

Water Recovery by Forward Osmosis from Challenging Industrial Effluents towards Zero Liquid Discharge: Selection of a Suitable Draw Solution

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Abstract

In the light of growing global water stress water, recycling is becoming ever more important. Zero liquid discharge is a concept that aims to recover all water from a wastewater stream. Since conventional thermal evaporation requires much energy, more efficient technologies are needed, such as forward osmosis (FO) in combination with draw solution (DS) recovery techniques. In this research, water from a real industrial secondary effluent was subjected to a treatment chain of ultrafiltration, reverse osmosis, and FO. The study aimed at the selection of a suitable DS. Fluxes and reverse solute flows of three 1 M DS (NaCl, Na₂SO₄, MgCl₂) were compared. The combination of water pre-treatment by softening methods, together with the use of MgCl₂ promises highest fluxes at low reverse solute flows.

Introduction

Ever increasing water stress levels demand for the development of efficient technologies to recover and recycle water. In some cases, industries may even be obliged to a zero liquid discharge (ZLD). ZLD is conventionally reached by applying energy-intensive thermal processes. The energy efficiency can be augmented by membrane technologies, such as reverse osmosis (RO), forward osmosis (FO) or membrane distillation (MD) [1].

Forward osmosis is a technology using an osmotic pressure π difference as driving force to draw specific constituents of a feed over a semi-permeable membrane. One advantage is lower irreversible fouling on the FO membrane compared to mechanical pressure driven RO [1–3]. Additionally, FO can be coupled i.e. with MD, allowing for the use of low grade heat for draw solution (DS) recovery [3].

However, the selection of a suitable DS salt is not easy: it should, besides other properties, be cheap, non-toxic, (completely) recoverable, have a low reverse solute flow, but a high mobility to minimize internal concentration polarization [3].

The objective of this study is to identify a suitable DS in lab tests for FO of secondary effluent from a real wastewater treatment plant (WWTP) of a chemical industry pre-concentrated by RO. The wastewater characteristics are discussed and pre-treatment methods suggested before FO. Fluxes and permeabilities of different 1 M DS are compared (NaCl, Na₂SO₄, MgCl₂) and corresponding reverse solute flows are investigated.

Material and Methods

A secondary effluent sample of the industrial WWTP was used for all FO lab-scale experiments. It was taken on 13.12.2016 and shipped to the lab without cooling within two weeks. The wastewater was analyzed by ICP-OES (Spectro Analytical Instruments). Anion concentrations were determined by the ion chromatograph ICS-2100 (Dionex, USA). Total organic carbon

(TOC) and total inorganic carbon (TIC) were measured on a Shimadzu TOC-V (Shimadzu Corp., Japan). PHREEQC (USGS, USA) was used with the included IInI database to predict potential scalants [4]. The osmotic pressure π of the feed was estimated by converting EC to π with online tools [5], [6], π of DS were calculated from the literature [7].

The wastewater was pre-treated by UF and RO up to individual recovery rates of 85% and 50%, respectively. The RO retentate was softened before further concentration by FO.

Soda ash treatment was performed by adjusting the pH to 9 – 10 with NaOH and Ca²⁺-overstoichiometric dosage of Na₂CO₃. After stirring for at least 0.5 h, the water was filtered (Whatman 589, GE Healthcare, UK), then adjusted to pH 3 – 4 with HCl and CO₂ was stripped by bubbling N₂ for at least one hour.

Draw solutions were prepared freshly on the day of use. Analytical-grade NaCl, Na₂SO₄ or MgCl₂ was mixed with deionized water in a 1 M concentration. For the DS make-up solution, the same solutions were prepared in higher concentrations. The experimental set-up was similar as in published research, i.e. [8].

Feed and DS were adjusted to 25 °C by a tempering bath. Gear pumps were set to a flow rate of 450 mL/min, corresponding to a Reynold's number of about 760 in the membrane cell for clean water. Experiments were performed in counter-current flow in FO mode.

UF membranes were purchased from MicroDyn Nadir, Germany. Commercially available RO membranes were provided by DOW Water & Process Solutions, Spain. PA composite flat sheet FO membranes were provided by Toray Chemical Korea Inc., Korea.

Results and Discussion

Average characteristics of the secondary WWTP effluent are summarized in table 1. The TOC is high, therefore strong organic fouling is expected. Calcium and carbonate concentrations pose very high scaling risks by calcium carbonates. PREEQC also predicts gypsum precipitation at recovery rates around 85%. It is hence necessary to pretreat the water e.g. by softening.

Table 1: Secondary WWTP effluent characteristics in the period of 29.12.2016 – 20.06.2017, provided by the WWTP operator.

Parameter	Unit	Average	Standard deviation
pH	-	7.9	0.2
EC	mS/cm	11.79	1.52
TOC	mg/L	147	56
COD	mg/L	463	122
BOD ₅	mg/L	26	14
Tot. N	mg/L	19	14
Tot. P	mg/L	1.0	0.5
Cl ⁻	mg/L	3203	1020
HCO ₃ ⁻	mg/L	524	130
SO ₄ ²⁻	mg/L	377	158
Li ⁺	mg/L	0.032	0.026
Na ⁺	mg/L	2053	500
Ca ²⁺	mg/L	196	74

Figure 1 shows the measured flux during FO treatment along with the corresponding osmotic pressure difference $\Delta \pi$ and permeability for MgCl₂ as DS. $\Delta \pi$ decreases linearly. This is explained by the increasing π in the feed during water recovery. In contrast, the flux shows a non-linear decreasing behavior due to more pronounced internal and external concentration polarizations at higher $\Delta \pi$, as described before [9].

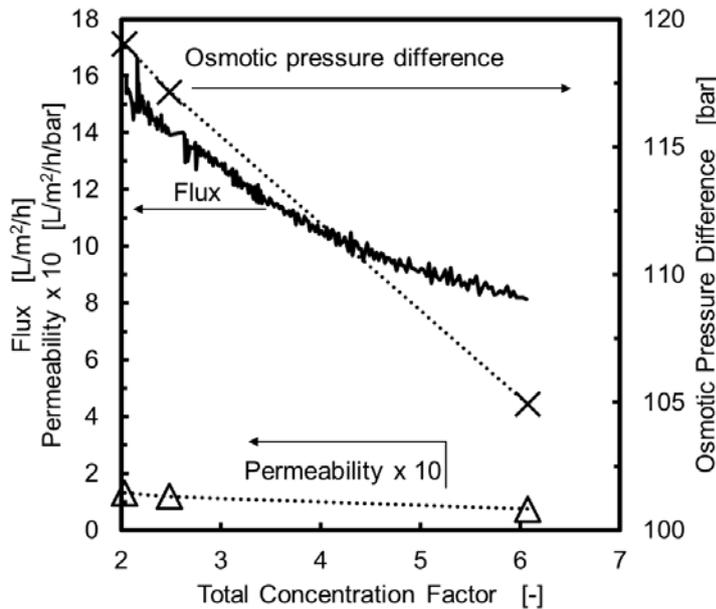


Figure 1: Recovering water from RO retentate by FO with 1 M MgCl₂ as DS. The total concentration factor starts at two due to pre-concentration of the feed by RO with 50 % recovery.

Table 2 compares interpolated fluxes and permeabilities for all investigated DS at a total concentration factor *CF* of 3. The *CF* compares initial and actual retentate volumes:

$$CF = \frac{V_{Ret,0}}{V_{Ret.}}$$

The Mg-salt provides the highest fluxes, since NaCl and Na₂SO₄ both have a π of around 50 bar in an 1 M solution compared to MgCl₂ with 128 bar [7]. However, the sodium salts have permeabilities of more than twice the value of MgCl₂ due to the described concentration polarization effects.

Table 2: Comparison of fluxes, osmotic pressure differences $\Delta \pi$ and permeabilities for tested draw solutions at total concentration factor of three (recovery: 67%). Results interpolated from measured data.

DS	Flux	Osmotic pressure difference	Permeability
[-]	L/(m ² ·h)	bar	L/(m ² ·h·bar)
MgCl ₂	13.0	115	0.113
Na ₂ SO ₄	8.08	33.4	0.242
NaCl	9.63	35.1	0.274

Some results allowing estimates about the RSF are shown in figure 3. Surplus species concentrations Δc_i were calculated by the following equation:

$$\Delta c_i = \frac{c_i - c_i^*}{CF_{FO}}$$

c_i denote the measured concentration of a species *i* after FO, c_i^* is the expected concentration of species *i* at the concentration factor CF_{FO} , and CF_{FO} signifies the factor by which the RO retentate is concentrated during FO.

$$c_i^* = c_{i,0} \times CF_{FO}$$

where $c_{i,0}$ is the concentration of species *i* at the beginning of FO treatment.

NaCl-species can be detected in the feed after FO concentration in much higher specific concentrations than those of both salts containing bivalent ions, namely SO₄²⁻ and Mg²⁺. These are hindered to pass the membrane due to the Donnan effect.

Na⁺ from NaCl and Na₂SO₄ apparently passes the membrane more easily than their salt counter-ions. This is explained by the pre-treatment at low pH to de-carbonize the wastewater. Feed and DS have different pH at the beginning of the FO (i.e. for NaCl, 4.3 and 5.9, respectively). Hence, H⁺ ions permeate from feed to DS to equalize the H⁺ concentration gradient. In order to maintain charge balance, Na⁺ reversely flows from the DS to the feed. For MgCl₂, this leads to very low RSFs, since the H⁺ substitute would be Mg²⁺, which is sterically hindered to pass the membrane.

RSF of a salt A_xB_y was calculated by the following equation:

$$j''_{\text{Rev}} = \min\left(\frac{\Delta c_A}{x}, \frac{\Delta c_B}{y}\right)$$

A and B describe chemical elements, x and y denote their count in one salt molecule. Assuming no precipitation on the feed side, a RSF of 20.2 mM/CF, 2.7 mM/CF and 1.5 mM/CF was measured for NaCl, Na₂SO₄ and MgCl₂, respectively. Surplus ions exceeding j''_{Rev} must be substitutions for H⁺ or other cations here, namely 39.6 mM/CF Na⁺, 5.5 mM/CF Na⁺ and 0.7 mM/CF Mg²⁺ for NaCl, Na₂SO₄ and MgCl₂, respectively. Substitution effects are expected to be of much lesser extend as soon as the pH values between feed and DS are equal. Changing pH in the feed may cause additional DS losses. A stable pH on the feed side is therefore a key to reduce RSF during long-term operation.

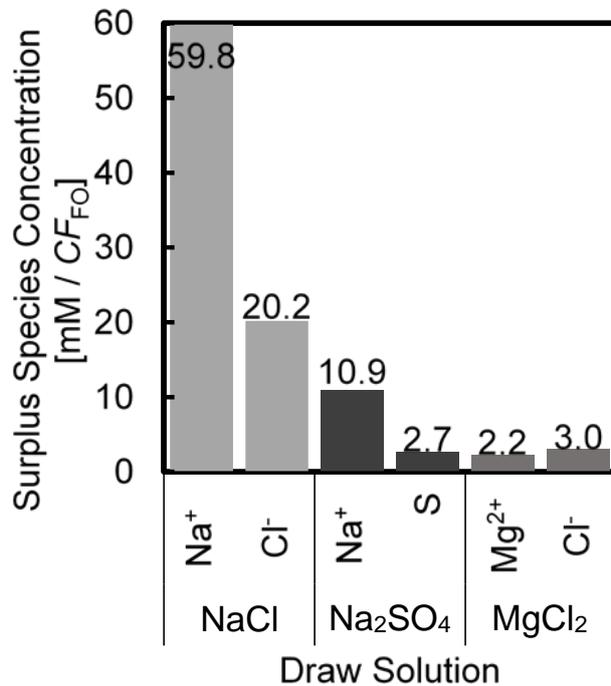


Figure 2: Surplus concentrations of 1 M draw solutions' species in the feed.

Conclusions

- As the investigated wastewater was very difficult (high risk of fouling and scaling), a pre-treatment with softening methods (soda ash treatment and de-carbonization) was suggested.
- The combination of the suggested pre-treatments along with MgCl₂ as a DS appears to be suitable for this specific case, allowing for a high flux at a low reverse solute flow.
- Further aspects have to be considered for an optimal process design, i.e. DS recovery. Lower π can enable more economic draw solution recovery strategies e.g. by RO or MD.

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