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Multi-walled carbon nanotubes with selected properties for dynamic filtration of pharmaceuticals and personal care products

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ABSTRACT

In this study, multi-walled carbon nanotubes (MWCNT) with selected properties, including pristine MWCNT, hydroxylated MWCNT (H-MWCNT), thin-walled MWCNT with large inner diameter (L-MWCNT), aminated MWCNT, and high-purity MWCNT were investigated for dynamic removal of eight pharmaceuticals and personal care products (PPCP). The removal ratios of different PPCP by the pristine MWCNT followed a decreasing order of triclosan (0.93) > prometryn (0.71) > 4-acetylamino-antipyrine (0.67) > carbendazim (0.65) > caffeine (0.42) > ibuprofen (0.34) > acetaminophen (0.29) at 100 min of filtration. Similar or even higher PPCP removals were obtained for all PPCP as the influent concentration decreased, suggesting potential consistent PPCP removals at environmental PPCP concentrations. The removal ratio of acetaminophen was increased to 0.74 by using H-MWCNT. SRFA (Suwannee River fulvic acid) suppressed PPCP adsorption to MWCNT, to greater extents with increasing SRFA concentrations. The L-MWCNT, despite a large inner diameter of 52 ± 3 nm, did not provide better resistance to the competitive adsorption of SRFA than MWCNT with a small inner diameter of 10 ± 2 nm. Future research will be conducted to minimize the effect of SRFA and facilitate application of MWCNT to the treatment of PPCP-contaminated water.

1. Introduction

Pharmaceuticals and personal care products (PPCP) have been constantly discharged into domestic wastewater and natural water due to their large quantity of consumption. (Kümmerer et al., 1997) Biological accumulation of PPCP in aquatic system has also given rise to the concentrations (up to 7051 ng L^{-1}) and frequent detections of PPCP in natural water. (Liu and Wong, 2013) Widespread attention has been paid to the identification of suitable techniques for efficient removal of PPCP and mitigate their ecotoxicity and potential human toxicity. (Abdelmelek et al., 2011).

Different treatment techniques including activated carbon adsorption (Kim et al., 2007), advanced oxidation process (Sillanpää et al., 2011), reverse osmosis (RO) (Grobert, 2007), and biodegradation have been investigated for PPCP removals. Liu et al., 2013 found that powdered activated carbon (PAC) effectively removed more nonpolar organic compounds, such as phthalic acid and catechol, than MWCNT, but the removal of polar organic compounds (salicylic acid) by MWCNT was 27.4 mmol L kg^{-1} higher than that by PAC. Moreover, PAC has distinct disadvantages such as difficulty to recover. (Yu et al., 2014) Comparatively, the higher cost and stronger toxicity of some intermediate products have limited the widespread use of the advanced oxidation. (Dewitte et al., 2008) Due to high energy consumption and complicated and costly process, RO technology has had difficulties in full-scale applications. As for biodegradation, most antibiotic drugs are recalcitrant to microbial degradation because of the presence of the stable naphthol ring in their structures. (Zhao et al., 2010) The limitations of these treatment techniques have necessitated the development of novel water purification technologies for PPCP.

Carbon nanotubes (CNT) have been reported to be one of the most promising adsorbents due to their superb adsorption properties, thereby being extensively studied in the last decade. (Iijima, 1991; Li et al., 2005) In our previous studies, adsorptive filtration with CNT has demonstrated good capabilities in removing aquatic natural organic matter (NOM), as well as triclosan, ibuprofen, and acetaminophen. (Wang et al., 2015; Cho et al., 2011) However, the

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removal efficiencies of CNT for different contaminants need to be optimized as the adsorption capacity of CNT can be greatly affected by the physicochemical properties of the feeding solution and the structure of CNT. For instance, the ubiquitous presence of NOM can greatly decrease PPCP removal due to competitive adsorption effect and/or blockage of internal CNT surfaces. (Joseph et al., 2011; Pan et al., 2013) Large organic molecules are typically adsorbed onto the outer surface of CNT, and comparatively, small molecules are adsorbed inside the micropores of the CNT structures in addition to their outer surface. (Crini and Badot, 2008) For small molecules, NOM is likely to block CNT micropores and restrict PPCP adsorption (Zhang et al., 2010). For adsorption of large molecules on the outer surface of CNT, similar π-π interactions can occur between CNT and aromatic contaminants or between CNT and NOM, (Wang et al., 2013) resulting in competitive adsorption (Wang et al., 2008).

Most of the existing studies concerning CNT adsorption of PPCP employed static adsorption experiments, and currently, there is little information in the literature in regard to the optimization of PPCP removal by utilizing CNT of different physical and chemical properties as filter media. Previous studies have shown that small ionic solutes from water are possible to be removed by changing CNT surface properties. For example, nearly 100% of $K_3Fe(CN)_6$ was removed by using carboxyl functional CNT arrays (Fornasiero et al., 2008). In addition, complete removals of Na^+ and Cl^- were obtained with functionalized CNT treated by plasma treatment containing −COOH and −OH groups (Yang et al., 2013). These studies have ubiquitously utilized house-made CNT samples that have not been available on the market. In order to promote technology innovation, it is beneficial to employ and assess commercially available CNT products for their potentials to water treatment.

Therefore, the primary objective of this study was to optimize the filtration of PPCP by selecting commercially available CNT products possessing a variety of physical and chemical properties. Eight representative types of PPCP, encompassing triclosan (TCS), ibuprofen (IBU), acetaminophen (AAP), carbamazepine (CBZ), 4-acetylamino-antipyrine (ATAP), caffeine (CAF), prometryn (PTN) and carbendazim (CBD) were filtered with membranes coated with one of five different types of commercially available, multi-walled CNT (MWCNT), including pristine MWCNT, hydroxylated MWCNT (H-MWCNT), thin-walled MWCNT with large inner diameter (L-MWCNT), high-purity MWCNT (HP-MWCNT), and aminated MWCNT (A-MWCNT) under controlled solution chemical conditions. The results demonstrated that optimized PPCP removal can be obtained by filtering through selected MWCNT, which sheds light on the application of MWCNT to the treatment of water and wastewater contaminated by PPCP. However, competitive adsorption of fulvic acids should be minimized in order to ensure efficient PPCP removal.

2. Experimental section

2.1. Natural organic matter and pharmaceuticals and personal care products

Reagent-grade TCS, IBU, AAP, CBZ and ATAP were bought from Tokyo Chemical Industry CO., and LTD, CAF, PTN and CBD were purchased from Aladdin Industrial Corporation. These chemicals were selected due to their high detection rates and levels in natural waters in Northern China (González-Naranjo and Boltes, 2014; Li et al., 2011). The physiochemical properties of the chemicals are presented in Table 1. Prior to filtration experiments, stock solutions of these chemicals were prepared by dissolving powdered chemicals into HPLC-grade methanol (Fisher Scientific) to desired concentrations according to their solubilities. In addition, Suwannee River fulvic acid (SRFA) standard II (Batch# 2S101F) was purchased from International Humic Substances Society (St. Paul, MN) and used to represent NOM in natural water.

2.2. Carbon nanotubes

Due to their low costs, MWCNTs were used extensively in this study. The pristine MWCNT employed in this study was purchased from Nanolab Inc., Waltham, MA, and were synthesized by virtue of the chemical vapor deposition technique as reported by the manufacturer. H-MWCNT, A-MWNT, L-MWCNT and HP-MWCNT used in the filtration experiments were purchased from Beijing Boyu Technology Corporation of High-tech New Materials. According to the manufacturer, H-MWCNT was prepared by using ultrasonic dispersion and centrifugal separation under the oxidation of H_2SO_4. For A-MWNT, carboxyl MWCNT served as a starting material, the carboxyl group was translated to amino group by ammoniation and then the carbonyl group was taken off at high temperature. For the synthesis of L-MWCNT, acetylene was used as the starting material and the targeted L-MWCNT was prepared by crackle reaction with nicked catalyst (Cho et al., 2009, 2008). HP-MWCNT was prepared with MWCNT under the oxidation of H_2SO_4 and $KMnO_4$. Characteristics of the CNT used in this study are summarized in Table 2.

2.3. Filtration experiments

Prior to each filtration experiment, 10 mg of MWCNT were massed with a digital microbalance (FA2004, Soptop, China) and dispersed in 10 mL of ultrapure water and sonicated for 30 min. The suspension was then filled into a glass syringe and pushed slowly through a flat-sheet polyvinylidene fluoride (PVDF) membrane (Durapore® HVLP, Millipore USA) with a nominal pore size of 0.22 μm and an effective membrane area of 4.52×10^{-4} m^2, resulting in a CNT loading of 22 g per m^2 membrane surface area. The CNT composite membrane was continuously rinsed with ultrapure water at a constant flow rate of 1 mL min^{-1} until a zero reading of UV_{254} absorbance was registered at the online UV detector.

Two different filtration systems were employed in this study, the first filtration system was used in filtration experiments with feed water containing 1 mg L^{-1} of PPCP, and comprised of a liquid delivery pump (Wufeng LC-100, China), a UV detector (Waters 486, USA), a syringe membrane filter, stainless steel tubing and a PVDF membrane with MWCNT (Fig. 1a). The second system consists a syringe pump with dual channels (RSP02-B, RISTRON, China), a syringe membrane filter, injection syringes (Fig. 1b), which was mainly employed in the filtration of feed solutions containing 100 μg L^{-1} of PPCP so as to minimize cross-contamination.

Feed solution consisting of 0.1 or 1 mg L^{-1} PPCP was prepared by spiking PPCP stock solution into an electrolyte solution containing 1.0 mM of NaCl. PPCP filtration was studied at two concentration levels to reveal potential effects of PPCP concentration on the removal efficiency. Moreover, SRFA was added to selected solutions to concentrations of 0.5, 5 or 10 mg L^{-1}. The pH of the solution was adjusted to 7.0 using 5 M NaOH and 5 M HCl.

The feed solution was then filtered through the CNT membrane with one of the filtration systems described above, at a constant flow rate of 1 mL min^{-1} for 120 min. The filtrate was collected at regular intervals for further analysis. All filtration experiments were conducted at a room temperature of 25 ± 2 °C and those with a feed PPCP concentration of 1 mg L^{-1} were repeated at least twice to test the repeatability of the results (Fig. S1 and Fig. S2, Supporting Information). A general run table, showing all the experiments conducted during this study has been present in Table 3.