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CHARACTERIZATION OF NANOFILTRATION MEMBRANES USED FOR THE SEPARATION OF AQUEOUS DYE–SALT SOLUTIONS

The process of desalination of aqueous dye–salt solutions by polymeric nanofiltration membranes using commercially available modules was studied. The influence of dye and salt concentration on the salt rejection and flux as well as comparison of individual NF membranes used for desalting purposes are presented. An extended Spiegler–Kedem model including the Donnan exclusion mechanism and the term of concentration dependence of salt permeability was used for predicting salt rejection.

The experimental results reveal a negative salt rejection during desalination and the influence of this phenomenon on permeate flux. It is also shown that the model can sufficiently predict salt rejection even at high concentration typical of desalting process.

Keywords: *nanofiltration, dye–salt solutions, desalination, modelling*

SYMBOLS

J_V – flux, m·s^{-1},
L_S – water permeability, m·s^{-1}·Pa^{-1},
P_S – salt permeability, m·s^{-1},
R_S – salt rejection,
r_p – effective pore radius, m,
X_d – effective membrane charge density, mol·m^{-3},
$\Delta x/A_k$ – effective membrane thickness/porosity ratio, m,
σ – reflection coefficient,
α – coefficient for salt permeability, m·s^{-1},
β – coefficient for concentration dependence of salt permeability.

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1. INTRODUCTION

Nanofiltration (NF) membranes are a new class of membranes, whose properties are between those for ultrafiltration (UF) and those for and reverse osmosis (RO). Their separation mechanisms involve both steric (sieving) effects and electrical (Donnan) effects. This combination allows NF membranes to be effective in a range of separation of mixtures of organic solutes (either neutral or charged) and salts.

The ability to predict the process performance of NF membrane separation would be very useful for the planning and optimisation of the processes. Such prediction would ideally take advantage of available physical characteristics of a process stream and a membrane.

In this article, an example of such prediction will be presented for the separation of dye–salt solutions using NF membranes. This kind of membranes is especially suitable for such a process since due to a combination of steric and Donnan effects the dye will be effectively rejected, while the salt may even be poorly rejected (concentrated in the permeate).

Two main approaches have been used thus far to model the transport of ionic species through NF membranes. One approach is based on the extended Nernst–Planck equation. In this approach, a system containing any number of n ions can be described using a set of $(3n + 2)$ equations. It is also assumed that the flux of every ions through the membrane is induced by pressure, concentration and electrical potentials. This model describes the transport of ions in terms of an effective pore radius r_p (m), an effective membrane thickness to porosity ratio $\Delta x/A_k$ (m) and an effective membrane charge density X_d (mol·m^{-3}). In order to determine the structural parameters of such a model, numerous experiments should be carried out; moreover, it is difficult to make use of it.

The second approach is the Spiegler–Kedem model [1]. This black-box approach allows the membranes to be characterised in terms of the salt permeability P_S and the reflection coefficient σ. Its use is limited to binary salt systems, and in the limiting case – to a binary salt system in the presence of completely rejected organic ions.

In this paper, the Spiegler–Kedem model was used for description of salt transport through NF membranes, even at high concentrations typical of industrial desalination of organic dyes.

2. EXPERIMENTAL

The batch experimental set-up was used. Both permeate and retentate streams recirculated to keep their concentration and volume constant during experiments. All experiments were carried out at 20 °C and the constant feed rate of 500 dm^3·h^{-1}.

2.1. MEMBRANE

Membrane used in this study is shown in the table.

Table

NF membrane used

Membrane	Material	Producer
Desal 5 DK	polyamide	GE Water Technologies

2.2. FEEDS

In the experiments, aqueous salt solutions and mixed aqueous dye–salt solutions (Acid Red 357) were used.

2.3. FLUX AND SALT REJECTION IN SINGLE SALT SOLUTIONS

The flux and the permeate concentration at various feed concentrations and at various transmembrane pressures (0.8, 1.0, 1.2 and 1.5 MPa) were measured for NaCl and $MgSO_4$ single salt solutions (concentrations of salt 2.5, 5.0, 10.0, 25.0, 50.0 $g \cdot dm^{-3}$).

2.4. FLUX, SALT AND DYE REJECTION IN MIXED DYE–SALT SOLUTIONS

In the case of Desal 5DK, the flux and the concentrations of NaCl and dye in permeate at various feed concentrations (10.2, 48.8, 102.5, 136.8, 191.1 g of dye per 1 dm^3 and 2.5; 5.0; 10.0; 25.0; 50.0 g of NaCl per 1 dm^3) were measured at the constant transmembrane pressure of 1.5 MPa.

3. RESULTS AND DISCUSSION

3.1. FLUX AND SALT REJECTION IN SINGLE SALT SOLUTIONS

Figure 1 shows the dependence of the transmembrane pressure on the flux for NaCl solutions with various content of salts. This dependence for every salt concentration is represented by a straight line. Thus we can assume that the concentration polarization is of no significance and therefore we can consider the bulk concentration equal to that on the membrane [2], which is required in model equations.

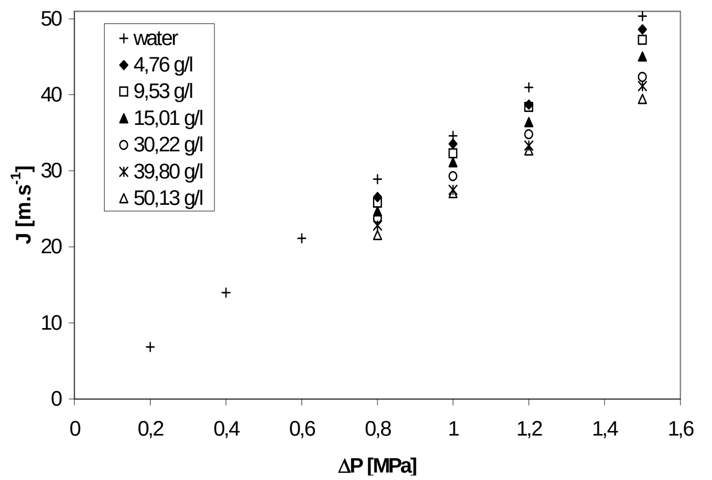

Fig. 1. Flux J as a function of transmembrane pressure ΔP for NaCl solutions with various salt contents (Desal 5DK)

Rejection versus flux (see figure 2) can be evaluated based on the extended Spiegler–Kedem model allowing us to obtain the parameters σ, α and β [3].

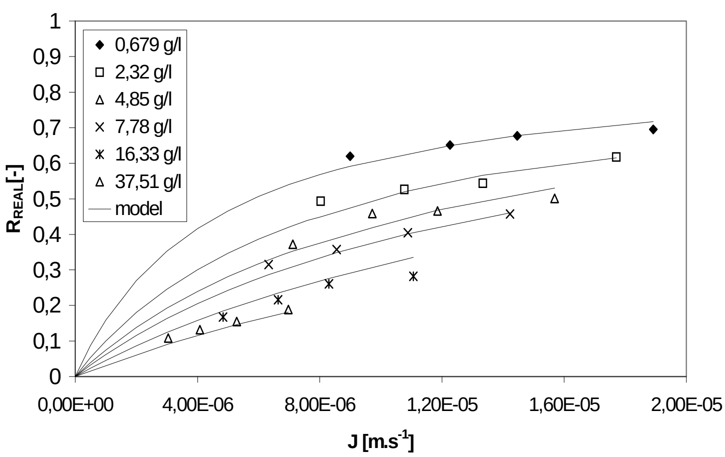

Fig. 2. Rejection R_{real} of NaCl as a function of flux J for NaCl solutions with various salt contents (Desal 5DK)

3.2. FLUX, SALT AND DYE REJECTION IN MIXED DYE–SALT SOLUTIONS

The aim of these experiments was to find the dependence of salt and dye rejection on the salt and dye concentration. In every experiment carried out in this work, the dye rejection was sufficiently high and almost equal to unity. The lowest value of the dye rejection measured was 0.999.

The salt rejection as a function of the dye and salt concentration is plotted in figure 3. It can be seen from this figure that the salt rejection decreases with a decrease in the salt concentration and with an increase in the dye concentration, corresponding to the Donnan equilibrium.

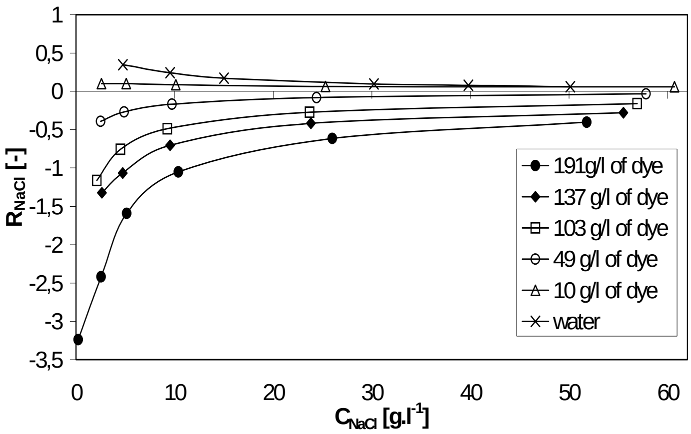

Fig. 3. Salt rejection R_{NaCl} as a function of salt concentration c_{NaCl} at different dye concentrations (Desal 5 DK, 1.5 MPa)

In the solution without the dye or with low dye content (positive rejection in both cases), we can observe a typical decline of salt rejection with an increase in salt concentration. At a higher dye content the salt rejection increases with an increase in the salt concentration due to shifting the Donnan equilibrium.

It is obvious (see figure 4) that the salt content has also a strong influence on the flux. In the case of single salt solution (without dye content), we can see a typical decrease of flux with an increase in the salt content. In the case of mixed dye–salt solutions, we can observe an initial increase in the flux and following decrease after reaching a maximum. The initial increase in the flux at high dye concentration and low salt concentration is due to negative rejection (see figure 3), which causes the difference in reverse osmotic pressure between permeate and feed sides of the membrane ($\Delta\pi > 0$). This difference in reverse osmosis pressure escalates the driving force of the process, thus the flux increases.

The experimental dependence of the salt rejection on flux can be evaluated by the extended Spiegler–Kedem model (see figure 5) in order to obtain σ_{NaCl}, α_{NaCl} and β_{NaCl} [3]. These parameters are characteristic of the transport of NaCl through a given membrane and also characteristic of a given dye in feed solution dye. The meaning of individual parameters is the same as in the case of the single salt transport.

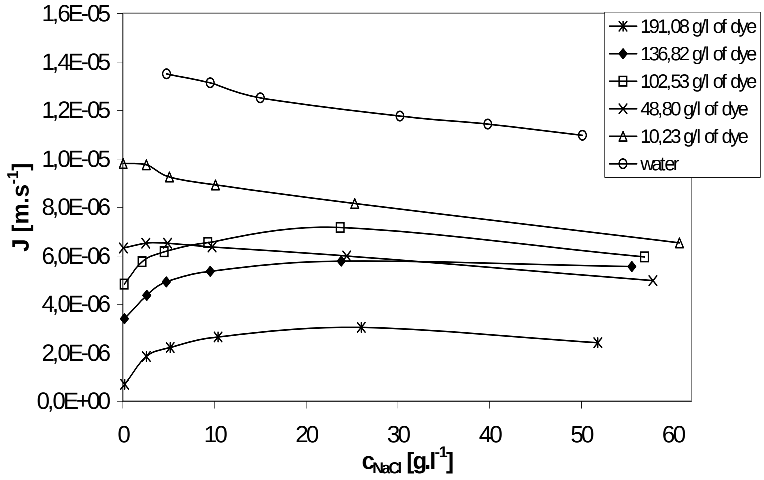

Fig. 4. Flux J as a function of salt concentration c_{NaCl} at different dye concentrations (Desal 5 DK, 1.5 MPa)

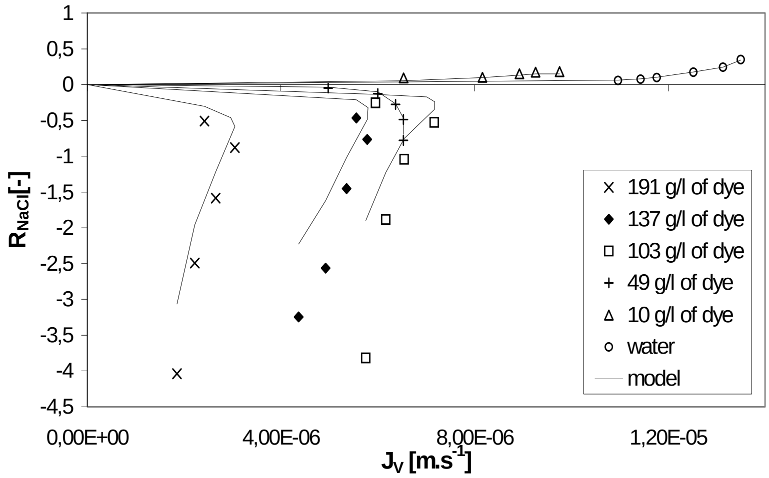

Fig. 5. Salt rejection R_{NaCl} as a function of flux J at different dye concentrations (Desal 5DK, 1.5 MPa); $\sigma_{\mathrm{NaCl}} = 0.87988$; $\alpha_{\mathrm{NaCl}} = 5.37851 \cdot 10^{-6}$ and $\beta_{\mathrm{NaCl}} = 0.62342$

Figure 5 depicted the experimental dependence of the salt rejection on the flux. The single curves represent the salt rejection as a function of the flux for a given dye content in the feed. The pressure difference was kept constant during all experiments and the flux was changed by changing the salt content in the feed (changing the difference in osmotic pressure).

It can be seen from figure 5 that based on the extended Spiegler–Kedem model we are not able to evaluate the rejection–flux data so accurately as it was in the case of the single salt transport. If the rejection values are within a fixed range, the prediction made based on this model is still sufficient.

4. CONCLUSIONS

The introduction of an exponential term to the concentration dependence expressing the salt permeability in the Spiegler–Kedem model allows very good prediction of the rejection of single salt solutions by nanofiltration membranes, depending on the feed concentration and permeates flux.

In the case of separation of mixed dye–salt solutions, the extended Spiegler–Kedem model including the Donnan equilibrium term (the Perry–Linder model) and the exponential concentration dependence term can be used for sufficient prediction of the salt rejection even at high dye concentrations typical of industrial desalination process.

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