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Nanofiltration membrane performance on fluoride removal from water

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Abstract

Fluoride concentration in drinking water is very important for human health. Optimal fluoride content is within the range of 0.5–1.0 mg/L. Nanofiltration (NF) membrane performance on fluoride removal from high fluoride content water was investigated in this study. The membranes used are negatively charged commercial thin-film composite (TFC) membranes (DS-5-DL, DS-51-HL and SR-1). The membrane performance was interpreted in terms of membrane parameters: pure water permeability (L_P), pore radius (r_P) and constant surface electrical potential (ψ). The parameters were obtained by fitting the 100 and 1000 ppm single salt (NaF) experimental data to a mathematical model that was developed based on the extended Nernst–Planck equation and the Grahame equation. The experimental results indicated that the rejection of NaF increased with the applied pressure and the solution flux increasing and the feed concentration decreasing. The experimental data were compared with the model developed. The model was also used to predict the membrane performance at 20 and 2000 ppm NaF solutions.

Keywords: Nanofiltration; Fluoride; Negatively charged; Rejection; Solution flux

1. Introduction

The amount of fluoride ion in the human body is an important factor that affects health. An excessive fluoride intake is detrimental to human health leading to serious problems, such as dental fluorosis [1] and skeleton fluorosis [2]. However, fluoride can effectively prevent dental caries when a relative low level is constantly maintained in the oral cavity [3]. Drinking water is the main source of daily fluoride intake for humans [4]. The World Health Organization (WHO) suggests that an optimal fluoride content in drinking water is within the range of 0.5–1.0 mg/L with this range being slightly adjusted for different parts of the world [5].

For source water with a fluoride content that is too high, some special water treatment should be employed. Reverse osmosis (RO) and electrodialysis (ED) are the widely used membrane processes in defluoridation of fluoride-rich waters at present [6–9]. The drawback of RO in treating fluoride-rich waters is that up to 99% of the salts in the water are rejected by the membrane, which means almost all fluoride is eliminated.

Compared to other membrane processes, like RO and microfiltration, nanofiltration (NF) is a relatively new process and is used to a lesser extent in the water industry. Although NF and RO processes are similar, NF is operated at lower pressures and can yield same permeate flux at lower pressure. In particular, in treating fluoride-rich waters, NF processes can provide a partial defluoridation and an optimal fluoride content in permeate can possibly be achieved by adjusting the operation conditions. Studies on NF performance on fluoride removal from water [10–12] are limited. The works of Kettunen and Keskitalo [10] and Lhassani et al. [11] were based on pilot studies. No details about the effect of the membrane intrinsic properties on the membrane performance were included. Choi et al. [12] have investigated influence of the co-existed ions on the fluoride rejection by two commercial nanofiltration membranes only considering the charge effect.

In this study, a mechanical mathematical model is developed to interpret the influence of the membrane structure and charge properties on the membrane performance. With the help of mathematical transport models, the fluoride level in water can be optimized by membrane selection and choice of operating conditions. There are at least two main approaches to modeling the behaviour of ion transport through NF membranes [13]. One approach is based on the Spiegler–Kedem equation. The other one is based on the extended Nernst–Planck equation. In this

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study, a model is developed through the second approach with inclusion of hindrance effects. The equilibrium on the membrane surface is described by the Donnan exclusion model.

In previous studies, the membrane charge effect was either described by the volume charge density [13,14], which lacked the detail on the electrical double layer formed on the membrane surface, or by the Gouy–Chapman equation [15] that related the volume charge density to the surface charge density. In the model development of this study, the Grahame equation is applied to relate the volume charge density to the surface electrical potential which is a function of the membrane fixed charges.

In applying these equations, several assumptions are introduced. Firstly, the NF membranes are assumed to consist of a bundle of uniform nanometer sized capillary pores. Considering that the separation properties of NF membranes lie in between ultrafiltration (UF) membranes and RO membranes, the assumption that NF membranes have a pore structure similar to those of UF membranes is plausible [15,16]. For instance, a direct measurement of NF membrane pore structure was conducted by Bowen et al. [17] using atomic force microscopy (AFM). Their results were quantitatively consistent with the existence of discrete pores in the membrane, although there were some dimensional differences between the results from the AFM images and from the model estimations. The second assumption is that the distribution of the electrical potential and the ion concentration across the pore radius is uniform. Using the non-linear Poisson–Boltzmann equation to describe the electrical potential and ion concentration distributions across the pore radius, Wang et al. [16] found that when the pore radius was less than 1.0 nm, the diffusion double layers could not be fully developed. Thus, the electrical potential variation across the pore radius is small. The third assumption is that the steric effect in the Donnan partitioning at the interface of the membrane is negligible. Based on the investigation of the rejection experiments, Bowen et al. [17] proposed that this assumption was reasonable for small ions.

The main objective of this paper is to further understand the NF membrane performance on fluoride removal. The study was divided into three parts: (1) develop a mathematical model to interpret the membrane behaviour, (2) estimate the membrane structural parameters and the membrane charge properties based on the single salt (NaF) experimental data and (3) compare the model calculations and predictions with the experimental data at different concentration solutions. The unique contributions of this paper are as follows. For the first time, the Grahame equation is used to describe the volumetric charge density in NF membrane transport. Although many studies exist on modelling salt transport in NF membranes, the study of NaF is unique, which is particularly interesting given the high electronegativety of F^- ion. Also, for the first time detailed data and modelling of two of the three membranes studied (HL and SR-1) are presented.

2. Theoretical background and model development

Membrane behaviour is generally characterized by flux and rejection. In this section, the nanofiltration performance is described, and then a transport model is developed based on the extended Nernst–Planck equation.

2.1. Process behaviour description

NF performance is usually described in terms of the pure water flux (J_W), the solution flux (J_V) and the rejection (R). The pure water flux, based on membrane area, can be related to the membrane structure and the solution viscosity at the operating temperature by the Hagen–Poiseuille equation [18]:

$$J_W = \frac{r_P^2 \Delta P}{8\mu(\Delta x/A_K)} \tag{1}$$

where r_P is the pore radius of the membrane, ΔP is the applied pressure, μ is the viscosity of the solution at the operating temperature and $\Delta x/A_K$ is the ratio of the membrane effective thickness to the membrane porosity. Thus, based on the Darcy's law, the pure water permeability (L_P) is given by Eq. (2) [19]:

$$L_P = \frac{r_P^2}{8\mu(\Delta x/A_K)} \tag{2}$$

In the presence of a solute, the volumetric solution flux (J_V), based on membrane area, is related to the applied pressure and the osmotic pressure ($\Delta\pi$). Kedem and Katchalsky [20] phenomenologically derived the following transport equation:

$$J_V = L_P(\Delta P - \sigma\Delta\pi) \tag{3}$$

where parameter σ is the reflection coefficient of the membrane for the particular solute.

In this study, cross flow was adopted for all experiments to eliminate the concentration polarization effect. Thus, for a species i, the membrane rejection is approximately equal to the observed rejection, and is defined as:

$$R = \frac{C_i^B - C_i^P}{C_i^B} \tag{4}$$

where C_i^B and C_i^P are the bulk concentrations in the feed and the permeate sides, respectively.

2.2. Development of the transport model

The extended Nernst–Planck equation has been used to describe the ion transport in RO membranes [21,22] and in NF membranes [13,14]. Including the hindrance diffusion and convection coefficients, the extended Nernst–Planck equation can be written as:

$$J_i(x) = -H_{i,d} D_{i,\infty} A_K \left(\frac{dC_{i,P}(x)}{dx} + z_i C_{i,P}(x) \frac{F}{RT} \frac{d\psi(x)}{dx} \right) + H_{i,c} C_{i,P}(x) J_V \tag{5}$$

where $J_i(x)$ is the ion flux at point x based on the membrane area, $H_{i,d}$ and $H_{i,c}$ are the hindrance diffusion and convective coefficients, respectively, $D_{i,\infty}$ is the diffusion coefficient of ion i in the bulk solution, $C_{i,P}$ is the ion concentration in the membrane pores, z_i is the electrochemical valence of the ion, R is the universal gas constant, T is the absolute temperature, ψ is the membrane surface electrical potential and F is the Faraday's constant.

Various calculation equations of the hindrance coefficients, as a function of the ratio (η) of the solute size to the pore size,