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Rejection and adsorption of trace pharmaceuticals by coating a forward osmosis membrane with TiO_2

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HIGHLIGHTS

- Contact angle, roughness and zeta potential decreased after TiO_2 modification.
- Modified FO membrane was firstly used to get high rejection efficiencies of PhACs.
- Modified membrane can alleviate the impact of pH changes and humic acid fouling.
- Adsorption played a significant role on rejection of TCS by the modified membrane.

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ABSTRACT

The active layer of a thin film composite polysulfonate forward osmosis (FO) membrane impregnated with nanoparticles of titanium dioxide (nano-TiO_2) using polydopamine was developed. A mass balance and adsorption thermodynamic analysis of selected pharmaceuticals in the FO process was investigated. Scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy were used to examine the physical and chemical properties of the modified membrane. The contact angle and zeta potential decreased significantly after modification. A small increase in rejection capacity for the selected pharmaceuticals after modification was observed. The modified membrane also displayed less tendency to be fouled by humic acid than the virgin one. The pH of the feed solution had less impact on the rejection of pharmaceuticals by the modified membrane than the virgin membrane, which was likely due to changes in the zeta potential and functional groups of the modified membrane. We demonstrated that adsorption plays a significant role in TCS removal but not in the removal of MTP and SMX.

1. Introduction

Pharmaceuticals have been detected as emerging contaminants in the effluents of wastewater treatment plants [1]. They are biologically active and can threaten the aquatic environment and human health due to their acute and chronic toxicity to aquatic organisms. They can also change the diversity of ecosystems and promote antibiotic resistance in wastewater treatment plants [2]. As a result, pharmaceutical pollutants in wastewater have received significant attention in recent years. Unfortunately, the removal efficiencies of trace pharmaceuticals are limited and usually they are only slightly transformed by conventional water treatment processes [3]. Various technologies have been used to remove pharmaceuticals including forward osmosis (FO), nanofiltration (NF), reverse osmosis (RO) and advanced oxidation [4–8]. Different from the NF and RO processes, FO utilizes an osmotic pressure difference as the driving force, thus there is no cake layer compaction [4]. FO can often achieve a high rejection efficiency for a wide range of pollutants [9]. Avoiding draw solution regeneration can bypass a significant energy cost in FO technology implementation and in this case the operational cost of FO will be much less than that of RO [10]. These advantages make FO a promising candidate for water reuse, especially for wastewater that contains emerging contaminants such as pharmaceuticals.

The rejection characteristics of an FO membrane are influenced by the membrane properties, target chemical (feed solution) characteristics and draw solution properties [11]. Rejection of emerging trace organic chemicals such as pharmaceuticals by the FO process has been demonstrated [12–14]. A comprehensive study on the

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rejection of trace organic chemicals by FO reported rejections of 40%–90% [12]. Linares et al. [13] also made a similar observation when they examined the removal of 13 emerging trace organic chemicals by FO. Xie et al. [14] elucidated the relationship between membrane properties and the rejection of trace organic contaminants by FO. However, they used a commercial cellulose triacetate (CTA) FO membrane, which could not endure a wide pH range. To the best of our knowledge, surface modification of existing FO membranes remains to be explored as an alternative strategy for improving the rejection of pharmaceuticals. The purpose of most of the previously reported NF or RO membrane modifications was to reduce membrane fouling by pollutants in the wastewater, or to increase water flux, and not to enhance the rejection of pharmaceuticals. The pH and humic acid (HA) are known to be very important factors in the transformation and transfer of pharmaceuticals and membrane fouling [4,12–14]; however, the effects of pH and HA on the rejection of pharmaceuticals by modified FO membranes are still unclear.

The incorporation of nano-sized titanium dioxide (nano-TiO_2) into membranes has been investigated in recent years [15]. This modification has been intensively studied as a means of membrane fabrication because of its excellent chemical stability and high hydrophilicity. Several strategies for integrating TiO_2 into thin film composite membranes have been reported by other researchers [15,16]. Because of its facile and versatile characteristics, the self-assembly method of coating TiO_2 onto membranes is preferred. However, the main drawback of this method is the weak binding force between the nano-TiO_2 and the membrane surface, and thus the application of the method is limited. Recently, polydopamine (PDA) has drawn much attention due to its hydrophilicity, biocompatibility and multifunctional groups (amino and catechol groups) [17–19]. PDA has also been found to be able to polymerize on the nano-TiO_2 surface, which facilitates the firm adherence of the nano-TiO_2 to the membrane surface [19]. Although robust binding of nano-TiO_2 on membranes using PDA has already been reported [20], the coating of nano-TiO_2 on an FO membrane and its impact on the rejection and adsorption of pharmaceuticals has not been studied.

Thus, the purposes of the present study were (i) to develop a modified FO membrane suitable for the removal of pharmaceuticals by integrating nano-TiO_2 using PDA for surface modification and (ii) to investigate the effects of pH and HA on the rejection of selected pharmaceuticals and also to do a mass balance analysis of the FO process. The surface characteristics of the modified membranes were analyzed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). Metoprolol (MTP), sulfamethoxazole (SMX) and triclosan (TCS) were selected as target pharmaceuticals because they have frequently been detected in the aquatic environment [21–24] and have similar molecular weights but different charges in aqueous solutions. The impacts of pH and HA were evaluated using a laboratory scale cross-flow FO mode system. The adsorption characteristics and a mass balance for each of the three pharmaceuticals were also investigated to determine the fate of the pharmaceuticals.

2. Methods and materials

2.1. Materials

The pharmaceuticals (MTP, SMX and TCS) were selected to be within the same molecular weight range but to have different physical chemical properties (e.g., surface charge) as shown in Table 1 [5,21–24]. The structures of the three pharmaceuticals were given in Fig. S1 (Supporting Information). MTP, SMX and TCS were purchased from Sigma–Aldrich (St. Louis, MO, USA) at greater than 98% purity and used without further purification. HA was purchased from MP Biomedicals, LLC (Solon, OH). Other chemical reagents were obtained from Fisher Scientific or Aldrich at greater than 98% purity and used without further purification. Nano-TiO_2 (particle size of less than 20 nm) were obtained from Sigma–Aldrich. Deionized (DI) water was used to prepare all feed stocks. The virgin membrane (thin film composite embedded with polysulfonate) was supplied by Hydration Technology Innovations (Albany, OR). It is an asymmetric membrane specifically designed for FO applications. The membrane was soaked in DI water for 1 h before use.

Table 1
Characteristics of selected pharmaceuticals.

Compound	MTP	SMX	TCS
Charge at pH = 8	Positive	Negative	Neutral
log K_{ow}[a]	1.88	0.89	5.17
pK_a[a]	9.49	1.7 and 5.8	7.8–8.14
M.W., g/mol[a]	267.4	253.3	289.6
Length, nm[a]	1.86	1.33	1.42
Eqwidth, nm[a]	0.73	0.64	0.72

[a] Data adopted from reference [5,21–24].

2.2. Preparation of a TiO_2 modified FO membrane

The virgin commercial membrane was dried with compressed air for 5 min and then mounted in the dead-end cell. Dopamine solution (2 mg mL^{-1}) was made by dissolving dopamine hydrochloride in Tris buffer solution (pH = 8.5 and 10 mM). A 15-mL dopamine solution (2 mg mL^{-1}) was poured into the dead-end cell and a deposition time of 30 min was allowed as described by Zhang et al. [20]. The membrane was then carefully removed from the dead-end cell and rinsed for 1 min with DI water in order to remove the residual unbound PDA. A modified coating method was employed to immobilize the nano-TiO_2 on the surface of the PDA-treated membrane, as described as follows [16]. First, a 0.2% suspension of TiO_2 nanoparticles in 2 L of Tris buffer solution (pH = 8.5, 10 mM) was prepared and sonicated (350 W, 50 Hz) for 120 min. Then the PDA treated membranes were immersed in the TiO_2 colloidal solution for 2 h. The TiO_2 colloidal solution was stirred continually during the coating process. Finally, the coated membrane samples were rinsed with DI water and dried at 60 °C for 5 min. This procedure is illustrated in Fig. S2. This coating method is proved to be capable of providing an efficient, strong and irreversible binding effect for TiO_2 nanoparticles by rinsing and wiped by a cloth [20]. It is found the quantity of TiO_2 clusters decreases a little as the rinsing time increase from 5 min to 60 min. The PDA layers maintain a uniform and complete coverage of TiO_2 nanoparticles on the membrane surfaces.

2.3. Characterization of the membranes

2.3.1. Contact angle and zeta potential measurements

The water contact angle was determined by a Ramé-hart Model 250 goniometer (Ramé-hart Instrument Co.). The contact angles were measured at five random locations for each sample and the average number is reported in order to minimize experimental error.

The zeta potential of the membrane was measured by a streaming current electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria). The size of membrane samples being examined was about 1 cm × 2 cm. The measurements were conducted in a background electrolyte solution (1 mM KCl). The same electrolyte solution was