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Separation of tetracycline from wastewater using forward osmosis process with thin film composite membrane – Implications for antibiotics recovery

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ABSTRACT

To minimize the risk of antibiotic wastewater generated by the pharmaceutical industries, the potential separation efficacy of tetracycline (TC) from aqueous solution using forward osmosis (FO) process with thin film composite membrane was systematically studied. First, the microstructure and transport properties of TFC membrane were characterized. Then, the effects of membrane orientation, feed velocity and solution pH on the behavior of the FO process for TC separation were studied. Finally, the performance of TFC membrane for TC separation in a long-term FO mode operation was investigated. The results showed that the membrane performance in FO mode (active layer facing the feed solution) and PRO mode (active layer facing the draw solution) was highly affected by solute resistivity (K) value. The water flux and TC rejection achieved over 20 LMH and 99.0% in FO mode, respectively. High TC concentration factor (CF) of 2.6 was obtained in FO mode, indicating the concentrated TC solution could be harnessed to recover the TC by conventional crystallization. However, severe water flux decline accompanied with low tetracycline CF was found in PRO mode, which was mainly attributed to serious fouling and high K value occurred in the porous support. With the flow velocity rising, the shear stress and mass transfer coefficient (k) on the membrane surface increased, alleviating the membrane fouling. Acidic environment would favor the separation due to the change of TC speciation and TFC membrane properties. A long-term testing demonstrated that more than 97% TC rejection and 74% water flux recovery were well maintained with simple hydraulic cleaning after 5 cycles FO mode operation. This work implied that the FO based technology could be developed as an effective alternative for the treatment of tetracycline antibiotic wastewater as well as the recovery of antibiotics from the wastewater.

1. Introduction

In the past decades, the extensive use of antibiotics for protecting human and animal health, as well as for improving the growth of livestock, has led to their excess accumulation in the environment [1]. In China, the annual production of antibiotics is about 210,000 tons [2]. Tetracycline (TC) antibiotics, including tetracycline, chlortetracycline and oxytetracycline, are the second class of antibiotics in production and usage worldwide, which are ranked first in China [3]. About 25–75% of tetracycline antibiotics are excreted and released in an unaltered form into the environment via urine and feces [4]. The emergence of tetracycline antibiotics in water has drawn a great attention due to the induced antibiotics resistance genes (ARGs), which have seriously jeopardized the human health and the ecological security [5,6].

Due to the large production of tetracycline, the wastewater from related pharmaceutical industries has become a serious pollutant source. The tetracycline antibiotics contaminated waste streams generated in manufacturing plants contains high level concentration of antibiotic from around 10 to 1000 mg/L [7–9]. Thus huge quantity of tetracycline antibiotics wasted in wastewater treatment process. If the tetracycline antibiotics could be reclaimed from wastewater, it would greatly reduce the amount of tetracycline antibiotics for disposal. Nevertheless, the traditional methods for wastewater treatment fail to remove tetracycline antibiotics effectively. To eliminate tetracycline antibiotics, advanced oxidation processes (AOPs) have been applied, including photochemical process, electrochemical process and photocatalytic process [1]. These processes are able to oxidize antibiotics

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by producing hydroxyl radicals from O_3/H_2O_2, UV/O_3 and UV–TiO_2. Though the AOPs could directly degrade tetracycline antibiotics, the methods could not recover the antibiotics from wastewater for reuse. Moreover, some AOPs need high operating cost due to the high energy consumption.

With the rapid development of membrane technology, membrane separation process has been gaining attention for antibiotic wastewater treatment. The reverse osmosis (RO) process, nanofiltration (NF) process and ultrafiltration (UF) process have been studied to remove tetracycline antibiotics from wastewater [8–10]. The rejection of examined antibiotics by some RO/NF membranes could achieve 98.5% [9]. More importantly, the tetracycline antibiotics in the RO or UF retentate can be recovered through conventional crystallization [8]. Nevertheless, RO, NF and UF are pressure-driven membrane processes, which are susceptible to membrane fouling [11]. Especially RO is still energy intensive process, in which 85% of energy consumption puts into the high pressure pumps [12]. Therefore, to explore other plausible membrane processes for tetracycline antibiotics separation with lower energy requirement and less membrane fouling is necessary.

Forward osmosis (FO), as a new membrane process, has been gaining popularity in the membrane separation area [11]. Unlike pressure-driven processes (RO and NF), FO is a natural process that utilized an osmotic pressure difference to drive water molecule across the membrane from a dilute feed solution into a concentrated draw solution [13]. Hence, FO possesses the advantages of low membrane fouling tendency due to the absence of hydraulic pressure [14,15]. Moreover, in FO system where recovery of draw solution is easy or unnecessary, FO will be energy-efficient [16–18]. Owing to these advantages, FO has been used for the treatment of municipal wastewater, oily wastewater and trace organic compounds (TOrCs) in water [19,20]. Furthermore, to produce fresh water and regenerate draw solution, FO could be combined with other membrane processes, such as RO and membrane distillation (MD) [21]. Especially, the FO can be utilized for the recovery of useful materials, such as nutrients and Na_2CO_3 [22,23]. The phosphorus in digested sludge centrate were extracted by FO process in the form of struvite ($MgNH_4PO_4{\cdot}6H_2O$) [22]. $Na_2CO_3{\cdot}10H_2O$ crystals were recovered from aqueous streams using FO process, and the purity of crystals was 99.98% [23]. Consequently, FO may be a promising technology for the recovery of tetracycline antibiotics from antibiotic wastewater.

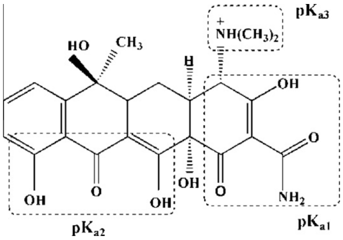
The application of FO process for the recoverable separation of TC from wastewater was proposed and studied in this study with commercial thin film composite (TFC) FO membrane. The effects of membrane orientation, feed velocity and the pH value of feed solution on TC separation were first investigated, followed by long-term studies of membrane cleaning and reuse for separation in FO process. To the best of our knowledge, this is the first time that FO process was studied to treat the TC wastewater, which may provide useful insights for the design of FO process for antibiotics separation from water during their production process.

2. Materials and methods

2.1. Solutions and FO membrane

Feed solution containing tetracycline for separation experiments was prepared from pure tetracycline hydrochloride powder (Beijing Solarbio Science & Technology, China). The main characteristics of TC hydrochloride are listed in Table 1. Solution of NaCl (Sinopharm Chemical Reagent, China) was used as draw solution. All the solutes were dissolved in deionized (DI) water, which has a conductivity of 5 μs/cm. The flat sheet TFC FO membrane obtained from Hydration Technology Hydration Innovations (HTI, USA) was recently commercialized. The main characteristics of this membrane are presented in Table 2. The parameters for *A* and *B* of TFC membrane are obtained from the Ref. [24].

Table 1
Characteristics of tetracycline molecule.

Structure	
Formula	$C_{22}H_{24}N_2O_8$
Molecular weight (g/mol)	444.44
pK_a[a]	3.3, 7.68, 9.3

[a] From Sassman and Lee [34].

2.2. Microscopic observation of TFC FO membrane

The micro-images of the membrane were obtained using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) with at an accelerating voltage of 5 kV. Before imaging, samples were coated with a thin layer of gold by a sputter coater (EMS150T ES, EMS, USA). For the cross section observation, the FO membrane was freeze-fractured in liquid nitrogen to obtain a clean edge.

2.3. Forward osmosis system

A schematic diagram of the laboratory-scale FO system was illustrated in Fig. 1. A custom-made cross-flow membrane cell with two identical and symmetrical flow chambers was utilized. The flow chamber had a total effective membrane area of 40 cm^2 with length, width and height of 100, 40, and 2 mm, respectively. The feed and draw solutions were circulated with peristaltic pumps (Longer, China). The draw solution tank was positioned on a digital balance (SF6001F, Ohaus, USA) connected to a computer, and weight changes were recorded automatically every minute to determine the permeate water flux. In addition, the conductivity of feed solution was monitored by a conductivity meter (Eutech Instruments, Singapore) for the calculation of reverse salt flux. The test was conducted at room temperature (23 ± 1 °C).

2.4. Measurement of water flux and reverse salt flux of the FO membrane

In order to fully saturate the membrane porous support by water, the membrane was soaked in a 50% solution of ethanol for 5 min at the beginning of tests, then rinsed in deionized water [25]. All the tests were carried out in the membrane channel without any spacer under counter-current crossflow direction. TC solution with concentration of 1000 mg/L was used as feed solution for TC separation experiments, while DI water was used for baseline experiments. The pH of TC solution was kept at about 3.05. 2 M NaCl solution was employed as draw solution in all tests. The initial volumes of draw and feed solutions were fixed at 2 L and 1 L, respectively. Both the solutions were supplied at crossflow velocity of 12.5 cm/s (600 mL/min or Reynolds number (*Re*) of 531). The experiments were conducted for 9 h.

The water flux (J_W, $Lm^{-2}\,h^{-1}$, abbreviated as LMH) and reverse salt flux (J_S, $gm^{-2}\,h^{-1}$, abbreviated as gMH) were calculated as follows:

Table 2
Transport properties of thin film composite (TFC) membranes.

Pure water permeability, A LMH/bar	Salt permeability coefficient, B LMH	NaCl rejection, R %	Mode	Water flux, J_W^F LMH	Reverse salt flux, J_S^F GMH	$K_{s/m}$
2.49[a]	0.39[a]	99.6[b]	FO[c]	21	15.5	4.22×10^5
			PRO[c]	50	22.35	3.82×10^5

[a] Values for and of TFC membrane are from Straub et al. [24].
[b] Nacl rejection of TFC membrane is provided by HTI.
[c] The water flux and reverse salt flux in FO and PRO mode were obtained with DI water as the feed and 2 M NaCl as the draw solution.

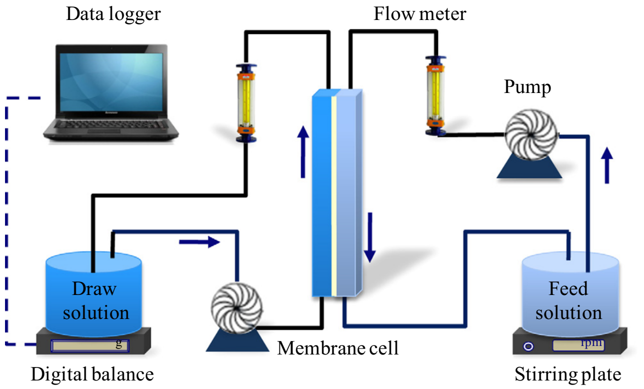


Fig. 1. A schematic diagram of the lab scale forward osmosis (FO) system.

$$J_W = \frac{\Delta V}{a\Delta t} \tag{1}$$

$$J_S = \frac{C_{S,t}V_{F,t} - C_{S,i}V_{F,i}}{a\Delta t} \tag{2}$$

where ΔV (L) is the volume of permeation water collected in a predetermined time Δt (h) during the test, and a is the effective membrane surface (m^2). $C_{S,t}$ (mg/L) and $V_{F,t}$ (L) refer to the salt concentration and total volume of the feed at the end of tests, respectively, while $C_{S,i}$ (mg/L) and $V_{F,i}$ (L) are the initial salt concentration and total volume at the beginning of tests.

2.5. Determination of TC rejection and concentration factor (CF)

The TC concentrations in the draw and feed solutions were determined by an ultraviolet (UV) spectrometer (T-18, Pgeneral, China) at the wavelength of 276 nm. The samples with approximate volume of 500 µL were taken from feed solution to measure the concentration every hour. The TC rejection can be determined from the following equation:

$$\text{Rejection} = \left(1 - \frac{C_P}{C_{F,i}}\right) \times 100\% \tag{3}$$

$C_{F,i}$ (mg/L) is the initial TC concentration in the feed solution, and C_P (mg/L) is the TC concentration in the permeate. Notably, unlike the conventional pressure-driven process, the permeate was obtained from the difference between TC initial and final concentrations in the draw solution. As a result, the C_P can be calculated using the following equation:

$$C_P = \frac{C_{D,t}(V_{D,i} + \Delta V) - C_{D,i}V_{D,i}}{\Delta V} \tag{4}$$

where $C_{D,t}$ (mg/L) is the TC concentration in the draw solution at the end of tests, $C_{D,i}$ (mg/L) is the TC concentration in the draw solution at the beginning, and $V_{D,i}$ (L) is the initial volume of draw solution.

In order to express the separation efficiency of TC, concentration factor abbreviated as CF is determined by follows:

$$\text{CF} = \frac{C_{F,t}}{C_{F,i}} \tag{5}$$

where $C_{F,t}$ (mg/L) is the TC concentration in feed solution at time t, and $C_{F,i}$ (mg/L) is the initial TC concentration of feed.

2.6. External concentration polarization and internal concentration polarization

The active layer facing the feed solution orientation in FO process is called as FO mode, while the active layer facing the draw solution orientation is named PRO (unpressurized pressure retarded osmosis) mode. The CP developed inside the porous layer is generally termed internal concentration polarization (ICP) as opposed to the external concentration polarization (ECP), which takes place outside the membrane [26].

The ICP in FO process can be characterized by the solute resistivity K, determined by the following equation [26]:

$$K = \frac{t\tau}{D\varepsilon} \tag{6}$$

where t, τ and ε are the thickness, tortuosity and porosity of membrane porous support layer, respectively. D is the diffusion coefficient of the solute. The K values in FO mode and PRO mode can be calculated by the following equations [27]:

$$K = \left(\frac{1}{J_W}\right) \ln \frac{B + A\pi_D}{B + J_W + A\pi_F} \quad \text{(FO mode)} \tag{7}$$

$$K = \left(\frac{1}{J_W}\right) \ln \frac{B + A\pi_D - J_W}{B + A\pi_F} \quad \text{(PRO mode)} \tag{8}$$

where A and B are pure water permeability and salt permeability coefficients of the active layer. The π_D and π_F are the osmotic pressures of the draw and feed solutions, respectively.

The mass transfer coefficient, k can be expressed the ECP in FO mode, given by the following relationship [28]:

$$k = \frac{ShD}{d_h} \tag{9}$$

where Sh is the Sherwood number and d_h refers to hydraulic diameter of the feed channel. The Sh of laminar flow can be obtained from the following equation:

$$Sh = 1.85\left(\text{Re}Sc\frac{d_h}{L}\right)^{0.33} \tag{10}$$

Re is the Reynolds number, Sc is the Schmidt number and L is the length of the flow channel.

3. Results and discussion

3.1. Membrane properties

Due to the high water permeability and good rejection to salts, the TFC FO membrane is widely used in desalination, wastewater treatment and water reuse. Representative scanning electron microscope (SEM) images of the TFC membrane were shown in Fig. 2. The polyamide active layer of the membrane surface, as exhibited in Fig. 2a, had a typical ridge-and-valley morphology formed using interfacial polymerization, which surface was relatively smoother than some lab-made ones [29]. As shown in Fig. 2b, the cross-sectional micrograph of the membrane revealed that the thickness of the polyamide layer was about 417 nm, respectively. The porous finger-like macrovoids spanned most of the support layer thickness. The porous structure could reduce the resistance to mass transfer, thus improving the water flux [30]. The TFC was embedded with bottom polyester screen support, forming large backside openings (Fig. 2c); the polyester screen support could enhance mechanical strength of the TFC membrane.

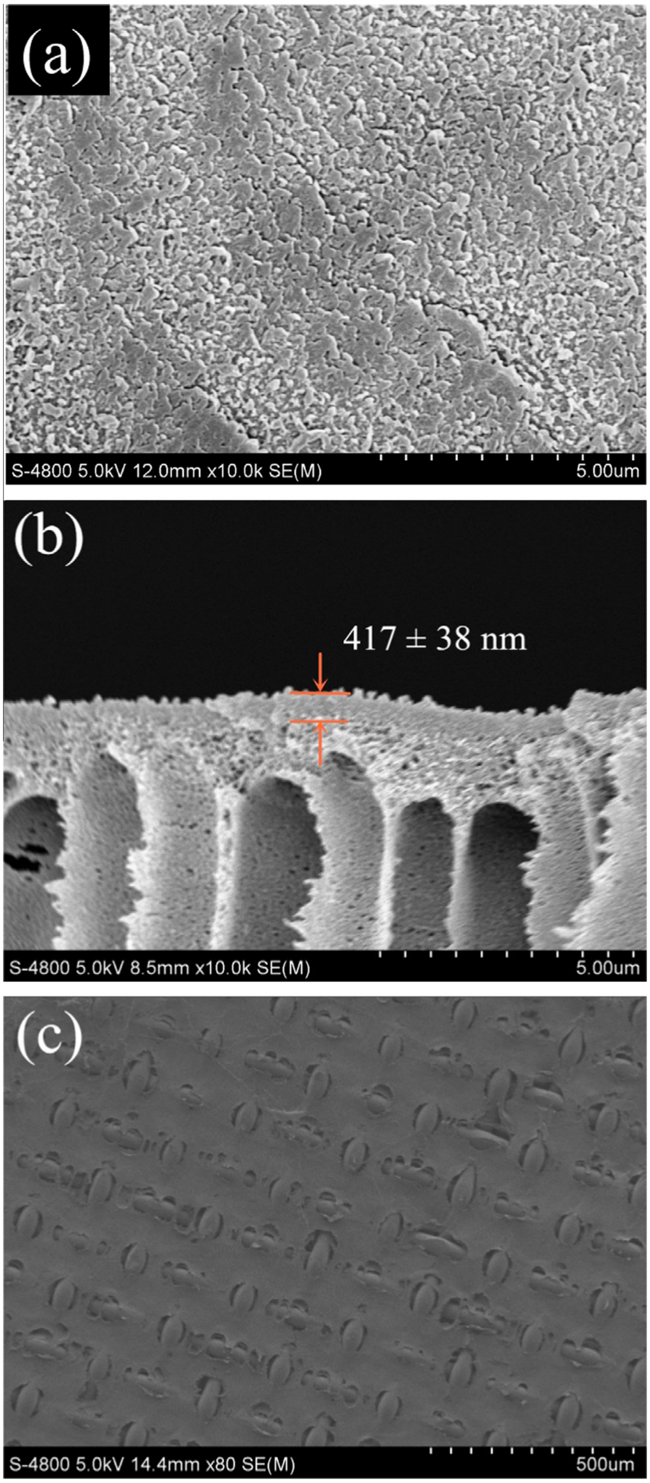


Fig. 2. SEM images of TFC membrane (a) active layer surface of the membrane, (b) cross-sectional SEM image of the membrane with a polyamide active layer (thickness of 417 ± 38 nm), and (c) bottom view of the support layer.

Table 2 listed the main transport properties of the TFC membrane. The mass transfer in two modes was evaluated with baseline tests, in which 2 M NaCl and DI water were used as draw solution and feed solution. The water flux and reverse salt flux in PRO mode were remarkably higher than that in FO mode, which mainly was attributed to the dilutive ICP in FO mode had a more significant effect on the effective osmotic pressure across the active layer than the concentrative ICP in the PRO mode [28]. Moreover, it was further demonstrated by the solute resistivity K values, which can characterize the ICP in FO process. As shown in Table 2, the solute resistivity K values, calculated from Eqs. (7) and (8), were 4.22×10^5 and 3.82×10^5 in FO and PRO modes, respectively. The reduction of K improved the water flux, so that the water flux in PRO mode was higher comparing to FO mode. Based on Eq. (6), a supporting layer with higher porosity and thinner thickness, as well as a solute of higher diffusion coefficient, could reduce the K.

The baseline curves in two modes were presented in Fig. 3. The sharp flux decline of baseline in PRO was contrast to the comparatively stable baseline flux in FO mode. Due to the diluted draw solution, the effective osmotic pressure for water flux kept decreasing and the large water flux would result in more reduced osmotic pressure. Therefore, the progressive decline of osmotic pressure coupled with the ICP caused the sharp flux baseline in PRO (Fig. 3). The results of baseline tests indicated that the membrane orientation significantly influenced the mass transport properties in FO process, which could be critical to the efficiency of TC separation.

3.2. Behavior and performance of TFC membrane for TC separation

3.2.1. Membrane orientation

The effect of membrane orientation on FO process for TC separation was demonstrated in Fig. 3. Under identical experiment concentrations, FO mode conducted significantly better for TC separation compared to the alternative mode. It was found the ini-

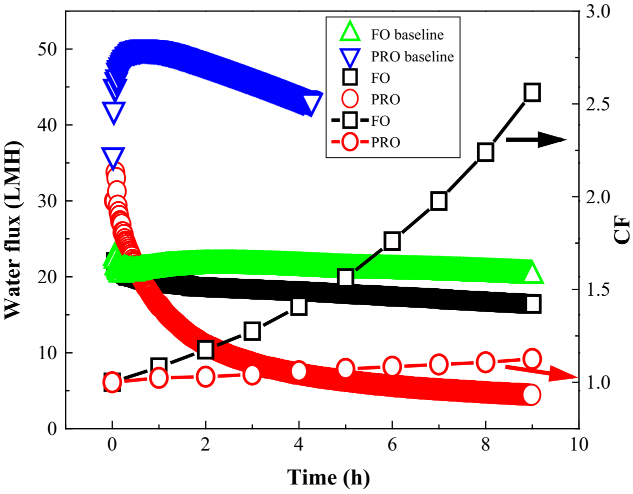


Fig. 3. Effect of membrane orientation on tetracycline (TC) separation. Experimental conditions: feed solution = 1000 mg/L TC; draw solution = 2 M NaCl; DI water used for baseline tests; CF: TC concentration factor; FO mode: active layer facing feed solution; PRO mode: active layer facing draw solution.

tial water flux of TC separation in PRO mode (about 30 LMH) was higher than that in FO mode (about 22 LMH). However, the water flux in PRO mode reduced drastically and became lower than that in FO mode after one hour. About 70% of water flux loss was observed in PRO mode during 9 h experiment, while a comparable slight flux decline was observed in FO mode (Fig. 3). The rapid flux decline in PRO mode indicated that the TC-induced membrane fouling was severer by contrast with FO mode. Such membrane fouling was dependent on the hydrodynamic conditions. The dominating hydrodynamic conditions controlling membrane fouling, such as permeation drag and hydrodynamic shear stress, were different when two membrane orientations were provided [31].

In the PRO mode, the TC molecules were dragged into the porous structure of support layer by the permeation drag. However, the influence of hydrodynamic shear stress was absent due to the cross-flow velocity vanishing within the porous support layer in PRO mode [31]. The high concentration of TC coupled with the larger hydrate solute sizes and lower diffusion coefficient of TC, resulting in the severe ICP in the porous structure. When the concentration on the membrane-feed interface was beyond the TC saturation concentration, the crystallization appeared. As illustrated in Fig. 4a, in FO mode, the TC crystals deposited on the surface of active layer. In contrast, in PRO mode, with the porous supporting layer against TC solution, we did not found obvious TC accumulation on the surface of supporting layer (Fig. 4b). However, it was clearly observed that TC crystals were deposited within the porous structure of the supporting layer (Fig. 4c), which led to the severe pore clogging. More importantly, the ICP mechanism, based on Eq. (6), was enhanced by reduced porosity and mass transfer coefficient resulted from the pore clogging. This phenomenon was responsible for drastic flux reduction in PRO configure.

The smoother and denser surface of the active layer could improve the hydrodynamic shear stress near the membrane surface and reduce the TC accumulation on the membrane. Therefore, compared to PRO mode, remarkable stability of water flux was observed in FO mode, even though there was lower initial water flux (Fig. 3). This observation was in good agreement earlier studies on application of FO for wastewater treatment [19,32].

The TC concentration factor (CF) in both modes against 2 M NaCl as a function of experiment time was also captured in Fig. 3. The CF behavior was corresponding to the water flux, the higher the water flux, the higher CF. The final CF of 2.6 in FO mode implied that 1000 mg/L TC feed solution could be concentrated to about 2600 mg/L, and the highly concentrated TC could be recovered by conventional crystallization [8]. In addition, it is worth noting that the rejection to TC was 99.3% in FO mode in contrast to 98.1% in PRO mode. The poorer rejection in PRO may owe to more severe ICP that could increase the diffusive driving force of TC from the porous support layer into the draw solution. A comparison of the performance in FO and PRO modes suggested that the FO mode was more suitable for TC separation in terms of transport stability and membrane fouling. So the following experiments were conducted in FO mode.

3.2.2. Feed flow velocity

The influence of flow velocity on TC separation in FO mode was demonstrated in Fig. 5. These experiments were conducted under the laminar flow with different flow velocities from 4.17 cm/s (*Re* of 177) to 16.67 cm/s (*Re* of 709) provided by flow rates from 200 mL/min to 800 mL/min. Results in Fig. 5a illustrated that flux decline was alleviated when higher velocities (i.e., larger *Re* Numbers) were employed. This was mainly ascribed to the lower fouling tendency of TC crystals accumulating on the membrane surface under the higher shear stress. On the other hand, with the increasing *Re* Numbers, the mass transfer coefficient k, increased according to Eqs. (9) and (10), and hence the ECP at the feed-membrane interface was reduced, ultimately leading to the increasing water flux.

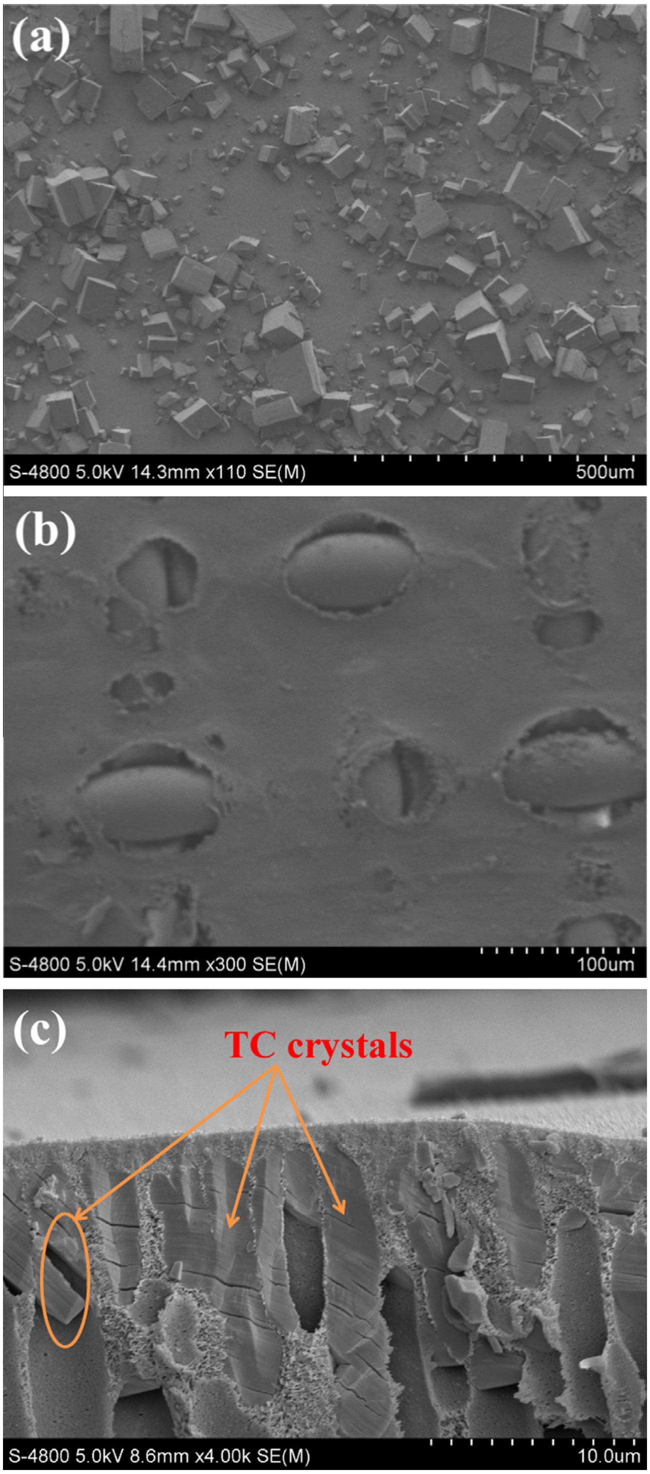


Fig. 4. SEM images of TFC membranes after experiments (a) active layer surface of the membrane in FO mode, (b) the bottom of support layer in PRO mode, and (c) cross-sectional image of the membrane with porous support layer in PRO mode. The arrows were used to point out the TC crystals in the pore.

Guided by the black dashed line drawn in Fig. 5a, it is found that the water flux under all different flow velocities performed similar trends against time. Two stages were presented in the flux pattern curve: the flux dropped to about 80% of its initial value in the first 2–3 h, followed by a relatively mild decline. The first stage decline

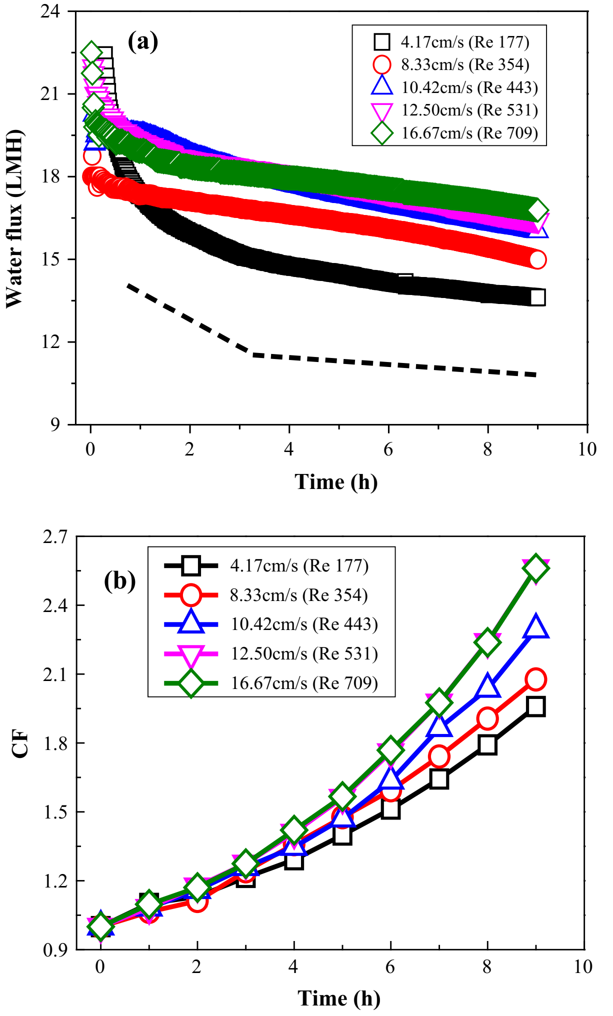


Fig. 5. Effect of flow velocity on (a) water flux, and (b) TC concentration factor. Dashed line in Fig. 5a was used to describe the water flux decline trend. Experimental conditions: draw solution = 2 M NaCl, feed solution = 1000 mg/L TC, FO mode.

was mainly due to the membrane fouling caused by the rapid deposition of TC on active layer. Since fouling cake layer was gradually formed at the end of the first stage, the flux decline of the later stage became milder. The diluted ICP in the porous support layer and the diluted draw solution mainly contributed to the flux decline in the second stage.

Nevertheless, the effect of feed flow velocities was more prominent at lower feed flow velocities (4.17 cm/s to 10.42 cm/s), while the water flux did not vary significantly at higher velocities (10.42 cm/s to 16.67 cm/s). It was probably because once the fouling cake layer formed, the fouling was less sensitive to further changes in hydrodynamic conditions [31,33].

It was worthy to note that all the rejections of TC at different velocities were more than 99%, indicating that the rejection was not affected by the changes of flow velocities in this study. Unlike the rejection, the concentration factor (CF) of TC at different velocities corresponded with the behavior of water flux (Fig. 5b). The main trend in CF was increasing from 1.9 to 2.6 with the higher velocities employed; however, there was scarcely any difference between the velocities of 12.50 cm/s and 16.67 cm/s. Both behaviors of water flux and CF demonstrated that the separation efficiency of TC was likely to reach a plateau with increasing feed flow velocity. Therefore, the additional benefits would not be derived at higher flow velocities after the plateau, but rather input energy be needed.

3.2.3. pH value

The results for TC separation at three different pH values (pH 3.05, 5.37, and 7.93) were displayed in Fig. 6. There were remarkable changes in water flux and CF under different pH values, which was related to different species of TC in the various pH ranges. TC has three pK_a values of 3.3, 7.7 and 9.3, respectively [34]. It may exist predominantly as a cation below pH 3.3 resulted from the protonated dimethylammonium group (pK_{a3}); as a zwitterions between pH 3.3 and 7.7 due to the deprotonated phenolic diketone moiety (pK_{a2}); as an anion because of the deprotonated tricarbonyl system (pK_{a1}) and phenolic diketone moiety (pK_{a2}) above pH 7.7 [34]. In addition, the polyamide active layer surface of FO membrane presented highly negatively charged as the dissociation of free or uncross-linked carboxylic groups above approximately pH 4.5, and it would become more negatively with pH value increasing [35,36]. Fig. 7 depicted the speciations of active layer of membrane and TC under different pH values at the beginning of tests.

Hence, based on Fig. 7, the electrostatic repulsion between TC anion and the negatively charged surface of TFC membrane probably was the major reason for the higher water flux at pH 7.93 than that at pH 3.05 during the initial five hours in Fig. 6. However, the decline of water flux was faster at pH 7.93 than that at pH 3.05 during the last four hours, which may be elucidated by the higher octanol/water partition coefficients (K_{ow}) of TC in alkaline environment. The higher K_{ow} indicated the TC was less hydrophilic, which was reflected by its lower water solubility [37,38]. The TC crystallization would accelerate with the reduced water solubility at pH 7.93, thereby promoting the membrane fouling and causing less water flux.

It was important noting TC was almost neutral as a zwitterion at about pH 5.5, where the TC solubility was the lowest [38]. Thus the TC dissolved partly when 1000 mg/L feed solution was prepared at pH 5.37. As shown in Fig. 7b, at the beginning of experiment, the undissolved TC particles immediately deposited on the membrane surface as a result of electrostatic adsorption, thereby leading to the fouling of active layer surface. As a result, a sharp reduce in water flux, about 75%, was observed at pH 5.37 (Fig. 6). Moreover, since the solution was always saturated, the CF curve as function of time at pH 5.73 paralleled to time.

The CF curves at pH 3.05 and 7.93 were also compared in Fig. 6. The CF at pH 3.05 was higher than that at pH 7.93, which corre-

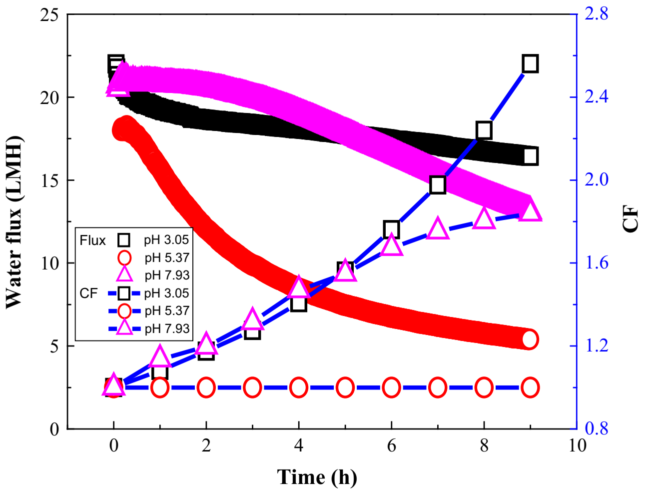


Fig. 6. Effect of pH on Tetracycline separation. Experimental conditions: draw solution = 2 M NaCl, feed solution = 1000 mg/L TC, FO mode.

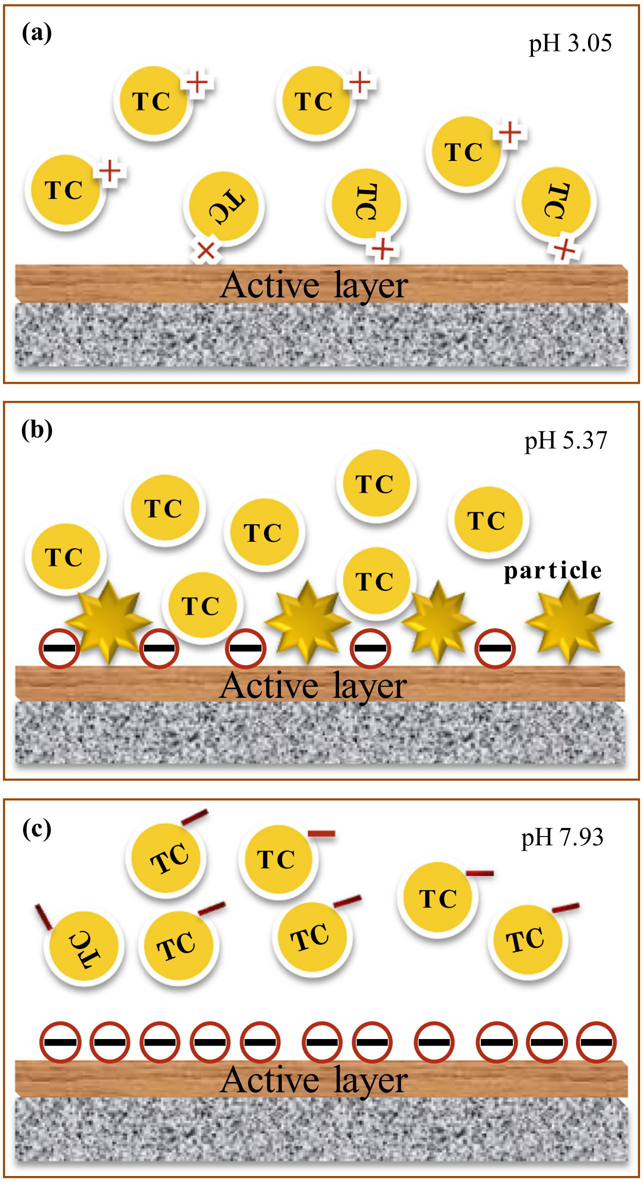


Fig. 7. Speciation of TC and membrane active layer under different pH. TC existed predominantly as (a) cation at pH 3.05, (b) zwitterion at pH 5.37 and (c) anion at pH 7.93. The active layer is more negatively charged at pH 7.93 than at pH 5.37, and TC could not dissolved completely at pH 5.37, resulting the TC particles absorbed on the active layer surface.

sponded to the changes of water flux. The rejection of TC was 99.3%, 99.3% and 99.8% at pH 3.05, 5.73, and 7.93, respectively. The rejection at pH 7.93 was a little higher than that at other pH, which may be ascribed to the electrostatic repulsion between the increasingly negatively charged membrane surface and TC. Consequently, the highly acidic environment was in favor of the TC recoverable separation, while membrane fouling was more subject to the neutral TC speciation at pH 5.73.

3.3. Long-term FO mode operation for TC separation

To investigate the behavior and performance of TFC membrane for TC separation in a long-term FO mode operation, cyclic process study with TC solution against 2 M NaCl was conducted. At the end of every testing, both the concentrated TC solution and diluted draw solution were replaced with deionized water that was recirculated for approximately 40 min to clean the membrane. At the beginning of next cycle, the draw and feed solutions were replaced with fresh ones, and every cycle underwent 9 h.

The water flux, TC rejection and CF in the cyclic process were studied, and the obtained results were shown in Fig. 8. The average water flux in Fig. 8a presented a moderated decline trend; about 26% flux reduction occurred from 18.6 LMH (cycle 1) to 13.7 LMH (cycle 5). In other words, 74% water flux could be retained after 5 cycles by deionized water cleaning. This result indicated that simple hydraulic cleaning could remove most cake layer of foulants that deposited on the surface of the membrane. Note, however, that the most part of flux reduction took place from cycle 1 to cycle 3, while the flux reduction from cycle 3 to cycle 5 was very slight. This was probably ascribed to that some TC crystals were not removed by the hydraulic cleaning, inducing the irreversible fouling which was likely to be stabilized at the end of cycle 4. So that, when irreversible fouling formed, the reduction of water flux could be milder after the reversible fouling was removed by backwash.

A slight decline of TC rejection from cycle 1 to cycle 5 was observed (Fig. 8a). The TC rejection could attain about 97.3% after four cycles, exhibiting usability of the TFC FO membrane. Consequently, the cyclic test demonstrated comparatively stable water flux and high TC rejection of the membrane could be maintained by simple hydraulic cleaning. However, a decrease of TC CF was

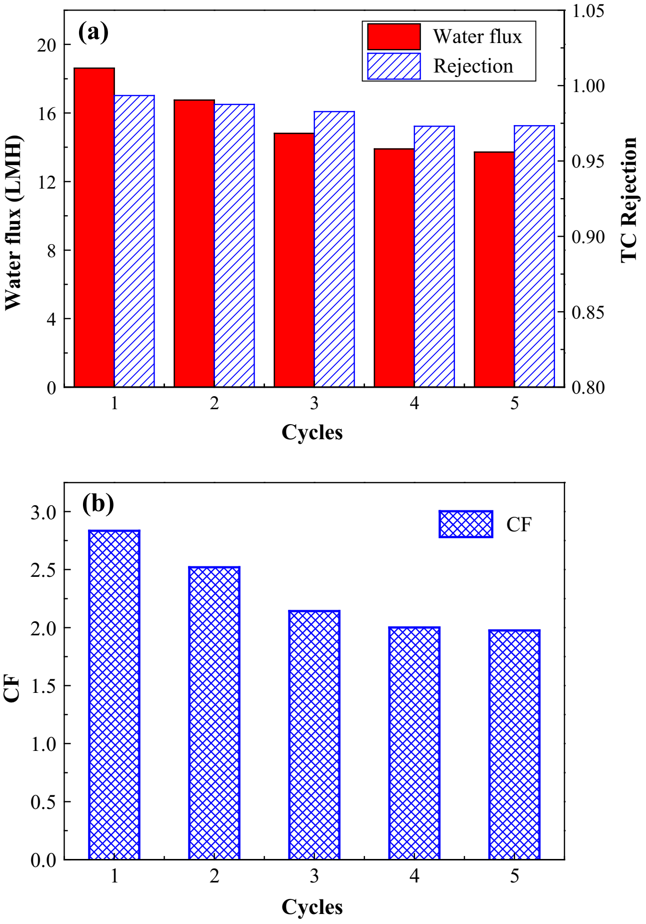


Fig. 8. (a) Water flux and TC rejection, (b) TC CF in the cyclic process. At the end of each cycle, hydraulic cleaning process was applied with deionized water for 40 min. Experimental conditions: draw solution = 2 M NaCl, feed solution = 1000 mg/L TC, FO mode.

observed due to the reduced water flux (Fig. 8b), and the TC CF needed to be further improved for the last two cycles. This indicated that longer cleaning time or other cleaning methods should be employed when the FO mode separation conducted for a much longer period.

Despite low energy consumption and low membrane fouling tendency, however, FO still faces the challenge of draw solution regeneration [39]. In order to regenerate the draw solution, FO needs to integrate with other membrane processes, such as MD or RO. The FO–MD hybrid process has been demonstrated to be an effective way for wastewater treatment and water recovery [19,21,22]. Thus, MD could be suitable to recover the draw solution and extract clean water from the antibiotic wastewater. Though such an evaluation is beyond the scope of this study, we will investigate the use of hybrid FO–MD, and evaluate the treatment efficiency in the future.

4. Conclusions

In summary, this work demonstrated that FO process was highly effective for the recoverable separation of tetracycline from pharmaceutical wastewater, and revealed that: (1) The membrane orientation played an important role in determining the water flux and concentration factor; FO mode was more suitable for the treatment of TC wastewater, and more severe fouling and ICP occurred in PRO mode. (2) As feed velocity raised, the shear stress and k value increased, which alleviated the membrane fouling; (3) The solution pH significantly influenced the water flux and membrane fouling due to the change of TC speciation and TFC membrane properties. Acidic condition enhanced the separation efficiency. (4) The TC rejection and water flux could be maintained with simple hydraulic cleaning in FO operation mode. More works, such as hybrid of FO–MD systems, should be conducted to study the regeneration of draw solution and the recovery of antibiotics.

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