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Influence of EfOM on simultaneous rejection and degradation of PhACs during a forward osmosis coupled with electrochemical oxidation process

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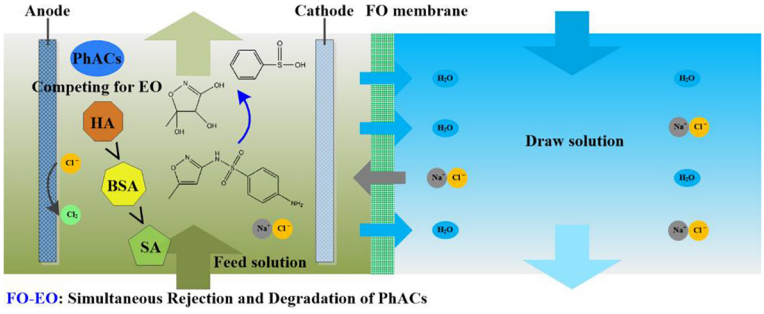
HIGHLIGHTS

- Removal of 15 PhACs using FO coupled with EO (FO-EO) process was studied.
- Impact of EfOM on rejection and degradation of PhACs was investigated.
- Negative impact on PhACs removal was in the order: NOM > proteins > polysaccharides.
- PhACs in actual secondary effluent were well removed by FO-EO processes.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a forward osmosis coupled with electrochemical oxidation (FO-EO) process was used to achieve simultaneous rejection and degradation of 15 pharmaceutically active compounds (PhACs) in wastewater. The influence of wastewater effluent organic matter (EfOM) on PhACs removal was investigated. Sodium alginate (SA), humic acid (HA) and bovine serum albumin (BSA) were used as model organics to represent major constituents of EfOM. Results demonstrated that a generally negative influence of SA on PhACs rejection was observed due to membrane fouling in FO processes. During FO-EO processes, high rejection (> 95%) and degradation efficiencies (> 94%) of 15 PhACs were achieved simultaneously. With the presence of model organics in feed, adverse impacts on PhACs degradation were observed in the order of HA > BSA > SA. Results of UV and EEM fluorescence spectroscopy detection verified the competition of EfOM with PhACs for electrochemical oxidation, further proving the role of natural organic matter (NOM) and proteins in impeding the PhACs removal in FO-EO processes. Moreover, degradation products of PhACs were identified. And the acute toxicity of the feed was decreased after treated by FO-EO processes although the mineralization of PhACs was partially achieved. Furthermore, PhACs in actual secondary effluent were well removed by FO-EO processes, exhibiting a desirable application performance.

1. Introduction

The widespread presence of pharmaceutically active compounds (PhACs) in the environment has received public concern in recent years. Although the reported concentrations of PhACs in the environmental samples were relatively low (between nanogram and microgram per liter in water or per kilogram in particles or soil) [1,2], their potential risk and threat to organisms should not be ignored. In fact, some

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PhACs at low level have been verified to exhibit adverse effects on some aquatic organisms. For instance, Brodin et al. [3] reported that a benzodiazepine anxiolytic drug (oxazepam) altered the behavior and feeding rate of the wild European perch (*Perca fluviatilis*) at concentrations encountered in effluent-influenced surface waters. Rodea-Palomares et al. [4] reported that mixtures of 16 PhACs at environmentally realistic low concentrations produced significant sublethal effects on a freshwater cyanobacterium (*Anabaena* sp. PCC7120 CPB4337; hereinafter *A.* CPB4337). Besides, PhACs have been detected in drinking source water [5], tap water [6] and bottled water [6], which could lead to potential risk to human health in long term. Therefore, it is necessary to control the discharge of PhACs from the sources. Since wastewater treatment plants (WWTPs) are generally considered as a hotspot source of PhACs due to their insufficient removal using traditional treatment processes [7], further treatment of WWTPs secondary effluent to eliminate PhACs could contribute to decreasing the discharge of PhACs, so as to reduce potential risk in the receiving aquatic environment.

Membrane technology is widely accepted as a means of wastewater treatment due to its promising high efficiency, ease of operation, and no use of chemicals [8]. Thus, various membrane processes, such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO), have been studied in recent years for removing emerging organic contaminants (EOCs), like PhACs, pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs) [9–11]. Compared with others, FO has advantages of lower fouling propensity, easier fouling removal and so on in the area of wastewater treatment [12]. Moreover, hybrid FO system, such as FO-RO and FO-NF, could potentially consume less energy compared to a standalone separation process especially when they are used for simultaneous wastewater treatment and seawater desalination [12]. With the commercial FO membranes developed by companies like Oasys Water, Porifera and Aquaporin Inside, applications of FO in desalination, wastewater treatment and osmotic energy harvest are promising.

Rejection of PhACs using FO membranes have been studied previously, and results demonstrated that FO membranes are efficient for rejecting a list of PhACs [11,13–18]. Meanwhile, factors influencing rejection were widely studied, such as physicochemical properties of PhACs [13], properties of membranes [17], membrane fouling [16], operating conditions [15], solution conditions [14], and so on. The main focus of these research was on the rejection efficiency and its affecting factors. However, accompanied with the successful rejection of PhACs by FO, one issue seems to be inevitable, which is the disposal of PhACs in FO concentrate. The treatment of membrane concentrate from WWTPs was studied by using advanced oxidation processes (AOPs), such as ozonation, Fenton process, photocatalysis, sonolysis and electrochemical oxidation [19,20]. Among them, electrochemical oxidation (EO) offers several advantages over other approaches, such as in-situ generation of oxidants without addition of chemicals, operation at ambient temperature and pressure [21]. And EO is capable of degrading a wide range of emerging organic contaminants in wastewater [19]. However, most of the studies about membrane concentrate treatment by EO are independent of membrane filtration processes, which means the concentrate is treated after membrane processes, thus two separate systems are needed for separation and degradation of contaminants. And this would lead to additional cost, land and time.

Compared with pressure-driven membrane processes, FO is operated at ambient pressure, which facilitates its combination with other technologies. Therefore, considering the structural similarity of FO filtrator and EO reactor, a FO coupled with EO process was established for the first time and tested for simultaneous rejection and degradation of pharmaceuticals in our previous study [22]. Both rejection and degradation of target pollutants were desirable, and a synergetic effect between FO and EO was observed, which was that pollutants rejection was enhanced due to their degradation in feed while degradation efficiencies of pollutants were improved due to favorable mass transfer by feed circulation and assist of active chlorine species transformed by oxidation of the reverse Cl^- from draw solution [22]. Nevertheless, the inadequacy of our last study lies in that the water matrix conditions of the synthetic wastewater are simple and the number of selected PhACs is limited as well. Since water matrix of actual wastewater is complex, it is necessary to investigate the influence of water matrix, especially wastewater effluent organic matter (EfOM), on PhACs removal during the treatment.

In this study, FO coupled with EO (FO-EO) process was further investigated for its capacity of simultaneous rejection and degradation of 15 PhACs with a wide range of molecular weight. And above all, this study investigated the influence of EfOM on rejection and degradation of PhACs during FO-EO processes. For this purpose, sodium alginate (SA), humic acid (HA) and bovine serum albumin (BSA) were used as model organics to represent polysaccharides, natural organic matter (NOM) and proteins, respectively, which are major constituents of EfOM. HPLC-MS was used to detect the PhACs concentration. UV and excitation-emission matrix (EEM) fluorescence spectroscopy were used to detect the change of EfOM in feed before and after treated. Furthermore, degradation products, acute toxicity and total organic carbon (TOC) were investigated for PhACs after treated by FO-EO processes.

2. Materials and methods

2.1. Representative PhACs and model organics

A total of 15 PhACs were selected to represent typical PhACs frequently detected in WWTPs effluent with a wide range of molecular weight and charge. Physicochemical properties of the 15 PhACs are shown in Table 1 and the chemical structures are shown in Table S1 in Supplementary Data. All pharmaceuticals were at purity of 98% or above. SA, HA and BSA were used as model organics to represent polysaccharides, NOM and proteins, respectively. Stock solutions of 500 mL for each PhAC with a concentration of 100 mg L^{-1} were prepared except for domperidone, carbamazepine, azithromycin and roxithromycin. Those four PhACs were prepared with a concentration of 10 mg L^{-1} for 2 L stock solutions due to their poor dissolvability in water. All the stock solutions were prepared with ultrapure water, and cinnarizine was dissolved with acid assist.

2.2. Forward osmosis membrane

A biomimetic aquaporin FO membrane is provided by Aquaporin A/S (Aquaporin A/S, Copenhagen, Denmark). Briefly, the aquaporin membrane is made as a thin film composite membrane where vesicles with embedded aquaporin proteins are stabilized by a polyamide layer supported by a porous support [23].

2.3. FO-EO reactor and schematic of the experimental set-up

The FO-EO reactor consists of two cells, namely FO-EO cell and draw solution cell, of which the dimensions are both 200 mm long, 20 mm wide, and 10 mm deep. FO membrane is set in the middle to separate the two cells. A titanium mesh is used as cathode, and horizontally placed above the FO membrane with a 2 mm gap in the FO-EO cell. The anode is above the cathode with a 5 mm gap. A commercial mesh electrode (titanium mesh coated by IrO_2-Ta_2O_5-SnO_2, provided by Long Sheng Electrode Co., China.), which exhibited excellent degradation efficiencies of several antibiotics in our previous study [22], is used as anode with a projected surface area of 40 cm^2 (20 × 2 cm). Silicone spacers are used to form the cells of feed and draw solution and seal up the cells. The internal schematic of the FO-EO reactor is shown in Fig. 1 as well as the schematic of the experimental set-up. Briefly, two peristaltic pumps are used to respectively pump the feed and draw solution in counter-current mode with a cross-flow velocity of 5 cm s^{-1}