M. Vanoppen, S. Derese, A. Bakelants, A. Verliefde

Abstract

Supplying fresh, potable water to an ever increasing world population is becoming a major challenge. One possibility is to produce fresh water from seawater by Reverse Osmosis (RO), a process that is very energy intensive. To reduce the energy demand of this process, osmotic dilution (OD)/osmotic energy recovery (OER) systems can be used as pre-treatment. Both Reverse Electrodialysis (RED) and Pressure Retarded Osmosis (PRO) and their non energy-producing counterparts short-circuited RED/ Forward Osmosis (scRED/FO) and assisted RED/FO (ARED/AFO) were modelled as OD/OER devices for RO, in a thermodynamic way. Different mixing ratios of impaired versus salt water (0.5, 1 and 2) were compared at a realistic RO recovery of 50%. A realistic approach for the RED/PRO-RO hybrid process was also modelled incorporating some major losses, to gain a more realistic insight into its possibilities. The thermodynamic modelling revealed that a significant reduction of the SEC is possible with all hybrid processes. The reduction in SEC is less for the non energy-producing systems, but these have the added advantage of requiring a lower membrane area to achieve a similar extent of seawater dilution. From preliminary results of the more realistic modelling, it seems that RED-RO scores better when losses are incorporated. Further thermodynamic and realistic modelling will focus on different RO recoveries, capital cost calculations based on membrane requirements and sensitivity analysis of the different parameters implemented.

Keywords

Desalination, Reverse Osmosis, Reverse Electrodialysis, Pressure Retarded Osmosis, Osmotic Energy Recovery, Osmotic Dilution

Introduction

In a world with a booming population and increasing environmental challenges, water and energy are two commodities which should be handled with the utmost care. Since much less than 1% of all water on earth is fresh water which is directly accessible for human use (1), more and more attention is directed towards alternative sources of fresh water, like seawater, which constitutes the majority of all water on earth. The major drawback of desalinating seawater for the production of fresh water is the enormous energy-demand of the processes used, for example reverse osmosis (RO). In reverse osmosis, water with a high salinity is forced through a semi-permeable membrane at high pressure, hereby retaining solutes (mainly salt). Up to 60 bars of pressure is needed to overcome the osmotic pressure difference between sea and potable water, leading to a power consumption of 2-3 kWh per $m³$ of produced potable water (2). In addition, the RO process produces a concentrated brine which has a salt concentration higher than that of seawater, leading to potential discharge problems (3). Another alternative abundant but yet largely unused source for fresh water is municipal wastewater, which has a rather negative connotation and can possibly contain traces of organic micro-pollutants such as pharmaceuticals or pesticides (4). As a result, the reuse of municipal wastewater for drinking water purposes is legally not allowed in many countries or preference is given to other sources.

The combination of municipal wastewater and seawater however, offers interesting perspectives. Although the direct use of wastewater may not be allowed for the production of drinking water, the controlled pre-dilution of seawater with impaired water might serve as a solution for the high energy demand. There are two possibilities for this pre-dilution. On the one hand, salt ions from the seawater could be transferred to the wastewater, lowering the osmotic pressure of the seawater. On the other hand, the water molecules of the wastewater could be transferred to the seawater, again effectively lowering its osmotic pressure. These techniques are called Reverse Electrodialysis (RED) and Pressure Retarded Osmosis (PRO) respectively, and both can be operated in such a way that energy is gained while the seawater is diluted. In RED, cation- and anion-selective membranes bordering alternating flow cells containing salty water (e.g., seawater) and fresh water (e.g., impaired water), create a potential difference which can generate an electrical current at electrodes by reduction-oxidation reactions. In a similar way, the transport of water from fresh water to pressurised salt water in PRO can be used to gain energy by relaxing the brackish solution with an elevated hydraulic pressure through a turbine. Both techniques have been described in literature (5– 10).

The general working principle of a potential hybrid process including RED or PRO (or any derivative process) as osmotic dilution (OD)/osmotic energy recovery (OER) system prior to RO is shown in [Figure 1.](#page-1-0)

Figure 1: schematic representation of the hybrid OD/OER-RO process

In this paper, some of the modelling work is presented that was carried out with the goal to compare both OD/OER systems based on the energy demand of the potential hybrid process as depicted above. In recent literature, Feinberg et al. (2013) already made some comparisons between RED and PRO as OER for RO, purely from a thermodynamic point of view (11). The modelling work presented here takes this effort further and not only includes the thermodynamic approach, but also a more realistic approach, incorporating losses in RED, PRO and RO due to the configuration and non-ideality of the components and systems. Furthermore, not only RED and PRO are considered as OD/OER, but also some of their non energy-producing processes (e.g. (A)FO, ARED, depicted in [Figure 2\)](#page-2-0), which were modelled in a thermodynamic way. In scRED/FO, no external resistance is applied, and thus no energy can be produced. This will result in a higher overall energy demand for the proposed hybrid process, but also in a lower required membrane area. By applying an additional driving force (an additional pressure in AFO, an additional voltage in ARED), a more extensive dilution of the seawater can be achieved. When compared to RED/PRO and scRED/FO, assisted hybrid processes have a higher energy demand and even lower required membrane area to reach a certain extent of dilution. In this paper, the specific energy consumption (SEC, in $kWh/m³$ potable water, defined as the energy needed to produce one m³ of potable water) of all of these different systems is compared.

Figure 2: schematic representation of derivative processes of RED (left) and of PRO (right)

Materials and methods

All modelling work was realised in MATLAB (The MathWorks Inc., USA), All used variables are explained in the equations below. Analogous equations were used in the modelling of the derivative processes.

Energy calculations

All thermodynamic modelling is based on the Gibbs free energy of mixing/separation ($\Delta G_{mix}/\Delta G_{sep}$ in J) of the streams involved. This energy of mixing is based on the entropy of mixing $(\Delta S_{mix}$ in J/K). For ideal solutions this entropy is given by Equation 1 for a three component system, such as the water/sodium/chloride system used for the thermodynamic modelling. n is the total amount of moles in the solution (mol), R is the universel gas constant (J/mol K) and x_i is the mole fraction of component i (-).

$$
\Delta S_{\text{mix}} = -n R [x_1 \ln(x_1) + x_2 \ln(x_2) + x_3 \ln(x_3)] \tag{1}
$$

To calculate the energy demand of an RO system, the Gibbs free energy of separating a solution into its components is determined (Equation 2). Here, T is the temperature in Kelvin.

$$
\Delta G_{\rm sep} = T \Delta S_{\rm mix} \tag{2}
$$

Similarly, for the OD/OER processes discussed, the Gibbs free energy of mixing can be calculated (Equation 3).

$$
\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}} \tag{3}
$$

By combining the equations above, the specific energy consumption (SEC, in kWh/m³ potable water) of the hybrid process can be calculated as shown in Equation 4, with V_p the volume of potable water produced in the RO unit.

$$
SECtot, thermodynamic = \frac{\Delta G_{sep} + \Delta G_{mix}}{V_p}
$$
 (4)

In the realistic modelling of RED and PRO, Equations 5 and 6 were used to calculate the produced energy. Here, I is the current through the RED system (A), R_{ext} is the external applied resistance (Ω), ΔV is the water transported in the PRO system and ΔP is the applied hydraulic pressure.

$$
W_{\text{RED,r}} = I^2 R_{\text{ext}} \tag{5}
$$

$$
W_{PRO,r} = \Delta V \Delta P \tag{6}
$$

The total specific energy demand (SEC, in $kWh/m³$) of the proposed hybrid system can then be calculated by Equation 7.

$$
SEC_{\text{tot,real}} = \frac{W_{\text{RO}} - W_{\text{RED/PRO}}}{V_{\text{p}}}
$$
\n(7)

Definition of operational parameters and variables

To allow for a fair comparison between RED and PRO, the SEC of the hybrid processes was determined in relation to the mixing ratio (M) as defined by Equation 8.

$$
M = \frac{Q_{\text{dilute}}}{Q_{\text{sea}}}
$$
 (8)

The mixing ratio M is defined to express the ratio of impaired water used for the pre-dilution to seawater. Here, Q_{sea} is the flow of the seawater and Q_{dilute} is the flow of impaired water, both in m³/s.

To define the extent of predilution, the mixing extent (r_{mix}), Equation 9, is used as defined by Feinberg et al. (2013) (11). When sea- and wastewater are considered separately, the mixing extent is zero. When the two are completely mixed until equilibrium concentration, the mixing extent is 1. Therefore, the initial (i) and final (f) concentration (c) of the seawater are compared to the equilibrium concentration (eq), Equation 10.

$$
r_{\text{mix}} = \frac{c_{\text{sea},i} - c_{\text{sea},f}}{c_{\text{sea},i} - c_{\text{eq}}}
$$
(9)

$$
c_{eq} = \frac{M C_{dilute,i} + C_{sea,i}}{M+1}
$$
 (10)

The assumptions made and constants used in the modelling are listed in [Table 1.](#page-3-0)

Variable	Explanation	Value
$C_{dilute,i}$	Initial dilute concentration	10 mol/m^3
$C_{sea,i}$	Initial seawater concentration	500 mol/ $m3$
М	Mixing ratio	$0.5, 1$ and 2
\mathbf{Q}_{sea}	Seawater flux RED	$0.36 \text{ m}^3/\text{h}$ (12)
	Seawater flux PRO	8 m ³ /h (13)
R	Gas constant	8.31 J/K mol
R_{RO}	Recovery RO	50%
т	Temperature	298K
ΔP_{min}	Overpressure applied in RO	5 bar

Table 1: assumptions and constants used in the modelling work

Incorporated losses in realistic modelling of RED and PRO

To gain a more realistic insight into the possibilities of both systems, losses due to the non-ideality of the systems must be included. For both systems, non-ideality of the membranes and losses due to incomplete mixing and friction (pressure losses) were incorporated. For RED, non-Ohmic and Ohmic losses were considered, and for PRO, the corresponding effects of concentration polarization and mass transfer were incorporated. All effects due to fouling of the membranes are neglected, as these are difficult to predict through model-based approaches.

Results and discussion

In the modelling work, PRO, RED and their derivative processes were considered as possible OD/OER technologies. All were modelled from a thermodynamic point of view first and further on, the RED and PRO models were expanded to include some major practical losses as discussed above. In this paper, the SEC of all the hybrid systems is discussed, for three different mixing ratios (0.5, 1 and 2) and assuming a conventional RO recovery of 50%. To allow a clear comparison of the different technologies, the thermodynamic SEC of a conventional RO unit with 50% recovery without predilution is used as a baseline.

Thermodynamic modelling of the OD/OER-processes

RED-RO vs PRO-RO

In a first approach, both PRO-RO and RED-RO were modelled in a thermodynamic way, excluding all possible losses, to gain a first insight in the theoretical possibilities of both techniques. As can be seen in [Figure 3,](#page-4-0) the OD/OER processes result in a significant drop in energy consumption for desalination. At higher mixing extents and mixing ratios, the energy consumption is even lower that 0 $kWh/m³$ of produced potable water, indicating that more energy is produced by the OD/OER system than is consumed by the RO. At mixing extent zero, a conventional RO is depicted, with a thermodynamic energy cost of approximately 0.85 kWh/m³ of produced permeate.

Figure 3: specific desalination energy for the thermodynamic reversible approach of the RED-RO and PRO-RO system for different mixing ratios (0.5, 1 and 2)

From [Figure 3](#page-4-0) it is clear that both RED-RO and PRO-RO attain a low SEC, with the advantage of RED-RO that the reduction in SEC occurs faster than in PRO-RO. This results in a lower SEC for the RED-RO system compared to the PRO-RO system for the same mixing extent. It is also clear that higher mixing ratios result in lower energy demands. This is due to the fact that a more extensive dilution can be achieved when more wastewater is used in respect to the amount of seawater, resulting in a lower

energy demand in the RO system due to the lower concentration in the feed solution. In practice, however, the wastewater stream will be limiting for the system, as seawater is an 'infinite' source. High mixing ratios are thus less likely to be implemented in practice, but even at a mixing ratio of 1 or 0.5 the reduction in energy demand is significant. These lower mixing ratios also result in higher overall recoveries (defined as the amount of potable water produced in respect with the amount of wastewater used). For example, if complete mixing is assumed, a mixing ratio of 2 results in an overall recovery of 0.5, while a mixing ratio of 0.5 results in an overall recovery of 2.

scRED-RO vs FO-RO

When no external resistance is applied, no energy can be gained from the system. However, as dilution occurs more quickly (due to the absence of an external resistance) compared to the RED/PRO-RO system, less membrane area is required to achieve a similar mixing extent, which results in lower capital costs compared to their energy producing couterparts. For RED, this system is called short circuited RED (scRED) and for PRO this system is called forward osmosis (FO). The advantage of these systems with respect to simple physical mixing of both streams, is that a selective barrier between seawater and wastewater is realised, preventing micropollutants and pathogens to be transported from the wastewater to the feed stream of the RO system.

Figure 4: specific desalination energy for the thermodynamic reversible approach of the scRED-RO and FO-RO system for different mixing ratios (0.5, 1 and 2)

Indeed, when comparing this system with the RED-RO and PRO-RO system [\(Figure 4\)](#page-5-0), the energy demand is higher than for the RED/PRO-RO system because no energy is harvested. The minimal SEC in the scRED-RO and FO-RO systems for is about 0.28 kWh/m³ potable water produced. Here, the SEC for both systems is comparable.

ARED-RO vs AFO-RO

To achieve even faster mixing, an additional driving force can be applied to the system. For RED, an extra voltage can be applied, resulting in a higher ion flux. For PRO, an additional pressure is applied to the dilute stream. These systems are called assisted RED/FO (ARED/AFO) respectively. This additional driving force is limited by the physical limitations of the systems and its energy demand should not cause the SEC to exceed that of a conventional RO. For the thermodynamic modelling, an additional driving force equivalent to 5 bar was applied $(\pm 1/5)$ of the osmotic pressure difference between the feed streams).

Figure 5: specific desalination energy for the thermodynamic reversible approach of the ARED-RO and AFO-RO system for different mixing ratios (0.5, 1 and 2)

Of course, the energy demand here is higher than in the previous cases because energy is consumed rather that produced. The possible advantage of this system is that an even smaller amount of membrane surface is needed to achieve a certain mixing extent, resulting in even lower capital costs. It is clear fro[m Figure 5](#page-6-0) that again SEC is similar for both systems.

Realistic modelling of RED-RO and PRO-RO

In the realistic approach, losses due to non-ideal behaviour (as discussed above) were incorporated to get a more realistic insight into the possibilities of the technologies compared to the thermodynamic approach.

Figure 6: specific desalination energy for the realistic approach of the PRO-RO and RED-RO system for different mixing ratios (0.5, 1 and 2). Extra lines were drawn on the PRO-RO figure to guide the eye from mixing extent 0 to 0.2

As can be seen in [Figure 6,](#page-6-1) the energy consumption in a more realistic situation is much higher than in the thermodynamic approach. This is mainly due to a lower energy production in the OD/OER system because of the losses incorporated. It is for example no longer possible to achieve an energy neutral/producing system with the assumptions made, except for the RED-RO system at mixing ratio 2. Also, mixing extents of 1 are no longer attainable due to concentration polarisation at the membranes. Although not always clear in the figures, the maximal mixing extent reached in RED-RO for example is now at around 0.96. When comparing PRO and RED, it is clear that using RED as OD/OER results in lower energy demands. At higher mixing extents, the SEC of the PRO-RO system even increases again, due to the additional energy needed to assure a sufficient hydraulic pressure of the feed streams going to the PRO modules. Since a lot of extra modules are needed to achieve high mixing extents, this energy is rather high and causes the SEC to rise again. These are, however, preliminary results from the modelling work, although the general trends are already clear. Further work is necessary to ensure a fair comparison between both realistic models, especially considering the included losses.

Conclusions

A hybrid OD/OER-RO process was modelled in a thermodynamic and more realistic way, comparing RED and PRO as OD/OER. Also different derivative processes were modelled thermodynamically. The specific energy demand for desalination was calculated and compared. Although all hybrid processes resulted in a significant reduction of the overall SEC, the energy producing OD/OERs clearly offer an energetic advantage. Although the other OD/OERs offer a lower reduction in specific energy, the faster mixing will result in a lower required membrane area for a similar mixing extent. This in turn will result in lower capital costs. The RED-RO and PRO-RO processes were also modelled incorporating some major losses. The results of this modelling indicate that it is realistic to achieve a significant reduction of the SEC in practice, especially when using RED as OD/OER. This process will however result in the highest membrane area and thus capital costs when compared to the non energy-producing couterparts.

Further modelling work will focus on the expansion of the realistic modelling and on different recoveries for the RO system, since higher recoveries can be achieved when the feed concentration is lowered. Also capital costs (modelled as the amount of membrane area needed) will be considered, since a trade-off between energy demand and capital costs will exist. Furthermore, a sensitivity analysis will be performed to identify the most critical process parameters.

References

- 1. S. L. Postel, C. Gretchen and P. R. Ehrlich. Human appropriation of renewable fresh water. Science 271 (1996) 785-788.
- 2. L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot, P. Moulin. Reverse osmosis desalination: water sources, technology, and today's challenges. Water research 43 (2009) 2317-2348.
- 3. M. Latorre. Environmental impact of brine disposal on Posidonia seagrasses. Desalination 182 (2005) 517-524.
- 4. S. A. Snyder, P. Westerhoff, Y. Yoon and D. L. Sedlak. Pharmaceuticals, personal care products and endocrine disruptors in water: implications for the water industry. Environmental Engineering Science 20 (2003) 449-469.
- 5. J. W. Post. Blue Energy: electricity production from salinity gradients by reverse electrodialysis. (2009) p. 224
- 6. J. Veerman, M. Saakes, S. J. Metz, G. J. Harmsen. Reverse electrodialysis: performance of a stack with 50 cells on the mixing of sea and river water. Journal of Membrane Science 327 (2009) 136-144.
- 7. D. A. Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer. Fouling in reverse electrodialysis under natural conditions. Water research (2012) 1-10.
- 8. T. Cath, A. Childress, M. Elimelech. Forward osmosis: principles, applications, and recent developments. Journal of Membrane Science 281 (2006) 70-87.
- 9. B. D. Coday, D. M. Heil, P. Xu, T. Y. Cath. Effects of transmembrane hydraulic pressure on performance of forward osmosis membranes. Environmental Science and Technology 47 (2013) 2386-2393.
- 10. J. W. Post, J. Veerman, H. V. M. Hamelers, G. J. W. Metz, K. Nijmeijer, et al. Salinity gradient power: evaluation of pressure-retarded osmosis and reverse electrodialysis. Journal of Membrane Science 288 (2007) 218-230.
- 11. B. J. Feinberg, G. Z. Ramon, E. M. V. Hoek. Thermodynamic analysis of osmotic energy recovery at a reverse osmosis desalination plant. Environmental Science and Technology 47 (2013) 2982-2989.
- 12. J. W. Post, H. V. M. Hamelers and C. J. N. Buisman. Energy recovery from controlled mixing of salt and fresh water with a reverse electrodialysis system. Environmental Science and Technology 42 (2008) 5785-5790.
- 13. DOW Filmtec RO specifications