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Desalination by capacitive deionization process using nitric acid-modified activated carbon as the electrodes

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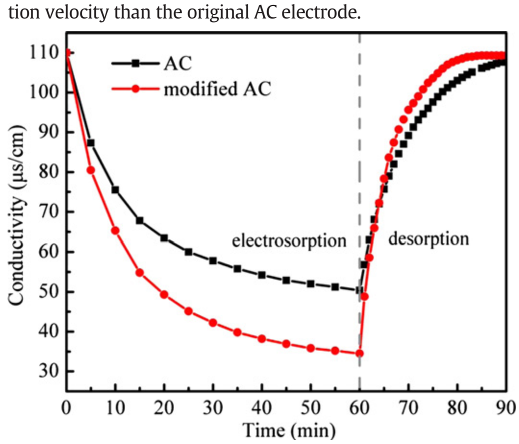
HIGHLIGHTS

- Nitric acid modified AC electrode achieved a higher desalination.
- The modification increased the sorption rate of electrolytic ions.
- The improvement was due to lower resistance and more oxygen functionalities.

GRAPHICAL ABSTRACT

The electrosorption/desorption of the CDI process at batch tests showed that the nitric acid modified AC achieved a higher desalination than the original AC as the electrodes. Also, the modified AC electrode had a much higher desorption velocity than the original AC electrode.



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ABSTRACT

In this work an activated carbon modified by nitric acid has been used as the electrodes in capacitive deionization (CDI) process for the desalination of an aqueous electrolytic solution. The experimental results have shown that the modification could greatly increase the salt removal from the solution. The desalination efficiency was increased about 15%, and the desalination kinetics was improved in the form of rate constant from 0.09208 to 0.09922. It has been found that the modification greatly increased the oxygen-containing functional groups on the surfaces of activated carbon, leading to the increases of the capacitance and the reduction of the charging resistance, which might be attributed to the improvement of the desalination.

1. Introduction

Capacitive deionization (CDI) is an electrosorption technology that developed recently for desalination. Ions are attracted to electrodes and then adsorbed electrostatically onto the surface when an electric

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potential is applied. Once the electric potential is off, the adsorbed ions are quickly released back into bulk solutions [1,2]. In this process the key point is the electrodes. Activated carbon (AC) is a commonly used material as the electrode for CDI because of the low cost and high specific surface area [3,4]. Recently, other carbon materials, such as carbon aerogels (CA) [5], carbon nanotube (CNT) [6] and graphene [7,8], have also been developed for effective CDI electrodes.

Normal activated carbons feature low capacitance, leading to a low ion removal, which limits the large-scale industrial application of CDI process. Accordingly, many studies have been conducted to improve the desalination performance of AC electrodes. It was reported that the improvement could be realized by adding a certain amount of mesoporous conductive carbon blacks [9], and by coating ion-exchange polymers on the electrode [10]. Surface modification of AC electrodes is another effective method to improve the desalination efficiency, which could be realized by the treatment using anhydrous ethanol solution containing metal alkoxides (such as titanium butoxide) [11–13], nitric acid [14,15], potassium hydroxide [16], sulfuric acid [17,18], sodium hypochlorite [19], permanganate [20], and hydrogen peroxide [18]. In this work, nitric acid-modified AC as the CDI electrodes was studied in order to improve CDI desalination. The objective is to obtain the understanding of the desalination performance and mechanisms of the modified AC as the electrodes in CDI process.

2. Material and methods

2.1. Materials

The AC powder used in this work was from the Proveedor de Laboratorios (Mexico). Nitric acid (HNO_3) for AC treatment, sodium chloride (NaCl) for the preparation of electrolytic solution, N-dimethylacetamide (DMAC) and polyvinylidene fluoride (PVDF) as the binder for electrode preparation used in this work were from Sigma Aldrich. The water used was distilled first, and then treated by passing through resin beds and a 0.2 μm filter.

2.2. Nitric acid treatment of AC

First, 10 g of raw AC powder and 100 ml of HNO_3 solution (10 mol/l) were mixed together and stirred for 4 h at 90 °C. Then, the AC powder was separated with filtration. The filter cake was washed with water until the filtrate became neutral. After that, the cake was dried at 60 °C, which was refereed as the modified AC.

2.3. Fabrication of AC electrodes

First, AC slurry was prepared by mixing 10 g of AC powder and 1 g of PVDF in 30 ml of DMAC solution for 4 h. After that, the slurry was uniformly casted on a graphite sheet with a blade to form electrodes with the dimensions of 10 × 3.7 cm. The casted electrodes were dried at 50 °C for 2 h, and then in a vacuum oven for 2 h to remove DMAC residual on the electrode. The weight of the AC electrode was 6 g.

2.4. Desalination test

Desalination tests were carried with a laboratory CDI set-up, which consisted of a CDI cell, a peristaltic pump, a conductivity meter and an external power supply. The schematic diagram of CDI unit cell was represented in Fig. 1. Brackish water circulated in the CDI cell with the volume of 300 ml, while ions absorbed in the electrical double layer on the interface of solution and electrodes if an electric field is applied to the electrodes.

A series of NaCl solutions with conductivities of 52, 110, 204, 510, 1020 μS/cm pass through the set-up in the flow rate of 25 ml/min at the voltage of 2 V. The conductivity of the solution at a given time was recorded, by which desalination efficiency can be calculated according to following equation:

$$\text{Desalination efficiency} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

where C_o and C_t are the initial conductivity and the conductivity at the duration of t, respectively.

2.5. Measurements

The specific surface area of the samples was determined by using a Quantachrome Autosorb-1 gas adsorption analyzer (USA) based on the BET method. A Thermo Nicolet Nexus Fourier Transform Infrared (FTIR) spectrometer (USA) was used to identify the chemical structure and the functional groups presented on the AC samples.

X-ray photoelectron spectra (XPS) for the determination of surface functional groups were obtained by using a Thermo Electron VG Multilab 2000 XPS analyzer (USA).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) that were obtained by using an Autolab PGSTAT30 electrochemical workstation (Netherlands) were used to examine the electrochemical properties of AC electrodes. In the measurements, the original AC and modified AC electrodes were used as the working

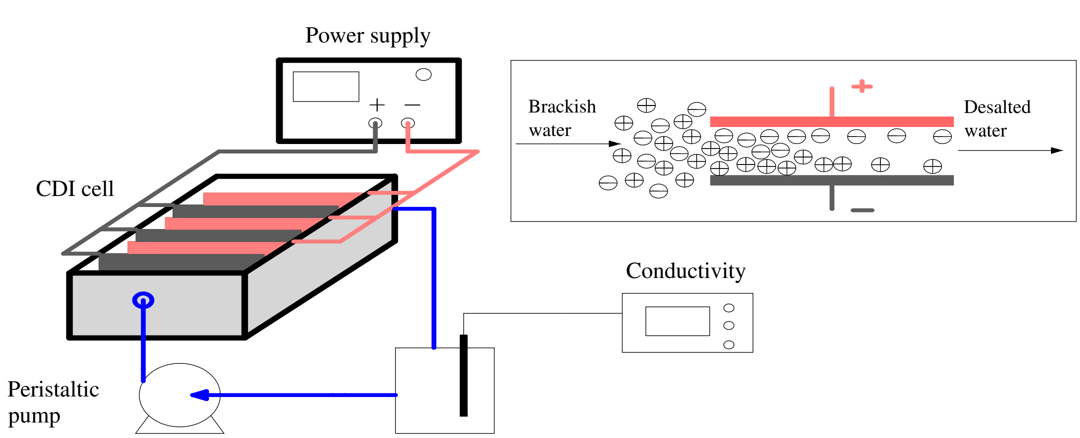

Fig. 1. Schematic representation of the CDI unit cell.