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Comparison of tetracycline rejection in reclaimed water by three kinds of forward osmosis membranes

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HIGHLIGHTS

- TC rejection and solution ionic strength increased with increasing water flux.
- NW-structure membranes could reduce TC rejection via increased flow velocity.
- Draw solution composition had an effect on TC rejection for hindering TC diffusion.

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ABSTRACT

Comparison of the rejection of trace tetracycline (TC) in the secondary effluent of an anoxic–oxic (AO) system by forward osmosis (FO) was investigated at the mini-lab scale. The effects of different operating conditions including membrane orientation, flow velocity, and draw solution concentration and solute on TC rejection were also explored. The results revealed that TC rejection increased with increasing water flux, but high reverse salt flux may reduce TC rejection through enhanced solution ionic strength. Membranes with a nonwoven structure could reduce TC rejection via increased flow velocity. In the pressure retarded osmosis (PRO) mode, rejection of charged TC was higher than in the FO mode because of enhanced electrostatic repulsion. In addition, the reverse draw solute could hinder the forward diffusion of TC, thus leading to a decline in TC rejection. The cellulose triacetate with embedded polyester screen (CTA-ES) membrane displayed consistently higher TC rejection than that of the cellulose triacetate with a cast nonwoven (CTA-NW) membrane, and the rejection of TC by a thin-film composite with embedded polyester screen (TFC-ES) membrane was relatively lower compared to CTA membranes. These findings provide further insight into TC rejection mechanisms and potentially can be useful for FO process operation in wastewater reclamation.

1. Introduction

Antibiotics are widely used for preventing and treating bacterial infections. The presence of low concentrations of antibiotics in wastewater will generate antibiotic resistant bacteria and antibiotic resistance genes, thus posing a great risk to human health and ecosystems [1–3]. Studies have shown that the sewage effluent of municipal sewage treatment plants is an important contamination source for antibiotic resistance. A number of investigations have explored mechanisms for the removal of antibiotics from municipal sewage treatment plants [4–6]. In fact, most conventional biological treatment processes can only partially remove these antibiotics from wastewater, and in some cases no removal is accomplished. Many studies have reported that the final concentrations of effluent antibiotics ranged from a few nanograms per liter (ng/L) to several micrograms per liter (μg/L) [7–9]. Advanced membrane treatment processes are commonly used in further treatment and reclaimed water recycling including nanofiltration (NF) [10], reverse osmosis (RO) [11], and combination process microfiltration — (MF)/RO [12], NF/RO [13], and membrane bioreactor (MBR) [14,15]. Although these advanced treatment technologies have been shown to achieve efficient removal of trace organic antibiotics from contaminated water, their limitations are that they are energy intensive and involve membrane fouling processes. Hence, new technologies that will better remove antibiotics from polluted water resources are needed.

Forward osmosis (FO) is a new emerging membrane process, operating at low or no hydraulic pressures, in which water is transported across a selectively permeable membrane from a less concentrated feed solution towards a more concentrated draw solution [16]. Because of its novel properties, it has become increasingly attractive in recent years. In contrast to pressure-driven membrane processes, such as ultrafiltration (UF) and RO, the FO process is associated with lower

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energy cost [17], less membrane fouling propensity [18], and higher contaminant recovery rates [19,20]. Consequently, the FO process has been investigated as a means of purifying a range of substrates, such as seawater, domestic wastewater, drilling wastewater, activated sludge solution, anaerobic digester concentrate, urban runoff, and materials from oil and gas operations [21–27].

The occurrence of trace organic contaminants (TrOCs) in secondary treated effluent is an important consideration in the recycling of wastewater. Numerous recent investigations have been conducted to study the removal of TrOCs using an FO process. Linares et al. [28] used secondary wastewater effluent as a feed solution and compared the effects on rejection caused by clean versus fouled membranes. The results suggested that the rejection of a hydrophilic neutral compound was enhanced by the presence of a fouling layer. Other studies investigated the effects of draw solution concentration on TrOC rejection. Alturki et al. [29] investigated the rejection of 40 TrOCs by a cellulose triacetate (CTA) membrane using 0.5 and 2 M NaCl as draw solutions. Their results revealed that, in the FO and pressure retarded osmosis (PRO) modes, the rejection of charged TrOCs was governed by both electrostatic interaction and size exclusion. Jin et al. [30] evaluated the rejection of four pharmaceutical compounds using a NaCl draw solution to increase water flux. Their finding was consistent with improved solute rejection with increasing water flux when the FO membrane active layer was facing the feed solution. A few studies examined the rejection of TrOCs by using different draw solution solutes. Xie et al. [31,32] investigated TrOC rejection using NaCl, $MgSO_4$, glucose, and urea as draw solutions at the same permeate water flux, in agreement with the retarded forward diffusion phenomenon. Several previous studies discussed the effects of membrane orientation on TrOC rejection. Alturki et al. [29] evaluated the rejection of 40 TrOCs as a function of membrane orientation, and they found that membrane orientation significantly impacted on TrOC rejection: in the PRO mode the compound showed poorer rejection than in the FO mode. Xie et al. [33] used CTA membranes to investigate the rejection of two TrOCs as a function of membrane orientation, and their report showed that negatively charged compounds were affected by the feed solution pH in both membrane orientations. Among TrOCs sulfamethoxazole, which is a sulfonamide antibiotic, was also studied as it is frequently detected in sewage effluent. Surveys indicated that many factors influence the removal efficiency of sulfamethoxazole by the FO process, including pH [33], membrane orientation [33], temperature [34], charge [35], molecular weight [35–37], and membrane fouling [32,38,39].

However, until recently there have been no direct investigations of the removal of tetracycline (TC) by different kinds of FO membranes. TC is a typical tetracycline antibiotic that is used extensively and is also associated with high detection frequencies in secondary effluent at low levels [40–42]. As a result, it is essential to understand the characteristics of TC rejection by different FO membranes.

The aim of this study was to investigate the effects of different operating conditions on the rejection of trace TC by different kinds of FO membranes. The basic properties of FO membranes were measured to better elucidate TC rejection behavior and comparison was also made between three different kinds of FO membrane.

2. Materials and methods

2.1. FO membranes

Three commercial FO membranes were provided by Hydration Technology Innovations (Albany, Oregon, USA), namely cellulose triacetate with embedded polyester screen (CTA-ES), cellulose triacetate with a cast nonwoven (CTA-NW), and a thin-film composite with embedded polyester screen (TFC-ES). The CTA membranes both have a cellulose triacetate active layer. According to the manufacturer, the operating pH value ranges of CTA-ES, CTA-NW, and TFC-ES membranes are from 3 to 8, 3 to 8, and 2 to 11, respectively.

2.2. Forward osmosis system

The mini-lab scale FO system utilized a membrane cell that was oriented vertically (Fig. 1). The membrane cell was made of polymethyl methacrylate, with co-current flow symmetric channels on both sides of the membrane. Each channel was 8 cm long, 3 cm wide, and 0.2 cm deep, providing a total effective membrane surface area of 24 cm^2. Two variable speed gear pumps (WT3000-1JA, LongerPump, China) were used to deliver the liquids of the feed and draw solutions in a closed loop. The draw solution rested on a digital balance (JA31002, Jinghai Instrument, Shanghai, China) and weight changes were recorded over time by a computer to calculate the permeated water flux. The conductivity, temperature, and pH of the feed solution were continuously measured using a conductivity meter (DDS-307, INESA Scientific Instrument, Shanghai, China) and a pH meter (Mettler Toledo, Shanghai, China).

2.3. Feed solution chemistry

The bench scale anoxic–oxic (AO) activated sludge treatment system was set up in an air-conditioned laboratory. The total working volume was 13.2 L, and the ratio of A:O was 1:2. The seed sludge (Shanghai Song-Jiang district WWPTs, China) was introduced into the reactors and domesticated with synthetic wastewater. The synthetic wastewater contained (mg/L): glucose (400), $CH_3COONa{\cdot}3H_2O$ (80), $NaHCO_3$ (125), KCl (4.7), $CaCl_2$ (2.5), NH_4Cl (120), KH_2PO_4 (24), and $MgSO_4{\cdot}7H_2O$ (27.5). The mineral salt solution contained (mg/L): $MnCl_2{\cdot}4H_2O$ (0.036), $FeCl_3$ (0.45), $CuSO_4{\cdot}5H_2O$ (0.09), H_3BO_3 (0.045), $ZnSO_4{\cdot}7H_2O$ (0.036), KI (0.054), and EDTA (3). Operating parameters of the AO process for optimum trace TC removal were as follows: the system hydraulic retention time (HRT) was 10 h and sludge retention time (SRT) was 15 d. Dissolved oxygen and mixed liquid suspended solids of A and O were 0.2–0.5 mg/L, 3–5 mg/L, 3500–4500 mg/L, and 3500–4500 mg/L, respectively. The internal circulation was 200%, and external circulation was 100%, and the temperature in the reactor was maintained at approximately 25 °C. The influent pH, chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) were 7.0 ± 0.2, 430 ± 10 mg/L, 31 ± 2 mg/L, and 5.6 ± 0.5 mg/L, respectively.

Tetracycline hydrochloride (Adamas Reagent, purity ≥ 99%) was spiked (500 μg/L) to the synthetic wastewater every day, after 100 days of AO operation. In the FO experiments, secondary effluent containing trace TC was collected as the feed solution and the water quality parameters are listed in Table 1. As the composition was likely to change daily, the same FO operating conditions were used for the same effluent sample. The key physico-chemical properties of TC are summarized in Table 2.

2.4. Experimental protocol

Trace TC rejection experiments were conducted in both FO and PRO modes. In the FO mode experiments, the active layer of the FO membrane faced the feed solution, and in the PRO mode experiments, the active layer of the FO membrane faced the draw solution. Analytical grade NaCl, $MgSO_4$, glucose, and urea (Sinopharm Chemical Reagent, China) were selected as draw solution solutes and the draw solutions were prepared in Milli-Q water. The initial volumes of the feed and draw solutions were both 1 L. The temperatures of the feed and draw solutions were kept constant at 25 ± 1 °C by air-conditioning. A new FO membrane was used for each experiment. Samples (600 mL) of the draw solution were taken for analysis after the rejection experiments had been conducted for 2 h [30].