Desalination 250 (2010) 682–687

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Mechanisms underlying the effects of membrane fouling on the nanofiltration of trace organic contaminants[☆]

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ARTICLE INFO

Article history:
Accepted 26 March 2009
Available online 12 October 2009

Keywords:
Nanofiltration
Organic fouling
Colloidal fouling
Trace organics
Water recycling

ABSTRACT

The influence of membrane fouling on the retention of four trace organic contaminants – namely sulfamethoxazole, ibuprofen, carbamazepine, and triclosan – by nanofiltration membranes was investigated in this study. Humic acid, alginate, bovine serum albumin, and silica colloids were selected as model foulants to simulate various organic fractions and colloidal matter that are found in secondary treated effluent and surface water. The effects of membrane fouling on the separation process was delineated by comparing retention values of clean and fouled membranes and relate them to the membrane properties (under both clean and fouled conditions) as well as physicochemical characteristics of the trace organic contaminants. Membrane fouling was dependent on the physicochemical properties of the model foulants. Initial foulant–membrane interaction could probably be a major factor governing the process of membrane fouling particularly by the organic foulants. Such membrane–foulant interaction was also a dominating factor governing the effects of membrane fouling on the membrane separation efficacy. In good agreement with our previous study (Nghiem and Hawkes, 2007 [1]), the effects of fouling on retention were found to be membrane pore size dependent. In addition, results reported here suggest that these effects could also be foulant dependent. It was probable that the influence of membrane fouling on trace organic retention could be governed by four distinctive mechanisms: modification of the membrane charge surface, pore blocking, cake enhanced concentration polarisation, and modification of the membrane hydrophobicity. The presence of the fouling layer could affect the retention behavior of charged solutes by altering the membrane surface charge density. While the effect of surface charge modification was clear for inorganic salts, it was less obvious for the negatively charged pharmaceutical species (sulfamethoxazole and ibuprofen) examined in this investigation, possibly due to the interference of the pore blocking mechanism. Evidence of the cake enhanced concentration polarisation effect was quite clear, particularly under colloidal fouling conditions. In addition, organic fouling could also interfere with the solute–membrane interaction, and therefore, exerted considerable influence on the separation process of the hydrophobic trace organic contaminant triclosan.

1. Introduction

Driven by more stringent water and wastewater treatment standards, applications employing membrane processes are increasing rapidly. Nanofiltration (NF), in particular, has been increasingly considered as a reliable and affordable technique for the production of high quality water from unconventional sources such as brackish water, polluted surface water, and secondary treated effluent where micropollutants are to be removed [2–5]. However, issues associated with membrane fouling remain quite problematic with respect to not just volume production but also treated water quality. The presence of the fouling layer can drastically alter the characteristics of the membrane surface including surface charge and hydrophobicity [6,7]. Consequently, in addition to a decline in permeate flux, membrane fouling can lead to considerable variation in the membrane separation efficiency.

It has been reported that membrane fouling can either improve or deteriorate permeate water quality. However, the influence of membrane fouling on trace organic retention by NF membranes is rather complex, and both increase and decrease in retention have been observed [1,7–10]. Xu et al. observed that retention behaviours of ionic, hydrophilic non-ionic and hydrophobic organics by fouled NF membranes were quite different from one another [7]. In another study, Ng and Elimelech reported that colloidal fouling of RO membranes caused a considerable decrease in the retention of the natural hormone estrone and estradiol [11]. In our previous study [1], it was also observed that magnitude of the influence of membrane fouling on the rejection of micropollutants (either positive or negative) decreased and the membrane pore size decreased. These studies clearly demonstrate the complexity of the mechanisms underlying different effects of fouling on

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[☆] Presented at the Conference on Membranes in Drinking and Industrial Water Production, 20–24 October 2008, Toulouse, France.

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doi:10.1016/j.desal.2009.03.025

retention of micropollutants and the need to improve our understanding in this important area.

This paper aims to study the influence of organic and colloidal fouling on the separation of four trace organic contaminants by nanofiltration membranes. Experiments were conducted with two commercially available NF membranes and four different model foulants, commonly encountered in water recycling applications. Membrane fouling was related to the membrane and foulant characteristics and subsequently the separation behaviour of the trace organic contaminants. On the basis of these results, effects of membrane fouling on sulfamethoxazole retention were delineated and relevant mechanisms were elucidated.

2. Materials and methods

2.1. Nanofiltration membrane

Two nanofiltration (NF) membranes – denoted NF-90 and NF-270 – were used in this investigation. These membranes were supplied by Dow FilmTec (Minneapolis, MN) and were stored dry. According to the manufacturers, both are thin-film composite polyamide membranes with a microporous polysulfone supporting layer. As can be seen from Table 1, these two NF membranes have relatively small pore sizes and correspondingly small values of molecular weight cut-off (MWCO). Both membranes are negatively charged at pH 8 with an isoelectric point at around pH 4.

2.2. Chemicals and reagents

Sodium alginate, humic acid, bovine serum albumin (BSA) and the colloidal silica Ludox HS-30 were selected as model foulants in this study. These chemicals were purchased from Sigma Aldrich (Castle Hill, Australia). This colloidal silica was supplied at 30% suspension in water and was stored in a refrigerator at 4 °C.

Analytical grade sulfamethoxazole, ibuprofen, carbamazepine, and triclosan were purchased from Sigma-Aldrich (Castle Hill, Australia) to represent trace organic contaminants frequently found in secondary treated effluent and sewage impacted water bodies at trace levels. The first three compounds are frequently prescribed pharmaceuticals while the last compound is widely used as an antimicrobial agent in many personal care products including toothpastes, soaps, shampoos, detergents, and disinfectants. These trace organics were first dissolved in pure methanol to make up stock solutions of 1 g/L. The stock solutions were stored at in a freezer at −18 °C and were used within 1 month. Sodium chloride (1 M), calcium chloride (0.1 M), and sodium bicarbonate (0.1 M) were used to prepare the background electrolytes. Adjustment of the feed water pH was carried out with sodium hydroxide (1 M) or hydrochloric acid (1 M). These chemicals were of analytical grade and were supplied by Sigma-Aldrich (Castle Hill, Australia). All aqueous solutions used in this investigation were prepared with laboratory grade MilliQ water.

2.3. Membrane filtration set-up and experimental protocol

A laboratory-scale crossflow NF/RO set-up was used in this study. This set up consisted of a stainless steel plate-and-frame membrane cell with an effective surface area of 4 cm × 10 cm, a stainless steel feed reservoir, and a high pressure pump. The concentrate flow rate was monitored by a rotameter. Feed pressure and crossflow velocity were controlled by means of a bypass valve and a back pressure regulator.

Table 1
Properties of the selected NF membranes.

Membrane	Pure water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Average pore diameter [a] (nm)	MWCO [b] (g/mol)	NaCl retention (%)	Zeta potential at pH 8 [a] (mV)
NF-270	13.5	0.84	150	40.0	−24.7
NF-90	6.4	0.68	100	85.0	−27.3

[a] Ref. [4].
[b] Ref. [12].

Membrane fouling and subsequent retention testing experimental protocol was conducted in three steps: compacting, fouling development, and retention measurement. First, the membrane was compacted using MilliQ water at 1800 kPa for approximately one to two hours until a stable baseline flux has been obtained. An electrolyte solution containing 20 mM NaCl, 1 mM $NaHCO_3$, and 1 mM $CaCl_2$ was introduced to the feed reservoir and the permeate flux was adjusted to 117 L/m^2h prior to the addition of foulant to make up a foulant cocktail having 20 mg/L of a model foulant. The fouling layer was then allowed to develop for 18 h and the feed solution was kept at pH 8. After the development of the organic fouling layer, the permeate flux was readjusted to 54 L/m^2h. A selected trace contaminant was spiked into the feed reservoir to make up a concentration of 750 μg/L and the filtration process continued for approximately 8 h to allow for the measurement of retention values. A small volume of feed and permeate samples was taken for analysis at specified time intervals. Analysis of trace organic concentrations in feed and permeate samples were conducted immediately on conclusion of the experiment using an HPLC system (Shimadzu, Kyoto, Japan). Further description of the HPLC analytical procedure can be found elsewhere [1]. Temperature of the experimental solution was kept constant at 20 ± 0.1 °C. Both the permeate and the concentrate were recirculated back to the feed reservoir throughout the entire experiment. To examine the retention of the trace organic contaminants by the clean membranes, a similar protocol but without the fouling development step was adapted. Observed retention is defined as $R = 100 \times (1 - C_P/C_F)$, where C_P and C_F are the permeate and the feed concentrations, respectively.

3. Results and discussions

3.1. Characteristics of the trace organics and model foulants

All four compounds selected for this study have relatively low molecular weights in the range from 206 g/mol to 290 g/mol. However, they are markedly different in their hydrophobicity values and dissociation constants (Table 2). As seen in Table 2, at pH 8 which is a typical pH of secondary effluent and surface water, sulfamethoxazole and ibuprofen are hydrophilic with very low effective log octanol–water-distribution ratios (Log D_{ow}) whereas carbamazepine is moderately hydrophobic. In contrast, triclosan is highly hydrophobic with a very high log D_{ow} value. As a result, triclosan has a very high affinity toward polymeric membranes.

Sodium alginate, humic acid, bovine serum albumin (BSA) and the colloidal silica Ludox HS-30 were selected to simulate polysaccharides, refractory organic matter, protein and colloidal particles that are ubiquitous in secondary treated effluent. These model foulants differ considerably in their physicochemical properties (Table 3) and hence allowing for a systematic examination of the role of the foulant in influencing the membrane separation performance. Both the sodium

Table 2
Physicochemical properties of the selected trace organic contaminants.

Compound	MW (g/mol)	pK_a	Charge at pH 8	Log D_{ow}	Molecular dimension (nm)	
					Width	Length
Ibuprofen	206.3	4.4	Negative	0.36	0.447	1.031
Sulfamethoxazole	253.3	1.7 and 5.8	Negative	−0.90	0.526	1.031
Carbamazepine	236.3	−0.49 and 13	Neutral	2.67	0.507	0.891
Triclosan	289.6	8.14	Neutral	4.70	0.693	1.419