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Adsorption behavior and mechanisms of ciprofloxacin from aqueous solution by ordered mesoporous carbon and bamboo-based carbon

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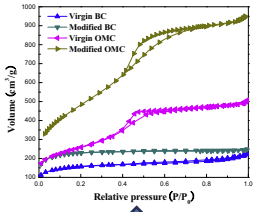
GRAPHICAL ABSTRACT



Sample	C1s (at %)	N1s (at %)	O1s (at %)
Virgin BC	92.41	0	6.47
Modified BC	90.12	4.37	3.52
Virgin OMC	96.37	0	2.87
Modified OMC	94.69	3.83	1.13

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ABSTRACT

The performances of ordered mesoporous carbon CMK-3 (OMC), bamboo-based carbon (BC), and these two kinds of adsorbents modified by thermal treatment in the ammonia atmosphere at high temperatures were evaluated for the removal fluoroquinolone antibiotic (ciprofloxacin) from aqueous solution. The adsorption behavior of ciprofloxacin (CIP) onto OMC and BC including adsorption isotherms and kinetics were investigated. The effect of various factors (pH, ionic strength and temperature) on the adsorption process was also investigated. The results demonstrated that the modified OMC and BC can further enhance the adsorption capacity due to introduce of alkaline nitrogen functionalities on the carbon surface. And their maximum adsorption capacity reached as high as 233.37 mg g^{-1} and 362.94 mg g^{-1} under the same experimental conditions, respectively. This is primarily ascribed to the positive effect of the surface basicity. The highest sorption was observed at the lowest solubility, which indicated that hydrophobic interaction was the dominant sorption mechanism for CIP uptake onto the four adsorbents. The adsorption data of antibiotics was analyzed by Langmuir and Freundlich model, and the better correlation was achieved by the Langmuir isotherm. The kinetic data showed that the adsorption of CIP onto OMC and BC follow closely the pseudo-second order model. The removal efficiency and adsorption capacity increased with increasing temperature. The results of thermodynamic study indicated that the adsorption process was a spontaneous and endothermic.

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1. Introduction

In recent years, antibiotics in environments including underground and surface water, soils, sludge and sediments have attracted extensive concern. Fluoroquinolone antibiotics (FQAS) are a group of synthetic antibiotics, widely used in the treatment of serious infections in humans and veterinary treatments, which presents high antibacterial activity against both Gram-negative and Gram-positive bacteria through inhibition of DNA gyrase [1]. This synthetic compound even under low concentrations may present a risk to human health through contaminated drinking water while present high antibacterial activity to the microbial and bacteria in the environments in the long-term period. Accordingly, it is necessary to develop new techniques to effectively remove FQAS in aquatic environments.

Bamboo is a large, woody-grasses member of Bambusoideae encompassing about 1250 species in 75 genera. Bamboo forests resource are widely dispersed in China, whose area reaches more than 48,400 h m^2. Besides it is estimated that annual output of bamboo is more than 12,600 h m^2 [2]. Bamboo, can be used as low-cost precursors to product bamboo-based activated carbon for sorption removal of contaminants from water such as metal ion [3], dye [4], organic and inorganic pollutants [5,6], which is proved to be a technologically feasible and economically viable manner.

Ordered mesoporous carbon CMK-3 is a member of CMK materials, can be synthesized by SBA-15 silica as template and all kinds of carbon sources as carbon precursor [7]. CMK-3 exhibits uniform mesopore size, high BET specific surface area and large total pore volume. In addition, CMK-3 shows characteristic features as for example the high stability in strong acids and bases, high mechanical stability and electric conductivity which is of particular importance in contrast to other ordered mesoporous carbon, so that it can be a promising carbon synthetic material as adsorbent for Macromolecular organic matter pollutant sorption from aqueous solution [8].

The sorption capacity of porous carbon depends on not only its surface area and pore structure, but also functional groups on its pore surface. The functional groups and pore structure of porous carbon commonly determine its application. The surface chemistry may be modified by various techniques, such as acid treatment, ammonization, and microwave treatment [9]. The nitrogen-containing groups generally provide basic property, which could enhance the interaction between porous carbon and acid molecules, which have a great effect on the surface chemistry of carbons material. Ammonization could introduce the basic groups, such as, C—H, C=N groups, amino, cyclic amides, nitrile groups, pyrrole-like structure [10].

In this study, we prepared ordered mesoporous carbon CMK-3 (OMC) by SBA-15 silica as template and furfuryl alcohol as carbon precursor and bamboo-based carbon (BC) was prepared using bamboo charcoal. Then, we designed a simple device to incorporate basic nitrogen-containing functional groups onto OMC and BC. We used ciprofloxacin (CIP), which was a synthetic FQAS antibacterial, as a model amphoteric antimicrobial to investigate sorption property with several types of referential carbon materials in this work. Moreover, the adsorption of CIP onto the OMC and BC mechanism was discussed, besides we also discuss and assess the influence of the chemical nature of the solution (such as pH, ionic strength and temperature) on the CIP adsorption process, as well as the adsorption kinetics and isotherms were investigated. In addition, the study focused on the interaction mechanism which dominated in the adsorption process.

2. Materials and methods

2.1. Materials

Ciprofloxacin (CIP), triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich),

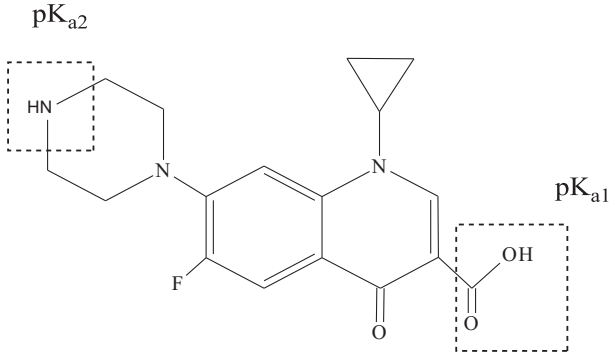

Fig. 1. Molecular structure of CIP (M = 331.35 g mol^{-1}; pK_{a1} = 5.9 ± 0.15, pK_{a2} = 8.89 ± 0.11).

furfuryl alcohol (FA, 90%, $C_5H_6O_2$), HCl, NaOH, H_2SO_4, H_3PO_4 were provided by Sigma–Aldrich. All other reagents were of analytical grade (see Fig. 1).

2.2. Synthesis of mesoporous carbon CMK-3

The CMK-3 samples were prepared by a nanocasting process using SBA-15 silica as template. Following the synthesis procedure reported by former work [11]. The SBA-15 template was synthesized using the triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich) as the template and tetraethyl orthosilicate (TEOS, 98%, Aldrich) as the silica source. At first, 2 g P123 was dissolved in 62.5 mL distilled water and 10.68 mL HCl (37 wt.%) solution at 35 °C and 4.3 g TEOS was then added. After the solution was magnetically stirred at 40 °C for 24 h, the mixture was stirred with magnetic until TEOS was completely dissolved and was transferred to an autoclave, and subsequently for 24 h at 100 °C under same condition. The product was filtrated and dried at 60 °C for 12 h and calcined at 550 °C for 12 h to remove the template.

The CMK-3 samples were fabricated by following the synthesis procedure: Briefly, About 2 g of furfuryl alcohol and 0.2 g of oxalic acid regards as catalyst were dissolved in 2.0 g of ethanol. Then 2 g of SBA-15 was added to a solution infiltrated by magnetic stirring dissolving at room temperature, the mixture was placed in a drying oven for 8 h at 100 °C, and subsequently the resultant mixture was calcinated at 350 °C under nitrogen gas condition. The sample, containing partially polymerized and carbonized, was treated again in the same way with the addition of 1.6 g of furfuryl alcohol, 0.6 g of oxalic acid and 8 g of ethanol mixture solution. Followed by calcination for 6 h at 350 °C under N_2 and sequentially carbonization for another 6 h at 900 °C under same condition, and the silica component was removed by stirring CMK-3 in 1.0 M NaOH solution (the volume ratio = 1:1) twice at 100 °C for 1 h. Finally, the carbon product was filtered and washed with water, and dried at 105 °C.

2.3. Preparation of bamboo-based carbon

The original bamboo charcoal was purchased from a local Charcoal company. The massive bamboo charcoal was ground and sieved to desired mesh size (1–2 mm). After sieving, sample was washed with hot distilled water to get rid of impurities and ash. The bamboo charcoal was dehydrated in oven for 24 h. Then the bamboo charcoals was pyrolysed in muffle furnace under flow of nitrogen gas (0.1 m^3/h) at 500 °C for 3 h. The product was separated and cooled at 25 °C overnight. Following sample was soaked with phosphoric acid (H_3PO_4) with the impregnation ratio of 1:1. The mixture sample was dried at 200 °C for 24 h. After cooling, the mixture was filtered and subsequently the mixture (BC) was repeatedly washed with distilled water until the pH close to 7 in