Forward osmosis for the treatment of reverse osmosis concentrate from water reclamation: process performance and fouling control

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ABSTRACT

While high quality water reuse based on dual membrane filtration (membrane filtration or ultrafiltration, followed by reverse osmosis) is expected to be progressively applied, treatment and sustainable management of the produced reverse osmosis concentrate (ROC) are still important issues. Forward osmosis (FO) is a promising technology for maximising water recovery and further dewatering ROC so that zero liquid discharge is produced. Elevated concentrations of organic and inorganic compounds may act as potential foulants of the concentrate desalting system, in that they consist of, for example, FO and a subsequent crystallizer. The present study investigated conditions under which the FO system can serve as concentration phase with the focus on its fouling propensity using model foulants and real ROC. Bulk organics from ROC consisted mainly of humic acids (HA) and building blocks since wastewater-derived biopolymers were retained by membrane filtration or ultrafiltration. Organic fouling of the FO system by ROC-derived bulk organics was low. HA was only adsorbed moderately at about 7% of the initial concentration, causing a minor flux decline of about 2–4%. However, scaling was a major impediment to this process if not properly controlled, for instance by pH adjustment or softening.

Key words | forward osmosis, fouling, RO concentrate treatment, scaling, water reclamation

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INTRODUCTION

While high quality water reuse based on dense membrane treatment is expected to be progressively applied in many regions of the world (GWI 2009), treatment and sustainable management of the produced reverse osmosis (RO) concentrate are still critical issues concerning dual membrane treatment. They limit the application especially in inland locations. High salinity alongside the concentrated organic and inorganic toxic compounds is dangerous to many plants and animals. Various concentrate treatment concepts have been proposed to minimize waste and maximize water recovery (Khan *et al.* 2009; Pérez-González *et al.* 2012). State-of-the-art treatment relies on evaporation ponds, falling film evaporators, crystallization, spray dryers, membrane distillation, discharge to the wastewater collection system, land application, deep well injection or disposal to surface waters (Asano *et al.* 2007). All available methods have serious shortcomings in terms of environmental and economic perspectives. It has been proposed that in the long term the only truly sustainable solution might be a complete recovery of the water and use of generated salts (Khan *et al.* 2009). This concept – known as zero liquid discharge, which has been applied to industrial water cycles (Vishnu *et al.* 2008) – typically involves energy-intense thermal processes to recover water and salts from the brine. Consequently the most pressing challenge to be overcome is the minimization of energy consumption.

As in other fields of application, membrane processes are promising treatment alternatives to thermal processes for further dewatering of reverse osmosis concentrate (ROC) with reduced energy demand. Besides electrodialysis and membrane distillation, forward osmosis (FO) has been studied as a strategy for sustainable brine treatment (Adham *et al.* 2007; Tang & Ng 2008; Martinetti *et al.* 2009; Zhao *et al.* 2012; McGinnis *et al.* 2013). Field & Wu (2013) contend that

water recovery from high salinity feeds is an important subject of future FO applications. Although attention has increasingly focused on FO for a number of applications in water and energy production, a number of critical challenges still prevail, particularly regarding the development of membranes with high flux, low fouling propensity and reverse solute diffusion, as well as design and implementation of draw solutions (DS) (Zhao *et al.* 2012; Klaysom *et al.* 2013). Another important aspect for FO in applying the zero liquid discharge principle is the impact of foulants on the concentrate desalting system, consisting of, for example, FO and a subsequent crystallizer (Adham *et al.* 2007) or a wind-aided intensified evaporation (WAIV) unit (Katzir *et al.* 2010).

Figure 1 presents an overview of the proposed potential treatment train involving FO and further crystallization stages. Insufficient removal of micropollutants by FO will require post-treatment of the FO permeate prior to blending with the RO permeate (Kazner *et al.* 2013).

Mi and Elimelech have studied several aspects of fouling and scaling, including organic fouling using model solutions (Mi & Elimelech 2010a), gypsum scaling (Mi & Elimelech 2010b) and silica scaling (Mi & Elimelech 2013). They have demonstrated the importance of appropriate arrangements to control fouling. While the general feasibility of FO for concentrate desalination has been studied to some degree (Adham *et al.* 2007; Tang & Ng 2008; Martinetti *et al.* 2009), the process behaviour concerning fouling and methods to prevent it when treating real ROC from water reclamation plants have received limited attention. The objective of this study is to elucidate under which conditions FO can dewater ROC leading to the production of zero liquid discharge where the focus is on the organic and inorganic fouling propensity of the FO system when treating real ROC from water reclamation.

MATERIALS AND METHODS

FO was applied for the dewatering of the ROC from the Sydney Olympic Park Authority's Water Reclamation and Management Scheme (WRAMS) water recycling plant. Tests were conducted in lab scale with a flat sheet FO unit using different membrane types (i.e. Hydration Technologies Inc. (HTI) cellulose triacetate (CTA) and thin-film composite (TFC) membranes) and reference model compounds (alginate and humic acids (HAs)) versus real ROC. Membrane performance was tested in FO mode and pressure-retarded osmosis mode.

Chemicals and reagents

For standard data evaluation and performance checking, analytical-reagent grade sodium chloride (NaCl) was supplied by Sigma Aldrich and used as received without any further treatment. DS and feed solution (FS) batches were prepared by dissolving measured quantities of these compounds in deionized water (DI) as described below. In all the experiments sodium chloride was used as DS as now applied in standard membrane characterization (Cath *et al.* 2013). The DS concentration was 1, 2, 3 or 4 molar HA was obtained as a commercial technical grade solid from Fluka (ash content 20%). A stock solution with a concentration of 4 g/L was prepared and filtered (Whatman filter paper 4) to remove any insoluble material. Subsequently its total organic carbon (TOC) concentration was measured and adjusted to the target concentration accordingly with DI water. Alginate was obtained from Sigma-Aldrich Australia. A 200 mg/L stock solution was prepared in DI water and diluted by adding DI to the required TOC concentration.
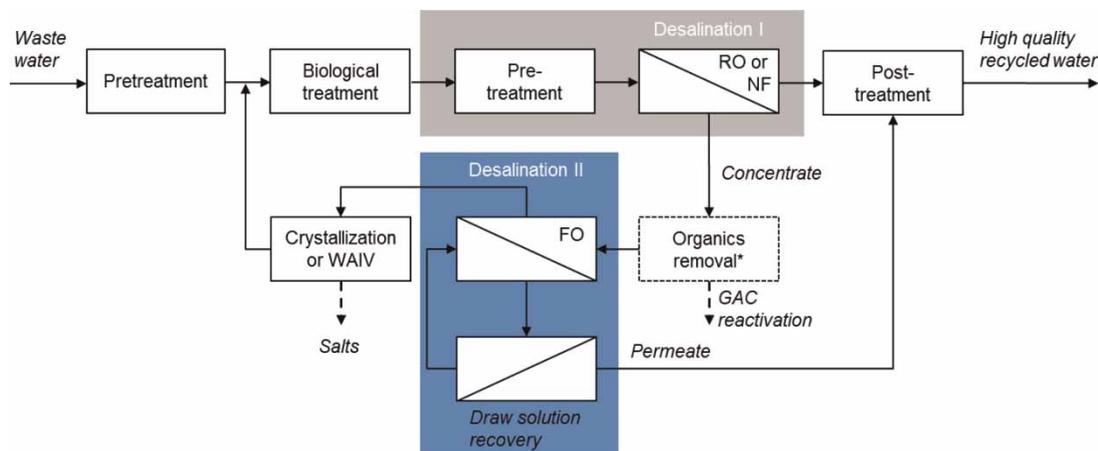

Figure 1 │ Schematic of proposed integrated water reuse concept (* = optional).

Characterization of the reverse osmosis concentrate

ROC was obtained from Sydney Olympic Park Authority's (SOPA) MF/RO water filtration plant, which operates with a volumetric feed flow of about 55 m³/h and a recovery of between 80 and 82%. Table 1 summarizes the typical levels of water quality and shows the concentrations of the sample used in this study. The sample was stored in 2 L glass bottles at 4 °C until usage in the respective tests.

Analytical methods

The electrical conductivity (EC) and pH of the draw and feed stream were measured using a manual pH meter (GMH 3430 Greisinger, Germany) and a manual conductivity meter (GMH 3530 Greisinger, Germany). All samples for chemical analysis were taken as grab samples at the beginning and end of the respective test runs. The samples were stored at 4 °C prior to analysis. The quantitative analysis of halogens (Cl^-, Br^-, F^-) was done using an ion chromatograph (IC-Metrohm 790 Personal IC, Herisau, Switzerland). Inductively coupled plasma optical emission spectrometry (Perkin Elmer OPTIMA 7300 DV, USA) was used to analyse a wider range of cationic and anionic elements in the ROC. Dissolved organic carbon (DOC) measurement was performed on a total organic carbon analyzer (multi N/C 3100, Analytik Jena AG, Jena, Germany). A liquid chromatography–organic carbon detection (LC-OCD) unit (DOC-Labor Dr. Huber, Germany) served for the advanced DOC characterization. The adsorbed TOC was determined as the difference between the initial TOC concentration and the normalized TOC concentration at the end of the test. The flux decline was calculated as the difference between the average flux during the fouling test and the average baseline flux, divided by the average baseline flux.

FO bench scale unit

A bench scale FO unit as shown in Figure 2 was employed for conducting the FO experiments. The cross-flow membrane unit featured a FO cell with a channel on both sides of the FO membrane (20 mm width × 3 mm height × 210 mm length), which transports the FS on one side of the membrane and the DS on the other side of the membrane. The flow velocity through each channel was controlled by a variable speed drive (Magnetic drive pump 316 SS, Cole-Parmer, USA). The targeted cross-flow rates for both the FS and the

Table 1 │ Average concentrations of water samples from SOPA's water treatment plant ($n = 3$, 2012) and ROC (2013) used in this study

		Typical concentrations in 2012				Sample for study
		MF Feed	RO Feed	RO Perm.	ROC	ROC
Recovery of RO					80%	82%
DOC	mg/L	6.58 ± 2	6.32 ± 0.6	0.19 ± 0.1	27.8 ± 1.5	38.0
UV254	1/m	0.17 ± 0.05	0.17 ± 0.01	0.01 ± 0.01	0.69 ± 0.02	0.78
pH	unit	6.8 ± 0.15	7.2 ± 0.34	5.6 ± 0.13	7.6 ± 0.16	7.8
EC	μS/cm	771 ± 273	723 ± 72	10.6 ± 3	3053 ± 673	3050
Calcium	mg/L	20.5 ± 0.8	22.2 ± 0.6	0.2 ± 0.1	95.2 ± 4.6	113
Magnesium	mg/L	7.3 ± 0.5	10.1 ± 0.4	0.08	44.6 ± 0.2	52.5
Potassium	mg/L	15.6 ± 0.7	15.6 ± 0.6	1.1 ± 0.1	64.3 ± 3.2	73.6
Sodium	mg/L	77.4 ± 2.2	88.1 ± 1.8	2.6 ± 0.2	372.5 ± 4.9	424
Iron	mg/L	0.13 ± 0.13	0.04 ± 0.03	< LOQ	0.15 ± 0.08	0.07
Silica as Si	mg/L	2.9 ± 0.1	2.7 ± 0.2	0.05	11.75 ± 0.6	11.6
Fluoride	mg/L	0.73 ± 0.1	0.85 ± 0.1	< LOQ	3.48 ± 0.7	5.8
Chloride	mg/L	116.8 ± 6.8	142.5 ± 5.7	1.31 ± 0.2	604.1 ± 13.6	310
Bromide	mg/L	0.38 ± 0.2	0.48 ± 0.1	< LOQ	1.57 ± 0.2	1.53
Nitrate as N	mg/L	1.91 ± 0.14	1.40 ± 0.08	0.09 ± 0.02	5.25 ± 0.37	10.8
Phosphate as P	mg/L	0.39 ± 0.26	0.52 ± 0.09	0.03 ± 0.03	2.79 ± 0.18	7.3
Sulphate	mg/L	38.4 ± 1.1	43.0 ± 1	0.3 ± 0.1	180.8 ± 1	251

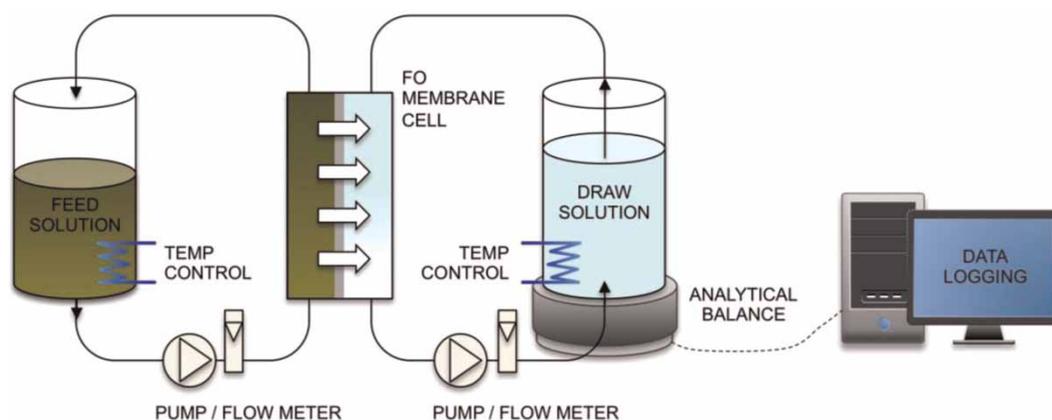Perm.: permeate; LOQ: limit of quantification.

Figure 2 │ Experimental set-up of the FO bench scale unit.

DS were adjusted manually with flow meters. Experiments were conducted with commercially available FO flat sheet membranes from HTI. Two types of membranes were applied: CTA and TFC polyamide (PA) membranes. The CTA membrane was used as a nonwoven (NW) support type and embedded screen (ES) type with the membrane embedded in a polyester woven mesh whereas the TFC membrane was used as ES type. The temperature of both solutions was kept constant at $25.0 \pm 0.2\,^{\circ}$C through a water bath, in which stainless steel coiled pipes were immersed. The water bath was connected to a temperature controller system (Thermoline BL-30) to maintain constant temperature. Flow meters (Cole-Parmer) were used to adjust the flow of both DS and FS streams. The initial volumes of the FS and DS were 2 L.

Experimental protocols

FO testing with model foulants

The tests were used to determine the specific fouling potential of the ROC's major components and their impact on the permeate flux. The tests were run for 15 hours for each membrane type and DS concentration using a new membrane for every test. Model foulants were used at elevated concentrations, which were about five to 10 times higher than the concentrations of the respective type of foulant in ROC, to accelerate the fouling effect and allow for clearer observations. A similar approach was chosen by Mi & Elimelech (2008). As all experiments were conducted in batch mode, initial baseline tests with DI water at the respective DS concentration were used to separate the flux decline due to the impact of fouling from the influence of decreasing osmotic driving force caused by progressive dilution of the DS (Mi & Elimelech 2008).

FO testing with ROC

The FO system was then tested with real ROC from the SOPA's WRAMS plant. The ROC was sampled on 1 day and then stored in glass bottles at $4\,^{\circ}$C until consumption for testing. Conductivity was monitored continuously. The concentrations of the organic and inorganic compounds were analysed for the initial and final solutions to identify organic and inorganic fouling.

FO testing with ROC at different pH values

As the ROC had a significant scaling potential, pH adjustment was studied as a method for reducing the risk of scaling.

RESULTS AND DISCUSSION

Tests with model foulants

Wastewater-derived effluent is mainly composed of natural organic matter (NOM), soluble microbial products (SMPs), and trace organic compounds (Shon *et al.* 2006). Humic acid was used to represent NOM while alginate represents polysaccharides, which form an important group of biopolymers derived from SMPs. In both membrane types, alginate indicated a significantly higher affinity to the membrane, particularly at higher fluxes (Figure 3, CTA NW membrane). These observations are in line with the results of Mi & Elimelech (2008). Irrespective of the applied osmotic pressure and flux about 30% of the initial alginate concentration was adsorbed after 15 hours of operation. The flux decrease due to alginate fouling increased from 2% at a DS concentration
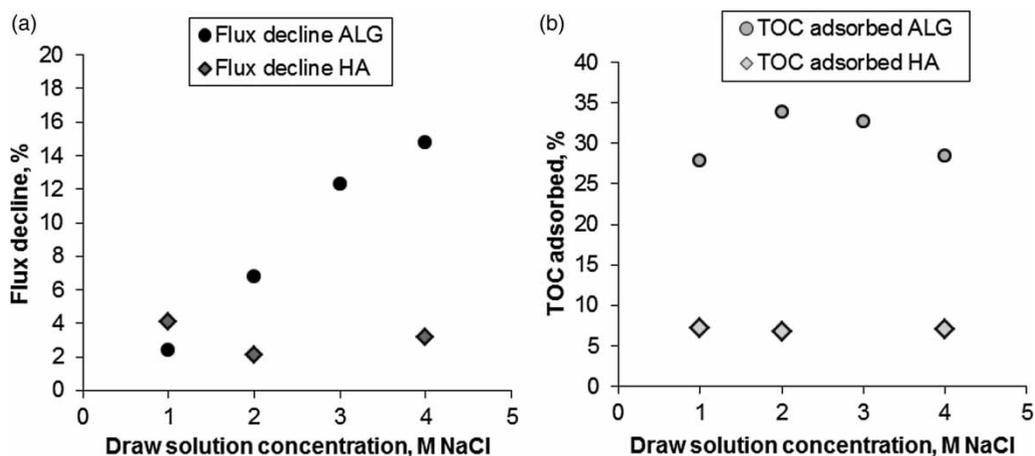
Figure 3 │ (a) Flux decline and (b) TOC adsorption of model foulants, humic acid (HA) and alginate (ALG) (CTA NW membrane, FO mode, model foulant in DI water).

of 1 M NaCl to about 15% at a DS concentration of 4 M NaCl. HA, however, caused only a minor flux decrease of 2 to 4%, which correlated to the flux. The adsorption of HA-based TOC was significantly less at about 7% during all tests with the CTA NW membrane (Figure 3). The HA adsorption to the CTA ES membrane (data not shown here) was slightly higher than the adsorption to the CTA NW membrane. The average adsorption of HA was between 9 and 10% of the initial TOC at fluxes about a factor of 2, which was larger than the fluxes achieved with the CTA NW membrane. HA-based flux decline was still moderate at values between 2 and 5%.

Tests with ROC

FO fouling tests with ROC showed a low organic fouling of the FO system. HAs were the dominating foulants in all studied membranes (Figure 4). Biopolymers such as polysaccharides (PS) were less fouling relevant, specifically because the ROC exhibits only low PS concentration due to the
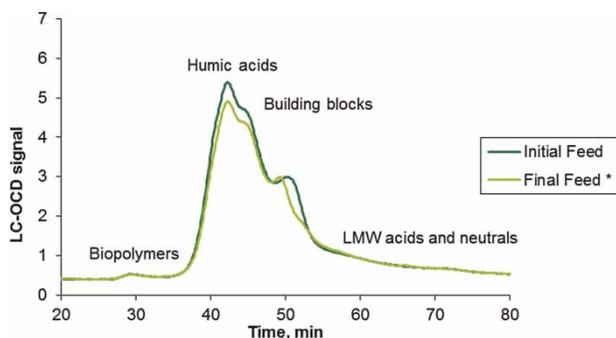

Figure 4 │ LC-OCD chromatogram of the FO feed solution at the beginning and the end (*normalized concentration) of 15-h laboratory test with ROC (TFC membrane polyamide, 25 °C, FS: ROC, DS: 2M NaCl, initial DOC = 38 mg/L, initial pH = 7.8). LMW = low molecular weight.

membrane pretreatment. After a filtration time lasting 15 hours, between 2 and 9% of the initial TOC (38 mg/L) was adsorbed with a slightly higher adsorption tendency at higher fluxes (Table 2).

Model solutions thus well indicated the fouling propensity of tested membrane types. Although organic fouling was insignificant, a rapid flux decline within the first 7 hours of operation was observed (Figure 5). Elemental analysis revealed a significant decrease in calcium and magnesium on the cation side as well as phosphate, carbonate and sulphate on the anion side. Modelling of the potential scaling with PHREEQC confirmed the high risk of formation of poorly soluble salts, particularly calcite, dolomite, and hydroxyapatite. Compared to the baseline filtration tests, the scaling led to a flux reduction of 10 to 25% (CTA membrane) and 35 to 55% (PA membrane). Hydraulic flushing and chemical cleaning could only partly recover the performance of the membrane.

To further reduce the risk of organic fouling, several methods can be employed to pretreat ROC including granular activated carbon (Kazner *et al.* 2013), or ozonation followed by biological activated carbon (Lee *et al.* 2009). This reduces the DOC concentration by 50 to 60% and further decreases the micropollutant load prior to FO. For long-term operation as studied by McGinnis *et al.* (2013), reducing bioavailable organics is particularly important to minimize organic fouling and biofouling.

Tests with ROC and pH adjustment

A moderate reduction of the FS pH was subsequently tested. When decreasing the initial FS pH to about 5, only a minor flux decline was observed that was comparable to the initial

Table 2 | Flux decline and TOC adsorption with ROC (CTA NW and TFC membranes, FO mode, ROC, pH = 7.8, unadjusted)

FS	DOC, initial mg/L	DS	Baseline flux avg. L/(m² h)	Flux with ROC avg. L/(m² h)	Flux decline %	TOC adsorbed %
CTA NW						
RO conc.	38	1 M NaCl	6.8	6.1	10.3	2.8
RO conc.	38	2 M NaCl	8.9	6.7	24.7	5.8
RO conc.	38	4 M NaCl	11.8	8.7	26.3	4.2
TFC (PA)						
RO conc.	38	1 M NaCl	14.3	9.3	34.9	2.1
RO conc.	38	2 M NaCl	18.9	10.0	47.1	8.7
RO conc.	38	4 M NaCl	22.1	10.0	54.7	6.1
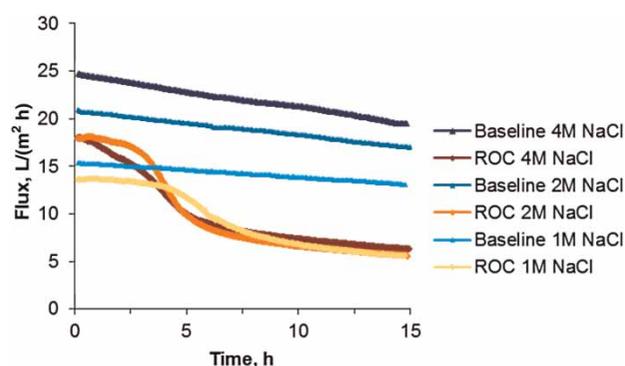
Figure 5 | Fouling of FO membrane by ROC with unadjusted pH (TFC PA membrane, 25 °C, initial pH = 7.8, final pH = 9.0).
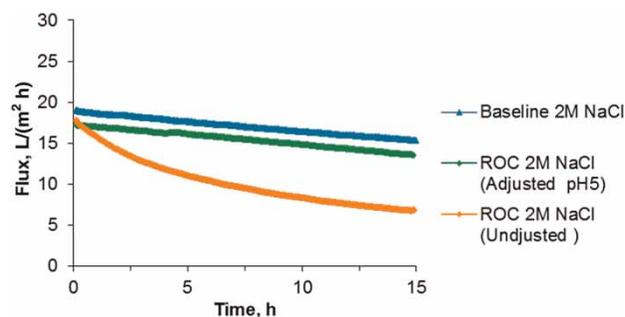
Figure 6 | Comparison of FO Fouling by ROC with adjusted and unadjusted pH (TFC PA membrane, 25 °C).

model foulant tests with HA (Figure 6). The difference between the pH-adjusted ROC test (initial pH of 5) and the baseline test can be attributed to the different osmotic pressure of the FS. It was further observed that the pH increased during the filtration test from initially pH 5.0 to pH 8.1 at the end of the test. The underlying phenomena are still subject to further investigation. Depending on the type of scalants, further scaling risk-reducing measures such as anti-scalants or softening might be necessary, as suggested by Adham *et al.* (2007) and Martinetti *et al.* (2009).

CONCLUSIONS

- FO appears to be a very promising technology for ROC treatment.
- Apart from selecting the proper DS and membrane, which must be regarded as the key questions, organics and inorganics play a major role in sustainable operation of FO systems.
- Scaling was a major impediment to the FO process and should be controlled, for instance by pH adjustment or softening.
- Low concentrations of critical scaling compounds such as phosphate, silica and carbonates in combination with well-controlled operational conditions are a prerequisite for high recovery and successful operation of FO for ROC treatment.
- Tests suggest that bulk organics have an impact on FO performance only to a minor extent in the short term, but may be removed prior to the concentration and desalting units, e.g. FO + crystallizer for sustainable long-term operation of the desalting systems and control of the level of refractory organics in the complete treatment system.

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