The role of membrane surface charge and solute physico-chemical properties in the rejection of organic acids by NF membranes

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Abstract

The objective of this study was to investigate the contribution of electrostatic interactions to the rejection of selected organic acids by nanofiltration membranes. Effective membrane surface charge (determined by two methods of zeta potential measurements) of two commercial nanofiltration membranes was examined at different pH values and feed water chemistries. Six different organic acids were selected for this study representing typical physico-chemical properties of emerging organic trace pollutants. Findings of this study indicated that the rejection of negatively charged organic acids was larger than expected based on steric exclusion and was primarily driven by the surface charge of the membrane and correlated with the degree of ionization of the solute. Increasing feed water pH resulted in an increased negative surface charge, an increased percentage of solutes in the deprotonated state and an increased rejection through electrostatic repulsion. The rejection of the pharmaceutical residue ibuprofen, an organic acid with hydrophobic properties, was also pH dependent, but at pH values below the pK_a ibuprofen adsorbed and partitioned through the membrane. At pH above the pK_a, adsorption of ibuprofen was minimal due to an increased solubility and the dominant role of electrostatic repulsion. The presence of calcium in the feed water lowered the effective membrane surface charge (as determined by electrophoretic mobility measurements) of both membranes tested, however, rejection of negatively charged organic solutes decreased only for membranes with a molecular weight cut-off larger than the solute molecular weight.
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1. Introduction

A partial rejection of organic micropollutants such as pesticides, endocrine disrupting compounds, or pharmaceutical residues is becoming an important concern during water and wastewater treatment applications where nanofiltration (NF) or reverse osmosis (RO) treatment is employed. Therefore, understanding the factors driving the rejection of organic micropollutants is essential in order to assess treatment efficiencies a priori. Previous studies on the rejection of organics by NF and ultra-low pressure reverse osmosis (ULPRO) membranes reported that the retention of solutes depends upon both solute properties (i.e., size, polarity and charge) and membrane properties (i.e., pore size, charge and hydrophobicity) [1–8]. Recent studies on the rejection of organic compounds by RO and NF membranes have reported a high rejection of negatively charged organic solutes as a result of electrostatic interactions between membrane and solute [1,7,9]. Investigations, however, on the mechanisms behind the rejection of organic acids, especially the role of membrane and solute properties, is limited. Ozaki and Huafang [9] and Berg et al. [1] reported that the rejection of organic acids increased with increasing pH relative to the solutes disassociation constant (pK_a). Numerous studies focusing on the role of membrane surface charge have reported that most thin film composite membranes have a negative charge at neutral pH due to deprotonated acidic functional groups which are added during the manufacturing process to increase the selectivity and flux of ULPRO and NF membranes [1,9–15]. Membrane surface charge has been found to vary between membranes and is dependent upon feed water chemistry including pH,

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electrolyte concentrations, and the presence of natural organic matter [12–19]. The rejection of inorganic ions such as sodium, magnesium, perchlorate (ClO_4^-), and heavy metals is reported to increase during conditions favoring a membrane surface charge that can electrostatically repulse the ion being studied [12,13,15–17]. Other researchers have reported that increasing the concentration of divalent cations in feed water can both reduce the charge of a membrane and the rejection of inorganic ions [13,16,17]. Recent studies by Childress and Elimelech [12], Yoon et al. [16,17] and Hagmeyer and Gimbel [20] have attempted to relate membrane surface charge properties to inorganic ion separation performance. However, little has been reported in terms of membrane surface charge and its role in the rejection of negatively charged organic solutes.

The scope of this study is to mechanistically investigate the effect of membrane surface charge of two commercial NF membranes on the rejection of selected organic acids representing a typical range of physico-chemical properties of emerging contaminants such as pharmaceutical residues and endocrine disrupting compounds. The surface charge of the two NF membranes was investigated as a function of feed water pH and calcium concentrations. The rejection of six organic acids representing different molecular weights (MW), molecular sizes (molecular width, MWd), acidities (i.e., pK_a), and hydrophobic properties (measured as the octanol–water distribution coefficient, K_{ow}) was studied for different feed water matrices.

2. Experimental approach

2.1. Membranes utilized in this study

Two thin film composite polyamide membranes (NF-90 and NF-200) were obtained from Dow/Filmtec (Midland, MI) and evaluated in this investigation. Both membranes were tested as flat sheet membrane specimens in a commercial SEPA II crossflow filtration test cell (Osmonics, Minnetonka, MN). Prior to experiments, specimens were thoroughly rinsed in Type I water (Milli-Q grade) and stored at 5 °C. The crossflow filtration test cell permitted testing of a single membrane cut-out (9.5 cm × 14.6 cm) under tangential feed flow conditions with a channel height of 0.79 mm. All relevant membrane properties are presented in

Table 1
Membrane characteristics

Membrane type	NF-90	NF-200
Manufacturer	Dow/Filmtec	Dow/Filmtec
Classified as	NF	NF
Material	Polyamide	Polyamide
MWCO (manufacturer)	200	300
NaCl rejection (%)	95	60
Test pressure (psi)	70	65
Recommended pH range (manufacturer)	4–11	4–11
Membrane charge (pH 7)	Negative	Negative
Pure water permeability (L/(m² day kPa) at 25 °C)	2.49	1.2
Contact angle (°)	63.2	30.3
Morphology description	Rough, fibrils, pores	Smooth, defects
Mean roughness (nm)	63.86	5.19
Surface outer pore size (nm)	38	Non-detectable
Standard deviation of pore size (nm)	28	Non-detectable
Surface porosity	1.59E−03	Non-detectable

Table 1. The NF-90 membrane was developed to achieve a high removal of salts, nitrate, iron and organic compounds from feed water. The NF-200 membrane is classified as a softening membrane that can remove a high percentage of organic compounds. All membrane experiments were carried out at a feed pressure of 550 kPa (80 psi) and a feed flow rate of 500 mL/min resulting in a superficial feed channel velocity of approximately 11 cm/s and a recovery of 9% for the NF-90 and 3% for the NF-200, respectively. Type I water (Milli-Q grade) was used to prepare synthetic water solutions for single solute rejection experiments.

2.2. Solute analysis

The organic acid solutes evaluated during this study were chosen to represent a range of molecular size parameters (MW and MWd) as well as acid dissociation constant (pK_a) values in order to investigate the influence of size and charge on rejection (Table 2). Additionally, the organic acids evaluated during this study have molecular size and acidic characteristics similar to many emerging trace organics found in water and wastewater. A Hewlett-Packard 1040A fluorescence detector (Palo Alto, CA) was employed to quantify 1,4-dihydroxybenzoic acid, 2-naphthalenesulfonic acid, 1,5-

Table 2
Physico-chemical properties of target compounds

Compound	MW (g/mol)	MWd (Å)[a]	pK_a	log K_{ow}
2,4-Dihydroxybenzoic acid	154	5.38	3.1, 9.1, 15.6	1.63
2-Naphthalenesulfonic acid, sodium salt	208	5.46	n/a	0.63
1,5-Naphthalenedisulfonic acid, disodium salt	288	7.13	n/a	−3.15
Ibuprofen	206	5.04	4.91	3.72 (pH 10), −0.4 (pH 1)
Glutaric acid	132	3.16	4.34, 5.41	−0.29
Acetic acid	60	3.08	4.76	−0.17

[a] Estimated using chemical molecular modeling software package Hyperchem 7.0 (Hypercube, Gainesville, FL).