Nanofiltration separation of polyvalent and monovalent anions in desalination brines

A. Pérez-González [a], R. Ibáñez [a], P. Gómez [b], A.M. Urtiaga [a], I. Ortiz [a,*], J.A. Irabien [a]

[a] Chemical and Biomolecular Engineering Department, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain
[b] APRIA Systems S.L., Polígono Trascueto, s/n, 29600 Camargo, Cantabria, Spain

ARTICLE INFO

ABSTRACT

This work, as part of a global membrane process for the recovery of alkali and acids from reverse osmosis (RO) desalination brines, focuses on the nanofiltration (NF) separation of polyvalent and monovalent anions, more specifically sulfate and chloride. This pretreatment stage plays a key role in the whole recovery process. Working with model brines simulating the concentration of RO concentrates, 0.2–1.2 M chloride concentration and 0.1 M sulfate concentration, the experimental performance and modeling of the NF separation is reported. The study has been carried out with the NF270 (Dow Filmtec) membrane. The effect of operating pressure (500–2000 kPa), ionic strength (0.4–1.3 M) and chloride initial concentration (0.2–1.2 M) on the membrane separation capacity has been investigated. Finally, the Donnan Steric Pore Model (DSPM) together with experimentally determined parameters, effective pore radius (r_p), thickness of the membrane effective layer (δ) and effective membrane charge density (X_d), was proved accurate enough to satisfactorily describe the experimental results. In this work we provide for the first time the analysis of partitioning effects and transport mechanism in the NF separation of sulfate and chloride anions in concentrations that simulate those found in RO desalination brines.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the context of desalination, RO membrane technology has been developed over the past 40 years, being the leading technology for new desalination installations. Water shortage problems in dry inland regions are increasingly satisfied through RO desalination of brackish groundwater's resources. Exploitation of brackish groundwaters is advantageous due to the lower salt concentration of the inlet water compared to seawater, which reduces the osmotic pressure to be overcome and the energy consumption [1]. However, the management of concentrates is an important drawback because brine discharges from inland installations still remains being a problem with not many feasible alternatives [2]. In coastal desalination plants, brines are directly discharged to the sea, posing adverse environmental effects on the receiving marine environment [3].

Alternatives aiming at zero liquid discharge, through combination of different technologies, are highlighted as the most promising management options [4]. In this work a sequential process based on the appropriate combination of membrane technologies is proposed with the aim of reducing the adverse environmental impact of brine discharge, together with the recovery of valuable products contained in the concentrated brine, namely alkali and acids. The strategy to achieve this goal implies, first, a pretreatment step of the brine to remove scaling salts and impurities, followed by bipolar membrane electrodialysis (BMED) to recover hydrochloric acid (HCl) and sodium hydroxide (NaOH). This technology has proved to be technically feasible for the production of 1.0 M or higher acid and alkali solutions [5].

Thus, this work is focused on the pretreatment stage, specifically on the separation of sulfate from the brine to avoid its negative effects in BMED. For this purpose, NF has been selected and considered a potential and effective alternative.

Nanofiltration is a pressure driven membrane separation process with intermediate separation effectiveness between RO and ultrafiltration (UF). NF membranes are typically polymeric, asymmetric and consist of a low resistance support layer with a functionally active porous top layer [6,7]. NF membranes have properties that combine size and electrical effects. The pores are typically near 1 nm in diameter and have fixed charges. Due to these characteristics, NF membranes retain multivalent complex ions and permeate small uncharged solutes and low charged ions [8–10]. This, along with the small energy consumption of the process and the high fluxes attained, makes NF membranes extremely useful in fractionation and selective removal of solutes

from complex process streams [11]. However, the description of membrane NF separations is extremely complex and is dependent on the micro-hydrodynamics and interfacial events occurring at the membrane surface and within the membrane nanopores [12]. There is significant debate as to the exact nature of these complex phenomena, and the rejection is typically attributed to a combination of steric and electrical effects [6]. Modeling of transport through membranes is an essential engineering aspect; although many models for nanofiltration have been proposed by several researchers [13–18], a realistic model that describes rejection of charged molecules has never been well established [19]. Thus, this work investigates experimentally and theoretically the NF separation of sulfate and chloride co-ions from highly concentrated solutions providing the tools needed for the design and optimization of the recovery of brackish and seawater RO desalination brines.

2. Experimental materials and methods

2.1. Chemical characterization of brines

The salinity of brackish groundwaters ranges from 1000 to 8000 mg/L of total dissolved solids (TDS) while the value for marine water is typically around 35,000 mg/L TDS [20]. However, constituent concentrations in the RO brines are found to be double or higher than in feed water. In this study, RO brines obtained from a brackish water desalination plant (Cuevas de Almanzora) and from two seawater desalination plants (Carboneras and Las Aguilas) located in Spain were taken as reference to set the ionic concentration (Table 1) of model brines used in NF experiments. The concentration of chloride, sulfate and nitrate was determined by ion chromatography (Dionex ICS-1100, Sunnyvale, CA, USA). The concentration of phosphate was determined by the ascorbic acid method according to Standard Methods 4500-PE. The concentration of cations was determined by Inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Perkin Elmer Plasma Emission Spectrometer ICP 400, Connecticut, USA), except for concentration of iron and manganese, which was determined by atomic absorption spectroscopy (AAS) (Perkin Elmer 3110, Connecticut, USA). The pH was measured by using a portable pH-meter (Crison pH 25) and conductivity and TDS with a portable conductivity meter (HACH sesION 5). Hardness was determined by EDTA titrimetric method according to Standard Methods 2340 C.

The concentration of carbonates and bicarbonates was measured by titration method according to Standard Method 2320 B.

Given the high ionic concentration of desalination brines of Table 1 it is concluded that any recovery process needs of the separation and purification steps where the valuable compound, chloride in the present case, is separated from other major and minor components. Alkali precipitation, with partial use of the recovered NaOH in BMED, would be the most suitable option for hardness removal at industrial level. The high concentration of sulfate in the analyzed brines is a consequence of the geological characteristics of the area, rich in gypsum. The experimental part of this study has been carried out using model brines with a fixed sulfate content of 8000 mg/L (0.1 M), the most unfavorable condition for its separation, and chloride concentrations in the range from 5000 mg/L to 40,000 mg/L (0.2–1.2 M) in order to cover the concentration range of brines from brackish water desalination to seawater desalination. Specifically, four synthetic brines with molar ratios chloride/sulfate: $\alpha = 1.7$, 5.1, 10.2 and 13.6 were prepared in order to evaluate the effect of operating pressure and ionic strength in sulfate and chloride rejection, and also the influence of initial chloride concentration in sulfate rejection was evaluated.

2.2. Streaming potential measurement

The streaming potential was measured with a SurPASS electrokinetic analyzer UAnton (Anton Paar, Barcelona; Spain). All the measurements were carried out at pH 6. Streaming potential is usually measured using as electrolyte KCl solutions in a low concentration range (0.001–0.01 M) as reported in literature for the membrane NF270 used in this study [21–27]. However, those electrolyte solutions are not representative of the conditions applied in this study during NF operation. So, in this work a somewhat modified procedure was followed based on the fundamentals of surface charge of NF membranes. It is known that a polymeric membrane acquires surface charge when brought into contact with an aqueous medium [28]. Therefore, NF270 membrane samples were immersed in the model brines for 24 h to allow the active layer to acquire the corresponding charge [29,30]. After this time, the streaming potential was determined using 0.1 M NaCl as electrolyte, that is the maximum acceptable concentration according to the operating restrictions of the equipment. This experimental protocol was developed to be able to measure the streaming potential established in high saline

Table 1
Average chemical characterization of the RO brines of three desalination plants: Cuevas de Almazora, Carboneras and Las Aguilas. Values of the standard deviation of the analytical techniques are given within brackets.

Parameter	Desalination plants		
	Cuevas de Almanzora	Carboneras	Las Aguilas
pH	7.9 (0.01)	8 (0.01)	9 (0.01)
Conductivity (µS/cm)	34,300 (0.5)	95,500 (0.5)	96,160 (0.5)
Hardness (mg CaCO$_3$/L)	13,000 (0.04)	18,000 (0.14)	16,400 (0.09)
TDS (mg/L)	20,700 (0.5)	70,000 (0.5)	70,488 (0.5)
Chloride (mg/L)	7279 (0.10)	37,955 (0.20)	38,887 (9.38)
Sulfate (mg/L)	8465 (0.06)	7243 (0.50)	5316 (0.29)
Nitrate (mg/L)	447 (0.01)	0 (0.00)	1.8 (0.04)
Phosphate (mg/L)	0.3 (0.03)	0.025 (0.01)	–
Sodium (mg/L)	5176 (0.24)	17,020 (0.29)	21,922 (5.85)
Magnesium (mg/L)	1589 (0.47)	2715 (0.40)	2479 (0.14)
Calcium (mg/L)	1828 (0.46)	796 (0.22)	791 (0.04)
Potassium (mg/L)	178 (0.59)	816 (0.51)	743 (0.25)
Carbonate (mg/L)	0 (0.00)	18 (0.00)	155 (0.00)
Bicarbonate (mg/L)	826 (0.07)	217 (0.04)	173 (0.07)