CHEMICAL ENGINEERING TRANSACTIONS

VOL. 60, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Luca Di Palma, Elisabetta Petrucci, Marco Stoller
Copyright © 2017, AIDIC Servizi S.r.l.
ISBN 978-88-95608- 50-1; **ISSN** 2283-9216

DOI: 10.3303/CET1760052

Experimental Analysis of a Continuously Operated Reverse Electrodialysis Unit Fed with Wastewaters

Javier Luque Di Salvo, Alessandro Cosenza, Andrea Cipollina, Alessandro Tamburini[a], Giorgio Micale

Dipartimento dell'Innovazione Industriale e Digitale (DIID) - Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo (UNIPA) – viale delle Scienze Ed.6, 90128 Palermo, Italy
alessandro.tamburini@unipa.it

Reverse Electrodialysis (RED) is one of the most promising technologies to convert salinity gradient chemical energy into electricity. RED units are traditionally operated with natural streams as river water and seawater thereby limiting the spread of the technology in sites far from coastal areas. Aim of the present work is that of exploring and expanding feed possibilities for RED systems by employing waste streams. Thus, an experimental study was performed by testing, for the first time, a Reverse Electrodialysis (RED) unit fed with a high salinity wastewater originated in a fish canning factory, and a low salinity wastewater from a sewage treatment plant. Uninterrupted, long duration experiments were carried out to evaluate time-evolution of the key electrical parameters. Power output was monitored over time along with pumping losses and electrical resistance. The effect of chemical backwashing was analysed in order to assess process maintenance. Results showed that fouling issues have a crucial impact on process performance and should be properly addressed before operating RED units fed by waste streams.

1. Introduction

In the framework of Salinity Gradient Power (SGP) technologies, Reverse ElectroDialysis (RED) is one of the most promising (Gurreri et al. 2016; Straub et al. 2016). In RED, two solutions of different salt concentration are fed into a series of alternate compartments, the one fed by the low salinity solution, the other by the high salinity solution. Compartments are separated by anion and cation exchange membranes alternatively piled to form a stack. Selective ion transport from the concentrate compartment to the dilute one across the membranes allows to generate an ionic current, which is eventually converted into electric current by means of suitable red-ox reactions occurring within the end electrodic compartments closing the stack.

Several options for the feed solutions are possible. Natural streams were first considered as a potential source of salinity gradient, such as: river water and seawater (Veerman et al. 2010) or concentrated brines and brackish waters (Tedesco et al. 2016, 2017). Another alternative is the use of suitable selected solutes and solvents in closed loop arrangement of SGP technologies, where the partially mixed solutions exiting from the SGP unit can then be regenerated by means of a thermally driven regeneration step. For instance, water solutions of thermolytic salts are among the most investigated in SGP heat engines (Bevacqua et al., 2016; Tamburini et al., 2016). A nascent, still less explored alternative is the use of different industrial wastewaters as feed solutions. In fact, in several different scenarios, waste streams to be disposed can actually represent a very effective source of salinity gradient to be exploited before the natural mixing with the receiving water body occurs (Lefebvre and Moletta 2006). In this sense, little is known about the behaviour of a RED unit fed with wastewaters. Recently, Wang et al. (2017) proposed a hybrid RED/Electrodialysis (RED/ED) process, where the RED stage is devoted to concentrating a waste, which is then recovered in the ED stage.

In the present work a high salinity waste brine from a fish processing factory and a low-salinity water from a sewage Membrane Bio Reactor (MBR) treatment plant were selected as feed solutions for a testing on a laboratory-scale RED unit. Two long-runs were performed, one using real wastewaters and another with artificial NaCl solutions having same electrical conductivity of wastewaters. The time-evolution of system performance parameters was registered and analysed in order to assess the relevant effect of the real feed

Please cite this article as: Luque Di Salvo J., Cosenza C., Cipollina C., Tamburini T., Micale M., 2017, Experimental analysis of a continuously operated reverse electrodialysis unit fed with wastewaters, Chemical Engineering Transactions, 60, 307-312 DOI: 10.3303/CET1760052

solutions. Also washing procedures were tested in order to highlight their effectiveness in controlling fouling phenomena, if any.

2. Experimental section

2.1 Wastewater feed solutions

Feed solutions used in this study came from treatment pilot plants at the Department of Civil, Environmental and Materials Engineering (DICAM) of the University of Palermo (Italy). Table 1 summarizes features of both wastewaters. The high salinity wastewater was originated in a fish canning industry located at Aspra, Sicily (Italy). The waste is characterized by high organic load, and because of the high salinity, active granular sludge biological treatment is preferred compared to the physical and chemical ones (He et al. 2017). In particular, the wastewater for this study was treated by Corsino et al. (2016) in a Sequence Batch Air Lift Reactor (SBALR) with an innovative simultaneous nitritation-denitritation technique, which shows a removal efficiency of Total Nitrogen (TN), COD and BOD over 90%. After this process, a wastewater with about 30 g/L of salinity is obtained. A post-treatment consisted in cartridge filtration (10 µm) to separate possible remaining solids, and mild acidification with HCl ($4 < pH < 5$) to prevent bacteria growth.

The low salinity feed originates from municipal wastewater, and was treated in a Moving-Bed Membrane Bio-Reactor (MB-MBR) pilot plant also located at DICAM. The treated effluent showed very low turbidity and no post-treatment was required to prepare the waste as feed. Tanks and pipes were suitably covered from light to prevent algae proliferation.

Table 1: Features of the wastewaters used in this work.

Features	High salinity wastewater	Low salinity wastewater
Cations (in ppm)	Na^+ (14,000) K^+ (390) Mg^{2+} (310) Ca^{2+} (0)	Na^+ (98.4) K^+ (22.4) Mg^{2+} (12.8) Ca^{2+} (60.6)
COD	650 mg/L	11 mg/L
BOD / Phosphorus	450 mg/L (BOD)	8 mg/l (Phosphorus)
Total Nitrogen	80 mg/L	24 mg/L
Salinity	30 g/L	0.6 g/L

2.2 Experimental apparatus and procedures

The RED stack consisted of 10 cell pairs each having an active membrane area of 0.01 m^2. Woven spacers made of polyamide (0.27 mm thick, Deukum GmbH) were interposed between the ionic exchange membranes (Gurreri et al. 2013), thus forming the channels for the feed solutions.

Ion Exchange Membranes were kindly supplied from FUJIFILM Manufacturing Europe BV (CEM and AEM Type I), whereas Nafion® CEMs were used as end membranes. A standard pre-conditioning procedure consisted in keeping IEMs in NaCl 0.5 mol/L for over 24h. Two Ru-Ir oxide-coated Ti electrodes from Magneto Special Anodes BV were placed in the electrode solution compartments. Electrode Rinse Solution (ERS) had a final concentration of 0.250 mol/L, with a composition of 0.100 mol/L $K_3[Fe(CN)_6]$ (Sigma Aldrich), 0.100 mol/L $K_4[Fe(CN)_6].3H_2O$ (Sigma Aldrich) and 0.050 mol/L of ultra-pure sodium chloride (NaCl 99.8%, Sigma Aldrich). Alkaline aqueous solutions (for backwashing cleaning procedure) was prepared with sodium hydroxide (solid NaOH > 99%, Sigma Aldrich).

The test rig for the experimental campaign is shown in Figure 1. A co-flow regime was adopted to feed the stack, by means of two independent peristaltic pumps (Cellai mod. 503U). The ERS reservoir and connecting pipes were well sealed and covered with aluminium paper to avoid air and light exposure (Scialdone et al. 2012). The ERS was recirculated with a flow rate of 13.5 L/h (peristaltic pump Verderflex R2S). Pressure gauges (M 40 PA, Cewal) were placed on each channel before entering the stack to measure pressure drops. A Multimeter Digimaster DM58B measured voltage difference.

Each day fresh samples of feeds were supplied to perform measurements. Besides electrical parameters, also electrical conductivity of inlet and outlet solutions, and pressure drops at both channels were measured. In order to maintain an uninterrupted alimentation with wastewaters, right after performing the relevant measurements a recycling feed-mode was adopted, i.e. the outlet meets the inlet tank. The recycling mode allowed to continuously feed the stack with the wastewaters, while operating with significantly lower volumes of waste. Fluid velocities were 1.0 cm/s and 0.5 cm/s for the low and the high salinity feeds, respectively. The long-run test lasted eight full days, and was partially stopped to perform an alkaline backwashing (pH = 9.6) when pressure drops were considered too high. Backwashing was applied (i) at inverted flow direction (i.e. entering from the outlet and exiting from the inlet) and (ii) at high flow rates to help physical unclogging of channels. The maximum fluid velocity during the alkaline backwashing was 3 cm/s (corresponding to about 500 ml/min), applied for short times (up to five minutes) between intervals of normal fluid velocities regime, i.e. 1.0 and 0.5 cm/s for the low and high channels, respectively.

An additional six days long-run with artificial NaCl solutions was performed adopting the same procedures to have a reference case. Artificial solutions were prepared with high purity salt (NaCl 99.8%, Sigma Aldrich), having final concentrations of 0.01 mol/L and 0.50 mol/L, based on the electrical conductivity of real wastewaters.

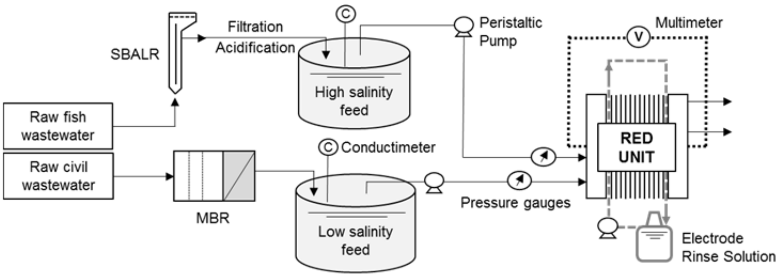

Figure 1: Scheme of the experimental setup. Wastewaters were received after biological treatments in pilot plants located at DICAM (University of Palermo, Italy).

The experiments were performed based on standard procedures for Reverse ElectroDialysis measurements presented in literature (Tedesco et al. 2015). The same consisted in measuring the voltage difference at OCV conditions and at different calibrated external loads (R_{ext}). The polarization curve (not shown for the sake of brevity) was used to derive stack resistance (R_{Stack}), Power density (P_d) and related parameters. More precisely, when an external load (R_{ext}) is connected in series with the electrode connections of the RED unit, a current passes through the circuit (I_{stack}) and an electrical potential drop (ΔE) occurs due the internal resistance of the stack (R_{stack}), as indicated by equation 1:

$$\Delta E = OCV - E_{Stack} = I_{Stack} \cdot R_{Stack} \tag{1}$$

Here the Open Circuit Voltage (OCV) is the voltage difference at open circuit conditions. The RED stack contains N repetitive units, named cell pairs. Each one is composed of a Cation Exchange Membrane (CEM), a high concentration solution compartment, an Anion Exchange Membrane (AEM) and a low concentration solution compartment. The gross power density ($P_{d,gross}$, W/m^2) normalized by the cell-pair membrane active area (A) is given by:

$$P_{d,\,gross} = \frac{E_{Stack}^2}{R_{ext} \cdot N \cdot A} \tag{2}$$

When considering extrapolation of the operating performance of a lab-scale RED unit to a larger stack piled with much larger number of cell pairs, the effect of “blank resistance” R_{Blank} (i.e. of the ohmic and non-ohmic resistances generated in the electrode compartments) becomes negligible. Thus, power density values measured in small laboratory stacks are typically “corrected” calculating the power potentially generable if the R_{Blank} were null.

A typical procedure for such correction is based on the subtraction of R_{Blank} from the stack resistance and the re-calculation of new values of E_{Stack} and I_{Stack} (Tedesco et al. 2015). The combination of such corrections with Eq (1) and Eq (2) gives the so-called “corrected power density”, $P_{d,corr}$:

$$P_{d,corr} = \frac{OCV^2}{N \cdot A \cdot R_{ext} \cdot \left(1 + \frac{R_{stack} - R_{blank}}{R_{ext}}\right)^2} \tag{3}$$

Finally, the power density required for pumping the solutions (P_{loss}) to the RED unit can be estimated by the following expression:

$$P_{loss} = \frac{\Delta P_{High} \cdot Q_{High} + \Delta P_{Low} \cdot Q_{Low}}{N \cdot A} \tag{4}$$

where ΔP indicates the pressure drop in the high or low concentration compartment and Q the relevant flow rate. By subtracting the pumping losses to the corrected power density, the corrected net power density, $P_{d,net,corr}$ is obtained:

$$P_{d,net,corr} = P_{d,corr} - P_{loss} \tag{5}$$

3. Results and Discussion

The performance of the RED stack was analysed by following the trends of selected parameters, i.e. stack resistance (R_{Stack}), pressure drops (p) and corrected net power density ($P_{d,corr,net}$). For the long-run with wastewaters, small variations in electrical conductivity were observed between samples used in different days. In particular, these oscillations have a direct effect on OCV and electrical performance of the RED system, especially because of the dilute compartment electrical resistance, which is the main contribution to the overall R_{Stack} (especially when very low salinity solutions are used, Veerman et al. 2009). In this sense, the long-run carried out with artificial solutions of fixed salinity served as reference. The results are organized as follows: first, a general picture of key parameters is presented; then, system maintenance is discussed; finally, power output and future outlook is reported.

3.1 RED response to wastewater feeds

One main effect of a continuous feeding of the stack is a progressive increase of pressure drops as observable in Figure 2A. This occurs also for the artificial solutions case maybe because of air bubbles accumulating inside the stack. As expected, this increment was more pronounced when wastewaters were used, with a sharper increase after four days of experiment. A direct way to control pressure drops levels would be the selection of fluid velocity. The use of high fluid velocities minimizes Concentration Polarization (CP), yet increasing pressure drops and the relevant pumping power (Pawlowski et al. 2014). Since the wastewater treatment plants are batch processes, and pressure drops were found to be critic with these particular feeds, flow rates were kept low. The increase in pressure drops can be explained based on the composition of the wastewaters, which may contain sub-micro particulate that can be aggregated in the meshed spacers, leading the channels to become obstructed.

The time-evolution of R_{Stack} for both long-runs is shown in Figure 2B. As it can be seen, a practical constant R_{Stack} (7.9 ± 0.4 Ω) was found with the artificial solutions, while it progressively increases in the case of real wastes. Very likely, remaining pollutants present in wastewaters not only can plug spacer compartments, but also may react with ion exchange material blocking ion passage, and thus increasing membrane electrical resistance. Long periods of continuous contact may result in stronger interactions between membranes and pollutants, which lead to fouling. When stack resistance and pressure drops were considered too high, the fouling control based on the use of alkaline solutions was performed.

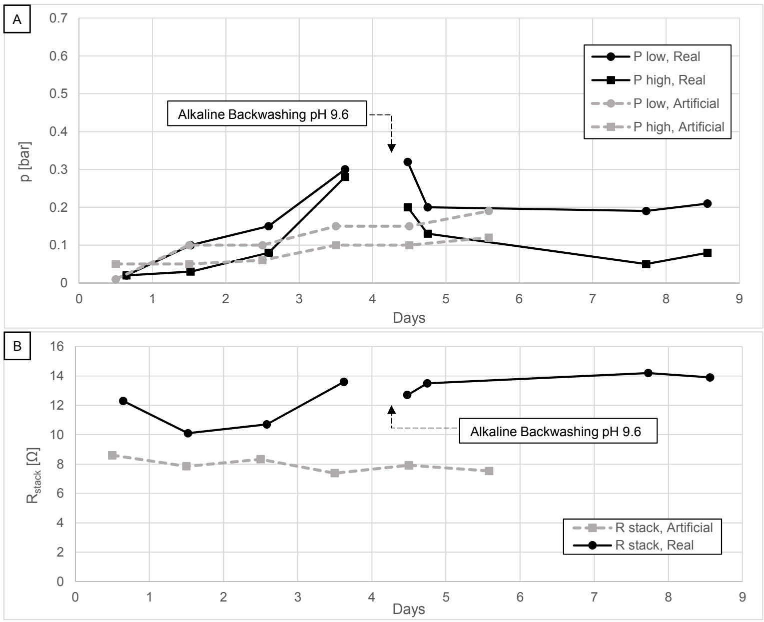

Figure 2: Time-evolution of (A) pressure drops and (B) stack resistance. Grey curves correspond to artificial solutions, black curves to real wastewaters.

3.2 Fouling control

In order to reverse fouling and lower pressure drops, a backwashing was implemented on the fifth day. For the backwashing, it was chosen an alkaline solution based on the presumable organic nature of foulants. The use of chemical agents is normally applied in the maintenance of industrial ED installations (Garcia-Vasquez et al.

2016). The backwashing did not succeed in reducing pressure and R_{Stack} to their initial values, thereby suggesting that fouling could not be fully reversible. However, a partial recovery of the initial performance was observed, as it can be inferred from pressure drops and stack resistance reduction. As shown in Figure 2, the decrease in pressure drops was the more evident. Such reduction is allegedly due to a physical unclogging of meshed spacers. R_{Stack} decrease is less evident and might be related to a partial removal of foulants from the membrane surface. Once the long-run with real wastewaters was finished, the RED stack was demounted to see the aspect of the membranes, observing that anion exchange membranes were dark-brown dyed while cation exchange membranes did not show perceptible changes at eye-sight inspection. This fact supports the idea of a predominant organic fouling, which, given the negative charge of organic compounds, selectively reacts with AEMs.

3.3 Power output

Generated power output was monitored by following the time-evolution of $P_{d,net,corr}$ according to Eq (5). It represents a realistic parameter when considering scale-up. The trend is shown in Figure 3, with positive values for the case with artificial solutions. When using real wastewaters, a positive response was obtained during the first days, with values up to 0.77 W/m^2, i.e. comparable to those obtained in the long-run with artificial solutions. After the fourth day, the increment in both pressure drops and stack resistance turned the balance and gave a negative $P_{d,net,corr}$.

The net power was improved after performing the backwashing because of pressure drops decrease, although it was not enough to give a positive balance. Interestingly, after the backwashing no significant further detriment of power output was observed up to the end of the long-run.

Notably, a discontinuity is reported for the $P_{d,net,corr}$ curve as during the backwashing no power can be produced.

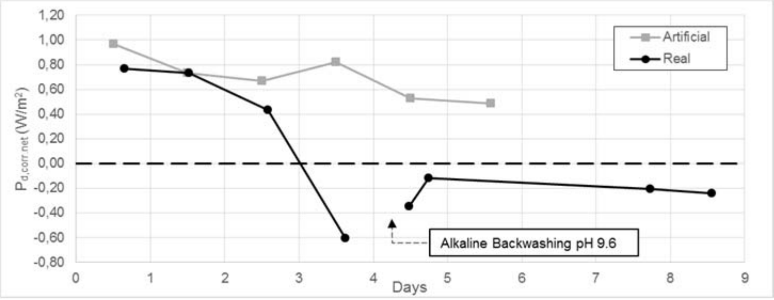

Figure 3: Power output of the two long-runs, according to Eq (5).

4. Conclusions

In this work, the performance of a lab-scale RED unit fed with treated fish wastewater and treated urban disposal water was analysed. A long-run test of eight days without interruptions was implemented. A positive power output, which accounts also for pumping losses, was obtained in the first days of experiment. System performance was dramatically affected by the use of the real wastes, very likely because of the remaining pollutants and/or sub-micro particulate contained in the wastewaters. Pressure drops was found as the main detrimental factor, due to a rapid physical clogging of feed spacers. Stack resistance was found also to increase with time, probably due to a more intimate interaction between pollutants and ion exchange membranes.

The alkaline backwashing was not enough to fully revert fouling, however, it showed promising results that should be further investigated. The main positive effect of the backwashing was a significant pressure drops decrease. Additional beneficial effects could come from a similar R_{Stack} reduction. This could be guaranteed by a more frequent backwashing application to prevent membrane fouling before it is largely produced. In this sense, also harder cleaning agents (i.e. higher pH solutions), higher temperatures and/or longer cleaning agent residence time should be tested, with the precaution of not compromising ion exchange membrane materials.

Overall, besides the negative power balance observed by the end of the long-run, the original set of experimental data represents a breaking point in the exploration of unconventional wastewater feeds for RED in a realistic context, highlighting the need of further related studies focused on membrane-fouling control. Indeed, by implementing RED in the end-process of (suitable) wastewater treatment can give value to an otherwise discard product.

Acknowledgments

This work has been carried out within the REvivED Water project (www.revivedwater.eu), financed by the European Union's Horizon 2020 research and innovation program under grant agreement No 685579.

The authors are grateful to their colleagues Prof. Michele Torregrossa, Prof. Giorgio Mannina, Prof. Gaspare Viviani and Dr. Marco Capodici, from the Department of Civil, Environmental and Materials Engineering (DICAM) of the University of Palermo, for providing the treated effluents used for the experimental campaign and for their advices, useful for optimizing the experimental procedure implemented in this work.

Reference

Bevacqua, M., Carubia, A., Cipollina, A., Tamburini, A., Tedesco, M., Micale, G., 2016, Performance of a RED system with ammonium hydrogen carbonate solutions, Desalination Water Treat., 57, 1-12, DOI: 10.1080/19443994.2015.1126410

Tamburini, A., Cipollina, A., Papapetrou, M., Piacentino, A., Micale, G. (2016), Salinity gradient engines, 219-252. Chapter 7 *in* Sustanable Energy from Salinity Gradients, Eds. Cipollina, A., Micale, G., Elsevier, Amsterdam, The Netherlands.

Corsino, S.F, Capodici, M., Morici, C., Torregrossa, M., Viviani, G., 2016, Simultaneous nitritation-denitritation for the treatment of high-strength nitrogen in hypersaline wastewater by aerobic granular sludge, Water Res., 88, 329-336, DOI: 10.1016/j.watres.2015.10.041

Garcia-Vasquez, W., Dammak, L., Larchet, C., Nikonenko, V., Grande, D., 2016, Effects of acid-base cleaning procedure on structure and properties of anion-exchange membranes used in electrodialysis, J. Membrane Sci., 507, 12-23, DOI: 10.1016/j.memsci.2016.02.006

Gurreri, L., Tamburini, A., Cipollina, A., Micale, G., Ciofalo, M., 2013, CFD Simulation of mass transfer phenomena in spacer filled channels for Reverse Electrodialysis applications, Chemical Engineering Transactions, 32, 1879-1884, DOI: 10.3303/CET1332314

Gurreri, L., Tamburini, A., Cipollina, A., Micale, G., Ciofalo, M., 2016, Flow and mass transfer in spacer-filled channels for reverse electrodialysis: a CFD parametrical study, J. Membrane Sci., 497, 300-317, DOI: 10.1016/j.memsci.2015.09.006

He, H., Chen, Y., Li, X., Cheng, Y., Yang, C., Zeng, G., 2017, Influence of salinity on microorganisms in Activated Sludge processes: A Review, International Biodeterioration & Biodegradation, 119, 520-527, DOI: 10.1016/j.ibiod.2016.10.007

Lefebvre, O., Moletta, R., 2006, Treatment of organic pollution in industrial saline wastewater: A literature Review, Water Res., 40, 3671-3682, DOI: 10.1016/j.watres.2006.08.027

Pawlowski, S., Crespo, J.G., Velizarov, S., 2014, Pressure drop in Reverse Electrodialysis: Experimental and modeling studies for stacks with variable number of cell pairs, J. Membrane Sci. 462, 96-111, DOI: 10.1016/j.memsci.2014.03.020

Scialdone, O., Guarisco, C., Grispo, S., Galia, A., 2012 Investigation of electrode material redox couple systems for reverse electrodialysis processes. Part I: iron redox couples, J. Electroanalytical Chem., 681, 66–75, DOI: 10.1016/j.jelechem.2012.05.017

Straub, A.P., Deshmukh, A., Elimelech, M., 2016, Pressure-Retarded Osmosis for power generation from Salinity Gradients: Is it viable?, Energy Environ. Sci 9(9), 31–48, DOI: 10.1039/c5ee02985f

Tedesco, M., Brauns, E., Cipollina, A., Micale, G., Modica, P., Russo, G., Helsen, J., 2015, Reverse Electrodialysis with saline waters and concentrated brines: A laboratory investigation towards technology scale-up, J. Membrane Sci., 492, 9-20, DOI: 10.1016/j.memsci.2015.05.020

Tedesco, M., Scalici, C., Vaccari, D., Cipollina, A., Tamburini, A., Micale, G., 2016, Performance of the first reverse electrodialysis pilot plant for power production from saline waters and concentrated brines, J. Membrane Sci., 500, 33-45, DOI: 10.1016/j.memsci.2015.10.057

Tedesco, M., Cipollina, A., Tamburini, A., Micale, G., 2017, Towards 1 kW power production in a Reverse Electrodialysis pilot plant with saline waters and concentrated brines, J. Membrane Sci., 522, 226-236, DOI: 10.1016/j.memsci.2016.09.015

Veerman, J., Saakes, M., Metz, S.J., Harmsen, G.J., 2009, Reverse Electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water, J. Membrane Sci., 327, 136-144, DOI: 10.1016/j.memsci.2008.11.015

Veerman, J., Saakes, M., Metz, S.J., Harmsen, G.J, 2010, Electrical power from sea and river water by Reverse Electrodialysis: A first step from the laboratory to a real power plant, Environ. Sci. and Technol., 44, 9207–9212, DOI: 10.1021/es1009345.

Wang, Q., Gao, X., Zhang, Y., He, Z., Ji, Z., Wang, X., Gao, C., 2017, Hybrid RED/ED system: Simultaneous osmotic energy recovery and desalination of high-salinity wastewater, Desalination, 405, 59-67, DOI: 10.1016/j.desal.2016.12.005