Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.780800

51 (2013) 6230–6237
September

Taylor & Francis
Taylor & Francis Group

Electrodialysis for desalination of brackish groundwater in coastal areas of Korea

Su Young Choi[a], Jeong Whon Yu[b], Ji Hyang Kweon[a,]*

[a]*Department of Environmental Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea*
Tel. +82 2 450 4053; Fax: +82 2 450 3542; email: jhkweon@konkuk.ac.kr
[b]*Department of Transportation Systems Engineering, Ajou University, Suwon, Gyungki-do 443-749, Korea*

Received 25 October 2012; Accepted 25 December 2012

ABSTRACT

Electrodialysis (ED) with ion-exchange membranes was applied for desalination of salted groundwaters from three places in coastal areas in Korea. The ED system produced high quality of permeate. However, substantial resistance built-up was identified in one particular groundwater sample. Possible causes of the fouling were sought for better understanding of brackish water desalination. Several model samples with different ion composition, that is, Na_2SO_4, $MgSO_4$, $CaSO_4$ at the same conductivity condition, that is, 1,200 μs/cm were tested to understand effects of monovalent and divalent ions on water quality and increases in resistance of the ED system. In addition, organic matter concentrations were compared in the sampled groundwaters. The ED performance of the three model solutions showed similar tendency in operation time and current curve and did not explain the discrepancy of ED performance of the groundwater. Dissolved organic carbon concentration results implied that organic matter in the groundwater played an important role in ED operation.

Keywords: Electrodialysis; Groundwater; Brackish water; Ion removal; Desalination

1. Introduction

Water resources in coastal areas and islands are substantially limited and have been mostly depended on seawater or groundwater under influence of seawater due to the lack of fresh surface water. For instance, Woodo area in Jeju Island, the biggest island in Korea, uses brackish water with total solid concentrations of 18,000 mg/L as intake water for 1,800 people in a village. In addition, brackishness of groundwater and/or surface water has been increasing with time. The phenomena become great significance in Korea due to the fact that three parts of Korean peninsula is surrounded by sea. A document by Korean Rural Community Corporation reported that water quality parameters indicated increases in sea water influences in the most of locations for inspection [1]. The water in coastal areas is salty and thus not directly drinkable. However, in some areas such as India, it is not always sufficiently available [2].

Several desalination processes can be considered including reverse osmosis (RO) membrane desalina-

*Corresponding author.

Presented at The Fifth Desalination Workshop (IDW 2012), 28–31 October, 2012, Jeju, Korea

1944-3994/1944-3986

tion, distillation, and electrodialysis (ED) process. Membrane-based processes for desalination of brackish water are gaining importance in comparison with traditional methods such as distillation process [2–4]. In Korea, 95 plants with membrane processes are being operated in coastal areas to supply water at a capacity of 8,000 m^3/day in 2010. Although RO is rapidly gaining the market share, thermal process still dominates this market due in general to the low cost of fossil-fuel based energy [4]. Several limitations remain in the use of membrane-based desalination technology. One of the major problems is membrane fouling associated with particulate matter, colloids, organic, inorganic compounds, and biological growth in the system. ED with ion-exchange membranes is applied to wastewater minimization, production of ultrapure water, concentration of dilute solutions in addition to desalination of salted waters [4–6]. ED is an electro-membrane process for the separation of ions across charged membranes from one solution to another under the influence of an electrical potential difference used as a driving force. In a typical ED cell, a series of anion and cation exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. When a direct current potential is applied between two electrodes, positively charged cations move toward the cathode, pass through the negatively charged cation-exchanged membrane and are retained by the positively charged anion-exchanged membrane. On the other hand, negatively charged anions move toward the anode pass through the positively charged anion-exchange membrane and are retained by the negatively charged cation-exchange membrane. At the end, ion concentration increases in alternate compartments with a simultaneous decrease of ion concentration in other compartments.

ED has been utilized for over 50 years for the production of potable water from brackish water sources [5]. The basic process has been significantly improved and several ED-related processes such as continuous electrodeionization, diffusion dialysis or capacitive deionization have been developed for a number of new applications in water and wastewater treatment. ED has many advantages such as compact footprint and low cost for installation and operation [6,7]. It was stated that ED could compete with RO system in the range of feed water salinity up to 8–10 g/L only because ED desalination cost is proportional to the amount of salt, which must be passed through membrane [8]. ED has been known to be a robust technology for brackish water and also for the removal of disinfection by product precursors such as bromide and organic matter [8,9]. These characteristics make the technology an attractive complement of RO to reduce the concentrate waste from an inland brackish groundwater desalination plant. Kim et al. performed a research with model simulation and experiments to understand hydrodynamic effects on ED for optimized ED operation [10]. Oren et al. studied a hybrid process combining RO and ED to recover 97–98% of brackish water as product water with chloride levels of 200 mg/L or less. In the process, ED is operated on the RO concentrate [11]. A researcher group in India also developed a system with ED, in which RO was added to increase TDS removal of ED product water [2]. The brackish water with 2,000–4,000 mg/L of TDS was treated to have product water with TDS level of 500 mg/L or less. In recent, ED has been expanded its application extensively to wastewater effluent and groundwater treatment [12]. However, none of a real-scale ED plant has been installed in Korea. Much effort should be made to apply ED to various water sources in Korea.

In this study, groundwater from several places in the coastal areas was sampled and treated with an ED system to assess its implementation as a new desalination process. Substantial resistance built-up was identified in one particular groundwater sample. Possible causes of the fouling were sought for better understanding of brackish water desalination. The ion composition ratio in each sample was compared. Several samples with different ion composition were tested to understand effects of monovalent and divalent ions on water quality and increases in resistance of the ED system. In addition, organic matter concentrations were compared in the sampled groundwaters.

2. Methods and materials

2.1. ED setup

The ED system consists of reservoirs, pumps, and ion-exchange membrane stack, power supply, and data acquisition system as shown in Fig. 1. The ED system was operated at a constant voltage and efficiency was measured as changes in current. The constant voltage mode was used due to the fact that the set-up of the system was fixed by the manufacture, although a constant current mode has been used in general operation. A pump (NH-3PX, Pan World, Ibarakiken, Japan) with a speed of 2,700–3,200 rpm are used to obtain a flowrate of 5 L/min.

2.2. Cell and membranes

The ED cell is packed with five pairs of ion-exchange membranes (cation and anion) and a pair of platinum electrodes (anode and cathode). Both electrodes are made of pure platinum. Area of each

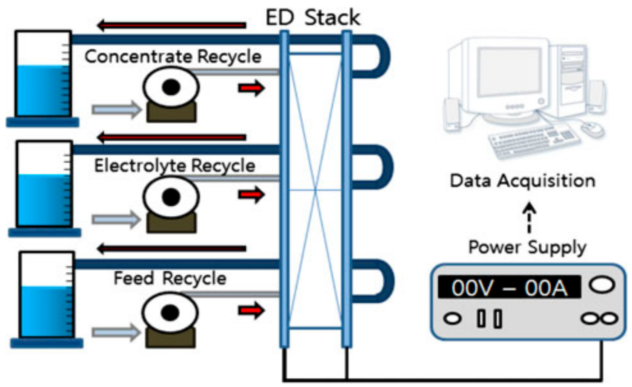

Fig. 1. Scheme of ED system in this study.

electrode is $4.7 \times 10.0\,cm^2$. The ion-exchange membranes are purchased from ASTOM Company (Neosepa, Tokyo, Japan). Neosepa CMX and AMX were used for cation- and anion- exchange membranes, respectively. Each membrane has an effective surface area of $55\,cm^2$. The thickness of CMX and AMX were 170 and 140 μm. Properties of the ion-exchange membranes are summarized in Table 1.

2.3. Feed waters

Three groundwaters were taken from JeBu, SungRoe, and PoSeung located in GyungKi province, Korea, and the water quality was measured and summarized in Table 2. JeBu and SungRoe waters showed greater conductivity than Poseung. Cation compositions for the sample waters were very different. For JeBu water, sodium, magnesium, and calcium evenly contributes the salts concentration and potassium concentration was relatively low. However, SungRoe water shows that most of cations were constituted from sodium ions and other cations was taken up only a small fraction. PoSeung water had relatively greater concentrations for potassium ions.

Table 1
Specification of ion-exchange membranes

	CMX	AMX
Characteristics	High intensity (Na^+)	High intensity (Cl^-)
Electrical resistance	3.0 ohm-cm^2	2.4 ohm-cm^2
Destructive strength	More than 0.40 MPa	More than 0.25 MPa
Thickness	0.17 mm	0.14 mm
Inter-membrane distance	0.73 mm	0.73 mm
Chamber volume	4.0 mL	4.0 mL

Table 2
Water quality of three groundwaters from JeBu, SungRoe and PoSeung

Location	JeBu	SungRoe	PoSeung
Na^+ (mg/L)	268.5	957.4	306.2
Mg^{2+} (mg/L)	177.4	1.24	55.7
K^+ (mg/L)	1.24	30.49	110.2
Ca^{2+} (mg/L)	375.94	41.49	112.7
SO_4^{2-} (mg/L)	81.1	196.8	–
Cl^- (mg/L)	1842.9	1534.9	649.3
HCO_3^{2-} (mg/L)	61	106.3	–
Conductivity (μs/cm)	5,520	5,640	2075
Na^+/Ca^{2+}	1.24	40.2	4.73
Cl^-/SO_4^{2-}	61.5	21.1	–
Cl^-/HCO_3	52.0	–	–

In addition to the measurements in the laboratory, a report from Korea Rural Community Corporation was obtained to evaluate the feed water properties. The annual report presents several water qualities from numerous sampling wells in seashores of Korean peninsula. The report was used to understand seawater influences on the groundwater and to give guidelines for vegetation. The conductivity and mole fraction of chloride vs. bicarbonate ions of the same sampling wells as the groundwaters used in this study were presented in Table 3. The guidelines for vegetation indicated that less than 2,000 μS/cm of conductivity can bear growth of all vegetation and more than 15,000 μS/cm of conductivity cannot be used for vegetation. In addition, if mole fraction of Cl^-/HCO_3^- is greater than 1.3, it specifies substantial effects of seawater intrusion. As shown in Table 3, the groundwater from SungRoe implied the less influence of seawater than those from JeBu and PoSeung. In addition, the mole fraction from the report for JeBu in Table 3 was similar to the result from the measurement in this laboratory shown in Table 2. It should be noted that the influence has been varied greatly year to year depending on conditions of local developments and pumping amounts from the wells.

In addition, several salt solutions including NaCl, $MgSO_4$, $CaSO_4$, and Na_2SO_4 were used to compare ED performance of the real groundwaters. Analytical grade salts were supplied by Sigma-Aldrich Company.

2.4. Analytical method

In all experiments, a conductometer (Thermo, Orion 5 star) was used to measure conductivity for the

Table 3
Results of conductivity and mole fraction of chloride and bicarbonate ions (modified from Kim et al. [1])

Location	Distance from sea (m)	Sampling depth (m)	Conductivity (μs/cm)			Mole fraction of Cl^-/HCO_3^-		
			2008	2009	2010	2008	2009	2010
JeBu	80	50	2,695	3,151	4,279	87.56	28.45	50.51
SungRoe	550	45	7,456	6,190	7,663	3.64	2.54	3.10
PoSeung	970	35	3,678	3,427	2,248	24.96	9.69	15.07

amount of salt in water. In addition to conductivity, pH (Orion 5 STAR, Thermo Fisher Scientific Inc. Beverly, USA) and current value were measured in each reservoir and recorded with data acquisition system. Ion chromatography was used to measure ion concentrations in the groundwater. A compact Dionex ICS-2000 ion chromatograph with an AD25 absorbance (230 nm) and a DS6 heated conductivity detector (35˚C) were used in series. Preceding the conductivity detector either a Dionex ASRS-UL TRA II 4-mm suppressor (131 mA) for anions, or a CSRS 300 suppressor for cations was attached. The data processing was done with the Dionex Chromelon software. The injection volume was 25 μL and the flow rate 1 μL/min. The separation of anions was achieved with a Dionex Ion Pac AG 18 (4 × 50 mm) guard and an IonPac AS 18 (4 × 250 mm) column. The separation of cations was achieved with a Dionex Ion Pac AG 18 (4 × 50 mm) guard and an IonPac CS 12a (4 × 250 mm) column. All columns were heated to 35˚C.

Dissolved organic carbon concentrations were analyzed using a TOC analyzer from Shimadzu (TOC-VCPH). The other physical and chemical parameters were analyzed by Standard Methods procedures.

3. Results and discussion

3.1. Desalination performance of the ED system for the brackish groundwaters

Groundwater was taken from three different locations and the water was treated by the ED in this study. Fig. 2 compares removal of main cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}), anions (Cl^-, NO_3^-, SO_4^{2-}, and Br^-) and conductivity by the ED. The ED system produced high quality of permeate. Removals of the specified ions were mostly achieved more than 90%. For instance, chloride concentrations in the permeate were 16.7 mg/L for JeBu, 106 mg/L for SungRoe, and 12.0 mg/L for PoSeung. Due to the seawater intrusion, chloride ion concentration in the feed was in the range of 649.3–1842.9 mg/L. The water quality standard of drinking water in Korea stated that chloride ion concentrations should be less than 250 mg/L.

It can be seen from Fig. 2 that monovalent anions (Cl^- and Br^-) are transported more easily through the AMX membrane than SO_4^{2-}. The preferential removal of the monovalent anions was more remarkable with the water from SungRoe, in which the sulfate removal was approximately only 78% and chloride removal was 93%. In general, SungRoe water showed the relatively lower removal that the two waters from JeBu and PoSeung. The cation removal of the waters from Jebu and PoSeung were almost the same but the removal of the water from SungRoe was lower than the two waters, which was consistent with the anion the removal. For instance, the sodium removal was 91% for SungRoe water, 98% or more for JeBu and PoSeung waters. It is also interesting to note that the monovalent cation removal of SungRoe water was less than the removal of divalent cations, which is opposite to the removal of anions.

3.2. Changes in conductivity and current during EDs

Specific requirements for total dissolved solid concentrations of feed water or for permeate water quality greatly affect selection of technologies for water desalination. It has been stated that ED may compete with RO or thermal methods in the range of

Table 4
Dissolved organic carbon concentrations for feed and permeate from the ED system

Location	JeBu		SungRoe		PoSeung	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
DOC (mg/L)	1.89	0.21	10.83	2.00	1.05	ND

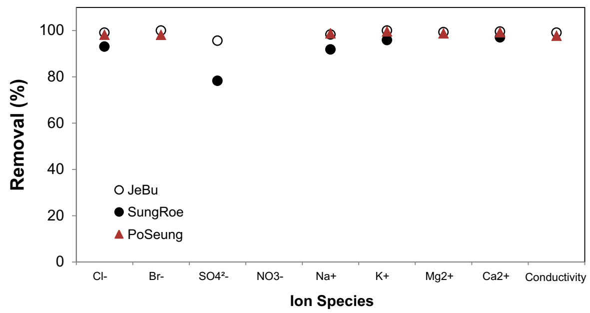

Fig. 2. Ion removal (%) by the ED in the laboratory system.

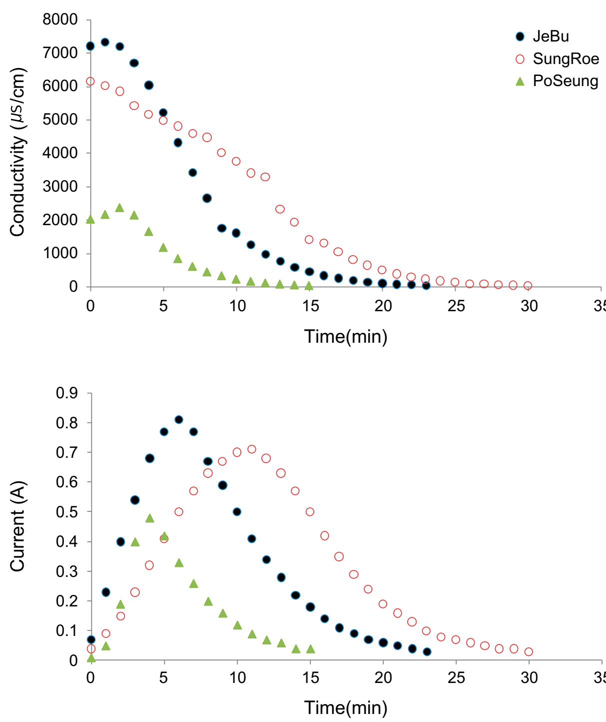

Fig. 3. Changes in conductivity and current during a batch mode of ED with a constant voltage operation (i.e. 12 V).

feed water salinity up to 8–10 g/L [8]. The total dissolved solids concentrations of the three groundwaters were 5,138 mg/L for JeBu, 3,179 mg/L for SungRoe, and 838 mg/L for PoSeung, which indicated that ED could be a feasible technology for desalination of the groundwater.

Performance of ED depends on factors such as salt concentration, ionic composition, applied voltage, temperature, and organic matter concentration. The conductivity was generally decreased with increasing operational time. It seemed that the behaviors of changes in the conductivity of the groundwaters from JeBu and PoSeung area seemed similar to each other whereas that of the groundwater from SungRoe were quite different, that is, delayed decrease of conductivity as shown in Fig. 3. The current changes also were corresponded with the conductivity results. The maximum current was occurred late, that is, after 12 min of the ED operation in contrast to the other results, which were showed the maximum current at approximately 4 or 7 min.

Possible cause of the difference could be presence of organic matter or effects of different ion compositions. Fouling of ED membranes by organic solutes is a well-known problem [13,14]. The fouling is registered as an increase in the membrane resistance and also causes a loss in selectivity of the membrane. Because most organic substances present in natural waters are negatively charged, it is almost always the anion selective membranes that are affected by fouling. The authors indicated that the exterior diffusion barrier formed outer surface of the membrane exhibited more severe fouling than a precipitate within the membrane. In addition, unlike seawater desalination, brackish groundwater desalination often involves substantial hardness removal. Thus, the competitive transport between divalent and monovalent cations affects the treatment efficiency [15]. The different composition between monovalent and divalent ions in the three groundwaters could also show variation in the ED performance.

3.3. Comparison of the ED performance of the groundwaters with NaCl solutions

Several model groundwaters were produced with NaCl solutions to show the same conductivity values as the three groundwaters. Therefore, approximately 4,000 mg/L of NaCl solutions was used to compare ED performance of JeBu and SungRoe groundwaters (Figs. 4 and 5). The conductivity was 5,520 μs/cm for JeBu, 5,640 μs/cm for SungRoe, respectively, although the conductivity from NaCl solution was relatively greater than the groundwaters. In addition, 600 mg/L of NaCl solution was made for comparison with PoSeung water (Fig. 6). The changes in conductivity during the ED operation for JeBu water and PoSeung were almost the same as the model NaCl solutions, whereas the changes for SungRoe were quite different from the model solution. For SungRoe water, the conductivity reduction was occurred slowly, the maximum current was low, and the time to reach for the maximum current was longer than NaCl solution. The comparison result of SungRoe indicated that some ions or organic matter, other than Na^+ and Cl^- determined the conductivity removal in the ED systems. Considering that the ionic compositions of SungRoe were very different from JeBu and PoSeung (Table 2), the difference might come from effects of competitive separation of monovalent and divalent ions in the ED system.

3.4. Effects of monovalent and divalent cations on ED performance

Divalent cations have been known to have a higher affinity to the ion-exchange membrane than monovalent cations due to valence effect [15,16]. Kim et al. explained competitive transports of divalent ions in ED: the selectivity of the cation-exchange membrane favors a divalent ion (i.e., calcium) due to the greater ionic charge and the boundary layer thickness gives preferential for a monovalent ion (i.e. potassium) due to its greater diffusivity [15]. The transport of the monovalent ion was enhanced where concentration polarization was attained (namely, non-Ohmic regime). In addition, the authors mentioned that for an electrodialyzer treating brackish groundwater, water flow should be increased for better hardness removal, which can be obtained by increasing the relative separation rate of divalent cations compared to monovalent cations. The explanation was consistent with higher calcium removal of groundwater from SungRoe shown in Fig. 2.

To understand ED performance for different cation ions, 1,000 mg/L of $MgSO_4$ and $CaSO_4$ solution and 800 mg/L of Na_2SO_4 solution were treated with ED (Fig. 7). The solutions exhibited the similar conductivity in a range of 1,250–1,350 µs/cm and also represented groundwater without organic matter. The ED was operated until the conductivity was reached to 50 µs/cm. The voltage was maintained constant at 12 V. The maximum current of $MgSO_4$, $CaSO_4$, and Na_2SO_4 solution was 0.43, 0.43, and 0.39 A and the desalination processing time was 20, 15, and 12 min, respectively. The pattern of the reduction of conductivity was similar for $CaSO_4$ and Na_2SO_4 and that of current was evenly apart. However, the pattern of the changes was not well corresponded to the results from SungRoe groundwater. It seems that monovalent and divalent ions might have some effects but could not fully explain the delayed reduction in SungRoe

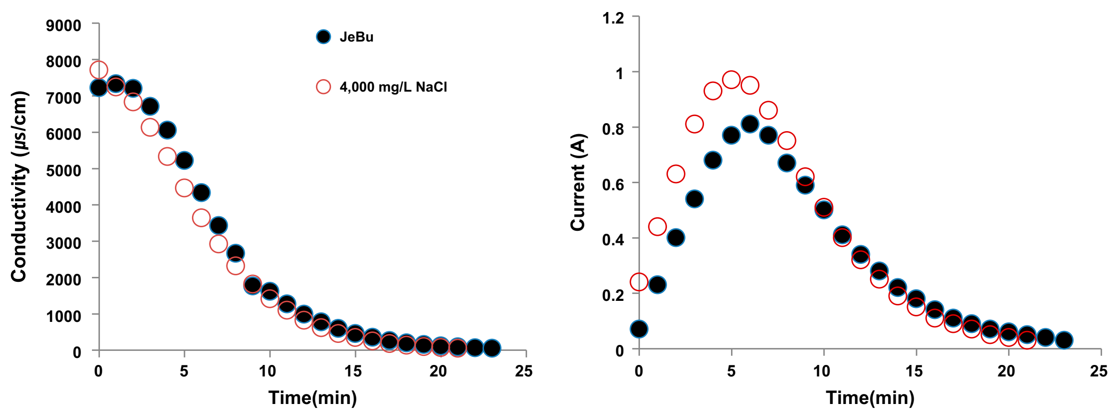

Fig. 4. Changes in conductivity and currents at 12 V with JeBu groundwater and NaCl solution of 4,000 mg/L.

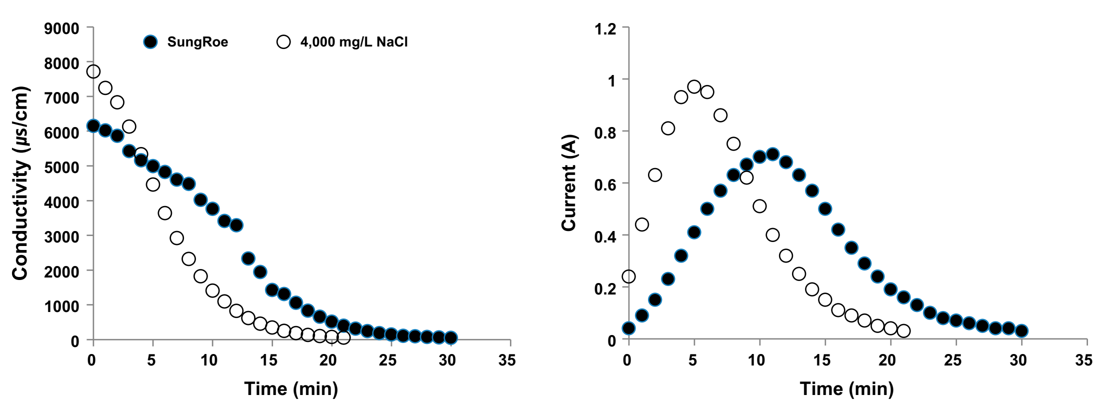

Fig. 5. Changes in conductivity and currents at 12 V with SungRoe groundwater and NaCl solution of 4,000 mg/L.

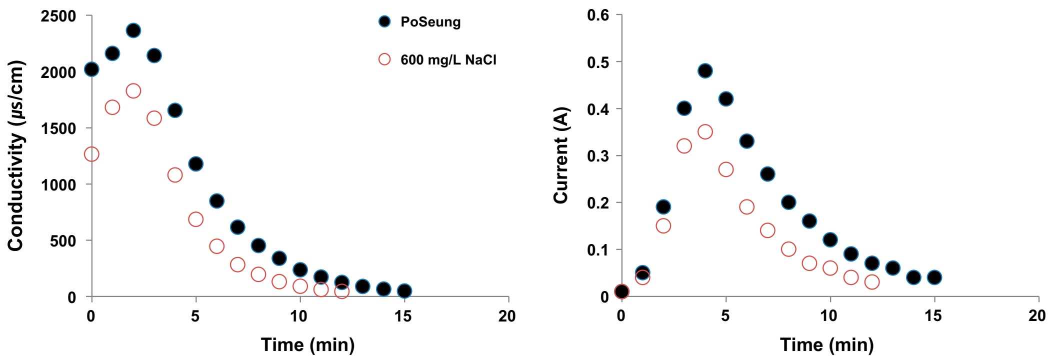

Fig. 6. Changes in conductivity and currents at 12 V with PoSeung groundwater and NaCl solution of 600 mg/L.

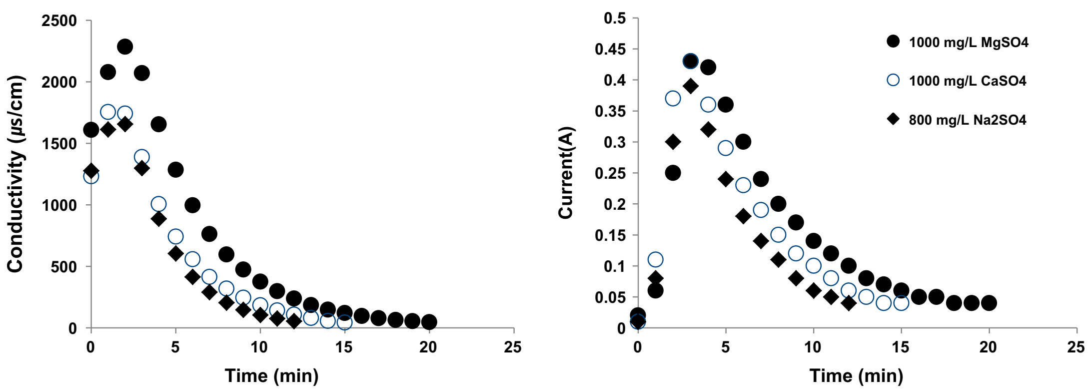

Fig. 7. Changes in conductivity and currents at 12 V with $MgSO_4$, $CaSO_4$, Na_2SO_4 solution of 1,000, 1,000, and 800 mg/L.

water. Dissolved organic carbon concentrations for the three groundwaters were measured by a TOC analyzer with 0.45 μm prefiltration. The results presented in Table 4 showed a greater value for SungRoe compared with other two groundwaters. It implied that organic matter in SungRoe water played an important role in the ED operation.

4. Conclusions

The ED system successfully produced high quality of permeate from the brackish groundwaters, for instance, 98–99% of conductivity removal in approximately 15–30 min of operation. In the range of 800–5,000 mg/L of total dissolved solid concentrations, ED was a feasible option for the desalination of brackish groundwater.

The groundwater from SungRoe showed a delayed decrease in conductivity, which was different from the groundwaters from JeBu and PoSeung. Possible causes of the difference were sought for better understanding of ED of the real groundwater. Membrane fouling by organic matter or competitive separation of monovalent and divalent cations were suspected for the difference. The conductivity reductions of sodium chloride solutions (i.e. 4,000 mg/L) with ion concentrations similar to the brackish groundwater were evaluated. The behavior was significantly different for SungRoe water. Cations were varied with monovalent sodium, divalent calcium and magnesium at the same conductivity condition, that is, 1,000 μs/cm. The ED performance of the three model solutions showed similar tendency in operation time and current curve and did not explain the discrepancy of the ED performance of the groundwater. Dissolved organic carbon concentration results implied that organic matter in SungRoe groundwater played an important role in electrodialysis operation. More research using anions such as HCO_3^- and SO_4^{2-} is needed to elucidate anion effects on electrodialysis performance of brackish groundwater.

Acknowledgment

This study was supported by Konkuk University in 2011.

References

[1] J.H. Kim, S.H. Song, K.S. Lee, B.S. Lee, Y.I. Kim, Project report of groundwater under influence of seawater Research. Korea Rural Community Corporation, Suwon 2010.

[2] S. Thampy, G.R. Dasale, V.K. Shahi, B.S. Makwana, P.K. Chosh, Development of hybrid electrodialysis-reverse osmosis domestic desalination unit for high recovery of product water, Desalination 282 (2011) 104–108.

[3] M. Sadrzadeh, T. Mohammadi, Sea water desalination using electrodialysis, Desalination 221 (2008) 440–447.

[4] R. Valavala, K. Sohn, J. Han, N. Her, Y. Yoon, Pretreatment in reverse osmosis seawater desalination: A short review, Environ. Eng. Res. 16(4) (2011) 205–212.

[5] V.A. Shapsshnik, K. Kesore, An early history of electrodialysis with permselective membranes, J. Membr. Sci. 136 (1997) 35–39.

[6] M. Sadrzadeh, T. Mohammadi, Treatment of sea water using electrodialysis: Current efficiency evaluation, Desalination 249 (2009) 279–285.

[7] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (2010) 268–288.

[8] M. Turek, Cost effective electrodialytic seawater desalination, Desalination 153 (2002) 371–376.

[9] F. Valero, R. Arbos, Desalination of brackish river water using electrodialysis reversal (EDR) control of the THMs formation in the Barcelona (NE Spain) area, Desalination 253 (2010) 170–174.

[10] Y. Kim, W.S. Walker, D.F. Lawer, Electrodialysis with spacer: Effects of variation and correlation of boundary layer thickness, Desalination 274 (2011) 54–63.

[11] Y. Oren, E. Korngold, N. Daltrophe, R. Messalem, Y. Volkman, L. Aronov, M. Weismann, N. Bouriakov, P. Glueckstern, J. Gilron, Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach, Desalination 261 (2010) 321–330.

[12] Y. Zhang, K. Ghyselbrecht, D. Meesschaert, L. Pinoy, B.V. Bruggen, Electrodialysis on RO concentrate to improve water recovery in wastewater reclamation, J. Membr. Sci. 378 (2011) 101–110.

[13] V. Lindstrand, G. Sundstrőm, A. Jőnsson, Fouling of electrodialysis membranes by organic substances, Desalination 128 (2000) 91–102.

[14] H.-J. Lee, S.-H. Moon, Fouling of ion exchange membranes and their fouling mitigation, Membrane journal 12(2) (2002) 55–66.

[15] Y. Kim, W.S. Walker, D.F. Lawler, Competitive separation of di- vs. mono-valent cations in electrodialysis: Effects of the boundary layer properties, Water Res. 46 (2012) 2042–2056.

[16] P.V. Vyas, P. Ray, G.S. Trivedi, S.K. Adhikary, R. Rangarajan, Studies on exchange equilibria of cations between cation-exchange membranes and electrolytic solutions, J. Colloid Interface Sci. 246(2) (2002) 366–371.