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Effect of operational conditions on post-treatment of RO permeate of geothermal water by using electrodeionization (EDI) method

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ABSTRACT

With the growing of electronics, semiconductors, food and pharmaceutical manufactures, the need of water quantity with high purity is increasing. The water quality needed should be with high electrical resistance and free of weakly ionized dissolved species. Integration of separation processes such as reverse osmosis (RO) and electrodeionization (EDI) was proven to be successful to produce water with high quality. This paper is about the applicability of EDI method for post-treatment of RO permeate of geothermal water. For this purpose, the effects of process parameters such as feed flow rate, electrical potential applied, type of ion exchange membranes, and cell number on reduction of electrical conductivity and the contents of boron, silicon and arsenic in EDI product water were investigated. In addition, pseudo first order and pseudo second order kinetics models, infinitive solution volume (ISV) and unreacted core (UCM) models were applied to determine the rate controlling steps of the removal of electrical conductivity and boron by EDI process. Obtained results revealed that a EDI product water containing $^{<}$0.20 mg B/L, $^{<}$0.05 mg Si/L and $^{<}$0.10 μg As/L was produced using a multi-cell EDI in which ion exchange resins in mixed bed configuration is placed between Neosepta CMX-AMX ion exchange membrane pair. These results were obtained when the optimum flow rate of 1.08 L/h and electrical potential of 20 V were applied to multi-cell EDI. At the optimal operational conditions, boron removal was found to be governed by second order kinetic model and the determining steps were film diffusion and liquid film according to ISV and UCM models, respectively. It was observed that thick ion exchange membranes were better than thin ion exchange membranes for polishing RO permeate of geothermal water by using EDI process.

1. Introduction

Various modern industrial applications require water quality free of weakly ionized species. The commonly concerned species vary from one industry to another. Generally, water purity preferred in most of the industrial applications is water with high electrical resistance and without silica, boron and arsenic contents. In electronics industry, silica is reported to have an impact of the material used, device performance and final product yielded [1,2]. Lower reliability of the oxide of the thermal growth, phosphor silica fog, voltage threshold variation and plasma breakdown are the drawbacks of using water containing silica in electronic industries [3]. The quality of the electronic tubes and solid state circuits is affected by silica present in water used in the manufacturing process. Because of its toxicity, arsenic is rigorously restricted in drinking water and food. Arsenic exists in different compartments of the environment in the form of inorganic and organic arsenics. The arsenic toxicity depends of the form in which it is present, the concentration level and the time of exposure. Inorganic arsenic compounds such found in water are more toxic than organic arsenic compounds such present in seafood. Arsenic and boron are considered as doping impurities added in silicon to control the electrical conductance of semiconductors. Although boron as one of the p-type impurities in silicon, it provides positively-charged holes to the valence band of semiconductors, much of it is reported to invert the n-type impurities in silicon and has an impact on concentration of carriers [3]. Therefore, ultrapure intended for use in various industrial applications should be free of silica, boron and arsenic.

Traditional separation methods reported for removal of these species from water are coagulation and electro-coagulation processes [4,5], adsorption [6,7], mixed bed ion exchange (IEX) [8–10], electrodialysis (ED) [11–13] and reverse osmosis (RO) [14–17]. However, a single method is not able to remove boron, silica and arsenic to the desired level for ultrapure water grade. Combination of two or more methods is the only choice to reduce these species at ultrapure water

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grade level. EDI itself is a combination of ED and mixed or layered bed ion exchange methods. Due to EDI feed water requirements, a pre-treatment step prior to EDI is necessary. In most cases, a single RO pass before EDI is enough to achieve this task.

In EDI process, the sample solution percolates through the ion exchange (IE) bed placed between a cation exchange and an anion exchange membranes. In dilute compartments of EDI, the resins reduce the sample solution resistance and then enhance the ion transport through ion exchange membranes to the electrodes under an electrical potential gradient. The ion exchange resins also participate in electrochemical reactions during which water is dissociated into proton and hydroxide ions [18]. The significant amounts of proton and hydroxide ions produced during the water splitting take part in electrochemical regeneration of resins and converting them into the forms of H^+ and OH^-. By the fact of water splitting during the EDI process, ion exchange resins are considered as a mixed bed ion exchange column that can be continuously regenerated by exchanging H^+ and OH^- ions with the ions present in dilute solution and adsorbed by the ion exchange resins [18,19]. Another effect of water splitting is that silica and boron in their neutral forms can be converted partially into their ionic forms (Eqs. (1–3)) [3], which leads to their transfer to adjacent concentrating compartments from dilute ones.

$$H_3BO_3 + OH^- \leftrightarrows B(OH)_4^- \quad (1)$$

$$SiO_2 + OH^- \leftrightarrows HSiO_3^- \quad (2)$$

$$HSiO_3^- + OH^- \leftrightarrows SiO_3^{2-} + H_2O \quad (3)$$

According to the recent literature, ultrapure water for semi-conductor industries with less amount of boron and silicon was produced by applying EDI process using RO permeate of water [3]. Demineralization of RO permeate from geothermal water by using EDI was also reported by Arar et al. [20–22]. According to the results obtained by Arar et al. [20], EDI in mixed bed configuration was less efficient for boron and silica removals from RO permeate of geothermal water than layered bed configuration mode.

In the present study, we focused on optimization of EDI operational parameters to improve the performance of EDI system with mixed bed configuration in terms of reduction of electrical conductivity, boron, silica and arsenic from RO permeate of geothermal water. RO permeate suitable of EDI feed was obtained by using a single pass RO operation from geothermal water. The parameters investigated in EDI with mixed bed configuration were feed flow rate, electrical potential, type of membrane and number of cell in EDI module. Moreover, conventional kinetic models (pseudo first order and pseudo second order kinetics models) and diffusional and reaction models (infinitive solution volume (ISV) models and unreacted core model (UCM)) were applied to determine the rate controlling steps for removal of electrical conductivity and boron from RO permeate by EDI method.

2. Materials and methods

In this study, a cross flow flat sheet membrane test unit (SEPA CF-II, GE) was used to obtain geothermal water RO permeate. Geothermal water was obtained from Izmir Geothermal Co. Izmir, Turkey. The RO permeate of geothermal water was produced using AG-BWRO membrane at 30 bar of applied pressure. The RO product water obtained was fed to EDI system. The characteristics of geothermal water and RO permeate were summarized in Table 1.

EDI experiments were carried out using a micro-flow EDI system in mixed bed configuration. The stack can be scaled up to a maximum of 4 cells and the dimensions of the micro-flow cell are 120 mm height, 70 mm width and 38 mm length. The effective area of the membranes inside the cell is 10.2 cm^2 (3.4 cm × 3.0 cm). The gap of the sample flow frame was 4 mm. The volume of solution used in the sample, concentrate and electrode compartments was 1 L. The cathode and anode electrodes were made of Nickel and DSA/O_2 coated on Ti, respectively. While the sample compartment was fed with geothermal RO permeate, the concentrate and electrode compartments were fed with a solution of Na_2SO_4 (± 500 µS/cm). The parameters investigated in EDI were feed flow rates (0.72, 1.08 and 1.80 L/h), electrical potential applied (10, 15, 20, 25 and 30 V), types of ion exchange membrane pairs employed (CMX-AMX, CMB-AMH, CMS-AHA and CMI7000-AMI7001) and cell number (SCEDI, DCEDI, TCEDI and MCEDI). The abbreviations of SCEDI, DCEDI, TCEDI and MCEDI represent EDI modules with single, double, triple and multi cells, respectively. The ion exchange membranes used in EDI system and their technical specifications were given in Table 2. The ion exchange resins placed in EDI dilute compartments and their physico-chemical properties were given in Table 3.

Table 1
Geothermal water and its RO permeate characteristics.

Characteristics	RO feed	RO permeate	LOQ*
EC (µS/cm)	1634–1743	18.1–36.0	–
pH	6.94–7.44	5.42–7.77	–
Na^+ (mg/L)	304–353	5.45	0.06
K^+ (mg/L)	27.1–28.6	< 0.60	0.60
Ca^{2+} (mg/L)	24.9–28.2	< 0.04	0.04
Mg^{2+} (mg/L)	5.15–10.2	< 0.02	0.02
HCO_3^- (mg/L)	724–750	25.9	–
SO_4^{2-} (mg/L)	212–215	0.182	0.15
Cl^- (mg/L)	157–162	2.15	0.31
B (mg/L)	9.82–10.44	3.98–5.36	0.10
Si (mg/L)	61.0	0.71	–
As (µg/L)	192.3	6.68	–

* LOQ: Limit of quantification.

Analyses of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^- and SO_4^{2-}) were performed with an ion chromatography equipment (Shimadzu-Prominence HIC-SP model). Boron was analyzed using Uv-visible spectrophotometer (Shimadzu UV-1800 model) by applying azomethine-H method. The contents of arsenic in the samples were determined by using a Shimadzu AA-7000 Model Atomic Absorption Spectrophotometer with a Hydride Vapor Generation. Silica analysis (as Si) was performed by using a spectrophotometer (Spectroquant Nova 60 spectrophotometer Merck Model).

3. Results and discussion

3.1. Effect of feed flow rate

The effect of feed flow rate on EDI system performance was investigated using EDI module with single cell. The cation and anion resins were placed in dilute compartment in mixed mode configuration. At an applied electrical potential of 20 V, the EDI performances at three different flow rates (0.72, 1.08 and 1.80 L/h) were monitored. As shown in Fig. 1, the conductivity rejection was influenced by the feed flow rate. Lower flow rate did not show a high rejection for conductivity, boron and silica (Table 4). The optimum feed flow rate was found to be 1.08 L/h. Boron and silica seem to be removed in EDI system through the adsorption by resins rather than ion transfer through ion exchange membrane. Similar optimum flow rate was obtained by Arar et al. [21], where a flow rate of 1.0 L/h was reported to be the optimum flow rate for a layered bed configuration system at applied voltage of 40 V. In mixed bed deionization systems, higher performances are normally achieved with longer contact time by reducing sample flow rate. Here different situation was observed due to the presence of electrical field. An increase in contact time in EDI may be achieved by increasing the cycle numbers of solution circulated in sample compartment of EDI, which reduces the effect of electrical field on the target elements. Therefore, an increase in flow rate results in an increase of cycle numbers of the solution in the sample compartment