxidation (Liu et al., 2017a; Liu et al., 2017b; Liu et al., 2018; Strasse, 2009; Zhao et al., 2017). Among these, adsorption is widely recognized as a large-scale and cost-effective method (Zhou et al., 2017c). However, for adsorption applications, it is still necessary to seek an economic, efficient, green, sustainable and easily separated adsorbent. Biochar is the carbon-rich solid that produced through the pyrolysis of biomass in anoxic environments (Shen et al., 2017; Wu et al., 2017). It has multi-empty structure and relatively abundant functional groups, (Liu et al., 2015), which is entrusted with adsorption performance.

Municipal sludge (MS) is a major by-product of municipal wastewater treatment facilities, considered solid waste contaminant. It is rich in organic matter that allows MS to have the potential to produce biochar (MS-biochar). However, the adsorption performance after single modification of MS-biochar is not satisfactory (Tang et al., 2018). Recently, based on the corresponding components of urban sludge, our previous studies have shown that TC can be effectively adsorbed by alkali-acid (AA) binding method modified MS-biochar (AAMS-biochar) and determine the optimal solution pH for TC adsorption is 7.0 (Tang et al., 2018). Comparing other adsorbents such as goethite adsorbents (1.92 mg/g) (Zhao et al., 2014), bamboo charcoal adsorbents (22.7 mg/g) (Liao et al., 2013), iron-montmorillonite adsorbents (37.21 mg/g) (Wu et al., 2016), and graphene oxide adsorbents (39.1 mg/g) (Lin et al., 2013), AAMS-biochar shows higher adsorption capacity for TC (286.913 mg/g at pH 7.0) (Tang et al., 2018). In addition, the magnetic properties of the AAMS-biochar itself can be effectively magnetically separated and recovered. Therefore, AAMS-biochar has good regeneration performance, the performance after five cycles decreased slightly (Tang et al., 2018). However, with respect to the kinetics of TC adsorption processes, systematic studies of temperature characteristics such as isotherms and adsorption energy have not yet been completed. It is crucial for research the mechanism of TC and AAMS-biochar adsorption and related application in the treatment of water contaminated with TCs and the like.

In the adsorption of sorbates from benzene rings, it has been proposed that the interaction of π-π electron-donor-receptor (EDA) is one of the main driving forces (Liao et al., 2013; Lin et al., 2013). The tetraphenyl ring structure is contained in the molecular structure of TC, the π-electron-acceptor is considered to the benzene ring of TC (Lin et al., 2013), while the π-electron-donors is aromatic groups on heterogeneous adsorbents (Liao et al., 2013; Liu et al., 2012). It remains to be further studied the effect of the π-π electron-donor-receptor interaction on TC adsorption. Moreover, it is helpful to understand the adsorption mechanism of the target molecule by analyzing the adsorption site energy distribution. The energy intensity of binding sites for TC adsorbed on the adsorbent is obtained from the curve of site energy distribution, which helps to elucidate the adsorption mechanism (Jin et al., 2016; Kumar et al., 2011). However, analysis of the effect of temperature on the energy of TC adsorption sites has not been completed.

Herein, in this work, the isotherms and adsorption kinetics involved in the TC adsorption on AAMS-biochar were studied at initial TC concentrations and different solution temperatures. The adsorption site energy distribution was determined by simulating the equilibrium TC adsorption data, and the interaction between the adsorbent and the energy non-uniformity at the adsorption site were analyzed.

2. Materials and methods

2.1. Materials preparation

The used materials and chemicals were presented in supporting information. The reported strategies (Tang et al., 2018). Typically, municipal sewage sludge was sieved through the 100 mesh sieve (0.15 mm) after drying and put into tube furnace (SK-G04123K, China) at a heating rate of 5 °C/min under nitrogen protection, calcining for 2 h. MS-biochar was obtained from an optimum pyrolysis temperature of 800 °C. First stir with sodium hydroxide (2 M) in a 90 °C water bath for 2 h, then soaked with concentrated nitric acid (14 M) at 10–15 °C, with magnetic stirring.

The structural information of SEM (Zeiss Merlin), the magnetic property, Fourier-transform infrared spectrum (FT-IR), and porosity and surface area of AAMS-biochar were described in our previous work (Tang et al., 2018). It showed that AAMS-biochar was rich in oxygen-containing functional groups and its average pores, pore volume and surface area were enhanced. The oxygen-containing functional group on the outside of the AAMS-biochar and the increased average pores, pore volume and surface area mean that they contain both hydrophilic and hydrophobic sites.

2.2. Batch experiments

For the batch adsorption studies, with the optimal pH value (pH 7.0), each sample contained 20 mg adsorbent and 20 mL TC solution at 298, 308, 318 K which shaking at 160 rpm. In the kinetic experiments, obtaining the kinetic data at 5, 10, 20, 30, 60, 120, 180, 300, 420, 600, 840, 960, 1080, 1200, 1320, and 1440 min with 200 mL initial TC concentration. In the adsorption site energy distribution analysis experiments, the initial concentrations of TC ranged from 50 to 800 mg/L, the TC solution temperatures were 298, 308 and 318 K, respectively. All samples were filtered with a 0.45 μm filter which was proved to have no intercepting effects for the TC molecule, and then analyzed by a UV-VIS absorbance at 357 nm, and calculated the standard deviation of the sample mean. All of the experiments were performed in triplicates.

2.3. Experimental data modeling

2.3.1. Kinetics analysis

The relationship between adsorption capacity and the number of active sites on the adsorbent was used the pseudo-second-order kinetics model to simulate (Zhou et al., 2017a). The pseudo-second-order kinetic model fitted well the adsorption of TC on modified biochar derived from sawdust (Zhou et al., 2017b). Adsorption of TC on AAMS-biochar will be simulated using this model in this work. The rate constant indicates k (g/(mg·h)), basic function equation is

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

at $t = 0$, integral with initial value $q_t = 0$ gives

$$t = \frac{tq_t}{q_e} + \frac{q_t}{kq_e^2} \tag{2}$$

where q_e is amount adsorbed of the adsorbate at equilibrium (mg/g), the effect of different temperatures can determine the rate constant by analyzing the adsorption kinetic data. By plotting the association of lnk and $1/T$, the activation energy can be determined, corresponding the *Arrhenius* equation (Eq. (3)) as follows,

$$lnk = -\frac{E_a}{RT} + lnA \tag{3}$$