Desalination of domestic wastewater effluents: phosphate removal as pretreatment

Ilan Katz, Carlos G. Dosoretz*

Faculty of Civil and Environmental Engineering and Grand Water Research Institute, Technion — Israel Institute of Technology, Haifa 32000, Israel
Tel. +972-4 8294962; Fax +972-4 8228898; email: carlosd@tx.technion.ac.il

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Abstract

Water shortage has become a global issue and not only a problem relevant to arid zones. In the past decade desalination of sea and brackish water has been found to be a technically and economically acceptable solution for water shortage. More recently, desalination of wastewater effluents has also begun to be considered for sustainable water reclamation and reuse.

Performance of membrane desalination processes, such as reverse osmosis (RO), is restricted by different fouling and clogging constraints, including inorganic scaling as well as organic fouling and biofouling. Utilization of effluents for desalination introduced to the membrane systems new feed water characteristics with reduced salinity but higher concentration of dissolved organic matter and predominant inorganic ions that are less common in seawater. Phosphate scaling is found to be a main obstacle for effluents desalination, mainly due to the lack of appropriate antiscalants to cope with its precipitation, especially at high recovery rates.

This work was aimed to study the chemical coagulation of phosphate from wastewater effluents as a pretreatment for RO desalination. Based on preliminary jar tests experiments, sodium aluminate (SAL) at concentrations of 20–30 mg/L, was found as an efficient coagulant for phosphate and turbidity reduction. SAL coagulation was tested either as simultaneous phosphate removal during membrane bioreactor (MBR) treatment or as post-removal of phosphate from secondary effluents from activated sludge process, followed by microfiltration. Both alternative treatments resulted in almost complete phosphate removal (≥99%).

Batch desalination of both kinds of pretreated effluents showed also that calcium carbonate was a second scaling agent upon phosphate removal. The simultaneous MBR-coagulation, which in addition to complete phosphate removal displayed a significant reduction of alkalinity (75%), produced higher quality effluents and reduced the effect of calcium carbonate scaling, as compared to the post-coagulation of secondary effluents. Furthermore, the simultaneous MBR-coagulation process showed no detrimental effects on the MBR membrane performance or on the biological activity and avoided the need of an additional sedimentation or filtration step.

*Corresponding author.

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prior to RO. In conclusion, the MBR-chemical coagulation process seems to be a technically feasible pretreatment of domestic effluents for further desalination.

Keywords: Phosphate scaling; Coagulation; Desalination; RO; MBR; Wastewater treatment

1. Introduction

Water scarcity is a fact of life in arid and semi-arid regions where agricultural, domestic and industrial demands compete for limited resources. Continuous population growth, rising standards of living, industrialization and urbanization limit the freshwater available for agricultural practices. In Israel, where total demand for fresh water already exceeds the average natural supply, the freshwater deficit in agriculture is already being replaced in a great extent by treated wastewater (30% of the total water used in agriculture today and approx. 50 in 2010 [1]). However, the treatment of effluents prior to its use in irrigation, as is presently practiced, is not adequate for sustaining long-term agricultural production. Irrigation with inadequately treated effluent generates a gradual deterioration of soil and groundwater properties, specifically soil and groundwater salinization, and soil structure deterioration.

Water qualifying for unrestricted irrigation can be safely reclaimed applying combined state-of-the-art pressure driven membrane separation technologies capable of generating effluents free of pathogens, colloids, dissolved solids and organic contaminants. Although pressure-driven membranes are known technologies, some issues regarding their application on a large practical scale for wastewater reclamation must be resolved, especially for reverse osmosis (RO).

The major constraints during RO of treated effluents, promoting fouling and thus limiting separation efficacy, are the presence of soluble organic matter that tends to adsorb producing organic fouling and to promote microbial fouling — biofouling — as well as the scaling forming salts such as phosphate, that cannot be easily avoided by use of antiscalants, and carbonate [2,3]. Also when organic matter and nutrients are almost completely removed and biofouling is hindered, in practical terms, calcium phosphate, and in part carbonate, scaling became the dominant factor for membrane fouling and flux decrease during desalination of secondary or tertiary effluents, limiting RO recovery rates [4]. Calcium phosphate scaling during secondary effluents desalination by RO was reported as limiting factor for RO recovery during desalination of treated effluents [5–7]. Williams et al. [8] reported that the major obstacle to operating an RO process for desalination of marginal or river water at high recoveries (above 85%) is the precipitation of sparingly soluble inorganic salts. Furthermore, at recoveries higher than 95%, as would be needed for feasible large-scale RO of marginal water, antiscalants are not effective and pH control does not prevent precipitation of minerals such as barium sulfate and calcium sulfate, which cannot be removed by chemical cleaning [3,7,9]. High recovery rate of treated effluents, especially in inland sites, is not required only in terms of high water recovery but also disposal of large brine volume is not feasible from either an economic or resource-conservation standpoint.

Chemical precipitation of phosphorous, which is mainly present as inorganic phosphates such as orthophosphates and polyphosphates, is a commonly used process in water treatment [10,11]. Simultaneous removal as well as post-precipitation of P is also applied in secondary activated sludge to supplement biological removal during wastewater treatment [12–17].

Al and Fe salts are conventionally considered as precipitants for P removal. At the pH of
wastewater, the use of Al or Fe(III) salts for phosphate removal may be related more to the coagulation mechanism rather than precipitation. In general, two major mechanisms have been considered to be linked to the coagulation of phosphate ions with Al/Fe(III) salts: formation of Al/Fe-hydroxo-phosphate complexes with general formula of the type Me(OH)$_{3-x}$(PO$_4$)$_x$, in which M indicates Al or Fe, and adsorption of phosphate ions with Al(OH)$_3$/Fe(OH)$_3$ flocs, which are the predominant hydrolysis species in wastewater treatment practices. The best flocculation effect for Al$^3+$ salts is generally experienced in the pH 6.0–8.0 range. The isoelectric point of Al in its hydroxide form is 7.4 pH, corresponding to the point of minimum solubility [10,14,15,18].

The flocs resulting from Al salts are less dense and slower to form than those from iron salts. However, the advantage of Al compounds is shown in a higher efficiency in the neutralization of surface charges and hence in coagulation/flocculation processes (e.g. removal of turbidity) [14]. With exception of aluminate — NaAlO$_2$ (SAL), all common Fe and Al coagulants are acid salts and, therefore, their addition consumes alkalinity and lowers the pH of the treated water/wastewater. This is important because pH affects both particle surface charge and floc precipitation during coagulation [10,15]. Since pH correction to a neutral pH would incur major additional chemical costs it is seldom practical to operate a wastewater treatment process with pH control.

The present work was aimed to study the chemical precipitation of phosphate with SAL as a pretreatment of RO feedwater during wastewater desalination. SAL coagulation was tested either as simultaneous P removal during MBR treatment or as post-removal of P from secondary effluents form activated sludge process. Although SAL coagulation significantly helped to maintain acceptable low flux decrease, feedwater acidification was still required to suppress flux decline during RO.

2. Materials and methods

2.1. Experimental setup and operational conditions

The experimental setup for effluents desalination applied for the research is described in Fig. 1, and included primary settling of raw wastewater followed by simultaneous production of tertiary effluents either by activated sludge (secondary treatment) plus microfiltration (MF) or by membrane bioreactor (MBR), and finally RO. Chemical precipitation was alternatively tested as simultaneous P removal during MBR treatment and as post-removal of P from activated sludge effluents, as indicated (see red circles in Fig. 1).

Raw wastewater was obtained from the Technion campus sewage collection system. Primary effluents were continuously produced by sedimentation of the raw wastewater in a stainless steel sedimentation tank of 1 m$^3$ designed to operate at 1 h retention time. Secondary effluents (approx. 3 m$^3$/day) were continuously produced in a sequential batch reactor (SBR) of 1.8 m$^3$ capacity with computerized control, operated in 5 cycles per day at an influent flowrate of 0.6 m$^3$.

Fig. 1. Outline of the research scheme for effluents desalination. AS: activated sludge; MBR: membrane bioreactor; MF: microfiltration; Pe: primary effluents; PS: primary settling; RO: reverse osmosis; Se: secondary effluents; UF: ultrafiltration. Circles denote the points where alternative coagulation was performed.
and aeration step of 2 h followed by 30 min anoxic stage, per cycle. MBR effluents (approx. 0.65 m³/day) were produced in a ZW-10 unit (Zenon, Canada), equipped with a 0.2 m³ feed tank and 0.9 m² UF-hollow fibers membranes of nominal MWCO of 0.04 µm. Filtration flux was approx. 28 L/m²/h and a backpulse cycle of 45 s was conducted every 15 min. The biological reactors were operated in continuous regime and the treated effluents exceeding the storage capacity were returned to the municipal sewage system.

Microfiltration was done on a Memtek (USA) unit equipped with four-1 m² polypropylene hollow fiber filters of 0.2 µm nominal pore size, assembled in parallel. The unit was operated in crossflow mode at an initial transmembrane pressure (TMP) of 0.5 bar. Reverse osmosis was performed on a unit comprising a 2.5" spiral wound module of 0.7 m² (FilmTec TW30-2514, Dow). The system was run at a TMP of 10 bar and operation mode was as follows: when an experiment was started, half of the permeate was discharged to obtain a twofold (50% recovery) or fourfold (75% recovery) feed concentration, then batch operation (full recycling of permeate and concentrate) was maintained for 24 h till a new batch was introduced. Temperature was maintained constant at 25 ± 2°C in all the units by means of a heat exchanger and a water chiller system.

Coagulation experiments were carried out at room temperature in a six paddle stirrer-jar test apparatus (RAE Motors Corp.) in jars of 2 L each, at the following conditions: mixing at 200 rpm for 2 min, then addition of coagulant followed by mixing at 200 rpm for 5 min and then at 25 rpm for 25 min, then settling for 30 min and finally decantation.

Coagulation of SBR effluents for in pilot scale for RO experiments was performed in a 150 L conical tank for decantation containing 100 L effluents, in a similar time frame as described above for the jar test experiments, with 30 mg/L SAL as coagulant. Low mixing was performed by gentle air sparging and fast mixing was performed by means of a centrifugal pump. Following decantation, the supernant was further filtered by MF for RO experiments. Simultaneous coagulation in MBR was performed by continuous dosing (80–90 mL per day) of SAL to maintain a nominal concentration of approx. 18 mg/L in the mixed liquor. Both coagulated Se and MBR-effluents were stored in the dark at room temperature during their use in RO experiments (1–3 days per run).

Unless otherwise indicated all coagulation experiments were performed without pH correction.

2.2. Analytical techniques

Conductivity and pH were measured using a Cyborscan (Eutech Instruments). Turbidity was measured with a 2100P turbidimeter (Hach). Total organic carbon (TOC) and total nitrogen (TN) were measured with an N/C 2100 multi analyzer (Analytik Jena). P, Ca, Mg and Na were assayed by ICP-emission spectrometry (Optima 3000 DV, Perkin Elmer). Alkalinity, expressed as mg/L CaCO₃, and water content in sludge were conducted according to Standard Methods [19].

2.3. Chemicals

Ferric chloride — FeCl₃ (60% w/w) was purchased from Spectrum Laboratory Products Inc. and sodium aluminate (12.5% w/v) was kindly received from SWDP Ltd. (Haifa, Israel).

3. Results and discussion

3.1. Jar test experiments

Ferric chloride and SAL were first tested for their ability for chemical clarification of either primary or secondary effluents in jar test experiments. Evaluation of coagulants dosage
was tested in the range of 5–50 mg/L for SAL and 40–100 mg/L for ferric chloride (Figs. 2 and 3). Although P reduction was chosen as the coagulation goal, removal of other parameters including turbidity, TOC, Ca, Mg and alkalinity were tested. SAL displayed a considerable better efficacy for Pe clarification than ferric chloride. Indeed, a concentration of approximately 25 mg/L SAL was sufficient for almost complete P removal whereas ferric chloride did remove only ~80% P, even at 100 mg/L dosage, and 50 mg/L SAL reduced 91% turbidity in contrast to only 78% reduction achieved at 100 mg/L for ferric chloride. Coagulation of Se with ferric chloride at pH 5.5 and 6.5 did not change significantly phosphate removal (data not shown). Addition of SAL resulted in increase of pH from 7.5 to 8.8 which was paralleled by a increase of alkalinity (24%), attributed to the basic nature of SAL, and a decrease in Ca and Mg content (20% and 18%, respectively), indicating further precipitation of the respective phosphates and carbonates at the alkaline pH. In contrast, addition of ferric chloride resulted in almost no pH change, as well as Ca and Mg content, due to a consumption of alkalinity (19%).

As presented in Fig. 3, ferric chloride exhibited better coagulation characteristics while treating Se compared to that with Pe and a similar or even slightly higher P reduction (97%) than SAL (95%), even if an higher dose was still required (100 vs. 50 mg/L, respectively). For secondary effluents, addition of SAL resulted again in increase of pH and alkalinity (22%) with a
concomitant decrease of Ca (25%) and Mg (15%) concentrations whereas coagulation with ferric chloride was denoted by a consumption of alkalinity (21%) paralleled by a decrease of pH with almost no change in Ca an Mg levels. Whereas TOC remained almost unchanged during coagulation of primary effluents with both coagulants, coagulation of secondary effluents was reflected by a reduction, being slight for SAL (~20%) and much more pronounced for ferric chloride (~60%), clearly denoting the different nature of the colloidal organic matter in both cases (see right panels in Figs. 2 and 3).

Kang et al. [20] also reported a higher efficiency for P removal from Se to levels below 0.1 mg/L applying Al$^{3+}$ salts compared to Fe$^{3+}$ salts. Lopez-Ramírez et al. [21] achieved a final turbidity of about 1–2 NTU during coagulation of Se, using 25 mg/L ferric chloride combined with 0.5–1 mg/L anionic charge flocculant (PASAFLOC FI-35) and lime at pH 10.5. Adin et al. [22] reported a reduction of membrane fouling permeate characteristic compared to nanofiltration while practicing precoagulation with ferric chloride of secondary effluents before UF. At pH 5.5, the optimal dose was between 150 and 200 mg/L, whereas, at pH 7.8 the efficiency increases with the dose up to 300 mg/L. Soffer et al. [23] compared ferric chloride and alum for coagulation of secondary effluents prior and in conjunction to UF. Precoagulation significantly reduced membrane fouling and increased separation performance, particularly at an optimum dose/pH condition. In ferric chloride coagulation...
negative turbidity removal at the lower doses increased with decrease in pH. Alum removed turbidity and colloidal particles at a relatively narrow pH range of 6–9, best at pH 6–7 whereas ferric chloride performs well is larger being 3–10.

3.2. SAL coagulation as pretreatment for RO desalination

Based on the jar test results, sodium aluminate was further applied to test simultaneous MBR-coagulation of primary effluents and post-coagulation of secondary effluents followed by MF, as pretreatment alternatives to generate high quality tertiary effluents as feedwater for RO desalination, in accordance to the wastewater treatment scheme outlined in Fig. 1. Accordingly, SAL concentrations applied were 18 mg/L for simultaneous coagulation (continuous operation) and 30 mg/L for post-coagulation (batch operation). The results are presented in Tables 1 and 2. Both alternative treatment resulted in almost complete removal of P, with a residual concentration of <0.1 mg/L, and turbidity. In both cases an increase in sodium concentration of 15–17% was noticed, in line with its content in SAL.

The simultaneous MBR coagulation operated with a dose of 18 mg/L SAL resulted in almost no change of pH but 74% reduction of alkalinity, and a slight reduction of Ca and especially Mg. The high decrease of alkalinity (corresponding to 5.6 meq) can be attributed to a high CO₂ stripping due the intensive aeration in the MBR combined with carbonate precipitation (Table 1).

Post-coagulation of SBR effluents with a SAL concentration of 30 mg/L SAL, followed by MF filtration, resulted in one unit pH increase and 28% reduction of alkalinity (corresponding to 1.7 meq) and 11% Ca removal (Table 2). Among coagulation and filtration, MF resulted mostly in a slight further decrease of TOC (approx. 15%) and turbidity. The decrease of alkalinity may be due to and carbonate precipitation at the alkaline pH and CO₂ stripping by air bubbling used for slow rate agitation in the coagulation process.

Mass balance in terms of molar equivalents shown in Table 1 reveals that for the case of simultaneous MBR-coagulation the reduction of

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TOC (mg/L)</th>
<th>Na (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>P (mg/L)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary effluent</td>
<td>7.6 ± 0.3</td>
<td>119.0 ± 14.1</td>
<td>65.4 ± 6.2</td>
<td>166.3 ± 7.8</td>
<td>62.6 ± 2.6</td>
<td>29.0 ± 1.6</td>
<td>9.7 ± 2.4</td>
<td>378.0 ± 9.2</td>
</tr>
<tr>
<td>MBR effluent</td>
<td>7.5 ± 0.2</td>
<td>1.3 ± 0.5</td>
<td>6.5 ± 1.1</td>
<td>195.8 ± 10.7</td>
<td>62.2 ± 4.2</td>
<td>26.9 ± 2.6</td>
<td>0.1 ± 0.1</td>
<td>97.1 ± 25.8</td>
</tr>
<tr>
<td>Coagulation reduction (%)</td>
<td>99</td>
<td>90</td>
<td>−17</td>
<td>1</td>
<td>7</td>
<td>99</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Reduction (meq)b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.1 ± 0.3</td>
<td>0.2 ± 0.1</td>
<td>0.9 ± 0.2</td>
<td>5.6 ± 0.5</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
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<td>P</td>
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</tr>
</tbody>
</table>

Values represent mean ± SD.

NaAlO₂ titer = 0.7 meq as Al³⁺.

As P-PO₄³⁻.
P and consumption of alkalinity surpass the expected stoichiometry of phosphate precipitation with aluminium according to the following primary and secondary reactions:

\[
\text{Al}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{AlPO}_4 + 2\text{H}^+ \quad (1)
\]

\[
\text{Al}^{3+} + 3\text{HCO}_3^- \rightarrow \text{Al(OH)}_3 + 3\text{CO}_2 \quad (2)
\]

both consuming alkalinity. This is interesting since the stoichiometric molar ratio of Al:P of 1:1 in AlPO$_4$ is never achieved in practice, and the actual ratio between Al dosed and P removed varies between 2:1 and 3:1, especially at phosphate lower than 10 mg P/L [10,14,15,18]. For the case of post-coagulation a ratio of Al:P of 2.75:1, coinciding with the theoretical expectations, whereas an Al:alkalinity ratio of 2:1 was obtained, in spite of the increase of pH (see Table 2). Hence, excess alkalinity removal is explained by CO$_2$ stripping due to intense aeration for both membrane operation and biological oxygen consumption in the MBR and sparging for slow rage agitation during post-coagulation combined with carbonate precipitation, as discussed before.

The effect of phosphorus co-precipitation with ferric chloride dosing on biological phosphorus along with carbon and nitrogen removal was investigated in a SBR for slaughterhouse wastewater treatment, however a residual P concentration of 3 mg/L was attained [24]. Chapman et al. [25] studied preflocculation of secondary effluents with ferric chloride in a static floating medium flocculator to enhance MF performance. Coagulant concentration for P and suspended solids removal were optimum at 90 mg/L whereas for turbidity removal at 20–30 NTU. They achieved 83% removal of turbidity, 97% of phosphorus 45% of TOC. As a result of the treatment, the permeate flux in MF was improved by 70% and a 30–70% higher removal of organics was observed.

Biological P removal in MBRs, and especially enhanced biological phosphate removal is getting increased interest, however this process is less robust than chemical P coagulation, and requires additional anaerobic and anoxic compartments [26]. The simultaneous coagulation within the MBR saved the necessity of a separate filtration step that was added to the SBR effluents coagulation before the feed to the RO.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TOC (mg/L)</th>
<th>Na (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>P (mg/L)</th>
<th>Alkalinity (mg/L as CaCO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR effluent</td>
<td>7.7 ± 0.1</td>
<td>2.5 ± 0.2</td>
<td>7.8 ± 0.8</td>
<td>156 ± 4.4</td>
<td>58.4 ± 1.3</td>
<td>26.7 ± 0.7</td>
<td>4.3 ± 0.1</td>
<td>300 ± 12.5</td>
</tr>
<tr>
<td>Coagulation + MF</td>
<td>8.7 ± 0.0</td>
<td>1.8 ± 0.7</td>
<td>6.5 ± 0.0</td>
<td>180 ± 1.7</td>
<td>51.9 ± 6.0</td>
<td>25.9 ± 2.0</td>
<td>0.1 ± 0.1</td>
<td>215 ± 2.5</td>
</tr>
</tbody>
</table>

<p>| Reduction (coagulation + MF) (%) | 29  | 17  | −15  | 11  | 3  | 99 | 28 |</p>
<table>
<thead>
<tr>
<th>Reduction (meq)$^b$</th>
<th>Ca</th>
<th>Mg</th>
<th>P$^c$</th>
<th>Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.3 ± 0.2</td>
<td>0.1 ± 0.1</td>
<td>0.4 ± 0.0</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>

$^a$Values represent mean ± SD.

$^b$NaAlO$_2$ titer = 1.1 meq (as Al$^{3+}$).

$^c$As P-PO$_4^{3−}$. 

The effect of phosphorus co-precipitation with ferric chloride dosing on biological phosphorus along with carbon and nitrogen removal was investigated in a SBR for slaughterhouse wastewater treatment, however a residual P concentration of 3 mg/L was attained [24]. Chapman et al. [25] studied preflocculation of secondary effluents with ferric chloride in a static floating medium flocculator to enhance MF performance. Coagulant concentration for P and suspended solids removal were optimum at 90 mg/L whereas for turbidity removal at 20–30 NTU. They achieved 83% removal of turbidity, 97% of phosphorus 45% of TOC. As a result of the treatment, the permeate flux in MF was improved by 70% and a 30–70% higher removal of organics was observed.

Biological P removal in MBRs, and especially enhanced biological phosphate removal is getting increased interest, however this process is less robust than chemical P coagulation, and requires additional anaerobic and anoxic compartments [26]. The simultaneous coagulation within the MBR saved the necessity of a separate filtration step that was added to the SBR effluents coagulation before the feed to the RO.
system. The coagulation with SAL within the MBR did not result detrimental to the biological process, and in addition a satisfactory P removal accompanied by alkalinity consumption at a suitable pH for biological activity was self-maintained. In addition, some improvement in the quality of the mixed liquor suspended solids (MLSS) was observed. In fact, a reduction in sludge volume index (SVI) from 180–250 mL/g without coagulation to 110–150 mL/g with coagulation was obtained. The dewatering characteristics of the biosolids was improved as well as a result of the coagulation, as reflected by the increase of the free water content at expenses of the decrease of interstitial water content, similar to the proportions found in activate sludge biosolids (Fig. 4). Nevertheless, the fixed solids content of the MLSS increased from 15–20% to 35–40% as result of the coagulation, which may be detrimental for the disposal and further utilization of the biosolids generated. Finally, the hydraulic performance of the MBR membranes was not significantly altered by the simultaneous coagulation in this study. Chemical coagulation for immersed UF membrane reactors, as for UF filtration of secondary effluents, may be advantageous, however, optimization of shear stresses close to the immersed membrane to minimize a deposit set up on the membrane surface is still required [23,27].

3.3. RO desalination of tertiary effluents

Effluents desalination was studied in a batch RO system at 50% recovery. The impact of the pretreatment on RO performance was assessed by the change in relative permeability and mass balance of precipitating species obtained by chemical analysis of the feedwater, concentrate and permeate.

The RO performance comparing simultaneous MBR-coagulation and post-coagulation of Se followed by MF is displayed in Fig. 5. MF-filtered Se without coagulation served as control. Membrane permeability declined rapidly when no coagulation was performed reaching 41% of its initial value after 48 h. Post-coagulation/MF of Se improved the performance of the RO separation and after 72 h of operation still 55% of the initial permeability was maintained.

![Fig. 4. Influence of simultaneous MBR-coagulation with SAL (MBR + SAL) on sludge volume and water holding capacity. MBR and SBR stand for controls without coagulation for membrane bioreactor and activated sludge, respectively. Sludge volumes were in the range of 0.1–0.5% and are not seen. Bar represent standard deviation.](image)

![Fig. 5. Influence of pretreatment on the relative RO permeability during desalination of tertiary effluents. MBR + SAL: simultaneous MBR-SAL coagulation; Se + SAL/MF: post-coagulation of SBR effluents and MF; control: SBR effluents after MF, without coagulation. RO was performed with full recycle of permeate and concentrate. Bars denote standard deviation.](image)
The best performance was attained by the simultaneous MBR-coagulation, in which after 72 h of operation still 90% of the initial permeability was maintained, clearly showing the advantage of this pretreatment in removing P but also considerably reducing alkalinity. Average rejection values were 92% of monovalent ions (Na, K), 97% rejection of divalent ions (Ca, Mg), 100% for P and 93% TOC.

The difference in permeability decline rate could be explained by mass balance calculations made from chemical analysis data of the feedwater, concentrate and permeate, suggesting inorganic scaling as the main cause for this decline (Fig. 6). Since the runs lasted only 1–3 days and TOC change was only 10–20%, permeability change cannot be attributed to organic fouling or biofouling. Nevertheless, organic fouling and the development of biofouling cannot be completely discarded as partially affecting the permeability, in spite of the short term of the experiments [28]. As seen in Fig. 6, the runs without coagulation (control) displayed complete precipitation of all the phosphate fed to the system, clearly indicating that phosphate scaling, and in part carbonate, was the most probably cause for the severe decrease of permeability. For both coagulation treatments, since phosphates were eliminated to almost completion, the mass balance indicates that calcium carbonate is the most likely secondary scaling specie, as evidenced by the change in calcium and alkalinity values, inline with previous reports [6,29].

The lower levels of Ca and alkalinity precipitated during RO fed with the simultaneous MBR-coagulation effluents in comparison to the post-coagulation ones are in line with the relative decrease of permeability (compare Figs. 5 and 6). However, since in both cases Ca disappearance equivalents exceed carbonate equivalents disappearance, other calcium salts seem to be being precipitated, such as sulfate which was not assayed. Calcium sulfate dihydrate (gypsum) has been reported to crystallize over RO membrane during desalination of Colorado River water [30]. Calculation of Langelier saturation index (LSI) of the both RO feeds displayed that post-coagulated Se, having higher LSI (1.3) and higher pH (8.5) than simultaneous MBR-coagulation (LSI = 0.75 and pH = 8.0), may have a higher potential for carbonate precipitation. These values are in complete agreement with the mass balance values presented in Fig. 6 and in line with the decrease of permeability presented in Fig. 5 as well as with the coagulation data presented in Tables 1 and 2, all showing the advantages of the simultaneous MBR-coagulation.
of the simultaneous MBR-coagulation (75% reduction of alkalinity in addition to complete phosphate removal).

To further reduce carbonate, and probably sulfate, precipitation, additional RO runs fed with simultaneous MBR-coagulation effluents were performed with pH adjustment to 6.5. The results are presented in Fig. 7. Under these circumstances, the slight decrease of permeability (<8%) observed for the acidified simultaneous coagulation-MBR effluent can be attributed to other fouling form than scaling. Moreover, these findings indicate the need for further acidification or high antiscalant dosing to reduce significantly reduce scaling during RO desalination of secondary effluents. A similar flux improvement for each one of the different pretreatments was achieved in RO experiments performed at 75% recovery, although a much more pronounced flux decline was evident for the control without coagulation and acidification (data not shown).

4. Conclusions

Utilization of effluents for desalination introduce to membrane systems feedwater of reduced salinity but higher concentration of dissolved organic matter and predominant inorganic ions that are less common in sea water. Although carbonate scaling is present, phosphate scaling appears to be a main obstacle for effluent desalination, mainly due to the lack of appropriate antiscalant to handle its precipitation, especially at high recovery rates. This work was aimed to study the chemical coagulation of phosphate as a pretreatment for RO of wastewater effluents. Based on preliminary jar test experiments, SAL at concentrations of 20–30 mg/L was found as an efficient coagulant for phosphate and turbidity reduction. SAL coagulation was tested either as simultaneous phosphate removal during MBR treatment or as post-removal of phosphate from activated sludge effluents followed by microfiltration. Both alternative treatments resulted in almost complete phosphate removal (≥99%). As well as being able to remove phosphate and reduce alkalinity, chemical coagulation is able to remove dissolved natural organic matter and other colloids, and especially humic substances, in the form of a colloidal metal–humate complex [10,31], which may increase membrane performance both during pretreatment and desalination stages.

Desalination of both kinds of pretreated effluents showed also that calcium carbonate was a second scaling agent following phosphate removal. The simultaneous MBR-coagulation, which in addition to complete phosphate removal displayed a significant reduction of alkalinity (75%), produced higher quality effluents and reduced the effect of calcium carbonate scaling, as compared to the post-coagulation of secondary effluents. Furthermore, the simultaneous MBR-coagulation process showed no detrimental effects on the MBR membrane performance or on the biological activity and avoided the need
of an additional sedimentation or filtration step prior to RO.

In conclusion, the MBR-chemical coagulation process seems to be a technically feasible pretreatment of domestic effluents for further RO desalination, generating soft effluents with low content of organic matter and nutrients.

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References


