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The negative rejection of H^+ in NF of carbonate solution and its influences on membrane performance

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Abstract

Nanofiltration (NF) experiments were conducted with simulated solution containing bicarbonate hardness and with three membranes: NF90, NF270 and NF-. The operating pressure was kept at 1.0 MPa, the water sample temperature was kept at 25 °C, the velocity on membrane surface was approximately 1 m s^{-1} and the feeding pH values were 6.0, 6.5, 7.0, 7.5 and 8.0. Except for sampling, both the concentrate and the permeate were cycled to the feeding tank in order to keep the concentration constant. Experimental results demonstrated that the flux of NF90 membrane was slightly affected by the feeding pH, while the flux of NF270 and NF membranes was augmented when the feeding was acidified. The permeate pH of each membrane was always lower than the concentrate pH, indicating that the H^+ was negative rejected. This phenomenon was observed not only in the filtration of carbonate solution, but also in the filtration of the NaCl solution and the tap water. It is assumed that the small positive H^+ can easily permeate the NF membranes having negative charges. The more charges the membrane has, the more H^+ is negative rejected. High permeability of H^+ can speed decomposition of HCO_3^- into CO_3^{2-} and then accelerate $CaCO_3$ crystallization on membrane surface, which is unfavorable for membrane performances. In NF processes, it is better to considerate the membrane's selection and the feeding's pretreatment simultaneously, and it is beneficial for preventing scaling when selecting the membranes with less negative charges if only the water qualify can meet the demands.

Keywords: Negative rejection; Nanofiltration; Ca^{2+} rejection; pH value; Scale

1. Introduction

Nanofiltration (NF) is a pressure-driven membrane process falling between reverse osmosis and ultra-filtration in its separation characteristics. NF membranes can reject many kinds of organic matters and multivalent ions while mono-valent ions such as Na^+ and Cl^- are relatively easy to permeate (Raman et al., 1994; Bowen and Mohammad, 1998; Van der Bruggen et al., 1999; Lee and Lee, 2000). NF is not only used widely in the concentration and separation processes, but also applied in the water supply to remove hardness, heavy ions and most of the organic matters.

The separation by NF membranes occurs primarily due to size exclusion and electrostatic interactions (Raman et al., 1994; Schäfer et al., 1998; Peeters et al., 1998, 1999; Childress and Limelech, 2000). For uncharged molecules, sieving or size exclusion is the most responsible for separation; for ionic species, both sieving and electrostatic interactions are responsible for separation. Membrane surface and pore charge characteristics play a significant role in the transportation of water and solute molecules through the NF membrane.

Membrane flux, J_v, determined by membrane properties and operating conditions, can be expressed by a non-equilibrium thermodynamic equation as shown in Eq. (1). (Schäfer et al., 1998; Pouliot et al., 1999; Mehiguene et al., 1999; Yamauchi et al., 2000):

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Nomenclature

A_k	the membrane porosity, dimensionless
J_s	the solute flux, mol m^{-2} s^{-1}
J_v	the volumetric permeate flux, m s^{-1}
$J_{v,p}$	the volumetric permeate flux of the pure water, m s^{-1}
$K_{s,p}$	the dissolvent constant of $CaCO_3$, dimensionless
L_p	the solvent permeability, m Pa^{-1} s^{-1}
MWCO	the Molecular Weight Cut-off of the NF membranes
P	the solute permeability, used in the non-equilibrium thermodynamic model, m s^{-1}
R	the gas constant (8.314 J K^{-1} mol^{-1})
R_{obs}	the observed solute rejection, $\leqslant 1$
R_{real}	the real membrane rejection to solute, $\leqslant 1$
T	the absolute temperature, K
X	the membrane charge density, mol m^{-3}
c_b and c_p	the solute concentration in bulk solution and in the permeated solution, mol m^{-3}
$c_{m,p}$	the concentration on the permeate side of NF membrane surface, mol m^{-3}
c_m	the concentration on the bulk side of membrane surface, mol m^{-3}
pH_{con}	the pH values of the membrane concentrate
pH_{per}	the pH values of the membrane permeate
r_p	the hydrodynamic membrane pore radius, m
Δp	the trans-membrane pressure (TMP), Pa
Δx	the membrane thickness, m
$\bar{c}_m$	the mean concentration over the membrane thickness, mol m^{-3}
$\frac{dc}{dx}$	the concentration profile in the concentration polarization layer, mol m^{-4}
δ	the thickness of polarization layer, m
ε	the membrane porosity, dimensionless
μ_p	the permeate viscosity of the solution, Pa s
σ	the reflection coefficient of the membrane towards a particular solute with $0 < \sigma < 1$

$$\begin{cases} J_v = L_p(\Delta p - \sigma \Delta \Pi_m) \\ J_s = P(c_m - c_p) + J_v(1-\sigma)\bar{c}_m \end{cases} \tag{1}$$

$$L_p = \left(\frac{r_p^2}{8\mu_p}\right)\left(\frac{A_k}{\Delta x}\right) \tag{2}$$

$$\Delta \Pi_m \approx c_m RT \tag{3}$$

$$\bar{c}_m = \frac{c_m - c_p}{\ln \frac{c_m}{c_p}} \tag{4}$$

Solute rejection, R_{obs} or R_{real}, is a function of concentration across NF membrane, and has no direct relationship with the operating pressure. They can be defined as Eqs. (5) and (6), respectively. c_b, c_p, c_m and $c_{m,p}$ are shown in Fig. 1, and as $c_m > c_b$, R_{real} would be higher than R_{obs}.

$$R_{obs} = \left(1 - \frac{c_p}{c_b}\right) \times 100\% \tag{5}$$

$$R_{real} = \left(1 - \frac{c_{m,p}}{c_m}\right) \times 100\% \approx \left(1 - \frac{c_p}{c_m}\right) \times 100\% \tag{6}$$

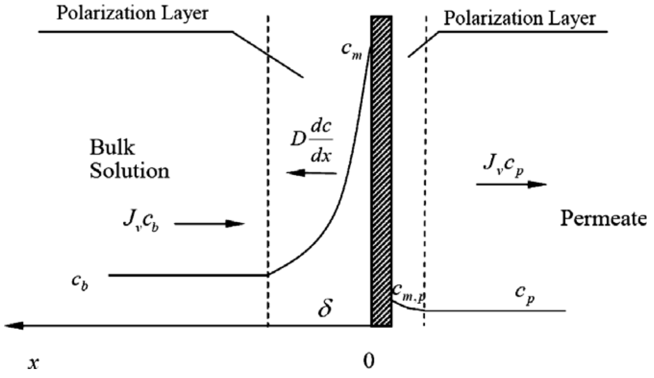

Fig. 1. Schematic diagram of the NF membrane filtration at certain moment (all of the solute exists as the ions).

NF membranes were initially developed for water softening. During the past decades, they are mainly applied to produce the drinking water (Van der Bruggen and Vandecasteele, 2003). While in water softening, scale caused by hardness ions often deteriorates the membrane performance, and pretreatments on membrane feeding are practically adopted for preventing the scaling. For example, acidification is a simple way to deter the formation of sparingly soluble salts such as the carbonate. It was found that acidification to membrane feeding could really improve membrane flux, while in our experiments, a very interesting phenomenon that H^+ was always negative rejected was observed, no matter what operation conditions were and what the feeding pH was. Although small ions such as Cl^- or low-molecular organic materials (e.g., carboxylic acid) were often observed to be negative rejected (Karode et al., 2000; Yaroshchuk, 2000; Gilron et al., 2001; Koops et al., 2001; Kang and Chang, 2005), the negative rejection of H^+ was rarely reported. It may be helpful for other researchers in this field if the phenomenon of the negative rejections of H^+ can be reported publicly.

In this paper, the NF processes were conducted with simulated bicarbonate solution under five pH conditions, and a theoretical discussion was made on the influence of H^+ permeability on membrane performances.

2. Experiments

2.1. Experimental process

The initial experimental objection was to compare membranes' performance on filtration of bicarbonate hardness solution under different feeding pH values, and a bench-scale NF unit, schematically represented in Fig. 2, was used