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Influence of wastewater precoagulation on adsorptive filtration of pharmaceutical and personal care products by carbon nanotube membranes

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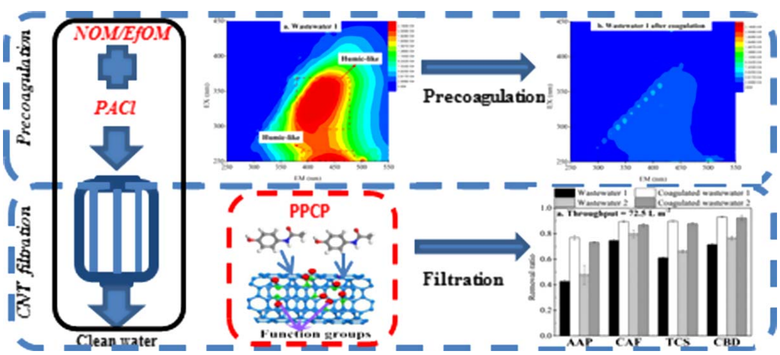
GRAPHICAL ABSTRACT



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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) have been widely studied for adsorption of pharmaceuticals and personal care products (PPCP). However, effluent organic matter (EfOM) is found to compete with PPCP for sorption sites on MWCNT, thereby markedly reducing the adsorptive capacities of MWCNT for PPCP in wastewater effluent. Herein, we report that precoagulation of secondary wastewater effluent effectively mitigated the competitive adsorption of EfOM and increased the adsorption capacities of MWCNT for acetaminophen, caffeine, triclosan, and carbendazim by up to 34%. Analyses of the coagulated waters using size exclusion chromatography and three-dimensional fluorescence spectrophotometry revealed that precoagulation primarily removed biopolymers and humic substances; the latter is known to suppress PPCP adsorption onto MWCNT. Moreover, the removal of EfOM by precoagulation reduced membrane permeability decrement and relieved membrane fouling. These results suggest that coagulation, a conventional technique widely used by water treatment plants, is a viable pretreatment approach for filtration of PPCP in wastewater by MWCNT. This finding also demonstrates the potential of integrating conventional technology and novel nanotechnology for cost-effective, advanced wastewater treatment.

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1. Introduction

Wastewater effluents contain a wide range of trace organics [1]. Among them, pharmaceuticals and personal care products (PPCP) serve as an important class of emerging contaminants due to their large quantities of consumption and increasing release into domestic wastewater [2]. PPCP include a diverse collection of chemical compounds, including antibiotic, disinfectants, fragrance, disinfectant, preservative, anti-inflammatory drug and so on [3]. Human exposure to antibiotics can result in serious threats to the ecosystem and human health [4]. Liu et al. found that consistent exposure to antibiotic and hormone drugs resulted in the emergence of resistant bacteria strains and increased human health risks [5]. Shen et al. [6] also demonstrated that carcinogenic nitrosamines can be generated during chlorine disinfection of water containing PPCP. Consequently, there is an increasing need for alternative wastewater treatment processes for PPCP removal that have high removal efficiencies at reasonable cost.

Various technologies have been studied for PPCP removal for advanced wastewater treatment. These technologies include ozonation [7], reverse osmosis [8], nanomaterials adsorption [4,5], and advanced oxidation processes [9]. Optimization of biological wastewater treatment (e.g., increasing sludge residence time) [10] has also been employed to enhance the removal of PPCP in wastewater. However, several studies found that these technologies demonstrate poor efficiency or have high operational costs [11–13].

Recently, carbon nanotubes (CNT) have been widely studied for PPCP adsorption because of their engineered nanostructures and superb adsorption capacities. However, the competitive adsorption between PPCP and NOM/EfOM impedes realistic application of nanomaterials. Engel et al. [14] found that competitive adsorption occurred between natural organic matter (NOM) and PPCP during their adsorption onto nanomaterials. Yu et al. [15] discovered that NOM negatively impacted the adsorption of pharmaceuticals onto CNT. Cho et al. [16] also observed decreased PPCP adsorption onto CNT in the presence of humic acid, an important component of NOM or effluent organic matter (EfOM). Therefore, competition of other organic matter for MWCNT adsorption of PPCP should be tackled from a technological standpoint.

Two potential approaches may be applied to control competitive adsorption of NOM or EfOM and enhance PPCP removal by CNT. From the perspective of material science, preparation of nanomaterials tailored to PPCP adsorption would be a plausible choice. However, previous studies have found that organic adsorption onto CNT involves various solute-CNT interactions, including π-π interaction, hydrophobic interaction, hydrogen-bonding interaction, and electrostatic interaction [17]. The magnitudes of these interactions depend not only upon the properties of CNT, but also upon the characteristics of organic adsorbates and solution chemistry. Considering the heterogeneous nature of EfOM, as well as the complexity of water quality, it will be difficult to identify a certain type of CNT that is capable of selectively adsorbing PPCP while leaving other EfOM component untouched.

Hence, removal of EfOM from the source water by wastewater pretreatment becomes a necessary option for PPCP removal by adsorptive nanomaterials. Various technologies have been developed for NOM or EfOM removal during full-scale water treatment. Among these technologies, enhanced coagulation is commonly employed by conventional water treatment plants or advanced water treatment plants [18,19]. For example, Yang et al. [20] found that coagulation with polyaluminum chloride removed up to 20% of TOC from the Luan River water and the Yellow River water. Vilgé-Ritter et al. [21] also found that coagulation was capable of removing 60% of NOM removal in Seine River water.

Therefore, the overarching aim of this study was to determine whether precoagulation was effective in removing active components of NOM or EfOM that were responsible for the competitive adsorption, thereby enhancing adsorptive removals of PPCP by CNT from biologically treated wastewater effluents. For this purpose, an oxidized MWCNT sample was selected from preliminary experiments and coated on a substrate ultrafiltration membrane to provide adsorptive filtration of PPCP compounds. Precoagulation of two batches of secondary wastewater effluents was conducted at predetermined optimal coagulant doses. Then after, PPCP compounds were spiked into the effluents with/without precoagulation, followed by adsorptive filtration of PPCP by the MWCNT membrane. It was found that precoagulation effectively removed humic-like substances, i.e., the EfOM components that were responsible for competing with PPCP for adsorption onto MWCNT, thereby significantly increasing adsorptive removal of PPCP by the MWCNT membrane. This important finding sheds light on the combination of conventional technology and nano-modified membrane for advanced treatment of wastewater effluent.

2. Experimental section

2.1. Chemicals and carbon nanotube membrane

Reagent-grade acetaminophen (AAP) and triclosan (TCS) were purchased from Tokyo Chemical Industry CO., caffeine (CAF) and carbendazim (CBD) were purchased from Aladdin Industrial Corporation, China. These chemicals were selected in this study due to their relatively high detection rates and levels in natural waters [22,23], as well as broad variations in molecular structures and physiochemical properties (Table 1). Stock solutions of these chemicals were prepared by dissolving powdered chemicals into HPLC-grade methanol (Fisher Scientific) to reach desired concentrations according to their solubility, namely, 1000 mg L^{-1} for AAP, CAF and CBD, and 500 mg L^{-1} for TCS, respectively. For the coagulation experiments, reagent-grade polyaluminum chloride (PACl) was purchased from Tianjin Guangfu Institute of Fine Chemicals and then diluted into a stock solution of 50 mg L^{-1} before use.

MWCNT used in the study was purchased from Beijing Boyu Technology Corporation of High-tech New Materials. This MWCNT possessed an average outer diameter of less than 8 nm, length of 10–30 μm, specific surface area of 360 m^{-1} g^{-1}, and a purity of 95%, and was selected in this study due to its high adsorption capacity for PPCP in the absence of EfOM as determined in a previous study [24]. Meanwhile, a commercially available, hollow fiber membrane was bought from the Litree Purifying Technology Co., Ltd, China and used as the substrate membrane. This membrane was made of polyvinyl chloride (PVC) and possessed an average pore size of 0.012 μm.

Prior to each filtration experiment, 14 mg of MWCNT were dispersed in 14 mL of ultrapure water by sonicating for 10 min with a probe sonicator (Ultrasonic processor FS-250N, Shanghai, China). The prepared CNT suspension was then pumped from inside-out through a pre-made, U-shaped PVC membrane module that had an effective membrane area of 6.9×10^{-4} m^2, resulting in a CNT loading of 22 g m^{-2} at the inside surface of the hollow fiber membrane. For the membrane permeability comparison, the two MWCNT membranes (membrane 1 and membrane 2) were prepared under identical conditions.

2.2. Wastewater effluents

One batch of secondary wastewater effluent was sampled in winter, December 2016 and the other batch in summer, June 2017, both from a local municipal wastewater treatment plant in Beijing, China, to represent municipal wastewater in different seasons. After being shipped to the laboratory, the wastewater sample was filtered immediately with binder-free glassfiber filters (Whatman, GF/1C) to remove particulate matters larger than a nominal pore size of 1.2 μm. The pre-coagulated wastewater was obtained by adding the PACl stock solution into the wastewater effluents at predetermined optimum doses of 2.5 mg L^{-1} for wastewater 1 and 2.1 mg L^{-1} for wastewater 2. The coagulant dose was determined by using jar tests (Fig. S1, Supporting information).