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Elucidating the mechanisms underlying the difference between chloride and nitrate rejection in nanofiltration

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ABSTRACT

Despite the strong similarity between chloride (Cl^-) and nitrate (NO_3^-) anions in terms of their hydrated radius and charge, Cl^- is rejected more favorably than NO_3^- by nanofiltration (NF) membranes. The main goal of this study is to provide a better understanding of the removal mechanisms favoring the higher rejection of Cl^- over NO_3^- in NF. A series of experiments with polyamide (NF270) and cellulose acetate (CK) NF membranes at different pH values, followed by calculation of the activation energies for Cl^- and NO_3^- passage through the membranes, showed that the higher Cl^- than NO_3^- rejection is attributed to both size-exclusion and Donnan (charge)-exclusion mechanisms. At a neutral membrane charge, a size-exclusion mechanism dominates the rejection of both anions. In this case, we observe higher rejection of Cl^- over NO_3^- due to the lower hydration energy of NO_3^-, which corresponds to higher degree of dehydration and thus higher rate of passage through the NF membrane pores. At a negative membrane charge, the smaller volume of Cl^- compared to NO_3^-, corresponding to higher ionic charge density, results in a stronger electrostatic repulsion of Cl^- by the negatively charged membrane and therefore higher Cl^- rejection than NO_3^-. The coupling of size- and Donnan-exclusion mechanisms with the NF270 membrane results in a maximum Cl^- to NO_3^- rejection ratio at near the isoelectric pH where the membrane is slightly negatively charged. At a positive membrane charge, the sodium (Na^+) counter ions dictate salt rejection independently of the anion type, resulting in almost similar rejections of Cl^- and NO_3^-. Based on the insight gained from these experiments, a layer-by-layer (LbL) polyelectrolyte modification was applied to the NF270 membrane to control its surface charge. This modification showed that shifting the isoelectric point of the NF270 membrane from its original value (pH 4–5) to higher values (pH 6–9) increased the Cl^- to NO_3^- rejection ratio at near neutral pH conditions, thus providing further support for our proposed mechanism underlying the difference between Cl^- and NO_3^- rejection by NF membranes.

1. Introduction

Nanofiltration (NF) is a membrane technology with separation characteristics between reverse osmosis (RO) and ultrafiltration (UF) [1–5]. Salt rejection in NF membranes is based mainly on size (steric)- and Donnan (charge)-exclusion mechanisms [6]. A unique feature of many NF membranes is their high selectivity for the passage of monovalent ions over larger ions and molecules, which is exploited in various applications for removing divalent salts and small organic molecules [3]. However, with respect to rejection of monovalent ions, the selectivity difference is much smaller and the mechanism for such selectivity difference is relatively poorly understood.

Chloride (Cl^-) and nitrate (NO_3^-) are common monovalent anions that are ubiquitous in natural waters and wastewaters. Nitrate is a major pollutant in groundwater and is associated with eutrophication of water bodies [7] and methemoglobinemia, known as the 'blue baby syndrome' [8]. Chloride is the major target anion in desalination processes [9,10] and can be harmful for crops above a certain level [11]. Despite the strong similarity between these two anions, especially in terms of their charge (−1 for both Cl^- and NO_3^-) and hydrated radius (0.33 and 0.34 nm for Cl^- and NO_3^-, respectively) [12,13], higher NF rejection of Cl^- than NO_3^- has been observed in numerous studies [14–20].

A first explanation suggested in several studies [14,15,21] is that NO_3^-, with a larger molar volume, would have a lower ionic charge density compared to Cl^-, which has a smaller molar volume. Thus, the repulsion of NO_3^- by a negatively charged membrane would be weaker and its rejection lower than the rejection of Cl^-. However, this

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explanation, relating the difference between the rejections of the two anions to the Donnan (charge)-exclusion mechanism, was never tested or validated.

Another explanation, associated more with a size-exclusion mechanism, attributed the higher Cl^- rejection to its higher hydration energy (−376 kJ/mol) compared to that of NO_3^- (−329 kJ/mol) [19,22,23]. This explanation is based on a theory suggesting that an ion with a lower hydration energy can strip and rearrange the water shells surrounding it and fit more easily into the membrane pores [24–27]. More recently, Richards et al. [28] used molecular dynamics simulations to show that partial dehydration controls the transport of several anions (including Cl^- and NO_3^-) through NF membranes. However, in a follow-up experimental investigation by the same group [29], the difference between the dehydration degree of Cl^- and NO_3^-, which was evaluated by determining the activation energy for the anion passage through the membrane, was found to be very small and inconsistent for different types of membranes.

Another explanation attributed the higher rejection of Cl^- to the higher degree of hydration of the NO_3^- ion, which reduces its effective surface charge and therefore also its retention [30,31]. However, this explanation is questionable since Cl^- has a higher hydration energy than NO_3^-. A couple of older studies speculated that NO_3^- has higher affinity to the membrane polymer than Cl^- [32,33]. The variety of explanations presented indicates that the reason for the difference in rejection of Cl^- and NO_3^- in NF is still not well understood and emphasizes the need for a more systematic investigation to address this issue.

The main objective of this study is to systematically investigate the mechanisms leading to the difference in rejection of Cl^- and NO_3^- in NF. Specifically, we have studied the effect of membrane charge on the rejection of the two anions by using a charged polyamide NF membrane and an uncharged cellulose acetate NF membrane. We also evaluated the activation energy for the passage of Cl^- and NO_3^- through the two membranes. Our results suggest that both charge- and size-exclusion mechanisms promote higher rejection of Cl^- than NO_3^- and lead to a maximum Cl^- to NO_3^- rejection ratio near the isoelectric pH. The implications of these results for membrane design, to increase the Cl^- to NO_3^- rejection ratio, were evaluated and discussed.

2. Materials and methods

2.1. Materials and chemicals

Two commercial NF membranes were used for the tests: polyamide NF270 (Dow FilmTec) and cellulose acetate CK (GE Osmonics). According to the manufacturers, the NF270 and CK membranes have molecular weight cut-offs of approximately 400 and 2000 Da, respectively. The NF270 membrane was also used as the substrate for membrane modification. Poly (sodium styrene sulfonate) (PSS; MW 70,000 g/mol), poly (diallyl dimethyl ammonium chloride) (PDADMAC; MW 150,000–200,000 g/mol, 20 wt% in water), poly (allyl amine hydrochloride) (PAH; MW 450,000 g/mol), poly (acrylic acid) (PAA; MW 100,000 g/mol), and sodium nitrate ($NaNO_3$) were purchased from Sigma-Aldrich. Sodium chloride (NaCl), isopropanol, and glycerol were purchased from J.T. Baker Chemicals. Hydrochloric acid (HCl) was purchased from AmericanBio, and sodium hydroxide (NaOH) was purchased from Macron Fine Chemicals. Deionized water (MilliPore Academic A-10, resistance 15 MΩ-cm) was used for preparing solutions, compaction of membranes, and rinsing the NF system.

2.2. Nanofiltration system and anion rejection experiments

A bench-scale system operating in cross-flow mode with a flat sheet membrane cell was used for all membrane tests. The total surface area of the membranes tested was 20.02 cm^2. Water was recirculated from the feed tank over the membrane cell with an applied inlet pressure between 3.4 and 5.5 bar (50 and 80 psi) (the specific pressure applied for each experiment is indicated in Section 3) and cross flow velocity of 21.4 cm/s. Before use, the commercial membranes were agitated in 25% isopropanol solution for 30 min using a rotating shaker. Then, the membranes were rinsed with deionized water three times (each time for 30 min) and kept overnight in deionized water to remove impurities. Prior to filtration, all membranes (commercial and modified) were compacted overnight under pressure between 4.8 and 6.9 bar (70–100 psi). Except for the experiments to determine the activation energy for anion transport through the membranes (Section 3.2), water temperature was maintained constant at 25 °C. For the experiments to determine the activation energy, temperature was increased gradually from 25 °C to 40 °C and samples were taken at four different temperatures of 25, 30, 35, and 40 °C. Feed solution pH was monitored and adjusted throughout all experiments using hydrochloric acid or sodium hydroxide. For each membrane test, feed and permeate were collected for Cl^- and NO_3^- analysis by ion chromatography (Dionex DX-500 with an AS14A IonPac column). All experiments were carried out with deionized water amended with NaCl and/or $NaNO_3$.

2.3. Determination of energy barrier for anion transport in NF

In order to calculate the activation energy for Cl^- and NO_3^- passage through the membrane, the solute flux (J_{solute}) was first calculated at four different temperatures of 25, 30, 35, and 40 °C using

$$J_{solute} = J_w C_p \tag{1}$$

where J_w is the water flux through the membrane (L m^{-2} h^{-1}) and C_p is the permeate anion concentration (mmol L^{-1}). The activation energy, E_a, was then calculated from the linearized form of the Arrhenius equation:

$$J_{solute} = B \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

$$\ln\left(J_{solute}\right) = \ln(B) - \frac{E_a}{R}\frac{1}{T} \tag{3}$$

where J_{solute} is the solute flux, B is the pre-exponential factor, R is the gas constant, and T is the absolute temperature.

2.4. Surface modification of NF membrane by layer-by-layer self-assembly process

Prior to membrane modification by layer-by-layer (LbL) assembly, the NF270 substrate was soaked in 25% v/v isopropanol solution as described in Section 2.2. The pristine membrane was carefully cut into a suitable size and placed on a handmade, specially designed rectangle holder with the active surface layer facing up and held tightly to expose the effective membrane area.

Four different polyelectrolyte solutions were used for surface modification via LbL assembly (Table 1). First, the aqueous solution of cationic polyelectrolyte was contacted with the active surface of the NF270 substrate for 30 min. The excess cationic polyelectrolyte

Table 1
Polyelectrolyte type, pH, polyelectrolyte concentration and salt concentration (sodium chloride) of the deposition solutions used during LbL assembly. The pH of the deposition solution was not adjusted. The polyelectrolyte and salt concentration used in this study were reported previously [35–37].

Solution	pH	Polyelectrolyte concentration (M)	Salt concentration (M)
PSS (-)	6.45	0.02	0.5
PAA (-)	3.15	0.02	0.5
PAH (+)	4.65	0.02	0.5
PDADMAC (+)	6.0	0.02	0.5
NaCl (rinsing solution)	5.6	–	0.5

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