Improvement of the energy generation by pressure retarded osmosis

Endre Nagy[*], József Dudás, Imre Hegedüs

University of Pannonia, Research Institute of Chemical and Process Engineering, Egyetem u. 10, H-8200, Veszprém, Hungary

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ABSTRACT

Applying the solute fluxes given for every single transport layer, namely external boundary layers, selective-, and the support layer, and even the cake layer, new expressions were developed to define the overall mass transfer coefficient and the interface solute concentrations. These equations make possible much deeper investigationof the mass transport process and process efficiency in pressure retarded osmosis system. It was stated that the effect of the feed side boundary layer on the energy generation must not be neglected without checking its effect. The extractable energy is dominated mainly by the membrane selectivity, structural parameter and also by the solute concentrations. Essential improvement of the membrane selectivity and/or decrease of the value of the structural parameter is needed to get more efficient pressure retarded osmosis process for energy extraction. Furthermore the increase of the draw solution concentration and/or decrease of the feed concentration should be regarded as an alternative process instead of seawater-river water pair.

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1. Introduction

Osmotically driven membrane processes as forward osmosis (FO) [1] and the pressure retarded osmosis processes (PRO) [2], or reverse electrodialysis [3] play very important roles in several industrial processes as producing fresh water from sea water [4], capturing clean energy [5], water and waste water treatment [6], foodstuff processing [7], etc. These promising membrane processes are intensively researched throughout the word proving by the rapidly increasing number research papers for both the FO [8] and PRO [9] processes. These osmotic processes operate on the principle of osmotic transport of water across a semi-permeable membrane from a low salinity feed solution (e.g. fresh water, river water) into a high salinity brine/draw solution (e.g. see water, brine water) [10]. The draw solution side is pressurized to obtain power by depressurizing the portion of water permeated through the membrane from the low salinity solution in case of PRO process. The performance of these processes strongly depends on the salt- and water transport rates. Recently Straub et al. [11] summarized the limited energetic efficiency of the PRO systems for seawater and river water pair. Accordingly, the volumetric energy density is relatively low ranging from 0.26 kWh/m^2 for seawater (0.6 M NaCl) and river water (0.015 M) to around 2.5 kWh/m^2 for hypersaline

(5.2 M, Dead Sea). They concluded that significant improvement of the membrane selectivity and operating conditions is needed for its economic application. Thus, the exact description of the mass transport through the osmotically driven membranes is crucially important for prediction and improvement of the process performance. Therefore the recent paper is focusing on the solute-, J_s, and water transport, J_w, and how they can depend on the membrane selectivity and the saline concentration of the draw and feed solutions. New expressions were developed for expression of the individual interface salt concentrations which make possible much deeper investigation of the effect of the operating parameters and membrane properties than the concentration differences of two interfaces defined in the literature until now.

Considering the literature data, recently Wang et al. [12] have summarized the most important transport models through osmotic membranes, among them, the solution-diffusion-convection models, as well. The first paper on pressure retarded osmosis was published by Lee et al. [13]. Their model expresses the solute and water transfer rates, solute permeability coefficient, B, and the energy generated taking into account the effect of the two membrane layers of the asymmetric membrane, only. Loeb et al. [14] applying the Lee's model, have developed equation for determination of the resistance to solute diffusion in the membrane support layer. Later it has been proved that not only the internal (ICP) but the external concentration polarizations (ECP) can have important role in the performance of the membrane processes [15]. Accordingly, the newly developed models by McCutcheon and

* Corresponding author.
  E-mail addresses: nagy@mukki.richem.hu, nagye@mik.vein.hu (E. Nagy).

Elimelech [16] and by Yip et al. [17] involve already the effect of the external mass transfer resistance at the draw solution's side. The former paper applies the $C_b = C_m \exp(J_w/k)$ approaching expression for the highly concentrated draw solution which is true only when, the salt permeability coefficient is equal to zero, as it also will be shown in this paper. These models are widely used in the literature [18,19]. Recent investigations have shown that the concentration polarization at the low-salinity feed solution can also affect the mass transfer rate [20]. Every four mass transfer resistance is taken into account in Nagy's model [20] and in the recently published one by Bui et al. [21] as well as in paper of Maisonneuve [22]. These models offer equations for prediction of the salt- and water transfer rates and the osmotic pressure difference. There is an essential difference in the mathematical methodology used by Nagy [20] and the other authors [23]. Nagy expressed the salt transfer rate for every single mass transfer layers, in his model, using the solution-diffusion-convection model, and thus, the resistance-in-series model can serve the overall salt- and water transfer rates, the concentration distribution in every layer, and the salt concentrations of the internal interfaces. This solution methodology can serve the individual internal concentrations, concentration distribution of every single transport layer, determination of the intrinsic membrane properties as well as deeper knowledge on the effect of membrane selectivity and operating conditions on the system efficiency. The need of significant improvement of the energy generation efficiency of a PRO system [11] assumes the production of more effective membrane and also the change of the saline concentration using rather brine draw solution instead of seawater and lower concentration feed solution as rainy water instead of river water.

Fouling can give rise to flux decline and shorten membrane lifetime [11]. The sources of water used in PRO will inevitably contain inorganic, organic, and microbial constituents that deposit on and adsorb to the membrane surface [24,25]. Fouling layer builds up in the support layer of the membrane, hydraulic resistance and concentration polarization increase, leading to diminished performance [26]. In PRO, the water flux decline can be greater than 30%. The draw side of the membrane has been shown to experience negligible fouling in studies using organic and microbial foulants. It can be attributed to the permeating water transporting foulants away from the membrane surface. Recently Tow et al. [27] measured and modeled the fouling based this latter on the transport expressions developed by Nagy [20].

The exergetic analysis of a PRO unit is important to predict the extractable specific energy. The Gibbs free energy of mixing represents the theoretical maximum energy, although today it is known as exergy, that is available for useful work by a reversible thermodynamic process. Hence, actual work output will always be less than the theoretical energy available because practical work extraction processes are irreversible in nature, thus, generates entropy [28]. Change in the Gibbs free energy of a system is equivalent to the work done by the system in an ideal reversible thermodynamic process. The water flux measurements and power density estimates from coupon-scale experiments are much higher than those that would occur in full-scale system. Important question is how coupon-scale measurements relate to productivity on a large scale [11]. Basically the so-called zero- and one-dimensional models are used for exergy analysis [29]. For zero-dimensional model, the osmotic pressure and permeate do not vary within the PRO device which is valid mostly only by labor experiments. One-dimensional model is used for a finite-size membrane module where the concentration and volume change causes change in the osmotic pressure and the permeate flux [30]. The large scale experiments can give significantly lower performance than that of the coupon-scale experiments [31]. The recent exergy studies,

however, do not still involve the effect of the reverse salt flux and the effect of the internal and external polarization layers.

The present study focuses on the mass transport efficiency during zero-dimensional model with the aim to increase the process performance of a PRO system. The aim of this paper is to discuss how the internal solute concentrations and the overall mass transfer coefficient change by the membrane properties, how the membrane selectivity and the draw and feed liquid concentration can improve the efficiency of the PRO system, the water flux and energy density, taking into account the effect of the four mass transport layers and thus that of both the external draw and feed boundary layers. It will be shown how strongly can negatively affect the salt permeability and the feed concentration the system efficiency indicating the right way for improving the process efficiency. It will also briefly discuss the effect of the fouling layer as well as the extractable energy using seawater-river water pair for energy production. At the end the model equations are validated by measured data.

2. Theory

The solution-diffusion-convection mass transport process, the overall mass transfer rate, mass transfer coefficient, taking into account all mass transfer resistances, will be analyzed as well as new equations are applied for prediction of the interface concentrations, C_m, C_{sk}, C_{sp} for PRO mode in this section.

2.1. Salt transport with simultaneous diffusive and convective flows in a single transport layer

The mass transfer rate for solution-diffusion-convection transport model is widely used for reverse osmosis, ultrafiltration, nanofiltration, gas separation membrane processes as well as for pressure retarded osmosis and forward osmosis for description of the concentration polarization [32]. The concentration distribution, illustrated in Fig. 1A, was firstly given by Nagy [20] for a single transport layer for these systems. Accordingly, the concentration distribution for a mass transport layer was obtained, as [20]:

$$C = \frac{(C_m - C_d)e^{(J_w/k)}}{1 - e^{(J_w/k)}}e^{-(J_w/k)y} + \frac{C_d - C_m e^{(J_w/k)}}{1 - e^{(J_w/k)}} \quad (1)$$

The value of k denotes the diffusive mass transfer coefficient, $k = D/\delta$, in the transport layer investigated, δ is its thickness, J_w is the water flux. Note, Eq. (1) differs completely from that given for ultrafiltration, nanofiltration or reverse osmosis [26] due to the presence of a diffusive flux at the outlet side of the transport layer, i.e. at $y = \delta$. This diffusive outlet flux does not exist in the case of ultrafiltration, nanofiltration, reverse osmosis or pervaporation. The overall partial mass salt transfer rate, namely the difference (obviously when the diffusive flux and the convective one have opposite directions) between the diffusive and convective fluxes, given it e.g. for the draw side boundary layer, is as [20]:

$$J_s = \beta^* \left(C_d - C_m e^{J_w/k_d} \right) \equiv \beta \left(C_d e^{-J_w/k_d} - C_m \right) \quad (2)$$

where

$$\beta^* = \frac{J_w}{1 - e^{J_w/k_d}}; \quad \beta = \frac{J_w e^{J_w/k}}{1 - e^{J_w/k}} \equiv \frac{J_w}{e^{-J_w/k} - 1}$$

As can be seen, in case of simultaneous diffusive and convective fluxes, the driving force depends also from the J_w/k value (traditionally $J_w/k = Pe$ (*Pe*: Peclet number) is used in chemical engineering processes but its usage is not the case in PRO or FO