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Competitive adsorption of PPCP and humic substances by carbon nanotube membranes: Effects of coagulation and PPCP properties

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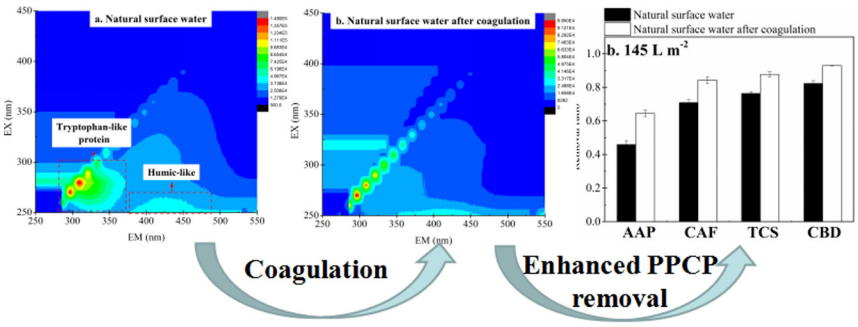
HIGHLIGHTS

- Natural organic matter (NOM) competed with PPCP for sorption sites and reduced PPCP removal.
- Humic acid (HA) water experiments further confirmed the active substances that competed with PPCP sorption.
- Precoagulation effectively mitigated the competitive adsorption of HA/NOM.
- Precoagulation increased PPCP removal by 7–69% for humic acid synthetic water and 11–18% for natural surface water.
- Biopolymers and humic substances were primarily removed by precoagulation.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural organic matter (NOM) and pharmaceuticals and personal care products (PPCP) are known to compete for adsorption sites on carbon nanotubes (CNT), resulting in decreasing PPCP adsorption onto CNT. In this study, four types of PPCP, as such acetaminophen (AAP), caffeine (CAF), triclosan (TCS), and carbendazim (CBD) were used to investigate the effects of PPCP properties and NOM coagulation on the competitive adsorption of PPCP and NOM. Coagulation preferentially removed HS from a natural surface water, thereby increasing adsorption of AAP, CAF, TCS and CBD by 19%, 13%, 17% and 11%, respectively. Similar trends were obtained with synthetic natural waters, for which the adsorption of AAP, CAF, TCS, and CBD increased by 29%, 7%, 44% and 69%, respectively, as humic acid (HA) concentration decreased from 10 mg L^{-1} to 0 mg L^{-1}. Furthermore, PPCP properties also affected their competition with NOM for adsorption by CNT membranes Because CAF existed in cationic form at pH ranging from 7 to 8.3, its adsorption was less affected by the presence/coagulation of NOM than AAP, CBD, and TCS. Based upon these findings, coagulation has the potential to be integrated with CNT adsorption for the removal of PPCP compounds during advanced drinking water treatment.

1. Introduction

Pharmaceuticals and personal care products (PPCP) exhibit adverse ecological impacts that have raised concern among public and regulatory groups about the fate of such compounds during potable water treatment and human exposure in drinking water (Singer et al., 2016; Bu et al., 2013; Li et al., 2014). Conventional drinking water treatment process

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including coagulation, sedimentation, and filtration is not efficient for PPCP removal due to the polarity and trace-level (parts per trillion) concentrations of PPCP compounds (Ternes et al., 2002; Alexander et al., 2012). Therefore, various advanced water treatment technologies, such as activated carbon adsorption, advanced oxidation process (McAvoy et al., 2002), reverse osmosis (RO) (Grobert, 2007) have been applied for PPCP removal from drinking water. Recently, nanomaterials have become promising absorbent materials for water treatment and desalination because of their peculiar nanostructures and superb adsorption capacities (Akbari et al., 2016; Das et al., 2014).

Carbon nanotubes (CNT) serve as a representative type of nano-adsorbent and have been widely used for the adsorption of aquatic contaminants. However, the competitive adsorption between natural organic matter (NOM) and PPCP significantly impedes realistic application of nano-adsorbents for PPCP removal (Petrović et al., 2003; Westerhoff et al., 2005). For example, Liu et al. found that ketoprofen (KEP) and carbamazepine (CBZ) adsorption on MWCNT decreased due to the decreasing adsorption sites through competition adsorption with humic acid (HA) (Liu et al., 2014).

Early works with activated carbon adsorption have revealed that the competitive effect of NOM on organic adsorption was related to the chemical structures and properties of the target organics. For example NOM competition more severely affected the adsorption of 2-phenylphenol with a nonplanar structure and hydrophilic property than the adsorption of phenanthrene with a planar structure and hydrophobic property (Guo et al., 2007; Zhang et al., 2011). In addition, functional groups present on PPCP compounds may also alter NOM competition through the electron-donating interaction (Oleszczuk et al., 2009).

Moreover, NOM removal is a priority for drinking water treatment because NOM consists of various substances that are important precursors of disinfection by-products (Singer, 1994). Various technologies have been developed for NOM removal. Among them, enhanced coagulation is commonly used by water treatment plants (Iijima, 1991; Pan and Xing, 2008). Yang et al. discovered that coagulation with polyaluminum chloride removed up to 20% of TOC from the Luan River water and the Yellow River water (Yang et al., 2012). Vilgé-Ritter et al. also found that coagulation was capable of removing 60% of NOM removal in Seine River water (Vilgé-Ritter et al., 1999). As a result, it is anticipated that coagulation may influence the competitive adsorption of NOM and PPCP by CNT materials by eliminating competition components in NOM. Indeed, our previous study demonstrated that precoagulation of wastewater effluents primarily removed humic-like components of effluent organic matter and enhanced PPCP adsorption by CNT (Wang et al., 2018). Therefore, it is important to determine whether similar effects exist for NOM during drinking water treatment.

Moreover, although competitive adsorption between PPCP and NOM has been widely reported in previous studies, few studies clarify the competition mechanisms that are manifested by the effects of NOM coagulation and PPCP properties when CNT are used as the adsorbents. Therefore, the main objectives of the present study were: 1) to investigate the effects of PPCP properties on their competitions with NOM for adsorption onto CNT membranes, 2) to determine the effects of NOM coagulation on competitive adsorption of PPCP, and 3) to assess the efficiency of integrated pre-coagulation and adsorptive CNT membrane microfiltration for removing PPCP under drinking water treatment conditions.

2. Experimental section

2.1. Chemicals

Reagent-grade acetaminophen (AAP) and triclosan (TCS) were purchased from Tokyo Chemical Industry CO., and caffeine (CAF) and carbendazim (CBD) were purchased from Aladdin Industrial Corporation, China. These chemicals were selected in this study because of their broad variations in molecular structures and physiochemical properties (Table S1, Supporting information). These compounds also possess relatively high detection rates and levels in natural waters (González-Naranjo and Boltes, 2014; Li et al., 2011). In addition, Suwannee River humic acid (Batch# A212001) was purchased from International Humic Substances Society (St. Paul, MN) and used to represent NOM in real water. For the coagulation experiments, reagent-grade polyaluminum chloride (PACl) was purchased from Tianjin Guangfu Institute of Fine Chemicals, China.

Stock solutions of selected PPCP compounds were prepared by dissolving powdered chemicals into HPLC-grade methanol (Fisher Scientific, USA) to reach desired concentrations, namely, 1000 mg L^{-1} for AAP, CAF and CBD, and 500 mg L^{-1} for TCS, respectively. For the preparation of HA stock solution, 10 mg HA was added into 100 mL ultrapure water to reach a mass concentration of 100 mg L^{-1}. For the preparation of PACl stock solution, the as-received PACl liquid was diluted into a stock solution of 50 mg L^{-1} with deionized water.

2.2. Carbon nanotube and membrane

The CNT material used in the study was purchased from Beijing Boyu Technology Corporation of High-tech New Materials, the characteristics of which are summarized in Table 2. This CNT belongs to multi-walled carbon nanotube and was selected in this study due to its relatively low costs and high adsorption capacity for PPCP in the absence of NOM as determined in a previous study (Wang et al., 2015). 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-250 N, Shanghai, China) and then pumped from inside-out through a pre-made, U-shaped PVC membrane module (Fig. 1). Each module had an effective membrane area of 6.9 $\times$ 10^{-4} m^2, resulting in a CNT loading of 22 g m^{-2} at membrane surfaces.

2.3. Feed water

For the preparation of synthetic surface water, the stock solution of HA was diluted into a background solution consisting of 0.01 M NaCl

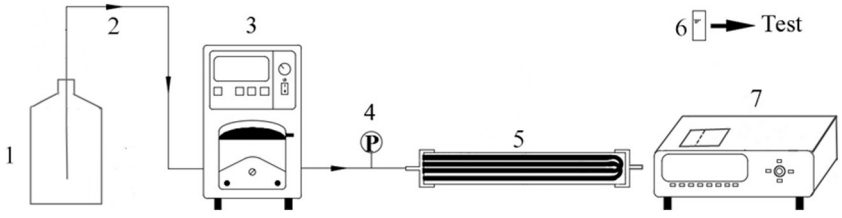

Fig. 1. A schematic diagram of the hollow fiber membrane filtration set-up: 1- feed water bottle; 2- connecting conduct; 3- peristaltic pump; 4- pressure gauge; 5- U-shaped composite hollow fiber membrane; 6- sample for measurement r; 7- ultraviolet spectrophotometer.