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Modelling the rejection of N-nitrosamines by a spiral-wound reverse osmosis system: Mathematical model development and validation

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ABSTRACT

A mathematical model was developed based on the irreversible thermodynamic principle and hydrodynamic calculation to predict the rejection of N-nitrosamines by spiral-wound reverse osmosis (RO) membrane systems. The developed model is able to accurately describe the rejection of N-nitrosamines under a range of permeate flux and system recovery conditions. The modelled N-nitrosamine rejections were in good agreement with values obtained experimentally using a pilot-scale RO filtration system. Simulation from the model revealed that an increase in permeate flux from 10 to 30 L/m^{2}h led to an increase in the rejection of low molecular weight N-nitrosamines such as N-nitrosodimethylamine (NDMA) (from 31% to 54%), which was validated by experimental results. The modelling results also revealed that an increase in recovery caused a decrease in the rejection of these N-nitrosamines, which is consistent with the experimental results. Further modelling investigations suggested that NDMA rejection by a spiral-wound system can drop from 49% to 35% when the overall recovery increased from 10% to 50%. The model developed from this study can be a useful tool for water utilities and regulators for system design and evaluating the removal of N-nitrosamine by RO membranes.

1. Introduction

Augmenting potable water sources using reclaimed water is an important part of the water management portfolio in many regions of the world [1]. The planned use of reclaimed water to augment water supply is stringently regulated for the protection of public health. Thus, reclaimed water is commonly treated by a series of advanced treatment processes before being added to aquifers or reservoirs as the source of potable water supply. In many cases, these include reverse osmosis (RO) filtration to ensure the removal of pathogenic organisms, total dissolved solids and trace organic chemicals [1–4]. N-nitrosodimethylamine (NDMA) is one of several trace organic chemicals that are of particular concern due to its highly variable rejection efficiency by RO membranes as reported in several recent pilot- and full-scale studies [5–7]. NDMA is a disinfection by-product formed during the chloramination of biologically treated effluent [8] and is often found in the RO feed at up to a few hundred parts per trillion [9]. In addition to NDMA, other N-nitrosamines that are often present in raw wastewater and secondary treated effluents including N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosodipropylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA) [10–12]. Several of these N-nitrosamines (including NDMA) have been classified as probable human carcinogens by the US EPA [13]. Thus, their concentrations in drinking water have been regulated by regulatory authorities around the world. For examples, the Australian Guidelines for Water Recycling have recommended their concentrations at 10 ng/L (NDMA and NDEA) and at 1 ng/L (NMOR) for the augmentation of drinking water sources [14].

Modelling the rejection of N-nitrosamines under various conditions is essential for the design of RO plants and compliance monitoring. NDMA and several other N-nitrosamines have been frequently detected in the feed water to RO treatment at concentration higher than the regulatory levels [15]. In addition, N-nitrosamine rejection by RO membranes is sensitive to operating conditions and feed solution characteristics [16]. Difficulties associated with analytical determination of N-nitrosamines in the permeate at regulatory concentrations (i.e. 1–10 ng/L) [5,17,18]

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also underscore the need for a model that can accurately describe the rejection of N-nitrosamines. N-nitrosamine concentrations in aqueous samples can be determined by chromatography (GC) or high pressure liquid chromatography (HPLC) with tandem mass spectrometry (MS/MS) detector. However, the number of commercial laboratories capable of trace level N-nitrosamine analysis is still limited and regular monitoring of N-nitrosamines remains difficult and expensive. Thus, a capacity to describe and predict the rejection of N-nitrosamines by the RO process is particularly useful for the management of these trace organic chemicals in water recycling applications.

The rejection of inorganic salts by multi-stage RO membrane systems can be simulated with a high level of accuracy using commercially available RO design software packages (e.g. IMSDesign, TorayDS/DS2, and ROSA provided by Hydranautics, Toray, and Dow/FilmTec, respectively). The development of mathematical models for simulating specific trace organic and inorganic chemicals by spiral wound RO membrane systems has been reported in several recent studies. Kim and co-workers have successfully developed a model for predicting boron rejection by applying the irreversible thermodynamic principle and sub-dividing a spiral wound element into a number of small sub-sections [19–21]. Using a similar approach, Verliefde et al. [22] have also developed a full-scale rejection model for several pharmaceutically active compounds (PhACs) using nanofiltration (NF) membranes. These models significantly enhance our understanding of the permeation of boron and PhACs through RO membranes under realistic conditions. However, to date, there have yet been any software packages or mathematical models that can simulate the rejection of N-nitrosamines.

The aim of this study was to develop a mathematical model to predict the rejection of N-nitrosamines by RO systems under a range of operating conditions. The developed model was validated using experimental data obtained from a pilot RO system. The potential application of this model for predicting N-nitrosamine rejection at full-scale level was also discussed.

2. Theoretical background

2.1. Membrane element characteristics

A commercial spiral-wound element has one or several membrane leaves. Each leaf consists of two flat sheet membranes sealed on three sides with the forth side attached to a perforated tube called the permeate collector. The membrane leaf is wound around the permeate collector. As a result, each spiral-wound element can essentially be presented by a large flat sheet membrane. In this study, each element is geometrically described with the length (L), width (W) and feed channel height (h_b) (Fig. 1). On the other hand, the irreversible thermodynamic principle can be used to model the rejection of N-nitrosamines by a small flat sheet membrane for a given hydrodynamic condition. Thus, the irreversible thermodynamic principle can also be used to model solute rejection by a spiral wound element. This can be done by sub-dividing the membrane area on each element smaller sections of the same size and using fluid mechanics to calculate and define the hydrodynamic condition for each sub-section. In this study, the membrane area on one each element is divided into 20 sub-sections ($m=20$) in a longitudinal direction where each sub-section length (Δx) is described as

$$\Delta x = \frac{L}{m} \tag{1}$$

It is noteworthy that the length of each sub-section selected here is similar to that of the flat sheet membrane coupon used in the laboratory-scale study. The membrane surface area attached to the feed spacers is assumed to be 10% and this area is not utilised for filtration. Thus, the active surface area in each sub-section (ΔS) is defined as

$$\Delta S = \frac{0.9S}{m} \tag{2}$$

The cross-section area of the feed channel (ΔS_c) is expressed as

$$\Delta S_c = W h_b \tag{3}$$

2.2. Hydrodynamics

The local permeate flux ($J_p(i)$), local permeate flow rate ($Q_p(i)$) and the overall permeate flow rate of a membrane element ($Q_{p,t}$) are calculated using Eqs. (4)–(6).

$$J_p(i) = L_p(\{P_f(i) - P_p(i)\} - \sigma \Delta\pi(i)) \tag{4}$$

$$Q_p(i) = J_p(i) \times \Delta S \tag{5}$$

$$Q_{p,t} = \sum_{i=1}^{m} Q_p(i) \tag{6}$$

where L_p=pure water permeability which is obtained from bench-scale tests and σ=reflection coefficient. Because permeate pressure (P_p) is negligible compared to feed pressure (P_f), local permeate pressure ($P_p(i)$) is assumed to be zero in this study. Local osmotic pressure ($\pi(i)$) shown in Eq. (4) is computed with feed solution temperature (T) and molar concentrations of ions ($m_{salt}(i)$).

$$\pi(i) = 1.19(T+273)\sum_{1}^{i} m(i) \tag{7}$$

Concentration of the solute ($m_{salt}(i)$) increases in the feed in the subsequent sub-sections since the solute is retained by the

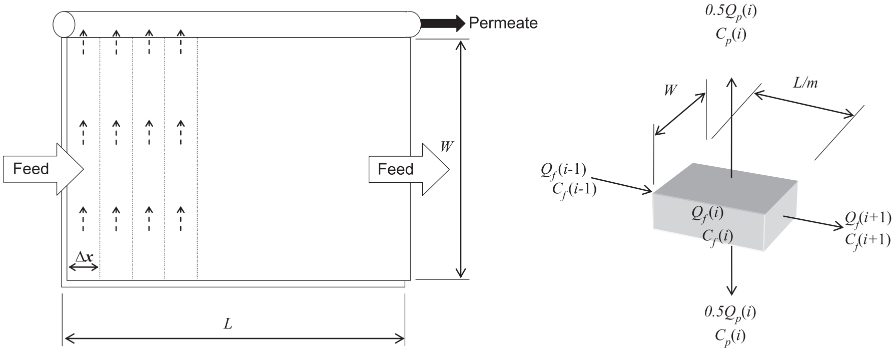

Fig. 1. Representation of a spiral-wound RO element as flat sheet configuration including the mass balance of a flat sheet sub-section.