Water Research 129 (2018) 394–401

Contents lists available at ScienceDirect

Water Research

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

Intrinsic tradeoff between kinetic and energetic efficiencies in membrane capacitive deionization

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ARTICLE INFO

Article history:
Received 29 July 2017
Received in revised form
2 November 2017
Accepted 11 November 2017
Available online 15 November 2017

Keywords:
Capacitive deionization
Energy consumption
Kinetic efficiency
Tradeoff
System optimization
Performance evaluation

ABSTRACT

Significant progress has been made over recent years in capacitive deionization (CDI) to develop novel system configurations, predictive theoretical models, and high-performance electrode materials. To bring CDI to large scale practical applications, it is important to quantitatively understand the intrinsic tradeoff between kinetic and energetic efficiencies, or the relationship between energy consumption and the mass transfer rate. In this study, we employed both experimental and modeling approaches to systematically investigate the tradeoff between kinetic and energetic efficiencies in membrane CDI (MCDI). Specifically, we assessed the relationship between the average salt adsorption rate and specific energy consumptions from MCDI experiments with different applied current densities but a constant effluent salinity. We investigated the impacts of feed salinity, diluted water salinity, diluted water volume per charging cycle, and electrode materials on the kinetics-energetics tradeoff. We also demonstrate how this tradeoff can be employed to optimize the design and operation of CDI systems and compare the performance of different electrode materials and CDI systems.

1. Introduction

Capacitive deionization (CDI) is an emerging desalination technology based on the formation of electrical double layer (EDL) in the electrode micropores (Porada et al., 2013; Biesheuvel et al., 2017). While the state-of-the-art desalination process still remains reverse osmosis (RO) (Elimelech and Phillip, 2011), it has been suggested that CDI may compete with RO for desalinating brackish water with low to moderate salinity (Zhao et al., 2013a; Anderson et al., 2010; Welgemoed and Schutte, 2005). Specifically, it has been suggested that, under certain circumstances, CDI is more energy efficient than RO for brackish water desalination. But more importantly, CDI has other operational advantages that may render it the technology of choice for desalinating inland brackish water, especially in remote areas where large scale infrastructure is not accessible (Oren, 2008; Mossad et al., 2013). For example, CDI does not have any high pressure or high temperature components, which reduces the capital cost especially for small scale treatment systems. CDI is also strongly adaptable: the operating conditions can be readily adjusted for different feed water quality and target product water quality (Zhao et al., 2012). In addition, the absence of pressure driven permeation in CDI and the presence of periodic reversal of electric field also render CDI less susceptible to fouling problems that are common in RO. Last but not least, CDI is compatible with renewable energy the supply of which is often highly intermittent (Forrestal et al., 2012).

The research field of CDI has experienced an exponential growth in the past decade, with progress made in multiple directions. Various system configurations (Suss et al., 2012; Porada et al., 2012a; Biesheuvel and van der Wal, 2010; Omosebi et al., 2014; Gao et al., 2015a) and operation modes (Zhao et al., 2012; Kim et al., 2015; Garcia-Quismondo et al., 2013; 2016; Zhao et al., 2013b) have been developed to enhance the energy efficiency (Zhao et al., 2012; Kim et al., 2015; Garcia-Quismondo et al., 2013; 2016) and mass transfer kinetics of CDI (Zhao et al., 2013b), to improve the electrodes' salt adsorption capacity (Kim and Choi, 2010; Gao et al., 2015b) and long-term chemical stability (Gao et al., 2015a, 2014), and to enable continuous operation (Suss et al., 2012; Porada et al., 2012a; Yang et al., 2016). In particular, the introduction of ion exchange membrane to CDI system to mitigate co-ion repulsion has been shown to significantly enhance the energy efficiency of CDI and enable the more flexible and efficient constant current operation (Biesheuvel and van der Wal,

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https://doi.org/10.1016/j.watres.2017.11.027
0043-1354/

2010; Lee et al., 2006). Such a configuration, namely membrane CDI (MCDI), has widely been adopted due to its higher energy efficiency over CDI without membranes (Zhao et al., 2012; Omosebi et al., 2014). Other active research areas in CDI include the development of high performance electrodes (Porada et al., 2012b; Nadakatti et al., 2011; Liu et al., 2017; Duan et al., 2017; Wang et al., 2017a; Zhao et al., 2016; Yasin et al., 2016), and advancing our fundamental understanding on the energy efficiency of, and mass transport phenomena in, CDI (Kim et al., 2015; Qu et al., 2016; Zhao et al., 2010; Tedesco et al., 2017; Hemmatifar et al., 2016).

For a given CDI system, there are several primary operating parameters to control, including applied voltage or current, flow rate, charging and discharge durations. Optimizing system design and operation of a CDI system requires understanding the impacts of these parameters on system performance. To attain such understanding, however, system performance first needs to be defined. Previous studies have investigated the effect of current density on the salt adsorption capacity (SAC) and mass transfer kinetics as quantified by average salt adsorption rate (ASAR) (Kim and Yoon, 2015). A tradeoff was identified between ASAR and SAC, which is analogous to the tradeoff between power density and energy density featured in the famous Ragone diagram for supercapacitor. However, while the SAC at a given of operating conditions might be a critical parameter in evaluating the performance of an electrode, its implication on practical CDI operations is limited. After all, what matters most to a desalination process are, among other factors, how fast the process occurs and how much energy it consumes. In other words, the kinetic and energetic efficiencies should be the central performance indicators.

The energy efficiency of a desalination process is often quantified using specific energy consumption (SEC), typically defined as the energy consumed to generate unit volume of product water (Zhu et al., 2009). For CDI, however, because effluent salinity varies significantly from one process to another, SEC is more often defined as the energy consumed to remove a unit mole (or mass) of salt (Zhao et al., 2012), which will be the definition adopted in this study. While many existing studies concerned the SEC of a CDI operation and reported different ways to improve it, the discussion of energy efficiency should not be divorced from that of kinetic efficiency as there is an inherent tradeoff between the two. Quantifying the tradeoff between kinetic and energetic efficiencies is essential to optimizing the design and operation of an RO system (Lin and Elimelech, 2017), which has not been systematically conducted for CDI. On the other hand, one cannot attain such a tradeoff by simply varying the current density of a CDI operation while maintaining all other parameters constant, because operations with different current densities may result in different effluent salinities and thus different underlying separations. Comparison of SEC between CDI processes resulting in different separations is problematic because different separations inherently require different Gibbs free energy of separation (Wang et al., 2017b; Biesheuvel, 2009 JCIS). Therefore, a rational comparison of kinetic and energetic performance between different CDI operations has to be conducted in a way that the effluent salinity and the underlying separations are kept constant.

In this study, we experimentally and theoretically quantify the kinetics-energetics tradeoff in MCDI. The configuration of MCDI is chosen because (1) it is significantly more energy efficient than CDI without ion exchange membrane and thus expected to be more widely adopted in practice; and (2) because it allows constant current charging which is the chosen operation mode in our study. The kinetics-energetics tradeoff is quantified using ASAR and the inverse of specific energy consumption (SEC^{-1}) from MCDI experiments in which the current density and flowrate are simultaneously adjusted to achieve the same separations with different kinetic efficiencies. We also systematically assess the impacts of several parameters on the kinetics-energetics tradeoff. These parameters include the feed salinity, diluted water salinity, diluted water volume per charging cycle, and electrode materials. Finally, we discuss the implications of these tradeoff curves and demonstrate how they can be employed for optimizing system design and operation and for comparing the performance of electrode materials.

2. Materials and methods

2.1. MCDI module

The MCDI stack comprised 4 parallel cells that were sandwiched in an acrylic housing. Two types of electrode, a film electrode casted with activated carbon particles, PACMM (PACMM 203, Material Methods, Irvine, CA, USA, $\delta e_1 = 290$ μm) and an activated carbon cloth FM10K (Zorflex®, Pittsburg, PA, USA, $\delta e_2 = 350$ μm), were used in this study. Each cell consists of a pair of graphite foil as current collectors (Alfa Aesar, thickness $\delta = 130$ μm), a pair of porous electrodes (PACMM or FM 10 K), a pair of anion- and cation-exchange membranes (Neosepta AMX, $\delta_{mem} = 140$ μm, and Neosepta CMX, $\delta_{mem} = 170$ μm, Tokuyama Co., Japan), and a glass fiber spacer (Whatman, $\delta = 250$ μm). Each electrode was cut to a 6×6 cm^2 square with a 1.5×1.5 cm^2 square hole at the center, yielding a total active electrode area of 270 cm^2 for the entire stack. A peristaltic pump drives the water to enter from the periphery of the square MCDI stack, flow along the spacers sandwiched between the ion exchange membrane/electrode assemblies, and exit from the center square hole. A schematic showing the MCDI structure and flow direction is provided in the Supplementary Information (Fig. S1). The total mass of the 4 pairs of electrodes were 2.56 g and 4.29 g for PACMM and FM 10 K, respectively.

2.2. Experimental methods and design

NaCl solutions were used as the model feed solution throughout the study. The feed solution was stored in a 10L feed tank with constant nitrogen purging to minimize the oxygen content for mitigating electrode oxidation. The feed solution was pumped through the MCDI stack by a peristaltic pump and the effluent of MCDI stack was sent back to the feed tank. The conductivity of the effluent was measured by a flow-through conductivity meter (isoPod EP357, eDAQ, Australia) installed right at the exit of the stack, which was further converted into salt concentration according to a pre-established calibration curve (Fig. S2). Although pH fluctuation has been observed in previous CDI experiments due to possible oxidation/reduction of the carbon electrodes (Dykstra et al., 2017; He et al., 2016), the measured concentrations of H^+ or OH^- in the effluent was orders of magnitude lower than the NaCl concentration used in our experiments. It is therefore reasonable to assume that the removal of NaCl by a pair of electrodes is symmetric, i.e., equal amount of Na^+ and Cl^- ions are removed in the CDI system. Desalination performance was evaluated with constant current charging and zero-voltage discharge as controlled using a potentiostat (SP 150, Bio-Logic, France) that recorded the real-time current and cell voltage.

To obtain a kinetics-energetics trade-off curve, we conducted MCDI experiments with different current densities and evaluated the ASAR (mg g min^{-1}), which represents the kinetic efficiency, and SEC (J mg^{-1}), which represents the energy efficiency. Previous studies using different current densities adopted an operation protocol that used a constant flow rate and terminated the charging when the cell voltage reached a pre-determined value (Zhao et al., 2012; Kim and Yoon, 2015). However, such a protocol led to