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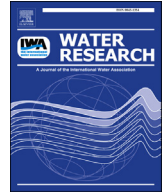
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# Desalination of brackish groundwater and reuse of wastewater by forward osmosis coupled with nanofiltration for draw solution recovery



Mattia Giagnorio<sup>a</sup>, Francesco Ricceri<sup>a</sup>, Alberto Tiraferri<sup>a, b, \*</sup>

<sup>a</sup> Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

<sup>b</sup> CleanWaterCenter@PoliTo, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

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## ABSTRACT

This study evaluates a treatment system centered on forward osmosis (FO) to extract high-quality water from real brackish groundwater and wastewater. The groundwater had salinity of 4 g/L, while the wastewater sample consisted of a secondary effluent. These feed solutions were treated first in a FO step, achieving a recovery of >60%. Subsequently, the diluted draw solutions were subject to a nanofiltration (NF) step to regenerate their original osmotic pressure and to simultaneously collect a final permeate product. Magnesium chloride and sodium sulfate were both suitable draw solutes for this application. MgCl<sub>2</sub> had a larger specific reverse salt flux and induced a more pronounced fouling-related flux decline with groundwater samples. Na<sub>2</sub>SO<sub>4</sub> was re-concentrated with a higher permeability NF membrane but may require the use of anti-scalants. The average fluxes obtained in high-recovery batch FO were between 5 and 11 L m<sup>-2</sup>h<sup>-1</sup> with an initial bulk draw osmotic pressure in the range of 12–15 bar. Relatively low flux decline was observed in fouling experiments with both samples, while physical cleaning proved promising to recover the related loss in productivity. The final product waters were all of very high quality, suggesting the potential of this coupled system for water reuse and desalination. Some challenges related to the relatively low water flux in the FO step, as well as the loss of draw solutes and the gradual change in composition of the draw solution, need further analysis to establish the technical and economic feasibility of the system.

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## 1. Introduction

Increasing quantities of water are required to sustain economic and population growth (Mekonnen and Hoekstra, 2016; Ridoutt and Pfister, 2010). At present, fresh groundwater and high salinity resources are the main sources of water for potable and irrigation uses. However, aquifers are being depleted due to their widespread exploitation (Taylor et al., 2013), while the purification of seawater requires energy-intensive technologies, e.g., reverse osmosis or thermal desalination, to remove salts and other contaminants (Elimelech and Phillip, 2011). Mid-salinity water resources, such as brackish groundwater or wastewater, are valuable alternatives to provide high-quality water.

The treatment of wastewater and of brackish groundwater has been achieved by applying different technologies (Qu et al., 2013), with membrane filtration among the most promising options. High-quality water can be extracted from wastewater through the application of membrane bio-reactors (MBR) or membranes coupled with advanced oxidation processes (Holloway et al., 2015; Hu et al., 2018; Minella et al., 2018; Skouteris et al., 2012). Nanofiltration (NF) and low-pressure reverse osmosis have been instead proposed as feasible technologies for the purification of brackish groundwaters (Phuntsho et al., 2013; Walha et al., 2007). However, fouling severely affects the lifetime of the membranes involved in pressure-driven filtration, thus increasing the overall cost of such systems (Guo et al., 2012). For this reason, current efforts are focused on the evaluation of innovative membrane-based processes exploiting different driving forces.

Within these efforts, promising results were reported for the application of forward osmosis (FO) to treat complex water sources (Akther et al., 2015; Coday et al. 2014a, 2014b; Linares et al., 2014;

\* Corresponding author. Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy.

E-mail address: [alberto.tiraferri@polito.it](mailto:alberto.tiraferri@polito.it) (A. Tiraferri).

Lutchmiah et al., 2014). Studies have demonstrated the feasibility to integrate FO membranes in MBR systems, thus exploiting the intrinsic low fouling tendency of the FO process (Achilli et al., 2009). Investigations have been carried out also to evaluate the application of FO in the food industry and in the oil and gas sector, with encouraging results for the treatment of different liquid foodstuffs, drilling mud, and fracturing flowback water (Chung et al., 2012; Garcia-Castello and McCutcheon, 2011; Hickenbottom et al., 2013; Klayson et al., 2013; Zhao et al., 2012b). The advantages related to FO drive a considerable amount of research around membrane development, module design, and the identification of the most applicable draw solutes (Chekli et al., 2012; Huang and McCutcheon, 2015; Shaffer et al., 2015; Xiao et al., 2012). Numerous membrane materials have been recently proposed to enhance the performance of FO by reducing fouling or the detrimental effect of internal concentration polarization (Madsen et al., 2015; Ren and McCutcheon 2014, 2018; Zhou et al., 2014). Both flat sheets and hollow fibres membranes are being developed (Hancock et al., 2013; Madsen et al., 2015; Ren and McCutcheon 2014, 2018; Setiawan et al., 2012). Related to the choice of the draw solutes, thermolytic solutes were proposed as promising compounds, owing to their possible recovery using distillation at relatively low temperature (Boo et al., 2015). Phuntsho et al. have studied fertilizers as DS for the treatment of brackish groundwater (Phuntsho et al., 2013), while Achilli et al. have presented a comprehensive study related to the most commercially available inorganic draw solutes (Achilli et al., 2010). All these studies have increased the understanding of the FO process and promoted its rapid development, but mainly focusing on the optimization of specific sections of the FO technology, e.g., the membrane or the draw solute. There are also processes related to the overall system functioning that are crucial for the effective implementation of FO, e.g., its rational coupling with the draw solute regeneration process and its achievable recovery rate, especially when treating real waters.

The literature provides theoretical calculations strengthening the economic and environmental potential of full-scale FO-based systems (Blandin et al. 2015, 2016a; Kim et al., 2018; Linares et al., 2016; Luo et al., 2014; Wan and Chung, 2018), but very few experimental reports exist on these issues. Examples include discussion on pilot-scale FO coupled with RO or NF treating wastewater effluents (Corzo et al., 2018; Hancock et al., 2013) and a FO-membrane distillation hybrid for sewer mining (Xie et al., 2013). In addition, Zhao et al. have presented promising results about the treatment of brackish water with an FO-NF system, but without providing many details on draw solution recovery and on the quality of the final product water (Zhao et al., 2012a). While more FO studies have recently involved the use or the modeling of pilot scale systems, the vast majority of this research is performed at low recovery rates and does not yet address the optimization of the combined system comprising also the draw solute regeneration step, thus overlooking also some of the phenomena involving the changes in the nature and composition of the draw solution during operation. Experimental research investigating these mechanisms is still relevant and should be conducted simultaneously with technological upscaling studies, to understand (i) the high-recovery performance of the system, (ii) the optimal operating conditions when FO is coupled to the draw solute recovery step, and (iii) the quality of both the recovered draw solution and the final water product.

The aim of this study is to evaluate a system to produce high-quality water from a real brackish groundwater sample and a real wastewater effluent through the integration of forward osmosis and nanofiltration. At first, different draw solutes are assessed and the most promising ones identified for this specific application. Following preliminary FO tests to choose the best operating

conditions, high-recovery experiments are presented. The two contaminated waters are first used as feed solutions in FO. Subsequently, the diluted draw solutions are treated in NF for regeneration and to obtain a high-quality permeate. The quality of the various aqueous streams entering and exiting both treatment steps are analyzed to discuss the overall performance of the coupled FO-NF system in terms of quality of the final product and effectiveness of draw solution recovery. The results of preliminary fouling tests are also presented, which provide further insight on the feasibility of the treatment system.

## 2. Materials and methods

### 2.1. Membranes and draw solutes

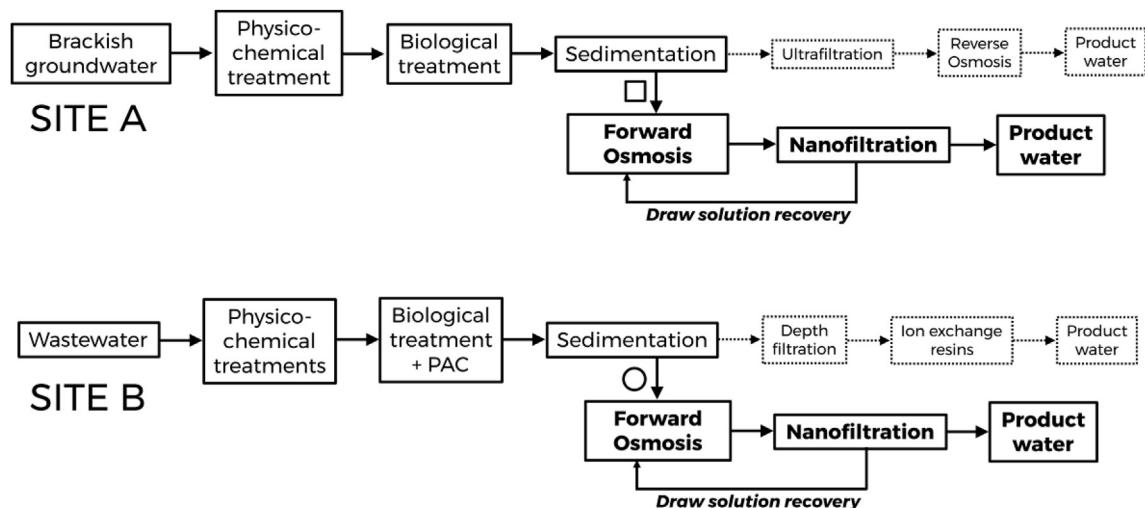
Two commercial membranes were used for nanofiltration (NF) tests: NF270 and NF90 (Dow Chemical Company, Midland, MI). The NF90 membrane has higher selectivity and lower permeance compared to the NF270, as reported in our previous work (Giagnorio et al., 2018). Commercial polyamide-based TFC forward osmosis (FO) membranes were acquired from Porifera Inc. (Hayward, CA, USA). The active layer water permeance,  $A$ , NaCl permeability coefficient,  $B^{NaCl}$ , and the support layer structural parameter,  $S$ , of the FO membranes were computed with NaCl as draw solution following the protocol reported by Tiraferrri et al., (2013). Their values were  $2.74 \pm 0.50 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ,  $0.94 \pm 0.25 \text{ L m}^{-2} \text{ h}^{-1}$ , and  $427 \pm 19 \mu\text{m}$ , respectively, resulting in a water flux of roughly  $15 \text{ L m}^{-2} \text{ h}^{-1}$  and a reverse salt flux of approximately  $0.09 \text{ mol m}^{-2} \text{ h}^{-1}$  ( $5 \text{ g m}^{-2} \text{ h}^{-1}$ ) using a draw solution of 485 mM NaCl and a feed solution of deionized water. Three inorganic salts and one organic compound were evaluated as draw solutes: magnesium chloride, sodium sulfate, magnesium sulfate, and glucose were all purchased from Carlo Erba (Milan, Italy). These solutes were chosen because of the possibility to regenerate the related draw solutions using NF, an established technology with already robust operational standards.

### 2.2. Feed water samples

Real water samples were collected from two separate treatment plants located in Italy. One of the two plants, referred to as “Site A”, treats contaminated brackish groundwater; the second plant (“Site B”) treats a mixture of civil and industrial wastewater. Specifically, samples exiting the secondary sedimentation step were collected from both sites (Fig. 1). The tests in this work aimed at assessing the possibility to substitute the following treatment steps, currently in place, with a coupled FO-NF system, with the specific goal to obtain water for high-end uses. Specifically, in site A the advantage of the FO-NF treatment train would be a potentially lower fouling compared to the UF-RO system currently in place, and a possible slightly higher quality of the product due to the nature of the membranes providing a double barrier in the FO-NF option. In site B, however, the FO-NF system would require an overall higher energy to be operated compared to the current configuration, but in contrast it would promote the beneficial reuse of this wastewater. The main characteristics of the feed samples are reported in Table 1 together with the respective osmotic pressures calculated with OLI System software.

### 2.3. Lab filtration setups

The NF experiments were performed with the same cross-flow system described in our previous publication (Giagnorio et al., 2018). The retentate stream was recirculated back to the feed reservoir while the permeate stream was continuously collected in



**Fig. 1.** Current and envisioned treatment trains for (top) site A and (bottom) site B. Scheme represents the main water line. In site A (square data points in the manuscript), the FO + NF system replaces ultrafiltration and reverse osmosis. In site B (circle data points), the FO + NF system replaces sand- and resin-based filtration steps.

**Table 1**

Characterization of water samples coming from Site A and Site B.

Parameter	Site A	Site B
Organic carbon (mg/L)	TOC: 4.4	DOC <sup>a</sup> : 22
pH	7.8	8.0
Cl <sup>-</sup> (mg/L)	2000	100
F <sup>-</sup> (mg/L)	2.5	0.1
PO <sub>4</sub> <sup>3-</sup> (mg/L)	2.5	1.5
NO <sub>3</sub> <sup>-</sup> (mg/L)	49	2.2
SO <sub>4</sub> <sup>2-</sup> (mg/L)	290	250
N-NH <sub>4</sub> (mg/L)	0.01	0.004
Ca <sup>2+</sup> (mg/L)	160	31
Mg <sup>2+</sup> (mg/L)	90	13
K <sup>+</sup> (mg/L)	45	15
Na <sup>+</sup> (mg/L)	1200	120
Al	n.d.	70
As	n.d.	4.2
Cr	n.d.	1.3
Fe	n.d.	16
Ni	n.d.	3.7
Conductivity (μS/cm)	6400	1100
TDS (mg/L)	3900	540
Osmotic pressure (bar)	3.0	0.5

n.d.: not detected or below detection limit.

<sup>a</sup> Measured following microfiltration (0.45 μm pores).

an external vessel. The FO setup was purchased from Sterlitech Corporation (Kent, WA, USA). It comprises two variable speed gear pumps (Cole-Parmer, Vernon Hills, IL), two reservoirs for the feed and draw solutions, a flat custom-made membrane cell, and a data acquisition system. The housing cell consists of a 146 mm (5.75 inches) long, 94.5 mm (3.72 inches) wide, and 1.5 mm (0.059 inches) deep rectangular channel for a total active area of the membrane sample of 140 cm<sup>2</sup> (21.7 in<sup>2</sup>). In all the experiments, the cross-flow rate was 1.8 L/min (0.34 m/s cross-flow velocity); the temperature and the conductivity of both solutions were measured through the programmable controller included in the system. The water flux across the membrane was computed based on the change of volume of the feed solution in time, which was measured with a computer-interfaced balance. Experiments were performed in batch, recirculating the feed and draw solutions to the respective reservoirs. All the tests were conducted with the membrane in FO configuration, i.e., active layer facing the feed solution, in co-current mode, and at a temperature of 23 °C.

#### 2.4. Preliminary forward osmosis tests and fouling tests

The different draw solutes were evaluated in initial tests, consisting of measuring the water and the reverse salt fluxes using deionized water on the feed side and upon variation of the osmotic pressure of the draw stream. The draw osmotic pressure was varied in five consecutive steps with bulk osmotic pressures of 4, 8, 12, 16, and 20 bar, respectively. Once the most promising draw solutes were chosen, MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>, a second set of tests was then conducted using solutions of either of these two salts on the draw side and the real samples from site A or B as feed solutions. These tests were analogous to those just described and comprised measurements of the water fluxes for five steps with varying driving force. Fouling experiments were also performed with the real samples as feed solutions and with a draw solution of a single salt of MgCl<sub>2</sub> or Na<sub>2</sub>SO<sub>4</sub> with a concentration suitable to achieve an initial flux of approximately 13–14 L m<sup>-2</sup> h<sup>-1</sup>. In these 8-h long fouling tests, the nominal driving force was kept constant by additions of appropriate volumes of a stock draw solution and of deionized water in the draw and feed reservoir, respectively, every 30 min. Some fouling experiments with the wastewater sample from site B also comprised physical cleaning steps to promote a larger shear stress at the membrane/solution interface, without backwashing: every 2 h, the cross-flow velocity was increased and a cleaning solution of 4.5 mM of Na<sub>2</sub>SO<sub>4</sub> or 1 mM of MgCl<sub>2</sub> was used both on the draw and on the feed side. Larger flow rates would translate into more significant pressure drops within the channels and higher energy requirements for pumping; in this study, the cross-flow velocity was only increased by 30% (to 0.45 m/s) during cleaning, representative of a mild process that would minimize the energy needs. After 20 min, the cleaning streams were replaced with previous draw and feed solutions and the fouling experiments carried on.

#### 2.5. High-recovery forward osmosis and nanofiltration tests

High-recovery FO tests were performed with either MgCl<sub>2</sub> or Na<sub>2</sub>SO<sub>4</sub> as draw solutes at an initial osmotic pressure of 15 bar (0.304/0.218 M of Na<sub>2</sub>SO<sub>4</sub>/ MgCl<sub>2</sub>) when treating the brackish groundwater from site A, and 12 bar (0.238/0.178 M of Na<sub>2</sub>SO<sub>4</sub>/ MgCl<sub>2</sub>) when treating the wastewater effluent from site B. The draw and feed reservoir contained 3.5 L of solution in the beginning of

the experiment. The water flux through the membrane was measured every 10 min and the tests were prolonged until roughly 65% of solution, i.e., 2.3 L, permeated from the feed to the draw side. At the end of each FO test, the diluted draw solution was processed in NF. The NF90 and NF270 membranes were used to re-concentrate  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$ , respectively, and to produce high-quality permeate water. The reported average ion-water internuclear distances, i.e., a measure for the size of the hydrated ion, for these species in aqueous solution are:  $\text{Mg}^{2+} = 0.21$  nm,  $\text{Cl}^- = 0.32$  nm,  $\text{Na}^+ = 0.236$  nm,  $\text{SO}_4^{2-} = 0.38$  nm (Marcus, 1988). NF membranes reject solutes by a combination of size-based separation mechanisms and electrostatic effects. The size and the valence of the ions in solution suggest the possibility to apply a looser NF270 to reject  $\text{Na}_2\text{SO}_4$  and a denser NF90 to reject  $\text{MgCl}_2$ . The applied pressure in the NF tests was kept constant at 20 bar or 16 bar to regenerate the draw solution coming from the treatment of the brackish groundwater and the wastewater effluent, respectively. The applied pressure in NF needs to be at least equal or higher than the osmotic pressure of the feed solution at the end of the test, i.e., 15 and 12 bar, respectively. The NF tests were prolonged until a relative recovery rate of 100% was achieved, i.e., 2.3 L of solution permeated from the feed side to the permeate side. Samples of the FO concentrate stream, FO draw solution, as well as NF feed and permeate solutions were collected at the end of each experiment and analyzed by an external accredited lab (Eurolab, Turin, Italy).

### 3. Results and discussion

#### 3.1. Choice of the draw solutes and of the operating conditions

The first set of tests aimed to select the most appropriate draw solutes. Four candidate compounds were evaluated, namely, magnesium chloride, magnesium sulfate, sodium sulfate, and glucose. They were selected based on the promising results discussed in the literature (Achilli et al., 2010; Chekli et al., 2012), being widely available and inexpensive, and owing to the possibility of being effectively recovered in nanofiltration (NF). Magnesium chloride,  $\text{MgCl}_2$ , and sodium sulfate,  $\text{Na}_2\text{SO}_4$ , have the largest osmolality among the four compounds. These two salts were also associated with the highest fluxes and the lowest specific reverse salt fluxes in forward osmosis (FO); see Fig. S1 of the Supporting Information. Specifically, the values of membrane  $B$  were 0.068 and  $0.059 \text{ L m}^{-2} \text{ h}^{-1}$  for  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$ , respectively, and the resulting reverse solute flux selectivities,  $J_w/J_s$ , were 1.5 and 1.9 L/mmol (16 and 13 L/g), obtained in experiments with deionized water as feed solution at 23 °C. Additionally, these two salts were rejected at high rate in NF with suitably high flux and were thus chosen to conduct our ensuing investigation. To maximize productivity, a denser NF membrane, NF90, and a looser membrane, NF270, were deployed to separate  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$ , respectively, during draw solute regeneration tests.

The purpose of preliminary low-recovery FO experiments was then to choose the concentration of these two draw solutes to be later applied in high-recovery tests. The two waters from site A and B were thus used as feed solutions and permeating fluxes measured as a function of bulk osmotic pressure of the draw solution. The trends displayed in Fig. 2 are consistent with theoretical expectations (Shaffer et al., 2015; Tiraferri et al., 2013). Similar FO fluxes were obtained with the two draw solutes, while higher productivity was observed when the less saline water was used as the feed solution, especially in the lower range of nominal osmotic driving force. At high values of draw bulk osmotic pressure, the results obtained with the two feed solutions evolved into similar values due to concentration polarization effects combined with reverse

salt flux (McCutcheon and Elimelech, 2006). The choice of the draw solution concentration for high-recovery tests is a compromise between the expected FO productivity and the hydraulic pressure to be applied in NF to restore this initial concentration value. Based on the profiles shown in Fig. 2, draw osmotic pressures of 15 bar and 12 bar were selected for subsequent experiments with water samples from site A and B, respectively.

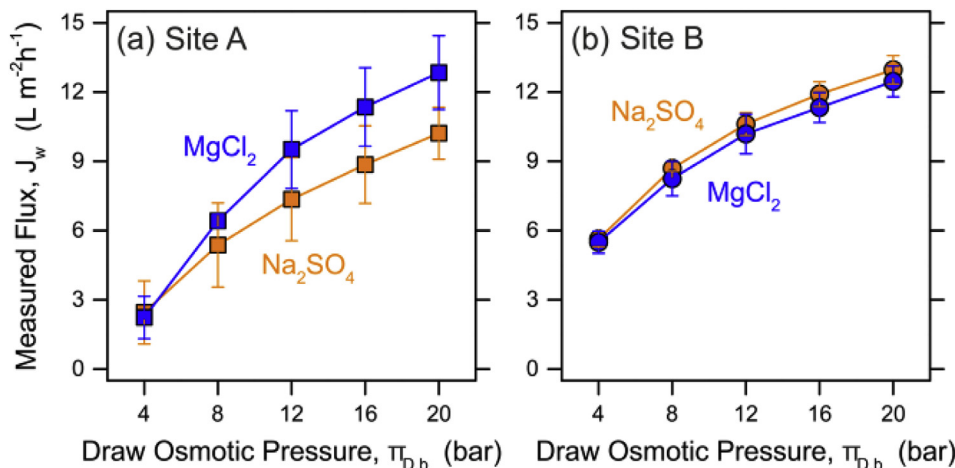
#### 3.2. Productivity of the coupled FO-NF system

The two contaminated waters from site A and B were first used as feed solutions in high-recovery FO test, using draw solutions of  $\text{MgCl}_2$  or  $\text{Na}_2\text{SO}_4$ . These tests were run until a recovery of roughly 65% was achieved. Subsequently, the diluted draw solutions were used as feed streams in NF tests, which were run until 100% of the dilution volume, that is, 100% of the approximate amount of permeated volume during the respective previous FO test, was collected as permeate. As a result, the draw solution was virtually completely regenerated and high-quality water was produced, the latter amounting to 65% of the volume of the initial feed of the FO test.

The fluxes measured in all the filtration experiments are reported in Fig. 3 as a function of recovery, at the initial draw osmotic pressures indicated in each graph. The rate of permeation in batch FO tests decreased gradually in time, caused both by a continuous reduction of the driving force and by fouling. The experiments were highly reproducible as displayed in Fig. S2 of the Supporting Information. In accordance with the data displayed in Fig. 2 and despite the lower initial draw osmotic pressure used to treat the wastewater effluent from site B, the average fluxes measured with this less saline feed water were significantly larger compared to those observed in tests treating the brackish solution from site A. Also, using sodium sulfate as draw solute instead of magnesium chloride resulted in slightly higher fluxes, possibly due to a more pronounced reverse salt diffusion of the latter salt (Achilli et al., 2010). Specifically, the average fluxes were  $6.4 \text{ L m}^{-2} \text{ h}^{-1}$  and  $5.2 \text{ L m}^{-2} \text{ h}^{-1}$  for brackish groundwater (site A) and  $11.1 \text{ L m}^{-2} \text{ h}^{-1}$  and  $9.7 \text{ L m}^{-2} \text{ h}^{-1}$  for the secondary wastewater effluent (site B). An implication of the relatively high fluxes displayed in Fig. 3b is the possibility to achieve significantly larger recovery values with wastewaters similar to those from site B, possibly up to 80%. The situation with brackish waters is the opposite, as lower recovery goals may be necessary to maintain high fluxes.

As shown in Fig. 3c and d, the fluxes observed in nanofiltration were larger than those observed in FO tests, owing to the different transport mechanisms and driving force involved in the two processes. The flux reduction observed in time as a function of recovery rate may be here entirely ascribed to the loss of driving force as the feed NF solution became more concentrated. A larger productivity was associated with the looser NF270 membrane, as expected from the intrinsic properties of the active materials characterizing the two NF membranes. The average fluxes in nanofiltration were  $86.2 \text{ L m}^{-2} \text{ h}^{-1}$  and  $54.9 \text{ L m}^{-2} \text{ h}^{-1}$  to recover the draw solution used to treat samples from site A (applied hydraulic pressure of 20 bar), and  $69.9 \text{ L m}^{-2} \text{ h}^{-1}$  and  $50.8 \text{ L m}^{-2} \text{ h}^{-1}$  in the case of site B (applied hydraulic pressure of 16 bar).

The average fluxes reported in the two paragraphs above were calculated simply by dividing the total cumulated permeated volumes by the duration of each respective experiment. When operating in batch mode in the laboratory, recovery increases with time. In real operation, recovery increases with space along the membrane module. Indeed, recovery may be used to tie the two modes of operation (Luo et al., 2014). Therefore, the fluxes discussed in this study may be regarded as those that would be obtained from the modules in a plant operating at the equivalent recovery rate of lab



**Fig. 2.** Fluxes measured in forward osmosis as a function of osmotic pressure of the bulk draw solution. The feed solution is (a: left) real brackish groundwater from site A and (b: right) real wastewater secondary effluent from site B. Blue and orange points depict data obtained with  $MgCl_2$  and  $Na_2SO_4$  as draw solutes, respectively. Average and standard deviation of two separate tests are shown. Lines are only intended as guide for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

tests and in co-current mode. As the NF productivity is larger than the FO productivity, the total active area needed to recover the draw solution is smaller than that necessary to treat the contaminated stream in FO, i.e., the capital costs of installation of the NF plant would be lower than for the associated FO plant. The data shown in Fig. 2 suggests that it would be possible to conveniently work with a larger initial osmotic pressure in the draw solution to maximize the productivity of the FO step while maintaining the same applied pressure in NF, thus reducing capital costs related to FO installation. Alternatively, or concurrently, the NF system may be configured to operate at lower applied pressure, resulting in energy savings for the overall system. Other possible options to optimize the system would be operating in counter-current mode in the FO stage, as well as working at larger flow rates of the draw compared to the feed solution, to achieve a lower dilution rate of the draw solutes at equivalent recovery: the excess flow of the draw would be treated in NF at higher fluxes compared to FO, thus producing larger volumes of high-quality water without greatly increasing the size of the plant. Clearly, scaling up of the system should take into account the piecing together of the two stages; a strategy that aims at optimizing the FO step alone and independently of the NF step will likely not achieve an optimal design. Such best configuration is expected to be accomplished by simultaneous optimization of both steps, possibly applying sub-optimal parameters in one of the two stages to maximize the overall utility.

### 3.3. Preliminary fouling results

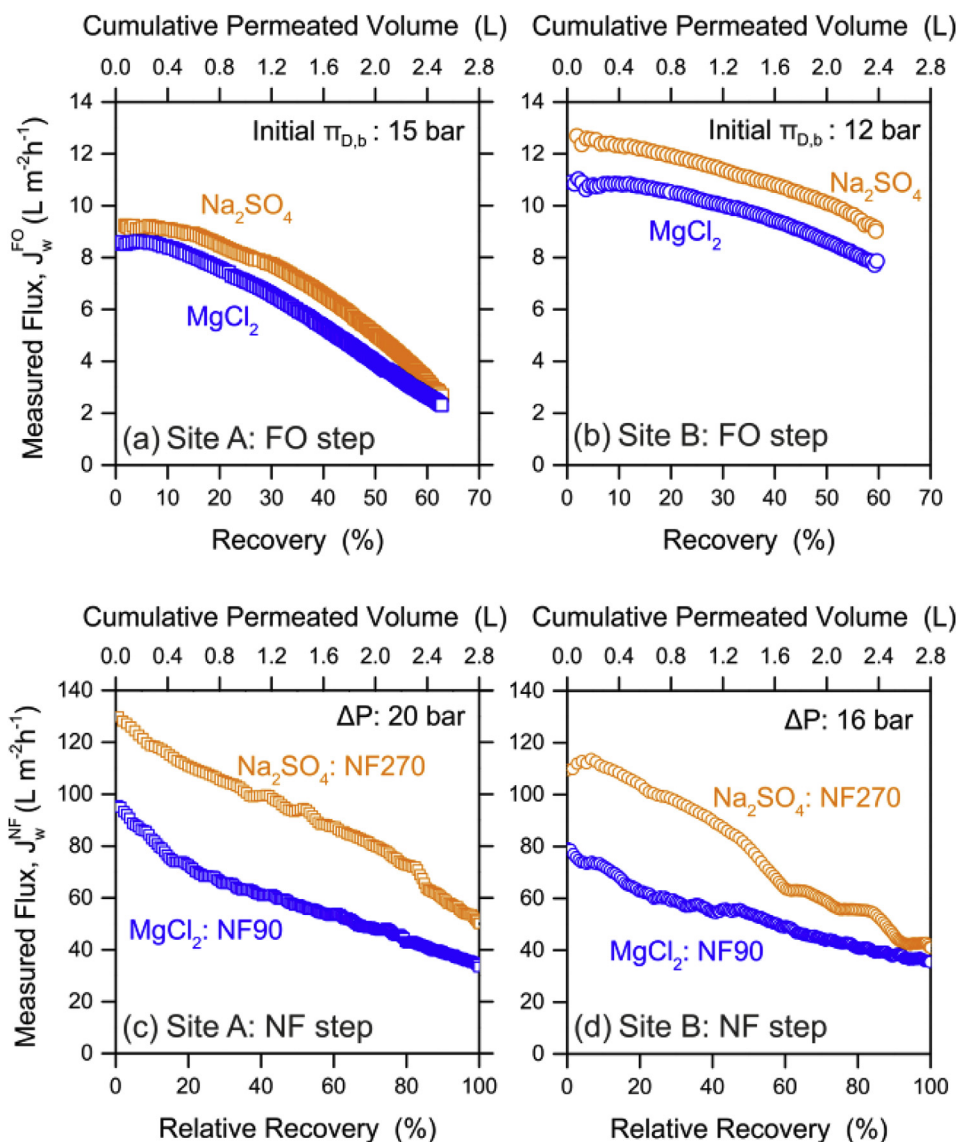
Fig. 4 presents experimental FO fluxes obtained from tests where their reduction was due solely to fouling-related effects. The flux decline observed with brackish groundwater as feed solution was moderate with  $MgCl_2$  as draw solute and very low with a draw solution of  $Na_2SO_4$ . The difference obtained with the two solutes, which also explains the slight dissimilarity of the data from high-recovery experiments with the same feed water from site A (Fig. 2a), may be rationalized with the negative effect of magnesium to enhance foulant deposition at the membrane/solution interface as this ion diffused to the feed side (Xie et al., 2014). A note of caution when comparing the performance of the two draw solutes is due here, as the use of sulfate may necessitate additions of antiscalants in real operation. The flux decline observed with secondary effluent was relatively more significant than that observed when

treating water from site A and this result is somewhat expected owing to the larger amount of organic molecules present in the wastewater samples (Table 1). The water fluxes measured after 8 h of test with samples from site B were 75–80% of the initial flux, regardless of the nature of the draw solution. The results suggest a role of magnesium chloride in promoting fouling when the brackish water from site A was used as feed stream: this observation may be rationalized with larger magnesium flux into the feed, possibly exacerbated by bidirectional ion transport mechanisms and exchanges with sodium ions contained at higher levels in water A compared to water B, and with specific interactions of magnesium with some of the components of the feed brackish water.

It is likely that the results shown in Fig. 4 overestimate the true prevalence of flux decline due to fouling. No provision was taken to minimize fouling during lab tests, viz., the cross-flow velocity was relatively low, spacers were not used, and the initial flux, strongly correlated to the extent of fouling (Blandin et al., 2016b), was intentionally in the higher range of typical FO fluxes. When simple and mild physical cleaning was performed with the feed wastewater from site B, part of the flux previously lost could be recovered and fluxes were generally higher compared to experiments without cleaning; see Fig. 4c. This result is consistent with previous studies, which showed partial recovery of the previously lost water flux thanks to physical cleaning using pure water (Blandin et al., 2016b; Mi and Elimelech, 2010). Even more important effects of cleaning are expected if the cross-velocity is increased at larger rates during real operation, at the expense of some energy costs. Additional observations can be made from the data in Fig. 4, which suggest the interesting behavior of the FO process in terms of fouling resistance: all the fluxes shown in the three graphs tended to stabilize within roughly one third of the experiment duration, suggesting that fouling may be minimal during operation after an initial influence on productivity. The observed decrease in flux at the onset of the tests may be also partly attributed to system equilibration. More in-depth fouling and cleaning experiments are certainly needed to provide further information and suggest operational modes.

### 3.4. Quality of the product waters, draw solution regeneration, and feasibility of the process

The composition of all the streams entering and exiting both the

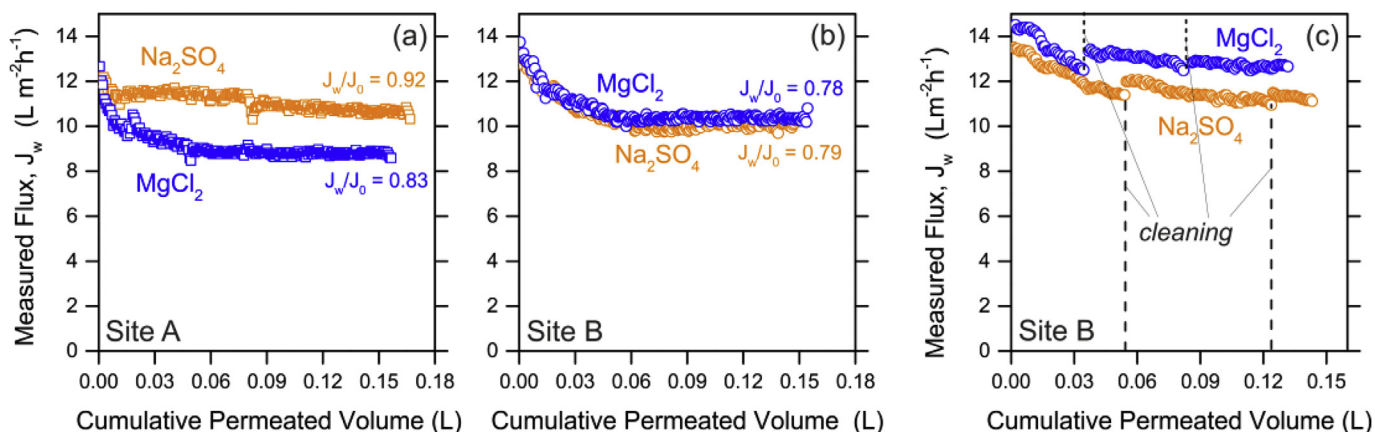


**Fig. 3.** Fluxes measured in the two treatment steps comprising the coupled system. (a, b: top row) Fluxes in batch forward osmosis as a function of absolute recovery: data points are average values of duplicate experiments. The draw solution bulk osmotic pressure in the beginning of the test was 15 bar for site A and 12 bar for site B. (c, d: bottom row) Fluxes in batch nanofiltration as a function of relative recovery, i.e., the amount of cumulative permeated volume relative to the amount of solution recovered in the previous FO step.  $MgCl_2$  and  $Na_2SO_4$  draw solutions were recovered in nanofiltration with NF90 and NF270 TFC membranes. The applied pressure was 20 and 16 bar (290 and 232 psi), respectively, for draw solutions obtained treating waters from site A and B, respectively.

FO and the NF systems was analyzed in terms of ionic species, organic carbon, and heavy metal concentrations. The three main issues related to water quality in the coupled system concern (i) the management of the FO concentrate, (ii) the end uses of the product, i.e., the NF permeate, and (iii) the regeneration of the draw solution, i.e., the NF retentate stream. While this study did not investigate the treatment of the FO retentate, the quality of these concentrated streams is here briefly commented in relation to their potential management strategy. The composition of the FO retentate streams collected in the high-recovery experiments is summarized in the Supporting Information, Tables S1 and S2. The concentrated brackish groundwaters had medium-high salinity, close to 10 g/L: the correct management of this solution may involve further concentration to recover salt or other resources, and for a more facile disposal. The concentrated secondary effluent comprised instead a considerable amount of organics, which would be even larger at higher advised recovery rates; see Table S2. Given the relatively low

salinity of this stream following FO treatment, it may be partly recycled within the treatment train and be subject to biological treatment, already present in site B, which would only need to remove organic carbon without problematic issues related to other nutrients, such as N or P.

Highly promising results of this work are related to the quality of the product waters, which is presented in Tables 2 and 3 for the treatment of feed waters from site A and B, respectively. In all the cases, the quality of the NF permeate was very high and this observation demonstrates the ability of the coupled system to desalinate brackish groundwater and to treat secondary effluents for high-end uses. In particular, the composition of one of the four product streams would allow its direct use as safe drinking water. The two waters produced using  $MgCl_2$  as draw solution may be readily used as high-quality irrigation water without restrictions, having a SAR value significantly lower than 3, being thus compatible with the most sensitive crops. Heavy metal concentrations



**Fig. 4.** Flux profile in forward osmosis fouling tests as a function of cumulative permeated volume with imposed initial flux of  $\sim 13\text{--}14\text{ L m}^{-2}\text{h}^{-1}$ . Flux decline observed with the feed solution from (a) site A and (b) site B. (c) Flux decline and recovery following cleaning with the wastewater effluent from site B; cleaning times are indicated by dash lines. Blue and orange points depict data obtained with  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$  as draw solutes, respectively. The value of flux at the end of the test, divided by the initial flux,  $J_w/J_0$ , is also reported near each curve. In these tests, the driving force was kept constant by addition of a concentrated draw solution and DI water in the draw and feed container, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**  
Characterization of the final product water obtained through the treatment of the brackish groundwater coming from Site A. Two replicate experiments were performed, showing comparable results. Here, we report data from one of the two replicates.

Parameter	Draw Solution: $\text{Na}_2\text{SO}_4$	Draw Solution: $\text{MgCl}_2$	Limits for use as irrigation water <sup>a</sup>	Limits for use as drinking water <sup>a</sup>
TOC (mg/L)	0.60	0.50		10
pH	8.5	9.2	5.5–9	6.5–9.5
$\text{Cl}^-$ (mg/L)	140	110	200	250
$\text{F}^-$ (mg/L)	n.d.	n.d.	1	1.5
$\text{PO}_4^{3-}$ (mg/L)	n.d.	n.d.	30	
$\text{NO}_3^-$ (mg/L)	15	n.d.	50	50
$\text{SO}_4^{2-}$ (mg/L)	270	0.04	2500	250
$\text{N-NH}_4$ (mg/L)	n.d.	n.d.		0.5
$\text{Ca}^{2+}$ (mg/L)	2.5	9.6	150	
$\text{Mg}^{2+}$ (mg/L)	0.35	13	35	
$\text{K}^+$ (mg/L)	0.64	5		
$\text{Na}^+$ (mg/L)	250	40	180	200
Conductivity ( $\mu\text{S}/\text{cm}$ )	1100	380	2500	2500
TDS (mg/L)	680	180	2000	
Hardness (mg $\text{CaCO}_3/\text{L}$ )	69	78		500
Alkalinity (mg/L)	62	16		
Aggressive Index	11.4	11.5		>10
SAR of irrigation water	39	1.98	Depends on crop	

n.d.: not detected or below detection limit.

<sup>a</sup> Limits for Italy.

were always below detection limit or at least one order of magnitude lower than the limits for potable water. These positive results are only partly surprising, as the FO and NF treatment steps in series involved the use of two selective membranes. Only in the case of use of  $\text{Na}_2\text{SO}_4$  as draw solute the values of SAR were relatively high, and the final concentrations of sodium and sulfate in the product water starting from feed waters from site A, 250 mg/L and 270 mg/L, respectively (Table 2), were larger than the limit value for potable water in Italy. These issues may be readily resolved by performing a second pass for only part of the NF permeate. On the other hand, the value of aggressive index slightly below 10 for one of the product waters from site B (Table 3) may be addressed by operating with a small bypass to mix the NF permeate with untreated water, still guaranteeing high quality of the final product.

Preliminary tests showed that similar product qualities may be obtained by directly applying significantly denser nanofiltration membranes, e.g., XLE membranes (Dow), to treat the influent feed waters. Comparable recovery rates and permeate fluxes to those observed in this study may be achieved by working at lower applied pressures (10–15 bar), but with more considerable

concerns related to fouling. The choice between the implementation of a coupled FO-NF system and a stand-alone NF system would require pilot-scale tests and evaluation of the various trade-offs of the two alternatives. Moreover, a system consisting of NF only would comprise only one high-selectivity barrier, while the coupled FO-NF is a two-barrier system that would potentially allow higher removal rates also of small organic compounds and micropollutants.

The third issue concerns the quality of the regenerated draw solutions. Reconcentrated draw streams should be ideally equivalent to the initial draw solution applied in the FO step, at least in terms of osmotic pressure. A comparison of the composition of the initial and regenerated draw streams is presented in Tables S3 and S4 of the Supporting Information. Following the two treatment steps in series, the regenerated draw solutions contained between 87 and 97% of the original TDS, vastly provided by the respective draw solutes, with only traces of different ions. The reduced amount of salinity translates into a nearly proportional loss of osmotic pressure compared to that of the initial draw solutions. The change in composition and in particular the decrease of TDS is

**Table 3**

Characterization of the final product water obtained through the treatment of the secondary wastewater effluent coming from Site B. Two replicate experiments were performed, showing comparable results. Here, we report data from one of the two replicates.

Parameter	Draw Solution: Na <sub>2</sub> SO <sub>4</sub>	Draw Solution: MgCl <sub>2</sub>	Limits for use as irrigation water	Limits for use as drinking water
TOC (mg/L)	1.1	0.33		10
pH	9.8	7.2	5.5–9	6.5–9.5
Cl <sup>-</sup> (mg/L)	7.4	55	200	250
F <sup>-</sup> (mg/L)	<i>n.d.</i>	<i>n.d.</i>	1	1.5
PO <sub>4</sub> <sup>3-</sup> (mg/L)	<i>n.d.</i>	<i>n.d.</i>	30	
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.24	<i>n.d.</i>	50	50
SO <sub>4</sub> <sup>2-</sup> (mg/L)	110	0.21	2500	250
N-NH <sub>4</sub> (mg/L)	0.022	0.0024		0.5
Ca <sup>2+</sup> (mg/L)	0.7	3.5	150	
Mg <sup>2+</sup> (mg/L)	0.065	16	35	
K <sup>+</sup> (mg/L)	0.16	2.5		
Na <sup>+</sup> (mg/L)	75	3.7	180	200
Conductivity (μS/cm)	350	190	2500	2500
TDS (mg/L)	190	80	2000	
Hardness (mg CaCO <sub>3</sub> /L)	43	83		500
Alkalinity (mg/L)	40	8.0		
Aggressive Index	12.3	9.3		>10
SAR of irrigation water	23	0.2	Depends on crop	

*n.d.*: not detected or below detection limit; <sup>a</sup>limits for Italy.

attributed to both reverse salt flux in FO, possible phenomena of scaling, and to incomplete (<100%) salt rejection in NF (Giagnorio et al., 2018). A larger relative loss of TDS was registered when treating wastewater from site B; in this case, the osmotic pressure of the NF retentate stream was roughly 10.5 bar instead of 12 bar. This result may be rationalized with a larger net salt flux to the feed stream in FO due to the largest salt gradient across the membrane, as the feed was characterized by lower salinity compared with experiments treating brackish solutions from site A. Generally, a larger relative loss of osmotic pressure was observed with MgCl<sub>2</sub>. An implication of these observations is the need to either add solute continuously to the draw stream entering the FO step to maintain the osmotic pressure constant, or the opportunity to reach relative recovery rates larger than 100% in the NF step. This latter step would possibly be advantageous as it would increase the overall system recovery, keeping in mind that a certain amount of draw solution would still have to be supplemented at the entrance of the FO step to maintain flow balance.

Another final important aspect related to the composition of the regenerated draw solution is the molar ratio of its constituting ions. The Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> ratios of the NF retentates were 1.87 and 1.98 (nominal ratio is 2) following the treatment of the brackish groundwater from site A and site B, respectively. The Cl<sup>-</sup>/Mg<sup>2+</sup> ratios were 2.08 and 2.04, respectively. These data imply larger loss of cations compared to each respective anion in the system. This result is rationalized with coupled and bidirectional ion transport across the FO and the NF membranes and with exchange mechanisms between feed and draw solutes in FO, which cause a departure of the draw solutions from the initial compositions due to the complex mixture of species present in the feed waters. Another aspect that was not observed in this study but that may cause further impairment of the solution in the draw loop is the possible accumulation of micropollutants and other undesired substances. This phenomenon is expected to be more significant when the draw regeneration process is more selective than that comprising the FO membrane (e.g., dense RO membranes), thus rejecting at high rates all the species that pass through the FO membrane. When NF is applied downstream of FO, this phenomenon should be thwarted and the system will still provide the advantages of a dual barrier to contaminants. In any case, the continuous alteration in the nature of the recirculated draw solution would perhaps require

more than simple additions of solutes to this stream and also involve partial or complete replacement of the draw solution periodically during operation. Ideal FO membranes that are more selective and capable of providing high fluxes using lower draw solute concentrations would be a step forward to address issues related to loss of osmotic pressure and alteration of draw solutions during operation.

#### 4. Conclusions

In this work, forward osmosis (FO) was evaluated in the treatment of a real sample of brackish groundwater and a real sample of wastewater effluent for the production of high-quality water. The most suitable draw solutions were magnesium chloride and sodium sulfate, used to obtain bulk osmotic pressures of 12 and 15 bar in the initial draw solutions, to provide feasible fluxes in the treatment of wastewater and groundwater samples, respectively. The diluted draw solutions, obtained following a recovery of 60% of the initial feed (2.3 L out of 4 L), were reconcentrated using medium-pressure nanofiltration (NF) where the totality of the recovered water (2.3 L) was collected in the permeate.

The results suggested that: (i) the combination of FO and NF allows the production of waters of quality suitable for potable uses or unrestricted irrigation; (ii) FO fluxes were in the order of 10 L m<sup>-2</sup> h<sup>-1</sup>, significantly lower than fluxes obtained in the NF step by applying a suitable hydraulic pressure to regenerate the initial draw solution osmotic pressure; (iii) reverse salt flux in FO and incomplete solute rejection in NF caused some loss of draw solutes, in the order of 5–10%; (iv) the regenerated draw solutions contained ions leaked from the initial feed samples and the stoichiometry of the two ionic species composing the initial draw solute were slightly off following regeneration; (v) the system may be further optimized by working at higher initial draw osmotic pressures and by increasing the recovery of the NF step. Very preliminary fouling and cleaning experiments suggested that the flux decline due to fouling may be low and mostly reversible during operation. Overall, these results imply that the implementation of full-scale FO still requires further improvements of this technology and of the coupling with the recovery process, although the potential of this novel technology remains high in treating contaminated streams of low and medium salinity to produce high-quality

water.

## Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.01.014>.

## Abbreviations

DI	deionized
DOC	dissolved organic carbon
DS	draw solution
FO	forward osmosis
FS	feed solution
MBR	membrane bioreactor
NF	nanofiltration
TFC	thin-film composite
TOC	total organic carbon

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