SEPARATION OF ORGANICS AND SALTS WITH ION-EXCHANGE MEMBRANES: EFFECT OF MATRIX AND ORGANICS

Marjolein Vanoppen[,a], Griet Stoffels[a], Lingshan Ma[a], Evelyn De Meyer[a], Klaas V.K.M. Schoutteten[a], Lynn Vanhaecke[b], Arne R.D. Verliefde[a]*

[a] *Particle and Interfacial Technology Group, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, University of Ghent, Belgium*
[b] *Laboratory of Chemical Analysis, Department of Veterinary Public Health and Food Safety, Faculty of Veterinary Medicine, University of Ghent, Merelbeke, Ghent*
[*] *Corresponding author email: marjolein.vanoppen@ugent.be, tel. +32 (0)9 264 99 11*

INTRODUCTION

Ion-exchange membranes are used in many processes, both in demineralization (e.g. process water, food industry) and in selective separation (e.g. microbial electrolysis cells). Oftentimes, the membranes are confronted with complex streams, containing a mixture of organic and inorganic components. One of the more recent developments in ion-exchange technologies is reverse electrodialysis (RED), a technology used to harvest the energy from salinity gradients.

In RED, ion-exchange membranes (IEM) are used to separate a high salinity water source (often seawater) from a fresh water source. The natural diffusion of salt ions from the high to the low concentration creates a potential difference across the membranes, that can be harvested as energy. Originally, the process was designed as a source of sustainable energy, with river water as a fresh water source, for which it is now being tested on pilot-scale(Vermaas et al. 2013; Güler et al. 2013). However, recently it was also suggested as a pre-desalination step for seawater RO, as shown in Figure 1(Vanoppen et al. 2016).
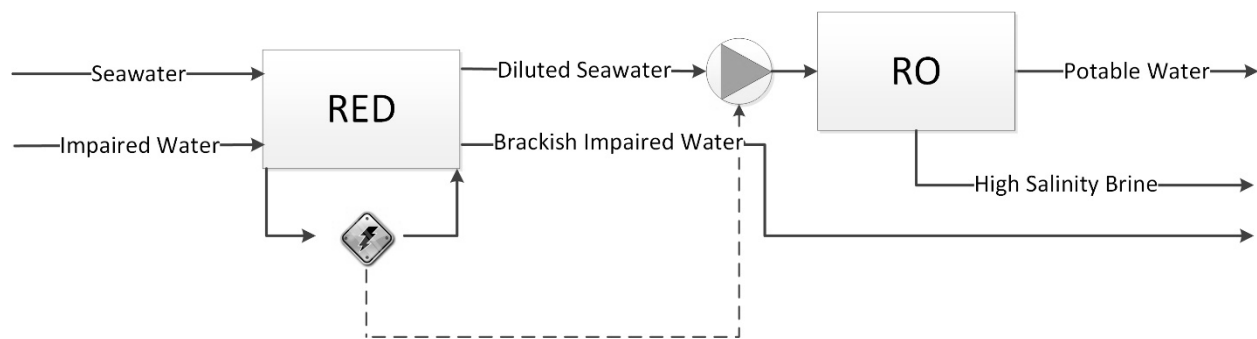
Figure 1 RED-RO hybrid scheme for energy efficient seawater desalination.

In this scheme, the seawater is used for the production of drinking water and impaired water, such as secondary effluent from a waste water treatment plant, is used as fresh water. The latter is deemed a suitable fresh water source here, as it is often unacceptable for the production of drinking water. The hybrid scheme has two advantages: energy is produced in the RED step and the

seawater concentration decreases, resulting in a lower energy demand in the RO step. As such, energy is saved in two ways.

However, the use of impaired water comes with a unique set of challenges. Not only is this type of water very diverse, it also contains a lot of contaminants. Of concern are mainly trace organic contaminants (TOrC), such as pesticides and pharmaceuticals, that are not removed in traditional waste water treatment systems. If these are transported from the impaired water to the seawater, they could pose a threat to the drinking water quality. This transport of organics through IEM has received relatively little attention in literature, although it is interesting to many processes utilizing IEMS, such as electrodialysis, microbial electrolysis cells, microbial fuel cells, and so on. Recent research has indicated however, that the transport or these organics in the presence of salts is mainly diffusion driven(Vanoppen et al. 2015). This paper continues in the fundamental research of organics transport in IEM, looking into the effect of different salts, the direction of the salt transport and organics with different properties.

MATERIALS AND METHODS

All experiments were carried out in DI water, to which the organics were added in the appropriate dosage. Experiments were carried out without current (diffusion experiments) and with a current density of 100 A/m², unless specified otherwise (ED experiments). An overview of the organics used with their general properties is given in Table 1. Three different salts were used: NaCl, $MgCl_2$ and Na_2SO_4.

Table 1 Overview of used organics and their properties.

Component	Charge (pH 7)	pKa (-)	MW (g/mol)	Log D (pH 7)	LOD (µg/l)
Carbamazepine	0	-	236.27	2.77	0.015625
Clofibric acid	-	3.4	214.65	-0.63	1
Dimethoate	0	-	229.26	0.34	1
Diuron	0	-	233.10	2.53	0.125
Ketoprofen	-	3.9	254.28	0.08	0.03125
Metoprolol	+	9.7	267.36	-0.79	0.25
Pirimicarb	0	5.0	238.29	1.79	0.5
Sulfamethoxazole	-	2.0	253.28	0.15	0.25
Lincomycin	+	7.97	406.54	-1.33	0.125
Lidocaine	+	7.75	234.34	2.02	1
Propanolol	+	9.67	259.34	0.04	1
Triclopyr	-	2.3	256.47	-0.83	1
Propionic acid	-	4.8	74.08	0.48	$12 \cdot 10^3$
Butyric acid	-	5.0	88.11	0.92	$14 \cdot 10^3$
Valeric acid	-	5.0	102.13	1.37	$17 \cdot 10^3$

All experiments were run for 48 hours (reaching a theoretical degree of desalination of 90% in the ED experiments) except for the desalination experiments with only organic acids, which were run for 8 hours (to avoid complete desalination). Samples were taken periodically in all experiments. The transport of the organics was calculated according to the following equation:

$$\text{transport}_t = \frac{C_{C,t} \cdot V_{C,t}}{C_{D,0} \cdot V_{D,0}} \times 100\% \tag{1}$$

With t the time at which the transport is determined, C the concentration of the organics (µg/l), V the volume (l) and C and D the concentrate and diluate respectively. To ensure comparable results, the concentrate always consisted of 0.17 eq/l and the diluate of 0.86 eq/l initially, supplemented with the 100 µg/l of the TOrC's or 1 or 10 g/l of the organic acids, depending on the specific experiment. An overview of the executed experiments is given in Table 2.

**Table 2** Experiments performed in this research

Experiment	Salt	Diluate (eq/l)	Concentrate (eq/l)
1	NaCl	0.86 + TOrC	0.17
2	NaCl	0.86	0.17 + TOrC
3	NaCl	1.71 + OA (1g/l)	0.17
4	NaCl	1.71 + OA (10 g/l)	0.17
5**	NaCl	OA (10 g/l)	0.17
6	MgCl$_2$	0.86 + TOrC	0.17
7	Na$_2$SO$_4$	0.86 + TOrC	0.17

RESULTS AND DISCUSSION

Influence of Multivalent Ions

Figure 2 shows the TOrC transport from diluate to concentrate after 48 hours in the presence of different salts. As expected, there is no influence of the salt type on the transport of neutral compounds, as these are not influenced by charge effects. It is however clear that the transport of negatively charged compounds is higher in the presence of sulphate. This is apparent for both the diffusion and ED experiments. This can be partially explained by the lower diffusion coefficient of sulphate compared to chloride (the diffusion constant at 25°C for Cl$^-$ is 20.3x10^{-10} m²/s and for SO$_4^{2-}$ is 10.7x10^{-10} m²/s(Ramadan et al. 2010)). As expected, the presence of Mg^{2+} does not have an effect on the transport of negatively charged compounds. However, for positively charged compounds, the transport increases both in the presence of SO$_4^{2-}$ and of Mg^{2+}. For Mg^{2+}, the reason can again be found in the diffusion coefficient, which is higher for Na$^+$ than for Mg^{2+} (the diffusion coefficient in water at 25°C for Na$^+$ is 13.3 x 10^{-10} m²/s and for Mg^{2+} is 7.05 x 10^{-10} m²/s(Ramadan et al. 2010)). Since Mg^{2+} diffuses slower than Na$^+$, relatively more positively charged organics will be transported to balance the equilibrium difference across the membrane when Mg^{2+} is present in the diluate than when Na$^+$ is present. Based on the data presented here, no clear reason can be found for the higher transport of positively charged compounds in the presence of SO$_4^{2-}$.

Figure 2 Transport of organics in the presence of multivalent ions during diffusion experiments (left) and ED experiments (right).
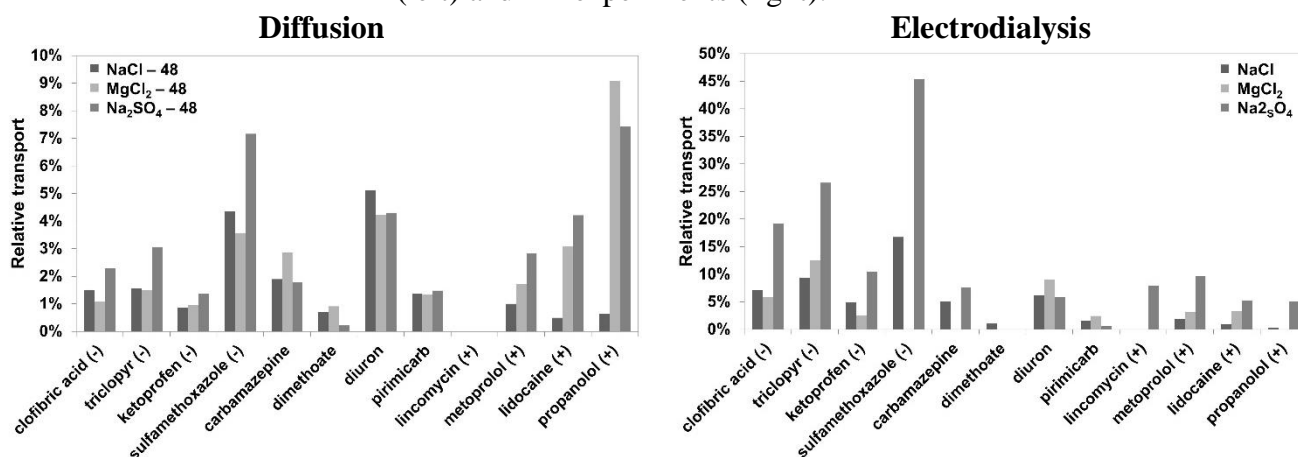
Influence of Relative Transport Direction

The organics don't necessarily have to be present in the diluate. In RED for example, waste water can be used as a sink for the ions and the diluate is seawater. It is expected that organic micropollutants are present in the waste water, and their transport to the seawater is undesired. Figure 3 shows the results for the transport of TOrCs when dosed to the diluate (D) or the concentrate (C), in both diffusion and electrodialysis experiments.

Figure 3 Transport of organics when dosed either to the diluate (transport in direction of salt transport) or to the concentrate (transport in opposite direction of salt transport) after 24 and 48 hours.
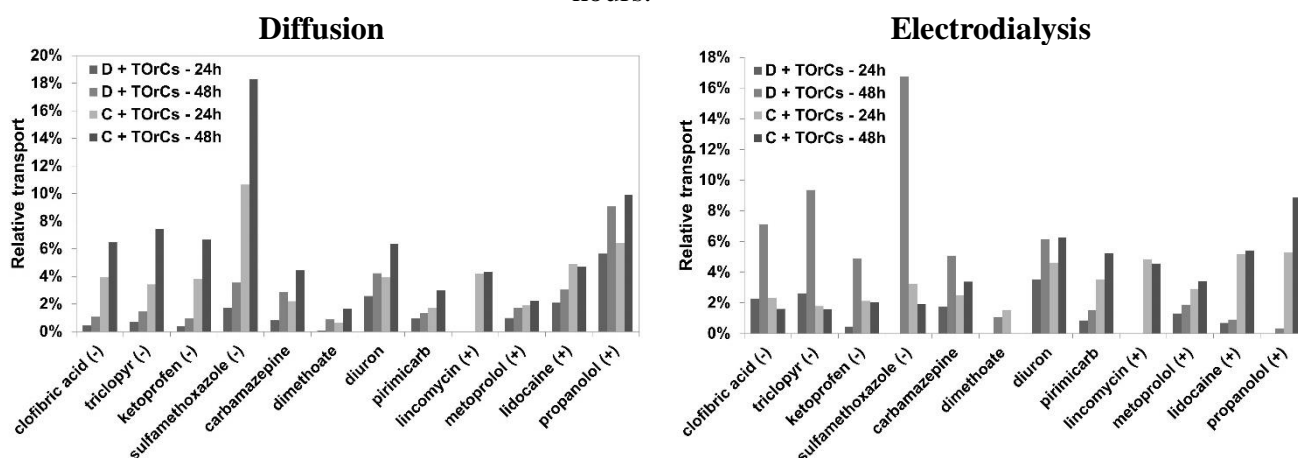

When dosed to the diluate, the transport of the organics is in the same direction as that of the dominant salts flux, while the opposite is true when they are dosed in the concentrate. This has a clear effect on the charged compounds, as shown in Figure 3, while there does not seem to be a significant difference in transport for the neutral compounds. During diffusion experiments, where no external potential is applied, the transport of especially negatively charged compounds is higher when they are dosed to the concentrate rather than the diluate. This can be explained by Donnan dialysis, where charged compounds of the same charge are exchange across IEM according to their difference in electrochemical potential. Because of the high electrochemical potential difference

between both solutions, Donnan dialysis plays a significant role. During ED, the trend is the opposite. Here, transport of negatively charged compounds is generally higher after 48 hours when dosed to the diluate. After 24 hours, there is no difference between dosing them in the concentrate or diluate. Positively charged compounds on the other hand seem to have a higher transport when dosed to the concentrate in the ED experiments. The latter can be explained by the higher crosslinking of the CEM, limiting easy transport of positively charged compounds.

Behavior of Organic Acids

To confirm previous findings with TOrCs indicating that organics transport is mainly diffusion driven, similar experiments with organic acids were conducted. Figure 4 shows the results of ED experiments with organic acids (OA) in the presence and absence of salts.

Figure 4 Diffusion and electromigration driven transport of organic acids in the presence and absence of NaCl.
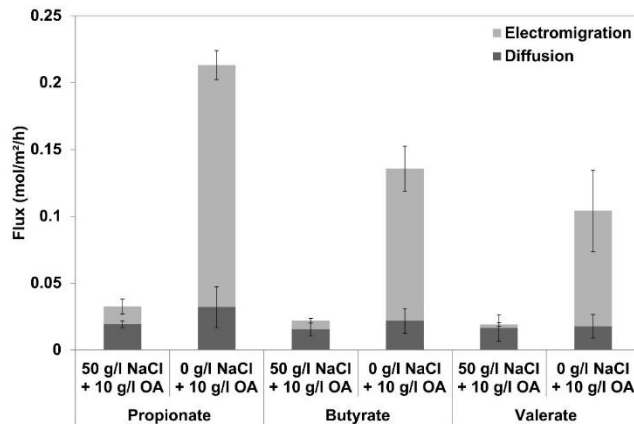
Transport in ED can be split into two parts; diffusion and electromigration, as expressed by the Nerns-Planck equation:

$$J_s = D \cdot \frac{\Delta C}{\Delta x} + \frac{F \cdot C}{R_g \cdot T} \cdot z \cdot D \cdot \frac{\Delta E}{\Delta x}$$

Here, J_s is the solute flux (mol/(m².h)), D the diffusion coefficient in the membrane (m²/h), ΔC the concentration difference across the membrane (mol/m³), Δx the thickness of the membrane (m), F the Faraday constant (96 485 J/(mol.K)), C the concentration in the diluate (mol/m³), R_g the universal gas constant (8.31 J/(mol.K)), T the temperature (K), z the ion valence (-) and ΔE the potential difference across the membrane. From this equation, it is clear that diffusion only depends on the diffusion coefficient in the membrane and on the concentration difference across the membrane. Hence, by comparing the diffusion and ED experiments with OA, transport by diffusion and electromigration could be distinguished, as shown in Figure 4. From this, it is clear that in the presence of salts the contribution of electromigration is very small, especially for larger compounds. This again shows that in the presence of salts, the transport of organics is mainly diffusion driven.

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