Electrodialytic Removal of Nitrates and Hardness from Simulated Mixtures Using Ion-Exchange Membranes

S. K. Nataraj, K. M. Hosamani, T. M. Aminabhavi

Membrane Separations Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India

ABSTRACT: A novel electrodialysis (ED) pilot plant unit coupled with a membrane stack containing 11 cation-exchange and 10 anion-exchange membranes is used for the removal of nitrates and hardness from simulated aqueous mixtures containing salts that are usually encountered in brackish water. The removal of high nitrates and water hardness is performed in 150 min of ED under three constant applied voltages at room temperature. The limiting current density is obtained for sodium nitrate and calcium chloride mixtures in dilute solution. In order to check the efficacy of the ED method, parameters like the applied potential are varied at constant flow rates. The efficiency of the ED method depends on the applied potential. Possible applications of ED are discussed for the removal of contaminants below the minimum contaminant level of drinking water. The ED method used here is satisfactory to produce good quality drinking water from a simulated mixture by removing the unwanted ions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1788–1794, 2006

Key words: electrodialysis; nitrate; chloride; limiting current density

INTRODUCTION

The shortage of drinking water is a major issue all around the globe. Electrodialysis (ED) is an effective process to remove the unwanted ions from wastewater streams.[1] ED is an ion-exchange membrane separation process in which electrical potential is used as the driving force for the separation. Separation by ED is simple and requires minimum energy consumption. In an ED stack, cation- and anion-exchange membranes are placed alternatively between the cathode and anode. When a potential difference is applied between both electrodes, cations move toward the cathode and anions toward the anode. The cations migrate through cation-exchange membranes, which have negative fixed groups, and they are retained by anion-exchange membranes and vice versa. This movement produces a rise in the concentration of ions in some compartments (concentrate) and a decrease in the adjacent compartment (diluate). However, the temperature may not have any effect on the rate of separation of salts from the mixed media and hence the ED can be operated continuously. These advantages make ED attractive, especially for desalination of brackish water and reconcentration of sodium chloride from seawater. In addition, this method has been widely used for production of table salt and organic acids, remediation of heavy metal polluted soil, sugar demineralization, blood treatment, and wine stabilization.[2–6]

Nitrogen is essential for all living things because it is a component of protein. Nitrogen exists in the environment in many forms and it changes its form when it moves through the nitrogen cycle. However, the excessive concentrations of nitrate-nitrogen or nitrite-nitrogen in drinking water can be hazardous to health, especially for infants and pregnant women. Nitrate is the oxidized form of a nitrogen-containing compound, which is commonly present in natural waters, because it is the product of aerobic decomposition of organic nitrogenous matters. The nitrate concentration in groundwater or surface freshwater reaches more than 100 mg/L in some places.[7] Significant sources of nitrates are chemical fertilizers, decayed vegetable and animal materials, domestic effluents like sewage sludge disposal on land and industrial discharge from refuse dumps, and atmospheric washout. The major concern affecting human health for infants less than 6 months of age is excessive nitrate concentration. More than a 10 mg/L nitrate concentration causes health hazards, especially in infants because of a bacterium that exists in their gastrointestinal tract, which converts nitrate to nitrite. The nitrite that is produced reacts with hemoglobin to form methemoglobin,

which does not carry oxygen. Consequently, the affected infant receives less oxygen to the brain, resulting in "blue baby" syndrome.[8,9] Even though the cancer-causing effects of nitrates are not well documented, nitrate reaction products (nitrosamines and nitrosamides) are strongly considered as potential human carcinogens.[10]

The U.S. Public Health Service[11] adopted drinking water standards and set acceptable limits for nitrate-nitrogen at 10 mg/L, whereas the World Health Organization[12] guidelines allow a maximum contaminant level of 50 ppm as NO_3. According to European Community standards, drinking water should not contain more than 50 mg/L of nitrate; the Bureau of Indian Standards has defined the acceptable limit of nitrates to be <45 mg/L, whereas a value of 25 mg/L is highly recommended.[13] Unlike virtually all other contaminant standards, drinking water standards for nitrates contain no margin of safety. Nearly every chemical standard in force today incorporates a 10- to 100-fold safety factor to ensure that sensitive members of the population are adequately protected.

Several researchers have studied nitrate recovery using ED membranes.[14–18] Kesore et al.[19] used an anion-exchange membrane coupled with a new inter-membrane spacer containing a nitrate-selectivity anion-exchange resin to improve the selectivity and effectiveness of nitrate removal from drinking water. Others[20,21] have studied the economical aspects of the ED process by analyzing the costs for different scale operations of ED units to produce drinking water. The total hardness of water comprises inorganic salts and small amounts of organic matter that are dissolved in water. The principal constituents are usually calcium, sodium, magnesium, and potassium cations as well as chloride and nitrate anions, particularly in groundwater from agricultural use, such as carbonate, bicarbonate, and sulfate. In this study the removal of nitrates and hardness of a synthetic (laboratory simulated) solution was studied by ED. The limiting current density (LCD) and the effect of working parameters on energy consumption were investigated using commercial ion-exchange membranes.

EXPERIMENTAL

Materials and feed preparation

Sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), and calcium chloride ($CaCl_2$) were purchased from S.D. Fine Chemicals (Membai, India). The $0.0016M$ solution of $NaNO_3$ and $0.012M$ solution of $CaCl_2$ were prepared in deionized water. Mixtures of the above two solutions were used in a ratio of 1 : 0.5 in the feed (tank 1) and concentrate (tank 2), respectively. Deionized water having a conductivity of 0.015 mS was used in the concentrate tank (50% of feed volume) to facil-

itate the ion transfer. About 5 L of 2.5 wt % Na_2SO_4 solution was used as an electrode wash in tank 3. The ED membranes were purchased from Membrane International Ltd. (Piscataway, NJ). The membrane stack was prepared in series by alternatively placing 10 anion- and 11 cation-exchange membranes and both ends were connected to the electrodes. The spacers used between the ED membranes are made of poly-(vinyl chloride).

Analytical methods

Concentrations of Na^+ and Ca^{2+} ions were determined by atomic absorption spectrometry (GBC Avanta 932, Dangenong, Victoria, Australia). The nitrate ion concentration was estimated by using a UV spectrophotometer (Anthellie model, Secomam). A standard curve of the absorbance versus concentration of $NaNO_3$ was established first and its slope was found to be 0.001. The eluted solutions from the ED stack were then measured for absorbance and their concentrations were calculated from the standard curve using the slope value. Samples of these solutions were collected at 15-min intervals for the spectral analysis. The conductivity and pH of the solutions were also measured by using a conductivity and pH meter (Jenway model 4330). The total dissolved solids (TDS) content (ppm) was estimated directly with a TDS meter (TDScan 1). The chloride ion concentration was estimated volumetrically.

ED setup

A schematic diagram of our ED apparatus (designed in-house) consisting of a membrane stack and spacers is shown in Figure 1. The system consists of three round-bottomed glass tanks, one each for feed (diluate), concentrate, and electrode wash solutions. Each tank is connected to centrifugal pumps that are magnetically coupled and driven by polypropylene wetted parts. Control valves and bypass valves are provided to adjust the flow rate independently in each line. Perforations in the edges of the gaskets and membranes match each other to provide pairs of internal hydraulic manifolds to carry fluid in and out of the compartments. One pair communicates with the depletion compartments and the other with the enrichment compartments. The ED stack consists of 11 cell pairs alternately arranged and containing positive and negative charges. Turbulence promoters made of flexible poly(vinyl chloride) wire mesh were used in the ED stack to reduce the concentration polarization effect. Energy is provided through a regulated dc power supply from a thyristor-type rectifier with 100-V and 30-A capacities.

Cowan and Brown's method was adopted to determine the LCD for the ED experiment.[22] The electrical
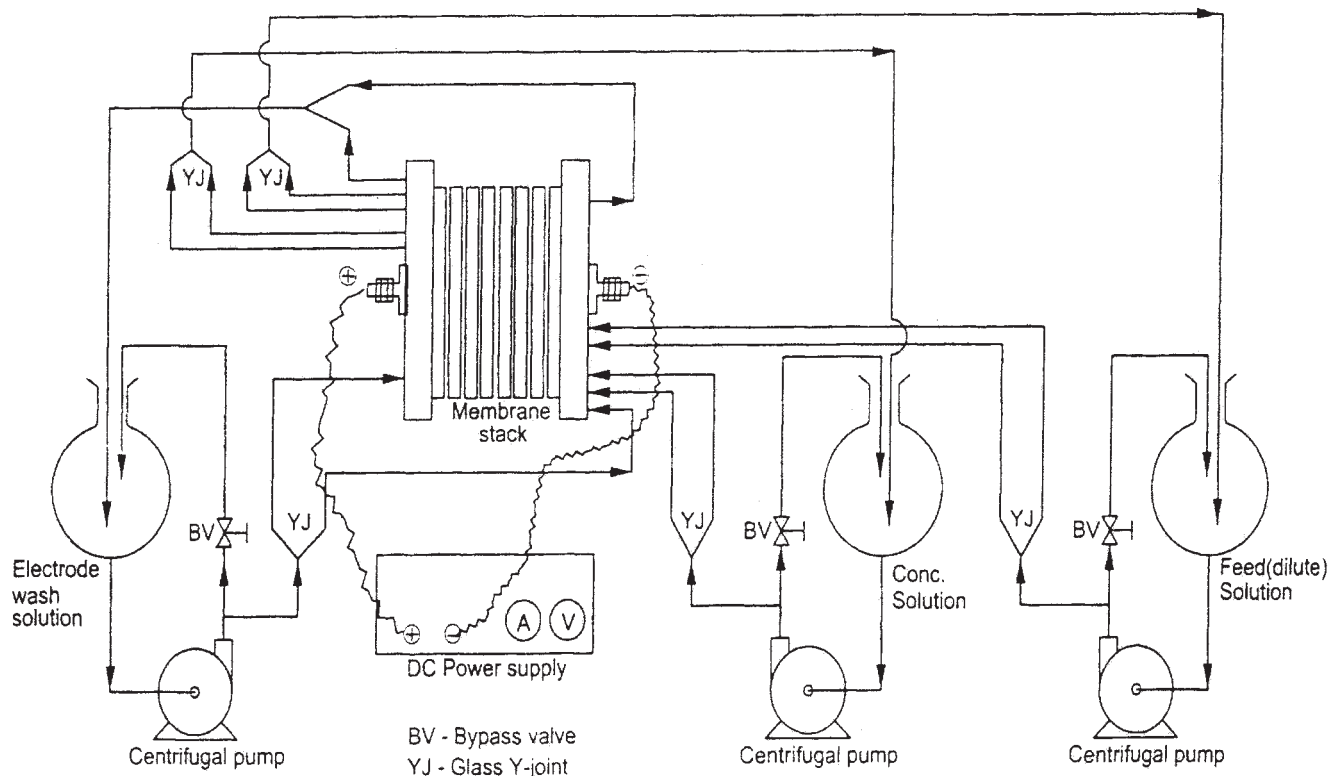
Figure 1 The electrodialysis experimental setup; BV, bypass valve; YJ, internal hydraulic manifolds.

current (I) across the ED stack was increased when the dc stack resistance ($R = V/I$) is measured. The electrical resistance was plotted versus the reciprocal electrical current ($1/I$). The point gives the limiting current where the electrical resistance starts to increase. The LCD was then calculated from the limiting current using the effective membrane area.[22,23]

RESULTS AND DISCUSSION

Specifications of the average feed composition used for the ED experiments are given in Table I. Experiments were performed at a constant flow rate of 0.8 L/min for the diluate and concentrate and 0.6 L/min for the electrode wash. The voltage was varied from 40 to 50 V, with an increment of 5 V. These values were chosen in order to not exceed the maximum values for the electric current and flows as recommended by the manufacturer of the ED membranes. The current intensity was read at each stage for every value of the applied voltage. In addition, the flow rates of the feed, concentrate, and wash streams were determined together with their respective electrical conductivities, pH, currents, and temperatures of all the solutions of the diluate stream; concentrates were recorded at constant time intervals, which are directly related to their respective saline concentrations. Samples of the solutions were collected every 15 min for the analysis. Table II shows the relative elimination of ions.

LCD

The LCD for the simulated diluate stream was determined as described previously.[22] When two straight lines are plotted for the measured data points, the intersection of these lines represents the LCD. For three constant voltages, the quantity $1/I$ as a function of the resistance is shown in Figure 2. A fourth-order polynomial regression of the data points was used in this experiment, where the absolute minimum of this regression was chosen to represent the LCD. For different potentials, the results of the minimum found reciprocal electrical current ($1/I$), limiting current

TABLE I
Feed Water Characteristics

Parameters	Concentration
Conductivity (mS/cm) at 25°C	4.2
pH	7.2
Total dissolved solids (mg/L)	2500
Calcium hardness as $CaCO_3$ (mg/L)	1380
Chloride (mg/L)	1780
Calcium (mg/L)	550
Sodium (mg/L)	550
Nitrate (mg/L)	420
Magnesium and potassium (mg/L)	<5

TABLE II
**Time and Voltage Dependence of Anion and Cation Concentrations of Feed Solution**

Time (min)	NO_3^- (ppm)			Cl^- (ppm)			Ca^{2+} (ppm)			Na^+ (ppm)			TDS (ppm)		
	50 V	45 V	40 V	50 V	45 V	40 V	50 V	45 V	40 V	50 V	45 V	40 V	50 V	45 V	40 V
0	424	420	434	1730	1810	1820	544	533	553	551	550	545	2560	2590	2550
15	332	310	379	1340	1760	1720	517	496	492	463	394	410	2470	2400	2380
30	290	271	294	1290	1620	1490	436	404	424	328	365	370	1730	2150	2170
45	241	226	221	1090	1490	1350	304	328	396	274	305	319	1570	1975	1940
60	198	190	191	930	1510	1140	252	292	384	231	269	286	1410	1799	1895
75	150	146	152	800	1230	930	236	252	288	196	236	265	1230	1596	1674
90	120	113	126	680	1060	810	188	228	252	159	206	231	1020	1430	1439
105	101	90	113	540	890	700	164	174	228	117	183	216	900	1282	1291
120	40	42	78	400	720	540	112	132	160	142	152	174	810	1101	1117
135	38	31	52	220	560	440	72	104	124	43	40	140	550	928	859
150	—	—	—	180	400	330	56	72	80	—	—	—	430	802	760

(I_{lim}), and LCD (i_{lim}, current ÷ effective membrane area = LCD) are given in Table III. A minimum limiting value of 9 mA/cm² was found for an electrical potential of 45 V. However, it should be noted that the LCD is not a constant value; it changes with the working conditions and operating time of the ED system.

Changes in electrical conductivity of the diluate stream (feed, Tank 1) as a function of time at three constant applied voltages are shown in Figure 3. The electrical conductivity of the dilute solution decreased exponentially with time. The continuous decrease in the electrical conductivity was mainly due to the deionization of the dilute solution. A significant difference is observed in the electrical conductivity of the diluate when operating the ED stack at different applied voltages; a higher transfer rate of ion is observed at 50 V.

The pH evolution in the diluate fraction during the ED experiment is shown in Figure 4 as a function of time. The average starting pH was noted as 7.7; at 50

V, the pH of the diluate stream decreased more significantly than the other applied potentials. This sudden decrease in pH to 3.1 after a linear slow decrease from 7.7 to 6.8 with time may be attributable to the dissociation of water molecules and liberation of hydrogen ions. Thus, the liberated hydrogen ions may be involved in the reduction of nitrate to nitrogen gas, which was indeed confirmed by the generation of gas bubbles observed in the diluate tank during the ED experiment according to the following chemical reactions:

$$H_2O \rightarrow H^+ + OH^-$$

$$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2 N_{2(g)} + 3H_2O$$
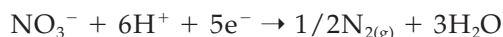
The removal of nitrate ions from the diluate as a function of time is shown in Figure 5. Ion exchange in the ED cells generally substitutes chloride anions for the nitrate anions without substantially changing the salinity of the feed water. Nitrate is thus preferentially removed and replaced by the chloride ions unless a special nitrate-selective resin is used. Because the membranes in this study are not completely selective and because of the batch nature of the process, the anion composition and pH of the product will change over the service cycle. Moreover, between 30 and 90 min of operation time, the nitrate removal rate at all potentials was similar. At the end of the experiment operated at 50 V, an increase in the volume of the concentrate was observed in the concentrate tank
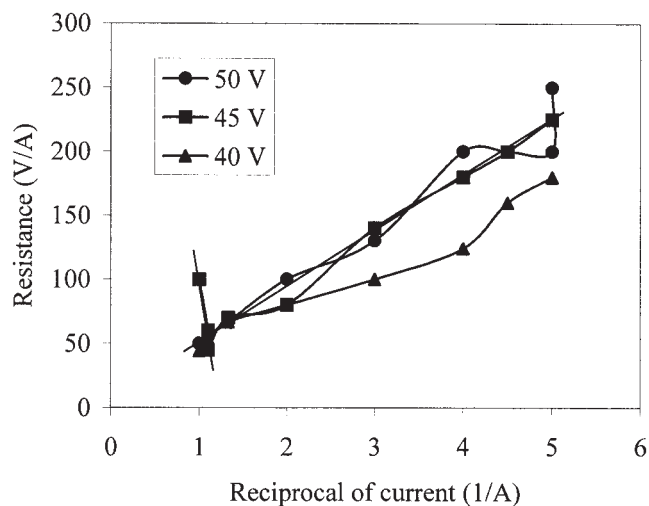

Figure 2 A plot of the reciprocal of the current versus resistance.

TABLE III
Limiting Current Density for Different Applied Voltages

Voltage (V)	I/I (1/A)	I_{lim} (A)	i_{lim} (mA/cm²)
40	1.0	1.11	11.11
45	1.1	0.9	9.0
50	1.0	1.0	10.0

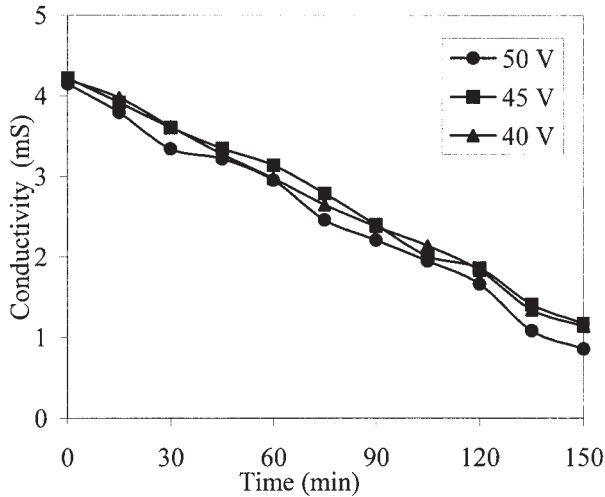**Figure 3** A plot of the conductivity versus time.

Figure 5 A plot of the nitrate ion concentration versus time.

(tank 2). This may be due to the osmosis (backdiffusion) of water from tank 1 to tank 2. In addition, at this voltage the active sites of the ED membranes are taken by the anions and thus the membrane selectivity decreases because of the poor mobility of the anions. However, at the lower voltage of 45 V, higher nitrate removal was achieved.

Figures 6 and 7 indicate the respective removal paths of the TDS and chlorides as a function of time at different applied voltages. Because salts are used for the regeneration of the ion exchanger, the diluate stream contains substantial amounts of sodium and chloride ions. As chloride is exchanged with nitrate in this process, the chloride level of the product is elevated and no sudden reduction of TDS was observed, as was the case in the nitrate ion concentration. At a higher voltage of 50 V, the sudden decrease in TDS at the initial time up to 30 min is observed because of the possible deionization of salt mixtures.
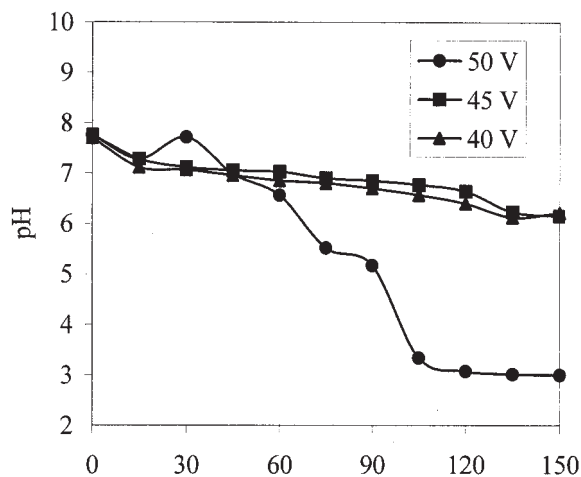
Specific ion transfer depends on the equivalent fraction of the corresponding ion in the raw water, the mobility of the ion, and the type of membrane. Figure 8 provides the results of a comparative study for the separation of monovalent (Na^+) and divalent (Ca^{2+}) ions by ED. Even though the operational time for both monovalent and divalent ions was the same, monovalent ions were removed at a higher rate than the divalent ions.

Excluding the capital and operating costs and considering the working parameters, the electrical energy consumption (EC) was calculated using the following equation:

$$EC = \frac{E_o \int_0^t I\,dt}{V_D} \tag{1}$$

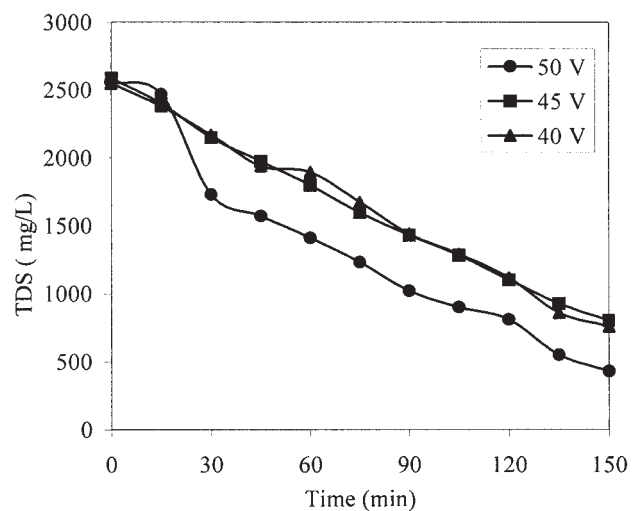**Figure 4** A plot of the pH as a function of time.

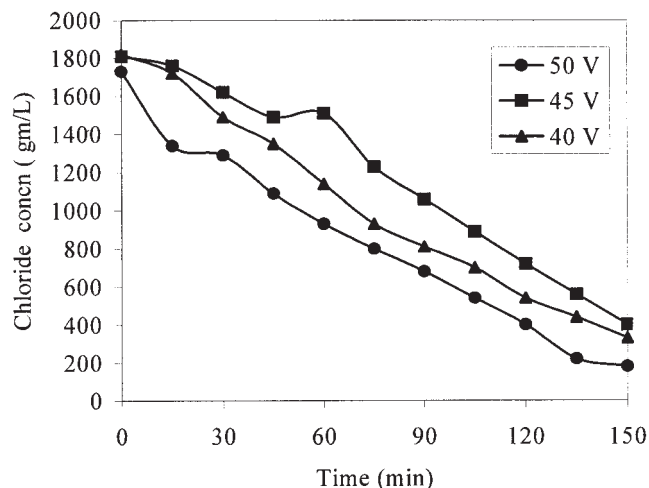**Figure 6** A plot of the total dissolved solids versus time.

Figure 7 A plot of the chloride ion concentration versus time.

where E is the potential, I is the current, V_D is the volume of diluate, and t is the time. At the optimum LCD, the electrical energy consumption (W/L) for the pilot plant is plotted against different applied potentials, as shown in Figure 9. This does not include the
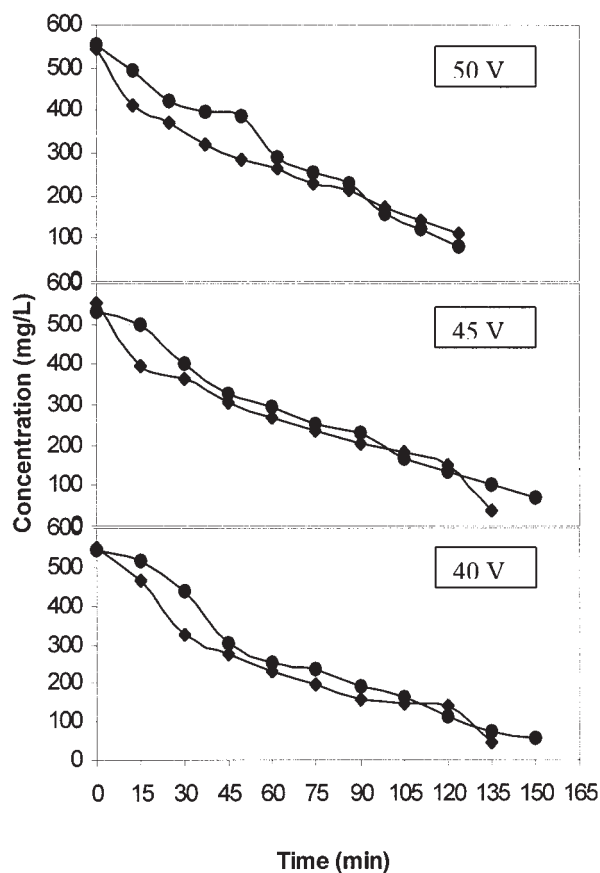

Figure 8 A plot of the (●) Na$^+$ and (♦) Ca^{2+} concentrations versus time at different applied potentials.
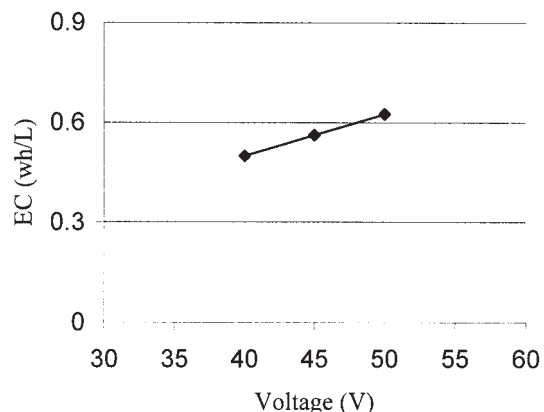

Figure 9 A plot of the energy consumption versus applied potential.

cost of energy for pumping during the production of drinking water. Energy consumption calculations were made for a final concentration of NO$_3^-$ in a dilute solution of 31 mg/L. When this concentration is reached, it can be assumed that water has been processed and is within the legal limits for drinking purposes. With this process the NO$_3^-$, Na$^+$, Ca^{2+} concentrations, as well as the Cl$^-$ ion concentrations are all within the minimum contaminant level for drinking water.

CONCLUSIONS

The present study demonstrates the effective usage of an ED process for the removal of nitrates from groundwater. The commercial ED membranes used in this study could greatly decrease the nitrate ion concentration to the level set by the World Health Organization for polluted groundwater. Even though the membranes are not completely selective for specific ions, the other harmful hardness-causing ions were easily removed. An optimal 9 A/cm^2 LCD was found for NaNO$_3$ and CaCl$_2$ mixtures of dilute solutions. At 50 V the removal of ions was slower because of the backdiffusion of solvent (water) resulting from membrane fouling and selectivity decreases, because these ions could occupy the active sites of the membrane. More than 94% of the nitrates, 89% of the chlorides, and 86% of the TDS were successfully removed after 150 min of operation of the ED.

References

1. Demkin, V. I.; Tubashov, T. A.; Panteleev, V. I.; Kaelin, Y. V. Desalination 1987, 64, 367.

2. Cherif, A. T.; Molenat, J.; Elmidaoui, A. J Appl Electrochem 1997, 27, 1069.

3. Colon, G.; Rosenau, J. R. Presented at the AIChE Annual Meeting, New York, 1987.

4. Shah, P. M.; Scamehorn, J. F. Ind Eng Chem Res 1987, 26, 269.

5. Urano, K.; Ase, T.; Naito, Y. Desalination 1984, 51, 213.

6. Elmidaoui, A.; Elhannouni, F.; Menkouchi, M. A.; Chay, L.; Elabbassi, H.; Hafsi, M.; Largeteau, D. Desalination 2001, 136, 325.

7. Jaafari, K.; Elmaleh, S.; Coma, J.; Berkhouja, K.; Water SA 2001, 27, 9.

8. Fonseca, A. D.; Crespo, J. G.; Almeida, J. S.; Reis, M. A. Environ Sci Technol 2000, 34, 677.

9. Dorsheimer, W. T.; Drewery, C. B.; Fritsch, D. P.; Williams, D. E. Water Eng Manage 1997, 144, 20.

10. Paekham, R. F. Presented at the International Workshop on Inorganic Nitrogen and Water Supply, Hamburg, Germany, 1991.

11. U.S. Environmental Protection Agency, Office of Water. 305(b) Report to Congress 1996/1998; U.S. Government Printing Office: Washington, DC, 1998.

12. World Health Organization. Guidelines for Drinking-Water Quality, 2nd ed. Health Criteria and Other Supporting Information; World Health Organization: Geneva, 1996; Vol. 2, p 940.

13. Salem, K. J.; Sandeaux, J.; Molenat, R.; Sandeaux, C. G. Desalination 1995, 101, 123.

14. Kneifel, K.; Luhrs, G. Desalination 1988, 68, 203.

15. Schoeman, J. J.; Buys, I. J. M.; Schute, I. B.; Macleod, H. Desalination 1988, 70, 407.

16. Eyal, A.; Kendem, O. J Membr Sci 1988, 38, 101.

17. Kapoor, A.; Viraraghavan, T. J Environ Eng 1997, 123, 371.

18. Miaam, Y. J Membr Sci 1990, 54, 233.

19. Kesore, K.; Janowski, F.; Shaposhnik, V. A. J Membr Sci 1997, 127, 17.

20. Kabay, N.; Demircioglu, M.; Ersiiz, E.; Kurucaovali, I. Desalination 2002, 149, 343.

21. Demircioglu, M.; Kabay, N.; Erosz, E.; Kurucaovali, I.; Safak, C.; Gizli, N. Desalination 2001, 136, 317.

22. Cowan, D. A.; Brown, J. H. Ind Eng Chem 1959, 51, 1445.

23. Lia, C. L.; Zhaoa, H. X.; Tsurua, T.; Zhoub, D.; Matsumura, M. J Membr Sci 1999, 157, 241.