

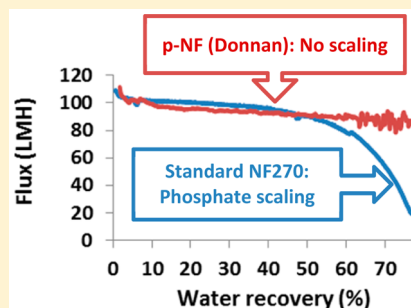
Breaking the Symmetry: Mitigating Scaling in Tertiary Treatment of Waste Effluents Using a Positively Charged Nanofiltration Membrane

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S Supporting Information

ABSTRACT: When salinity of municipal wastewater increases and approaches the limits of toxicity for plants, moderate desalting of wastewater becomes vital for keeping it suitable for irrigation. Nanofiltration (NF) is an attractive solution, as it partially removes NaCl. Unfortunately, commercial NF membranes (e.g., NF270) strongly reject multivalent ions present in wastewater, especially, scale-forming calcium and phosphate. This results in undesired demineralization, severe membrane scaling, and unacceptably low water recovery. To address this problem, we report here that a positively charged NF (p-NF) performs significantly better than NF270, owing to overall lower rejection of scale-forming ions. Therefore, for a commensurate flux and NaCl rejection, p-NF shows much less scaling than NF270, even at recoveries as large as 80%–85%. This suggests that p-NF may have an advantage over standard NF for moderate desalting of wastewater and other water sources with high scaling potential.



1. INTRODUCTION

The current standard for wastewater treatment is secondary bioremediation, which removes most organics but leaves the salt content unchanged. When the wastewater salinity approaches the limits of toxicity for crops, a tertiary treatment becomes vital. Since salinity needs to be reduced only moderately, partial desalting using nanofiltration (NF) membranes could be attractive for upgrading the quality of secondary effluents for unrestricted irrigation.^{1,2} Such treatment could also remove some micropollutants.^{3–5}

The main purpose of tertiary desalting is removal of NaCl, whereas other commonly present ions, such as phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) as well as Ca^{2+} and Mg^{2+} , need not be removed. Moreover, these nutrient ions may be an asset for agriculture and municipal irrigation. Unfortunately, NF-treated water gets strongly depleted of these ions due to high rejection by NF. Thus, this incurs significant remineralization costs and, more importantly, causes severe membrane scaling and, as a result, limits water recovery.

In case studies performed at Shafdan Wastewater Treatment Site (Israel), scaling by calcium phosphate, present at a supersaturation level in the feed, has been identified as the major problem in desalination of secondary wastewater.^{6,7} Rejection by NF and concentration polarization yield a still higher supersaturation at the membrane surface and, ultimately, severe scaling, which could only be prevented by an unacceptably low recovery, ~50%.

The problem is traced back to the high rejection of calcium and phosphate, which is an inherent feature of NF membranes commercially available today. Indeed, most commercial NF membranes are negatively charged. As a typical example, a widely used NF270 by Dow has a polyamide layer containing a

significant amount of negative carboxylic charges.⁸ Compared to ~50% rejection of chloride, this membrane retains >98% multivalent anions due to strong Donnan exclusion.^{9,10} One might expect that Donnan exclusion by negative charges would result in a low rejection of divalent cations Ca^{2+} and Mg^{2+} ; however, dielectric exclusion^{11–18} enhances their rejection as well, exacerbating scaling.

The key idea presented here is that scaling may be mitigated by using an NF membrane with a different ion rejection pattern. We suggest an open positively charged NF membrane (p-NF) as an attractive alternative. Positively charged NF membranes are known^{19–22} but have not been previously considered in wastewater desalting. At first glance, one might expect that rejection of multivalent cations and anions by p-NF would be a mirror image of a negatively charged membrane,²³ yielding no benefits. However, more thorough examination reveals that this symmetry is broken. First, cation and anion sizes differ significantly; therefore, the dielectric exclusion, which is ion size dependent, affects rejection of cations and anions differently. Thus, Ca^{2+} rejection by NF270 is higher than Na^+ since dielectric exclusion overrides the Donnan one.^{11–18} On the other hand, much larger phosphate and sulfate should be less affected by dielectric exclusion and more likely to follow the regular Donnan scenario, i.e., be weakly rejected by p-NF. Second, the ion content in water is asymmetric, i.e., phosphate is much more dilute than calcium. As a result, kinetics of scaling may be more sensitive to phosphate than calcium, and reduced

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phosphate rejection may be more beneficial for mitigating scaling.

To examine this hypothesis, we prepared a positively charged NF membrane with NaCl rejection similar to NF270 and tested its separation performance and scaling behavior versus NF270. Experiments ultimately reveal that broken symmetry of ion rejection by p-NF yields less scaling, higher recovery, and smaller permeate depletion of nutrient ions.

2. MATERIALS AND METHODS

A poly(ether sulfone) (PES) ultrafiltration support membrane was kindly supplied as flat sheets by Dr. Peter Eriksson of GE-Osmonics. An NF270 membrane was supplied by Dow. Polyethileneimine (PEI), cross-linker glycerol diglycidyl ether (GDE), and inorganic salts and humic acid (HA) were purchased from Aldrich. Deionized water was used throughout.

A PEI–ethanol coating solution (20 g/L PEI, 2.5 g/L GDE and 50 g/L glycerol) was prepared by dissolving PEI, GDE, and glycerol in ethanol and stirred for 2 h before coating. Ethanol was a preferred solvent, as it dissolves PEI, GDE, and glycerol and does not affect PES support; it also better wets the PES surface and dries faster, yielding a more uniform and reproducible coating. The addition of glycerol helped prevent collapse of support pores and permeability loss during drying. Prior to coating the PES support, PES coupons were immersed in ethanol for 24 h to remove soluble components and then in the coating solution for 1 min. Thereafter, the membrane was removed and hung vertically with a clip holder in a convection oven and dry-cured at 30 °C for 24 h. Thus, prepared p-NF membranes had water permeability of 5–6 LMH/bar. Fouled p-NF membranes were prepared by filtering a 10 mg/L HA solution until a 30% drop in permeability and rinsed before testing.

IR spectra of the membranes (average of 64 scans at 4 cm^{−1} resolution) were recorded on a Nicolet 8700 FT-IR spectrometer with a MIRacle ATR diamond smart accessory (Pike). Cross-sectional morphology was examined by SEM (Zeiss Ultra-Plus, Germany) using samples dried at 30 °C for 12 h, freeze-fractured in liquid nitrogen, and coated with gold. Surface ζ-potential was measured using a SurPASS electrokinetic analyzer with a clamping cell (Anton Paar).

Membrane testing and scaling experiments were performed on a laboratory crossflow setup. Single-salt feeds contained 2 g/L NaCl, MgCl₂, or Na₂SO₄. A mixed feed used for high recovery/scaling experiments corresponded to Shafdan secondary wastewater.²⁴ The feed pressure was adjusted to have an initial flux 90–100 LMH to address different permeabilities (12–13, 5–6, and 4–4.2 LMH/bar for NF270, p-NF, and fouled p-NF, respectively). Ion compositions of feed, permeate, and brine were determined by inductively coupled plasma (ICP). The chloride concentration was deduced from charge balance. The permeate was collected until a desired recovery and weighed continuously using a digital balance interfaced to a computer to monitor the permeate flux (see [Supporting Information](#) for more detail). The effective rejection for each species, *R*, was calculated as follows

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (1)$$

where *C_p* and *C_f* are concentrations in total collected permeate (after reaching final recovery) and initial feed concentration, respectively. Note for single salt tests the permeate volume was

small, and then initial and final feed compositions were nearly identical. For concentration/scaling tests, the recovery was large, 80%–85%; thus, feed and permeate became more concentrated toward the end of the run, reducing effective rejection defined by eq 1.

3. RESULTS AND DISCUSSION

Figure 1a shows the cross section of a p-NF membrane. A dense selective PEI layer, 150–200 nm thick, on top of a

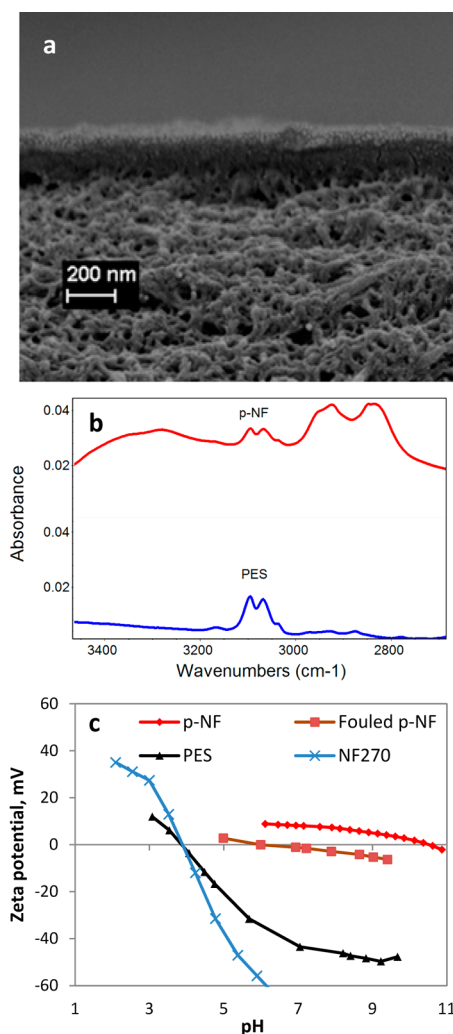


Figure 1. (a) SEM micrograph of the PEI-coated PES membrane cross section. (b) ATR-FTIR spectra of unmodified PES membrane (bottom, red) and PES membrane coated with PEI polymer (top, blue). (c) ζ-potential of the p-NF membrane, pristine and fouled with humic acid, and polyestersulfone UF membranes as a function of pH.

supporting membrane is clearly observed. The PEI charge is due to amine groups, which show a range of *pK_b* values in water with 50%–80% ionization at pH ~ 7.^{25,26} ATR-FTIR spectra in Figure 1b display distinct 2830 and 2938 cm^{−1} bands, absent in PES support and assigned to stretching of aliphatic C–H bonds of PEI, and a wide 3200–3400 cm^{−1} band due to primary and secondary NH groups. Streaming potential (Figure 1c) confirms a positive charge of p-NF up to pH 10.5 (isoelectric point, IEP), while PES support and NF270²⁷ show a negative charge down to IEP ~ 4.

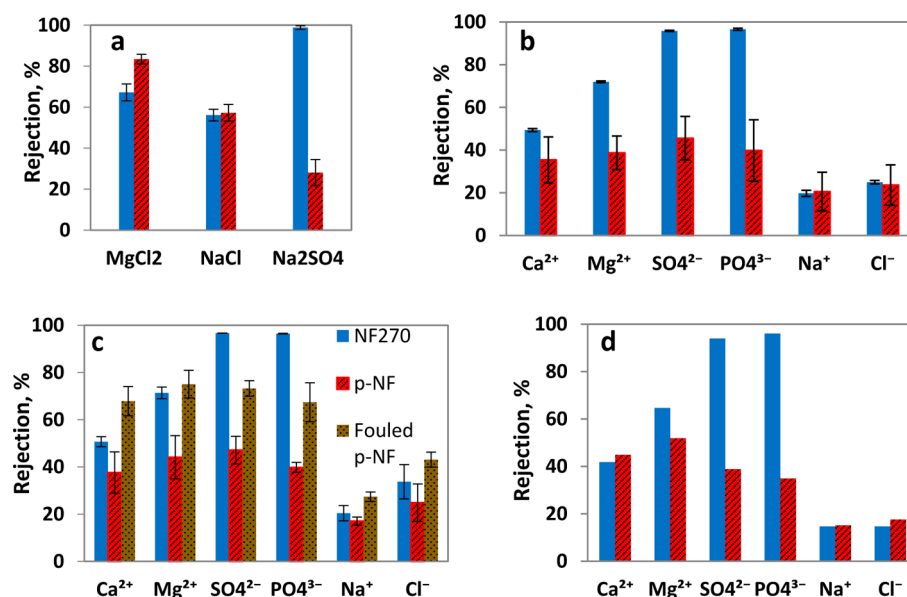


Figure 2. Single salt rejection and effective rejection of different ions by NF270, p-NF, and p-NF fouled by humic acid for (a) single salt feed solutions, recovery 1.5%, (b) a mixed feed representing Shafdan secondary wastewater ion concentration after 80% water recovery, (c) a mixed feed with phosphate concentration increased 4X relative to Shafdan effluent after 80% water recovery, (d) a mixed feed with 4X phosphate and 7X NaCl after 85% water recovery. Rejections are as defined by eq 1. The shown standard deviations from (a) to (c) correspond to three replicate experiments.

Figure 2a displays MgCl_2 , NaCl , and Na_2SO_4 rejection of p-NF and NF270 for single salt feeds. Both membranes show a commensurate NaCl rejection and a much stronger rejection of the salts containing a *divalent co-ion*, i.e., MgCl_2 for p-NF and Na_2SO_4 for NF270. However, in the case of a *divalent counterion*, NF270 rejects MgCl_2 stronger than NaCl , while p-NF rejects Na_2SO_4 less than NaCl . The order is then $R[\text{MgCl}_2] > R[\text{NaCl}] > R[\text{Na}_2\text{SO}_4]$ for p-NF, but it is $R[\text{Na}_2\text{SO}_4] \sim R[\text{MgCl}_2] > R[\text{NaCl}]$ for NF270 and not simply reversed compared to p-NF. This symmetry-breaking reflects the role of dielectric exclusion (probably, combined with size effect) in NF270, which indiscriminately enhances rejection of divalent ions more than monovalent ones. Clearly, such enhancement is not desired when calcium phosphate precipitation is an issue. In contrast, Donnan rejection of divalent co-ions is stronger, but that of divalent counterions is weaker than that of their monovalent counterparts. Then, in p-NF, a higher rejection of MgCl_2 compared to NaCl is balanced by low rejection of Na_2SO_4 . This makes p-NF more favorable for treatment of calcium- and phosphate-rich effluents prone to scaling, as demonstrated below.

The difference in rejection mechanism may be explained by different pore sizes and the PEI layer being more hydrophilic and not as strongly cross-linked as polyamide in NF270. The effective pore size for NF270 is ~ 0.22 nm, as estimated from its water permeability, thickness, and porosity.¹⁵ An analogous estimate for p-NF places it in the range from 0.27 to 0.48 nm (Supporting Information). This suggests a weaker dielectric^{11–18} and size exclusion in p-NF, yet its positive charge still allows a substantial NaCl rejection.

Experiments simulating tertiary treatment were first conducted using solutions with a mineral composition representative of Shafdan effluent, which contains about 6 mg/L phosphate,⁶ and even at this level is supersaturated (Supporting Information). Analysis using the geochemical software PHREEQC³ indicates that the actual supersaturated calcium

phosphate species is hydroxyapatite, whose saturation index (SI) at feed pH 7.4 is already positive, $\text{SI} = 3.59$. Nevertheless, concentration up to 80% water recovery showed scaling for neither NF270 nor p-NF, even though SI in concentrate reached ~ 6.6 . The flux showed some decline, similar to the p-NF in Figure 3a, probably due to membrane compaction and deswelling at increasing ionic strength.²⁹ Since the filtration was

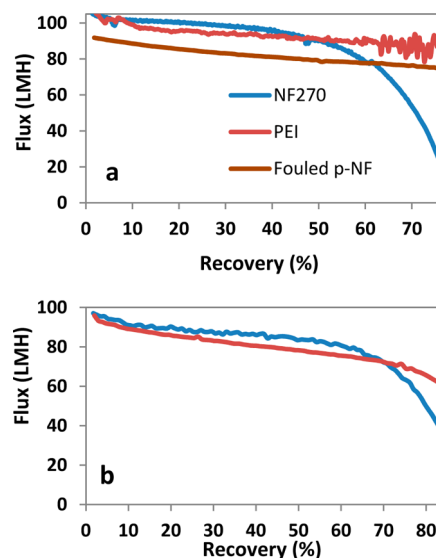


Figure 3. Water of flux as a function of recovery comparison between NF270, p-NF, and fouled p-NF membranes during recovery tests: (a) Secondary water with 4-fold increased phosphate concentration. (b) Secondary water with 4-fold and 7-fold increased phosphate and NaCl concentrations, respectively. Feed pH was 7.4 ± 0.2 . Each curve shows a representative single run, confirmed in duplicate experiments. Due to different water permeabilities (Materials and Methods section), the feed pressure was adjusted to have initial flux in the range of 90–100 LMH.

in a batch regime and hydroxyapatite is known to nucleate slowly,³⁰ the membrane was probably not exposed to a supersaturated solution for a sufficient time to initiate scaling. The situation is therefore not as challenging as in continuous NF treatment, where parts of the membrane are *permanently* exposed to the same supersaturated solution; thus, hydroxyapatite nucleation and scaling is only a matter of time. To make scaling observable, we performed more demanding tests using the same composition but with phosphate increased 4-fold to 24 mg/L, still realistic for fluctuating wastewater composition.

Figure 3a shows flux versus recovery for 24 mg/L phosphate. Apparently, rapid flux decline in the NF270 membrane after reaching ~55% recovery indicates severe scaling. On the other hand, no sign of scaling was observed for the p-NF membrane. As explained previously, a lower rejection of phosphate in the p-NF membrane leads to lower concentration and less polarization compared to NF270, which delays scaling. Figure 2b and c compare the effective (overall) ion rejections measured for two phosphate levels after 80% recovery. It can be seen that the pattern is similar in both experiments. As expected, the negatively charged NF270 membrane strongly rejects sulfate and phosphate. However, p-NF showed no such high rejection of calcium and magnesium. Hydroxyapatite SI in concentrate increased for both NF270 and p-NF membranes to 8.14 and 6.21, respectively. Apparently, ~1.9 unit difference (note logarithmic SI scale) was substantial for preventing hydroxyapatite scaling for p-NF.

On the other hand, effective NaCl removal, roughly by half, was almost the same for both membranes in both experiments and sufficient for foreseeable tertiary treatment. The salinity reduction in the p-NF permeate was commensurate with depletion of phosphate and sulfate; thereby, p-NF may minimize or even eliminate the need for remineralization of the permeate. This is in stark contrast with NF270, where these ions content in the permeate was ~20 times lower than in the feed.

Some applications or still higher recoveries may involve a higher initial NaCl concentration than above; thus, the Donnan effect may weaken. In order to estimate how that may affect ion separation, another test was performed for up to 85% recovery with NaCl concentration increased 7-fold. Increased NaCl only slightly reduced phosphate and sulfate rejection for NF270 (Figure 2d); therefore, the concentration factor for multivalent ions was similar at both salinities. The flux then declined with recovery in a similar manner, and at ~60% recovery started dropping precipitously indicating onset of scaling (Figure 3b). In contrast, the p-NF membrane showed a moderate decline for the entire recovery range, probably caused by the combined effect of osmotic pressure, compaction, and deswelling, with somewhat faster decline only close to 80% recovery. It is shown that the NaCl rejection in Figure 2d was lower than in Figure 2c and probably insufficient for overall salinity reduction (this could be tunable via cross-linking). Although NaCl rejection was similar for both membranes, p-NF showed far less depletion of phosphate and sulfate, making p-NF a more attractive option.

A potential concern for use of p-NF in wastewater treatment is fouling by natural organic matter, especially, negatively charged, which may modify membranes charge and rejection.³¹ To examine this point, p-NF was similarly tested after it was fouled with HA until 30% flux reduction. Figure 1c shows that IEP of the fouled membrane shifted to slightly acidic pH 6.

Figure 2c indicates that fouling increased ion rejections for the same feed by 10%–25%; however, the overall pattern was well preserved. Most importantly, phosphate/sulfate rejection remained far below that of NF270. As a result, similar to pristine p-NF and unlike NF270, fouled p-NF showed no sign of scaling (Figure 3a). Notably, this result may also suggest that scaling was unrelated to surface charge and mainly dictated by ion rejections.

In summary, the prepared positively charged p-NF PEI membrane performed significantly better than NF-270 in terms of scaling and recovery for effluents supersaturated with scale-forming species. Such membranes may therefore be a preferable option for mild desalting and reclamation of wastewater and other moderately saline water sources with a high scaling potential, e.g., brackish groundwater.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00283.

Setup used in filtration, pore size estimates, and chemical composition of the solutions in scaling (high water recovery) experiments. (PDF)

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Notes

The authors declare no competing financial interest.

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