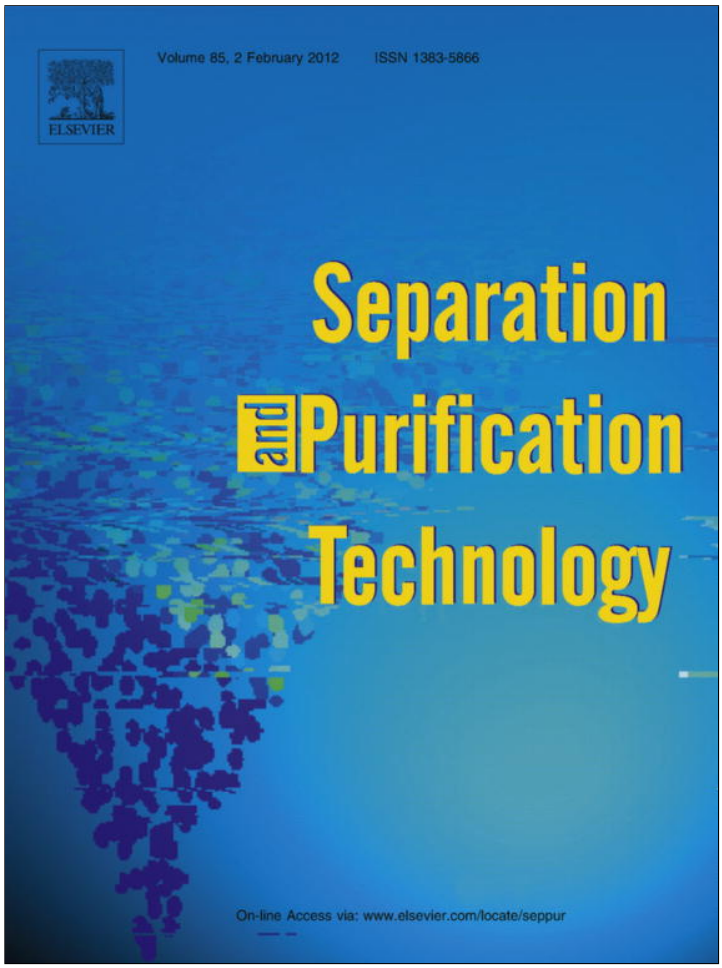


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# Rejection of pharmaceutically active compounds by forward osmosis: Role of solution pH and membrane orientation

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ABSTRACT

The effects of feed solution pH and membrane orientation on water flux and the rejection of carbamazepine and sulfamethoxazole were investigated using a bench scale forward osmosis (FO) system. Water flux was pH-dependent in both membrane orientations. In addition, water flux increased while the specific reverse salt flux and hydrogen ion flux decreased with increasing feed solution pH. Water flux was lower in the normal FO mode compared to that in the pressure retarded osmosis (PRO) mode because osmotic pressure differential was reduced due to the internal concentration polarisation (ICP) phenomenon. The rejection of neutral carbamazepine was generally pH independent in both membrane orientations. The rejection of carbamazepine in the PRO mode was lower than that in the FO mode due to the higher concentration gradient caused by concentrative ICP in porous supporting layer. Steric hindrance was probably the main separation mechanism for the neutral carbamazepine in the FO process. On the other hand, the rejection of sulfamethoxazole was significantly affected by the feed solution pH in both membrane orientations. Variation in the rejection sulfamethoxazole could be attributed to the electrostatic repulsion between the negatively charged FO membrane surface and varying effective charge of the sulfamethoxazole molecule.



## 1. Introduction

The last two decades have seen the shortage of drinking water supply further exacerbated due to population growth, irregular weather patterns as a result of climate change, and environmental contamination [1,2]. At the same time, trace organic contaminants of anthropogenic origin have also emerged. These trace organic contaminants have been frequently detected at trace level ranging from a few nanogram per litre (ng/L) to several microgram per litre (μg/L) in sewage, effluent from sewage treatment plants, water bodies, and in some cases, even drinking water [3–6]. Some of these contaminants are pharmaceutically active or can potentially induce a range of adverse endocrine disrupting effects on vertebrates at environmentally relevant concentrations (i.e., several ng/L). Not surprisingly, many dedicated studies have been focused on the use of advanced water treatment technologies for effective removal these trace organic contaminants, thus allowing for the utilisation of non-conventional water sources such as treated effluent. Around the world, a number of water reclamation facilities have been built to provide a supplementary source of water supply [7,8]. In many countries including the USA, Singapore, and several European states, water recycling has been shown to be a successful strategy to ensure the replenishment of catchment or reservoir for potable water supply and reduce dependency on sources vulnerable to climate change [1,8,9]. Examples of advanced treatment technologies widely used in water recycling applications to ensure sufficient removal of trace organic contaminants include nanofiltration or reverse osmosis, and ultraviolet radiation [8,10]. Although these advanced treatment processes demonstrate efficient removal of a wide range of trace organic contaminants from impaired water resources, they can be energy intensive. As a result, several new treatment technologies have been proposed and investigated in recent years.

Forward osmosis (FO) is one such emerging water treatment technology. FO utilises an osmotic pressure differential to drive the permeation of clean water across the membrane into the draw solution [11]. FO is highly attractive for water treatment due to its low fouling propensity [12], simple configuration, and low energy consumption [13,14]. Consequently, a number of investigations have focused on the use of FO in wastewater treatment. The effectiveness of FO has been demonstrated by the treatment of landfill leachate [15], anaerobic digester concentrate [16], activated sludge solution [17,18], and domestic wastewater [19]. In most cases, FO is used as an advanced pre-treatment technique in conjunction with a draw solution recovery process, such as reverse osmosis (RO) and membrane distillation (MD). In a recent study, Cath

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et al. [20] proposed such a hybrid FO–RO system to combine wastewater reclamation and seawater desalination. In this hybrid system, treated effluent with low osmotic pressure (low salinity) is first treated by an FO membrane and clean water is drawn into a seawater draw solution. The diluted draw solution is subsequently desalinated by RO to produce fresh water suitable for beneficial uses. In another study, Wang et al. [21] demonstrated a hybrid FO–MD system to treat highly viscous protein solution where FO is employed for dewatering protein solutions while MD is used for draw solution recovery. These hybrid systems are capable of providing a dual-barrier treatment against trace organic contaminants and largely reducing the treatment burden of downstream processes. In addition, because FO has very low fouling propensity, these hybrid systems can be used to treat feed water of low quality. Hancock et al. [22] recently conducted a life cycle assessment exercise to compare the environmental impact of the FO–RO dual-barrier concept and RO technology for seawater desalination application. They reported that, if the full technical potential of FO technology can be realised, the environment impact of an FO–RO hybrid system is 25% less than that of the current state-of-the-art RO process [22]. It is noteworthy that a draw solution recovery process is not required in all cases. When the draw solute can add value to the extracted water, the diluted draw solution can be directly consumed without any further treatment [23]. Examples of these applications include several FO water purification products (such as X-pack, Life Pack, Expedition, and Hydro-Well) that are commercially available from Hydration Technology Innovations (www.htiwater.com) and even the extraction of water from urine for direct consumption by astronauts during their space mission [24]. In these applications, it is essential that trace organic contaminants are effectively removed by the FO process.

Little is known about the removal behaviours of trace organic contaminants during the FO process. Cartinella et al. [25] demonstrated that FO can completely remove the steroid hormones estrone and estradiol. Cath et al. [20] investigated the removal of diclofenac, gemfibrozil, naproxen and salicylic acid by an FO membrane and reported rejection values of 99%, 80%, 90% and 72%, respectively. Similar rejection of 13 trace organic contaminants by FO membrane was observed as well [26]. Hancock et al. [27] revealed significant variation in the rejection of trace organic contaminants by the FO process in the range from 40% (tris-(2-carboxyethyl)-phosphine (TCEP)) to more than 95% (sulfamethoxazole) when they examined the separation of 30 compounds using a bench scale FO system. Given the similarity between the molecular weight of TCEP (250 g/mol) and sulfamethoxazole (253 g/mol), the underlying reasons for their significantly different rejection behaviours remain largely unknown. In addition, because mass transfer in the FO process is driven exclusively by a chemical concentration gradient, the transport mechanisms of the FO and pressure driven filtration processes such as NF and RO may not be the same. In fact, Xie et al. [28] has demonstrated that at the same permeate flux, rejection of some hydrophobic trace organics under the FO mode was higher than that under the RO mode. The authors attributed this observation to the retarded forward diffusion phenomenon that could occur in the FO process at high draw solute flux.

The FO membrane can be operated in two different configurations, namely the normal FO mode and pressure retarded osmosis (PRO) mode. The former refers to a configuration in which the active layer of the FO membrane is placed against the feed solution, while the latter refers to a configuration in which the active layer of the FO membrane is placed against the draw solution. Jin et al. [29] through a modelling study showed that the boron flux in the PRO mode was higher than that in the FO mode. Mi and Elimelech [30] experimentally demonstrated that membrane fouling was more severe in the PRO mode than that in the FO mode. Tang et al. [31] have subsequently reported similar observations. However, there remains a lack of systematic and mechanistic understanding of the rejection of trace organic contaminants by FO in the two membrane orientations. Such understanding is essential for further development of the FO technology, especially when it is used to purify water contaminated with trace organics.

In this study, we examined the water flux behaviour and rejection of two PhACs – namely sulfamethoxazole and carbamazepine – by an FO membrane. The water flux, reverse salt flux, and hydrogen ion flux were systematically related to the surface charge and hydrophobicity of the membrane at different feed solution pH and two membrane orientations. Experimental results were analysed to elucidate the effects of solution pH and membrane orientation on water flux and PhACs rejection, thus providing further insight into the rejection mechanisms of trace organic contaminants by FO membrane.

## 2. Materials and methods

### 2.1. FO membrane

An asymmetric FO membrane acquired from Hydration Technology Innovations (HTI, Albany, OR) was used in this investigation. According to the manufacturer, the operational pH range of this membrane is from pH 3.5 to 7.5. This membrane exhibited comparably lower water permeability and higher salt rejection than a typical commercial NF membrane. Although the actual composition of the membrane is proprietary information, it has been suggested that the membrane has a dense cellulose-based active layer embedded in polyester mesh providing mechanical support. A detailed description of the membrane is provided elsewhere [11].

### 2.2. Laboratory scale FO system

FO experiments were conducted using a closed-loop bench-scale flat plate FO membrane system (Supplementary Data, Fig. S1). The membrane cell was made of acrylic plastic. The dimensions of the channels were 13 cm long, 9.5 cm wide, and 0.2 cm deep. The total effective membrane area for mass transfer was 123.5 $cm^2$.

Two variable speed gear pumps (Micropump, Vancouver, WA) were used to circulate the feed and draw solutions. Flow rates of the feed and draw solution flow were monitored using two rotameters and kept constant at 1 L/min (corresponding to a cross flow velocity of 9 cm/s). The draw solution reservoir was placed on a digital balance (Mettler Toledo Inc., Hightstown, NJ) and weight changes were recorded by a computer to calculate the permeate flux. The conductivity of the draw solution was continuously measured using a cell constant of $K = 1\ cm^{-1}$ conductivity probe (Cole-Parmer, Vernon Hills, Illinois). To maintain constant draw solution concentration, a peristaltic pump was regulated by a conductivity controller to intermittently dose a small volume of a high concentration draw solution (6 M) into the draw solution reservoir (control accuracy ±0.1 mS/cm). The concentrated draw solution makeup reservoir was also placed on the same digital balance. The transfer of liquid between the two reservoirs did not interfere with the measurement of permeate flux and the system could be operated with a constant osmotic pressure.

### 2.3. Experimental protocol

The feed was prepared by spiking carbamazepine and sulfamethoxazole (Sigma–Aldrich, Saint Louis, MO) into a background electrolyte solution (20 mM NaCl and 1 mM $NaHCO_3$) to generate a concentration of 250 μg/L. These background electrolytes were

selected to simulate the typical composition in the treated secondary effluent and to maintain the constant pH of the feed solution [32,33]. Either HCl (1 M) or NaOH (1 M) was used to adjust the pH value of the feed solution. Analytical grade NaCl (Fisher Scientific, Pittsburgh, PA) was used to prepare the draw solution in Milli-Q water. The volumes of the feed solution and draw solution were 4 and 1 L, respectively. Temperatures of the feed and draw solutions were kept constant at 23 ± 0.1 °C using a temperature control unit (Thermo Fisher Scientific, Waltham, MA) in all experiments. Both FO and PRO mode experiments were conducted. In the FO mode experiments, the active layer of the FO membrane was placed against the feed solution, and in the PRO mode experiments, the active layer of the FO membrane was placed against the draw solution. A new FO membrane sample was used for each experiment. Approximately 1 mL of samples from both the feed tank and draw solution tank were taken at specific intervals for HPLC analysis.

### 2.4. Contact angle measurement

Contact angle measurements were conducted using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) and employed a standard sessile drop method. FO membrane samples were submerged into a pH-adjusted electrolyte background solution (20 mM NaCl and 1 mM $NaHCO_3$) ranging from pH 3.5 to 7.5 for 10 h. After removing excess liquid, the membrane samples were fixed onto a glass slide using double-sided adhesive tape and then dried in a desiccator for at least 24 h prior to contact angle measurements. pH-adjusted Milli-Q water was used as the reference solvent for the corresponding pH-adjusted membrane sample. Ten water droplets were used on each membrane sample and contact angles on both sides of the droplet were analysed.

### 2.5. Zeta potential measurement

The zeta potential of the membrane surface was determined using a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The zeta potential of each membrane surface was calculated from the measured streaming potential using the Fairbrother-Mastin approach. All streaming potential measurements were conducted in a background electrolyte solution containing 10 mM KCl. Hydrochloric acid and potassium hydroxide were used to adjust pH by means of automatic titration. The test solution was used to flush the cell thoroughly prior to the pH adjustment for each measurement. All streaming potential measurements were performed at room temperature (approximately 22 °C), which was monitored by the temperature probe of the instrument.

### 2.6. Representative PhACs

Two pharmaceuticals, namely sulfamethoxazole and carbamazepine, were selected for this study. Their key physicochemical properties together with molecular structures are presented in Table 1. Sulfamethoxazole and carbamazepine are frequently detected in secondary treated effluent, sewage affected water bodies, and recycled water for non-potable purposes (see for example: [34,35]). They represent two different drug categories. Sulfamethoxazole is a frequently used antibiotic while carbamazepine is a widely used anti-epileptic drug. These compounds were purchased from Sigma–Aldrich (St. Louis, MO) and their reported purities were 99% or higher. The pharmaceuticals were first dissolved in pure methanol to make up stock solutions of 1 g/L. The stock solutions were stored at −18 °C and were used within one month.

### 2.7. Analytical methods

A Shimadzu HPLC system (Shimadzu, Kyoto, Japan) equipped with a Supelco Drug Discovery C-18 column (with diameter, length, and pore size of 4.6 mm, 300 mm, and 5 μm, respectively) and a UV–vis detector was used to measure the concentrations of the sulfamethoxazole and carbamazepine in the feed and draw solutions. The detection wavelength was 280 nm and sample injection volume was 50 μL [36]. The mobile phase composed of acetonitrile and Milli-Q grade deionised water buffered with 25 mM $KH_2PO_4$. Two eluents, namely, eluent A (80% acetonitrile + 20% buffer, v/v) and eluent B (20% acetonitrile + 80% buffer, v/v) were delivered at 1.0 mL/min through the column in time-dependent gradient proportions for 20 min. The detailed eluent gradient time program is provided in the Supplementary Data, Table S1. Calibration generally yielded standard curves with coefficients of determination ($R^2$) greater than 0.99 within the range of experimental concentrations used. The analysis was carried out immediately upon the conclusion of each experiment. A sample injection volume of 50 μL was used considering the salt tolerance of C18 column. The quantification limit for all the analytes under investigation using these conditions was approximately 10 μg/L.

Conductivity and pH of the feed and draw solutions were measured using an Orion 4-Star Plus pH/conductivity metre (Thermo Fisher Scientific, Waltham, MA).

### 2.8. Rejection calculation

In a typical FO process, the permeate concentration of target solute is diluted by the draw solution. Therefore, the apparent concentration of the target solute in the draw solution overestimates the actual rejection performance. To evaluate the real performance of the FO process, the actual (corrected) concentration of the target solute, $C_{s(t)}$ can be recalculated by taking the dilution into account using mass balance:

$$C_{s(t)} = \frac{C_{ds(t)}V_{ds(t)} - C_{ds(t-1)}V_{ds(t-1)}}{V_{w(t)}} \quad (1)$$

where $V_{w(t)}$ is the permeate volume of water to the draw solution at time $t$, $V_{ds(t-1)}$ is the volume of draw solution at time ($t$-1), $V_{ds(t)}$ is the volume of draw solution at time $t$, $C_{ds(t)}$ is the measured concentration of target solute in the draw solution at time $t$, and $C_{ds(t-1)}$ is the measured concentration of target solute in the draw solution at time ($t$-1). Subsequently, the solute rejection in the FO process is calculated using the actual (corrected) permeate concentration, yielding:

$$R_{FO} = \left(1 - \frac{C_{s(t)}}{C_{f(t)}}\right)100\% \quad (2)$$

where $C_{f(t)}$ is the concentration of the target solute in the feed at $t$ time.

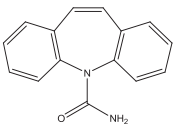
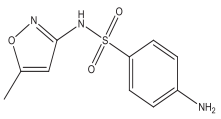
## 3. Results and discussion

### 3.1. Flux behaviour

#### 3.1.1. Permeate water flux

The asymmetric membrane can be operated in two different orientations, namely FO and PRO modes. The water flux obtained from the PRO mode was considerably higher than that in the FO mode (Fig. 1). This difference in water flux is due to the internal concentration polarisation (ICP) phenomenon which has been described in detail in several previous studies [37,38]. ICP occurs when the solute concentration within the membrane supporting layer differs from that of the bulk solution. In the FO mode, the

**Table 1**
Key physicochemical properties of PhACs used in this study.

| Pharmaceutical | Carbamazepine | Sulfamethoxazole |
|---|---|---|
| Structure |  |  |
| Molecular weight (Da) | 236.3 | 253.3 |
| $pK_a$[a] | 9.73 | 1.7, 5.8 |
| Log $K_{ow}$[a] | 2.45 | 0.89 |
| Dipole moment (Debye)[b] | 3.6 | 5.4 |
| Stokes radius (nm) | 0.37 | 0.38 |
| Molecular length (nm)[b] | 0.891 | 1.031 |
| Molecular width (nm)[b] | 0.529 | 0.587 |
| Molecular depth (nm)[b] | 0.507 | 0.526 |

[a] From the SciFinder Scholar (ACS) database.
[b] Molecular dimension and the dipole moment were calculated using Molecular Modelling Pro Version 6.3.3 (Chem SW Inc.).

draw solution inside the porous supporting layer becomes diluted as water permeates from the feed through the active layer into the protective confines of the membrane supporting structure. In the PRO mode, the feed solute is concentrated within the porous supporting layer, thus reducing the overall osmotic gradient across the membrane. McCutcheon and Elimelech [38] referred to these two phenomena as dilutive and concentrative ICP, respectively. Because the osmotic pressure of the feed solution was much smaller than that of the draw solution, the dilutive ICP in the FO mode is more pronounced than concentrative ICP in the PRO mode, which substantially reduces the effective osmotic driving force for water flux. While the ICP phenomenon may not impact the osmotic pressure at the feed side in the PRO mode, it can lead to the build-up of PhACs within the supporting layer of the membrane at the feed side, thus influencing the rejection of the PhACs. Effects of the ICP phenomenon on the rejection of sulfamethoxazole and carbamazepine will be discussed in detail in section 3.2.

Water flux was a function of the feed solution pH in both orientations (Fig. 1). The water flux increased by 27.6% and 7.5% in the FO and PRO modes, respectively, as the feed solution pH increased from 3.5 to 7.5. This behaviour may be attributed to conformational changes of the cross-linked membrane polymer structure and changes in the membrane hydrophobicity as a function of the solution pH. These two possible mechanisms can be elucidated by membrane surface charge characteristics, especially the zeta potential profiles of the active layer (Fig. 1a) and supporting layer (Fig. 1b) as well as the hydrophobicity (Table 2) of the FO membrane. It is hypothesised that the electrostatic repulsion between ionisable functional groups of the membrane polymeric matrix increases as the solution pH increase, thereby leading to an increased average pore size and higher permeate flux. Indeed, the zeta potential of both the active layer and the supporting layer became more negatively charged with increasing feed solution pH. The results reported in Fig. 1 are also in good agreement with the pH-dependent water flux response in some nanofiltration processes [39,40]. It is also noted that the FO membrane surface becomes more hydrophilic through dissociation of carboxyl functional groups ($COO^-$) of the active layer as the solution pH increased (Table 2). A more hydrophilic membrane could favour water transport. In fact, this hypothesis is consistent with the correlation between hydrophobicity of FO membrane and water flux observed by McCutcheon and Elimelech [41].

**Table 2**
Contact angle of the active and supporting layers of the FO membrane at different pH values (mean ± standard deviation of ten repeated measurements).

| pH | Active layer (°) | Supporting layer (°) |
|---|---|---|
| 3.5 | 70.9 ± 3.1 | 79.7 ± 1.0 |
| 4.5 | 66.7 ± 3.6 | 75.0 ± 3.2 |
| 5.5 | 64.8 ± 2.9 | 70.8 ± 3.2 |
| 6.5 | 62.8 ± 3.9 | 71.1 ± 1.8 |
| 7.5 | 60.2 ± 3.4 | 69.7 ± 3.4 |

### 3.1.2. Reverse salt flux and hydrogen ion flux

The specific reverse salt flux ($J_s/J_w$) is a quantitative indicator for bi-directional diffusion in the FO process. Higher specific reverse salt flux reflects a decrease in the selectivity of the membrane

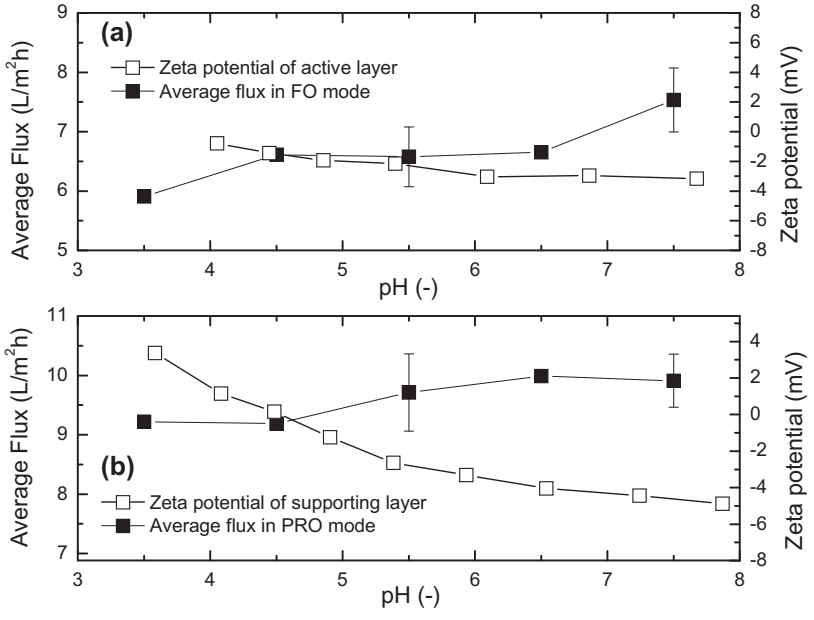



**Fig. 1.** The water flux as a function of feed pH in FO and PRO modes. Experimental conditions were: 1 M NaCl as draw solution, the cross flow rate was 1 L/min for both sides, and the cross flow velocity was 9 cm/s. The temperature of both sides was kept at 23 ± 0.1 °C. Zeta potential of active and supporting layer of the HTI FO membrane was measured with background electrolyte of 1 mM KCl. The error bar represents the standard deviation from duplicate experiments.

and the lower efficiency of the process [42]. In both the FO and PRO modes, the specific reverse salt flux decreased with increasing feed solution pH (Fig. 2). This implies that better selectivity and efficiency are expected with a basic feed solution rather than that with an acidic one. This decrease in the specific reverse salt flux is mostly driven by the increase in water flux. The water flux increases significantly at higher pH whilst the salt flux is suppressed by the more negatively charged FO membrane.

The pH of the feed solution consistently increased during the course of each experiment (Fig. 3). Due to the feed volume reduction during the FO process, the measured changes in the feed pH during the experiment may not reflect the transport of hydrogen ion. Thus, the molar flux of hydrogen ion out of the feed solution is used to describe the hydrogen ion transport. Similar feed pH variation was also observed by Hancock et al. [42] and Phuntsho et al. [43]. This pH variation can be explained by charge neutrality and concentration gradient driven diffusion. Hydrogen ion diffuses through the FO membrane to maintain feed solution electroneutrality when sodium permeates into the feed side. Therefore, higher specific reverse salt flux in the FO mode (Fig. 2) leads to the higher hydrogen ion flux. In addition, according to Fick's law, the hydrogen ion flux is directly proportional to the difference in ion concentrations across the membrane [44]. The hydrogen ion concentration gradient decreases with increasing feed pH, and thus a decreased hydrogen ion flux is expected as observed in this study.

### 3.2. Rejection of PhACs

#### 3.2.1. General behaviour

The feed solution pH and membrane orientation play key roles in the rejection of carbamazepine and sulfamethoxazole. The rejection profile of carbamazepine is relatively pH-independent, while that of sulfamethoxazole is strongly pH-dependent within the pH range of this study. The stable rejection of carbamazepine (Fig. 4a) can be ascribed to its neutral form in the pH range investigated here. In contrast, feed solution pH had a considerable effect on the rejection of sulfamethoxazole (Fig. 4b). At near neutral pH values (pH 6.5 and 7.5), the rejection of sulfamethoxazole was above 90 % and constant throughout the experiment. However, at acidic pH values (i.e., pH 3.5, 4.5, and 5.5), the rejection of sulfamethoxazole was low and decreased gradually over the first few hours of experiment. This pH-dependence behaviour resulted from the speciation of sulfamethoxazole ($pK_a$ of sulfamethoxazole = 5.8), from a neutral species at high pH to a negatively charged one at lower pH [45,46]. The initial and gradual decrease in sulfamethoxazole rejection at low pH observed in Fig. 4 may be attributed to the hydrogen ion flux from the feed to the draw solution (Fig. 3) which may result in a higher localised pH immediately at the membrane surface. Further investigation is required to fully substantiate this phenomenon.

Membrane orientation had a direct impact on the rejection profiles of the two compounds. The rejection of carbamazepine was

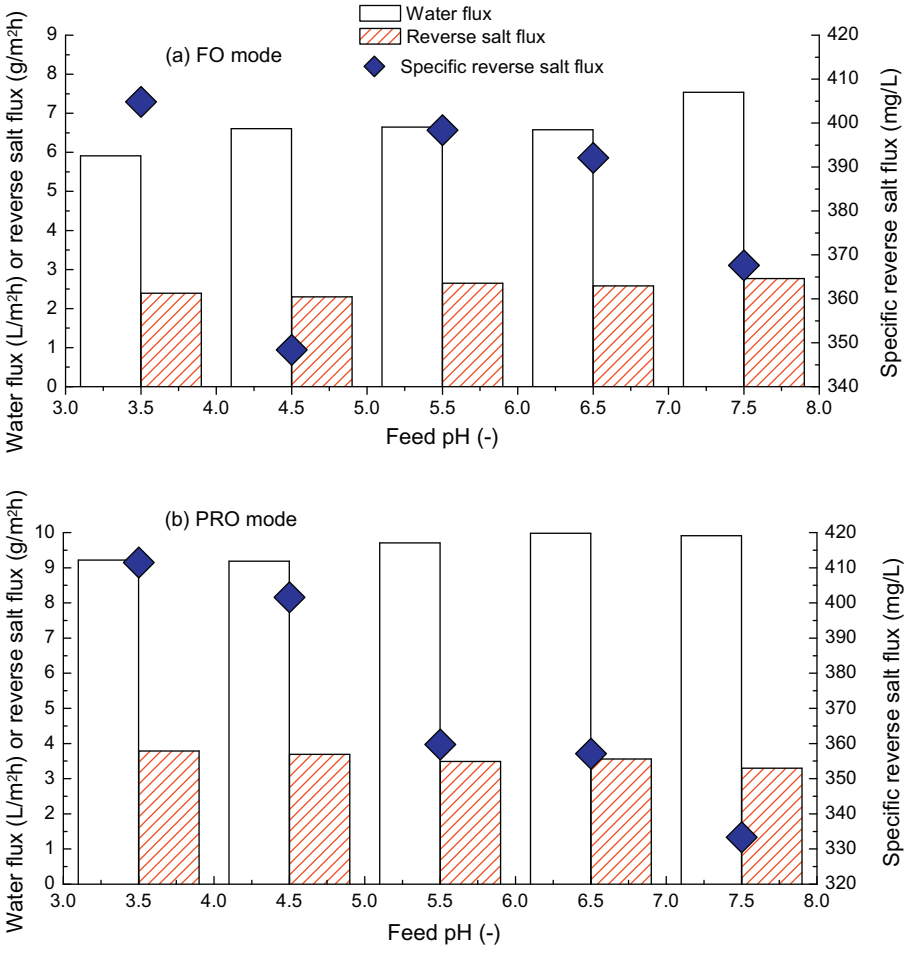



**Fig. 2.** Permeate of hydrogen ion flux from the feed as a function of initial feed pH in FO and PRO modes. Hydrogen ion flux was calculated based on the pH change of the feed at the end of a 10-hour experiment. The draw solution (1 M NaCl) pH was 6.25.

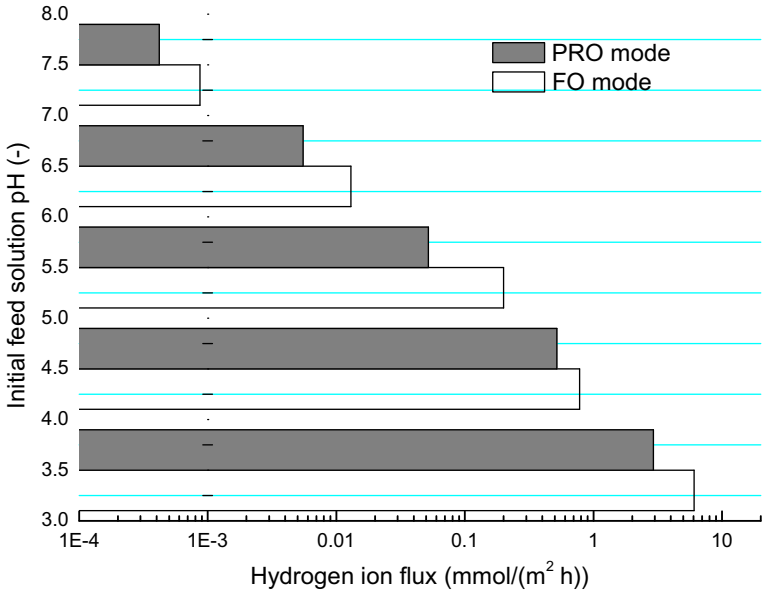



**Fig. 3.** Water, reverse salt (NaCl) and specific reverse salt fluxes in the FO and PRO modes at different feed pH values. The experimental conditions were described as in Fig. 1.

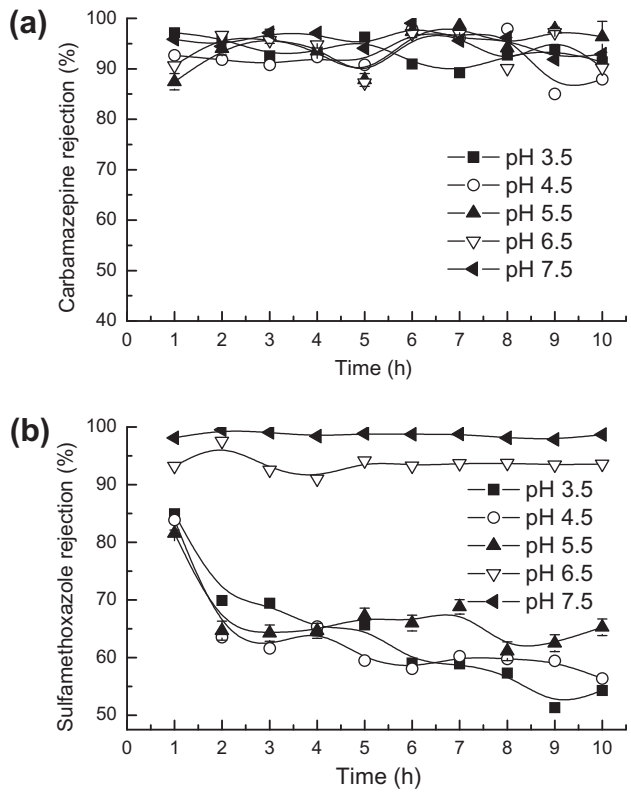



**Fig. 4.** The rejection of (a) carbamazepine, and (b) sulfamethoxazole as a function of time at different feed pH in FO mode (concentration of carbamazepine and sulfamethoxazole = 250 μg/L in the feed, the background electrolyte contained 20 mM NaCl and 1 mM $NaHCO_3$, draw solution = 1 M NaCl; cross flow velocity on either sides of the membrane = 9 cm/s; feed and draw solution temperature = 23 ± 0.1 °C). The error bar represents the standard deviation from duplicate experiments.

approximately 90% in the FO mode (Fig. 4a), while a rejection of only 70% was obtained in the PRO mode (Fig. 5a). The rejection behaviour of sulfamethoxazole was also notably different in the two membrane orientations. At unfavourable acidic pH values, more than 50% of sulfamethoxazole was removed in the FO mode (Fig. 4b), but only 20% rejection of sulfamethoxazole was found for the PRO mode (Fig. 5b).

### 3.2.2. Effect of solution pH

The feed pH appears to be a major parameter governing the rejection of sulfamethoxazole in the FO process. Results presented in Fig. 6a are consistent with the behaviour of sulfamethoxazole during nanofiltration processes [45] and may be attributed to a combination of the speciation of the compound, membrane surface charge, and feed solution pH. Carbamazepine, with p$K_a$ value of 9.73, is a neutral compound in the investigated pH range of 3.5 to 7.5. Thus, steric hindrance (and not electrostatic interaction) is the dominant rejection mechanism for carbamazepine. This hypothesis is supported by the constant rejection value of carbamazepine of approximately 90% regardless of the feed solution pH. It is noteworthy that rejection of the neutral sulfamethoxazole (at pH 3.5 and 4.5) is lower than carbamazepine (Figs. 4 and 5) while the molecular weight of sulfamethoxazole is comparable to that of carbamazepine (Table 1). This different rejection behaviour may be due to the dipole moment and molecular shape of these two compounds. In the absence of electrostatic interaction, sulfamethoxazole facilitated with a high dipole-fixed charge interaction is more likely to be attracted to the membrane pores [47]. In addition, sulfamethoxazole is cylindrical in shape with large molecular length and small molecular width and depth (Table 1). Nghiem et al. [46] have also reported lower rejection of the neutral sulfamethoxazole compared to that of carbamazepine by an NF filtration process.

On the other hand, sulfamethoxazole can dissociate from a neutral species to a negatively charged anion as the feed pH becomes increasingly more acidic below its p$K_a$ value of 5.8. The active layer of the membrane becomes more negatively charged with increasing feed pH [30]. Hence, the rejection mechanism is controlled by both steric hindrance and electrostatic repulsion between the negatively charged active layer of FO membrane and anionic sulfamethoxazole. These interactions result in a near complete rejection of sulfamethoxazole at pH values beyond its p$K_a$. It is interesting to note that the sigmoidal rejection curve of sulfamethoxazole as a function of feed pH resembles the shape of its speciation (Fig. 6c). This further suggests that electrostatic repulsion is a sig-

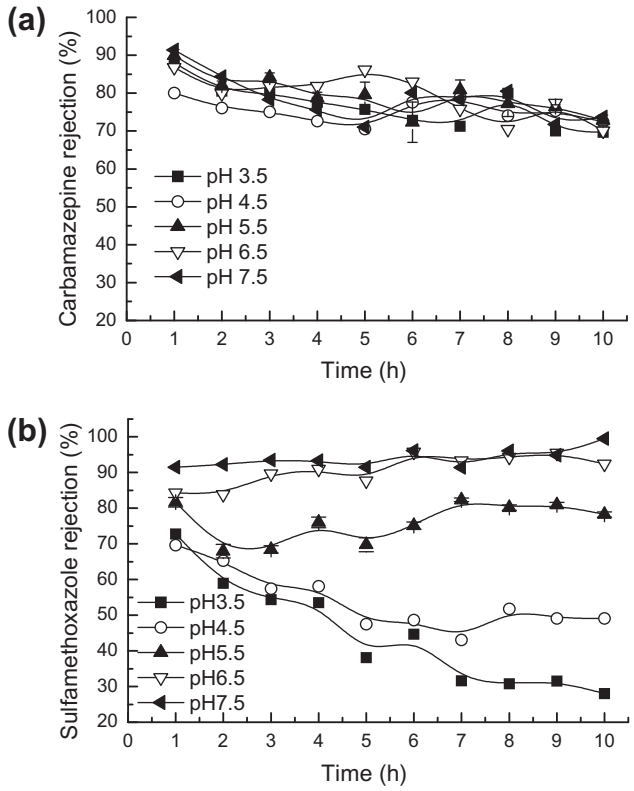



**Fig. 5.** The rejection of (a) carbamazepine, and (b) sulfamethoxazole as a function of time at different feed pH in PRO mode (experimental conditions were as per Fig. 4). The error bar represents the standard deviation from duplicate experiments.

nificant governing mechanism in the separation of sulfamethoxazole by FO membrane.

### 3.2.3. Effect of membrane orientation

Membrane orientation can exert some impact on the rejection of carbamazepine and sulfamethoxazole during the FO process. For the neutral compound carbamazepine, the rejection in the FO mode was 20% higher than that in the PRO mode (Fig. 6). The different rejection behaviour of carbamazepine in the FO and PRO modes is attributed to the ICP effect. Because the ICP phenomenon may not significantly impact the osmotic pressure gradient in the PRO mode, the effective mass transfer driving force in the PRO mode is higher than that in the FO mode. In addition, in the PRO mode, carbamazepine is subjected to the concentrative ICP within the porous supporting layer of the membrane [29] leading to a higher concentration gradient across the dense active layer of the membrane. Therefore, the ICP phenomenon can negatively affect the rejection of carbamazepine in a similar fashion to that caused by the normal concentration polarisation phenomenon. At pH 3.5 and 4.5, the rejection of sulfamethoxazole in the PRO mode was lower than that in the FO mode, but with the increase of feed solution pH, the rejection of sulfamethoxazole increased with insignificant difference in sulfamethoxazole rejection between the two membrane orientations. It is noted that the supporting layer of the membrane was more negatively charged than the active layer when the pH was above 5.5 (Fig. 1). Thus, the rejection of sulfamethoxazole was enhanced by electrostatic repulsion between the negatively charged supporting layer and the negatively charged compound. This enhanced electrostatic repulsion between the ionised sulfamethoxazole and the FO membrane could lead to the deformed sigmoidal rejection curve as observed in Fig. 6b. This

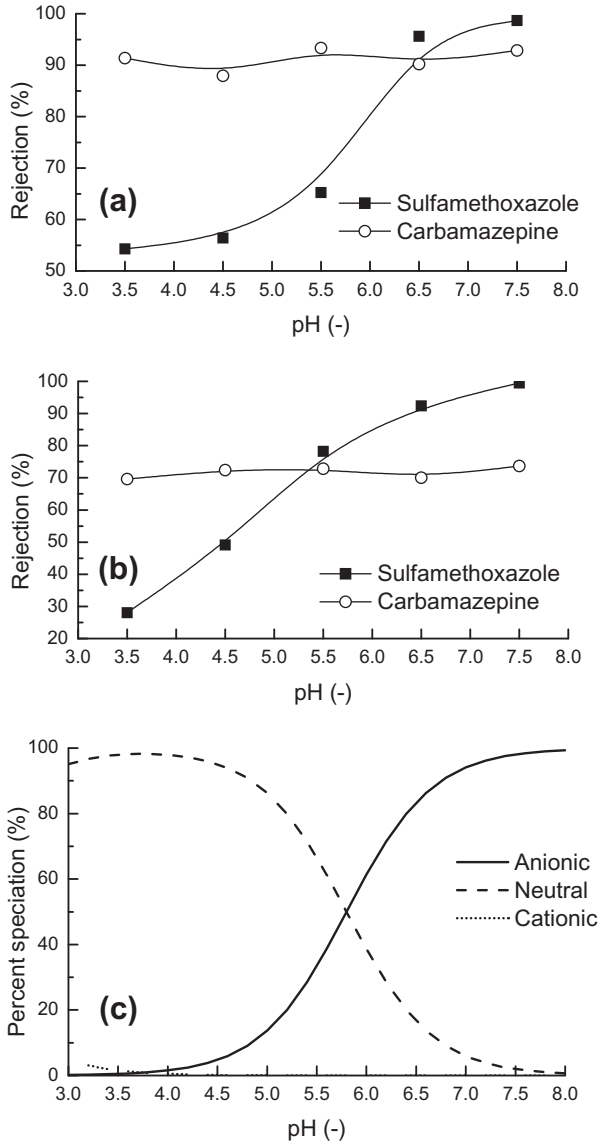



**Fig. 6.** Rejection sulfamethoxazole and carbamazepine in (a) FO mode, (b) PRO mode as a function of feed pH and (c) the speciation of sulfamethoxazole as a function of pH. The data points represented the rejection at the end of 10-h experiments (experimental conditions were as per Fig. 4).

observed enhanced rejection performance is also consistent with the decreased specific salt flux discussed in section 3.1.2.

## 4. Conclusion

In this study, we investigated the effects of membrane orientation and feed solution pH on permeate flux and rejection of carbamazepine and sulfamethoxazole by an FO membrane. The following conclusions could be drawn: (i) water flux was pH-dependent in both membrane orientations. An increase in water flux was observed with the increase of the feed solution pH, and the specific reverse salt flux and hydrogen ion flux were hindered in the basic pH range. These observations agreed well with the zeta potential measurements of the FO membrane; (ii) the feed solution pH induced different rejection behaviour for carbamazepine and sulfamethoxazole. Rejection of the neutral carbamazepine compound was independent of pH, while rejection of sulfamethoxazole was significantly affected by pH as the speciation of sulfamethox-

azole varied with pH; (iii) membrane orientation played an important role in both water flux and PhACs rejection behaviour. Due to concentrative and dilutive ICP effects, water flux was higher in the PRO mode than that with the FO mode. In the PRO mode, concentrative ICP in the porous supporting layer of the FO membrane resulted in a lower PhACs rejection value than that in the FO mode.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2012.03.030.

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