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Desalination using Electrodialysis as a Function of Voltage and Salt Concentration

Laura J. Banasiak[1], Thomas W. Kruttschnitt[2] and Andrea I. Schäfer[3]

[1] Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, AUSTRALIA
pH +61 2 4221 3491; fax +61 2 4221 3143; ljb15@uow.edu.au
[2] University of Applied Sciences, 74081 Heilbronn, GERMANY
thomas.kruttschnitt@web.de
[3] School of Engineering and Electronics, University of Edinburgh, Edinburgh EH9 3JL, UNITED KINGDOM
pH +44 (0) 131 650 7209; fax +44 (0) 131 650 6781; Andrea.Schaefer@ed.ac.uk

Abstract

Electrodialysis is a process that competes with reverse osmosis for desalination and the removal of specific inorganic contaminants. Desalination experiments were carried out on aqueous solutions containing 5 and 10 g/L NaCl to determine the optimum operating conditions of an electrodialysis (ED) system. Further desalination of aqueous solutions containing 1, 5, 10, 20, 25 and 35 g/L NaCl at an optimum applied voltage of 12 V was conducted to determine the influence of initial salt concentration on the desalination process. The possibility of removing fluoride and nitrate from a groundwater containing about 4.3 g/L NaCl, as well as 2.8 and 31.3 mg/L of fluoride and nitrate respectively, as a function of applied voltage was also investigated. A laboratory electrodialysis stack containing seven cation-exchange membranes and six anion-exchange membranes of 56 cm^2 effective area was used. From these studies it is demonstrated that electrodialysis is an effective method for the removal of fluoride and nitrate from brackish groundwater and that real groundwater showed a slower desalination behaviour. Fouling of the membranes was observed.

Keywords: Desalination, electrodialysis, defluoridation, denitrification, brackish groundwater

1   Introduction

Electrodialysis (ED), which involves the preferential transport of ions through ion exchange membranes under the influence of an electrical field, is used mainly for the desalination of saline solutions producing concentrated brines and salt depleted waters; such as the production of potable water mainly from brackish water [1, 2], seawater [3] and industrial water [4] sources. ED has found to be feasible when the salinity of the feed water is not more than about 6 g/L of dissolved solids [5]. For waters with relatively low salt concentrations (less than 5 g/L), electrodialysis is generally the most economic process in comparison to reverse osmosis (RO) [2]. However, the desalination of waters with higher concentrations of dissolved solids (30 g/L) can successfully be performed through ED [6, 7].

A wide range of trace contaminants, including fluoride and nitrate, can usually be found in surface waters, groundwater and brackish water. While the concentrations of fluoride in surface water are relatively low (<0.1-0.5 mg/L) [8], higher concentrations have been found in ground waters (up to 20 mg/L) [9]. The harmful effects of excess concentrations of fluoride on teeth and the skeletal system have been widely studied. Dental and skeletal fluorosis is widespread in populations with drinking water directly supplied from groundwater [10]. Nitrate concentrations in surface and ground water have increased significantly in almost all areas of the world, as a result of the heavy utilization of artificial fertilizers and the penetration of large quantities of nitrates into ground and surface waters [11]. The concentration of nitrate ions in groundwater of some places exceeds 50 mg/L [12]. Deleterious health effects have been attributed to nitrate, including infantile methemoglobinaemia or 'blue-baby' syndrome as it is known. Long term consumption of elevated levels of nitrate can also affect the health of adults and older children causing cancer risks due to nitrosamines or nitrosamides [13]. According to the World Health Organization (WHO) and the Australian Drinking Water Guidelines, the maximum acceptable concentration levels for fluoride and nitrate in drinking water are 1.5 and 50 mg/L [8, 14]. However, for nitrate a level of 25 mg/L has been recommended [8].

ED has to date not been frequently used for the removal of fluoride and nitrate due to high operating costs. However, due to the high selectivity and low chemical demand of ED it has proved to be a reliable and efficient method for both desalination and the removal of fluoride and nitrate [15-17]. The development of new ion-exchange membranes with better selectivity, lower electrical resistance, and improved thermal, chemical, and mechanical properties have also created further interest in electrodialysis [18]. In this study the performance of ED for the desalination of different salt solutions and the removal of fluoride and nitrate removal from a brackish ground water was conducted. The influence of applied voltage and initial salt concentration of a solution was also determined. The aim of this study is the direct comparison of ED with reverse osmosis (RO) and nanofiltration (NF) for the removal of inorganic trace contaminants.

2   Materials and Methods

2.2   Electrodialysis System

The layout of the ED system used in the experiments and a close-up of the ED stack and its components is illustrated in Figure 1 and Figure 2. The apparatus used in this experiment consisted of a BEL-500 electrodialysis unit (supplied by Berghof, Eningen, Germany). The membrane stack was connected to a DC electric potential through TiO$_2$-coated titanium electrodes. The stack consisted of seven cation-exchange membranes and six anion-exchange membranes, providing for each an available membrane area of 58 cm^2 (effective area). Membranes were all manufactured by Tokuyama Soda Co and supplied by Eurodia. The power supply had a maximum output voltage of 18 V and a maximum output current of 10 A. There were three pumps and three solution tanks of 10 L holding the concentrate, diluate and the electrode rinse solutions. The flow range for the pumps for the concentrate and diluate solutions was 0.12 to 13 L/min. The electrode rinse pump had a maximum flow rate of 2.5 L/min with a maximum pressure of 21 psi.
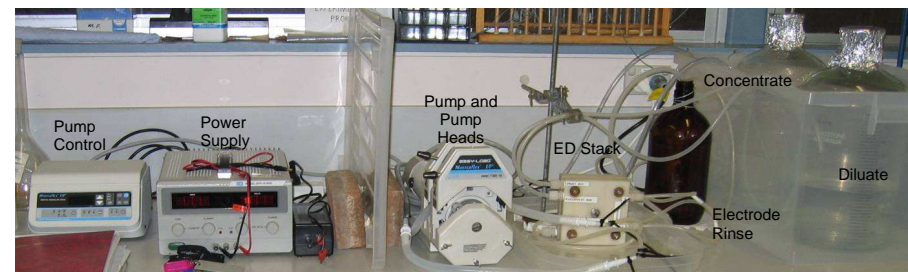

Figure 1 Electrodialysis System Layout with pump control, power supply, pump, ED stack, and three containers with electrode rinse, concentrate and diluate.
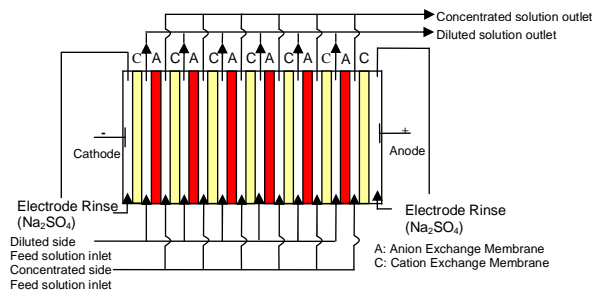
Figure 2 Electrodialysis stack with cation and anion exchange membranes in alternating series between two electrodes.

2.3 Pine Hill Water Situation

In arid areas drinking water is very scarce and the establishment of human populations in these areas depends on how potable water can be made available. Water quality in remote locations is a serious problem within Australia. For this study a groundwater that contains a series of inorganic contaminants and a total dissolved solids concentration of about 5 g/L was selected for testing. Electrodialysis of groundwater from Pine Hill Farm (140 km northwest of Alice Springs) (See Figure 3Figure 3) was undertaken, of which the results for fluoride and nitrate removal are outlined in this paper. As can be seen in Table 1 water quality parameters for both fluoride and nitrate concentration exceeded drinking water guidelines with initial fluoride and nitrate concentrations of 2.8 and 31.1 mg/L respectively.

Figure 3 Pine Hill Farm in Central Australia, Northern Territory.

Table 1 Water Quality at Pine Hill Farm in comparison with World Health Organization 1993 and Australian Drinking Water Quality Guidelines 2004 [8, 14]

Parameter	Unit	Sample Value	Drinking Water Guideline Value
Fluoride (F⁻)	mg/L	2.8	1.5
Nitrate (NO₃⁻)	mg/L	31.1	25
pH	-	8.4	6.5 - 8.5
Electrical Conductivity (EC)	mS/cm	7.77	-
Sodium Chloride (NaCl)	mg/L	4255	500

2.4 Experimental Protocol

The applied cell voltage is a critical operating condition in electrodialysis processes as the voltage determines the current in the cell and hence the desalination efficiency as well as energy consumption. Desalination experiments using ED were undertaken to determine the performance of the system at three applied voltages; 9, 12 and 18 V. Two sets of experiments were carried out, one at a initial salt concentration of 5 g/L NaCl and one at 10 g/L NaCl. To study the impact of initial salt concentration the desalination process experiments were carried out with salt concentrations of 1, 5, 10, 20, 25 and 35 g/L NaCl at an optimum applied voltage of 12 V (determined from the experiments mentioned above). To determine the influence of electrodialysis on the removal of fluoride and nitrate within the Pine Hill bore water, the effect of applied voltage was tested at 12 and 18 volts.

The ED system was operated in continuous operation mode during the experiments. In this mode the feed water (initially filled in both diluate and concentrate containers) was recirculated throughout the concentrate and diluate streams until the desired product was achieved. Both the concentrate and diluate were fed into the electrodialysis stack at a flow rate of 3 L/min. A solution of 0.5 M Na₂SO₄ was used as the electrode rinse solution instead of NaCl, at a flow rate of 2.5 L/min, in order to prevent the generation of chlorine or hypochlorite which could be hazardous for the electrodes. Experiments were conducted at room temperature. Samples were taken at time intervals from both diluate and concentrate streams for testing of conductivity, pH, temperature and ion concentrations. The stack was flushed with solutions of 0.1 N alkali and acid, and Milli-Q water in between experiments in order to remove precipitated salts and prevent fouling and scaling of the membranes.

2.5 Analytical Methods

Fluoride and nitrate were measured using Metrohm 781 Ion Meter with fluoride and nitrate ion-selective electrodes (ISE). Conductivity (mS/cm) readings that were taken during all experiments were converted to NaCl concentration from the following equation (determined from standard NaCl solutions); where EC is the electrical conductivity in µS/cm and the NaCl concentration is expressed in mg/L.

$$NaCl\ Concentration = \frac{EC - 89.4}{1.8}$$

3 Results and Discussion

3.1 Effect of Voltage on Desalination Kinetics

The concentration of NaCl in the diluate stream as a function of time and voltage and an initial salt concentration of 5 g/L NaCl is shown in Figure 4. As can be seen, the time it takes to reach the NaCl guideline value of 500 mg/L for drinking water decreases as the applied voltage is increased (70, 50, and 27 min at 9, 12, and 18V, respectively). The same trend was also seen in the experiments with the initial salt concentration of 10 g/L NaCl (73 and 37 min at 12 and 18 V) (See Figure 5). In the experiment with the initial salt concentration of 10 g/L NaCl and applied voltage of 9V the water was not desalinated to below the guideline value. Both Figure 4 and Figure 5 the NaCl concentration in the diluate rapidly decreases within the initial 30 minutes. After this point the decrease in salt concentration slowed down and an accompanying smaller incremental decrease in the current between the two electrodes within the stack was noted. This can be explained with both concentration polarization in the

membrane boundary layer as well as depletion of electron carriers in the diluate. For desalination to occur in electrodialysis there needs to be sufficient current between the cathode and anode. It is possible that in the experiment with an initial salt concentration of 10 g/L NaCl, the current across the stack after 180 mins (results not shown) was insufficient to continue the desalination process. For this reason an applied voltage of 12 V was determined to be an optimum operating parameter of this electrodialysis system.
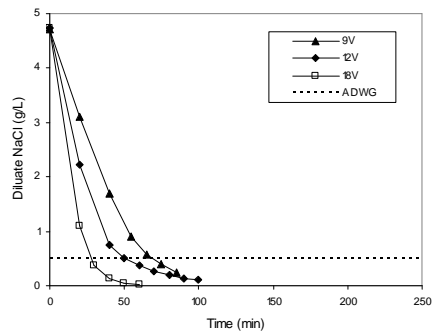

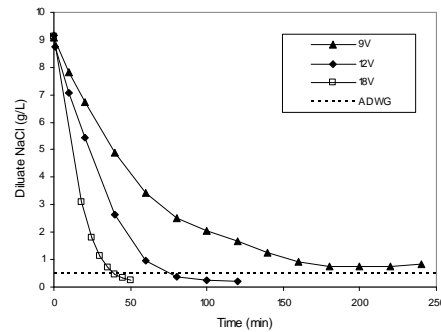Figure 4 Diluate salt concentration as a function of voltage. Initial feed solution concentration of 5 g/L NaCl

Figure 5 Diluate salt concentration as a function of voltage. Initial feed solution concentration of 10 g/L NaCl

3.2   Effect of Feed Salt Concentration on Desalination Kinetics

The feed salt concentration was tested as a variable in order to determine the scope of electrodialysis for a range of groundwater salinities. The results are shown in Figure 6. The NaCl guideline value for drinking water was reached only in the experiments with an initial salt concentration of 1 g/L NaCl (17 min, 50% removal), 5 g/L NaCl (60 min, 90% removal) and 10 g/L NaCl (115 min, 95% removal). In the experiments with an initial salt concentration of 20, 25 and 35 g/L NaCl the guideline value was not reached using this system and applied voltage, however a removal of between 97.5-98.5% NaCl was achieved. After 90 to 120 min the desalination becomes marginal.
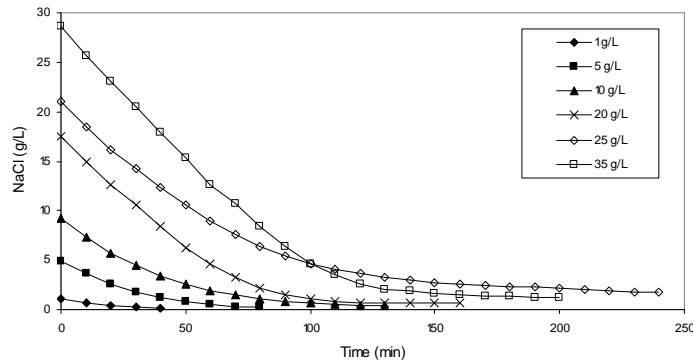

Figure 6 Diluate salt concentration as a function of initial feed salt concentration

3.3   Desalination Kinetics of Pine Hill Bore Water

To evaluate the relevance of laboratory experiments in comparison with real bore water pine Hill bore water was used for a series of experiments. Naturally, this bore water consists of a variety of ions and hence the NaCl equivalent is not a correct measure. For this reason electrical conductivity was presented also. The electrical conductivity and NaCl concentration within the diluate stream in the desalination of Pine Hill bore water is shown in Figure 7. The NaCl concentration decreases linearly with time until 100 minutes after which the variation decreases and levels slightly. These results show that the bore water can be sufficiently desalinated within 83 minutes, which is significantly longer than the 50 minutes required for synthetic saline solution (see Figure 4). Such a decrease in the kinetics can be explained with the presence of a variety of ions that may not transport as fast as NaCl as well as a decreased efficiency due to the formation of membrane deposits.
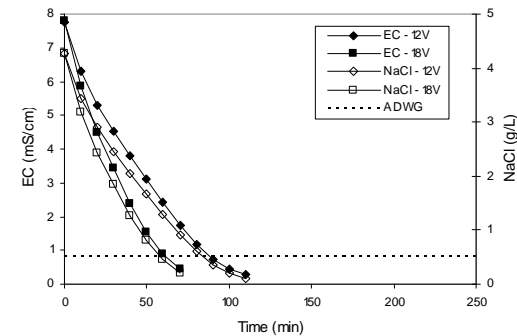

Figure 7 Diluate concentration as NaCl equivalent and electrical conductivity (EC) of Pine Hill Bore Water

3.4   Fluoride and Nitrate Removal from Pine Hill Bore Water

The variation of fluoride and nitrate concentration with time and within the diluate stream is shown in Figure 8 and Figure 9, respectively. Fluoride removal kinetics increased with increasing voltage (73 min at 12V and 49 min at 18V), while the nitrate removal kinetics were not drastically influenced by the applied voltage (3.5 min at 12V and 5 min at 18V). The initial concentration of nitrate in the bore water (31.1 mg/L) was close to the recommended maximum concentration level (25 mg/L). Therefore, a minimal removal (about 19%) nitrate was required in this case to meet the guideline value. Fluoride required a removal of about 50% which was also achieved. The kinetics for both compounds are very different and those differences may be a result of concentration or ion characteristics.

Scaling of the cation-exchange membranes was an issue in the Pine Hill bore water experiments. Figure 10 shows a picture of a clean cation- exchange membrane before use and the same membrane after use. Scaling is the precipitation of crystalline divalent and trivalent ion hydroxides such as $CaCO_3$, $MgCO_3$, $Mg(OH)_2$ and $CaSO_4$ on the concentrate side of the cation-exchange, and to a lesser extent on the anion-exchange membranes [19]. Membrane fouling during ED is a major limiting factor in its use for water treatment as the long-term chemical stability of membranes is influenced by the occurrence of scaling and further work is in progress to characterise the deposits and investigate fouling mechanisms in detail.
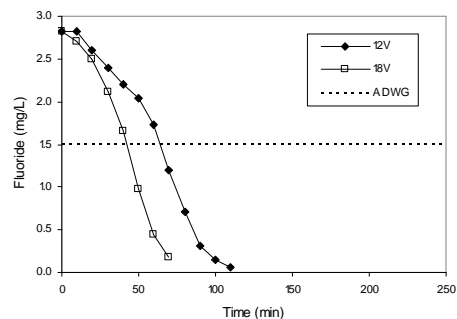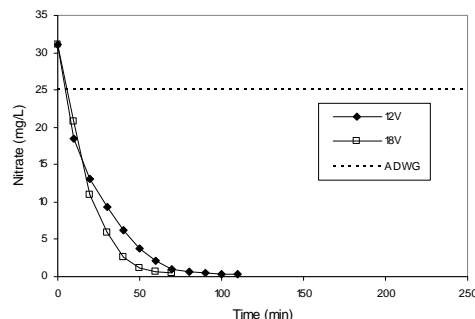
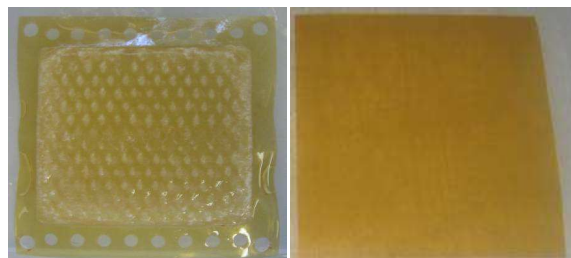Figure 8 Fluoride removal from Pine Hill Bore Water   Figure 9 Nitrate removal from Pine Hill Bore Water

Figure 10 Picture of a clean (right) and fouled (left) cation-exchange electrodialysis membrane.

4   Conclusions

The results of this study show that electrodialysis is capable of being used to desalinate brackish water was well as water with higher salt concentrations up to about 35 g/L NaCl, i.e. seawater. Fluoride and nitrate removal by electrodialysis was conducted on brackish bore water from Pine Hill in Central Australia which has a fluoride and nitrate content of 2.8 and 31.1 mg/L respectively. This study showed that desired drinking water can be obtained by the electrodialysis of ground water with fluoride and nitrate concentrations above Drinking Water Guidelines levels. Further work is required to determine fouling mechanisms as well as trace contaminant removal mechanisms.

5   Acknowledgements

6   References

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