Separation of nutrient ions and organic compounds from salts in RO concentrates by standard and monovalent selective ion-exchange membranes used in electrodialysis

Yang Zhang [a], Bart Van der Bruggen [a,*], Luc Pinoy [b,d], Boudewijn Meesschaert [c,d]

[a] Department of Chemical Engineering, Laboratory for Applied Physical Chemistry and Environmental Technology, K.U.Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium
[b] Department of Industrial Engineering, Laboratory for Chemical Process Technology, KaHo St.-Lieven (Associated to the K.U.Leuven as Faculty of Industrial Sciences, Technologie Campus, Gebroeders Desmetstraat 1, B-9000 Gent, Belgium and M²S, K.U.Leuven Association, K.U.Leuven), Belgium
[c] Department of Industrial Sciences and Technology, Katholieke Hogeschool Brugge-Oostende (Associated to the K.U.Leuven as Faculty of Industrial Sciences, Zeedijk 101, B-8400 Oostende), Belgium
[d] Department of Molecular and Microbial Sciences, K.U.Leuven, Arenberg Park 20, B-3001 Leuven, Belgium

ARTICLE INFO

ABSTRACT

To allow water recycling and nutrient recovery from reverse osmosis (RO) concentrates from a food industry plant, separation of salts from the organic fraction and from nutrient anions is required. In this study, the use of ion-exchange membranes in electrodialysis was investigated to this purpose. Two types of anion-exchange membranes from PCA, Germany, were investigated: a nonselective membrane (SA) and a membrane selective for monovalent anions (MVA). Different approaches including lowering the initial current density and increasing the initial pH were applied. The transport properties of different anions and different small charged organic compounds through ion-exchange membranes were discussed. The separation efficiency, which represents the selectivity, was compared under different conditions. The results show that separation of non-nutrient anions from nitrate and phosphate was difficult, whereas separation of salts from the organic fraction was feasible provided that the organic solutes are similar to uncharged test solutes used in the experiments; it was shown that a higher molar mass of the organic solute has a positive effect on the separation. Lowering the current density can increase the separation efficiency of monovalent/multivalent anions with either the SA membrane (a nonselective membrane) or the MVA membrane (a monovalent selective membrane). When the initial pH was increased, the separation efficiency of monovalent/multivalent anions can be improved for the MVA membrane, however, no obvious change was found for the SA membrane. Finally, experiments on real RO concentrates proved that the separation of salts from organics by electrodialysis is similar to the separation of salts from uncharged solutes and therefore feasible.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

During the past 50 years, electrodialysis has been developed and applied for desalination and concentration of industrial streams [1]. Nowadays, water shortage and shrinkage of mineral reserves have become global issues. With the innovation of technologies, water reclamation and nutrient (or mineral) recovery from waste streams become technically and economically possible. Specifically, some waste streams, e.g. fermentation waste, farming waste and agricultural waste, contain organic compounds, nutrient salts and other dissolved solids, which can possibly be selectively removed with water recovery. Electrodialysis process is generally the most economic process compared with reverse osmosis (RO) when the salinity of target water is less than about $5\,g\,L^{-1}$ [2]. However, the desalination of high salinity waters (up to about $35\,g\,L^{-1}$) was also successfully performed through electrodialysis [3]. Electrodialysis is one of the technologies that give a possibility to separate different charged organic and inorganic components. Therefore, electrodialysis gets more and more attention for water reuse and nutrients recovery.

Different possibilities for nutrient salts recovery by electrodialysis and other technologies have been suggested in the literature. Pronk et al. [4] and Maurer et al. [5] suggested that recovery of nitrogen and phosphate and separation of micropollutants from urine by electrodialysis are feasible. They also mentioned that nanofiltration is an alternative. For nutrient recovery and water reuse of black water (concentrated household wastewater), van Voorthuizen et al. discussed three kinds of pretreatment processes

including UASB (Upflow Anaerobic Sludge Blanket) plus membrane filtration, anaerobic Membrane Bioreactor (MBR) and aerobic MBR [6]; and studied nutrient removal efficiency by nanofiltration and reverse osmosis membranes [7]. Results show that the rejection of phosphate was 74–99%, which was sufficient for the desired purpose. Kumar et al. [8] demonstrated that polymeric ligand exchange resins (PLEs) can be used successfully to remove phosphate from RO concentrate. In both Pronk's and Kumar's research, struvite precipitation was chosen for concentrated phosphate recovery. Shu et al. [9] made an economic evaluation of struvite crystallization for phosphate recovery and obtained a positive conclusion. The work from Mondor et al. [10] showed the potential interest to recover ammonia from swine manure by RO and electrodialysis.

In order to separate multivalent ions and monovalent ions (such as the separation of potassium from magnesium, phosphate from chloride or the separation of nitrate from sulfate), different kinds of ion-exchange membranes (such as monovalent selective cation or anion-exchange membranes) are required, when membrane technologies are considered. Moreover, it is necessary to investigate the selectivity of the ions with the same charge sign by ion-exchange membranes for salts separation.

Sata [11] proposed that the selectivity of ion-exchange membranes for a specific ion can be caused by three different mechanisms: control of the permselectivity of ions with the same charge on the basis of their size; rejection of certain ions by a thin surface layer on the membrane with the same charge as the ions; and specific interactions between the ion-exchange groups of the membrane and the mobile ions.

For migration of ions with the same charge, Van der Bruggen et al. [12] showed that nitrate removal was slower than chloride in electrodialysis when different salts (NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$ and $NaNO_3$) were separated by AMV/CMV Selemion membranes and ACS/CMS Tokuyama membranes in electrodialysis. Elmldaoui et al. [13] found the anion selectivity in the following order: $NO_3^- > Cl^- > HCO_3^- > SO_4^{2-}$ when they studied the removal of nitrate from ground water of Morocco by ACS anion-exchange membrane (Tokuyama Soda Co., Japan). Monovalent and bivalent anion selectivity was reported in various articles [14–17], which can be ascribed to the size and charge effects. Ion competition also takes an important role on ion selectivity in electrodialysis process on mixed salts solutions. Kabay et al. [14] studied the separation of fluoride from the binary mixture (F^-:Cl^-), (F^-:SO_4^{2-}) and the ternary mixture (F^-:Cl^-:SO_4^{2-}) by Neosepta® AMX (anion exchange) membranes and found that the competition between fluoride and chloride ions was much greater than the competition between fluoride and sulfate ions. Although various researches have been done on ion selectivity, further systematic discussion may be needed.

Nanofiltration is another option to separate monovalent from multivalent ions. Ions with different size and charge can be separated by nanofiltration by means of size elimination (by membrane pore size) and electrical repulsion (by charged nanofiltration membranes), which has been investigated in various publications [18–21,34]. However, the selectivity for the ions with similar size and charge (e.g. Cl^-/NO_3^-) is much lower. Some studies showed the possibilities to separate nitrate from chloride [22,23] by nanofiltration, but the results were not sufficient for industrial application.

Different investigations have been done to compare the separation efficiencies between nanofiltration and electrodialysis. Van der Bruggen et al. [12,24] compared separation efficiencies of monovalent and divalent anions and cations of different nanofiltration membranes and ion-exchange membranes. They concluded that the properties of the ion-exchange membrane resin are the main parameters for separation efficiency by electrodialysis; while pore size and charge of membrane are important factors for ion separation efficiency by nanofiltration. They also pointed out that, compared with nanofiltration, electrodialysis could remove ions

down to any concentration, if a longer residence time is applied and the limiting current is not reached. This is regarded as an advantage of electrodialysis to nanofiltration for ion separation.

Organic compounds are often an unignorable fraction in waste streams. Some compounds are charged and could migrate by an electrical field. Moon et al. [25] studied a mixture of formic, acetic, lactic and succinic acid during separation by monoselective and nonselective anion-exchange membranes. Montiel et al. [26] successfully retained aromatic amino acid from high concentrations of sulfate and phosphate: they removed 78% of sulfate and 84% of phosphate and recovered 87% of aromatic amino acid by using electrodialysis in a long term (319 h) experiment. Due to the fact that charged organics in aqueous environment are always weak acids, weak bases or zwitterions, migration mechanisms in ED are deeply affected by pH. Singlande et al. [27] showed that acetic acid as a neutral compound (pH not mentioned) was retained in ED in the presence of salt (NaCl or Na_2SO_4). Results showed that mass transfer of acetic acid as a neutral compound is only due to diffusion and affected by salt nature.

Charged small organics (several hundred Daltons) in natural water or wastewater could penetrate through the membrane or block the pores [28–30]. Apparently, organic compounds are important, and could contaminate the product or foul the membrane. However, transport mechanisms of charged organics in electrodialysis are not well investigated yet.

In this study, wastewater from a food industry plant was treated by ultrafiltration and RO to fulfill the discharge requirement in Belgium. But in the RO concentrate, salts, nutrients and organic compounds are concentrated several times compared to the feed streams. In this case, the concentration of phosphate and organic compounds in the concentrate stream is about $120 \, mg \, L^{-1}$ (phosphate) and $120 \, mg \, L^{-1}$ (organic compounds measured as TOC). Therefore, the concentrate streams cannot be discharged directly to natural water body and have to be treated. On the other hand, as the concentration of nutrients is high, nutrient salts may be separated and recovered by electrodialysis.

In this work, synthetic waters, simulating this RO concentrate, are used to study the behavior of nutrient anions and organic compounds in an electrodialysis stack containing standard cation and standard or monovalent selective anion-exchange membranes. Theoretically, separation of specific anions (e.g., separation of multivalent from monovalent anions) can be effectively achieved if preparation methods of the ion-exchange membranes and/or electrodialysis methods to permeate specific ions are established [31]. This work evaluates the separation of multivalent anions from monovalent anions. Furthermore, the behavior of small and larger organic molecules and ions is studied to determine the size and charge effect. Acetic acid, aspartic acid, glycine, methylamine and lysine are chosen to achieve this aim. During the experiment at a neutral pH, acetate and aspartate are negatively charged, methylammonium ion and protonated lysine are positively charged and glycine is a zwitterion. Thus, in neutral solution, acetate or aspartate should penetrate through the anion-exchange membranes and methylammonium ion or protonated lysine should penetrate through the cation-exchange membranes during electrodialysis, however, glycine should be retained in the feed (diluate). From the results, mechanisms of selectivity in ion-exchange membranes and migration of charged small organic compounds will also be discussed.

2. Materials and methods

2.1. Electrodialysis equipment and membranes

A lab-scale electrodialysis apparatus was used in all experiments. For each membrane, the active surface area is $0.0064 \, m^2$

Table 1
Information on PCA standard cation and anion-exchange membranes and monovalent selective anion-exchange membranes.

Membrane	Thickness (µm)	Ion-exchange capacity (mequiv./g)	Chemical stability (pH)	Permselectivity	Functional groups	Surface potential (Ω cm^2)
PC-SK	130	ca. 1	0–11	>0.96	$-SO_3Na$	0.75–3
PC-SA	90–130	ca.1.5	0–9	>0.93	$-NR_4Cl$	1–1.5
PC-MVA	100	ca. 1	0–7	>0.97	N/A	N/A

Table 2
Components and concentrations in synthetic waters.

Salt	Concentration (mmol L^{-1})
$MgSO_4$	4.46
NaCl	7.63
$NaNO_3$	0.31
$NaHCO_3$	8.20
Na_2HPO_4	0.44
Organic compounds	0 or 120 g L^{-1} TOC

and the flow channel width between two membranes is 0.5 mm. There are five cell pairs in the stack, each containing a diluate and a concentrate compartment, so in total five pieces of anion-exchange membranes and six pieces of cation-exchange membranes were used. PCA SK standard cation-exchange membranes and PCA standard (SA) or monovalent selective (MVA) anion-exchange membranes are used in the stack. Information about the membranes is given in Table 1, which was supported by the manufacturer. The membranes and the stack were supplied by PCA-Polymerchemie Altmeier GmbH and PCCell GmbH, Heusweiler, Germany. The configuration of stacks can also affect the performance of electrodialysis [32], but it will not be discussed in this article.

2.2. Experimental procedure

The composition of the synthetic feed waters is given in Table 2. The organic compounds used in the experiments are shown in Fig. 1.

During the experiments, the volume of diluate, concentrate and electrode rinse solution was 7 L. As initial concentrate and diluate, the same solution was used. As electrolyte solution circulating in electrode compartments (electrode rinse solution), 0.1 M H_2SO_4 was used. Operation parameters for experiments are referred in the operation manual of the stack [33]: the maximum applied voltage was 2 V for each cell pair, i.e., the applied voltage to the stack should not be over 10 V. Total voltage drop, including voltage drop in the membrane stack as well as on the electrodes, was measured in the experiments. Flow rate of diluate and concentrate were both 30 L h^{-1}; flow rate of electrode rinse solution was 150 L h^{-1}.
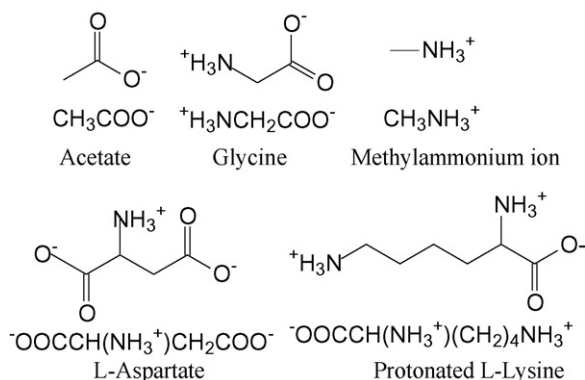

Fig. 1. Structural formula and molecular formula of acetate, glycine, methylammonium ion, L-aspartate, and protonated L-lysine.

The applied current started from 0.5 A, and was held constant until the voltage reaches 10 V. Then the current was decreased with 0.1 A. This sequence was repeated until the current was only 0.1 A. To investigate the effect of the current efficiency on ion selectivity, in some experiments the applied current started from 0.3 A.

Prior to the experiments in neutral environment, pH was corrected by HCl or NaOH, especially when methylammonium ion, acetic acid, aspartic acid or protonated lysine was used in the experiment. In some experiments, the initial pH was adjusted to 9.

2.3. Analytical methods

All the chemicals in the experiments are analytical grade. Samples are collected every 30 min and when current is lowered. Anion concentration is measured by ion chromatography (DX-120 Ionchromatography with IONPAC AS12A Analytical Column, DIONEX, USA). The eluent contains 1.8 mmol L^{-1} CO_3^{2-} and 0.2 mmol L^{-1} HCO_3^{-}.

The concentration of bicarbonate and organic compounds are measured as ionic carbon (IC) and total organic carbon (TOC) using a TOC Analyzer (TOC 5000A TOC Analyzer and autosampler, Shimadzu, Japan).

2.4. Data analysis

All figures and tables refer to concentration changes in the diluate. The mass balance of the ions present in the feed solution was verified for diluate, concentrate and electrode rinse solution. Thus, data for concentrate and electrode rinse solution will not be presented in this article.

As current (density) decrease in time during the experiments, mean values are determined using

$$I = \sum_j \frac{\Delta t_j I_j}{\sum_j \Delta t_j}$$

where I is the mean current [A] and I_j the constant current [A] in a time interval Δt_j [s] during the experiment.

Ion migration can be quantitatively expressed by means of current efficiency. The current efficiency is the fraction of the current that is used to transfer a certain ion. In this work, the average current efficiency of different anions is discussed. This average current efficiency is calculated by the following equation:

$$\eta = \sum_j \frac{\Delta t_j \eta_j}{\sum_j \Delta t_j}$$

whereby η is the current efficiency [%].

Selectivity, represented as separation efficiency, was calculated by the method introduced in the literature by Van der Bruggen et al. [12] In this method, the separation efficiency S between component A and B is evaluated as:

$$S(t)(\%) = \frac{(c_A(t)/c_A(0)) - (c_B(t)/c_B(0))}{(1 - c_A(t)/c_A(0)) + (1 - (c_B(t)/c_B(0)))} \times 100$$

The average separation efficiency is calculated to express the selectivity of the membranes during the experiments:

$$S = \sum_j \frac{\Delta t_j S_j}{\sum_j \Delta t_j}$$

3. Results and discussion

3.1. Anion transport by the SA and the MVA membrane under different conditions

To recycle reverse osmosis concentrates, it is necessary to separate nutrient anions (i.e., nitrate and phosphate) from other anions. The anion separation was carried out using a nonselective membrane (SA) and a monovalent selective membrane (MVA) at initial neutral pH and an initial current of 0.5 A (reference conditions). The effect of pH was studied by increasing the initial pH to 9 at the same initial current (0.5 A). The effect of current density was studied by lowering the initial value to 0.3 A at initial neutral pH. Furthermore, membrane permselectivity will be compared by means of separation efficiency of different pairs of anions.

3.1.1. Comparison of nonselective membrane and monovalent selective membrane

Fig. 2 shows the decrease of the concentrations in the diluate components as a function of time during the experiments. Phosphate ions exist as a mixed composition of $H_2PO_4^-$ and HPO_4^{2-}. Thus, $H_xPO_4^{y-}$ is used to express the phosphate ions. It can be seen that the concentration decrease of monovalent ions (Cl^-, NO_3^- and HCO_3^-) is similar for both the SA and the MVA membrane, while the differences in concentration profiles are large for multivalent ions ($H_xPO_4^{y-}$ and SO_4^{2-}). After 200 min, the concentration reduction of the monovalent ions, i.e., Cl^-, NO_3^- and HCO_3^- is 96%, 92% and 95%, respectively; while the concentration reduction of multivalent ions, i.e., $H_xPO_4^{y-}$ and SO_4^{2-}, is 86% and 95%, respectively when the standard membrane SA is used. For the monoselective membrane MVA, the concentration reduction of Cl^-, NO_3^- and HCO_3^- is 98%, 98% and 95%; while for $H_xPO_4^{y-}$ and SO_4^{2-} this is 56% and 77%. These results suggest that the MVA membrane can effectively separate multivalent ions from monovalent ions in contrast to the SA membrane.

Selectivity towards ions with a different valence is due to the fact that the monovalent selective membrane (MVA) has a permselective layer. The principle of the monovalent anion-permselective membrane functional layer is argued between steric-hindrance and electric-repulsion [34]. Above results may exhibit both the steric-hindrance effect (size of multivalent ions is larger than monovalent ions) and electric-repulsion (charge of multivalent ions is higher than monovalent ions).

3.1.2. Effect of current and pH

In Fig. 3, the concentration decrease of the anions is compared for the reference conditions (i.e., initial neutral pH and initial current 0.5 A) with that obtained with a lower current density (i.e., initial neutral pH and initial current 0.3 A).

A lower current density results in a lower concentration decrease for all anions. However, in Fig. 3(a) for the SA membrane, for monovalent ions, the effect is relatively small (i.e., less than 10% of monovalent ions were retained at the end of the experiment). But for multivalent ions, the effect is extreme: more than 80% of $H_xPO_4^{y-}$ and SO_4^{2-} was retained in the diluate compartment after 200 min when the initial current was decreased to 0.3 A. Similar results were observed in Fig. 3(b), for the MVA membrane, a lower current density resulting in a lower concentration decrease for Cl^- and NO_3^-. Again, the influence of current density is bigger for the
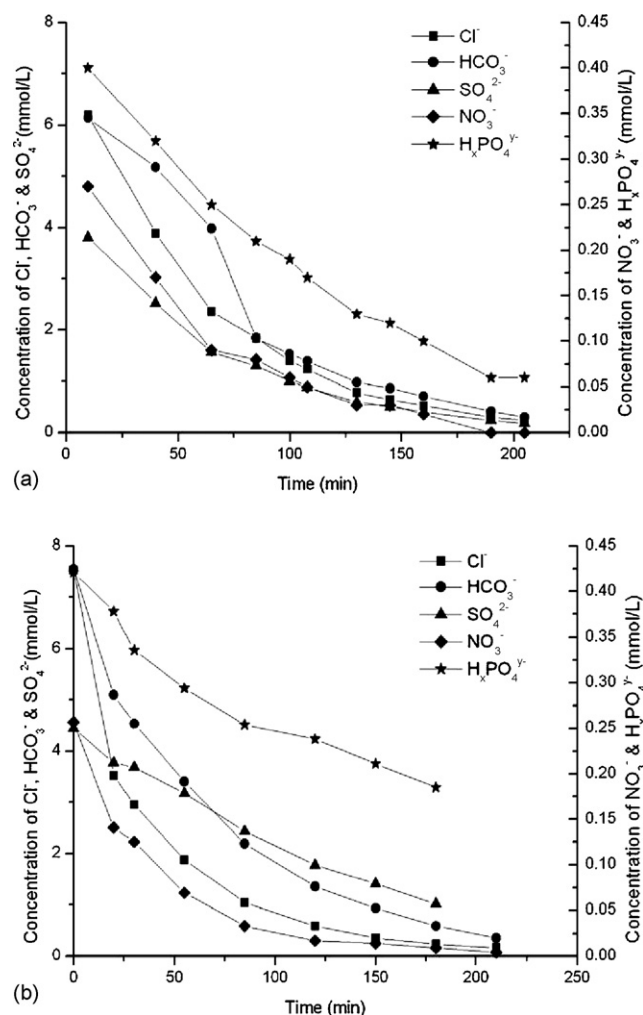

Fig. 2. (a and b) Concentration decrease of ions by SA and MVA membranes. (a) Reflects the concentration decrease by the SA membrane and (b) reflects the concentration decrease by the MVA membrane. The left axis shows the concentration of Cl^-, HCO_3^- and SO_4^{2-} and the right axis shows the concentration of NO_3^- and $H_xPO_4^{y-}$.

multivalent ions SO_4^{2-} and $H_xPO_4^{y-}$. Almost none of these ions permeated through the membranes when the initial current was 0.3 A. The results imply that a lower current density can separate multivalent anions from monovalent anions, to some extent, even when a nonselective membrane (SA) is used. For the MVA membranes also, the separation between monovalent and multivalent ions is significantly improved when the current is lowered. This is due to the fact that a lower current causes a lower flux of ions through the membrane. With respect to this lower current, the flux of the bigger sized multivalent ions is affected more than for the monovalent ions.

Table 3 depicts the current efficiencies, calculated as discussed above. The values are strongly dependent of the (initial) concentration of the different ions during the experiment. For example, values for nitrate are never high, due to the very low concentration of nitrate in the diluate (Table 2). Furthermore, the mean value for the current of the different experiments is added, as this factor also influences current efficiencies. When the initial current was lowered to 0.3 A, the current efficiency of multivalent anions (i.e., $H_xPO_4^{y-}$ and SO_4^{2-}) was severely decreased for both the SA membrane and the MVA membrane. However, the current efficiency of monovalent anions (i.e., HCO_3^-, Cl^- and NO_3^-) was increased from 16.8 to 37.0, 17.4 to 30.0 and 0.9 to 1.5, respectively,
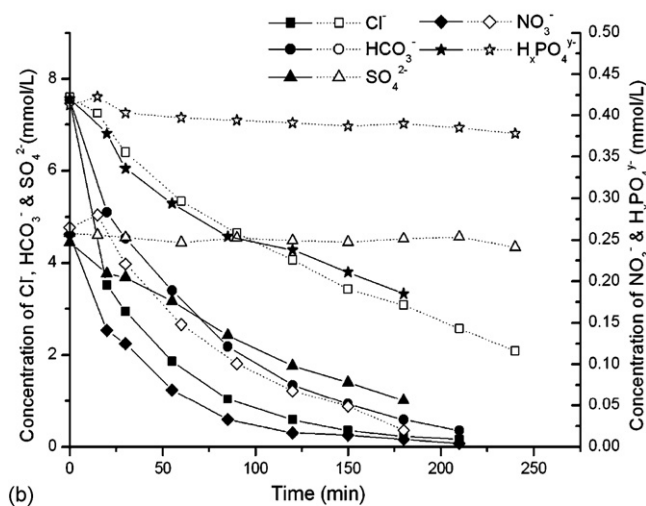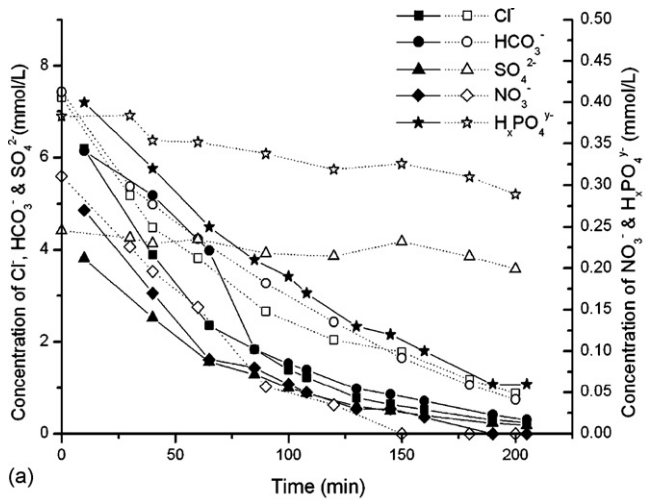
(a)

(a)

(b)

Fig. 3. (a and b) Influence of initial current density on the ion concentrations as a function of time by the SA (a) and the MVA (b) membranes. The reference conditions are initial pH neutral, initial current 0.5 A. The left axis shows the concentration of Cl^-, HCO_3^- and SO_4^{2-} and the right axis shows the concentration of NO_3^- and $H_xPO_4^{y-}$ (solid symbols: reference conditions; hollow symbols: initial pH neutral, initial current 0.3 A).
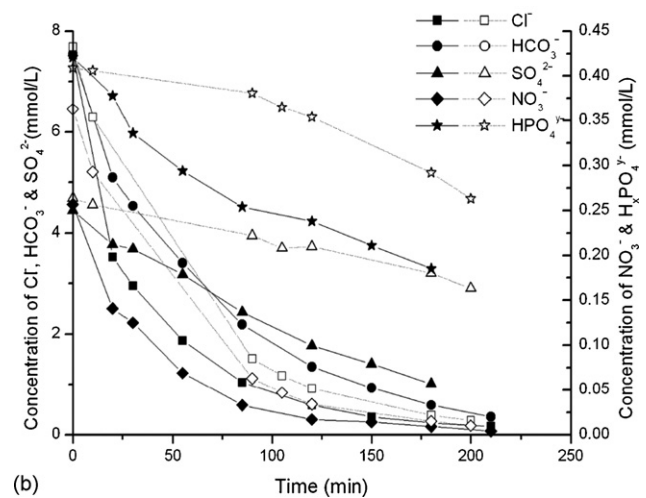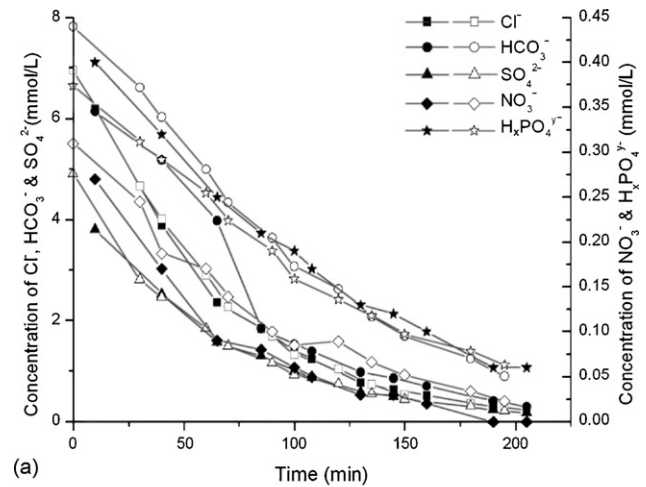

(b)

Fig. 4. (a and b) Influence of initial pH on the ion concentrations as a function of time by the SA (a) and the MVA (b) membranes. The reference conditions refer to the following conditions: initial pH neutral, initial current 0.5 A. The left axis shows the concentration of Cl^-, HCO_3^- and SO_4^{2-} and the right axis shows the concentration of NO_3^- and $H_xPO_4^{y-}$ (solid symbols: reference conditions; hollow symbols: initial pH 9, initial current 0.5 A)

for the SA membrane. For the MVA membrane, there was a slight change for NO_3^- and HCO_3^-, from 0.5 to 1.3 and from 21.0 to 21.7, respectively. However, a significant difference is found for Cl^- (from 16.7 to 28.6). These results imply that transport of multivalent anions is strongly affected by the electrical field, especially for the nonselective membrane. When the electrical field is lowered; the decrease in flux for $H_xPO_4^{y-}$ and SO_4^{2-} is much larger than the decrease in flux for the monovalent ions i.e., HCO_3^-, Cl^- and NO_3^-.

When comparing the concentration decreases between the experiments at neutral pH and pH 9, it can be seen from Fig. 4(a)

that the concentration difference between neutral pH and pH 9 of monovalent and multivalent ions after 200 min is below 10%, i.e., a higher pH does not affect the transport of anions through the standard membrane SA. Table 3 also shows that there is no obvious difference towards the current efficiencies of Cl^-, NO_3^-, $H_xPO_4^{y-}$ and SO_4^{2-} by the SA membrane in these two different conditions. Fig. 4(b) shows that at pH 9, the retention of all monovalent anions is very low, while the retention of $H_xPO_4^{y-}$ and SO_4^{2-} is improved a lot by increasing the pH. This indicates that increasing the pH can improve the permselectivity of the MVA membrane but cannot affect the performance of the SA membrane. This effect can be due to changes in the anion-exchange membrane surface charge

Table 3
Current efficiency and mean current for experiments concerning influence of pH and initial current density.

Membrane	Initial conditions	HCO_3^-	Cl^-	NO_3^-	$H_xPO_4^{y-}$	SO_4^{2-}	$I_{average}$
SA	$I = 0.5$ A, pH neutral	16.8	17.4	0.9	1.9	22.4	0.28
SA	$I = 0.3$ A, pH neutral	37.0	30.0	1.5	0.7	7.6	0.17
SA	$I = 0.5$ A, pH 9	21.4	17.4	0.8	1.5	21.4	0.28
MVA	$I = 0.5$ A, pH neutral	21.0	16.7	0.5	1.7	18.9	0.23
MVA	$I = 0.3$ A, pH neutral	21.7	28.6	1.3	0.2	3.5	0.14
MVA	$I = 0.5$ A, pH 9	n.m.	25.9	1.3	1.8	16.0	0.20

n.m.: not measured.

and the solute charge for $H_xPO_4{}^{y-}$: on the one hand, an anion-exchange membrane will be less positively charged when the pH is increased, while on the other hand, a shift from $H_2PO_4{}^-$ to $HPO_4{}^{2-}$ ($pK_{a2} = 7.2$) occurs. By the calculation of CurTiPot [35], the fraction of $HPO_4{}^{2-}$ changed from around 60% (pH neutral) to around 98% (pH 9). Hence, the electrical attraction between the multivalent anions (i.e., $H_xPO_4{}^{y-}$ and $SO_4{}^{2-}$) and the anion-exchange membrane is decreased. Referring to Table 3, the current efficiency of $SO_4{}^{2-}$ decreased from 18.9 till 16.0 when pH was increased from neutral to 9. Therefore, the lower concentration decrease towards $H_xPO_4{}^{y-}$ and $SO_4{}^{2-}$ by the MVA membrane in high pH environment may indicate that the main effect is due to a change of the MVA membrane charge itself.

On the other hand, current efficiency of different anions in Table 3 can be explained by the theory of competitive ion transport in electrodialysis, which was developed by Nikonenko et al. [36,37] and Zabolotsky et al. [38]. This theory states that a membrane specific selectivity can be achieved for ion-exchange membrane at low current density (lower than the limiting current density); whereas when the current density approaches the limiting current density or even higher, the effective transport numbers of the ions will be close to the values in the bulk solution. As Table 3 shows, at initial current 0.5 A and neutral pH for the SA membrane, the current efficiency of $HCO_3{}^-$, Cl^-, $NO_3{}^-$, $H_xPO_4{}^{y-}$ and $SO_4{}^{2-}$ was 16.8, 17.4, 0.9, 1.9 and 22.4, respectively. Those ratios are very similar with the ratios of the ion concentration in Table 2 multiplies the charges it carry (i.e., at pH 7.5, $HCO_3{}^-$ $8.20 \times 1 \times 0.9 + 8.20 \times 0 \times 0.1 = 7.38\ mol\ L^{-1}$, Cl^- $7.63\ mol\ L^{-1}$, $NO_3{}^-$ $0.31\ mol\ L^{-1}$, $H_xPO_4{}^{y-}$ $0.44 \times 1 \times 0.3 + 0.44 \times 2 \times 0.7 = 0.75\ mol\ L^{-1}$, $SO_4{}^{2-}$ $4.46 \times 2 = 8.92\ mol\ L^{-1}$); however, at initial current 0.3 A and neutral pH for SA, the current efficiencies of monovalent anions were increased ($HCO_3{}^-$, Cl^-, and $NO_3{}^-$ was 37.0, 30.0 and 1.5, respectively) and were decreased for multivalent ions ($H_xPO_4{}^{y-}$ and $SO_4{}^{2-}$ was 0.7 and 7.6). A similar trend was also observed for the MVA membrane although which is a selective membrane. Based on the theory of competitive ion transport in electrodialysis, the results reveal that the membrane's specific selectivity was achieved at lower initial current (0.3 A), whereas the selectivity was shielded at higher initial current (0.5 A), which approached to the limiting current.

3.1.3. Membrane selectivity

Separation efficiencies (range from -1 to $+1$) of different pairs of monovalent and multivalent ions in the experiments are shown in Table 4. In this table, a more positive value means that the latter ion is more retained at the diluate side, while a more negative value means that the former ion is more retained at the diluate side. According to the aims of the project, separation of nutrient anions from other anions is needed. Thus, Cl^-:$H_xPO_4{}^{y-}$, Cl^-:$NO_3{}^-$, and $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ should be emphasized.

From Table 4, it can be concluded that the SA membrane has no selectivity towards Cl^-:$NO_3{}^-$ and Cl^-:$SO_4{}^{2-}$ since the values are close to zero, but is slightly selective to Cl^-:$H_xPO_4{}^{y-}$ and $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ in pH neutral and initial current 0.5 A (reference experiment). However, when the current density was lowered,

the separation efficiency of Cl^-:$H_xPO_4{}^{y-}$ and Cl^-:$SO_4{}^{2-}$ increased to 0.75 and 0.84, respectively. The selectivity of $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ decreased from 0.18 to -0.05. It means that for larger sized ions, although having a higher valence, the flux through the membrane decreases more than for smaller monovalent ions when the electrical field is lowered. Thus, the multivalent ions were more retained at the feed side, which corresponds with a higher selectivity.

In the reference condition ($I_i = 0.5$ A, pH neutral), the MVA membrane showed a good permselectivity to monovalent ions (Cl^-:$SO_4{}^{2-}$ 0.33, Cl^-:$H_xPO_4{}^{y-}$ 0.50) and a slight selectivity to $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ (0.21). Lowering the initial current to 0.3 A resulted in an increase of selectivity in monovalent ions to multivalent ions, similar to the SA membrane. On the other hand and again similar with what happens when the SA membrane is used, the separation efficiency of $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ decreased from 0.21 to -0.16.

As Table 4 shows, increasing the initial pH to 9 did not result in a selectivity change for Cl^-:$SO_4{}^{2-}$ and Cl^-:$H_xPO_4{}^{y-}$ towards the SA membrane. However, selectivity changes were found for Cl^-:$NO_3{}^-$ (-0.05 to 0.28). It can be concluded that a less positive surface charge can affect the penetration of nitrate through the SA membrane. Increasing the pH also results in a slight separation of Cl^-:$HCO_3{}^-$ (0.20). From the results, it can be concluded that the increase of pH cannot change the SA membrane separation efficiency of monovalent to multivalent ions.

Table 4 also shows that an increase of the pH can enhance the separation efficiency of Cl^-:$SO_4{}^{2-}$ (0.33–0.50) and Cl^-:$H_xPO_4{}^{y-}$ (0.50–0.67) and slightly decrease the selectivity of $SO_4{}^{2-}$:$H_xPO_4{}^{y-}$ (0.21–0.06) by the MVA membrane.

These results show that multivalent anions can be separated from monovalent anions and retained in the diluate compartment by the selective membrane (MVA). The separation efficiency of the MVA membrane can be improved either by increasing pH or decreasing the applied current. The results also show that the non-selective membrane (SA) can also have some selectivity by reducing the applied current. However, no significant evidence supports the selective separation of the same (similar) charged anions (i.e., separating $NO_3{}^-$ from Cl^- and $H_xPO_4{}^{y-}$ from $SO_4{}^{2-}$) by the membranes applied in this work.

3.2. Behavior of organic compounds in the electrodialysis stack

Besides the topic of the behavior of nutrient and non-nutrient anions in the stack, the separation of inorganic ions from charged and uncharged organics is important for recycling the nutrient rich fraction. To simulate this, a selection of test solutes was made in view of studying negatively charged, positively charged and neutral (zwitterion) organic solutes. These compounds were tested in the stack using standard as well as monovalent selective anion-exchange membranes. As cation membranes, the standard SK membranes were always used.

Fig. 5(a and b) shows the concentration decrease of different organic ions (anion, cation and zwitterion) during electrodialysis with standard membranes (SA) and monovalent selective membranes (MVA). As can be seen in Fig. 1, acetate and aspartate are negatively charged organic ions, methylammonium and protonated

Table 4
Separation efficiency of monovalent and multivalent ions.

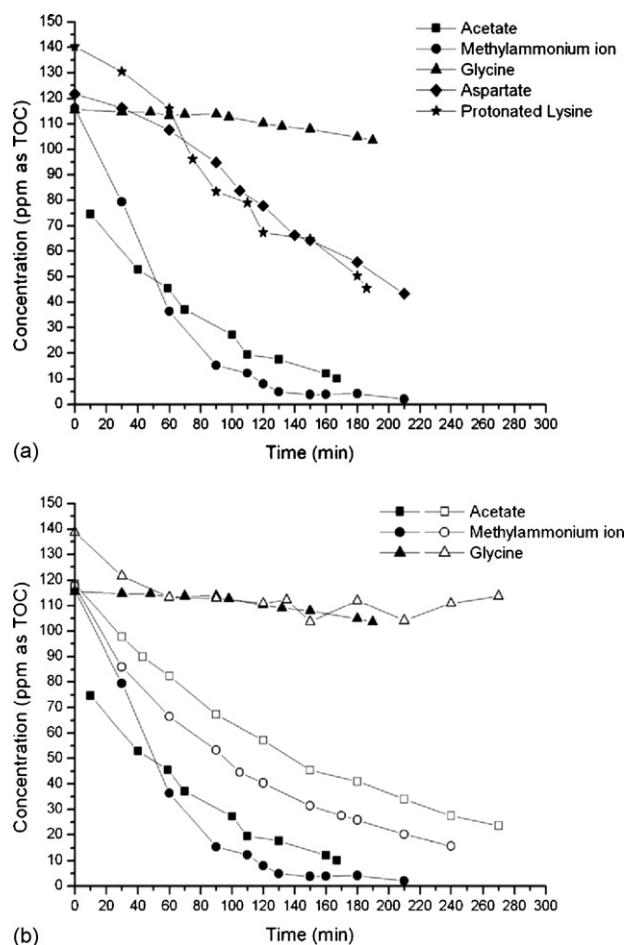| Membrane	Initial conditions	Cl^-:$SO_4{}^{2-}$	Cl^-:$H_xPO_4{}^{y-}$	Cl^-:$HCO_3{}^-$	Cl^-:$NO_3{}^-$	$SO_4{}^{2-}$:$H_xPO_4{}^{y-}$
SA	$I = 0.5$ A, pH neutral	0.02	0.21	-0.01	-0.05	0.18
SA	$I = 0.3$ A, pH neutral	0.84	0.75	-0.04	-0.23	-0.05
SA	$I = 0.5$ A, pH 9	0.02	0.28	0.20	0.28	0.22
MVA	$I = 0.5$ A, pH neutral	0.33	0.50	0.07	-0.03	0.21
MVA	$I = 0.3$ A, pH neutral	0.89	0.99	0.01	-0.04	-0.16
MVA	$I = 0.5$ A, pH 9	0.50	0.67	n.m.	0.08	0.06

n.m.: not measured.

Fig. 5. (a and b) Concentration decrease of organic ions by electrodialysis under reference conditions (initial pH neutral, initial current 0.5 A. (a) Experiments with SA/SK membranes and (b) comparison between SA/SK and MVA/SK stack (solid symbols: SA membrane; hollow symbols: MVA membrane).

lysine are positively charged organic ions, and glycine is a zwitterion.

As shown in Fig. 5(a) (using the SA membrane), for the organic anions, i.e., acetate and aspartate, both concentrations in the feed compartment decreased with time. During the first 150 min of the experiments, the concentrations of acetate and aspartate decreased with 85% and 53%, respectively. Just to compare, it is mentioned that after the same time in all the experiments with the SA membrane, the concentration of chloride decreased over 90%. The fact that acetate is removed faster than aspartate can be attributed to a molar mass effect. The molar mass of acetate is 59 g mol^{-1} and the molar mass of aspartate is 132 g mol^{-1}. With the same (net) charge of acetate and aspartate, the difference of molecular weight seems to cause a different solute flux in the electrical field [21]. On

the other hand, as Fig. 1 shows, the L-aspartate has one positively charged functional amino group in the molecule. Although the net charge of L-aspartate is negative, the positive functional group can also affect the organic anion transport through the anion-exchange membrane due to the positively charged membrane.

The membrane type can also affect the transport of organic anions. Fig. 5(b) shows the differences in concentration decrease of acetate by the nonselective membrane (SA) and the selective membrane (MVA). It can be seen that the SA membrane permeated more acetate than the MVA membrane (around 20% more acetate was removed). A first reason for this difference is found in the mean current densities during those two experiments. Because of the fact that the electrical resistance of the MVA membrane is higher, the limiting voltage drop of 10 V was reached earlier when the MVA membrane was used. As a result, the mean current for the experiment with the SA and the MVA membranes was respectively 0.27 and 0.20, as seen in Table 5, resulting in less driving force for the permeation of acetate in case of the MVA membranes. A second reason can be size exclusion. The MVA membrane is probably more dense than the SA membrane, thus, both the diffusion and the electrical transport are affected by the smaller pores of the MVA membrane.

For the organic cations, i.e., methylammonium ion and protonated lysine, both of their concentration in the feed compartment decreased with time, which is similar as for the organic anions mentioned above. The concentration decrease in the feed compartment of smaller organic cation (methylammonium ion, MM = 30 g mol^{-1}) was faster than the larger one (protonated lysine, MM = 147 g mol^{-1}), i.e., 97% of methylammonium ion was removed and 54% of protonated lysine was removed by the stack, which leads to the same conclusion as the organic anions mentioned above. Thus, it can be concluded that the size effect takes an important role in the transport of organic ions in electrodialysis. Comparing the experiments with the SA and MVA membranes, again it is found that the removal rate is higher in the case of SA membranes in the stack. For both experiments, the same SK membranes were used. So, this effect is solely due to the fact that the mean current for the stack lowered from 0.33 to 0.25 when the SA membranes are replaced by the MVA membranes.

From Fig. 5(a and b), it can be seen that for glycine, the concentration in the diluate changed by less than 8% by both the stacks containing SA membranes and MVA membranes. If it is assumed that glycine is not transported by the electrical field (being overall neutral), the only transport mechanism is by Fickion diffusion. Since the electrodialysis membranes are relatively tight [28], diffusion coefficients are assumably low. This is confirmed by the experimental results for the SA as well as for the MVA membrane.

In Table 5, the separation efficiency of salts to organic ions is compared to evaluate how efficiently salts are separated from different small organic ions by electrodialysis. Average separation efficiency of SO$_4{}^{2-}$/TOC and Cl$^-$/TOC is calculated by the same method as in Table 4.

Table 5 shows that the separation efficiencies of SO$_4{}^{2-}$ and Cl$^-$ to acetate by the SA membrane are the same, which shows

Table 5
Separation efficiency of SO$_4{}^{2-}$ and Cl$^-$ to organic ions and mean current under reference conditions (experiments concerning removal of organic compounds).

Compound	Acetate	Methylammonium ion	Glycine	Aspartate	Protonated lysine
SA anion membrane in stack					
SO$_4{}^{2-}$/organic solute	0.17	0.03	0.91	0.43	0.27
Cl$^-$/organic solute	0.17	0.07	0.91	0.52	0.44
$I_{average}$	0.27	0.33	0.28	0.29	0.31
MVA anion membrane in stack					
SO$_4{}^{2-}$/organic solute	−0.15	−0.54	0.76		
Cl$^-$/organic solute	0.30	0.19	0.90		
$I_{average}$	0.20	0.25	0.18		

that a slight separation of salts to acetate can be achieved. The separation efficiencies of SO_4^{2-} and Cl^- to methylammonium ion (positively charged organic ion) by the electrodialysis stack are both close to zero, which means that the inorganic ions cannot be separated from methylammonium ion by electrodialysis. The separation efficiency of these ions to glycine by the stack containing SA membranes is satisfying (over 0.90). This is due to the fact that glycine is a zwitterion, which cannot migrate in the electrical field. Aspartate and protonated lysine show similar separation efficiencies to the same inorganic ion by the stack, SO_4^{2-}/aspartate and SO_4^{2-}/protonated lysine is 0.43 and 0.27, respectively; Cl^-/aspartate and Cl^-/protonated lysine is 0.52 and 0.44, respectively. This means that concerning the larger organic ions (aspartate is larger than acetate), the separation between salts and those organic ions is better.

When the selective membrane MVA is applied in the electrodialysis stack, a different conclusion can be drawn from Table 5: separation of Cl^- to acetate and methylammonium ion can still be slightly achieved (0.30 and 0.19, respectively), but separation efficiency of SO_4^{2-}/acetate and SO_4^{2-}/methylammonium ion is negative (-0.15 and -0.54, respectively), which means that more organic ions (acetate and methylammonium ion) than sulfate ions were transported to the concentrate compartment. This is because the selective membrane (MVA) can retain more multivalent ions and permit more monovalent ions penetrating through it.
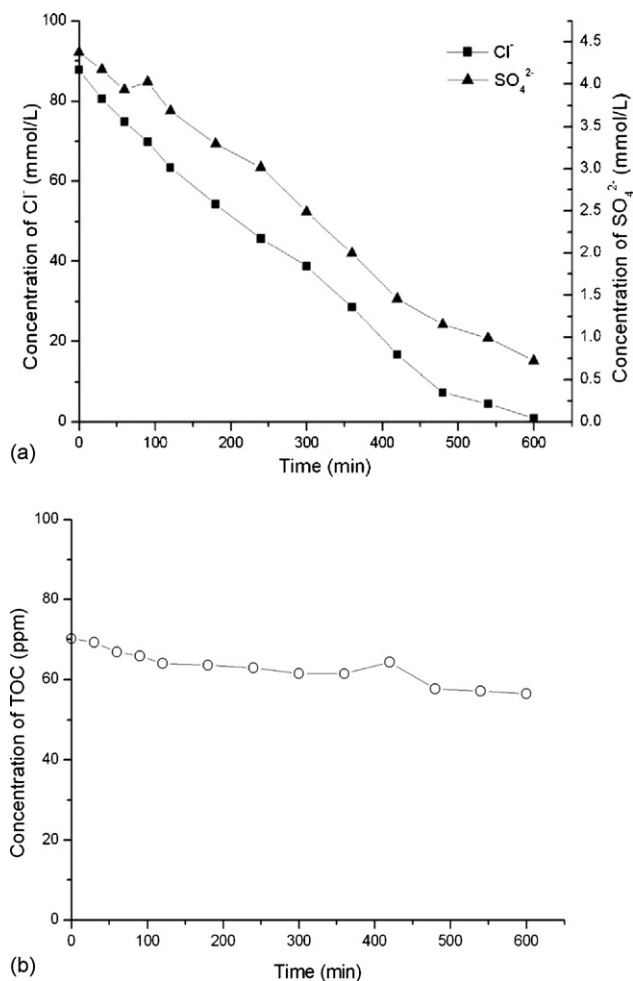
3.3. Electrodialysis of real RO concentrates

Experiments on real RO concentrates using the nonselective anion SA and cation SK membranes were performed to evaluate the separation of salts from organic solutes by electrodialysis in a realistic matrix.

Fig. 6(a and b) shows the concentration decrease of Cl^-, SO_4^{2-} and TOC in diluate of a real RO concentrate stream by electrodialysis.

It can be seen from Fig. 6 that the concentration decrease of salts (i.e. Cl^- and SO_4^{2-}) is similar, however, the concentration decrease of TOC is very slow and most (over 85%) of the organic fraction was retained at the feed side. This can be explained by the organic compounds transport experiments above: most of the organic solutes in the real RO concentrates can be assumed to have a large size, be zwitterions, or be uncharged. Thus, by the SA membrane in electrodialysis, salts can be successfully separated to the concentrate compartment while keeping the organic fraction at the feed side.

4. Conclusions

In this study, the separation of nutrients and organic solutes from inorganic ions was investigated. Anion transport properties through a nonselective anion-exchange membrane (SA) and a monovalent selective anion-exchange membrane (MVA) under different conditions (by changing initial pH or initial current density) were studied to investigate the separation efficiencies of monovalent ions to multivalent ions. It was found that lowering the current density can separate the monovalent anions from the multivalent anions with either the SA (nonselective) or the MVA (selective) membranes. Furthermore, lowering the current is more effective than increasing pH to improve the permselectivity of the MVA membrane. However, it is difficult to separate NO_3^- from Cl^- and $H_xPO_4^{y-}$ from SO_4^{2-}, i.e., to separate the anions with similar size and charge. Hence, further research on the improvement of selectivity on Cl^-/NO_3^- and $H_xPO_4^{y-}$/SO_4^{2-} by electrodialysis is necessary.

Moreover, to separate the salts from organic compounds, small organic ions transport mechanisms through the SA membrane and the MVA membrane were investigated. Larger ions are retained more efficiently than smaller ones, which points in a direction of a size-exclusion effect. On the other hand, zwitterions are retained almost completely in the diluate side.

Finally, an experiment was performed to prove the separation of salts from organic solutes in the real RO concentrate streams by electrodialysis. The fact that more than 85% of the organic fraction in the real RO concentrate was kept at the feed side strongly suggests that the separation of salts from organics by electrodialysis is feasible.

Acknowledgement

References

[1] H. Strathmann, Ion-exchange Membrane Separation Processes, vol. 9, Membr. Sci. Technol., Elsevier, 2004.
[2] H. Strathmann, Membrane separation processes, J. Membr. Sci. 9 (1981) 121.
[3] L.J. Banasiak, T.W. Kruttschnitt, A.I. Schäfer, Desalination using electrodialysis as a function of voltage and salt concentration, Desalination 205 (2007) 38.
[4] W. Pronk, M. Biebow, M. Boller, Electrodialysis for recovering salts from a urine solution containing micropollutants, Environ. Sci. Technol. 40 (2006) 2414.
[5] M. Maurer, W. Pronk, T.A. Larsen, Treatment processes for source-separated urine, Water Res. 40 (2006) 3151.

Fig. 6. (a and b) Concentration decrease of Cl^-, SO_4^{2-} (a) and TOC (b) in diluate of real RO concentrate stream by electrodialysis. The left axis in (a) shows the concentration of Cl^- and the right axis shows the concentration of SO_4^{2-}.

[6] E. van Voorthuizen, A. Zwijnenburg, W. van der Meer, H. Temmink, Biological black water treatment combined with membrane separation, Water Res. 42 (2008) 4334.

[7] E. van Voorthuizen, A. Zwijnenburg, M. Wessling, Nutrient removal by NF and RO membranes in a decentralized sanitation system, Water Res. 39 (2005) 3657.

[8] M. Kumar, M. Badruzzaman, S. Adham, et al., Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE), Water Res. 41 (2007) 2211.

[9] L. Shu, P. Schneider, V. Jegatheesan, et al., An economic evaluation of phosphorus recovery as struvite from digester supernatant, Bioresour. Technol. 97 (2006) 2211.

[10] M. Mondor, L. Masse, D. Ippersiel, et al., Use of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure, Bioresour. Technol. 99 (2008) 7363.

[11] T. Sata, Studies on ion exchange membranes with permselectivity for specific ions in electrodialysis, J. Membr. Sci. 93 (1994) 117.

[12] B. Van der Bruggen, A. Koninckx, C. Vandecasteele, Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration, Water Res. 38 (2004) 1347.

[13] A. Elmidaoui, F. Elhannouni, M.A. Menkouchi Sahli, et al., Pollution of nitrate in Moroccan ground water: removal by electrodialysis, Desalination 136 (2001) 325.

[14] N. Kabay, Ö. Arar, S. Samatya, et al., Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species, J. Hazard. Mater. 153 (2008) 107.

[15] N. Kabay, H. Kahveci, Ö. İpek, et al., Separation of monovalent and divalent ions from binary mixtures by electrodialysis, Desalination 198 (2006) 74.

[16] N. Kabay, Ö. İpek, H. Kahveci, et al., Effect of salt combination on separation of monovalent and divalent salts by electrodialysis, Desalination 198 (2006) 81.

[17] R.S. Gartner, F.G. Wilhelm, G.J. Witkamp, M. Wessling, Regeneration of mixed solvents by electrodialysis: selective removal of chloride and sulfate, J. Membr. Sci. 250 (2005) 113.

[18] J. Schaep, B. Van der Bruggen, C. Vandecasteele, D. Wilms, Influence of ion size and charge in nanofiltration, Sep. Purif. Technol. 14 (1998) 155–162.

[19] J.M.M. Peeters, J.P. Boom, M.H.V. Mulder, H. Starathmann, Retention measurements of nanofiltration membranes with electrolytes solutions, J. Membr. Sci. 145 (1998) 99–209.

[20] C. Labbez, P. Fievet, A. Szymczyk, et al., Retention of mineral salts by a polyamide nanofiltration membrane, Sep. Purif. Technol. 30 (2003) 47–55.

[21] J. Tanninen, M. Mänttär, M. Nyström, Effect of salt mixture concentration on fractionation with NF membranes, J. Membr. Sci. 283 (2006) 57–64.

[22] L. Paugam, C.K. Diawara, J.P. Schlumpf, et al., Transfer of monovalent anions and nitrates especially through nanofiltration membranes in brackish water conditions, Sep. Purif. Technol. 40 (2004) 237–242.

[23] F. Garcia, D. Ciceron, A. Saboni, S. Alexandrova, Nitrate ions elimination from drinking water by nanofiltration: membrane choice, Sep. Purif. Technol. 52 (2006) 196–200.

[24] B. Van der Bruggen, R. Milis, C. Vandecasteele, et al., Electrodialysis and nanofiltration of surface water for subsequent use as infiltration water, Water Res. 37 (2003) 3867.

[25] P.J. Moon, S.J. Parulekar, S.P. Tsai, Competitive anion transport in desalting of mixtures of organic acids by batch electrodialysis, J. Membr. Sci. 141 (1998) 75.

[26] V. Montiel, V. Garcia-Garcia, J. Gonzalez-Garcia, et al., Recovery by means of electrodialysis of an aromatic amino acid from a solution with a high concentration of sulphates and phosphates, J. Membr. Sci. 140 (1998) 243.

[27] E. Singlande, H.R. Balmann, X. Lefevbre, et al., Improvement of the treatment of salted liquid waste by integrated electrodialysis upstream biological treatment, Desalination 199 (2006) 64.

[28] V. Lindstrand, G. Sundström, A. Jönsson, Fouling of electrodialysis membranes by organic substances, Desalination 128 (2000) 91.

[29] D. Kim, S. Moon, J. Cho, Investigation of the adsorption and transport of natural organic matter (NOM) in ion-exchange membranes, Desalination 151 (2002) 11.

[30] H. Lee, D. Kim, J. Cho, et al., Characterization of anion exchange membranes with natural organic matter (NOM) during electrodialysis, Desalination 151 (2002) 43.

[31] T. Sata, Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis—effect of hydrophilicity of anion exchange membranes on permselectivity of anions, J. Membr. Sci. 167 (2000) 1.

[32] F. Li, W. Meindersma, A.B. de Haan, et al., Novel spacers for mass transfer enhancement in membrane separations, J. Membr. Sci. 253 (2005) 1.

[33] PCCell ED ED 64 0 02, Operation and Maintenance Instruction, PCCell GmbH, Heusweiler, Germany, Version, August 06.

[34] M. Mulder, Basic Principles of Membrane Technology, 2nd edition, Kluwer, Dordrecht, The Netherlands, 1996.

[35] CurTiPot, Version 3.3.2, accessed and downloaded in August 10, 2008.

[36] V.V. Nikonenko, V.I. Zabolotskii, N.P. Gnusin, K.A. Lebedev, Effect of stationary external electric fields on ion-exchange membrane selectivity, Sov. Electrochem. 16 (1980) 472.

[37] V.V. Nikonenko, V.I. Zabolotskii, K.A. Lebedev, Model for the competitive transport of ions through ion exchange membranes with a modified surface, Rus. J. Electrochem. 32 (1996) 234.

[38] V.I. Zabolotsky, J.A. Manzanares, V.V. Nikonenko, et al., Space charge effect on competitive ion transport through ion-exchange membranes, Desalination 147 (2002) 387.