Desalination 417 (2017) 36–51

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Improvement of MCDI operation and design through experiment and modelling: Regeneration with brine and optimum residence time

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ARTICLE INFO

Keywords:
Membrane capacitive deionization
Brine regeneration
Water recovery

ABSTRACT

Membrane Capacitive Deionization (MCDI) is an energy efficient, electrochemical desalination technology, in which ions are removed from a salty stream upon applying a constant voltage or current. The ions are stored in carbon electrodes and then released back into the stream by reversing the polarity. In this work, we aimed to assess the feasibility of using a brine stream to regenerate the MCDI unit in order to improve water recovery. We further aimed to determine the optimum residence time in the MCDI unit. To achieve these objectives, we first enhanced the ion transport model previously developed for MCDI by independently measuring the counter-ion and co-ion diffusion coefficients in the ion-exchange membranes. These experiments allowed for an asymmetric model of the MCDI unit where the voltage drop across the cation exchange membrane was greater than that across the anion exchange membrane. Using this revised model, we found that in batch operation, a brine to feed water concentration ratio of around two was optimum. In continuous operation, over 40% enhancement in water recovery could be achieved when the regeneration brine was partially recycled, but water productivity dropped. We further showed that the maximum desalination capacity did not increase beyond a critical residence time in the MCDI cell, while the water recovery decreased.

1. Introduction

Desalination of sea and brackish water has become more common over the past decades to meet freshwater requirements for domestic, agricultural and industrial demands. Desalination capacity, energy demand, regeneration method and water recovery are the main features distinguishing the technologies developed for this purpose, which are generally thermally or membrane based [1,2]. Capacitive Deionization (CDI) is an alternative, electrochemical water treatment method in which ions are temporarily adsorbed in electrical double layers of two oppositely charged porous carbon electrodes [3]. Therefore the desalination capacity is reliant on the carbon material used in the electrode fabrication [4,5]. To enhance the performance of CDI, Membrane Capacitive Deionization (MCDI) has also been proposed, where ion-exchange membranes (IEMs) are placed in front of the charged electrodes to inhibit the co-ions, i.e. ions carrying the same charge as the surface, from reaching the electrodes [6,7]. In CDI or MCDI, ions or other charged species are removed from the concentrated feed. However, this is not the case for most other desalination technologies in which water is separated from the polluted stream. It is thus apparent that at lower concentrations of the charged species in comparison with that of water, the energy consumption of CDI based processes will be significantly lower than the latter [8]. Therefore, CDI or MCDI is mostly employed as an energy-efficient method for brackish water remediation where the salinity is limited to 1000 mg L^{-1} [9].

Once the carbon pores reach their saturation limit, the CDI or MCDI unit is not capable of adsorbing ions anymore. Therefore, a regeneration step is required to deplete the electrode materials of the charged species. In CDI, the previously adsorbed ions are released back to the liquid phase by dropping the system voltage to zero, while in MCDI it is more common to release these ions by reversing the polarity. As a result the stack undergoes repetitive adsorption/desorption cycles [10]. Ease of regeneration adds to the merits of this promising desalination method [11].

While many attempts have been made towards synthesis of novel carbon materials with improved physico-chemical properties for CDI processes [12,13], less research has been conducted on the operational aspects of both CDI and MCDI. Zhao et al. [14] were the first to optimize the salt adsorption in MCDI by varying operational variables within both constant voltage and constant current modes. Recently, García-Quismondo et al. [15] considered new operational modes to increase energy efficiency in CDI by varying charge and discharge

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http://dx.doi.org/10.1016/j.desal.2017.05.004
Received 6 March 2017; Received in revised form 27 April 2017; Accepted 3 May 2017

current densities and also investigated the use of a concentrated brine stream during discharge. Yet more research is needed to improve the design aspects of MCDI. To illustrate, feed water recovery, i.e. the volumetric ratio of desalinated water produced to that of the feed water, is one such operational metric used to evaluate water treatment processes [16]. In the field of MCDI, the higher the feed water recovery, the less feed water volume is wasted during the desorption step. In this work, we specifically consider the potential of regenerating the MCDI unit with a stream of higher salt concentration than the feed to increase the feed water recovery. Since this is a very critical question, more exploration is required to determine its feasibility especially in the presence of ion-exchange membranes. If a more concentrated stream can be utilised in the desorption step, a certain amount of the water for regeneration can be recycled a number of times which then leads to much greater water recovery.

In this paper, we explore this concept using both experimental techniques and a theoretical model. The modified Donnan Theory developed by Biesheuvel et al. [17,18] is the most well developed model available in the literature to describe the storage of ions in the EDLs of micropores (< 2 nm) of carbon electrodes. The same research group has also proposed a dynamic ion transport model to describe the performance of the MCDI unit [17,19,20]. Tang et al. [21] has recently used a similar approach to model the removal of fluoride in CDI. This ion transport model includes all the mass and charge balances throughout the MCDI unit and is combined with modified Donnan theory to describe the ion storage in the electrical double layers (EDLs). Nonetheless, this theoretical method is based on various simplifying assumptions. In this work we avoid some of these assumptions by (i) measuring the diffusion coefficients in the ion-exchange membranes; (ii) using these values to adjust the voltage distribution across the two half-cells and (iii) including the ion activity coefficient in the solution and the membrane phases. The novel features introduced into the mathematical approach strengthen the model, as estimation of some parameters is replaced with direct measurements. The improved ion transport model was then utilised to determine the impact of partially recycling the regeneration brine, and further to determine the optimum residence time in the MCDI unit.

2. MCDI model

To describe the deionization process the modified Donnan (mD) Theory proposed by Biesheuvel et al. [18] is used to describe the ion storage in the electrical double layers (EDLs) of the carbon electrode (Section 2.1). Mass transfer equations then enable the prediction of the ion flux from the flow channel formed by a spacer through the ion-exchange membranes to access these EDLs (Section 2.2). In this approach, the effect of faradaic reactions and also the contribution of hydronium and hydroxyl ions have been neglected. Fig. 1 gives an overview of the MCDI arrangement of one of two half-cells that is described by the model. While macro and micro-pores are distributed within the carbon electrode, to better demonstrate the concentration and potential drop, they are drawn in series in Fig. 1.

2.1. Modified Donnan theory in the micropores

Modified Donnan theory uses the Boltzmann distribution to correlate the concentration in the micropores of the carbon where a surface charge is applied, to that of the macropores where the concentration of anions and cations is identical. A term μ_{att} is introduced to account for the physical adsorption of ion i onto the carbon surface at zero voltage (Eq. (1)) [17]:

$$C_{i,Mi} = C_{Ma}\cdot exp\left(-z_i\cdot\Delta\varphi_{electrode,Don} + \mu_{att}\right) = C_{Ma}\cdot exp\left(-z_i\cdot\Psi/V_T + \mu_{att}\right) \quad (1)$$

where $C_{i,Mi}$ is the concentration of ion i in the micropores of the carbon, C_{Ma} is the salt concentration in the macropores, and z_i is the valency of ion type i, $\Delta\varphi_{electrode,Don}$ is the Donnan potential difference, which in turn can be expressed in terms of the electrical potential difference (Ψ) between the macro and micro pores, and the thermal voltage $V_T = k_B T/e$ (≈ 25.5 mV at room temperature), where e is the electrical charge of an electron, k_B is the Boltzmann constant and T is the absolute temperature [18]. In contrast to the conventional EDL model of Gouy-Chapman-Stern where a distribution of the electrical potential is considered inside the pores, modified Donnan Theory considers $\Delta\varphi_{electrode,Don}$ as a constant. The reason behind this assumption is that the micropore size within the carbon material used is commonly small enough to result in overlapping EDLs.

The charge concentration ($C_{charge,Mi}$) is defined as the difference between the concentration of cations in the micropores with that of the anions. For a monovalent salt, $C_{charge,Mi}$ can be calculated from Eq. (2) as

$$C_{charge,Mi} = C_{cation,Mi} - C_{anion,Mi} = -2.\ C_{Ma}.\ exp\left(\mu_{att}\right).\ sinh\left(\Delta\varphi_{electrode,Don}\right) \quad (2)$$

According to the modified Donnan Theory [22], this charge concentration is proportional to the Stern layer potential difference ($\Delta\varphi_{St}$) as Eq. (3).

$$\Delta\varphi_{St}\cdot V_T\cdot\left(C_{St,0} + \alpha\cdot C_{Charge,Mi}^2\right) = -F.C_{charge,Mi} \quad (3)$$

where F is the Faraday constant, $C_{St,0}$ is the Stern layer capacitance at zero voltage and α demonstrates the charge dependency of the Stern layer capacity.

2.2. Dynamic ion transport model of MCDI

During the adsorption step, the salt concentration falls along the direction of the flow in the MCDI unit as the ions are being removed from the bulk stream. Neglecting axial dispersion, one can write Eq.(4) to describe the concentration in the spacer compartment (C_{spacer})

$$\frac{\partial C_{spacer}}{\partial t} = -\mathrm{v}\cdot\frac{\partial C_{spacer}}{\partial x} - \frac{j_{iy}}{\delta_{spacer}} \quad (4)$$

where δ_{spacer} is the thickness of the spacer which defines the flow channel width, v is the velocity in the flow channel and j_{iy} is the flux of ion type i moving in direction y, perpendicular to the flow direction, to reach the ion-exchange membrane. Assuming a quasi-steady-state

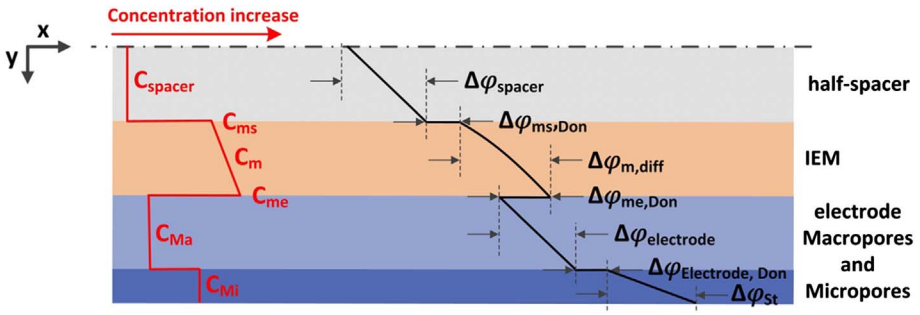

Fig. 1. Schematic illustration of counter-ion concentration (C) and dimensionless voltage (φ) distribution over a half-cell.