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Removal of sulfamethoxazole and sulfapyridine by carbon nanotubes in fixed-bed columns

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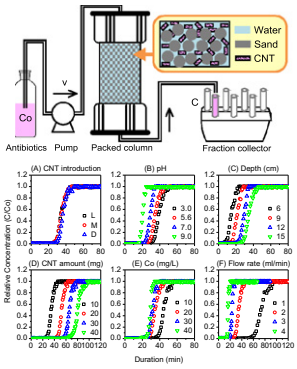
HIGHLIGHTS

- CNT/sand columns can effectively remove SMX and SPY from water.
- Multiple factors influence the CNT/sand column removal efficiency.
- Spent CNT/sand columns can be regenerated to remove SMX and SPY.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfamethoxazole (SMX) and sulfapyridine (SPY), two representative sulfonamide antibiotics, have gained increasing attention because of the ecological risks these substances pose to plants, animals, and humans. This work systematically investigated the removal of SMX and SPY by carbon nanotubes (CNTs) in fixed-bed columns under a broad range of conditions including: CNT incorporation method, solution pH, bed depth, adsorbent dosage, adsorbate initial concentration, and flow rate. Fixed-bed experiments showed that pH is a key factor that affects the adsorption capacity of antibiotics to CNTs. The Bed Depth Service Time model describes well the relationship between service time and bed depth and can be used to design appropriate column parameters. During fixed-bed regeneration, small amounts of SMX (3%) and SPY (9%) were irreversibly bonded to the CNT/sand porous media, thus reducing the column capacity for subsequent reuse from 67.9 to 50.4 mg g^{-1} for SMX and from 91.9 to 72.9 mg g^{-1} for SPY. The reduced column capacity resulted from the decrease in available adsorption sites and resulting repulsion (i.e., blocking) of incoming antibiotics from those previously adsorbed. Findings from this study demonstrate that fixed-bed columns packed with CNTs can be efficiently used and regenerated to remove antibiotics from water.

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1. Introduction

Sulfonamide antibiotics are widely used as human and veterinary pharmaceuticals (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Thiele-Bruhn, 2003). Sulfamethoxazole (SMX) and sulfapyridine (SPY) are two commonly used sulfonamide antibiotics primarily used for treating human patients, and are well known to bioaccumulate up the food chain and trigger acute as well as chronic adverse effects (Göbel et al., 2005). Recent findings indicate that simultaneous exposure to multiple antibiotics could result in the enhanced toxic effects (Park and Choi, 2008). A general concern for public health is the development of antibiotic resistance from chronic exposure to antibiotic contaminated water. Therefore, it is urgent to investigate the pathways through which SMX and SPY disperse in the environment, and develop systems that can efficiently remove these dissolved substances from water.

Entry pathways of sulfonamide antibiotics to aquatic environments include aquaculture activity, pharmaceutical manufacturing, and medical waste disposal. Additionally, access could be indirectly gained to surface and subsurface waters from leached waste of livestock receiving antibiotic treatment (Baran et al., 2011). Precipitation events could further accelerate the release of antibiotics concentrated in animal manure, which, once dissolved in surface waters, could mix and load groundwater within the soil profile. The protection of surface and groundwater quality, as two primary sources for drinking water, from contamination of leached antibiotics is of great priority for public and environmental health.

A variety of physiochemical techniques have been developed to remove or destroy antibiotics from water sources, including oxidation (Beltrán et al., 2008), ion exchange (Choi et al., 2007), reverse osmosis (Adams et al., 2002), and adsorption (Ternes et al., 2002). Adsorption is a standard method used to remove dissolved contaminants from water. Adsorbents, such as clay (Avisar et al., 2010), zeolite (Braschi et al., 2010), and activated carbon (Caliskan and Gokturk, 2010), have been examined for their removal efficiency of sulfonamide antibiotics in aqueous solutions. Solution chemistry has been shown to strongly affect the removal efficiency of these adsorbents with particular importance placed on solution pH (Lertpaitoonpan et al., 2009), ionic strength (Gao and Pedersen, 2005), and presence of competitive sulfonamide antibiotics (Gao and Pedersen, 2010).

Carbon nanotubes (CNTs), as novel sorbents, have gained increasing attention because of their exceptional sorbing properties. CNTs have hollow and layered structures with a characteristically large surface area, thus endowing CNTs with great potential for superior sorption capability (Wang et al., 2009). Previous studies have demonstrated high adsorption ability of CNTs to both heavy metals (Stafiej and Pyrzynska, 2007) and organic pollutants (Zhang et al., 2010). Investigations on the adsorption of sulfonamide antibiotics by CNTs have reported that removal efficiency varies according to the quantity of walls making up the CNTs as well as to chemical pretreatment of the CNTs (Ji et al., 2009, 2010). Pretreatment of CNTs (e.g., by surface functionalization) is widely used to improve the dispersion of these nanoparticles in aqueous solutions (Tian et al., 2011). The introduction of functional groups also increases the ion-exchange capacity of the CNTs, thereby augmenting the number of available sites that can participate in electrostatic adsorption (Atieh et al., 2010). As such, functionalized CNTs have been reported to exhibit greater potential for removing antibiotics from aqueous environments than pristine CNTs (Zhang et al., 2010).

The current application of CNTs for antibiotic removal from water has been restricted to batch sorption methods. Two key disadvantages of batch methods include difficulty to collect exhausted/spent adsorbents and interruptions incurred when integrated to existing continuous processes (Eckenfelder, 2000). For example, the *in situ* removal of antibiotics in the environment (e.g., an agricultural field) requires a continuous flow setup to cope with the intermittent discharge of antibiotic-loaded runoff. It is thus necessary to develop and optimize CNT-enabled water treatment methods that take advantage of the large sorption capacity of CNTs in a setup that can be deployed in the field.

Unlike batch sorption systems, fixed-bed filters permit continuous flow and adsorption of antibiotics from solution; thus, opening a wealth of opportunities for *in situ* water treatment. The fixed-bed filters enabled by high performance adsorbents exploit the high sorption capacity of the adsorbent, while enabling the practicalities of continuous flow operation. Despite the above-mentioned benefits of fixed-bed systems and great sorption potential of CNTs (Tian et al., 2012b), to the authors' knowledge, the removal of antibiotics from aquatic environment using CNT-enabled fixed-bed columns has not been explored.

In this work, we used CNT-enabled fixed-bed column methods to investigate the removal of SMX and SPY from aqueous solutions under various conditions. Our overarching objective was to investigate the removal efficiency of SMX and SPY by CNTs in a fixed-bed system under various physicochemical conditions. The specific objectives of the work were to (1) examine the removal of SMX and SPY from aqueous solutions by trickling antibiotic-contaminated water through a CNT/sand fixed-bed column under conditions of varying pH, CNT incorporation method, adsorbent dosage, bed depth, adsorbate initial concentration, and flow rate and (2) evaluate the efficiency of regeneration of the fixed-bed columns for reuse.

2. Materials and methods

2.1. Bed materials and conditions

Functionalized multi-walled carbon nanotubes (CNTs) (Cheap Tubes Inc., Brattleboro, VT) and quartz sand were used as filter materials in the fix-bed columns. Three methods of CNT incorporation to the sandy medium were tested (layered, mixed, and deposited), bed depths tested ranged from 6 to 15 cm, and flow rates ranged from 1 to 2 mL min^{-1}. Chemical conditions tested for fixed-bed experiments were 3.0–9.0 pH, 10–40 mg adsorbent dosage, and 10–40 mg L^{-1} of antibiotic concentration.

CNTs were produced using a chemical vapor deposition method with nickel and magnesium catalysts. Subsequent functionalization was achieved with an acid mixture of concentrated sulfuric and nitric acids (3:1, v:v) to introduce carboxyl and hydroxyl functional groups to the nanotube surface (Zhang et al., 2011). A batch of the functionalized CNTs were used in the dry powder form (undispersed CNTs), while a second batch was dispersed in water to create a suspension of CNTs (dispersed CNTs). To make the dispersion, 16 mg of the synthesized CNT powder were dispersed in 1000 mL deionized water and subsequently sonicated for 30 min in a Misonix S3000 ultrasonicator (QSonica, Newtown, CT).

Thorough characterization of the CNTs for physiochemical properties was performed for the following properties. Surface area of undispersed CNTs was measured using the NOVA 1200 surface area analyzer (Quantachrome Instruments, Boynton Beach, FL), following the Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77 K. Point of zero charge (PZC) of the undispersed CNTs was determined using the mass titration method (Noh and Schwarz, 1990). Hydrodynamic diameter of dispersed CNTs was determined by dynamic light scattering with a Brookhaven Zeta-Plus (Brookhaven Instruments Corporation, Holtsville, NY). CNT concentration in suspension was calibrated by measuring the total absorption of light at wavelengths of 255 nm using Evolution 60 UV–Vis Spectrophotometer (Thermo Scientific, Waltham, MA).