Desalination 258 (2010) 159–163

Contents lists available at ScienceDirect

Desalination

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

Electrode reactions and adsorption/desorption performance related to the applied potential in a capacitive deionization process

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ARTICLE INFO

Article history:
Received 7 September 2009
Received in revised form 7 March 2010
Accepted 11 March 2010
Available online 10 April 2010

Keywords:
Desalination
Capacitive deionization
Carbon electrode
Electrode potential
Salt-removal efficiency

ABSTRACT

Desalination experiments were performed by constructing a capacitive deionization (CDI) unit cell with a carbon electrode prepared from activated carbon powder (ACP). Through CDI experiments, the mechanism of adsorption, desorption and electrode reactions were investigated by measuring conductivity, effluent pH, and the current passed through the cell under different electrode potentials. The salt-removal efficiency increased with increasing potential at the range of 0.8–1.5 V. Additionally, the pH of the solution varied significantly with a change in potential. At potentials less than 1.0 V, the pH increased due to the reduction of dissolved oxygen and the pH decreased at potentials over 1.2 V due to oxidation reactions at the anode. The change in current revealed that adsorbed ions were not completely desorbed and a fraction of ions were retained at the carbon electrode. These accumulated ions were re-adsorbed at the electrode surface when a potential was re-applied, which led to a decrease in the salt-removal efficiency of CDI.

1. Introduction

Due to the recent focus on issues related to energy and the environment, the study of capacitive deionization (CDI), a salt-removal technology, is actively pursued [1–3]. CDI uses the principles of ionic adsorption on the electrode surface due to electrostatic force. When the electrode is charged, ions with opposite electric charge move to the electrode and form an electric double layer (EDL). When the electrode is discharged, ions are desorbed from the electrode surface and move back into bulk solution [4].

The CDI process is simple to operate because ions can be readily adsorbed or desorbed by changing the potential of the electrode. CDI is an environmentally friendly process because contaminants are not produced during the regeneration of electrodes. Energy consumption is also greatly reduced because CDI is operated at a low potential and electrolysis does not occur at the electrode [5–8].

Most studies related to CDI have focused on the preparation of electrodes in order to increase capacitance. Various carbon materials with a high specific surface area and good conductivity have been used to produce electrodes for CDI. High-performance carbon electrodes have been developed with materials such as carbon cloth, carbon nanotubes, and carbon aerogels [9–15].

To increase the capacitance of the electrode, the efficiency of salt-removal in CDI must be improved. However, even if an electrode has a constant capacitance, the efficiency of salt-removal can vary greatly depending on the mechanism of adsorption and desorption on the electrode surface. If all ions adsorbed onto the electrode cannot move back into the bulk solution during the desorption process, the ion concentration on the electrode surface will increase. Thus, when a potential is applied, ions present on the electrode surface are re-adsorbed onto the electrode and the amount of ions transported into the bulk solution is reduced, leading to lower salt-removal efficiency. Therefore, the mechanisms of ion adsorption and desorption, which are related to the applied potential, effect the efficiency of desalination in CDI, and information regarding these processes can be used to improve performance. While most studies related to CDI have focused on improving the performance of the electrode, to date, there have been almost no studies on ionic adsorption and desorption mechanisms relating to the applied potential.

CDI should be operated at the highest possible potential to adsorb more ions onto the electrode. However, an increase in electrode potential is limited because electrode reactions can occur at higher potentials, which not only decrease the efficiency of salt-removal, but also cause serious problems in CDI operation. For example, if hard species or heavy-metal ions are present in the influent, scale can be deposited on the electrode surface as the pH increases. While electrode reactions are obviously an important factor in CDI, to date, no reports on the interpretation of electrode reactions have been published.

In this study, a salt-removal experiment was performed with a CDI unit cell made with a carbon electrode prepared from activated carbon powder. Salt-removal efficiency and electrode reactions were investigated in relation to the applied potential by measuring the electrical conductivity and effluent pH at different applied potentials.

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0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.03.020

Adsorption and desorption performances were analyzed by interpreting the correlation between the current passed through the cell and the conductivity of the effluent.

2. Experimental

2.1. Fabrication of porous carbon electrode

To fabricate a carbon electrode, a carbon slurry was prepared by mixing activated carbon powder (P-60, Daedong AC Corp., specific surface area = 1260 m^2/g) and poly(vinylidene fluoride) (PVdF, M.W. = 530,000, Aldrich) dissolved in dimethylacetamide (DMAc, Aldrich). The mixture was stirred for 12 h to ensure homogeneity. The slurry was then cast onto a graphite sheet (F02511, Dongbang Carbon Corp., Korea) using a doctor blade. The coated electrode was dried at 50 °C in a drying oven for 2 h and then in a vacuum oven at 50 °C for 2 h to remove all organic solvents remaining in the micropores of the electrode. The PVdF polymer content of the dried carbon electrode was 10 wt.%.

2.2. Capacitive deionization experiments

Capacitive deionization experiments were conducted in a flow-through system, depicted in Fig. 1. The system consisted of a reservoir, peristaltic pump, CDI unit cell, and conductivity meter. The CDI unit cell consisted of two parallel carbon electrode sheets separated by a non-conductive spacer (nylon cloth, 100 μm thick). This prevented an electrical short and allowed liquid to flow. The size of the carbon electrode was 100 mm × 100 mm. Graphite sheets were used as inert current collectors on the back side of the carbon electrodes. A Plexiglas plate was used to assemble the upper and lower parts of the unit cell.

A flow channel was created by punching a hole with a diameter of 1 cm in the center of the electrode so that the solution was in contact with all sides of the electrode and could flow through a spacer to the central hole. A solution with 200 mg/L NaCl was supplied to the cell using a peristaltic pump at a flow rate of 20 mL/min.

A given potential was applied to the CDI cell using a potentiostat (WPG100, WonA Tech Corp.). An adsorption test was conducted while applying a pre-established potential for 10 min and a desorption test was conducted for 5 min immediately following the adsorption test by changing the electrode potential to 0 V. The conductivity and pH of the effluent passing through the cell were measured by connecting a conductivity (CON-BTA, Vernier Corp.) and pH sensor (Orion 8102BNUWP, Thermo Electron Corp.) to the exact location of the cell where the solution was released. The conductivity and pH were automatically measured at intervals of 1.0 s by connecting the conductivity and pH sensor to the interface (LabQuest, Vernier Corp.). CDI was conducted at 0.8, 1.0, 1.2, and 1.5 V potentials to compare the efficiency of salt-removal at these potentials.

3. Results and discussion

3.1. Conductivity changes of effluent with varying applied potential

Fig. 2 shows the conductivity of the effluent as the applied potential was varied from 0.8 to 1.5 V.

As soon as a potential was applied, conductivity was abruptly reduced as ions were adsorbed onto the surface of the electrode. As the potential increased, a further reduction in conductivity was observed. When potentials of 0.8, 1.0, 1.2, and 1.5 V were applied to the CDI cell, the conductivities were reduced by 112, 94, 63, and 29 μS/cm, respectively. The conductivity increased slowly as the sorption capacity of the electrode became saturated. As calculated from conductivity results, the amounts of NaCl adsorbed over 10 min under varying potentials were 5.64, 8.24, 12.22, and 15.42 mg, respectively. Thus, the amount of NaCl adsorbed increased linearly as the potential increased.

Changes in the conductivity of effluent during desorption are also shown in Fig. 2. Here, a potential was applied for 10 min and a desorption potential of 0.0 V was applied immediately after adsorption. Conductivity rapidly increased after the desorption potential was applied, as ions were immediately desorbed. The amount of desorbed ions increased according to the prior adsorption potential and when 1.5 V of potential was applied, the conductivity increased up to 2653 μS/cm during desorption. In the desorption process, most of the adsorbed ions were desorbed within 2 min of applying a desorption potential. This indicates that desorption proceeded rapidly and the regeneration of the electrode during CDI was facile. Thus, the recovery ratio of the influent can be increased by reducing desorption time.

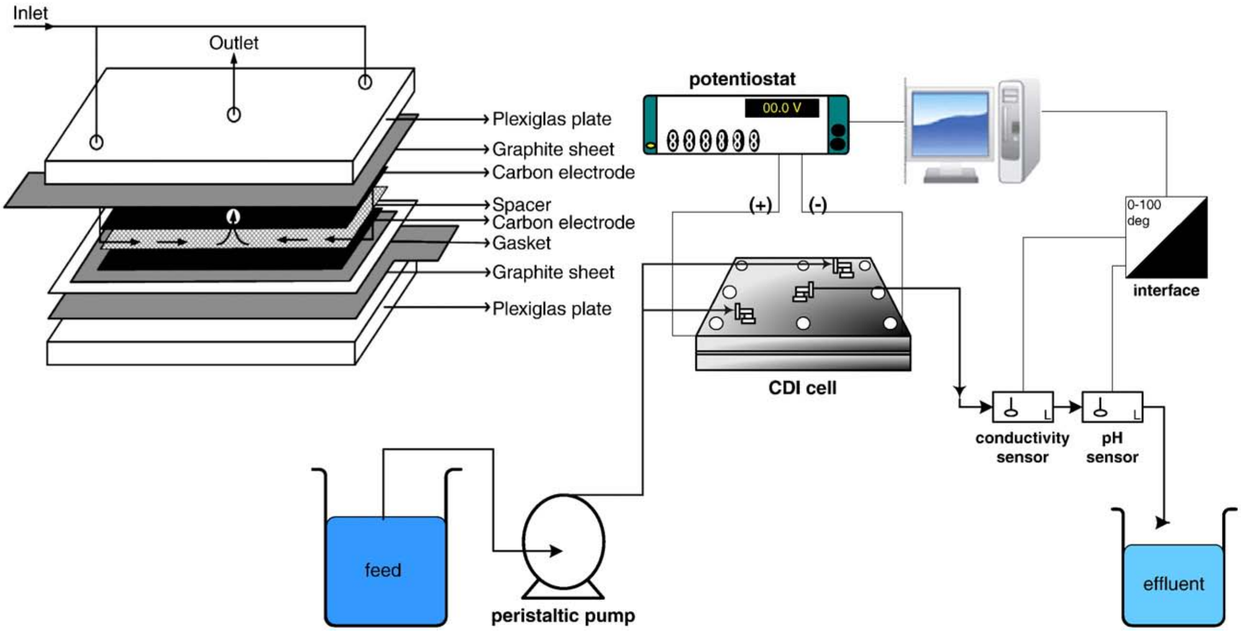

Fig. 1. Schematic diagram of capacitive deionization (CDI) experiments.