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Pressure Retarded Osmosis: a Membrane Process for Environmental Sustainability

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Salinity Gradient Power (SGP) based on the controlled mixing between two solutions at different salinities is a viable alternative to produce power from renewable sources. Pressure Retarded Osmosis (PRO) is one of the most promising technologies proposed so far for the exploitation of such energy source. Apart from the typical source of salinity gradients, namely river water and seawater, more and more interest has been raised recently towards the use of non-conventional saline solutions. In this work, water originating from a sewage treatment plant is used as the dilute solution (feed solution), while brine exiting from a desalination plant is used as the concentrate (draw solution), thus being efficiently diluted before the discharge into the sea. Aim of this work is to investigate the performance of PRO modules arranged in series via a purposely developed process model based on transport and balance equations. Detrimental effects due non-ideal phenomena as salt diffusion through the membrane, concentration polarization were taken into account. Pumping power was also accounted for. Geometrical data were derived from existing spiral wound membrane modules typically employed in Reverse Osmosis. The effect of solution velocity, number of PRO units and operative hydraulic pressure (applied on the draw solution channel) on the process performance was investigated.
Results show that the dependence of the net power on velocity and applied pressure is not monotonic thereby exhibiting a maximum: under optimized conditions, a maximum net power of ~1.5kW corresponding to a net power density of ~6.6 W/m^2 can be obtained with six identical PRO modules. Along with this power production, a simultaneous brine dilution of more than 22% was found at the same conditions. However, despite the potential shown by the model, the main limitation for a real process might be the real performances of the osmotic membranes in terms of mechanical robustness and resistance against fouling phenomena. In this regard, valuable contributions may come from nanotechnologies ad-hoc developed.

1. Introduction

From the last century, nanomaterials have had an important impact on technological and industrial development. Significant innovations have been brought in the environmental applications and in particular in the water treatment processes. Membranes with increasing efficiency have been proposed for both water desalination and energy production by salinity gradient (SGP). The latter is a sustainable source for energy exploiting the concentration gradient between two solutions (Logan and Elimelech, 2012). This renewable energy can be converted into available electric current by a suitable technology based on membrane processes. Reverse Electrodialysis (RED) makes use of ionic exchange membranes along with red-ox reactions at electrodic compartments to produce electric current (Tamburini et al., 2015). In Pressure Retarded Osmosis, water from a low salinity feed solution permeates through an osmotic membrane into a pressurized high salinity draw solution, thus naturally increasing the pressure energy of the pressurized stream (convertible into electric current within a hydro turbine) (Achilli and Childress, 2010).
Both technologies are usually operated with seawater and river water. Such common choice may have some limitations: for example, (i) river water may be scarcely available and (ii) the available driving force may result into a very low amount of produced energy when all energy consumption contributions (e.g. pumping, pre-treatment) are taken into account. Therefore, in recent years interest is moving also towards non-conventional

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salinity gradients (Helfer et al., 2014). Just as an example, higher performances have been reached by RED units fed by brackish water and almost saturated brine coming from saltworks (Tedesco et al. 2015, 2016). In this regard, the brine coming from a desalination plant could be a valuable alternative as concentrated solution. Moreover, water originating from a waste-water treatment plant could be used as the dilute solution, a valuable alternative to river water when this is scarcely available. Brine and treated-water are waste streams whose direct discharge into the sea may result into shocks for the marine ecosystems. Their employment within a PRO unit would guarantee the simultaneous reduction of the environmental impact of these two "waste streams" as well as the production of green energy. Notably, PRO might be more suitable than RED to deal with a treated water stream because of its possible low conductivity.
Therefore, the aim of the present work is proposing a model able to assess the performance of one or more spiral-wound PRO modules (put in series) in terms of both power production and brine dilution.

2. Model

The model is based on transport and mass balance equations. The transport equations describe the osmotic phenomena through the membrane and fluid dynamics in the channels. The balance equations describe the variation of the fluid concentrations along the channels.

2.1 Transport Equations

The water flux (J_w) through the asymmetric membrane is function of the osmotic pressure difference between the two channels ($\Delta\pi$), the hydraulic pressure applied (Δp_h), the fluid dynamics in the draw solution channel (through the mass transfer coefficient *k*), the salt diffusivity in the porous support of the membrane (*D*) and three membrane parameters that characterize the membrane. The membrane parameters are: water permeability (A), salt permeability (B) and the structure parameter of the porous support layer (S). The subscripts *D* and *F* identify the concentrated Draw (i.e. brine) and the diluted Feed (i.e. treated sewage) solutions, respectively; *b* and *m* identify the solution bulk and the solution-membrane interface, respectively.

$$J_w = A\left\{\frac{\pi_{D,b}\exp\left(-\frac{J_w}{k}\right)-\pi_{F,b}\exp\left(\frac{J_w S}{D}\right)}{1+\frac{B}{J_w}\left[\exp\left(\frac{J_w S}{D}\right)-\exp\left(-\frac{J_w}{k}\right)\right]}-\Delta p_h\right\} \quad (1)$$

Undesired phenomena which reduce the theoretical driving force of the process concern external and internal concentration polarization and salt flux through the membrane. The internal and external polarization concentration (ICP and ECP_D) can be assessed respectively as:

$$C_{D,m} = C_{D,b}\exp\left(-\frac{J_w}{k}\right)-\frac{B}{J_w}(C_{D,m}-C_{F,m})\left[1-\exp\left(-\frac{J_w}{k}\right)\right] \quad (2)$$

$$C_{F,m} = C_{F,b}\exp\left(\frac{J_w S}{D}\right)+\frac{B}{J_w}(C_{D,m}-C_{F,m})\left[\exp\left(\frac{J_w S}{D}\right)-1\right] \quad (3)$$

where *C* is salt concentration. Notably, the ECP_F in the diluted channel (i.e. the treated sewage one) is not accounted for as it is expected to be negligible. The salt flux (J_s) is determined by the concentration difference between the two solutions at the membrane-solution interfaces ($C_{D,m}$-$C_{F,m}$):

$$J_s = B(C_{D,m}-C_{F,m}) \quad (4)$$

The pressure of the solutions decrease along the channels due to the pressure drops:

$$p_{out} = p_{in}-(\Delta p_{m,D}+\Delta p_{m,F}) \quad (5)$$

$$\frac{\Delta p_m}{L} = \frac{1}{2d_h}\lambda\rho v^2 \quad (6)$$

The pressure drops per unit length of the module ($\Delta p_m/L$) depend on the velocity square (v), on the hydraulic diameter (d_h) and on the attrition coefficient (λ) obtainable from dimensionless correlations. Given the preliminary nature of the present work, v, d_h and resulting λ and Δp_m were considered equal for both solutions.

2.2 Mass Balance equations

The flow rates and the concentrations of the solutions along the channels change due to water and salt flux. These variations can be obtained by solving easy mass balances for the two channels:

Global and salt mass balances in the brine channel:

$$Q_{D,out} = Q_{D,in} + J_w A_m S_f \quad (7)$$

$$Q_{D,out} C_{D,out} = Q_{D,in} C_{D,in} - J_s A_m S_f \quad (8)$$

Global and salt mass balances in the treated-wastewater channel:

$$Q_{F,out} = Q_{F,in} - J_w A_m S_f \quad (9)$$

$$Q_{F,out} C_{F,out} = Q_{F,in} C_{F,in} + J_s A_m S_f \quad (10)$$

in which Q identifies the flow rate, A_m the membrane area and S_f the spacer shadow factor.

2.3 Performance parameters

The Gross Power (P) and the Gross Power Density (PD) are:

$$P = J_w A_m S_f \Delta p_h \quad (11)$$

$$PD = J_w \Delta p_h \quad (12)$$

The Net Power (NP) and the Net Power Density (NPD) can be obtained by simply subtracting the pumping power for both channels to P and PD, respectively:

$$NP = J_w A_m S_f \Delta p_h - Q_F \Delta p_{m,F} - Q_D \Delta p_{m,D} \quad (13)$$

$$NPD = NP / A_m \quad (14)$$

3. Model input and validation

The proposed model requires a number of input data. (i) Firstly, module geometrical features are needed: the total length of the module was 1m and model equations were discretized along the main flow direction (Δx=0.01m). The geometry of the module modelled derives from the analysis of real spiral wound (SW) modules used for Reverse Osmosis. In particular, membrane area was 38m^2 and a *Naltex 1228* overlapped spacer was employed for both channels. Its features are: thickness of 0.75mm, mesh length of 3mm, porosity equal to 0.9, hydraulic diameter d_h=0.96 and shadow factor equal to 0.76 (Schock and Miquel,1987).
(ii) Other inputs concern solution physical properties, in particular the initial concentration of the two solutions: $C_{D,in}$=1.120M=65g/l is typical of a brine exiting from a desalination plant in Sicily (Italy), $C_{f,in}$=0.017M=1g/l is typical of a water coming from a sewage treatment plant in the same region.
(iii) Once the spacer features have been chosen, the resulting spacer-filled channel mass transfer coefficient *k* and the friction factor λ can be assessed via correlations available in the literature. According to Schock and Miquel (1987), $\lambda = 6.23 Re^{-0.3}$ and $k = \frac{Sh\, D}{d_h} = (0.065 Re^{-0.875} Sc^{0.25}) \frac{D}{d_h}$.
(iv) Other inputs concern membrane features: as it can be easily inferred from equation 1, parameters A, B and S are needed. A real thin film composite (TFC) membrane provided by *HTI technologies* was employed. Its parameters were assessed by a simplified procedure based on experiments carried out on a lab-scale planar geometry module. The procedure along with the experiments performed is minutely described in another work by our group (Cipollina et al., 2016), details are not reported for the sake of brevity. The resulting membrane parameters used here as input for the model are: A=5.55E-7m/s bar, B= 2.70E-7 m/s, S= 463 μm.
The model has been validated via data collected on a different geometry consisting of a lab-scale cylindrical module described in Cipollina et al. (2016) and reported in Figure 1a: as it can be seen in Figure 1b, the measured water fluxes are well predicted by the model.

Results and Discussion

The proposed model allows the estimate of the membrane module (PRO) performance in terms of energy production and brine dilution. As it can be seen in Figure 2, when the imposed Δp_h is increased from zero, the water flux decreases as expected on the basis of eq.1. Conversely, the produced power which is proportional

to the product between the water flux and the applied Δp_h (eq.11) shows an increasing-decreasing trend exhibiting at maximum at $\Delta p_h=\Delta\pi/2$ (under ideal conditions). Under these conditions, the maximum power density produced is about 9.3 W/m^2 (corresponding to NPD_{max}≈7.9 W/m^2), while brine dilution is still poor: in particular its concentration passes from 1.12 M to 1.06M (5% of reduction), while treated wastewater concentration passes from 0.017 M to 0.025 M (~50% of increment).
The two exiting solutions still have a quite different concentration, which can be exploited for a further energy production. Thus, some identical PRO modules (each 1m length) can be put in series in order to increase the total (i.e. cumulative) power production along with the brine dilution. With six modules, a cumulative P of about 1.7 KW is obtained (Figure 3a), while the cumulative NP increases more slowly due to the additional pressure drops. Clearly, PD and NPD decrease as the number of modules increases (Figure 3b) because of the driving force reduction due to the gradual mixing of the two solutions.

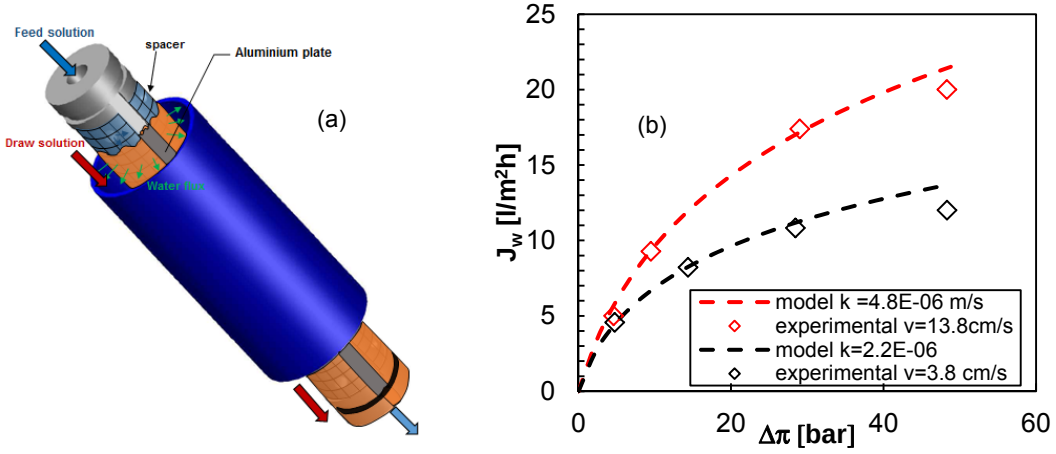

Figure 1: (a) Sketch of the lab-scale cylindrical geometry module by Cipollina et al. (2016) (b) Model validation via experimental data: water flux vs osmotic pressure difference.

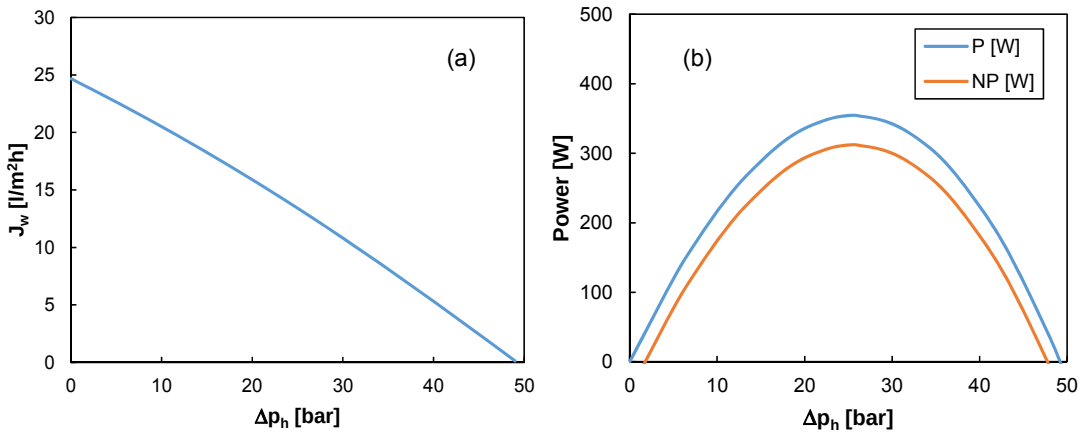

Figure 2: (a) Water flux through the membrane and (b) relevant gross and net power produced as a function of the applied hydraulic pressure for a single PRO module 1m length and v=10cm/s.

More interestingly, when six modules are put in series, the brine concentration passes from 1.12M to 0.88M (21% of reduction), thus suggesting how the PRO process can efficiently convert environmental issues into valuable power. This occurrence can be easily inferred from Figure 4a, where both the bulk and the interface concentration profiles of the two solutions along the modules are shown: the difference between the bulk and the corresponding interface (i.e. membrane) value represents the concentration polarization responsible for the driving force reduction. As it can be seen, the higher the driving force and the water flux, the higher the polarization observed, thus, high-performance membranes based on advanced nanotechnology should be developed in the future together with methods for polarization reduction.
All the results described so far are relevant to a specific velocity of the two solutions (i.e. 10 cm/s): this parameter has a crucial impact on the PRO modules performances in terms of both brine dilution and power

production. In particular, different effects simultaneously occur: the first one is observable in Figure 4b, which shows the brine dilution as a function of the fluid velocity and the applied hydraulic pressure. Clearly, the higher the flow rate, the lower the brine dilution due to the lower residence time.
The effect of velocity on gross and net power is shown in Figure 5a. The gross power increases with the velocity thanks to the concentration polarization reduction: the ECP_D is reduced by the increase of velocity components perpendicular to the membrane (Gurreri et al., 2013; Gurreri et al., 2016) while ICP, arising within the membrane porous layer, is substantially independent of fluid dynamics in the feed spacer-filled channel. At larger velocities than those reported in Figure 5a, gross power is expected to reach a plateau corresponding to the case where bulk and membrane draw solution concentration coincide. On the other hand, velocity increase leads pressure drop to increase as well. These two competitive effects results into a non-monotonic trend with a maximum which in our case occurs at v=10cm/s (the value adopted for all the previous figures).

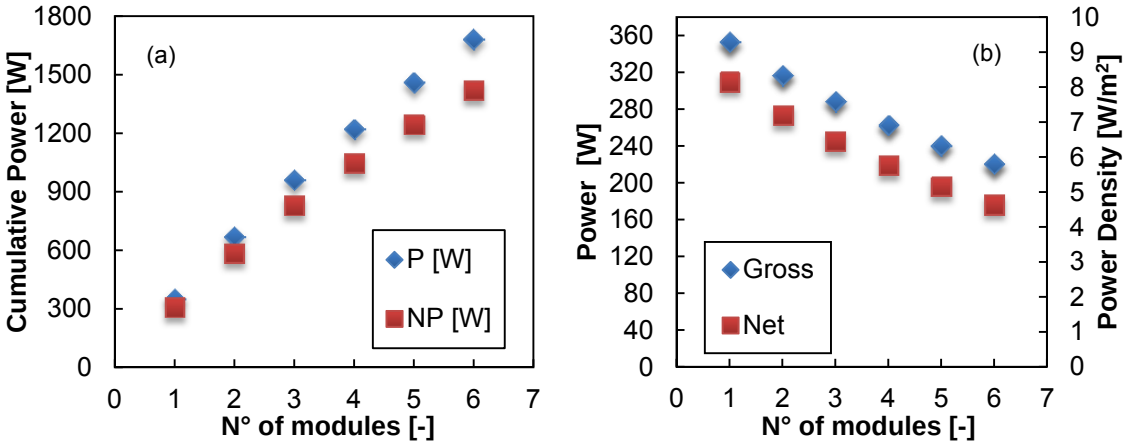

Figure 3: Power produced vs the number of equal 1m length PRO modules in series and v=10cm/s. (a) Cumulative power and net power; (b) gross power density (PD) and net power density (NPD).

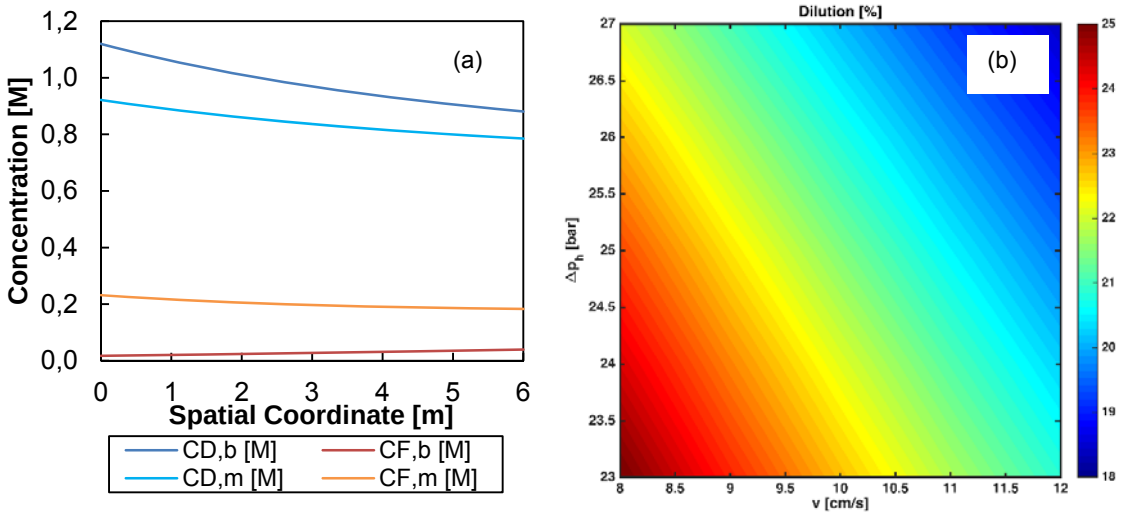

Figure 4: (a) bulk and membrane-solution interface concentrations for both solutions along the six PRO modules (v=10cm/s); (b) brine dilution percentage as a function of Δp_h and v.

4. Conclusions

A model simulating the performance of a number of PRO modules, each one 1m long and provided with $38m^2$ of membrane, was devised and validated with experimental data. The effect of solution velocity, number of PRO units and operative hydraulic pressure on the process performance was investigated. Results show that a maximum net power of about 1.5 kW (≈6.6 W/m^2) can be obtained at a velocity of both solutions equal to 10 cm/s and, as expected, at a pressure equal to half of the osmotic pressure difference. These conditions also

guarantee a brine dilution of more than 22%. Such findings suggest that PRO could be used as a valuable technology to produce green and sustainable energy from waste streams. However, additional work is needed to experimentally assess, at the same conditions, the membrane performance in terms of mechanical robustness and fouling resistance, which might be the main actual limitation for the process.

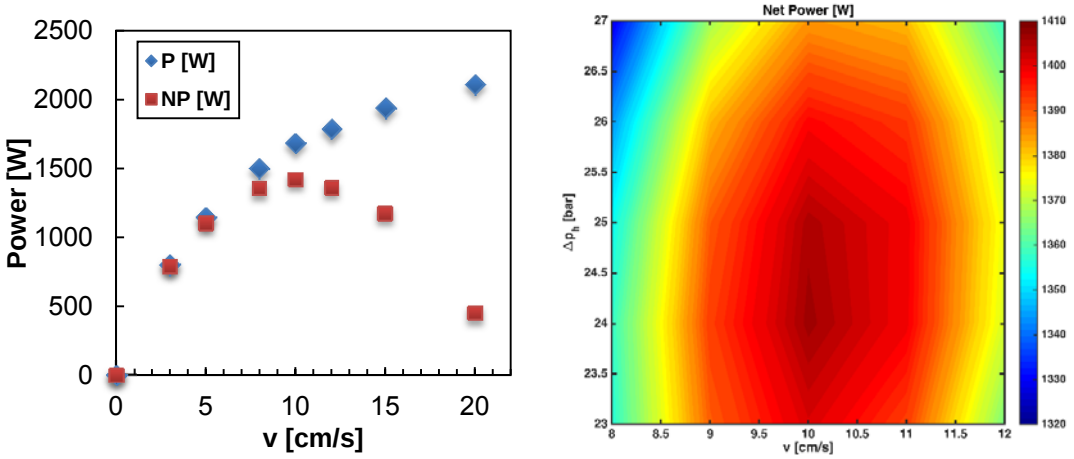

Figure 5. Left: gross and net power produced by the six PRO modules vs solution velocity. Right: net power as a function of Δp_h and v.

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