Rejection and modeling of arsenate by nanofiltration: Contributions of convection, diffusion and electromigration to arsenic transport

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ABSTRACT

Nanofiltration (NF) membranes, DK and DL, were characterized by attenuated total reflection-Fourier transform infrared spectroscopy, surface charge titration, pore size determination and salt rejection. The results showed both membranes have amide I and carbonyl groups on their surfaces, and have the same basic structure of polyamide layer sitting on the top of a polysulfone layer. The DK membrane carries more negative charges in the entire pH range investigated. Arsenate rejections by the NF membranes were evaluated with a crossflow test setup. The effects of pH, ionic strength, operating pressure, arsenate initial concentration on the membrane performance were investigated. Mass transfer coefficients of the membranes were determined experimentally. The Donann Steric Pore Model and concentration polarization film theory were applied to calculate the arsenic rejection rate. The rejection mechanism was interpreted by calculating the contributions of convection, diffusion, and electrostatic migration to arsenic transport through the membranes. The calculated results showed that the contribution of diffusive transport dominated at low flux, and convection and electromigrative transport, especially the latter, play an increasingly important role at a high flux.

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1. Introduction

Nanofiltration (NF) has attracted increasing attention over the recent years due to the development of new applications. Moreover, new polymer chemistry and manufacturing processes have dramatically lowered the membrane operating pressures and reduced costs. NF membranes are now widely used in various fields such as pharmaceutical manufacturing [1,2], decolorization of textile dye waste [3], treatment of metal contained in waste waters from metal finishing industries [4–6], paper and plating industries [7,8], and drinking water production [9,10]. Membrane characterization showed that the effective pore sizes of NF membranes range from less than 1 nm to a few nanometers, and by molecular weight cut-off between reverse osmosis membranes and ultrafiltration membranes. Another feature is that most of NF membranes are charged either negatively or positively, generally due to dissociation of functional groups of membrane or adsorption of charged species from solution onto membranes. Therefore, the separation principles of NF include steric exclusion for neutral species, or steric and charge exclusion between inorganic ions and the membrane, and consequently, different models have been proposed to describe NF membranes process [11–15].

Early model descriptions of the NF processes were derived from the work of Spiegler and Kedem concerning irreversible thermo-dynamics. These approaches were originally applied for dense reverse osmosis membranes. The membranes were assumed as a black box, no transport information is needed or obtained, and electrostatic potential of the membrane system was not considered. Thus the model could not be used to characterize the structural and electrical properties of the membrane. Nernst–Planck equation has been modified by Wang et al. allowing the evaluation of membrane charge so that convection and diffusion as well as electrostatic migration were taken into account to predict the membrane performance [16]. Donann Steric Pore model (DSPM) developed by Bowen et al. has proven to be particularly useful in interpreting the retention properties of NF membranes. The model was based on the extended Nernst–Planck equation with electroneutrality conditions inside the membrane, and Donann equilibrium modified with a steric effect was combined to describe the partitioning of components on both solution/membrane interfaces. In this model the main equation (the extended Nernst–Planck equation) describing the solute transport through the membranes consists of contributions from diffusion, electromigration, and convection, as follows:

$$J_i = \left(-D_{i,p}\frac{dc_i}{dx} \right) - \left(D_{i,p}z_ic_i\frac{F}{RT}\frac{d\psi}{dx} \right) + (K_{i,c}c_iJ_v) \tag{1}$$

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in which the hindered diffusivity ($D_{i,p}$) equals the product of hindrance factor for diffusion ($K_{i,d}$) and bulk diffusivity ($D_{i,\infty}$), $K_{i,c}$ represents hindrance factor for convection, c_i the concentration of solute i at the surface of the membrane, z_i the valance of solute i, F Faraday's constant, R the gas constant, T the temperature, ψ the electric potential, and J_v the volume flux [17]. Some authors have successfully applied this model to further detail the dominant mechanism for solute transport through membrane under different conditions [5,18–21]. Lee et al. explained the rejection of nitrogen compounds by integrating experimental results with the calculations using DSPM. More importantly, the significances of various transport mechanisms, diffusion, convection, and electromigration, were determined [19]. Szymczyk et al. investigated the dominant mechanism for the transport of symmetrical electrolytes under various conditions of effective charge density, permeate volume flux, membrane pore size and membrane thickness to porosity ratio [22].

Arsenic, usually existing in natural waters in forms of As(III) and As(V) oxidation states, is now recognized as one of the most serious inorganic contaminants in drinking water on a worldwide basis. NF membranes have been actively used for arsenic removal due to its high separation efficiency and stable performance [23–30]. However, the assessments of membrane separation for arsenic remediation could not be simply accomplished since specific NF systems differ from case to case in terms of membrane types, operating parameters and application conditions. Some studies on the NF membrane performance for arsenic removal have led to different or contradictory observations and explanations. For example, Sato et al. reported the arsenate rejection by three types of NF membranes, ES-10, NTR-729HF, and NTR-7250, increased with the increase of operating pressure [26], whereas arsenate rejection by 192-NF 300, a spiral wound thin film composite polyamide membrane, was independent of transmembrane pressure in the range of 310–7241 kPa [27]. Hering and Elimelech indicated that pH did not affect the removal of arsenic by the NF-70 and TFC-HR membranes in the range of 5.5–8.5 [31]; however, it was observed that As(V) rejection by a sulfonated polysulfone thin-film composite membrane denoted BQ01 significantly decreased from 85% at pH 8.5 to only 8% at pH 4.5 [25]. Further investigations on different NF membranes and various operating parameters are thus of interest for the development of an arsenic removal strategy. Moreover, optimization of NF process, including membrane selection or improvement of the operating conditions, requires a fundamental understanding of the chemical and physical mechanisms governing the arsenic rejection by NF. A useful model is, therefore, needed.

In this paper, NF membranes, DK and DL, were characterized in terms of membrane permeability, potentiometric titration, contact angle measurement, ATR-FTIR spectra, pore size determination, and salt retention. The arsenic rejection by the DK and DL membranes was evaluated as a function of operating pressure, arsenic initial concentration, ionic strength and pH in a cross flow membrane system. The experiments were performed by using only the arsenate species, As(V). This is a more easily removable form of arsenic, but the result can be considered relevant since As(III) can be oxidized to As(V) by using a pre-oxidation step with chemical oxidants [32–34]. The DSPM model and the concentration polarization film theory were applied to predict the arsenate rejection by the membranes. In particular, no studies, to our best of knowledge, have been performed to interpret the contributions of the different transport mechanisms – diffusion, convection, and electromigration – to arsenic transport through NF membranes; the model calculation was, therefore, applied to identify the dominant transport mechanisms in certain circumstances during the arsenic rejection and provide further insights useful for practical membrane applications such as treatment plant design, membrane selection and improvement of the operating conditions for arsenic removal.

2. Experimental section

2.1. Materials

All chemicals were of regent grade and solutions were prepared by Milli-Q water (Millipore Corp. with resistivity of 18.2 MΩ cm). Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was obtained from Sigma-Aldrich. The stock solution of 100.0 mg/L As(V) was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ in water and filtering through a 0.22 μm membrane. Two commercial NF membranes, DK and DL, were purchased from GE Osmonics.

2.2. Characterization of the membranes

Pure water flux of the membrane was measured at a pressure range from 551.6 kPa (80 psi) to 1379 kPa (200 psi) to evaluate the membrane permeability. Flux was determined gravimetrically by weighing the mass of permeate collected at predetermined time intervals. The permeability was calculated as the slope of the linear flux versus pressure line. The static contact angles of membrane samples were measured by projecting an image of an automatic sessile droplet resting on the surface with a VCA-2500XE Video Contact Angle System (AST Products, Inc.). ATR-FTIR Spectra were obtained from 650 to 4000 cm^{-1} at a resolution of 2 cm^{-1} using Nicolet FTIR 6700 (Thermo Electron Corporation; Waltham, MA) equipped with a germanium ATR element. The instrument was purged with dry nitrogen to prevent interference of atmospheric moisture with the spectra. The potentiometric titration measurement was performed to determine the fixed charge density of the membranes. The titration was carried out using a Titrino 798 microburette (Metrohm, Switzerland) interfaced to a PC computer utilizing Datalog software.

Rejections of uncharged glucose solutes were performed to estimate the pore size of the membrane, and the sugar concentrations in permeate and feed samples were analyzed using a colorimetric method [35]. It should be noted that the effect of concentration polarization (CP) cannot be neglected during the model calculation when the mass transfer coefficient is in the same order magnitude of the permeate flux. Therefore, the intrinsic rejection should be used in model calculation. By assuming that the CP layer quickly reaches a steady state and the transverse solute flux through the CP layer is constant, one can evaluate the solvent flux (J_v) by the one-dimensional, steady-state mass balance across the CP layer [36]. After some mathematical manipulations, the intrinsic rejection can be given as follows:

$$\ln\left(\frac{1-R_o}{R_o}\right) = \ln\left(\frac{1-R_i}{R_i}\right) + \frac{J_v}{k} \tag{2}$$

where R_o is observed rejection, R_i intrinsic rejection, and k mass transfer coefficient. The determination of the mass transfer coefficient is described later in next section. The intrinsic rejection data were fit to Spiegler and Kedem-Steric Hindrance Pore model to yield the pore radius and membrane thickness to porosity ratio of the membranes, the hypothesis and calculation procedures of the model have been detailed elsewhere [12,13].

2.3. Experiment set-up and operation protocol

2.3.1. Membrane units

A lab-scale plate-and-frame stainless steel membrane system with an effective membrane surface area of 138.7 cm^2 was operated in a conventional cross-flow mode, with a variable-speed HydraCell diaphragm pump (model D-03, Minneapolis, MN) capable of providing pressure up to 6.89 MPa (1000 psi) and a maximum flow rate of 6.81 L/min (Fig. 1). Feed solution was pumped through the membrane channel from a 10 L of plastic tank in closed loop