

PROPERTIES GOVERNING THE TRANSPORT OF ORGANIC POLLUTANTS THROUGH ION-EXCHANGE MEMBRANES USING DESALINATION OF COMPLEX WASTE STREAMS IN ED

Marjolein Vanoppen, Particle and Interfacial Technology Group, Faculty of Bioscience Engineering, University of Ghent, Coupure Links 653, 9000 Ghent, Belgium,

marjolein.vanoppen@ugent.be, 0032 (0)9 264 99 11

Dorien Gaublomme, University of Ghent, Ghent, Belgium

Klaas Schoutteten, University of Ghent, Ghent, Belgium

Lynn Vanhaecke, University of Ghent, Ghent Belgium

Julie Vanden Bussche, University of Ghent, Ghent, Belgium

Arne R.D. Verliefde, University of Ghent, Ghent, Belgium

Introduction

Industrial wastewaters often consist of complex mixtures of inorganic salts and organic materials. Examples are found in the food industry, where the treatment of potatoes, olives, cheeses, ... results in complex waste streams, but also in other applications. One typical complex stream is the brine of reverse osmosis installations operating on wastewater effluent, which can result in a concentrated mixture of salts and organics. (Kabsch-Korbutowicz et al. 2011; Kim 2011) The high salt concentration in these complex streams limits the treatability with conventional biological purification, while the organic matter restricts the applicability of conventional physico-chemical techniques to recover the inorganics. (Lefebvre & Moletta 2006; Deorsola et al. 2013) Adequate treatment of these streams could lead to the reuse and/or valorisation of both organic and inorganic fractions. One possibility to achieve this is the application of electro-driven membrane processes, such as electrodialysis (ED) or membrane capacitive deionisation (MCDI). Both use ion exchange membranes (IEM) to perform a selective separation.

ED, more than MCDI, has been finding its way into industrial applications, from the food industry to biotechnology-applications and many more. (Strathmann 2010) As with other membrane processes, fouling of the IEM has been identified as one of the most important limiting factors for the application of ED. Research has so far mainly focused on inorganic scaling (Araya-Farias & Bazinet 2006; Bazinet & Araya-Farias 2005; Casademont et al. 2008; Casademont et al. 2007) and organic fouling (Tanaka et al. 2012; Banasiak et al. 2011; H.-J. Lee et al. 2002; H. Lee et al. 2002) in IEM. However, the phenomena governing transport of organics through IEM has received little attention in literature (Banasiak 2009), even though experiments indicate that this transport can be significant. A more thorough understanding of transport phenomena of organics through IEM is thus required and could lead to the design and development of more efficient membranes to separate inorganic and organic substances in

complex waste streams. That's why this research focusses on the transport of trace organic contaminants (TOrcs), as a model for a wide range of organics, through IEM in the well know ED process. This allows the identification of the dominant solute, solution and membrane properties governing transport of organics through IEM. This will benefit a wide range of IEM-applications, such as ED, MCDI, membrane electrolysis cells, membrane fuel cells, and many more.

Materials and Methods

ED set-up

The PCCell ED 64004 (PCA GmbH, Germany) was used. This ED cell contains two titanium electrodes coated with a platinum/iridium mixed metal oxide coating for the cathode and anode respectively. Fujifilm cation and anion exchange membranes (CEM and AEM) were used to form four cell pairs with an active membrane area of 64 cm² per membrane. The properties of the membranes used are given in Table 1, as provided by the manufacturer. Diluate and concentrate compartments were formed using 0.5 mm silicone/polyethylene spacers.

Table 1. Properties of the used cation and anion exchange membranes as given by the manufacturer.

Properties	AEM	CEM
Thickness (μm)	160	160
Permselectivity (%)	95	96
Electrical resistance ($\Omega\cdot\text{cm}^2$)	3.5	6.1
Water permeability ($\text{ml}/\text{bar}\cdot\text{m}^2\cdot\text{hr}$)	3	3.5
Burst strength	5	4.7

TOrcs

A set of 16 TOrcs with a wide variety of physico-chemical properties (such as size, hydrophobicity, charge, ...) was selected. A stock solution of 2 mg/l TOrcs, with a minimal purity of 98% (Sigma Aldrich, USA), was prepared and stored at 4°C before dilution prior to each experiment. An overview of the used TOrcs and their properties is given in Table 2.

Table 2. Properties of the 16 used TOrCs

Component	Charge (@ pH 7)	pKa (-)	MW (g/mol)	Log D (@ pH 7)
Atrazine	0	3.2	215.68	2.20
Carbamazepine	0	-	236.27	2.77
Chloridazon	0	-	215.68	1.11
Clofibric acid	-	3.4	214.65	-0.63
Diclofenac	-	4.0	296.15	0.73
Dimethoate	0	-	229.26	0.34
Diuron	0	-	233.10	2.53
Ketoprofen	-	3.9	254.28	0.08
Metoprolol	+	9.7	267.36	-0.79
Paracetamol	0	9.5	151.16	0.91
Phenazone	0	-	188.23	1.22
Pirimicarb	0	5.0	238.29	1.79
Simazine	0	3.2	201.66	1.78
Sulfamethoxazole	-	2.0	253.28	0.15
Theophylline	-	7.8	180.16	-0.81
Triclopyr	-	2.3	256.47	-0.83

The TOrC concentration was determined using UHPLC-HR-OrbitrapTM-MS (Benchtop Exactive OrbitrapTM mass-spectrometer, Thermo Fisher Scientific, USA). Prior to analysis, the salts were removed from the samples by a solid phase extraction with Oasis HLB cartridges (6cc, 200 mg of sorbent, Waters Corporation, Ireland).

Experimental protocol

The experiments were divided into two parts. In a first part, the transport behaviour of the TOrCs in the absence of an electrical potential was investigated. Different NaCl concentrations in both the diluate and concentrate compartments were used to investigate the effect of salts on the diffusion behaviour of the TOrCs. In a second part, three different current densities were applied to a model waste water containing 100 g/l NaCl and 100 µg/l TOrCs, with a 10 g/l NaCl solution as the concentrate. The membranes for the first set of tests were reused for the ED tests and flushed with TOrC solution for an additional 24 hours, ensuring full saturation of the membranes with TOrCs. The ED experiments were run in batch mode until a total desalination extent of 95% was reached. Samples for TOrC analysis were taken at 0, 25, 50, 75 and 95% desalination. Desalination was monitored by monitoring the conductivity and weight (as an indication for water transport) of the diluate compartment.

Results and Discussion

Transport of TOrCs without an electrical potential

In Figure 1, the net transport at the end of the different transport experiments without an electrical potential is shown. It is clear from this that in the absence of NaCl, the transport is much higher for charged molecules. The relatively high transport of paracetamol could be explained by its small size, although no clear correlation with size was found for the other components. The lower transport in the presence of salt is explained by the preferential interaction of the membranes with Na^+ and Cl^- . These ions are not only much smaller and more mobile than the TOrCs, their concentration is also much higher, causing their preferential transport at the expense of TOrCs. Another possible explanation is that the diffusion coefficient of organics tends to decrease in the presence of salts. This phenomenon has been found to decrease the self-diffusion coefficient by up to 27% at high NaCl concentrations during tests in our laboratory. A decrease of up to 12% can be expected at the concentrations used in our research, which could partially explain the lower transport of TOrCs in the presence of NaCl.

Figure 1. Transport of TOrCs (%) in the presence of different salt concentrations in the diluate | concentrate compartments. Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$.

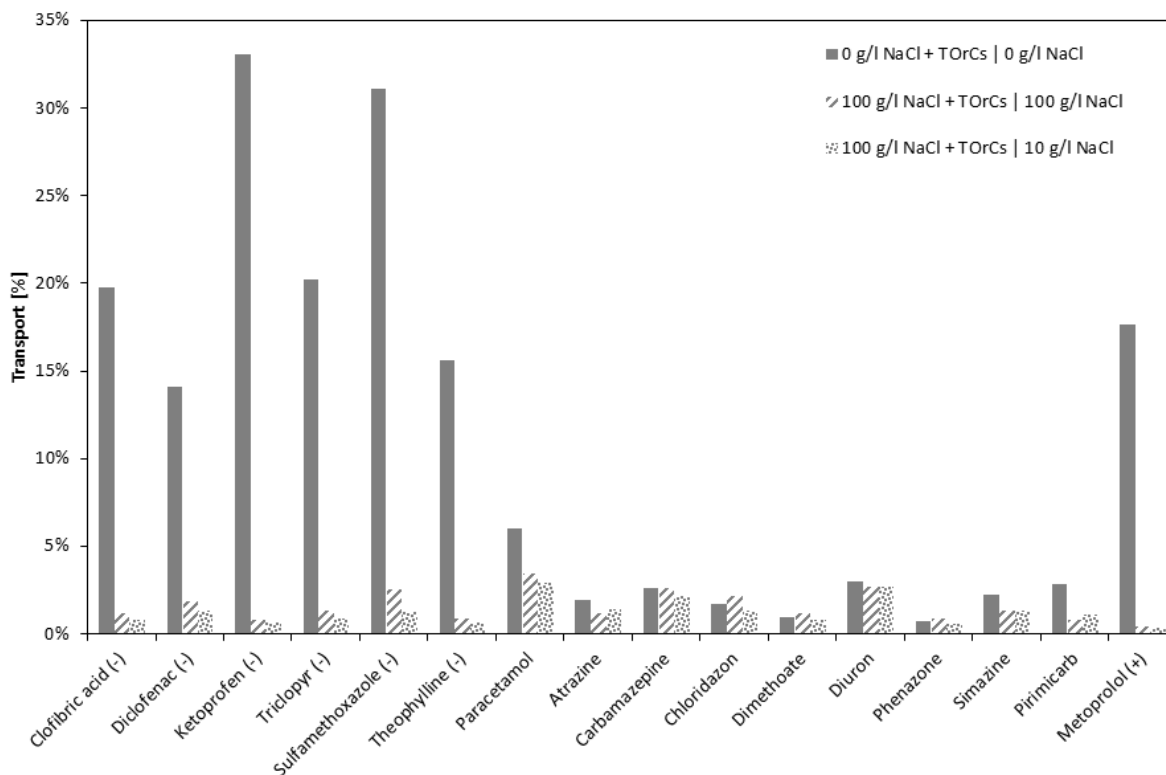
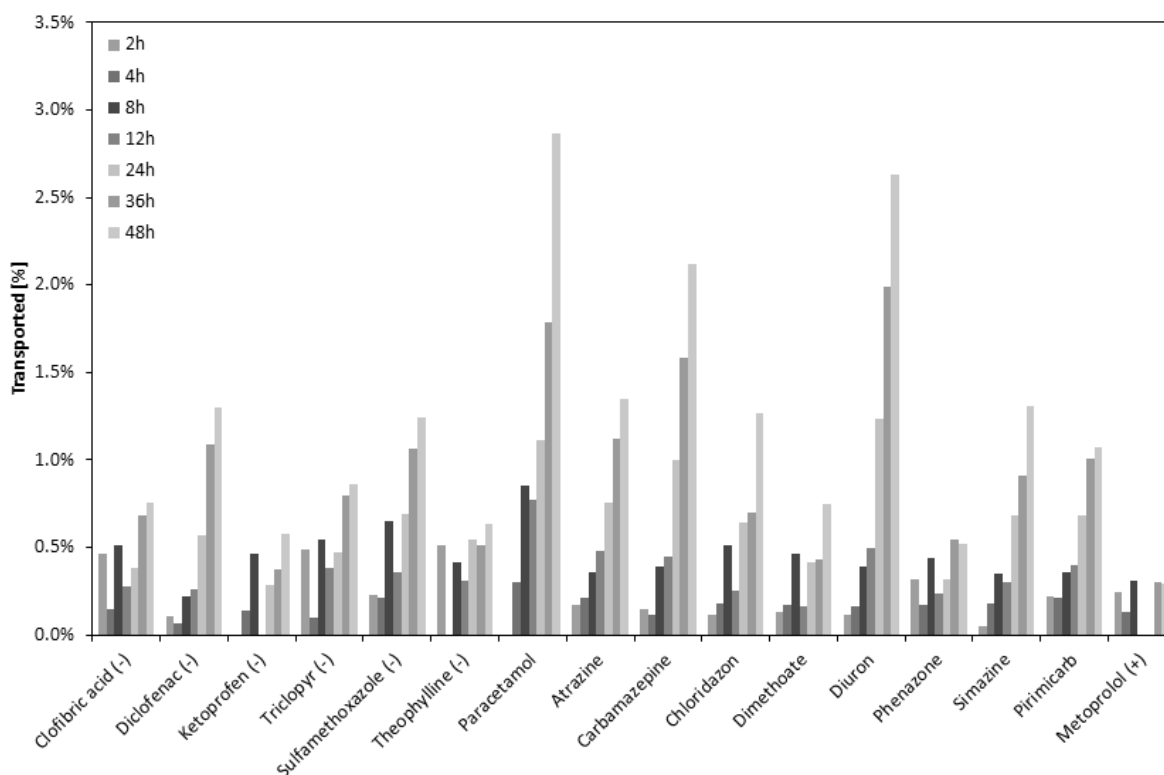


Figure 2. Transport (%) versus time (h) with a 100 g/l NaCl + TOrCs | 10 g/l NaCl diluate | concentrate concentration difference. Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$



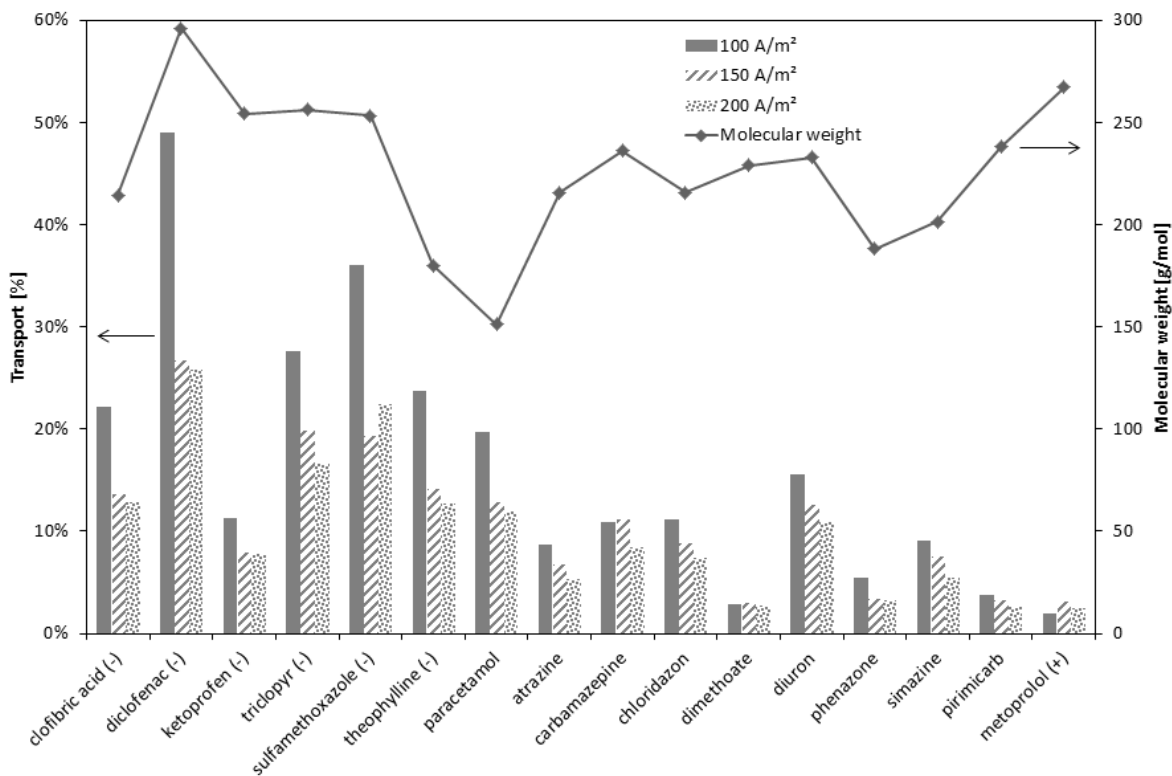
Taking a closer look at the transport during the 100 g/l NaCl + TOrCs | 10 g/l NaCl, as shown in **Error! Reference source not found.**, we can see a linear trend for the neutral compounds (with an average R^2 of 0.9 ± 0.1 for the linear regression). This indicates a purely diffusion driven transport of these compounds, which is expected since the interaction with the membrane is probably limited due to their lack of charge. For the charged compounds, the average R^2 is 0.7 ± 0.2 and 0.1 ± 0.1 for negatively and positively charged TOrCs respectively. This indicates that besides diffusion, other phenomena also play a role in their transport. The low transport of metoprolol is probably explained by the high crosslinking of the membrane (indicated by its high resistance) and the high molecular weight of metoprolol, hindering its transport across the membrane. For the negatively charged compounds, other interactions, such as charge and electron donor-acceptor interactions, are important. This is in agreement with earlier work by Banasiak et al. (Banasiak 2009)

Transport of TOrCs during electro dialysis

The total transport during the ED experiments, with three different current densities, is given in Figure 3. These experiments were conducted with 100 g/l NaCl and 100 μ g/l TOrCs in the initial diluate and 10 g/l NaCl in the initial concentrate, chosen to mimic an industrial waste stream. ED results in two main drivers for transport; the concentration difference between the compartments

and the applied current densities. From the graph it is clear that more transport occurs at lower current densities. Theoretically however, one would expect more transport to occur at higher current densities because of the higher driving force. This indicates that the transport is only partially influenced by the electrical potential, but that the main driver for transport is simple diffusion. Since the 100 A/m² experiments ran for approximately double the time of the 200 A/m² experiments, there was more time for diffusion during these experiments. This hypothesis is also supported by the linear transport of TOrcs over time, with an average correlation coefficient of 0.94 ± 0.06 for all compounds. If the electrical potential difference would have a significant effect, one would expect the transport to be more exponential, increasing with a decreasing NaCl concentration during desalination. It is hypothesized that the electrical potential only plays a major role for TOrc transport at the end of the desalination process, when much less salt is available for charge transfer. This is why the difference between the 150 and 200 A/m² experiments is a lot lower.

Figure 3. Net transport (%) at 95% desalination for electro dialysis at three different current densities (100, 150 and 200 A/m²) as a function of molecular weight (g/mol). Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$



Conclusions

Overall, this research shows that the main interactions between charged TOrcs and the membrane are electrostatic interactions. The electrical potential seems to have only a minor effect on the transport of TOrc up to the point that the salts are almost completely depleted from

the diluate. Further research will focus on non-electrostatic interactions (interfacial energy) and different membrane characteristics influencing membrane-TOrC interactions.

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