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Optimized removal of antibiotic drugs from aqueous solutions using single, double and multi-walled carbon nanotubes

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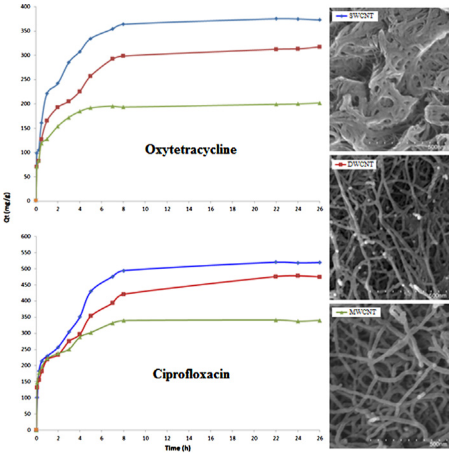
HIGHLIGHTS

- Efficient removal of antibiotics from aquatic environments is needed.
- Various carbon nanotubes showed promising potentialities for this task.
- Highest removal capacities were registered using SWCNTs for both antibiotics.
- Ultrasonication helped increasing the removal performance.
- Ethanol was the solvent that induced the highest desorption.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, experiments were carried out to investigate the use of as-synthesized single-walled (SWCNT), double-walled (DWCNT) and multi-walled carbon nanotubes (MWCNT) agglomerates for the removal of two antibiotics, Oxytetracycline (OXY) and Ciprofloxacin (CIP) from aqueous solution. The variations of key operating parameters on the removal process were assessed in order to find out the optimum conditions. It includes exposure time, solution pH, temperature, ultrasound assistance and desorption assays. The experimental results revealed that a moderate increase in adsorption was registered between pH 3 and 7 for both antibiotics. The application of ultrasound helped enhancing the removal capacities of OXY for all tested CNTs. For the case of MWCNTs, 1 h of ultrasonication increased the adsorption capacity by 44.6%. As for CIP, the ultrasonic treatment did not enhance the overall adsorption, especially for the case of DWCNTS. The Brouers–Sotolongo equation was the best fitting isotherm model. The highest removal capacities were registered using SWCNTS for both antibiotics (724 mg/g for CIP and 554 mg/g for OXY). In addition, ethanol was the solvent that induced the highest desorption percent for the case of CIP (52% for MWCNTs). However, the desorption of OXY was negligible for all solvents (maximum 3.3% for DWCNTs using ethanol).

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1. Introduction

Various emerging pollutants including pharmaceutical drugs, endocrine disrupters, polycyclic hydrocarbons, as well as surfactants, are commonly found in aquatic environments [1], marine sediments and treated wastewaters [2]. During the last decades, numerous research studies were conducted to investigate the occurrence, fate and ecotoxicology of many emerging pollutants in wastewaters and aquatic environments [3]. Considering their serious menace to the environment and their inherent health risk to human beings, the development of efficient removal techniques is becoming an urgent matter to be addressed. Thus, different treatment techniques including adsorption [4], advanced oxidation process [5], membrane separation [6] and bioremediation [7] were investigated.

Among those techniques, adsorption seems to have interesting potentialities for emerging pollutants remediation, considering its versatility and removal efficiency. The main aim of this study is to focus on emerging pollutants in order to anticipate the application of the adsorption technique in future water treatment procedures targeting this kind of pollution. Antibiotics were targeted as pollutants of emerging concern since several studies revealed that most antibiotic drugs are difficult to be biodegraded due to the stable naphthol ring in their structures [8]. As well, their extensive use induced the so-called antibiotic-resistance among several bacterial strains, thus, reducing the therapeutic efficiency of antibiotics which resulted in disturbing the function of the ecosystem [9].

Carbon nanotubes (CNT) are reported in the literature as one of the most promising adsorbents applied in water and wastewater treatment [10]. However, two major limitations confined their large scale application in water treatment: (i) their hydrophobicity [11] and (ii) production cost [12].

The goal of this study is to examine and compare the efficiency of single, double and multi-walled CNT to remediate antibiotics-related pollution via adsorption. The investigation aims to optimize the operating conditions affecting the removal of two antibiotics (Oxytetracycline and Ciprofloxacin) from aqueous solutions using as-synthesized and untreated CNTs.

2. Materials and methods

2.1. Carbon nanotubes

SWCNTs, DWCNTs and MWCNTs, produced via catalytic chemical vapour deposition, were purchased from Sigma–Aldrich, with purity above 95%. The as-synthesized nanotubes agglomerates were thoroughly washed with ultrapure water, then dried at 80 °C for 24 h and stored in desiccators for further use.

All CNTs were used without prior thermal and/or chemical treatment. Such choice was made in order to monitor the removal capacities of each of the untreated nanotubes to remove antibiotics. This is an important step to justify later if pretreatment procedures are needed (or not) to improve the overall removal, considering the associated extra cost (energy consumption and/or chemicals purchase). In addition, as nanotubes tend to aggregate and form interesting porous network due to the entanglement of thousands of individual tubes [13], it is worth experimenting the three types of CNTs in their synthesized form (i.e. agglomerates with heterogeneous sizes).

2.2. Antibiotics

Two USP grade antibiotics (>95% purity) were investigated in this study: Oxytetracycline hydrochloride (OXY) and Ciprofloxacin hydrochloride (CIP). Their molecular structures and chemical properties are shown in Table 1.

Synthetic solutions for each antibiotic were prepared separately by dissolving accurately weighed amounts of powdered compound in ultrapure water. Subsequent dilutions were made to obtain the required concentrations. Spectrophotometric scanning of dilute solutions was performed and absorbance maxima for each antibiotic were identified as 360 nm for OXY and 273 nm for CIP.

2.3. CNTs characterization

2.3.1. BET (Brunauer, Emmett and Teller) analysis

The BET surface area and pore size distribution of the studied CNTs were estimated via nitrogen adsorption at 77 K using a Micromeritics® surface area and porosimetry analyzer (model Gemini 2380 V1.00). Samples were first degassed to remove any moisture. Then, the built-in software provided the BET surface area (S_{BET}). The pore size distribution was estimated using the Barrett–Joiner–Halenda (BJH) equation during the desorption phase [16].

2.3.2. SEM (scanning electron microscopy) analysis

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalysis (Hitachi SEM/EDS S-4800) was used to determine the surface of the tested CNTs and the porous structure of the agglomerated network. The CNTs were firstly mounted on an aluminium stub and the microscope was operated at an accelerating voltage of 20 kV.

2.4. Sorption experimental procedure

All adsorption experiments were carried out by stirring the desired amount of untreated single, double and multi-walled CNTs with 10 mL of the antibiotic-loaded solution. 15 mL round bottom glass tubes were used and the stirring was performed in a thermo-regulated oscillatory shaker. The removal efficiency was studied under various exposure times (up to 26 h), pH values (3–11), temperatures (15–45 °C) and ultrasonic assistance (0–60 min using an ultrasonic frequency of 40 kHz). As well, various initial antibiotic concentrations (5–100 mg/L) were tested for the isotherm experiments.

After a pre-determined time interval (for kinetics) or at equilibrium time (for isotherms), a solution sample was extracted, filtered (using a 0.2 μm syringe filter) and analysed for residual antibiotic concentration. Sample analyses were carried out using the spectrophotometric technique at the corresponding wavelengths. Blank assays (i.e. antibiotics solution without CNTs) did not show any significant loss of pollutant from the solution.

Regarding the desorption assays; the antibiotics-loaded CNTs were recovered after the adsorption stage. The mixture was decanted for 6 h and the aqueous phase removed using a syringe. The recuperated CNTs were gently washed with ultrapure water to remove the unadsorbed fraction of the antibiotic molecules and dried at 45 °C for 12 h. Then, 1 mg of antibiotic-loaded CNTs was mixed with 10 mL of solvent (water, ethanol, methanol, 50% water/50% ethanol and 50% water/50% methanol). First, the desorption using all solvents was applied for the best adsorbing CNTs (i.e. SWCNTs). Then, the solvent enabling the highest recovery was applied for the other CNTs (i.e. DWCNTs and MWCNTs).

The quantity of adsorbed antibiotics per unit weight of the CNTs, Q (mg/g), was calculated as follows:

$$Q = (C_0 - C) \times \frac{V}{M}$$

Where, C_0 (mg/L) is the initial antibiotic concentration, C (mg/L) is the estimated concentration at a definite time (C_t) or at equilibrium