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Single and simultaneous adsorption of pefloxacin and Cu(II) ions from aqueous solutions by oxidized multiwalled carbon nanotube

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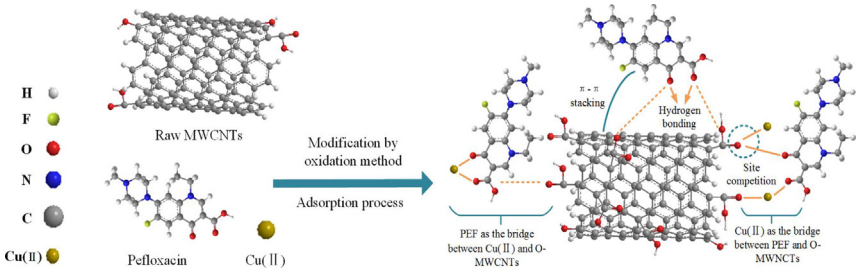
HIGHLIGHTS

- Raw MWCNTs was successfully modified by acid treatment.
- The adsorption of pefloxacin and Cu(II) on O-MWCNTs exists site competition and enhancement.
- Well explained the role of Cu(II) as the bridge between pefloxacin and O-MWCNTs.
- The adsorption mechanism for PEF and Cu(II) adsorption onto O-MWCNTs was thoroughly investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the oxidized multiwalled carbon nanotube (O-MWCNTs) was obtained by a simple method, and investigated by various techniques (SEM, TEM, FT-IR, XPS and zeta potential) for the removal of pefloxacin and Cu (II). The mutual effects of their adsorption onto O-MWCNTs were comprehensively clarified with sole and binary systems with adsorption kinetics, sorption thermodynamic and sorption isotherm models. The results indicated that there are site enhancement and competition of pefloxacin and Cu(II) on O-MWCNTs. According to mechanism investigation on the adsorption of pefloxacin and Cu(II) by XPS analysis, pH impact study, electrostatic interaction and π–π interactions, the low concentration of Cu(II)/pefloxacin could act as a bridge between pefloxacin/Cu(II) and O-MWCNTs, which significantly enhances the adsorption of pefloxacin/Cu(II). This study provided effective method and valuable reference for the elimination of pefloxacin/Cu(II) from aquatic environments.

1. Introduction

Fluoroquinolones-type antibiotics are emerging pollutants of rising concern due to their widespread application in human and animal medicine. Recent research has shown that in the presence of divalent cations, antimicrobial effects of fluoroquinolones are changed (Feng et al., 2016). Fluoroquinolones also affect trace metal metabolism by inhibiting copper- and zinc-dependent enzymes (Doorslaer et al., 2014; Skov et al., 2015). Fluoroquinolones play an important biological role by chelating with certain metal ions with the carbonyl and the carboxyl group of the molecule (Doorslaer et al., 2014). Pefloxacin (PEF) (1 ethyl-6-fluoro-7-(4-methylpiperazin-1-yl)-4-oxo-quinoline-3-carboxylic acid), is a member of second generation fluoroquinolone antibiotics, with high activity against both of the Gram-negative and Gram-positive bacteria, and also shows significant activity against anaerobic bacteria (Sharma et al., 2017). As it can be used for medical treatment

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such as lepromatous leprosy (Burgos et al., 2011), systemic bacterial infections (Singh et al., 2018) and various types of infectious diseases (Burgos et al., 2011), this drug exist in the environment as the parent compound or metabolites due to its slurry on agricultural land and the spreading of manure, or direct deposition by livestock (Zhang et al., 2015). PEF causes contamination to the environment and detected in industrial effluents, sanitary sewage and livestock and poultry breeding wastewater, which forms a serious threat to human health and ecology environment (Zhang et al., 2017).

Cu(II) ions is considered as vital transition metal ion because it involves in several biological processes like iron transport, oxidative stress protection, respiration, blood clotting and pigmentation (Awual and Hasan, 2015). Also, the active centers of numbers of metalloproteins require the participation of Cu(II) ions. In addition, their complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents. Cu(II) ions are essential to human life and health but, like all heavy metals, are potentially toxic (Awual and Hasan, 2015; Ochoa-Herrera et al., 2011; Yargıç et al., 2015). Furthermore, they usually exist in environment as an element of heavy metal pollution and tend to combine with PEF to form complex contaminants, which poses more serious toxicological residual to the environment (Soayed et al., 2014). Therefore, it is necessary to develop integrated techniques realizing the simultaneous elimination of Cu(II) and PEF.

Several methods (e.g., advanced oxidation, adsorption, biological treatment, and electrochemical methods) have been widely applied to the removal of antibiotics and/or heavy metals (Ahmed et al., 2017; Chen et al., 2017; Liu et al., 2017; Zhou et al., 2017a; Zhou et al., 2017c). Actually, the adsorption technology is a priority option due to a synthetic consideration of removal safety, simplicity, efficiency and economic feasibility in the treatment processes (Yu et al., 2017). Various adsorbents, such as polystyrene-divinylbenzene resin (Ling et al., 2016), graphene-based materials (Huang et al., 2017), biochar (Zhou et al., 2017b) and etc. have been adopted to remove the coexisting pollutants of antibiotics and/or heavy metals with a positive effect (Fasfous et al., 2010; Hadavifar et al., 2014; Hu et al., 2012; Ji et al., 2012; Yu et al., 2011; Zhang et al., 2014).

As a new type of adsorbent, carbon nanotubes (CNTs) have attracted widespread attention for the pollutants' removal, such as ions (e.g., Cd^{2+} (Li et al., 2017), Pb^{2+} (Li et al., 2017), Zn^{2+} (Mubarak et al., 2013), and Ni^{2+} (Lasheen et al., 2015)) and antibiotic (e.g., ciprofloxacin (Li et al., 2014) and norfloxacin (Wang et al., 2010)). Unlike many adsorbents, CNTs are advantageous due to their large surface areas, well developed mesopores and significant π-π electrostatic interactions (Zhang et al., 2014). In addition, appropriate modification of CNTs could increase its surface functional groups, and generate more open tubes by opening some of the end caps (Li et al., 2014). For examples, Ma and coworkers reported alkali-activated multi-walled carbon nanotubes have excellent removal capacity for methylene blue (399 mg/g) and methyl orange (149 mg/g) (Ma et al., 2012). Yang et al. used diamine functionalized mesoporous silica on multi-walled carbon nanotubes (NN-mSiO_2@MWCNTs) for the adsorption of Cu(II), Ni(II), Pb(II) and Zn(II) in aqueous solution with highly sorption capacity (Yang et al., 2013). However, few study has been reported for the simultaneous adsorption of Cu(II) and PEF.

Herein, in this work, the carbon nano-materials were oxidized by the method of acidification, and characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), fourier transformation infrared spectrum (FT-IR) and zeta potential. Meanwhile, to fully understand the sorption behavior of Cu(II) and/or PEF onto O-MWCNTs, and how pH and Cu(II)/PEF affect PEF/Cu(II) adsorption on the O-MWCNTs, batch adsorption experiments were conducted. The adsorption mechanism was investigated by analysis of X-ray photoelectron spectroscopy (XPS). This work indicates that O-MWCNTs exhibit tremendous performance for effective removal of Cu(II) and PEF in aqueous solution simultaneously.

2. Materials and methods

2.1. Materials and chemicals

Multiwalled carbon nanotubes (MWCNTs, purity > 95%) with 10–20 nm outer diameter were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences. Pefloxacin (PEF, purity > 99%). Hydrogen nitrate (HNO_3), sulfuric acid (H_2SO_4), cupric nitrate (Cu_2NO_3), hydrochloric acid (HCl), sodium hydroxide (NaOH) and copper stock solution used in this study were analytical reagent grade. Doubly distilled water was used throughout.

2.2. Instrumentation and analytical method

The surface morphology and microstructure of the raw and modified MWCNTs were analyzed by scanning electron microscopy (SEM, QUANTA250, USA), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). Zeta potential was used to measure the force between particles (including repulsion and attraction) which was determined with a zeta potential analyzer (Zetasizer Nano, UK). By its change, the dispersion mechanism was further understood. The surface functional groups of raw and modified MWCNTs were detected with a FT-IR Spectrometer (NICOLET 5700, USA) from 1000 to 4000 cm^{-1}.

2.3. Preparation of O-MWCNTs

The O-MWCNTs were prepared according to the strategy reported previously (Zhao et al., 2014). First, 3 g purchased multi-walled carbon nanotubes were added to a 2 L beaker, and then a pre-equipped concentrated H_2SO_4/HNO_3 mixed solution (3:1 by volume) was slowly added in a fume hood. After ultrasonically dispersed for 20 min, the solution was constantly stirred for 24 h with magnetic stirrer to obtain a better and evenly dispersed oxidation reaction. Then, the complex was separated by a vacuum suction filter apparatus, where the obtained oxidized multi-walled carbon nanotubes were repeatedly washed until neutral and then placed in a blast oven at 105 °C, dried for 48 h, grounded into a powder and stored for use in a mortar.

2.4. Batch adsorption experiments

All experiments were conducted in 100 mL polyethylene plastic bottles at 298 K. After 4 h of reaction, the supernatant was filtered and diluted for detection. The concentration of PEF before and after adsorption was detected by a UV spectrophotometer (UV1101, SHIMADZU, Japan). The Cu(II) concentrations were determined by a flame atomic absorption spectrometry (AA-6880, SHIMADZU, Japan). The details of the experiment are presented in the supporting information.

All the samples in the experiments were repeated three times, and the results were reported according to average values. Preliminary experiments (adsorbent free) showed that the loss of PEF was <5% during the whole experimental process.

2.5. Experimental data modeling

Two kinetic models: the pseudo-first-order, pseudo-second-order, and two isothermal models were used to test experimental data to examine the adsorption kinetics and mechanism (Kaman et al., 2017; Saha et al., 2018). The details are presented in the supporting information.