

Contents lists available at ScienceDirect

### Chemical Engineering Journal



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

# Simultaneous analysis of electrosorption capacity and kinetics for CDI desalination using different electrode configurations



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#### G R A P H I C A L A B S T R A C T



#### ARTICLE INFO

Keywords: Desalination CDI Optimized salt removal Electrode configuration Polyaniline activated carbon

#### ABSTRACT

Capacitive deionization (CDI) offers an affordable technology for the reduction of salt concentrations in brackish water. However, there are still drawbacks concerning electrode capacity and energy consumption, compared to other well-established technologies such as reverse osmosis or electrodialysis. This study investigates high-ad-sorption electrodes based on polyaniline-activated carbon, applying different configurations (symmetric and asymmetric electrodes, and membrane CDI) to optimize electrosorption capacity and energy consumption. A new approach called *OSR* (optimized salt removal) is proposed, based on simultaneous analysis of the electrosorption capacity and the adsorption/desorption kinetics. This technique was used to evaluate different electrode configurations. The best performance was obtained using MCDI, which improved the electrode capacity from 14.9 to 20.0 mg g<sup>-1</sup>, while reducing the specific energy consumption by 21%. It was demonstrated that the performance of the electrosorption and desorption curves using a pseudo-first order kinetic model and applying the *OSR* method showed that the best desalination was achieved using MCDI at 1.2 V. This configuration did not present the highest *SAC* or the fastest electrosorption/desorption kinetics, but a good balance was obtained between these two variables.

#### 1. Introduction

Capacitive deionization is a low-cost technology that can be used for the desalination of brackish water (with salt concentration lower than  $10 \text{ g L}^{-1}$ ). Recent advances in electrode materials and energy efficiency

make CDI competitive with other well-established technologies such as reverse osmosis or reverse electrodialysis [1]. The main advantage of CDI is the low energy consumption resulting from the use of low cell voltages (1.2–1.4 V) for desalination [2]. This process employs the electric double layer (EDL) formed inside the pores of carbon electrodes

http://dx.doi.org/10.1016/j.cej.2017.09.067 Received 6 September 2017; Accepted 9 September 2017 Available online 11 September 2017 1385-8947/ © 2017 Elsevier B.V. All rights reserved.

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for ion storage when a potential bias is applied. Therefore, properties of the material such as specific surface area (SSA), pore size distribution (PSD), and conductivity have important effects on desalination performance [3]. In addition, the electrode wettability, which is highly dependent on the surface groups of the material, plays a crucial role in the electrode capacity, since greater hydrophilicity of the electrode enables easier access of water to the pores [4,5].

The development of new low-cost electrodes is still challenging. Several electrode materials have already been studied in attempts to increase desalination capacity and the kinetics of electrosorption, while reducing energy consumption. Nitrogen-doped activated carbons (Ndoped AC) offer high performance electrode materials, due to the high specific adsorption capacity (SAC) attributed to surface nitrogen groups, which promotes salt adsorption and increases conductivity [6]. For example, N-doped graphene and N-doped graphene sponge presented SAC values of 21.9 and 21.0 mg  $g^{-1}$ , respectively, while a value of 16.1 mg  $g^{-1}$  was obtained using N-doped carbon sponge derived from cotton [6-8]. Although these capacities are impressive, the cost of these electrodes, related to the high activation temperature and nitrogen doping with ammonia [8], means that they remain too expensive for large-scale applications. Another procedure to obtain N-doped AC is the use of precursors containing nitrogen atoms, avoiding the expense associated with doping using NH3. To this end, glucosamine hydrochloride [9], polyacrylonitrile [10], polyaniline (PAni) [11-13], and polypyrrole [14] have been investigated as N-doping precursors.

Although the search for materials with high electrosorption capacity has intensified in the CDI field, the electrode kinetics has been little explored. Despite the paramount importance of the electrode *SAC*, the electrosorption and desorption kinetics can be decisive, since this influences the number of cycles possible in a given operational time. For instance, an inexpensive electrode with poor or moderate *SAC* can achieve good desalination performance if the electrosorption and desorption kinetics are sufficiently fast. Therefore, optimization of the electrosorption time could enable a greater number of adsorption/ desorption cycles in the same operational time, resulting in the electrode performance being comparable to that of an electrode with higher *SAC*.

The modified Ragone plot proposed by Kim and Yoon [15] provides an important tool for simultaneous evaluation of the electrosorption capacity and the kinetics of the process, but it only considers the average salt adsorption rate (*ASAR*), without taking the desorption time into account. To the best of our knowledge, the present work is the first to describe a new approach, called *OSR* (optimized salt removal), for analysis of CDI electrode performance, simultaneously considering both the electrosorption capacity and the electrosorption and desorption kinetics. Instead of a plot, this method considers an optimized value for the mass of salt removed during a given operational time. The *OSR* method was used to evaluate different electrode configurations, facilitating their comparison and providing an easy way to identify the most promising desalination process.

Desalination was carried out with an N-doped AC electrode previously prepared using a PAni precursor. The AC derived from PAni (PAC) was chosen due to the advantages of PAni as an AC precursor, including low monomer cost, ease of synthesis, and high nitrogen content (~15 wt%), as well as the similarity of its structure to graphite, which facilitated the insertion of nitrogen into the carbon matrix. In a previous study, Zornitta et al. [16] successfully synthesized PAC derived from PAni doped with different anions (PAC) and obtained high-performance electrodes for CDI desalination. Using PAni doped with p-toluenesulfonate as precursor, the AC electrodes (PAC/PTS) showed high electrosorption capacity (14.9 mg g<sup>-1</sup> at 1.4 V). The electrodes were modified by surface treatment and were used in symmetric and asymmetric configurations and in membrane CDI. The best electrode configuration was determined considering the desalination performance in terms of *OSR* per day.

Recent studies have found that the use of asymmetric electrodes

improves desalination performance for two main reasons: (i) shift of the  $E_{pzc}$  of the electrodes, which maximizes the effective electrode potential used to adsorb ions [17,18]; and (ii) introduction of additional attractive forces that act to remove the ions from the electrolyte solution [19]. This strategy has been reported to optimize SAC, even in longterm experiments [18]. Another strategy widely employed to enhance CDI performance is the use of ion-selective membranes (MCDI) to improve charge efficiency [20]. In a typical CDI process, most of the electrosorption occurs within the carbon particles (in the micropores and mesopores), while the contribution of the macropores to the EDL is negligible [21]. During electrode polarization, co-ions (ions with the same charge as the polarized electrode) are repelled from the micropores, but are inhibited from leaving the electrode due to the presence of the membrane. Hence, these co-ions remain stored in the macropores in order to maintain electroneutrality, and more counterions are removed from the electrolyte. Therefore, part of the charge that would be wasted in eliminating the co-ions is compensated by the use of the macropores as reservoirs of counterions. Different to conventional CDI, in which the charge efficiency is far from unity due to the elimination of co-ions, MCDI usually presents high charge efficiency values [20,21].

In summary, in this study, symmetric and asymmetric CDI and MCDI were employed along with PAC electrodes in an attempt to maximize charge efficiency, increase electrode capacity, and reduce energy consumption. The different configurations were evaluated in a desalination process, employing a new methodology for simultaneous analyses of *SAC*, electrosorption kinetics, and desorption kinetics.

#### 1.1. Simultaneous analysis of electrosorption capacity and kinetics

In a CDI process operating under real conditions, both electrosorption and desorption processes must be considered when selecting the best electrodes for desalination, with the electrode kinetics and capacity being most important in terms of electrode performance. In the CDI field, electrode capacity is commonly evaluated using the salt adsorption capacity (SAC), which is the amount of salt removed per active mass of the carbon electrode. The kinetics of electrosorption can be evaluated using techniques such as the CDI Ragone plot [15] and pseudo-first or second order models [22-30]. The CDI Ragone plot provides information about SAC, ASAR, and the electrosorption time, with optimization of both parameters obtained from the top-right position in the plot. The fitting of electrosorption data using pseudo-first and second order kinetic models provides numeric information from the kinetic constant. It is widely accepted that this way of evaluating kinetics provides accurate information (high correlation coefficients) and is a straightforward technique for comparison of electrode kinetics.

Here, equations were developed in order to maximize electrode capacity by optimizing the electrosorption time, considering both capacity and kinetics. It has been widely reported that pseudo-first order kinetics provides good fits to CDI electrosorption data, so the development of the equations was based on fitting using the pseudo-first order kinetic model (Eq. (1)). Nevertheless, it is also possible to use other fittings, such as the pseudo-second order kinetic equation, as shown in the Appendix.

$$C_0 = C_0 \exp(-kt) \tag{1}$$

In order to describe both electrosorption and desorption using an exponential relationship, the variation of the electrode capacity in terms of *SAC* was modified using Eq. (2):

$$SAC'(t) = SAC_m - SAC(t) \tag{2}$$

In this equation, SAC'(t) is the difference between the maximum SAC ( $SAC_m$ ) and SAC at a given time t.

Fig. 1 illustrates a typical *SAC*'(t) curve fitted to Eq. (1). In order to provide both electrosorption and desorption curves in the same figure, Eq. (1) was rewritten as Eqs. (3) and (4), where t(t) was replaced by *SAC*'(t) and *SDC*(t) (salt desorption concentration), respectively,  $C_0$  was

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