



A mechanistic model for electrochemical nutrient recovery systems



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ABSTRACT

Electrochemical membrane technologies such as electrodialysis have been identified as key technologies to enable nutrient recovery from wastewater. However, current electrochemical models are focused on simpler solutions than wastewater and omit key outputs such as pH, or total cell potential. A combined physico-chemical and electrochemical model was developed which includes the mechanisms of competitive transport of ions, implicit inclusion of H^+ and OH^- , pH (including ionic activity and ion pairing), different factors contributing to total cell potential and a novel method for ion exchange membrane transport. The model outputs compare well with measurements from experiments and simulate secondary effects such as electrode reactions and current leakage. Results found that membrane, rather than boundary layer or bulk resistance was the major contributor to potential drop, and that apparent boundary layers were relatively thick (3 ± 1 mm). Non-ideal solution effects such as ion-pairing and ionic activity had a major impact, particularly on multi-valent Ca^{2+} ions, which enhances the capability of electrodialysis to recover monovalent nutrient ions such as K^+ and NH_4^+ . Decreased resistivity of ion exchange membranes to specific ions (for example, in this case nitrate) could also be detected. The methods here are validated using a comparatively simple synthetic solution of five ionic components, but are able to be easily scaled for a more complex solution, and are also compatible with additional mechanisms such as precipitation, fouling, and scaling.

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1. Introduction

For several decades, electrochemical processes have been used in the areas of desalination of brackish water, water purification and industrial contaminant removal (Strathmann, 2010). Electrodialysis (ED) in particular has the potential for further application in a variety of industries due to its ability to concentrate ions from solution without introducing external chemicals. A comparatively recent electrochemical application is for concentrating nutrient ions, including potassium, ammonium and phosphate, from waste streams (Mehta et al., 2015). This concentrate could be used as a liquid fertilizer, undergo further treatment, such as absorption or stripping to form a more refined fertilizer product (Ippersiel et al., 2012) or form a solid nutrient product (Ledezma et al., 2015). Compared to traditional feed sources such as brackish or sea-water, wastewater has a complex solution composition and a high propensity for membrane fouling and scaling (Mondor et al., 2009).

Using wastewater presents difficulties compared to traditional electrochemical feed sources.

Models describing electrochemical membrane systems have been developed (Zabolotskii et al., 2013; Kodym et al., 2012; Lee et al., 2006; Kraaijeveld et al., 1995; Mohammadi et al., 2005; Moon et al., 2004; Kim et al., 2012; Tanaka, 2013; Nikonenko et al., 2003, 2010; Bawomruttanaboonya et al., 2015). However, the majority of existing models are focused on describing the fluxes of single salts (Lee et al., 2006; Mohammadi et al., 2005; Moon et al., 2004; Tanaka, 2013; Ortiz et al., 2005), or only have the capacity to model up to three of the same charged ions in solution (Kraaijeveld et al., 1995; Kim et al., 2012; Nikonenko et al., 2003). Some models have taken into account the effects of pH on mass transport in the system (Zabolotskii et al., 2013; Kraaijeveld et al., 1995; Nikonenko et al., 2003, 2010), but none have simulated the pH through the system and how this effects mass transport and acid-base dissociation of complex species. In particular, the phenomena of current leakage, or transfer of proton and hydroxide ions across the membranes is critical (Nikonenko et al., 2010). Acid-base reactions involving bicarbonate have been modelled across a single ion-exchange membrane (IEM) (Nikonenko et al., 2003, 2010), but

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Nomenclature

z_i	charge of ion i (–)	E_{IC}	total internal cell potential drop (V)
C_i	concentration of ion i (mol m ⁻³)	w	width of the spatial area (in the x -direction, perpendicular to the membranes) to which the potential gradient applies (m)
a_i	ionic activity of ion i (mol m ⁻³)	E_{cell}	total cell potential (V)
μ	ionic strength of solution (mol m ⁻³)	E_{rev}	reversible potential of the electrodes (V)
γ_i	ionic activity coefficient of ion i (–)	E_{act}	activation overpotential of the electrodes (V)
D_i	diffusion coefficient of ion i (m ² s ⁻¹)	E_{conc}	potential loss from concentration polarization (V)
F	Faraday's constant (C mol ⁻¹)	J_{crit}	95% confidence objective function surface
R	gas constant (J mol ⁻¹ K ⁻¹)	p	number of parameters to fit in the parameter estimation
T	temperature (K)	n_{data}	number of experimental data points used in the parameter estimation
ϕ	potential (V)	$F_{0.95,p,n_{data}-p}$	cumulative F distribution value for 95% confidence
u_y	fluid velocity (m s ⁻¹)	<i>Subscript Ai</i>	referring to anion i
V	spatial volume (m ³)	<i>Subscript Ci</i>	referring to cation i
P	Permselectivity fraction of counter-ions (–)	<i>Subscript res</i>	referring to in the reservoir
X	membrane capacity (meq m ⁻³)	<i>Subscript DBL</i>	referring to in the diffusion boundary layer
x	membrane ionic activity (meq m ⁻³)	<i>Subscript A</i>	referring to total amount of anions
I	applied current density (A m ⁻²)	<i>Subscript C</i>	referring to total amount of cations
E	electric field strength (N C ⁻¹)	<i>Subscript AEM</i>	referring to within the anion exchange membrane
E_{Donnan}	Donnan exclusion potential (V)	<i>Subscript CEM</i>	referring to within the cation exchange membrane
a_{i-}^S and a_{i-}^M	activities of anion i in the solution and the membrane surface, respectively (mol m ⁻³)		
a_{i+}^S and a_{i+}^M	concentrations of cation i in the solution and membrane surface, respectively (mol m ⁻³)		

this is not generally scalable to more complex systems, and does not include effects such as ionic activity and ion-pairing, which are critical to determine ion availability. Existing models do not have the capacity to accurately describe complex physicochemical processes such as acid-base dissociation and ion-pairing, and there have not been mechanistic studies which couple the modeling of mass and charge transport as well as pH for electrochemical membrane processes using complex solutions.

A limitation in existing electrochemical modelling is the lack of integration between existing electrochemistry theory and a robust physico-chemical process simulation framework such as that developed by Solon et al. (2015) and Flores-Alsina et al. (2015). The aim of this study is to develop a physico-chemical modeling approach for electrochemical membrane systems which includes, and accounts for the relationships between the following mechanisms:

- Mass transfer based on charge transport of ions (including ionic activity correction);
- pH effects including current transport by hydrogen and hydroxide ions (current leakage);
- Ion-pairing and acid-base dissociation; and
- Total cell potential, including the effect of solution resistance, membrane resistance, and electrode resistance.

While each topic listed above is complex in its own right, a complete electrochemical process model requires all mechanisms to be addressed in an integrated way. For example, the mass transfer of a key cation, for example, the Ca²⁺ in a calcium sulfate solution will be competitively transported with H⁺. Therefore mass transport is related to the pH of the system. The electrode reactions in a simple water splitting system are also related to the pH because they produce H⁺ or OH⁻ in proportion to applied current. The rate of transport of Ca²⁺ is also dependent on the speciation of the Ca²⁺ component as aqueous, paired chemical species CaOH⁺, Ca(OH)_{2(aq)} and CaSO_{4(aq)}, as well as to the electrochemical potential.

Electrochemical technologies which use wastewater may need substantial modifications to current technologies, which commonly use thin chambers (1–2 mm) and spacers, as the risk of blockage from solids fouling, precipitation and biofouling are far higher with wastewater (Mondor et al., 2009). Instead, thicker, free-standing chambers may be used. Thicker chambers reduce requirement of pre-treatment and related costs to remove suspended solids from the wastewater (Goodman et al., 2013). Wider membrane distances will result in a different type of flow regime compared to conventional processes. Hence a key outcome of this study will be to determine whether using wider membrane distances of 12 mm will cause prohibitively high potential losses. However, the model developed in this paper is also applicable to systems with narrow chamber widths, spacers and non-laminar flows.

The focus of this work was to develop a combined physico-chemical and electrochemical model and to validate it using a simple single pair ED unit. However, the model could be expanded for a conventional full-scale ED unit with multiple cell pairs, narrow flow channels with spacers, and high (but below limiting) current density. The model has direct application to other electrochemical process, with wider membrane distances and where low current density is applied, such as ammonium recovery at the cathode from human urine (Luther et al., 2015) and sewage wastewater (Desloover et al., 2015) and in-reactor precipitation using a single pair electrochemical reactor (Ledezma et al., 2015). The focus of this study is to develop and integrate physico-chemical and electrochemical modelling processes.

2. Modeling methods

2.1. Model domain and controlling mechanisms

Both the model and experiments have the same configuration outlined in Fig. 1. That is, a batch process in a three membrane (four chamber) electrodialysis stack without spacers. Two chambers are for the electrolyte, one for the feed and one for the product, with

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