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Dynamic adsorption of ciprofloxacin on carbon nanofibers: Quantitative measurement by in situ fluorescence

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ABSTRACT

Antibiotics have been considered to be a potential risk to human and ecological health. In an effort to develop convenient and effective treatment technology for the removal of fluoroquinoline antibiotics ciprofloxacin (CIP) from aqueous solution, a dynamic adsorption experimental apparatus based on carbon nanofibers (CNFs) was built and the adsorption of CIP was quantitatively measured by in situ fluorescence (FL) for the first time. The experimental results show that the adsorption kinetics and isotherms match well with the pseudo-second-order model and the Langmuir model, respectively. The adsorption equilibrium accomplished within 4 h, which is much shorter than the adsorption of CIP on the other carbon materials reported before. The maximum adsorption capacity (q_m) is 10.36 mg/g, which is similar to the q_m of CIP adsorption on biocomposite fibers. The strong adsorption affinity exhibited by CNFs was ascribed to the contributions of π–π electron–donor–acceptor (EDA) interaction, hydrophobic interaction and electrostatic interaction. The dynamic adsorption of CIP on CNFs provides a novel and effective approach for CIP removal, implying the potential practical application of CNFs in the field of water treatment.

1. Introduction

Ciprofloxacin (CIP) is one of the most commonly used fluoroquinoline antibiotics for treating bacterial infection. The world annual sales of CIP were over $1 billion by the end of 1990s [1]. Due to the incomplete metabolism of CIP in humans and the discharge of drug manufacture effluent, CIP has been detected frequently from surface water and underground water within the concentration range from ng/L to μg/L [2–4]. Much higher concentrations of CIP up to 150 μg/L and 50 mg/L have been detected in the effluents of hospitals and drug production facilities, respectively [5–8]. Since the presence of CIP in water environment leads to increasing antibiotics resistant bacteria [2,7,9] and deleterious effects on water quality [10], it is highly desirable to develop effective control strategies for CIP removal in wastewater treatment process.

Wastewater treatment generally consists of a primary stage, a secondary stage, and sometimes an advanced treatment stage and different biological, physical and chemical processes are involved. Concerning the removal of antibiotics from aqueous solution, conventional wastewater treatment processes such as biological degradation and adsorption on sewage sludge have been proved to be ineffective [11,12]. Moreover, the chlorine disinfection and the ozonation oxidation processes may increase the toxicity of antibiotics and produce more serious threat to water quality [13,14]. In comparison, given the advantages of easy operation, low cost and repeated utilization, adsorption on carbon materials is a relatively ideal treatment process for trace CIP removal from wastewater [15].

Carbon nanofibers (CNFs) represent a new form of carbon adsorbents, which are microporous materials in the form of woven fabrics with large surface area and narrow pore size distribution. Since the adsorption energy could be enhanced by low-size pores [16], CNFs are considered as a promising material for highly efficient adsorption [17,18]. Furthermore, the exposure of micropores on the large surface could potentially benefit the adsorption rate [19].

CNFs have been used for toluene and activated dyes adsorption [20,21]. However, the study on the adsorption of CIP with CNFs was not reported. The goal of this work is to remove CIP effectively by dynamic CNFs adsorption. In order to gain insight into the dynamic adsorption, the experiment was carried out in a cylindrical CNFs packed cell, to simulate a full-scale adsorption tower of

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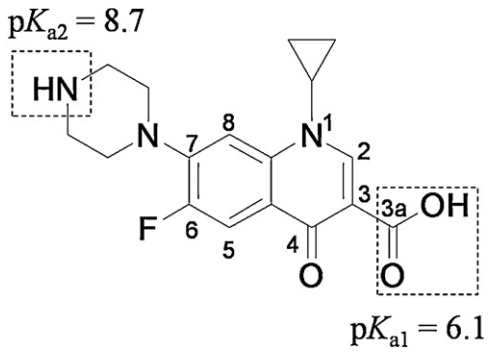

Fig. 1. The structure of CIP.

water treatment. The cell was linked with a fluorescence (FL) spectrophotometer for in situ monitoring the concentration of CIP, and a PC-based data acquisition system was connected to the spectrophotometer. The adsorption kinetics and isotherms were investigated, and the influence of the solution pH was explored. Adsorption mechanisms were proposed on the basis of these results.

2. Experimental

2.1. Materials

The untreated CNFs (thickness: 5 mm) made from polyacrylonitrile were obtained in the form of woven fabrics from Jiangsu Kejing carbon fiber Co., China. To remove the fine and inorganic ions produced from the manufacturer, the CNFs were first sonicated in 1 M HCl for 1 h, then sonicated in 1 M NaCl for another 1 h. At last, treated CNFs were washed with Milli Q water for several times until the pH value closed to neutral and dried at 105 °C, and stored in desiccators before use. CIP (99%) was purchased from Dalian Meilun biology technology Co., China. The structure of CIP was given in Fig. 1. The properties of CIP were summarized in Table 1. As CIP can exist as cation, zwitterion and anion under different pH conditions, and the neutral molecule is only sparingly soluble in water (shown in Table 1), the stock solution of CIP (1 g/L) was prepared by dissolving the solid standards in methanol and water (1:9) at pH 2.5.

2.2. CNFs characterizations

Scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai G2 S-Twin) images were observed to investigate the surface morphology of CNFs, respectively. The nitrogen adsorption and desorption isotherms were measured at 77 K on a Quantachrome instrument Quadrasor SI. The specific surface area (S_{BET}) and total pore volume (V_{total}) were calculated by multi-point BET and BJH methods, respectively. The micropore volume was calculated by V–t plot method. Fourier-transform infrared spectroscopy (FT-IR) of CNFs was recorded on a Shimadzu IR prestige-21 spectrometer. Zeta potential of CNFs at different pH was measured according to the method reported in our previous study [24] using a zetasizer nano ZS equipment (Malvern instrument company, USA).

2.3. Batch-mode adsorption experiment

To investigate the adsorption capacity of CNFs for CIP, batch-mode experiments were conducted in a continuously recirculating system including CNFs packed adsorption unit cell and a FL spectrophotometer for quantitative measurement of CIP. A schematic diagram of the apparatus was shown in Fig. 2. In each experiment, the CIP solution was continuously pumped from a peristaltic pump into the cell. The CNFs were filled on a fixed baffle plate with circular hole, and the weight of CNFs in each experiment was about 300 mg. To avoid the CNFs flowing into the effluent, a plastic grid was covered on the CNFs. The concentration of effluent after adsorption was continuously monitored by in situ FL. Finally, the effluent was returned to the feed container.

For the study of adsorption kinetics and isotherms, the aqueous solution of CIP containing 0.5 mM $CaCl_2$ was maintained with a total volume of 2 L. The temperature was kept at 25 °C. The pH value of the CIP solution diluted from CIP stock solution (1 g/L) is 5.0. The flow rate of CIP was kept at 50 mL/min. The kinetics studies were carried out at CIP initial concentration of 500 μg/L, 750 μg/L and 3.0 mg/L, respectively. The isotherm experiments were conducted in CIP concentration range of 100 μg/L to 3 mg/L. The adsorption time was set as 4 h, which is enough to reach adsorption equilibrium according to the results of kinetics experiments. The concentration of effluent was determined by the intensity of in situ FL. The uptake of CIP at time t and equilibrium, q_t and q_e (μmol/g), was calculated by the following equation respectively:

$$q_t = V \cdot \frac{C_0 - C_t}{m} \quad (1)$$

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

where C_0, C_t and C_e are the initial, time t and equilibrium concentrations of CIP (μmol/L) in solution, respectively; V is the volume of the solution (L) and m is the weight of CNFs (g).

In the experiments of pH effect, Ca^{2+} concentration was set as 0.5 mM. The solution pHs were adjusted in the range of 2.0–8.0 by adding either HCl (0.5 M and 0.05 M) or NaOH (0.05 M) after mixing of CIP with CNFs, which did not change during the adsorption process.

2.4. CIP determination

The concentration of CIP was determined by photometry mode of FL spectrophotometer (F-4500, Hitch Co., Japan). The adsorption unit cell was connected with the profile of the sample cell. The CIP solution was pumped into the sample cell of the FL spectrometer by peristaltic pump. After FL detection, CIP solution flowed out from the top of the cell. The maximum excitation (Ex) and emission (Em) wavelengths of CIP was 280 nm and 445 nm, respectively. The FL intensities of CIP in the concentration range of 50 μg/L to 3 mg/L were measured to obtain the calibration curve for quantification. The concentrations of CIP under different adsorption experiments were obtained by in situ FL monitoring and fitting with

Table 1
Selected physicochemical properties of CIP.

Chemical	Molecular weight (g/mol)	pK_a	Solubility (mg/L)	Log K_{ow}	Molecular size (Å)	Configuration
Ciprofloxacin (CIP)	331.4	pK_{a1} = 6.1, pK_{a2} = 8.7[a]	150[b]	0.42[c]	13.5 × 3 × 7.4[a]	Planar

[a] Ref. [1].
[b] Ref. [22], at 37 °C (pH = 7).
[c] Ref. [23], at 25 °C.