



Electrodialysis on RO concentrate to improve water recovery in wastewater reclamation

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ABSTRACT

Over-consumption of groundwater in coastal areas causes seawater intrusion and soil salinization, which is a threat to residents, to agricultural activity and to the ecological system. In this study, a more sustainable approach is investigated based on groundwater recharge of the unconfined aquifer in the dune water catchment area in the western part of the Flemish coast. Ultrafiltration (UF) followed by reverse osmosis (RO) is currently applied to treat the secondary effluent from a wastewater treatment plant (WWTP) for infiltration (groundwater recharge). This paper investigates the feasibility of electrodialysis (ED) on the RO concentrate to reduce the volume of salty water discharge and to improve the overall water recovery to produce infiltration water for groundwater recharge. In the pilot system, the decarbonation process was used to reduce scaling potential of the feed or the concentrate stream of the ED. Based on various experiments in batch and in feed-and-bleed mode, ion transport mechanisms were studied to monitor the effluent water compositions. Meanwhile, a factor named critical scaling concentration (CSC) was established to predict the potential occurrence of scaling. Ozonation was used to improve the biodegradability of the ED effluent hence to reduce the potential of organic compounds accumulation in the recirculation system. Thus, ED was found to be a good option to treat RO concentrates.

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1. Introduction

Nowadays, water shortage has become a global issue [1]. Water reuse, wastewater reclamation and desalination of saline water are crucial strategies to generate water needed for economical development [2–4]. It is recognized that water supply and sanitation in developing countries is even more important, in view of the Millennium Development Goals (MDG) [5]. Thus, water and wastewater treatment technologies are to be developed and applied to fulfill the higher requirements on water quantities and quality. Apart from being the fastest growing process for desalination, reverse osmosis (RO) now also increasingly used in other applications [6,7] due to the high and stable quality of the water produced and the relatively low cost.

However, there are still some drawbacks for RO application. One of the most important issues is the treatment of the concentrated waste drain from RO due to the high salinity of this RO

concentrate. Traditionally, the RO concentrate is discharged into the natural water body (with or without dilution, depending on the local discharge regulations to avoid degradation of the water body) or treated by evaporation. The former method is not environmentally friendly and the latter process is very costly (when conventional energy is used for evaporation, potentially even less environmentally friendly). In the mid-1990s, a survey of membrane drinking water plant disposal methods in the United States was conducted [8] for plants with a capacity above 25,000 gal/day (95 m³/day). In this survey, 78% of the 137 installations were RO, 11% were NF (nanofiltration) and the rest 11% were electrodialysis. The survey showed that roughly half (48%) of the 137 installations chose to discharge their concentrate directly in surface water; in 23% of the cases, the concentrate was mixed with sewage wastewater effluent and discharged in the water body; only in 6% of them it was chosen to discharge the concentrate to evaporation ponds. In 1999, a follow-up survey [9] showed that 60% of the installations discharged their concentrate directly into surface water. However, investigation shows that the standard limit for surface water discharge require that the salinity difference should be less than 10% [10].

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More recently, new processes have been developed for treating and recycling the brine from the RO process. Van der Bruggen et al. [11] reviewed the possibilities to treat or to discharge the pressure-driven membrane concentrates and pointed out that distillation, electrodialysis, or an integrated membrane operation can be applied to minimize the waste fraction from the brine. Greenlee et al. [12] concluded that zero liquid discharge processes (including thermal evaporators, crystallizers, brine concentrators, and spray dryers) for RO concentrate recovery are technically feasible but more efforts have to be done to reduce the capital and operational cost.

On the other hand, rather than considering to minimize RO concentrate waste disposal, an integrated system allows to reclaim the RO concentrate with the aim of: (i) producing chemicals from the solutes and (ii) water reclamation or recycle to the treatment system. Some investigations had been carried out to make the RO concentrate “valuable”. Electrodialysis (ED) or electrodialysis reversal (EDR) has been proposed as part of such system. Mavrov et al. [13] treated RO/EDR/ion exchanger concentrates from a surface water desalination plant by electrodialysis with bipolar membranes (EDBMs) to produce mixed acid and mixed base for regeneration of the ion exchangers in the plant. Badruzzaman et al. [14] investigated the feasibility to produce mixed acid and mixed base by EDBM process from an RO concentrate stream from the wastewater treatment plant in Rio Rancho, U.S. After 10 h operation of the EDBM stack (PCCell GmbH, Germany), the production (mixed acid and mixed base) quality was comparable with technical grade and the NF (US National Formulary) grade acids and bases. Thus, it was proved that the use of EDBM to treat and produce mixed acid and mixed base is technically feasible. Xu and Huang [15] reviewed ED-based separation processes and concluded the applications of ED/EDBM integrated RO/NF process for brine minimization and chemical production. Furthermore, a novel type of electrodialysis, named electrostatic shielding electrodialysis (ESE) can be a promising option to minimize RO concentrate and to produce acids and bases without chemical and thermo sensitive polymeric ion-exchange membranes or bipolar membranes [16–19]. The ESE stack has proven to treat electroplating rinse waters [17], brackish water [18,19] and to produce acid and base [19]. Further investigation on treating RO concentrate should be interesting since membrane fouling and scaling can be eliminated [16].

Reahl [20] reported the design and the operation of an UF–RO–EDR system to reinsert 85% of the RO concentrate to the UF–RO system and to improve the overall water recovery to 97%. Similarly, an RO–EDR system was applied to treat the brackish water with high scaling potential from the Sahel region in Tunisia; the system overall water recovery reached 91.6% [21]. Korngold et al. [22,23] investigated the treatment of the concentrate from an RO unit fed by brackish water, by a pilot ED installation with a separated gypsum precipitator to reduce the scaling problem in ED. The salts in the RO concentrate were partially removed by the ED and the produced water was mixed together with the RO permeate, thus, the overall recovery of the RO unit was improved; furthermore, the volume of brine in the combined process was reduced, at the same time increasing its salt concentration. The salt concentration in the brine increased from 1.5% to 10% and the RO unit overall recovery increased to 97–98% [23]. More recently, Oren et al. [24] investigated a pilot study on an RO–EDR process with a side loop crystallizer to improve water recovery and produce mineral byproducts on brackish groundwater from the Negev Highland, Israel. It is reported that the overall water recovery reached over 98% and the treatment cost was significantly less than the Israel water tariff and competitive with the cost of conventional RO [24].

In conclusion, ED (or EDR) shows remarkable advantages technically and economically on treating RO concentrate streams.

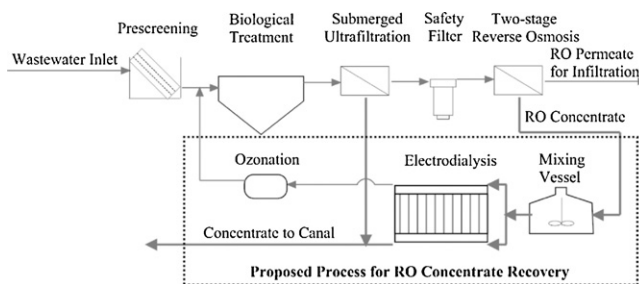


Fig. 1. Schematic diagram of I.W.V.A. wastewater treatment process.

Although some investigations on the treatment of RO concentrate by ED have been done, further study on the details of the process is needed, in view of fully understanding the influence of operational parameters and transport of the inorganic and the organic compounds through the membranes. Furthermore, scaling on the membranes and fouling remain potential hurdles.

In July 2002 the Intermunicipal Water Company of the Veurne region (I.W.V.A., Wulpen, Belgium) has started to treat wastewater for producing infiltration water for groundwater recharge of the dune water catchment ‘St-André’. As this water is recharged in a dune area, which is of high ecological value, the infiltration water must have low levels of salts and nutrients. Based upon the quality parameters set for the infiltration water, a combination of membrane filtration (UF and RO) was chosen to treat the (mainly domestic) wastewater effluent. The schematic diagram of the wastewater treatment process is shown in Fig. 1. The intake of the wastewater first passes a mechanical screen with 1 mm openings to remove all larger particles. After conventional biological (anaerobic–aerobic) treatment, the water is clarified and flows to the submerged hollow fiber UF units. From the UF filtrate reservoir the water first passes the cartridge safety filters with pore sizes of 15 μm , and is then pumped to the RO system. The recovery of the RO system is around 75% and is varied according to the feed water conductivity. Finally, the RO product (permeate) is pumped for infiltration; the RO brine (concentrate) is mixed with the UF concentrate and discharged to the canal.

To improve the overall water recovery of the RO process for producing infiltration water, an ED installation is proposed to treat the RO concentrate and to re-insert the product, i.e., the diluate of the ED, into the biological treatment process. The proposed procedure is shown in Fig. 1: RO concentrate flows into a mixing vessel with acid to reduce the scaling potential, then it is pumped to the ED installation for desalting. The ED product (diluate) is ozonated prior to be re-inserted into the biological treatment process. The ED brine (concentrate) is mixed with the UF concentrate to meet regulations and is discharged to the canal.

In this work, a systematic investigation was done to study a pilot scale ED installation to treat RO concentrate with high scaling potential from a WWTP, in view of improving the overall water recovery of the system. As proposed, the ED product (effluent) will be recycled into the biological treatment unit of the WWTP and the RO overall water recovery can be improved from 75% to around 95%. To achieve this, some basic requirements have to be fulfilled:

1. the pilot system can be long-term operating in a stable way;
2. the salt removal should be around 75% and the ED effluent conductivity should be similar as the influent of the biological treatment unit;
3. besides conductivity, the ED effluent quality should be similar as the influent of the biological treatment unit, i.e., concentration of different cations and anions, pH, biodegradability of organic compounds.

Table 1
Characteristics of the PCA standard cation and anion exchange membrane.

Membrane	Thickness (μm)	Ion exchange capacity (mequiv./g)	Chemical stability (pH)	Permselectivity	Functional groups	Surface Potential (Ωcm^2)
PC-SK	130	ca. 1	0–11	>0.96	$-\text{SO}_3\text{Na}$	0.75–3
PC-SA	90–130	ca.1.5	0–9	>0.93	$-\text{NR}_4\text{Cl}$	1–1.5

In view of these objectives, different experiments and analyses that were carried out are described in this article. Due to high scaling potential of the RO concentrate (ED feed), decarbonation by hydrochloric acid in either the ED feed or the ED concentrate has been investigated. During the experiments, transport mechanisms of the inorganic ions and the organic compounds were studied to evaluate the effects on the water composition of the ED effluent. Due to high concentrations of organic compounds in the ED effluent, ozonation as a post-treatment was studied to improve the biodegradability.

2. Materials and methods

2.1. Membrane characteristics

Standard anion exchange membranes (PC-SA) and standard cation exchange membranes (PC-SK) were installed in the pilot scale ED stack. PC-SA and PC-SK are homogeneous membranes; characteristics of the membranes as given by the manufacturer (PCA – Polymerchemie Altmeier GmbH, Heusweiler, Germany) are shown in Table 1.

PC-SA membrane surface and cross-section micrographs (Fig. 2) were taken by scanning electron microscope (SEM) (XL30 Phillips, Eindhoven, the Netherlands). It can be seen that PC-SA membrane has a polymeric backbone; the membrane's functional layer is around 20 μm thick.

2.2. Pilot experiment set-up and the feed waters

A PCCell ED 1000H (PCCell GmbH, Heusweiler, Germany) electrodialysis stack was installed in the pilot scale skid (IECNV, Riemst, Belgium). The set-up consists of three separated circuits with three 200 L vessels for the diluate, the concentrate and the electrode rinsing solution. For each membrane, the active surface area was 0.1 m^2 and the flow channel width between two membranes is 0.5 mm. There are 25 cell pairs in the stack, each containing a diluate and a concentrate compartment, so in total 25 pieces of anion exchange membranes and 26 pieces of cation exchange membranes are used. Thus, the total anionic membrane surface area in the stack is 2.5 m^2 . During the experiments, the RO concentrate was used for the diluate and the concentrate streams in the ED (except specified with NaCl as the concentrate). H_2SO_4 (0.1 M) was used as the electrode rinsing solution.

In average, the RO concentrate (ED feed) has following characteristics: pH 7.5, conductivity 5 mS cm^{-1} , TOC 40 mg L^{-1} , Ca^{2+} 400 mg L^{-1} , Mg^{2+} 35 mg L^{-1} , bicarbonate 1300–1600 mg L^{-1} . Due to the high scaling potential caused by the high concentration of calcium and carbonate ions present in the RO concentrate, HCl was added in the ED feed or the ED concentrate vessel to adjust pH to 5.5–6.5. Due to rainfall and seasonal variation, the RO concentrate conductivity varies between 3.0 and 5.8 mS cm^{-1} .

The pilot scale experiments were conducted in three different operational modes: batch mode, feed-and-bleed mode and continuous mode.

2.2.1. Batch mode

Batch mode operation was carried out with two objectives: (1) to verify the modeling results based upon laboratory experiments and hence optimize the operational parameters of the pilot system; (2) to be used before the long-term feed-and-bleed operation to reduce the start-up salt concentration. During batch mode, the diluate, the concentrate and the electrode rinsing solution were recirculated in the system at constant current until the salt removal reached around 75% of the initial value.

2.2.2. Feed-and-bleed mode

Feed-and-bleed mode was applied for long-term operation to produce an effluent (product) with 75% of salt removal. During feed-and-bleed mode, the ED concentrate and the electrode rinsing solution were recirculated and the diluate was discharged in an intermittent way. The applied current and the circulation flow rate (500 L h^{-1}) of the three circuits were the same as applied in batch mode. A not flow rate of 75 L h^{-1} from the diluate was used. Under optimized conditions, this stream should contain around 25% conductivity of the RO concentrate (the feed stream). This stream was regarded as the product of the ED system and it is proposed to be re-inserted into the biological treatment unit of the WWTP.

2.2.3. Continuous mode

The continuous mode was used for cost analyses of the system. During this mode, the ED concentrate and the electrode rinsing solution were recirculated while the diluate through the stack was continuously discharged without recirculation. Different flow rates and currents were applied to compare the operational cost under various conditions.

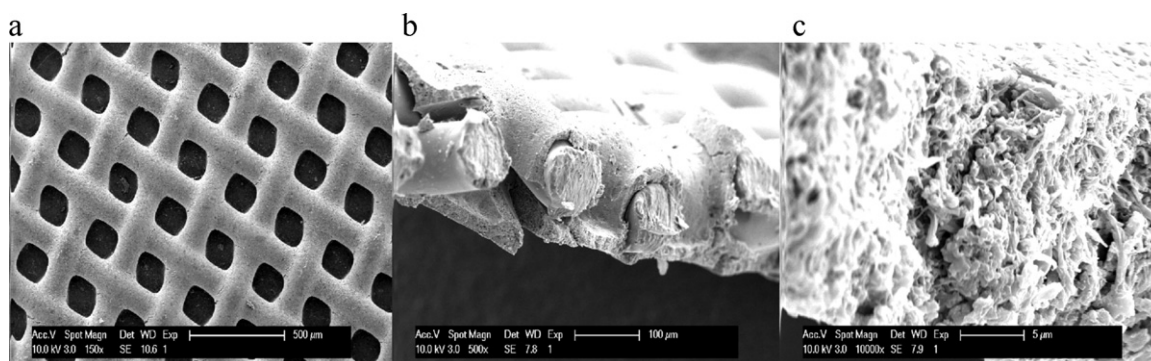


Fig. 2. SEM micrographs of PC-SA membrane surface (a, 150 \times magnification, 10 kV) and cross-section (b, 500 \times magnification, 10 kV; c, 10,000 \times magnification, 10 kV).

2.3. Post-treatment: ozonation process

Ozonation is the post-treatment of the electrodialysis effluent (product) stream to improve the biodegradability. A lab scale ozone generator (Fisher OZ500, Germany) with a pure oxygen gas flow (Praxair, Belgium) was used in the experiments. The gas flow rate was set at 60 L h^{-1} at room temperature and atmospheric pressure. A glass reactor with a working volume of 1 L was used in the experiments. The ozone–oxygen mixing gas from the generator was introduced to the bottom of the glass reactor through a Pyrex fritted glass diffuser and mixed with the target water by a magnetic stirrer. During the experiments, 1 L min^{-1} of mixed ozone–oxygen gas ($24 \text{ mg min}^{-1} \text{ O}_3$) was dosed into the target water. The original and ozonated ED diluates (products) were analyzed for TOC, BOD₅ and ultraviolet absorbance at 254 nm (UV₂₅₄) to examine the effect of the ozonation process on the organic compounds and their biodegradability.

2.4. Analytical methods

All chemicals in the experiments were analytical grade, except hydrochloric acid for decarbonation, which was industrial grade. Samples from the pilot scale experiments were collected every 1-h or when necessary.

For the samples from the pilot experiments, pH was measured by Ankersmit 420A pH meter (Orion, Boston, USA) and conductivity was measured by ORION 160 conductivity meter (Orion, Boston, USA). The ion (anion and cation) concentration was measured by ion chromatography (DIONEX series 4500i with IONPAC AS14 analytical column for anion analysis and DIONEX DX-100 with IONPAC CS14 for cation analysis, DIONEX, USA). The eluent for anion analysis contained $3.5 \text{ mmol L}^{-1} \text{ CO}_3^{2-}$ and $1.0 \text{ mmol L}^{-1} \text{ HCO}_3^-$; and the eluent for cation analysis contained $10 \text{ mmol L}^{-1} \text{ CH}_3\text{SO}_2\text{OH}$. The concentration of inorganic and organic carbon were measured using a TOC Analyzer (TOC-V CPN E200V TOC Analyzer, Shimadzu, Japan).

For the samples from the ozonation process, TOC was measured by a TOC analyzer (TOC 5000A TOC Analyzer and autosampler, Shimadzu, Japan). The procedure for BOD₅ measurement was carried out by Standard Method 5210 B [25]. UV₂₅₄ was measured by a Shimadzu UV-1601 double beam spectrophotometer at 254 nm.

2.5. Data analysis

2.5.1. Membrane selectivity (S_B^A) and current efficiency (η)

Membrane selectivity, represented as membrane separation efficiency, was calculated by the method introduced by Van der Bruggen et al. [26]. In this method, the separation efficiency S between component A and B is evaluated as

$$S_B^A(t) = \frac{(c_A(t)/c_A(0)) - (c_B(t)/c_B(0))}{(1 - c_A(t)/c_A(0)) + (1 - (c_B(t)/c_B(0)))} \quad (1)$$

The range of S_B^A is from -1 to 1 . If ion A is transported slower than ion B , the S_B^A value is between 0 and 1 ; if ion B is transported slower, then the S_B^A is between -1 and 0 .

The current efficiency of ion A is defined as the ratio of the electrical charge used for the transport of ion A to the total electrical current charge. Assuming the applied current being constant, the current efficiency of ion A (η_A) can be calculated as

$$\eta_A = \frac{z(\Delta m_A(t)/M_A)F}{nIt} \times 100(\%) \quad (2)$$

In a continuous test it is calculated as

$$\eta_A = \frac{zQ_f(c_i - c_0)F}{nI} \times 100(\%) \quad (3)$$

where $\Delta m_A(t)$ is the weight of transferred ion, z is the charge number of ion A , M_A is molar mass of ion A , F is the Faraday constant, I is the applied current, t is the time period, Q_f is the diluate flow rate through the stack, c_0 and c_i is the feed and the effluent concentration in the diluate compartment, n is the number of cell pairs in the ED stack. $\Delta m_A(t)$ can be calculated from equation below:

$$\Delta m_A(t) = RA_t = m_A^d - c_A^d(t)V_0^d \quad (4)$$

2.5.2. CaSO₄ saturation Index and CaCO₃ (Langelier) saturation index (LSI)

Due to the high concentrations of Ca^{2+} , SO_4^{2-} and CO_3^{2-} in the RO concentrate, it is possible that scaling at the diluate and/or concentrate side of the membrane can affect the ED system operation. Therefore, the saturation levels of CaSO_4 and CaCO_3 in the experimented waters were calculated.

The calcium sulphate saturation level can be calculated by the following equation [27]:

$$\delta_{\text{CaSO}_4} = \frac{C_{\text{Ca}^{2+}} C_{\text{SO}_4^{2-}} \gamma_{\pm}^2 C_w^2}{K_{sp}} \quad (5)$$

where γ_{\pm} is the mean calcium sulphate activity coefficient, $\gamma_{\pm}^2 = \gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}}$; $K_{sp}(\text{CaSO}_4)$ is the solubility product of CaSO_4 , $K_{sp}(\text{CaSO}_4) = 4.93 \times 10^{-5}$ at 25°C [28]. γ_{\pm} can be calculated by Debye–Hückel theory [29]:

$$-\log \gamma_i = \frac{Az_i^2 \mu^{1/2}}{1 + B\alpha_i \mu^{1/2}} \quad (6)$$

γ_i is the activity coefficient of ion i , μ is the ionic strength of the solution, z_i is the charge number of ion i , α_i is the effective ionic radius of ion i (in nm). At 25°C , $A = 0.5115$, $B = 0.3291$ [28].

Thus

$$-\log \gamma_i = \frac{0.5115z_i^2 \mu^{1/2}}{1 + 0.3291\alpha_i \mu^{1/2}} \quad (7)$$

The ionic strength μ of a solution is calculated by

$$\mu = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (8)$$

where c_i is the molar concentration of ion i , z_i is charge number of ion i .

α_i effective ionic radius, for calcium: $\text{Ca}_{\alpha}^{2+} = 0.6 \text{ nm}$, sulphate: $\text{SO}_{4\alpha}^{2-} = 0.4 \text{ nm}$ [28].

At pH 6.5–9.5, the Langelier saturation index (LSI) [30] is used to indicate the scaling potential of water containing carbonates, which is expressed by

$$\text{LSI} = \text{pH} - \text{pH}_S \quad (9)$$

where pH_S is the “saturation pH” at which the water is saturated with calcium carbonate. pH_S is defined as

$$\text{pH}_S = (9.3 + A + B) - (C + D) \quad (10)$$

where $A = (\log_{10} [\text{TDS}] - 1)/10$, $[\text{TDS}]$ is the concentration of total dissolved solids (mg L^{-1}); $B = -13.12 \times \log_{10}(T) + 34.55$, T is the Kelvin temperature (K); $C = \log_{10}[C_{\text{Ca}^{2+}}^*] - 0.4$, $[C_{\text{Ca}^{2+}}^*]$ is the concentration of Ca^{2+} as CaCO_3 (mg L^{-1}); $D = \log_{10}[\text{Alk}^*]$, $[\text{Alk}^*]$ is the concentration of alkalinity as CaCO_3 (mg L^{-1}).

3. Results and discussion

3.1. Decarbonation for anti-scaling

As the ED feed water, the RO concentrate has a high concentration of calcium and carbonates (around 1300–1600 ppm as

Table 2
Typical feed water and the simulated concentrated water ($\times 10$) ions content and the scaling potential evaluation at pH 7.8, 25 °C.

	Ion concentration (mg L^{-1})								Scaling potential	
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	δ (%)	LSI
Feed	722	154	426	49	974	113	1377	433	5.4	2.21
Simulated concentrate	7220	1540	4260	490	9740	1130	13,770	4330	105.1	4.11

carbonates). Table 2 shows the concentration of the main ions in the typical ED feed water (RO concentrate). The calcium sulphate saturation level (δ) and calcium carbonate saturation index (LSI, i.e., Langelier saturation index), calculated by Eqs. (5) and (9), indicate that the ions that cause the scaling potential are calcium, magnesium and carbonate, since the LSI of the feed water reached 2.21, which means the scaling potential of Ca²⁺ and Mg²⁺ carbonates is high. If concentrated 10 times, the LSI will reach 4.11. The scaling potential of SO₄²⁻ is relatively low in the feed water, the saturation level δ is only 5.4%, even concentrated 10 times, it just reaches saturation (105.1%).

According to CO₃²⁻ – HCO₃²⁻ – H₂CO₃ equilibrium, the pH of the RO concentrate (ED feed) should be adjusted to 5.5–6.5 to ensure that most of the inorganic carbon is present as bicarbonate (HCO₃⁻), which will not cause scaling. On the other hand, since carbonate (CO₃²⁻) continuously migrates from the diluate to the concentrate compartment, the diluate compartment will not have scaling problem. Therefore, only acidifying the ED concentrate stream is an alternative method to prevent scaling. In this work, both methods were used: acidification of the ED feed (called decarbonated RO concentrate – DROC, ⊙ in Fig. 3) and of the ED concentrate (called decarbonated ED concentrate – DEDC, ⊗ in Fig. 3) by adding HCl. Differences between these two methods and implications will be discussed in the following sections.

3.2. Pilot scale ED operation

3.2.1. Ion removal in batch experiment with decarbonated feed

In this paper, the batch mode was applied to desalinate the RO concentrate to the target concentration (around 75% of salt removal) prior to the feed-and-bleed mode. Ion removal efficiency (%) was studied in batch experiments on different decarbonated feed water compositions (pH 5.5–6.5, conductivity 3.51–5.46 mS cm⁻¹). In the experiments, water conductivity was reduced by 75%. Fig. 4 compares the removal efficiency of the main cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, NO₃⁻, SO₄²⁻) by the ED. It can be seen from Fig. 4 that the monovalent anions (NO₃⁻ and Cl⁻) are transported more easily through the PC-SA membrane than SO₄²⁻, which is a confirmation of a previous study [31]; however, K⁺, Ca²⁺ and Mg²⁺ are transported more easily than Na⁺ through the PC-SK membrane. The anions and cations were removed from the diluate in the following order:

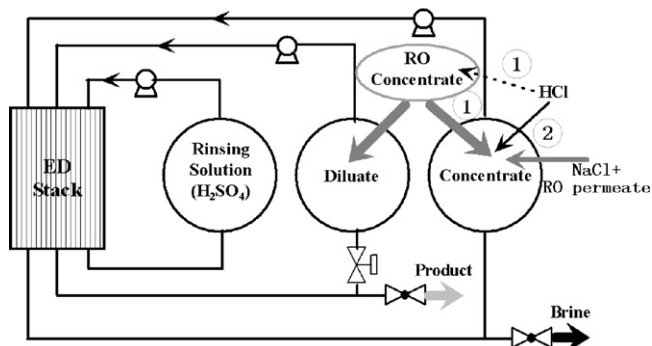


Fig. 3. Schematic diagram of the pilot ED installation and decarbonation.

NO₃⁻ > Cl⁻ > SO₄²⁻ and Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ (further explanation in the next section). Due to the decarbonation of feed water in these experiments, transport of bicarbonate did not occur.

It should be noticed that the feed water pH was adjusted to a value between 5.5 and 6.5 in the batch experiments, which apparently did not affect ion selectivity of the ion exchange membranes. This is a confirmation of the research by Zhang et al. [31].

3.2.2. Operation and ion transport in feed-and-bleed experiment

After reduction of the conductivity by 75% in the batch process, the feed-and-bleed operation was experimented to produce a constant stream (ED effluent) with around 75% salt removal. Three flow rates 50 L h⁻¹, 75 L h⁻¹ and 100 L h⁻¹ of the effluent were experimented in the feed-and-bleed mode to optimize the effluent salt concentration, the salt removal rate was 85%, 75% and 55%, respectively. Thus, a flow rate of 75 L h⁻¹ was chosen to produce overall ED effluent at 75% salt removal.

Long-term experiments by feed-and-bleed mode were run to examine the system stability and effluent quality. In the experiments, the decarbonation on the ED feed (i.e., RO concentrate, DROC, as shown in ⊙ of Fig. 3) and on the ED concentrate (DEDC, as shown in ⊗ of Fig. 3) was compared, as shown in Fig. 5. In the DROC experiment, the ED feed conductivity was around 3.5 mS cm⁻¹, the pH was adjusted to 5.8, the applied current was 3 A due to the lower conductivity; in the DEDC experiment, the ED feed conductivity was 5.6 mS cm⁻¹, the pH of ED feed was 7.6 and was not acidified, instead, the ED concentrate pH was adjusted to 6.0, the applied current was 5 A.

Although those two experiments had large differences in feed water conductivity, pH, decarbonation method and the operational current, it can be seen from Fig. 5 that the conductivity was reduced from 3.5 mS cm⁻¹ to 0.8 mS cm⁻¹ in the DROC experiment and from 5.6 mS cm⁻¹ to 1.5 mS cm⁻¹ in the DEDC experiment and both of the experiments had a constant effluent of 75% salt removal regardless the feed pH and conductivity. This means that the pilot ED installation can work in a stable way in a long-term feed-and-bleed operation with either the feed or the ED concentrate decarbonation.

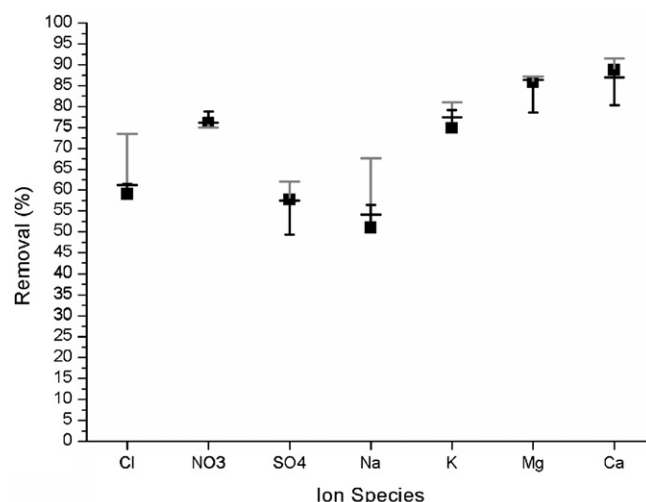


Fig. 4. Ion removal (%) by the pilot ED with around 75% desalting in batch mode.

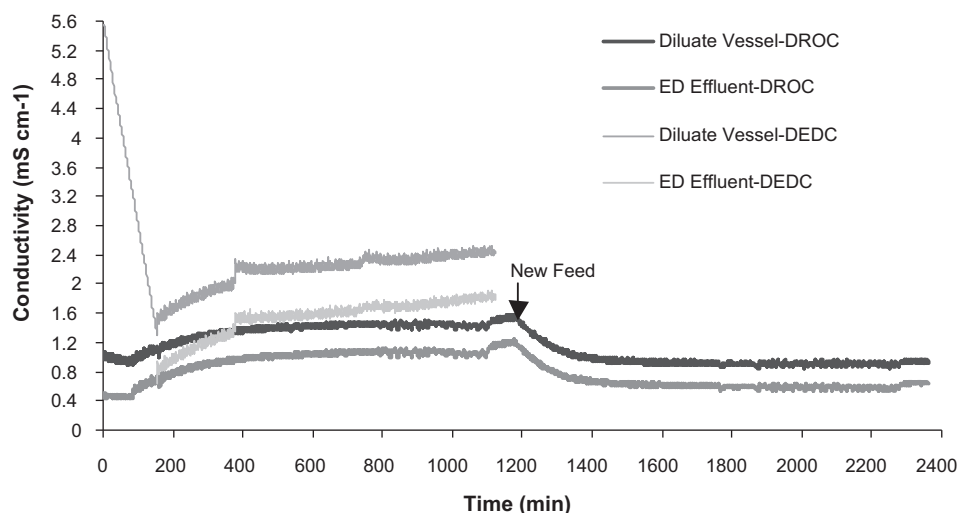


Fig. 5. Conductivity of the diluate and the effluent as a function of time.

On the other hand, ion removal efficiency as a function of time is compared for these two experiments. As shown in Table 3, the removal rates of the same ion in these two experiments are similar except the rate of SO_4^{2-} and Na^+ . The removal rate of SO_4^{2-} and Na^+ in DROC experiment (R_{DROC}) is 47.0% and 74.5%, respectively; and the removal rate of the two ions in DEDC (R_{DEDC}) is 59.1% and 54.8%, respectively. The reason of a lower removal rate of SO_4^{2-} and a higher removal rate of Na^+ in DROC experiment may be attributed to the lower current (3 A, from 1.5 h to 40 h). Lowering the current density can effectively reduce the mobility of multivalent ions (both cation and anion) more than for the monovalent ions, i.e., in this case the mobility of SO_4^{2-} , Mg^{2+} and Ca^{2+} in DROC experiment is relatively lower than the mobility of those in DEDC experiment. Moreover, as the multivalent cations move slower in the DROC experiment, the ion transport competition results in a relatively higher mobility of Na^+ . Both experiments exhibit a same anion removal order: $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, which is also the same as shown in the batch experiments. As shown in Table 3, SO_4^{2-} has the largest molar conductivity but also has the largest hydrated ionic radius: the size effect is dominant in this case since SO_4^{2-} has the lowest mobility. The cation removal order, however, was different: $\text{Ca}^{2+} \approx \text{K}^+ > \text{Mg}^{2+} > \text{Na}^+$ in the DROC experiment and $\text{Ca}^{2+} > \text{Mg}^{2+} \approx \text{K}^+ > \text{Na}^+$ in the DEDC experiment. The cation removal order can be affected in different ways: as shown in Table 3, K^+ has a lower hydrated ionic radius and a higher molar conductivity, thus K^+ moves faster than Na^+ ; Mg^{2+} and Ca^{2+} have high hydrated ionic radii typical for multivalent ions, and high molar conductivities, thus the mobility is dependent on the applied electrical field. If comparing Mg^{2+} with Ca^{2+} , the latter one has a lower hydrated ionic radius and a higher molar conductivity, thus Ca^{2+} moves faster. On the other hand, due to the fact that PC-SK membrane fixed charges (sulphonate functional group, $-\text{SO}_3^-$) have larger affinity to the

multivalent ions, this also makes Ca^{2+} and Mg^{2+} migrate faster than K^+ and Na^+ .

Ion migration can be quantitatively expressed by means of current efficiency, i.e., the fraction of the current that is used to transfer a certain ion. In this work, the average current efficiency (η , %), which is calculated by Eq. (3), is discussed. Fig. 6 compares the overall current efficiency and the current efficiency of Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} as a function of time in the DROC and DEDC experiments.

As seen in Fig. 6, the overall current efficiency of DROC was 80% during the first period and dropped to around 60% after new decarbonated ED feed was added; similarly, the overall current efficiency of DEDC was 80% during 17 h of the experiment. Regardless of these differences, it can be concluded that the ED system can be long-term operated with a high overall current efficiency by both decarbonation methods. It can also be seen from Fig. 6 that the current efficiencies of Na^+ , Cl^- and SO_4^{2-} in DROC and DEDC are within a similar range except that of Ca^{2+} , which is remarkably higher in DEDC (around 55%) than in DROC (around 40% during the first 19 h and decreased to around 20% from 19 h till the end). This is probably because a higher current was applied in DEDC, which led to a higher mobility of Ca^{2+} .

Since it is observed that PC-SK membrane exhibits a selectivity for the cations and PC-SA membrane shows a selectivity for the anions, during the batch and long-term feed-and-bleed operation, detailed analysis is necessary to investigate how much and to what extent the ions are selectively removed. This is essential to ensure that the lower permeable ions will not excessively remain in the ED effluent to affect biological treatment unit when re-inserted into the WWTP. Fig. 7 shows the selectivity of the main cations and anions by the ion exchange membranes in the long-term feed-and-bleed DROC and DEDC experiments. It is observed that the selectivity of $\text{SO}_4^{2-}/\text{Cl}^-$ is mostly a moderate positive value

Table 3

Stokes radius (r_{Stokes}), molar conductivity (λ) and average removal rate (R) of the ions in the experiments.

	Anion			Cation			
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
r_{Stokes}^a (m)	0.121	0.129	0.231	0.183	0.125	0.346	0.308
λ^b ($10^4 \text{ S m}^2 \text{ mol}^{-1}$)	76.3	71.4	159.6	50.1	73.5	106.1	119.0
R_{DROC} (%)	73.4	86.2	47.0	74.5	85.4	79.9	84.0
R_{DEDC} (%)	76.9	86.4	59.1	54.8	80.2	80.7	85.3

^a Stokes radius [32,33].

^b Molar conductivity [32,34].

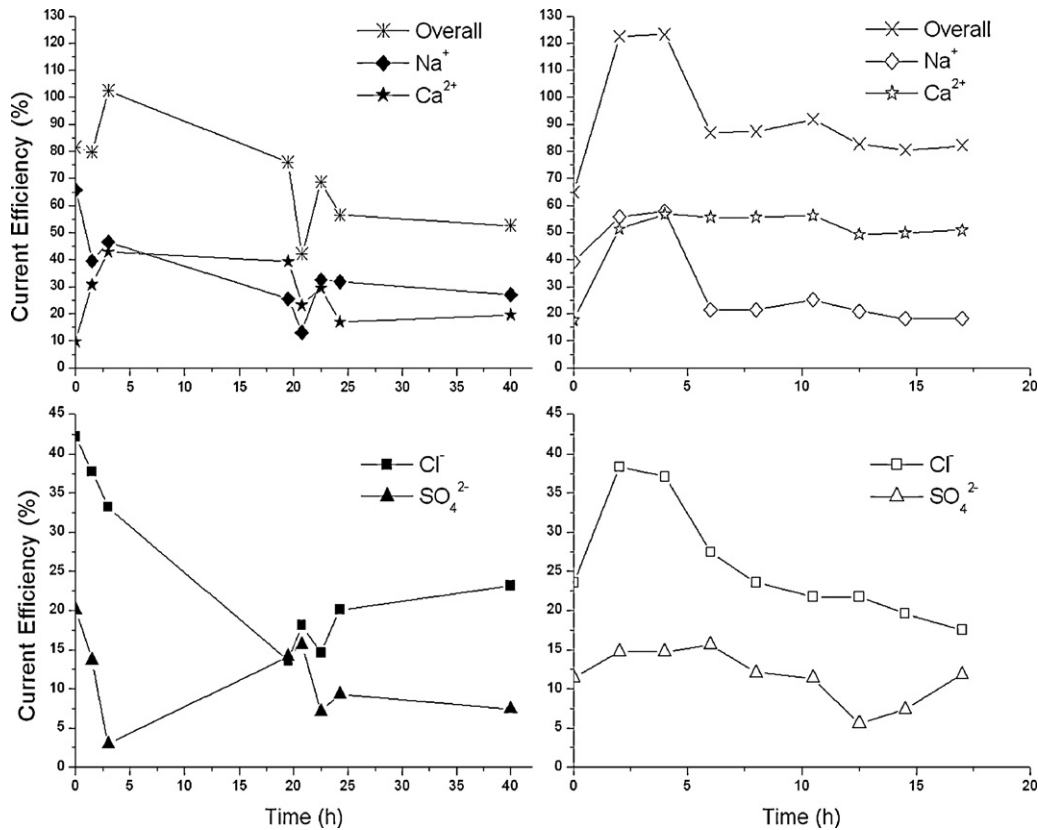


Fig. 6. The overall current efficiency and the current efficiency of the cations and anions as a function of time in the DROC (the left curves, solid dots) and DEDC (the right curves, hollow dots) experiments.

(around 0.4) in both experiments; the selectivity of $\text{Ca}^{2+}/\text{Na}^{+}$ has a high deviation in the DROC experiment: the first 19 h has a moderate value (around -0.4), however after a new decarbonated ED feed was added, a low selectivity was observed. On the other hand, a moderate to high value (around -0.6) was observed from 5 h to the end of DEDC experiment.

As discussed, a higher current was applied in DEDC experiment, which caused a higher mobility of the multivalent cations and anions. As seen in Fig. 7, the DEDC experiment shows a higher (negative) selectivity of $\text{Ca}^{2+}/\text{Na}^{+}$. However, no obvious differences between these two experiments are found on the selectivity of

$\text{SO}_4^{2-}/\text{Cl}^{-}$, which may due to the fact that the selectivity is already quite low.

3.2.3. Transport of carbonates in batch and feed-and-bleed experiments

Decarbonation of either the ED feed or the ED concentrate is essential to ensure that the system runs stable in a long-term operation; the RO concentrate has a high scaling potential, as described in the previous section. Therefore, transport of carbonates (bicarbonate and/or carbonate, depending upon the pH value) is crucial to be investigated and discussed. Since the decarbonation on ED feed removes most of the carbonates, those experiments with decarbonated ED feed will not be studied in this part, i.e., only the experiments with ED concentrate decarbonation are discussed.

The pH of ED concentrate was adjusted (in the batch mode) and maintained (in the feed-and-bleed mode) at 6.5, 6.0 and 5.5 by dosing HCl into the concentrate vessel. By adjusting the pH to the range of 5.5–6.5, CO_3^{2-} (carbonate) can be converted to HCO_3^{-} (bicarbonate) to minimize the scaling potential of the ED concentrate.

All of the experiments were operated under a constant current of 5 A and with a flow rate of 500 L h^{-1} . Fig. 8 shows the concentration profile of carbonates (as bicarbonate, HCO_3^{-}) as a function of time in the experiment with pH 6.5, 6.0 and 5.5, respectively.

As shown in Fig. 8, the profiles of the bicarbonate concentration change in the feed vessel of the three experiments are relatively similar: after the batch operation, around 65% of bicarbonate was removed from the feed (vessel); during the feed-and-bleed operation, over 50% of bicarbonate was removed from the vessel. The similar profiles in the ED effluents can be seen in Fig. 8 (the hollow circle symbols), which corresponds to a constant salt removal efficiency (around 20%) achieved from the feed stream. However, the profiles in the ED concentrates are different (see Fig. 8): a low

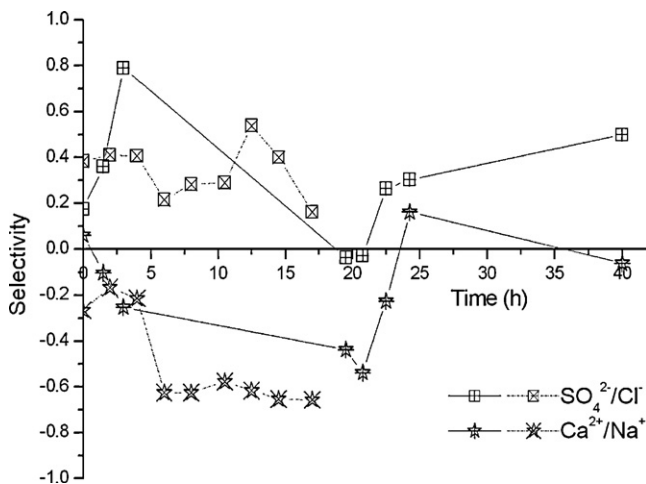


Fig. 7. Selectivity of PC-SK membrane to $\text{Ca}^{2+}/\text{Na}^{+}$ and of PC-SA membrane to $\text{SO}_4^{2-}/\text{Cl}^{-}$ in the DROC (hollow with “+” symbol) and DEDC (hollow with “x” symbol) experiments.

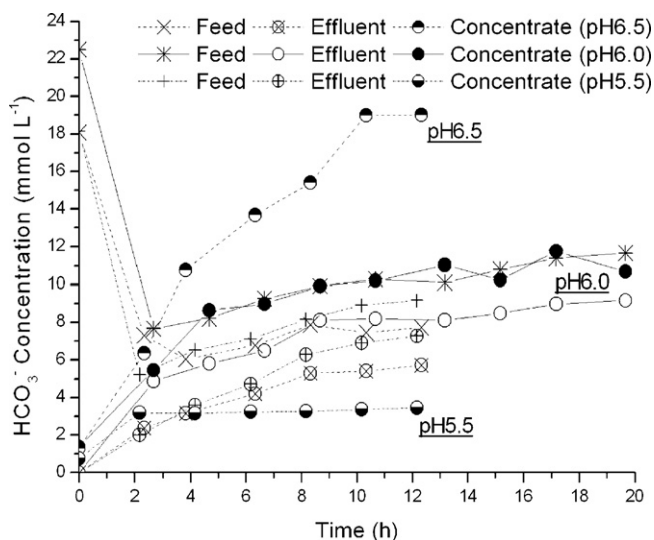


Fig. 8. Bicarbonate concentration profile under different pH of ED concentrate by batch and feed-and-bleed experiment.

bicarbonate level was kept at pH 5.5; a moderate bicarbonate concentration was achieved at pH 6.0; a high level was reached at pH 6.5, and the concentration reached around the same level of the feed. No scaling problem was observed in the experiments with decarbonated ED concentrate at pH 6.0 and 5.5, but problems were encountered at pH 6.5.

Fig. 9 shows a detailed observation on the scaling problem during the experiment with a decarbonated concentrate at pH 6.5. The Langelier saturation index (LSI) of each sample was calculated by the method and equations from Section 2.5.2. The critical scaling concentration (CSC) is defined as the concentration of bicarbonate which causes the solution to the critical scaling point ($LSI = 1.00$) under a specific pH ($6.5 \leq pH \leq 9.0$), ionic strength and hardness. The CSC represents the lowest concentration of bicarbonate that causes scaling under the specific conditions. It is calculated by the method and equations from Section 2.5.2 with the pH, ionic strength and hardness as the samples. Scaling will not occur if the real experimental value is lower than the CSC value, otherwise it will occur. Fig. 9 shows that conditions for scaling were favorable after around 6 h of the experiment and even when the concentration of bicarbonate stabilized after 10 h, the LSI value still increased

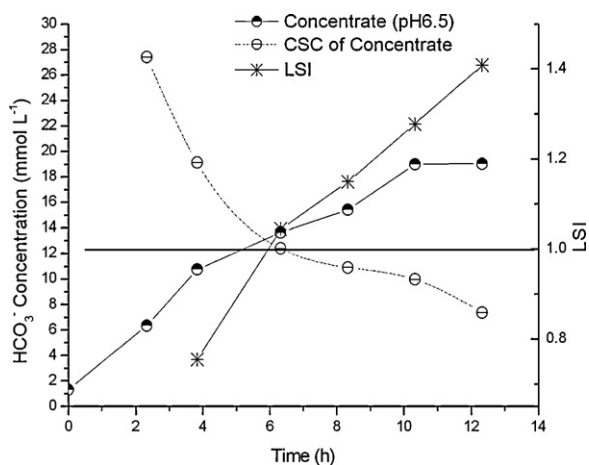


Fig. 9. Bicarbonate concentration profile, the corresponded Langelier saturation index (LSI) and the critical scaling concentration (CSC) of bicarbonate as a function of time of experiment with a decarbonated concentrate at pH 6.5.

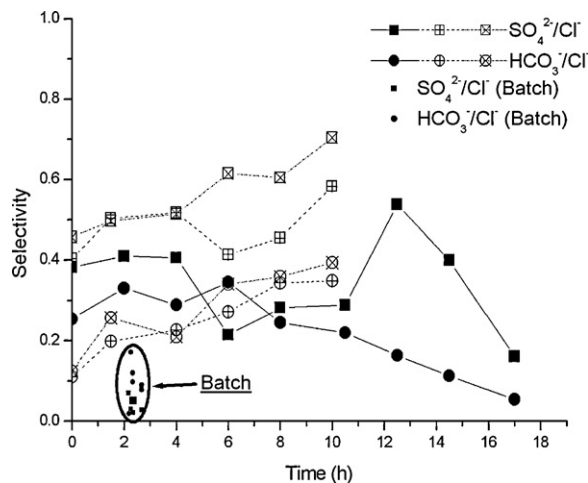


Fig. 10. Selectivity of SO_4^{2-}/Cl^- and HCO_3^-/Cl^- in batch and feed-and-bleed experiments with original RO concentrate as the feed and pH adjustment on the ED concentrate. Data obtained from the analysis on the ion concentration of the feed vessel.

due to the concentration increase of Ca^{2+} and Mg^{2+} . According to the CSC value, the bicarbonate concentration should be below 10 mmol L^{-1} at 10 h and below 7.5 mmol L^{-1} at 12 h to prevent scaling.

3.2.4. Comparison of anion selectivity in batch and feed-and-bleed experiments

The selectivity of PC-SA membrane to the main anions was analyzed in both batch and feed-and-bleed experiments with original RO concentrate as the feed and pH adjustment on the ED concentrate. The ion concentration in the feed vessel was determined. As shown in Fig. 10, the selectivity of SO_4^{2-}/Cl^- and HCO_3^-/Cl^- is similar and in the range of 0–0.2 in batch mode, which means that the selectivity is low. On the contrary, the selectivity of SO_4^{2-}/Cl^- and HCO_3^-/Cl^- in feed-and-bleed mode is mostly higher than 0.2, and the value of SO_4^{2-}/Cl^- is always higher than that of HCO_3^-/Cl^- . This means that the mobility order of the anions in the feed-and-bleed mode is: $Cl^- > HCO_3^- > SO_4^{2-}$, and more SO_4^{2-} and HCO_3^- remain at the diluate side in feed-and-bleed mode than in batch mode.

3.3. ED product quality and ozonation as the post-treatment

RO concentrate (ED feed) and ED product (effluent) quality from a typical experiment is compared with the WWTP effluent to show the difference of these three kinds of streams. As the ED product (effluent) is to be recycled to the WWTP biological treatment unit, the WWTP effluent quality can be used to monitor the concentration of different ions. From Table 4, it can be calculated that in this case the conductivity of ED product is around 31% of the ED feed. If the ED product is compared with the WWTP effluent, one may conclude that all parameters are similar except for the TOC. The ED process can only remove around 10% of the organic compounds from the feed. Furthermore, the organic compounds are originally from the WWTP effluent and have a small biodegradability. This means that further treatment of the ED product should be considered to minimize the effect of the recycle stream on the biological unit and the whole system. Therefore, ozonation on the ED product was applied to reduce the TOC concentration and improve the biodegradability of the recycled stream.

Table 5 evaluates the samples' biodegradability (BOD_5 and UV-254) and organic compounds concentration (as TOC) at different pH and ozone dosage. The samples below pH 7.8 (samples 3 and 4) have

Table 4

Comparison of the RO concentrate (ED feed), ED product (effluent) and WWTP effluent (the mean value and max–min value).

Parameter	RO concentrate ^a	ED product ^a	WWTP effluent [35]
pH	7.43	7.06	7.67 (7.28–8.26)
TOC (mg L ⁻¹)	38.23	33.86	18 (5–43)
Conductivity (mS cm ⁻¹)	4.82	1.52	1.645 (0.524–2.670)
Sodium (mg L ⁻¹)	579	206	210 (60–379)
Potassium (mg L ⁻¹)	121	28	34 (2–100)
Magnesium (mg L ⁻¹)	34	7	18 (3–30)
Calcium (mg L ⁻¹)	395	49	131 (56–184)
Chloride (mg L ⁻¹)	596	127	320 (90–776)
Nitrate (mg L ⁻¹)	74	15	23 (4–45)
IC ^b (mg L ⁻¹)	1088	437	367 (110–543)
Sulphate (mg L ⁻¹)	426	190	145 (11–281)

^a The RO concentrate and ED product (effluent) data was obtained from a typical experiment.^b Inorganic carbon.**Table 5**Ozone dosage and the BOD₅, TOC, UV-254 value of the ED product.

Sample	pH	O ₃ dosage (mg L ⁻¹)	BOD ₅ (mg L ⁻¹)	TOC (mg L ⁻¹)	UV-254 (cm ⁻¹)	TOC/UV-254 ratio
1	7.8	0	14.1	35.3	0.834	42.3
2	7.8	120	16.8	31.6	0.437	72.3
3	7.8	288	21.9	28.7	0.32	89.7
4	7.8	576	21.7	26.7	0.245	108.8
5	6.5	288	18.9	29.1	0.33	88.1
6	6.5	576	21.0	27.3	0.236	115.9

a slightly higher BOD₅ and a slightly lower TOC than those below pH 6.5 (samples 5 and 6) with the same ozone dosage. Thus, a higher pH can slightly improve ozone oxidation efficiency. On the other hand, comparing samples 1–4 and 5–6, a remarkable increase of BOD₅ and a decrease of TOC and UV-254 can be seen as an increase of ozone dosage. However, the values are very similar if BOD₅ of samples 3 and 4 is compared, that means that further dosage of ozone may not improve the biodegradability.

Furthermore, as Tambo and Kamei reported [36], a TOC/UV-254 ratio over 30 is advisable for biological treatment. The results show that the TOC/UV-254 ratio can be improved from 42.3 to around 110 (108.8 for sample 4 and 115.9 for sample 6) with the increase of ozone dosage. This means that further ozone dosage may still improve the biodegradability, which is contradictory with the BOD₅ results and may need further experimental investigation.

4. Conclusions

A pilot ED system was used for RO concentrate treatment in a WWTP to improve the overall water recovery. In the pilot system, the decarbonation process sufficiently reduced the scaling potential of the feed or the concentrate stream of the ED. After this decarbonation it was possible to operate the ED installation under a steady state for a long-term experiment (42 h) with a satisfying salt removal. Generally, a moderate selectivity was observed between SO₄²⁻/Cl⁻ and HCO₃⁻/Cl⁻, and a moderate to high selectivity was found between Ca²⁺/Na⁺ by using the non-selective anion- and cation-exchange membranes, which is a confirmation of the previous investigation. The mobility orders of the anions and cations are: NO₃⁻ > Cl⁻ > HCO₃⁻ > SO₄²⁻ and Ca²⁺ > Mg²⁺ > K⁺ > Na⁺. The critical scaling concentration (CSC) of Ca²⁺ can be used to predict scaling problems. The ED product (effluent) quality is similar as the WWTP effluent except a higher TOC value is found. Ozonation can successfully improve the biodegradability of ED effluent and hence can reduce the accumulation of organic compounds in the circulation system. A high overall water recovery (95%) of the WWTP system can be achieved from the integrated RO–ED system. Thus, in this case, ED can both technically be considered to be a good option to treat RO concentrates.

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