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A phenomenological model to evaluate the performances of electrodialysis for the desalination of saline water containing organic solutes

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ABSTRACT

Electrodialysis is promising to treat saline solutions containing organic solutes. However, there is still a need for a model to describe the desalination performances according to the process parameters. In this work a phenomenological model is proposed based on the analysis of the different contributions to the mass transfer of salt, water, and organic compounds. Once the characteristic parameters are determined experimentally, it is possible to predict the salt and organic concentrations in both compartments according to the operating conditions. The methodology is illustrated for the evaluation of electrodialysis performances considering a case study, and the effect of the current and solution compositions are discussed. To remove a fixed salt quantity, a lower current gives a higher organic solute transfer due to a higher time dependent solute diffusion, the additional transfer, fixed by the quantity of charge, remaining constant. Regarding the influence of the inorganic salts, higher transfer of organics, like glucose, acetic acid or acetate, are observed with sulfate compared to chloride, while a contrary behavior is obtained with phenol. This model also permits to discuss the influence of possible pre-treatments to change the pH or the salt composition in order to improve the electrodialysis performances.

1. Introduction

Aqueous waste streams of increasing quantities are often complex, containing salt and organic matter (OM) [1]. Membrane processes like nanofiltration (NF) or electrodialysis (ED) are very promising for the separation of the organic compounds and the salt, leading to a feasible treatment, reuse and/or valorization of these fractions. ED can be better option due to process availability in varying salinity range and flexibility for process control e.g. on current [2,3]. In addition, successful applications of ED for desalting complex saline solutions in varying fields of biotechnological, chemical industries and water treatment systems are reported, with solution containing both organic solute and salt [4–7]. In each case, two different streams are produced, as shown in Fig. 1.

Considering further integration of the produced streams, ED desalination can have many different objectives. Concerning the organic content, the solute decomposition or recovery could be the objective depending whether it is a pollutant or valuable fraction. Meanwhile, concerning the salt extracted in the concentrate, further utilization such as production of raw materials or exploitation salinity gradient energy is of great interest [8]. Nevertheless, it is noteworthy that desalination and organic solute transfer occur simultaneously. The process control

regarding the solution impurity in the diluate and concentrate should be given to great attention, as it may limit the integrated process followed.

In fact, previous ED studies mainly focus on partial factors like solute concentration and nature, membrane type selection, operating current, pH and system running mode etc. [7,9–13], while a systematic investigation concerning ED performance for the separation of the organic solute/salt is still lacked. Moreover, in such cases, the membranes, the salt and organic solute together build a complex system, making process performance hard to predict [14]. For instance, the salt transfer (to be maximized) and the simultaneous organic solute transfer (to be minimized) are reported to be highly linked due to the water electroosmosis and the applied current in ED [14,15]. Furthermore, modification on both the ion-exchange membrane (IEM) structural [16] and the solute hydration [17] by salt has been reported, possibly resulting to unexpected poor performance of ED. Thus, considering a complex interaction among salt-solute-membrane involved, a theoretic model in order to better predict/understand ED performance is urgently necessary. However, few studies focus on the predicted model for ED process [6], with only limited solution investigated such as in agroprocessing field [18,19]. Furthermore, the model based on Nernst-Planck equation integrating many parameters is often hard to use in
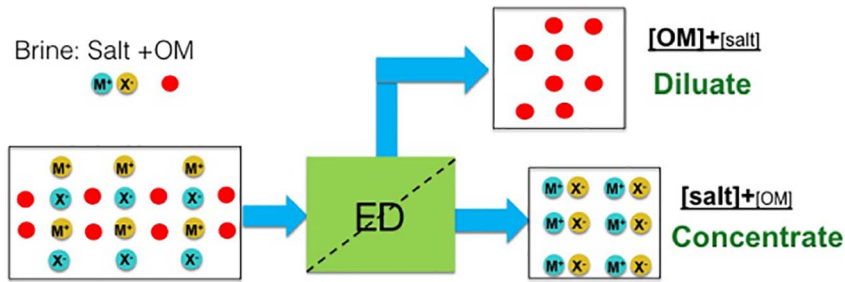

Fig. 1. Schematic drawing of ED desalting saline solution containing organic solute.

real practice of different aspects [20].

The aim of this study is to propose a simple, phenomenological model to evaluate the ED performance desalting various saline brines containing organic solute. Synthetic saline solutions consisting of different salt (NaCl, MgCl$_2$, Na$_2$SO$_4$, respectively) mixed with varying organic compounds (namely acetic acid, phenol and glucose as neutral compounds and acetate as charged one) are used. Based on the mass transfer investigation, characteristic parameters of the proposed model are experimentally obtained. Then, according to the model, the ED process performance is discussed concerning the influence of the current and solution composition (the salt and organic solute), on the variation of solute concentration for both two streams, i.e., diluate and concentrate.

2. Phenomenological modelling based on mass transfer

A phenomenological model in the ED process is depicted according to the transfer of inorganic salt, water and organic compound. Then, the variation of the solute concentration in each compartment can be predicted with the proposed model, enabling to further evaluate the process performance.

2.1. Inorganic salt and water transfer

The salt flux in ED, j_s (eq·m^{-2}·s^{-1}), is reported to be dominated by migration due to the electrical potential gradient, j^{mig}, which is proportional to the current [2,6,19]. The salt flux density is expressed as in Eq. (1), introducing the current coefficient α (eq·m^{-2}·s^{-1}·A^{-1}):

$$j_s \approx j^{mig} = \alpha I \tag{1}$$

In the same manner, it is reported that the water transfer, j_w (m^3·m^{-2}·s^{-1}), is dominated by the electroosmotic flux (j^{eo}), i.e. the water transfer owing to the migration of ion species, corresponding to the ion hydration [2,6,21,22]. Due to its relation with the salt transfer, electroosmosis j^{eo} varies linearly with the current. Then, the water flux density is given by Eq. (2), by introducing an electroosmotic coefficient, β (m^3·m^{-2}·s^{-1}·A^{-1}):

$$j_w \approx j^{eo} = \beta I \tag{2}$$

2.2. Organic solute transfer

It is documented that the mass transfer of the organic compound can be owing to the diffusion driven by the concentration gradient [23]. But an additional contribution was demonstrated to be also involved (convection for neutral solute and migration for charged solute) and that it is not negligible compared to diffusion, which is further discussed later [6,12,24–26]. The flux of organic solute, j_{OM}, consisting of the diffusion flux, j^{diff}, and the additional flux, $j^{additional}$ is given by Eq. (3):

$$j_{OM} = j^{diff} + j^{additional} \tag{3}$$

Concerning the diffusion transfer, it can be further expressed as:

$$j^{diff} = P_{OM} \Delta C_{OM} \tag{4}$$

where ΔC_{OM} is the concentration gradient ($\Delta C_{OM} = C_{OM,D}{}^0 - C_{OM,C}{}^0$) and P_{OM} (m·s^{-1}) is the solute permeability. ΔC_{OM} is assumed to be constant in this study, with the value equal to $C_{OM,D}{}^0$, the initial organic solute concentration in diluate (feed). Indeed, comparing with the initial amount added in the diluate, this amount of transferred organic compound is negligible which will be further discussed in Section 4.2.

Concerning the additional transfer, it corresponds to two cases, considering different solute charge nature. For a neutral organic solute, the additional transfer was reported to be convection due to electroosmosis which is proportional to the current [14,15]. A charged organic solute is supposed to migrate under current, same to inorganic charged species above mentioned. Thus, the migration of the charged solute is also proportional to the current, referred to Eq. (1).

Therefore, the additional transfer of organic solute, whatever charge nature, can be expressed as follows:

$$j^{additional} = \gamma I \tag{5}$$

introducing γ (mol·m^{-2}·s^{-1}·A^{-1}) as the additional transfer characteristic coefficient.

The total flux of solute transfer, shown as Eq. (3) can be rewritten as Eq. (6):

$$j_{OM} = j^{diff} + j^{additional} = P_{OM} C_{OM,D}^0 + \gamma I \tag{6}$$

consisting of diffusion, which is characterized by coefficient P_{OM} (m·s^{-1}), and an additional transfer, characterized by γ (mol·m^{-2}·s^{-1}·A^{-1}).

2.3. Solute concentration variation

Knowing the transfer of solute and water across the ion-exchange membrane, the quantity of the solute and water in real time in the two compartments can be calculated, based on mass balance analysis for an ED experiment run in a batch mode. Then, the concentration of salt (C_S, eq·m^{-3}) and concentration of organic solute (C_{OM}, mol·m^{-3}) resepctively are given by:

for the concentrate compartment:

$$C_s^C = \frac{C_{s,C}^0 V_C^0 + \alpha I S_m t}{V_C^0 + 2\beta I S_m t} \tag{7}$$

$$C_{OM}^C = \frac{(P_{OM} C_{OM,D}^0 + \gamma I) 2 S_m t}{V_C^0 + 2\beta I S_m t} \tag{8}$$

then based on the mass balance, for the diluate compartment:

$$C_s^D = \frac{C_{s,D}^0 V_D^0 - \alpha I S_m t}{V_D^0 - 2\beta I S_m t} \tag{9}$$

$$C_{OM}^D = \frac{C_{OM}^0 V_D^0 - (P_{OM} C_{OM,D}^0 + \gamma I) 2 S_m t}{V_D^0 - 2\beta I S_m t} \tag{10}$$

The numerators and denominators describe the solute quantity and solvent quantity at each time t, respectively. The four characteristic parameters for solute and solvent transfer (α, β, P_{OM} and γ) are obtained