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Long Nghiem

University of Wollongong, longn@uow.edu.au

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Influence of feed water chemistry on the removal of ionisable and neutral trace organics by a loose nanofiltration membrane

Long D. Nghiem*

School of Civil, Mining & Environmental Engineering The University of Wollongong, Australia NSW 2522

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Abstract. This study examined the effects of feed water chemistry and membrane fouling on the rejection of trace organics by a loose nanofiltration membrane. One ionisable and one non-ionisable trace organics were selected for investigation. Results reported here indicate that the solution pH and ionic strength can markedly influence the removal of the ionisable trace organic compound sulfamethoxazole. These observations were explained by electrostatic interactions between the solutes and the membrane surface and by the speciation of the ionisable compound. On the other hand, no appreciable effects of solution pH and ionic strength on the rejection of the neutral compound carbamazepine were observed in this study. In addition, membrane fouling has also been shown to exert some considerable impact on the rejection of trace organics. However, the underlying mechanisms remain somewhat unclear and are subject to on-going investigation.

Keywords: nanofiltration; trace organics; operating conditions; water recycling; membrane fouling.

1. Introduction

Membrane processes such as nanofiltration (NF) and reverse osmosis (RO) play an important role in the production of high quality reclaimed water where trace organic contaminants are to be removed. Examples of water recycling schemes using NF/RO processes are quite numerous and include a diverse range of water reuse applications such as managed aquifer recharge, municipal dual-reticulation systems, as well as industrial and agricultural uses (Nghiem and Schäfer 2005). Applications of NF/RO treatment processes for indirect potable recycling (IPR) have also been demonstrated in several countries including Singapore, Belgium, and the USA (Seah, *et al.* 2003, Bixio, *et al.* 2006). The use of RO for large-scale IPR is currently under serious consideration in several Australian cities. In such schemes, the produced NF/RO filtrate is injected into either a water supply aquifer or reservoir, recaptured after a certain environmental residence time and then repurified in a drinking water production facility (Seah, *et al.* 2003, Bixio, *et al.* 2006). The satisfactory elimination of trace organic contaminants is of paramount importance for the protection of public health (Nghiem and Schäfer 2005, Dong, *et al.* 2008). It is well known that a vast number of trace organic contaminants are continuously released to sewage (Khan and Ongerth 2004). However, removal of these compounds during conventional biological sewage treatment varies greatly, ranging from almost no removal (for some compounds such as carbamazepine) to nearly complete removal

* Ph.D. E-mail: longn@uow.edu.au

(Ternes, *et al.* 2004). Membrane filtration such as NF and RO can act as a very reliable barrier for the removal of pathogenic agents and an array of inorganic contaminants (Ratanatamskul, *et al.* 1998, Thanuttamavong, *et al.* 2001). The efficiency of NF and RO processes with respect to trace organic contaminant removal has been extensively investigated (Verliefde, *et al.* 2007, Van der Bruggen, *et al.* 2006). Based on extensive literature and a large body of experimental data, Van der Bruggen, *et al.* (2006) have successfully developed a predictive framework for qualitative assessment of the rejection of trace organic contaminants by NF membranes. The framework takes into account both membrane characteristics and the properties of the trace organic contaminants. Nevertheless, apart from solution pH, this framework does not consider any other operational parameters (such as ionic strength and membrane fouling). Indeed, the understanding of the influence of operating conditions on the removal of trace contaminants during long term operation remains rather limited.

Operating conditions are essential in maintaining the performance of any membrane filtration process in both contaminant removal efficiency and water production rate. Variation in operating conditions may have considerable effects on the membrane performance in terms of flux and total dissolved solids removal. To date this particular issue has attracted a number of dedicated investigations. Most of these investigations focused on the rate of water production and have resulted in several benchmark parameters, which are widely used in the membrane industry. One of the most well known examples is the critical flux concept (Fane, *et al.* 1999, Nyström, *et al.* 2003, Bacchin, *et al.* 2005). In fact, membrane manufacturers typically associate their product warranty within a range of several acceptable operating parameters such as feed flow rate, pressure, permeate flux, and recovery. However, these criteria remain vague and broadly conservative. While the hydraulic operating condition can be manipulated and kept relatively stable by the operators, it is not possible to maintain a constant feed water composition. For example, Zhang, *et al.* (2004) reported clear effects of solution matrix on pesticide rejection when they examined atrazine and simazine rejection in distilled, tap, and river water matrices, although the precise underlying mechanisms remain unclear (Zhang, *et al.* 2004). Furthermore, membrane fouling, which is a problematic and inevitable issue in membrane filtration, can drastically alter the membrane properties and thus its separation efficiency.

The aim of this study was to investigate the effects of the operating conditions including feed water chemistry and membrane fouling on the rejection of trace organics by NF/RO processes. A very loose nanofiltration membrane was selected for this investigation in order to minimise rejection by size-exclusions and thus better observe the likely effects. Experiments were conducted with two pharmaceuticals representing the emerging trace organics commonly encountered in secondary effluent and freshwater bodies using a crossflow membrane filtration test unit. Their rejection behaviour was delineated with respect to the membrane properties, speciation of the compounds, and particularly the operating conditions (feed solution pH, ionic strength, and membrane fouling).

2. Materials and methods

2.1. Representative membrane

Flat sheet samples of a loose thin film composite NF membrane – denoted TFC-SR2 (Koch Membrane Systems, San Diego, CA) – were used in this investigation. This membrane is composed of a thin polyamide skin layer on top of a microporous polysulfone support. This membrane was selected because of its low salt and high organic matter rejection, which makes it a very desirable

Table 1 Properties of the TFC-SR2 membrane (Nghiem and Schäfer 2005)

Pure water permeability ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Average pore diameter (nm)	NaCl rejection (%)	Virgin membrane zeta potential (mV)		
			pH 4	pH 6	pH 8
15.4	1.28	9.8	-4.7	-9.8	-10.4

Table 2 Physicochemical properties of pharmaceuticals

	Sulfamethoxazole	Carbamazepine
Molecular weight (g/mol)	253.3	236.3
Molecular width ^a (nm)	0.526	0.507
Molecular height ^a (nm)	0.587	0.529
Molecular length ^a (nm)	1.031	0.891
Dissociation constant ^b	$pK_{a1} = 1.4, pK_{a2} = 5.8$	$pK_a = 2.3$

^aCalculated using ChemOffice (CambridgeSoft Corporation).

^bSciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994–2007 ACD/Labs)

membrane if desalination or hardness removal is not required. Key properties of this membrane are presented in Table 1. It was received as flat sheet samples and was stored dry at 4°C.

2.2. Chemical standards and reagents

Two common pharmaceuticals – sulfamethoxazole and carbamazepine – were selected for this study to represent polar trace organic contaminants. Their molecular weights, dimensions, and dissociation constants are presented in Table 2. The molecular length was defined as the distance between the two most distant atoms in the molecule and molecular width and height were dimensions perpendicular to the molecule longitudinal axis. These values were computed using the ChemOffice program based on the most stable configuration of the molecule. These pharmaceuticals are among the most commonly reported trace contaminants in secondary treated effluent and sewage impacted water bodies. Analytical standards were purchased from Sigma-Aldrich (Saint Louis, MO) with purity of 99% or higher. Pharmaceuticals stock solutions were prepared in pure methanol at 1 g/L. The stock solutions were stored at < 4°C and were used within 1 month. Sigma-Aldrich humic acid (St. Louis, MO) was selected as a model organic foulant for this study. This humic acid was derived from soil peat. It is readily available, well characterised, and has been widely used in membrane fouling investigations (Yuan and Zydney 2000, Tang, *et al.* 2007). This Sigma-Aldrich humic acid has an elemental composition of 60% C, 4.47% H, 34.5% O, and 0.96% N (Mao and Hu 1998). All other chemicals and reagents were of analytical grade. Sodium chloride, calcium chloride, and sodium bicarbonate were used to prepare the background electrolytes. pH adjustment was carried out with sodium hydroxide (1 M) or hydrochloric acid (1 M).

2.3. Filtration protocol

Filtration experiments were conducted with a NF/RO cross flow rig as shown in Fig. 1. In preparation for each experiment, the membrane was stabilised at 12 bar (176.4 psi) using deionised (DI) water until the permeate flux attained a constant value. The feed reservoir temperature was

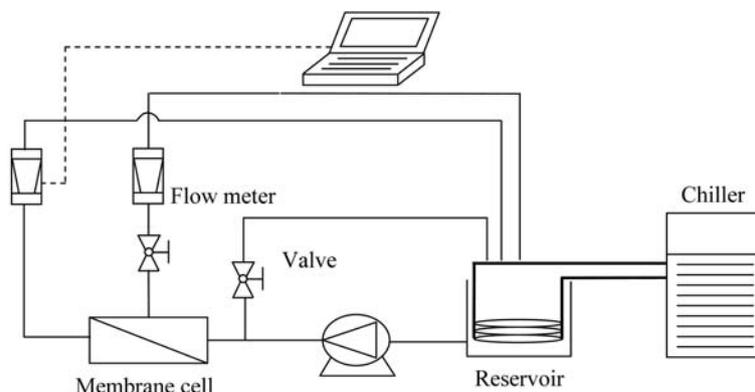


Fig. 1 Schematic diagram of the NF/RO filtration test unit

kept at $20 \pm 0.1^\circ\text{C}$ throughout the experiment. Unless otherwise stated, permeate was recycled back to the feed reservoir.

After stabilising the membrane, 7 L of electrolyte solution containing 20 mM NaCl and 1 mM NaHCO_3 was introduced to the feed reservoir. The cross flow and the permeate flux were adjusted to 30.4 cm/s and $15 \mu\text{m/s}$ ($54 \text{ L/m}^2\text{h}$), respectively. The trace contaminants were separately spiked into the feed reservoir to make up a concentration of 500 to 750 $\mu\text{g/L}$. Analysis was conducted immediately on conclusion of the experiment using an HPLC (Shimadzu, Kyoto, Japan) system. For experiments involving fouled membranes, the fouling layer was developed for 18 hours using a foulant cocktail containing 20 mM NaCl, 1 mM CaCl_2 , 1 mM NaHCO_3 and 20 mg/L of Aldrich humic acid prior to the introduction of the trace contaminants. Feed and permeate samples (1 mL each) were taken for analysis at specified time intervals. When the solution pH was varied, the system was equilibrated for at least one hour prior to sample collection.

3. Results and discussions

3.1. Speciation of trace organics

Some inorganic and organic chemicals may exist in aqueous solution in various forms (species) and the distribution of these species (or the speciation process) often strongly depends on the specific solution conditions of pH, temperature, pressure, ionic strength, and to some extent the presence of other entities in the solution (Waite 2004). Understanding the speciation process is critical since the various species may behave quite differently during membrane filtration processes due to a range of factors including size and charge, amongst other more complex physicochemical properties of the particular species. Although the effects of chemical speciation of numerous inorganics have been extensively discussed by Waite (Waite 2004), understanding of trace organic speciation influence on rejection is still limited. Species distribution can be influenced by various mechanisms such as acid-base transformation, complexation, precipitation, and oxidation-reduction. Amongst these, acid-base transformation is often the most important mechanism leading to significant changes in physical/chemical properties of trace organics during NF/RO membrane filtration processes. Acid-base transformations of sulfamethoxazole and carbamazepine are presented in Fig. 2.

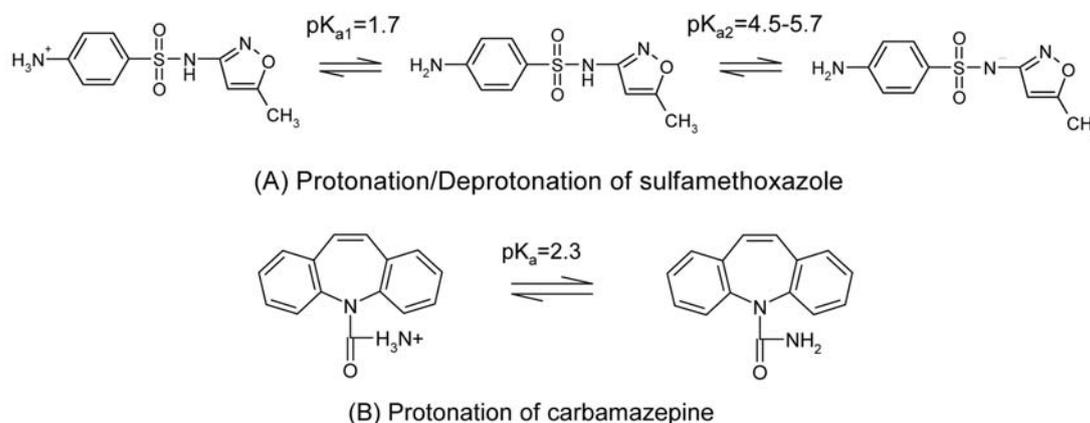


Fig. 2 Protonation/deprotonation of (A) sulfamethoxazole and (B) carbamazepine

In a typical membrane filtration process where temperature, pressure and ionic strength vary within a moderate range, speciation of many chemicals depends primarily on the solution pH. Functional moieties of many trace organics are readily dissociable in accordance with the solution pH. Those that contain acidic functional groups such as carboxyls or phenols may be deprotonated to gain a negative charge, while those with basic functional groups such as amines may be protonated to gain a positive charge. Such speciation processes depend on the acid dissociation constant (pK_a) as depicted in Fig. 2.

3.2. Nanofiltration of hydrophilic trace organics

To examine the hypothesis that charge repulsion can enhance rejection, a set of experiments was conducted for the two pharmaceutically active compounds (PhACs) at pH 8.0. At this pH, carbamazepine exists almost exclusively in its neutral (uncharged) form while sulfamethoxazole exists predominantly as anionic species (see Fig. 2). A mass balance analysis indicated that sulfamethoxazole and carbamazepine did not adsorb, to any appreciable degree, to the membrane surface. This can be explained by their relative hydrophilicity as well as electrostatic charge repulsion with the membrane surface. This behaviour was also reflected by stable rejection values over time as shown in Fig. 3. More importantly, the results clearly indicate that electrostatic repulsion between charged solute and the membrane surface has considerably enhanced the separation process. Despite the fact that sulfamethoxazole and carbamazepine examined in this study have very similar molecular dimensions (see Table 2), their rejection by the TFC-SR2 membrane differs distinctively. Rejection of the neutral compound carbamazepine is low and steric interaction (or size exclusion) is expected to be the only separation mechanism involved. In contrast, sulfamethoxazole rejection is significantly higher, most likely due to the additional Donnan exclusion effect resulting from electrostatic interaction between these negatively charged species and the membrane surface. These observations indicate that nanofiltration membranes may be used effectively to remove ionisable trace organics at lower pressures than those required by tighter membranes. This has important implications for water recycling practice since some ionisable trace organics are often poorly removed during biological treatment process of conventional wastewater treatment plants, hence are more likely to be present in secondary treated effluents than some of their more hydrophobic counterparts.

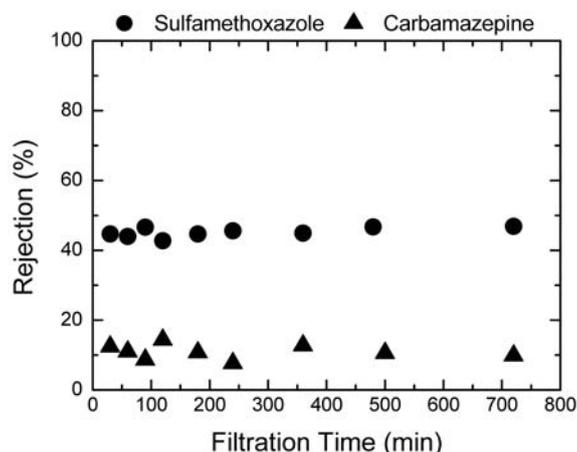


Fig. 3 Rejection of sulfamethoxazole, and carbamazepine by the TFC-SR2 membrane as a function of time ($\text{pH} \approx 8.0$)

3.3. Effect of pH on rejection

The solution pH can have a dramatic effect on the membrane surface charge (see Table 1). This in turn will have a significant influence on charge interaction between the membrane surface and charged solutes, and hence the contribution of charge repulsion toward the rejection of charged solutes. As discussed above, speciation of certain trace organics can also be strongly dependent on solution pH. The combination of these effects can also influence charge interaction between the membrane surface and charged solutes. Consequently, the solution pH can be a critical factor governing electrostatic interaction in a nanofiltration membrane filtration system involving ionisable trace organics.

Rejection of sulfamethoxazole and carbamazepine by the TFC-SR2 membrane, as a function of solution pH, is presented in Fig. 4. Because carbamazepine is neutral at all pH values examined here, carbamazepine rejection was constant and independent of solution pH (and membrane charge). In contrast, rejection of sulfamethoxazole varied considerably, resembling their speciation behaviours in accordance with variation of the solution pH. Sulfamethoxazole rejection rose from almost nil to as high as 70% for the TFC-SR2 membrane as the solution pH was increased from 3.5 to 10.5. In this example, it is evident that electrostatic repulsion is the dominant removal mechanism for this very loose NF membrane.

3.4. Effect of ionic strength on rejection

The solution ionic strength significantly affects the Debye length or the double layer thickness at the membrane surface. This, in turn, governs electrostatic interaction in the NF/RO membrane filtration system, and is therefore expected to exhibit some influence on the separation process of charged solutes. Indeed, experimental data presented in Fig. 5 appear to strongly support such an assumption. As ionic strength increases, the solution Debye length is shortened. In other words, electrostatic interaction is reduced resulting in a decrease in sulfamethoxazole rejection as at high ionic strengths (and pH 8). The influence of ionic strength on rejection is absent when sulfamethoxazole exists predominantly in a neutral form (at pH 4). This again consistently confirms that the effect of

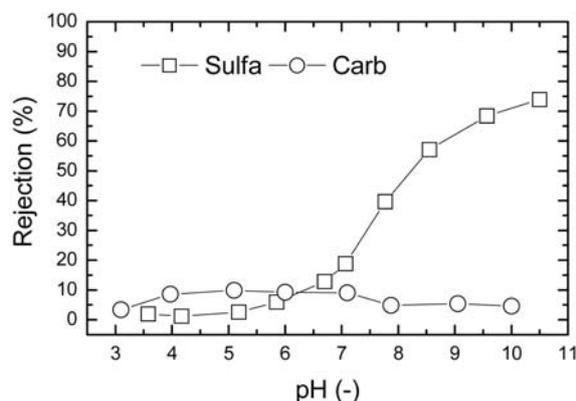


Fig. 4 Rejection of sulfamethoxazole and carbamazepine by the TFC-SR2 membrane as a function of solution pH

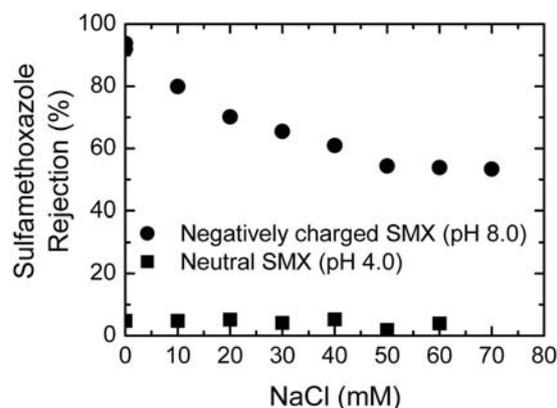


Fig. 5 Sulfamethoxazole rejection by the TFC-SR2 membrane as a function ionic strength at pH 8.0 and 4.0

ionic strength on rejection of negatively charged sulfamethoxazole is induced by the suppression of electrostatic interaction.

Results reported here also highlight the importance of charge repulsion as a removal mechanism of charged solutes in NF membrane filtration processes. At low ionic strength, a considerable rejection can be achieved with negatively charged sulfamethoxazole while rejection of the neutral species appears negligible (see Fig. 5). For most water recycling applications, ionic strength or salinity of the secondary treated effluent is relatively low (< 0.5 g/L). However, salt concentrations in the vicinity of RO and NF membranes can vary by two important means. The most obvious is variation in the feedwater. The other mechanism is known as ‘concentration polarisation’ and is localised to the membrane surface (Song and Elimelech 1995). Based on the results of this experiment, both of these effects may be expected to influence the rejection of some trace organic chemicals.

3.5. Effect of membrane fouling on rejection

In order to achieve an accelerated fouling condition, filtration experiments were conducted with the presence of 20 mg/L humic acid in an electrolyte solution containing 1 mM of Ca^{2+} . While there was no fouling in the absence of the organic foulants, severe membrane fouling could be observed when the feed solution contained a mixture of humic acids and calcium ions. Membrane fouling was fully developed after 18 hours. At this stage, a stable permeate flux was been achieved and the flux had been reduced by 70%. The formation of a fouling layer was confirmed by visual observation at the end of each experiment, which showed a dark brown layer of organic materials firmly attached to the membrane surface.

Difference in rejection behaviour by the membranes under clean and fouled conditions was observed. Rejection behaviour of the pharmaceuticals by fouled membranes as a function of pH closely resembled that under clean membrane conditions. While fouling may alter the surface charge of the membrane, it appears that sulfamethoxazole rejection by both fouled and clean membranes is strongly dependant on the compound’s speciation behaviour. Rejection of both sulfamethoxazole and carbamazepine by the TFC-SR2 membrane improved considerably under fouled conditions (Fig. 6). This observed increase in rejection for the TFC-SR2 membrane which has a large pore size (average

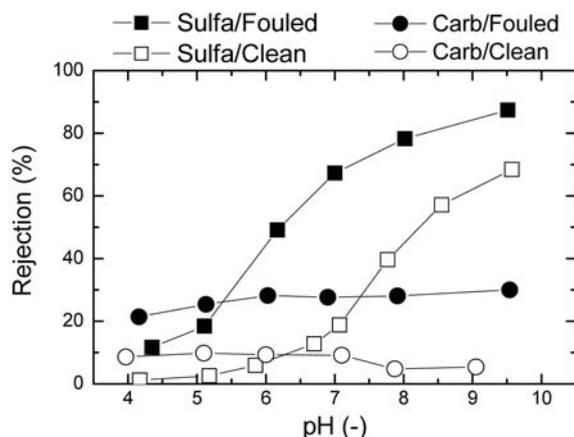


Fig. 6 Sulfamethoxazole and carbamazepine rejection by clean and fouled TFC-SR2 membranes as a function of pH. (Electrolyte solution contains: 20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂; crossflow velocity 30.4 cm/s; fouling was developed for 18 hrs with feed solution containing 20 mg/L humic acids.)

pore diameter of 1.28 nm) is possibly attributable to pore plugging and possible deposition of organic matter on the pore walls. Fouling on and within the pores of the TFC-SR2 membrane is proposed to result in reduced porosity and area available for the passage of pharmaceutical molecules. It is noteworthy that this phenomenon is also likely to be observed in ultrafiltration processes.

4. Conclusions

This study examined the effects of the operating conditions including feed water chemistry and membrane fouling on the rejection of trace organics by a loose nanofiltration membrane. Results reported here indicate that the solution pH and ionic strength can markedly influence the removal of ionisable trace organic compounds while the rejection of neutral trace organics remains unaffected by these parameters. These observations were explained by steric and electrostatic interactions between the solutes and the membrane surface and by the speciation of the ionisable compounds. Solution pH governs the speciation (or charge) behaviour of the compound and therefore the rejection mechanisms. Pharmaceutical rejection increases dramatically as the compound transforms from a neutral to a negatively charged species as solution pH increases above the compound's pK_a value. Ionic strength screens the molecule and membrane charges and therefore reduces the effectiveness of electrostatic repulsion as a major rejection mechanism by the loose nanofiltration TFC-SR2 membrane. In addition, membrane fouling has also been shown to exert some considerable impact on the rejection of trace organics with a clear improvement in rejection by the fouled TFC-SR2 membrane. This is possibly due to the improved sieving effect due to pore plugging and adsorption of foulants on the surface of the membrane pores.

Acknowledgements

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