A model of electrodialysis for multi-ion systems

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Summary of key findings

The underlying mechanisms for competitive mass transport of ions as well as pH variation in multi-ion electrodialysis were experimentally characterised and successfully modelled. This included the development of a novel current proportioning method for calculating the flux of ions in a multicomponent solution, pH effects and parameters for membrane permselectivity and membrane ion exchange capacity. It was shown that a conventional diffusion boundary layer model can accurately describe ionic mass transfer in equipment with large inter-membrane distances. In addition, diffusion boundary layer thickness was estimated for the first time in non-traditional electrodialysis applications.

Background and relevance

The nitrogen, phosphorous and potassium present in wastewater have the capacity to significantly reduce reliance on, and even replace, traditional fertilizer sources (Batstone et al. 2014). In reject wastewater from the anaerobic digestion phase of wastewater treatment, the water has already been treated, so the nutrients are in a soluble form (NH_4^+, PO_4^{3-}, K^+) and there are low amounts of organics present. However, the nutrient ions must be concentrated prior to undertaking any commercial recovery operation (Mehta et al. 2013). Electrodialysis has been used to concentrate salts from water for several decades. Electrodialysis has been identified as having the potential to succeed in a variety of unconventional applications due to its ability to concentrate ions from solution without altering the quality of the solutes or solvent. One of these potential applications is the concentration of nutrients from wastewater.

Although models of electrodialysis have been developed, the majority of these models concern simple solutions, with little explanation of the mechanisms essential for modelling electrochemical systems with more complex solutions like domestic or agri-business wastewater. Existing models do not have the capacity to accurately simulate the complex physico-chemical processes which occur. In addition, there have not been mechanistic studies which couple the modelling of mass and charge transport as well as pH and precipitation.

The aim of this study was to develop a physico-chemical modelling approach for the separation and concentration of nutrient ions from synthetic wastewater. Key mechanisms include ion transport through diffusion and migration (Nernst-Planck equation), the influence of pH on the competitive charge transport of ions, ion transport through ion exchange membranes based on the ion-exchange capacity and permselectivity of the membranes, and total cell potential including the contribution of resistance from the solutions, membranes and electrodes. Also included is the phenomenon of diffusion boundary layers, which are layers of solution immediately adjacent to the membranes and electrodes in which no convection occurs. Key mechanisms are shown in Figure 1.1.

The model can be used to identify and evaluate limiting factors in the process. For example, when using electrodialysis to concentrate nutrients from wastewater the equipment will be more prone to fouling and scaling compared to traditional applications. Therefore the traditional design of separating the membranes by only 1–2 mm using spacers will not be appropriate. Instead, thicker (10–15 mm) free-standing chambers must be used. The larger inter-membrane distance may result in a different type of flow regime and it is important to identify any limitations of this type of system in terms of solution resistance and ionic transport. Therefore another aim is to use the model to determine if there are differences in mass transport limitations in a system with wider inter-membrane distances compared with the distances commonly found in more traditional electrodialysis applications.
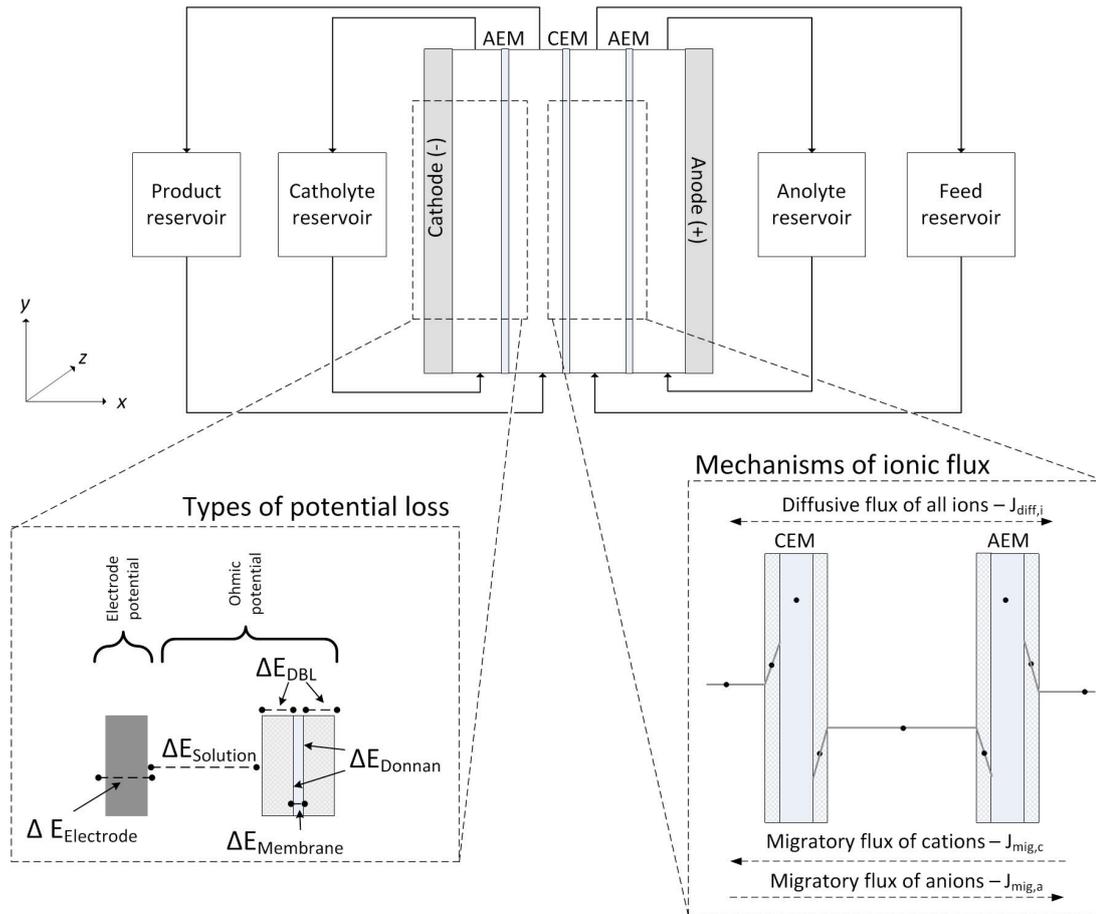
Figure 1.1 Overview of model and experimental configuration. The inlay on the left shows the types of potential losses incorporated in the model. The inlay on the right shows the mechanisms of ionic flux (J) in the x-direction. The shaded areas either side of the cation exchange membrane (CEM) and anion exchange membrane (AEM) indicate the diffusion boundary layers (DBLs) and the black dots indicate areas where concentration and pH are calculated in the model.

Results

To determine the diffusion boundary layer thickness the model output was fitted to experimental data by minimizing the residual sum of squares. A diffusion boundary layer thickness of 3.0 mm was determined to be optimum, with upper and lower 95% confidence intervals of 4.0 and 2.6 mm, respectively. This value is higher than values found in literature, which is not unexpected considering the wider inter-membrane distances used here (Choi, Park & Moon 2002; Kim, Walker & 81 Lawler 2012).

Figure 1.2 shows the feed and product outlet concentrations and pH for the model compared to experimental data, using the optimized diffusion boundary layer thickness. This particular system contains synthetic wastewater comprised of calcium sulfate and potassium sulfate as the feed and product solutions, and sodium nitrate as the electrolyte. These results show that this mechanistic model adequately represents empirical observations.

A residual sum of squares ANOVA analysis shows that a model with diffusion boundary layers has significantly better fit compared with a model without diffusion boundary layers included. This indicates that despite the increased inter-membrane distance, similar mechanisms are governing the process compared to traditional electrodialysis applications with small inter-membrane distances and higher flow rates.
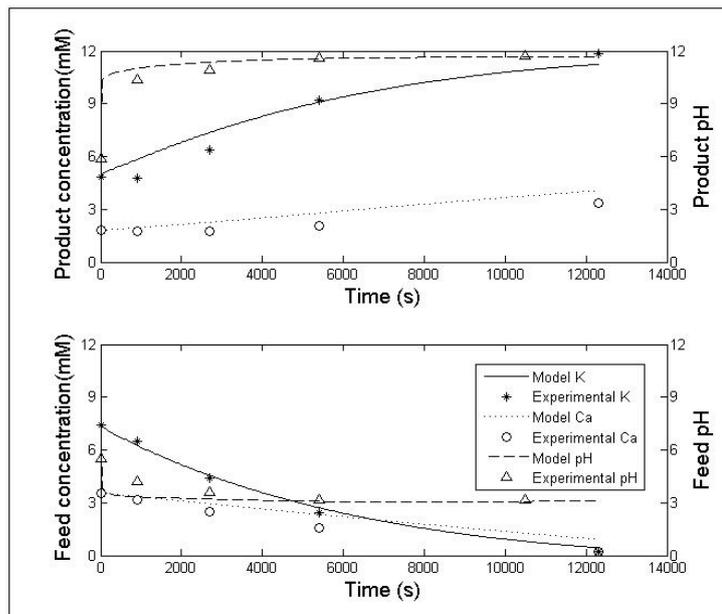
Figure 1.2 Modelled and experimental potassium and calcium concentrations as well as pH in the outlet of a laboratory scale unit.

Discussion

The results show that the proposed mechanisms of charge proportioning between different ions, the pH calculations and the contribution of protons and hydroxide ions to competitive mass transport effectively describe the experimental data. The phenomenon of current leakage, a mechanism which contributes to the inefficiency of the process, is fundamentally incorporated into the model through the competitive transport of proton and hydroxide ions. The optimum diffusion boundary layer thickness was found to be larger than values found in literature. However, this was expected compared to more traditional electrodialysis applications which have smaller intermembrane distances, spacers and faster fluid flow. The model also includes the membrane parameters of permselectivity and ion-exchange capacity, which enables determination of membrane resistance in different solution compositions as well as for ion exchange membranes with different characteristics. Future work will extend the model to account for ionic speciation, ion-pairing and precipitation in synthetic and real wastewater solutions.

References

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