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Desalination of water with high conductivity using membrane-free electrodeionization

Xiaolan Shen, Tianjun Li, Xiaping Jiang, Xueming Chen *

Environmental Engineering Department, Zhejiang University, 388 Yuhangtang Road, Hangzhou 310058, China

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ABSTRACT

Our previous work has shown that membrane-free electrodeionization (MFEDI) is a promising process for high purity water (HPW) production. However, this technique was only suitable to feed water with low conductivity, usually below 20 μs/cm. To extend the applicable range, type I strong base resin was used together with type II strong base resin in this work, due to the high capacity and easy regeneration of type II strong base resin and the excellent purification performance of type I strong base resin. It was demonstrated that although the conductivity of the feed water increased to 50 μS/cm, effective purification was still achieved, with effluent conductivity being 0.056–0.066 μS/cm only. The average conductivity of the concentrate collected during regeneration was over 380 μS/cm, indicating high regenerating efficiency. The water recovery reached 86% and the power consumption was 1.5 kW h/m^3 water. In addition, repetitive experimental results showed that the MFEDI system could work stably.

1. Introduction

Nowadays, HPW is widely used in semiconductors and pharmaceuticals production, electric power generation, and chemical and biochemical laboratories [1–4]. With the rapid development of relevant industries, the demand for HPW is increasing greatly. Generally, HPW production involves in a series of operations. Among them, the mixed bed ion exchange (MBIE), which works as a polishing step, plays a very important role in ensuring the quality of HPW [5]. In despite of high efficiency [6], MBIE requires periodical regeneration using alkali and acid. This produces concentrated waste stream containing high concentration of strong acid, strong alkali and salt. Furthermore, the operations of resins separation, respective regeneration of anion and cation exchange resins and remix of the resins are laborious [7–11].

An alternative technique to MBIE is electrodeionization (EDI), which is a hybrid system combining ion exchange (IE) and electrodialysis (ED). EDI has many advantages including no need of chemicals to regenerate the ion exchange resins, environmental friendliness and easy operation [12–15]. Nevertheless, EDI needs selective ion exchange membranes, and thus a series of membrane-associated problems, such as concentrating polarity, chemical precipitation, and membrane fouling, may occur [16–19].

In our previous work, a novel MFEDI process was investigated for high purity water production [20]. This process is different from the electrically regenerated ion exchange invented by Davis and Hills [21] that used ion exchange fabrics and had a complex configuration. It is also different from the one reported before by our group [22] that required at least a pair of ion exchange membranes.

MFEDI is operated in batch, that is, the purification and electrical regeneration are alternated. The purification process is illustrated below:

$$R-H+Na^+ \rightarrow R-Na+H^+ \quad (1)$$

$$R-OH+Cl^- \rightarrow R-Cl+OH^- \quad (2)$$

where R–H represents H-type cation exchange resin and R–OH represents OH-type anion exchange resin. After the effluent conductivity is over a specific value, electricity is supplied to restore the exchange capacity of the resin. Hereafter, high concentration of hydrogen ions and hydroxide ions are produced by water dissociation and water electrolysis. These ions would exchange with salt ions in resin phase to regenerate the resin. The electrical regeneration process is described below:

$$H_2O \rightarrow H^+ + OH^- \quad \text{electrically enhanced water dissociation} \quad (3)$$

$$2H_2O-4e \rightarrow 4H^+ + O_2\uparrow \text{ at the anode} \quad (4)$$

$$2H_2O+2e \rightarrow 2OH^- + H_2\uparrow \text{ at the cathode} \quad (5)$$

* Corresponding author. Tel.:+86 57187951239; fax: +86 57187952771.
E-mail address: chenxm@zju.edu.cn (X. Chen).

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$$OH^- + R - Cl \rightarrow R - OH + Cl^- \quad (6)$$

$$H^+ + R - Na \rightarrow R - H + Na^+ \quad (7)$$

The MFEDI process shows many advantages. Firstly, membranes are not used in MFEDI system and problems associated with membranes can be avoided. Secondly, MFEDI combines the advantages of MBIE and EDI: on the one hand, the conductivity of the MFEDI effluent is close to pure water; on the other hand, ion exchange resins in MFEDI column can be regenerated electrically in situ and the concentrates produced during regeneration can be recycled to RO. Furthermore, the operation and configuration of MFEDI are simpler than MBIE and EDI.

However, MFEDI was only suitable to feed water with low conductivity, usually below 20 μS/cm. To extend the applicable range, type I strong base resin was used together with type II strong base resin in this work. As we know, type I strong base resin is superior in purification. Nonetheless, this type of resin is low in capacity and difficult to be regenerated. On contrast, type II strong base resin is high in capacity and easy in regeneration, but it is poor in purification. The combination of the two types of strong base resins allows the full use of their advantages. In the purification stage, the large capacity of type II strong base resin helps to absorb more ions, and the excellent purification performance of type I strong base resin assists to guarantee the HPW quality; in the electrical regeneration stage, the good regeneration property of type II strong base resin facilitates restoring more capacity.

The major objectives of this study are to evaluate the performance of the resins selected for producing HPW from the water with high conductivity, to examine the efficiency of the electrical regeneration, and to investigate the resins stability.

2. Materials and methods

2.1. Resins pretreatment

Main physiochemical properties of the gel-type strong-base cation exchange resin (Monosphere 550A, Dow Co., Shanghai, China), gel-type strong-base II cation exchange resin (Monosphere 202, Zhengguang Co., Hangzhou, China) and macroporous-type weak-acid anion exchange resin (Monosphere D113, Zhengguang Co., Hangzhou, China) are presented in Table 1. Before use, type I strong base resin and type II strong base resin were washed with deionized water until neutral pH, and weak acid resin was first soaked in 4% NaOH for 6 h, then washed with deionized water, regenerated fully with 5% HCl, and finally washed with deionized water again.

2.2. Electrodes preparation

Mesh electrodes used in MFEDI system were prepared as following: $H_2PtCl_6{\cdot}H_2O$ (99%, Adamas Reagent Co., Shanghai, China) was dissolved in isopropanol (99.5%, Adamas Reagent Co., Shanghai, China) with a concentration of 0.5 M [23]. Titanium meshes, 3 cm in diameter, with an effective area of 7.1 cm^2, were used as substrates. The electrodes were fabricated using a thermal decomposition method. The detailed fabrication procedures can be found elsewhere [24].

2.3. Experimental setup for equilibrium investigation and resistivity measurement

The experimental setup for equilibrium investigation and resistivity measurement is shown in Fig. 1. A pair of Ti/Pt electrodes was installed in a column, which had a diameter of 3 cm. The net spacing of the electrodes was 3 cm, and about 30 mL of mixed ion exchange resins including 10 mL of cation exchange resin and 20 mL of anion exchange resin, were packed between the electrodes. A spring was used to compress the resin layer. A reservoir was used to store the circulation solution. The solution temperature was maintained using a water bath. Nitrogen gas was purged into the solution to eliminate the interference of the carbon dioxide.

The equilibrium investigation was conducted in a cyclic manner including an adsorbing stage and a releasing stage. Initially, 600 mL of 0.5 M NaCl solution was circulated to the system and no electricity was supplied. After the ion exchange equilibrium reached, that is, the solution conductivity was unchanged any more, DC electricity was supplied to the resin layer at a current density of 280 A/m^2 until a new equilibrium reached. The resistivity was measured by examining the variation of voltage with current density.

2.4. MFEDI system

The MFEDI system for HPW production is schematically shown in Fig. 2. The inner diameter of the MFEDI column was also 3 cm. The whole column was divided into two parts: the lower part, 70 cm in effective height, was packed with the mixed weak acid and type II strong base resins with a ratio of 1:2; while the upper part, 30 cm in effective height, was packed with the mixed weak acid and type I strong base resins also with a ratio of 1:2.

The MFEDI system was operated in a batch mode including a purification stage and a regeneration stage. In the purification stage, no electricity was supplied, and 50 μS/cm NaCl feed solution passed the MFEDI column upward with a flow velocity of 10 m/h; in the regeneration stage, electricity was supplied at a constant voltage of 1400 V, and deionized water passed the MFEDI column downward with a flow velocity of 15 m/h. To improve regeneration efficiency and to neutralize the concentrate, the electrodes were reversed during regeneration. In the first 20 min of the regeneration, the top electrode worked as a cathode and the bottom electrode worked as an anode. In the latter 40 min of the regeneration, the top electrode worked as an anode and the bottom electrode worked as a cathode.

2.5. Analysis

Conductivity was measured using a conductivity meter (Orion 3 Star, Thermo Scientific, Singapore, for MFEDI effluent, resolution: 0.001 μS/cm; and Sension 5, Hach, OH, for the others, resolution: 0.01 μS/cm). pH values and Na^+ concentrations were measured using a pH/ISE meter (Orion Dual StarTM, Thermo Scientific, Singa-

Table 1
Properties of ion exchange resins.[a]

Designation	Type	Matrix structure	Functional group	Capacity (mol/L)
D113	Weak-acid	Polyacrylic acid	Carboxyl	4.3
550A	Type I strong-base	Polystyrene	Quaternary amine	1.4
202	Type II strong-base	Polystyrene	Quaternary amine	1.3

[a] Obtained from manufacturers.