



Adsorption removal of ciprofloxacin by multi-walled carbon nanotubes with different oxygen contents from aqueous solutions



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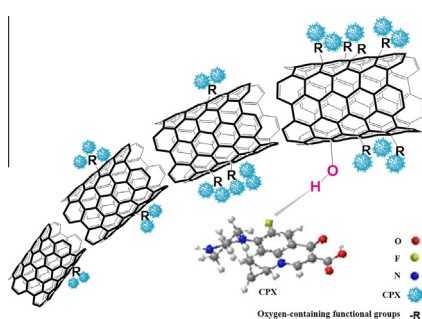
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HIGHLIGHTS

- Carbon nanotube adsorbents with different oxygen content were synthesized.
- Oxidized carbon nanotube have excellent adsorption properties.
- Investigated relationship between adsorption properties and oxygen content.
- Adsorption mechanism and effect of environmental factors were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidized multi-walled carbon nanotubes (MCNTs) were used as adsorbents to investigate the effects of oxygen contents on adsorption properties of ciprofloxacin (CPX). With the oxygen content increasing from 2.0% to 5.9%, the normalized maximum adsorption capacity of CPX appeared growing state. However, the increment rate became slower, which is mainly attributed to π - π electron donor-acceptor interaction. The promotion of hydrophilicity and dispersibility, and the inhibition of water cluster had played a coordinate role in the whole adsorption process of CPX onto MCNTs. The isotherm adsorption data were more appropriate to Dubinin–Radushkevich and Langmuir model. Moreover, the MCNTs with the best adsorption properties was chosen to investigate adsorption kinetics and the effect of environmental factors (dosage, and pH, ionic strength) on CPX adsorption. The experimental kinetic data showed that intra-particle diffusion and outer diffusion may both present in the removal process to control the adsorption rate. CPX adsorption strongly depended on the pH of the solution. The alkaline condition was not conducive to the adsorption of CPX on MCNTs. However, the ionic strength had no significant effect on the adsorption capacity of CPX onto MCNTs. Therefore, the electrostatic interaction may be the main adsorption mechanism in the adsorption process.

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1. Introduction

With the widespread use of antibiotics, pharmaceutical effluents containing antibiotics have recently attracted wide attentions

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since it has potential adverse effects. Although the injuriousness of antibiotics is not so intuitive like other environmental pollution, residues of the antibiotic drug have become a seriously ignored problem. The abuse of antibiotics can damage the immune function of animals, when again infected, and then they need more antibiotics to treat. Thus, it could sink into a vicious cycle [1]. Ciprofloxacin (CPX, $C_{17}H_{18}FN_3O_3$), one of the extensively used antibiotics in the world, can lead to the growing of

antibiotic-resistant bacteria even if the concentration is lower. Meanwhile, CPX is difficultly biodegradable substance. Once released into the aquatic environment, CPX easily enriches to induce resistant strains, which will have a serious impact on the ecological environment. Therefore, before being discharged into the drainage system, CPX must be removed to a permissible level from the wastewater [2]. For antibiotic contaminants with such characteristics, relatively stable, non-biodegradable, highly toxic, and cumulative effect, adsorption may be an effective way to remove antibiotics due to low cost, high efficiency, and good feasibility.

For MCNTs have the unique structure of the porous and hollow, large specific surface area, and exist multiple interactions between the contaminants and MCNTs, which has an excellent potential for the removal of organic contaminants in aqueous phase, causing widespread concerns [3–14]. Moreover, surface chemical functionalization of MCNTs can have an impact on adsorption of target pollutants [15–18]. Carabineiro et al. [4] selected three types of carbon-based materials: activated carbon, carbon nanotubes, and carbon xerogel as adsorbents for the removal of CPX, the above results showed that MCNTs exhibited the most excellent adsorption properties for per specific surface area (SSA). Sheng et al. [17] conducted a compared adsorption experiment of as-prepared and oxidized MCNTs, finding that the adsorption capacity became lower after oxidation treatment. In addition to the repulsion of negative charges, π – π dispersion forces caused by the introduction of carboxyl group between MCNTs and the aromatic ring of ionizable aromatic compounds, which may also obstruct adsorption. Recently, the adsorption of organics on MCNTs was mainly focused on improving the adsorption performance, exploring divergence caused by different physical and chemical properties of organic pollutant itself. However, few studies had reported the influence of MCNTs' properties on organics adsorption. Carbon nanotubes were oxidized and modified by sodium hypochlorite, which can effectively improve the adsorption performance of organic pollutants on MCNTs [19]. However, relatively few studies had reported effects and mechanisms of oxygen content and surface functional groups of carbon nanotubes on adsorption performance [20,21].

MCNTs as adsorbents and released to the environment after adsorption process, which may be contacted with some oxidant, and then functionalized and purified. Therefore, a clear understanding of adsorption properties and the effect of oxygen content on the surface of oxidized carbon nanotubes play a significant role in assessing the environmental risks. MCNTs with different oxygen contents were obtained by regulating the concentration of NaClO solution, and then they were chosen as adsorbents to study adsorption characteristics of CPX on MCNTs with different oxygen contents. From the perspective of surface oxygen content and oxygen-containing functional groups of the adsorbent material, we studied the intrinsic link between characteristics of MCNTs with different oxygen contents and adsorption properties of CPX. Moreover, we investigated the interaction mechanism between carbon nanotubes and CPX. To ensure the accuracy of the adsorption properties of the adsorbent in actual wastewater treatment, we chose MCNTs with 4.7% oxygen contents (CNTs-4.7%O), which exhibit the best adsorption properties, as an adsorbent to investigate the effect of different environmental factors (pH, ionic strength, and dosage) on CPX adsorption.

2. Materials and methods

MCNTs were oxidized by different concentrations of sodium hypochlorite (NaClO) to be loaded different oxygen contents. The oxygen content were measured by X-ray photoelectron spectro-

scopic (XPS), XPS analysis was carried out in a Kratos Axis Ultra DLD Spectrometer, using monochromated Al K α X-rays, at a base pressure of 1×10^{-9} Torr. The MCNTs with different oxygen content, which are prepared in the previous studies [19], used in this study were named CNTs-2.0%O, CNTs-3.2%O, CNTs-4.7%O, and CNTs-5.9%O. Ciprofloxacin, of assay >90% were purchased from Sigma, Yanyu (Shanghai) Chemical Reagent Co., Ltd. All other reagents were analytical grade and were used as received.

All adsorption experiments were carried out in a series of 150 ml flasks containing 20 mg MCNTs and 40 ml CPX solutions. To obtain adsorption isotherms, 20 mg MCNTs were contacted with 40 ml of different concentrations of CPX solutions (10–160 mg/L). The mixtures were then shaken at 180 r/min for 24 h at 298 K. When reaching adsorption equilibrium, the appropriate solution was gathered to filter using a syringe with 0.45 μ m filter membrane and then determine by UV–Vis spectrophotometer (UV759UV-VIS, Shanghai Precision & Scientific Instrument Co. Ltd.) at 275 nm. Simultaneously conducting blank experiments was CPX solution without adsorbent to eliminate the effects caused by agents.

In the adsorption kinetics experiment, 20 mg of MCNTs were added to 40 ml of 150 mg/L constant concentration CPX solution at 298 K. At predetermined time intervals, the MCNTs were collected through a 0.45 μ m membrane filter and the filtrate was analyzed by UV–Vis method.

Furthermore, additional experiments were also carried out to detect the influence of dosage, pH, and ionic strength on the adsorption properties. The effect of dosage was performed to select an adsorbent dose of 10, 20, 30, and 40 mg. The effect of pH on CPX sorption by MCNTs was evaluated by adjusting the pH values of the solutions to the designated values. Used in the experiment was 0.01 M HCl or 0.01 M NaOH with the initial concentration of 150 mg/L of CPX. To study the effect of ionic strength, predetermined amounts of NaCl were added to obtain 0.05 M, 0.1 M, 0.2 M, and 0.4 M ionic strength solutions with a CPX concentration of 150 mg/L at 298 K. All adsorption experiments were performed to ensure a single variable.

The equilibrium adsorption amount of CPX was calculated as follows:

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

where C_0 and C_e are the CPX concentrations (mg/L) in the initial solution and at equilibrium, respectively; V is the volume of the solution and m represents the weight of the MCNTs used for adsorption studies.

The nonlinear forms of Langmuir and Freundlich models were expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_f C_e^{1/n} \quad (3)$$

where C_e and q_e are the concentrations of adsorbate in water, and the amount of adsorbate adsorbed to adsorbent when the adsorption equilibrium is reached, respectively. q_m is the maximum adsorption capacity, and K_L is Langmuir constant (L/mg) related to the energy of adsorption and the affinity of the binding sites. Moreover, K_f is Freundlich constant, also known as a capacity factor associated with adsorption capacity ((mg/g)(L/mg) $^{1/n}$). $1/n$ related to adsorption intensity, which is a dimensionless empirical parameter.

To deepen the understanding of adsorption mechanism, the Dubinin–Radushkevich (D–R) isotherm model was chosen to apply on adsorption study. The linear form of D–R model was expressed as follows:

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