UDK 628.161:546.16

**Rangappa S. Keri, Kallappa M. Hosamani,**
**Harisha R. Seetharama Reddy,**
**Sanna Kotrappanavar Nataraj, Tejraj M. Aminabhavi**

# APPLICATION OF ELECTRODIALYTIC PILOT PLANT FOR FLUORIDE REMOVAL

*Removal of fluorine from water was investigated by electrodialysis method. In order to check the efficacy of ED unit, parameters like applied potential, pH; initial fluoride concentrations and flow rates were varied. Significant results were obtained with concentrations of less than 10 ppm. Results were satisfactory in meeting the maximum contaminate level (MCL) of 0.01 ppm for fluoride. Effect of working parameters on energy consumption was investigated using ion-exchange membranes. Results of this study are useful for designing and operating different capacities of ED plants for recovering different ions. The ED plant was found to be satisfactory to produce a good quality drinking water from the simulated mixture by removing the unwanted ions.*

**Keywords:** fluoride, electrodialysis, limiting current density, membranes.

## INTRODUCTION

Fluoride in minute quantity is an essential component for normal mineralization of bones and formation of dental enamel [1]. However, its excessive intake may result in slow, progressive crippling scourge known as fluorosis. There are more than 20 developed and developing nations that are endemic for fluorosis.

These are Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria, India, etc. [2 – 7]. In India, it was first detected in Nellore district of Andhra Pradesh in 1937 [8]. Since then considerable work has been done in different parts of India to explore the fluoride laden water sources and their impacts on human as well on animals. The safe limit of fluoride in drinking water is 1.0 mg/L [9]. The endemic fluorosis in India is largely of hydro-geochemical origin. It has been observed that low calcium and high bicarbonate alkalinity favor high fluoride content in groundwater [10, 11].

Water with high fluoride content is generally soft, has high pH and contains large amount of silica. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature, the action of other chemicals and the depth of wells. Due to large number of variables, the fluoride concentrations in groundwater range from well under 1.0 mg/L to more than 35.0 mg/L [12].

Fluorine is highly reactive and is found naturally as $CaF_2$. It is an essential constituent in minerals like topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite, etc. The fluoride is found in the atmosphere, soil and water. It enters the soil through weathering of rocks, precipitation or waste run off. Surface waters generally do not contain more than 0.3 mg/L of fluoride unless they are polluted from external sources. Though drinking water is the major contributor (75 – 90% of daily intake), other sources of fluoride poisoning are food, industrial exposure, drugs, cosmetics, etc. [13]. The principal objective of this paper is to investigate in detail the application of ED process consisting a set of a ion-exchange membranes used to separate fluoride from the drinking water.

Reverse osmosis (RO) and electrodialysis (ED) are the widely used membrane processes in defluoridation of fluoride-rich waters at present, some of including pilot scale studies [14 – 21]. The drawback of RO in treating fluoride-rich waters is that up to 99% of the salts in the water are rejected by the membrane, which means almost all fluoride is eliminated. NF is operated at lower pressures and can yield same permeate flux at lower pressure. In particular, in treating fluoride-rich waters, NF processes can provide a partial defluoridation and an optimal fluoride content in permeate can possibly be achieved by adjusting the operation conditions. In this present work, electrodialytic pilot plant was tested for its potential application in removing fluoride from ground water and simulated mixtures. The limiting current density (LCD) was calculated for different potentials to understand the efficiency of the ED process in saving electrical energy requirements. The effects of working parameters like initial concentration, electrical potential and flow rates were varied in an effort to reserve the energy consumption.

## EXPERIMENTAL

***Materials and feed preparation.*** Calcium Fluoride ($CaF_2$) was purchased from S.D. Fine Chemicals (Mumbai India). 0.012M solution of $CaF_2$ was prepared in deionized water. The prepared Calcium fluoride (1ppm, 5ppm, 10 ppm) solution is taken in the feed (tank 1). Deionized water having a conductivity of 0.694 mS was used in the concentrate tank (50% of feed volume) to facilitate 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. Specifications of mixture ground water samples and simulated prepared for this study is shown in Table 1.

***Analytical methods.*** Ion-selective Electrode Method was adopted to measure the concentration of fluoride. 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 (TDScan1)

*Table 1. Specifications of the average feed composition used for the ED experiments*

| Parameters | Concentration |
|---|---|
| Conductivity mS/cm at 25°C | 4.2 |
| pH | 7.2 |
| Total dissolved solids (TDS), mg/L | 2050 |
| Calcium hardness as $CaCO_3$, mg/L | 1380 |
| Chloride, mg/L | 180 |
| Sodium, mg/L | 50 |

***ED setup***. A schematic diagram of our ED apparatus (designed in-house) consisting of a membrane stack and spacers is shown in Fig. 1. The system consists of three round-bottomed glass tanks, one each for feed (dilute), 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.

***Limiting current density***. Cowan and Brown's method was adopted to determine the LCD for the ED experiment. Electrical current, $I$, across the ED stack was increased when the DC stack resistance, $R = V/I$ was measured. Electrical resistance was then plotted Vs reciprocal electrical current ($1/I$). The point gives the limiting current where electrical resistance starts to increase. LCD was then calculated from the limiting current using the effective membrane area.

***Energy consumption.*** The energy consumption (EC) required in an ED process is the sum of electrical energy to transfer the ionic species through ion selective membranes and the energy required to pump various solutions through the ED stack. It is a measure of the power consumed in Watts per liter (W/L) for transportation of ions and was calculated by using the equation:

$$\mathrm{EC} = \frac{E\int_0^t I dt}{V_D} ,$$

where $E$ is potential, $I$ is current, $V_D$ is volume of the dilute and $t$ is time.

## RESULTS AND DISCUSSION

One of the most important parameters pertaining to the application of ED is electrical potential. Applied voltage and reduction in concentration of fluoride with time in the ED process is summarized in Table 1. Experiments were performed at a constant flow rate of 0.8 L/min for the dilute 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, currents, and temperatures of all the solutions of the dilute 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 2 shows the relative elimination of ions.

Changes in electrical conductivity of the dilute stream (feed, Tank 1) as a function of time at three constant applied voltages is shown in Fig. 2. Electrical conductivity of the diluate solution decreased exponentially with time. In cases where 40 and 50 V continuously decrease in electrical conductivity was due to the deionization of dilute solution. However, only in case of 60 V, the unusual trend with more than the initial value was noted.

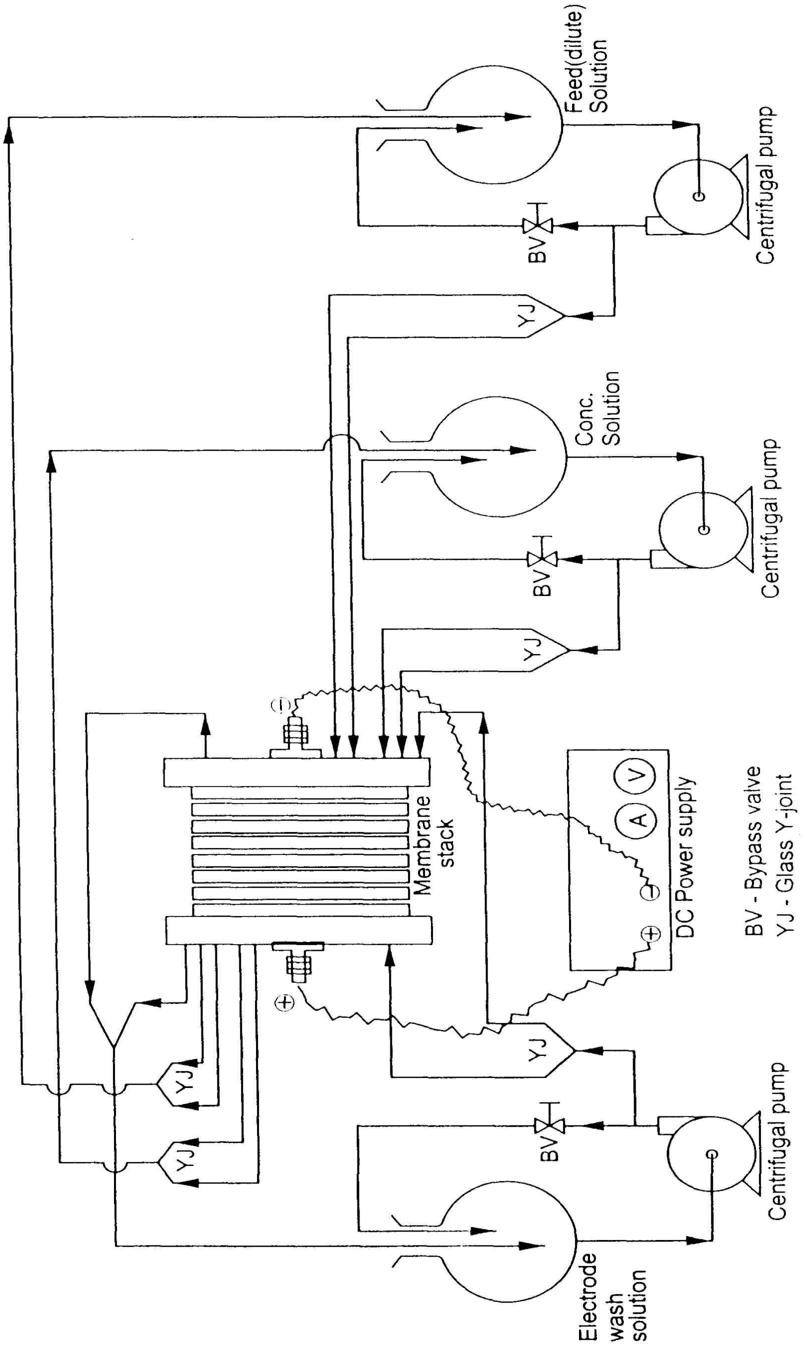

*Fig. 1. Electrodialysis experimental set-up*

*Table 2. Time and voltage dependence of anion and cation concentrations of the feed solution*

| Time (min) | $Cl^-$ (ppm) | | | $Ca^{2+}$ (ppm) | | | $Na^+$ (ppm) | | | TDS (ppm) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50v | 45v | 40v | 50v | 45v | 40v | 50v | 45v | 40v | 50v | 45v | 40v |
| 0 | 170 | 180 | 180 | 544 | 533 | 553 | 551 | 550 | 545 | 2060 | 2090 | 2050 |
| 30 | 120 | 160 | 140 | 436 | 404 | 424 | 328 | 365 | 370 | 1730 | 2150 | 2170 |
| 60 | 90 | 150 | 110 | 252 | 292 | 384 | 231 | 269 | 286 | 1410 | 1799 | 1895 |
| 90 | 60 | 100 | 80 | 188 | 228 | 252 | 159 | 206 | 231 | 1020 | 1430 | 1439 |
| 105 | 50 | 80 | 70 | 164 | 174 | 228 | 117 | 183 | 216 | 900 | 1282 | 1291 |
| 120 | 40 | 70 | 50 | 112 | 132 | 160 | 142 | 152 | 174 | 810 | 1101 | 1117 |
| 135 | 20 | 50 | 40 | 72 | 104 | 124 | 43 | 40 | 140 | 550 | 928 | 859 |
| 150 | 10 | 40 | 30 | 56 | 72 | 80 | – | – | – | 430 | 802 | 760 |

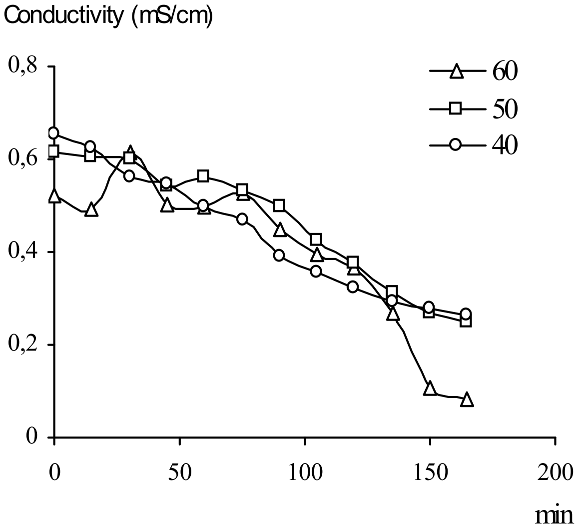

*Fig. 2. Conductivity as function of time at 40 V*

This is due to the osmotic pressure in the diluate side and concentrated tanks, i.e., the concentration gradient in its initial stage may force the solvent transport into the concentrate tank. Also, the dissociation of solvent itself may cause an increase in conductivity at higher potential. However, this is observed through a sudden increase in the level of concentrate tank. A significant difference was observed in electrical conductivity of the diluate at the end of the operation for 60 V with the higher transfer rates of ion and back-flow of the solvent, which has resulted in achieving a very low conductivity of 0.084 μS.

***Limiting current density.*** Since current affects the performance of the ED system, the selection of rigorous current density holds an important role, which is always influenced by the power sources and membrane specification. Conversely, it should be noted that LCD is not a constant value, it will change with working conditions and operating time of the ED system. In the present study, LCD for the simulated dilute stream was determined as described before. When two straight lines were plotted for the measured data points, the intersection of these lines represents the LCD as shown in Fig. 3.

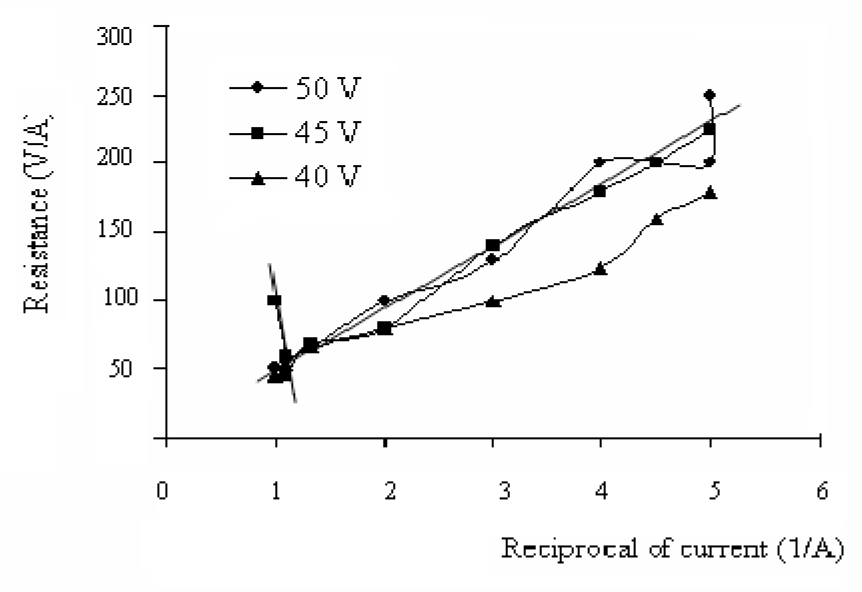

*Fig. 3. Plot of reciprocal of current vs resistance*

The fourth-order polynomial regression of data points was used in this experiment, where the absolute minimum of this regression was chosen to represent the LCD. For different potentials, results of minimum found for reciprocal electrical current (*1/I*), limiting current ($I_{lim}$) and limiting current density ($i_{lim}$) (current divided by the effective membrane area gives LCD) are given in Table 3.

*Table 3. Limiting Current Density for Different Applied Voltages*

| Voltage (volts) | *1/I* (1/A) | $I_{lim}$ (A) | $i_{lim}$ (mA/cm$^2$) |
|---|---|---|---|
| 40 | 1.0 | 1.11 | 11.11 |
| 45 | 1.1 | 0.9 | 9.0 |
| 50 | 1.0 | 1.0 | 10.0 |

The minimum limiting value of 10 mA/cm$^2$ was found for an electrical potential of 50 V. However, as noted before LCD is not a constant value; it will change with working conditions and operating time of the ED system.

To check the effectiveness of the new system for different potential applications, we have carried out ED experiments with 50, 20 and 10 mg/L initial concentrations. These results are displayed in Fig. 4.

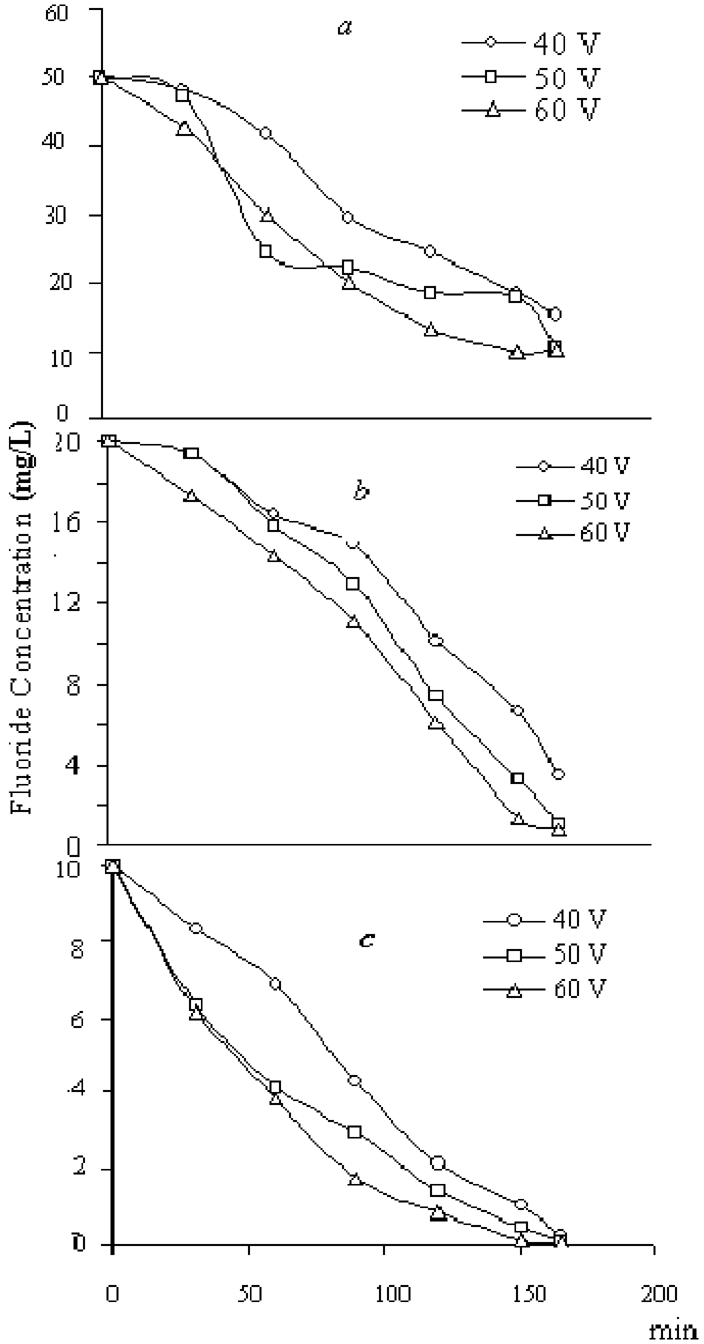

*Fig. 4. Plot of fluoride ion concentration vs time*

With the operation time of 165 min and of 50 mg/L concentration, a highest of 79.22 % was achieved at 50 V potential. For 20 mg/L initial concentration, the rejection rate was extended up to 82 % at 40 V, 94.45 % at 50 V and 95.95 at 60 V. Even though at higher potential the same trend was observed at 50 V, which was indeed optimal. For lower initial concentration of 10 ppm, the ED stack was found to be highly effective in achieving 99 % of rejection and these values are much below the MCL. Analytical observations illustrate the efficient removal up to 97 %, 99.2 % and 99.6 %, respectively at 40, 50 and 60 V with 10 mg/L initial concentration in contaminated water sources. The elevation of current efficiency from 97 to 99.6 % is explainable by a constant voltage and the decreasing concentration of ions. The optimization of voltage or current applied during separation will increase the process efficiency. However, the most important parameter is the duration of separation itself, which has to be considered in connection with the product volume and purity. It is demonstrated that high fluoride and other impurities of water can be removed in 165 min of the full ED operation performed under three constant applied voltages at the ambient temperature.

Fig. 5 and 6 respectively, indicate the removal path of the TDS and chlorides as a function of time at different applied voltages.

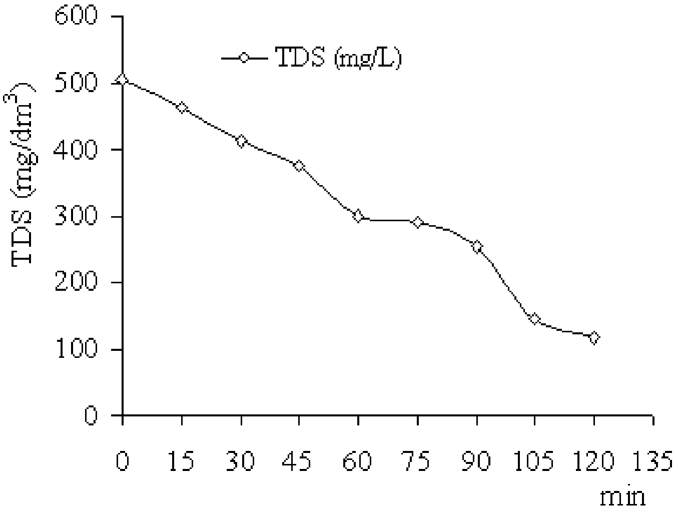

*Fig. 5. Plot of TDS vs time*

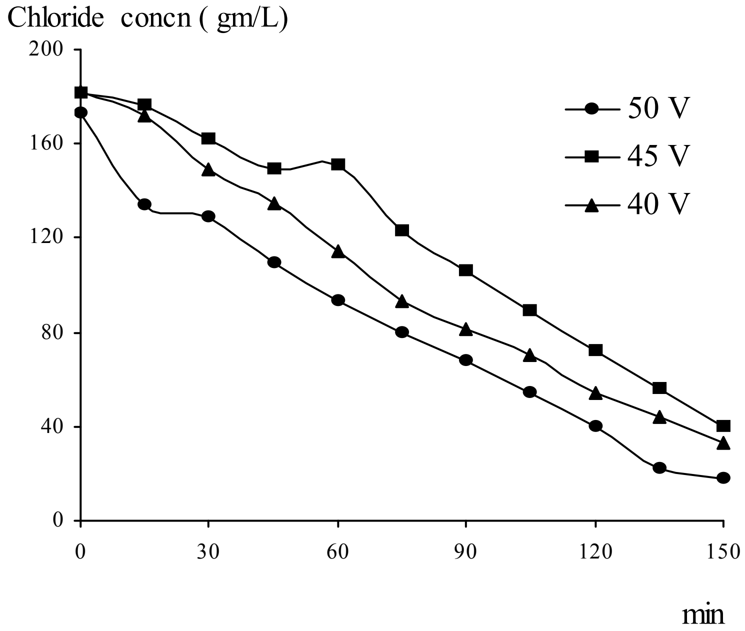

*Fig. 6. Plot of chloride ion concentration vs time*

Since salts are used for the regeneration of the ion exchanger, the diluate stream contains substantial amount of sodium and chloride ions. As chloride is exchanged as counter ion in this process, the chloride level of the product is elevated. At higher voltage of 50 V, the sudden decrease in TDS at the initial time up to 30 min is observed due to the possible deionization of salt mixtures.

The energy consumption in an ED process is related to the amount of desired ionic species that are transferred through the membranes. Excluding the capital, operating costs as well as considering the working parameters, calculated values confirmed that energy consumption increases with an increase in the applied voltage as expected. At optimum LCD values, the electrical energy consumption in Watts per liter (*Wh*/*L*) for the pilot plant is plotted in Fig. 7 vs. different potentials applied.

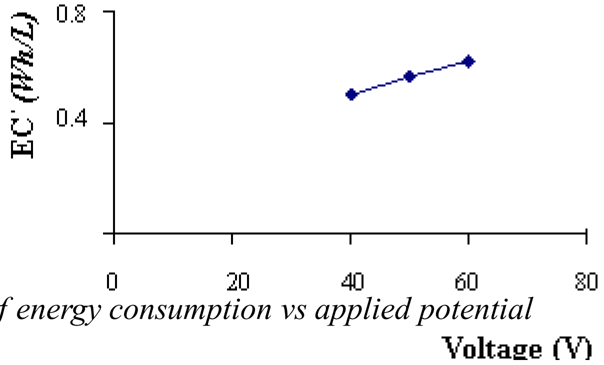

*Fig. 7. Plot of energy consumption vs applied potential*

The effect of flow rate on separation performance was not so apparent. For different flow rates of 0.4, 0.8 and 1.2 L/min studied, separation was almost the same as documented for most of the selected concentrations and applied potentials. However, the specific ion transfer depends on equivalent fraction of the corresponding ion in raw water, but mobility depends upon the type of membranes used.

## CONCLUSIONS

The present study demonstrates the effective usage of an ED process for the removal of fluoride from groundwater. The commercial ED membranes used in this study could greatly decrease the fluoride 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. At 50 V the removal of ions was slower because of the back diffusion of solvent (water) resulting from membrane fouling and selectivity decreases, because these ions could occupy the active sites of the membrane.

### ACKNOWLEDGMENTS

This research work is financially supported by the Department of Science & Technology (DST), New Delhi - 110 016. (Ref. No SR/S1/OC-08/2005 dated 05-09-2005).

**Резюме.** Исследовано удаление фтора из воды методом электродиализа. Для проверки эффективности электродиализной установки варьировали приложенную разность потенциалов, начальную концентрацию фторида и скорость потока. Важные результаты были получены при начальной концентрации фторида <10 мг/дм$^3$. С использованием ионообменных мембран исследовано влияние рабочих параметров на энергопотребление. Результаты данной работы будут полезны для разработки и планирования производительности электродиализной установки при выделении различных ионов. Электродиализная установка оказалась эффективной для получения питьевой воды хорошего качества из модельных растворов путем удаления нежелательных ионов.

**Резюме**. Досліджено видалення фтору з води методом електродіалізу. Для перевірки ефективності електродіалізної установки варіювали прикладену різницю потенціалів, початкову концентра цію фторидута швидкість потоку. Важливі результати були отримані при початковій концентрації фториду <10 мг/дм$^{3.}$ З використанням іонообмінних мембран досліджено вплив робочих параметрів на енергоспоживання. Результати цієї роботи будуть корисні длярозробки та планування продуктивності електродіалізної установки при виділенні різних іонів.Електродіалізна установка виявилася ефективною для отримання питної води хорошої якості з модельних розчинів шляхом видалення - небажани х онів

1. *Kass A., Yechieli Gavrieli Y., Vengosh A., Starinsky A.* // J. Hydrol. – 2005. – **300**. – P. 314 – 331.
2. *Amina C., Lhadi L.K., Younsi A., Murdy J.* // J. Afr. Earth Sci. – 2004. – **39**, N 3/5. – P. 509 – 516.
3. *Oren O., Yechieli Y., Bohlke J.K., Dody A.* // J. Hydrol. – 2004. – **290**, N 3/4. – P. 312 – 328.
4. *Anwar F.*// Waste Manage. – 2003.– **23**, N 9. – P.817– 824.
5. *Liu A., Ming J., Ankumah R.O.* // Sci. Tot. Environ. – 2005. – **346**, N1/3. – P. 112 – 120.
6. *Charles F.H., Swartz C.H., Badruzzaman A.B.M., Nicole K.B., Yu W., Ali A., Jay J., Beckie R., Niedan V., Brabander D.* // Comptes Rendus Geosci. –2005. – **337**, N1/2. – P. 285 – 296.
7. *Mameri N., Yeddou A.R., Lounici H., Grib H., Bariou B. D.*// Water Res. – 1998. – **32**, N 5. – P.1604 – 1610.
8. *Pandit C.G., Raghavachari T., Rao D.S., Murthy K.* // Ind. J. Med. Res. – 1940. – **28** – P. 533 – 558.
9. *Rukah A., Alsokhny K.* // Chem. Erde Geochem. – 2004. – **64**, N2. – P. 171 – 181.
10. *Mulligan C.N., Yong R.N., Gibbs B.F.*// Eng. Geol. – 2001. – **60**, N1/4. – P. 93 – 200.
11. *Demkin V. I., Tubashov T. A., Panteleev V. I., Kaelin Y. V.* // Desalination. – 1987. – **64**. – P. 367 – 374.
12. *Cherif A. T., Molenat J., Elmidaoui A. J.* //Appl. Electrochem. – 1997.– **27**. – P.1069 –1074.
13. *WHO* (World Health Organization), Guidelines for Drinking Water Quality (II): ealth Criteria and Supporting Information, World Health Organization, Geneva, Switzerland, 1984.
14. *Hichour M., Persin F., Sandeaux J., Gavach C., Hichour M., Persin F., Sandeaux J., Gavach C.* // Separ.Purif.Technol.– 2000. – **18**. – P.1 – 11.
15. *Jane Huang C., Liu J.C.*// Water Res. – 1999. – **33**. – P. 3403 – 3412.
16. *Azbar N., Turkman A.* //Water Sci. and Technol. – 2000. – **42**, N1/2. – P. 403 – 407.
17. *Amor Z., Malki S., Taky M., Bariou B., Mameri N., Elmidaoui A.*//Desalination. – 1998. – **120**. – P. 263 – 271.
18. *Rumeau M., Pontie M.* Rencontre Internationale sur les Fluorures, les Nitrates et les Pesticides dans les Eaux du Bassin Mediterraneen: Problemes et Traitements, Kenitra, 1997.
19. *Wang H., Ji J., Chen J.* //Environ. Geosci.– Paper No. 83 – 18, Booth 18,

Denver Annual Meeting, 2002.
20. *Killedar D. J., Bhargava, D.S.* // Ind. J. Environ. Health. – 1993.– **35**, N 2. – P. 81– 87.
21. *Sinha S., Sa R., Singh S.* // Bull. Environ. Contan. Toxical. – 2000. – **65.** – P. 683 – 690.

P.G. Department of Studies in Chemistry,
Karnatak University,
Membrane Separation Division,
Center of Excellence in Polimer Science,
Karnatak University, Dharwad, India

Recieved 06.04.2009