ELECTRODIALYTIC REMOVAL OF NITRATE AND HARDNESS FROM SIMULATED MIXTURES USING ION-EXCHANGE MEMBRANES

ABSTRACT
An indigenously built electrodialysis (ED) pilot plant unit coupled with the membrane stack containing 11 cation exchange and 10 anion exchange membranes was used for the removal of nitrate and hardness from the simulated aqueous mixtures containing salts that are usually encountered in brackish water. It is demonstrated that high nitrate and hardness of water could be removed in 150 min of ED operation performed under three constant applied voltages at room temperature. Limiting current density (LCD) was obtained for \( \text{NaNO}_3 \) and \( \text{CaCl}_2 \) mixtures in dilute solution. In order to check the efficacy of ED method, parameter like applied potential was varied at constant flow rates. The efficiency of the ED method depends upon the applied potential. Potential applications of ED are discussed for the removal of contaminants below the minimum contaminant level (MCL) of drinking water. The ED method used here is found to be satisfactory to produce good quality drinking water from the simulated mixture by removing the unwanted ions.

Results of this chapter are published in *Journal of Applied Polymer Science*, 99 (2006) 1788–1794
III.A.1. INTRODUCTION

Shortage of drinking water is a major issue all around the globe. Electrodialysis (ED) is an effective process to remove the unwanted ions from the wastewater streams [1]. When a potential difference is applied between both the electrodes, cations move towards cathode and anions towards 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 decrease in the adjacent compartment (diluate). However, temperature may not have any effect on the rate of separation of salts from the mixed media and hence, the ED can be operative continuously. These advantages make ED attractive especially for desalination of brackish water and re-concentration of sodium chloride from seawater. In addition, this method has been widely used for production of table salt, organic acids, remediation of heavy metal polluted soil, sugar demineralization, blood treatment and wine stabilization [2-6].

Nitrogen is essential for all living things as 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 nitrogen containing compound, commonly present in natural waters, because it is the product of aerobic decomposition of organic nitrogenous matters. Nitrate concentration in groundwater or surface freshwater reaches, in some places² more than 100 mg/L. Significant sources of nitrate are chemical fertilizers, decayed vegetables and animal matters, domestic effluents sewage sludge disposal to land and industrial discharge from refuse dumps and atmospheric washout. The major concern affecting human health pertains to
infants less than six months of age is the excessive nitrate concentration. More than 10 mg/L of the nitrate concentration will cause health hazards, especially in infants due to a bacterium that exists in their gastrointestinal tract, which converts nitrate to nitrite. The nitrite produced reacts with hemoglobin to form methemoglobin that 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, but nitrate reaction products, nitrosamines and nitrosamides are strongly considered as potential human carcinogens [10].

U.S. Public Health Service [11] adopted drinking water standards and set acceptable limit for nitrate-nitrogen at 10 mg/L, while WHO [12] guidelines allow maximum contaminant level (MLC) of 50 ppm as NO₃. According to European Community (EC) standards, drinking water should not contain > 50 mg/L of nitrate; the Bureau of Indian Standards has defined the desirable limit of nitrate to be < 45 mg/L, while a value of 25 mg/L is highly recommended [13]. Nearly, every chemical standard in force today incorporates a ten to 100-fold safety factor to ensure that sensitive members of the population are adequately protected.

Several researchers have studied the nitrate recovery using ED membranes [14, 15]. Kesore et al. [16] used the anion exchange membrane coupled with a new inter-membrane spacer containing nitrate-selectivity anion exchange resin to improve the selectivity and effectiveness of nitrate removal from drinking water. 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, carbonate, bicarbonate and sulfate. In this study, the removal of nitrate and hardness of synthetic (laboratory simulated) solution was studied by ED. Limiting current density (LCD) and the effect of working parameters
on energy consumption was investigated using the commercial ion-exchange membranes.

III.A.2. RESULTS AND DISCUSSION

Specifications of average feed composition used for ED experiments are given in Table III.A.1. Experiments were performed at a constant flow rate of 0.8 L/min for diluate, concentrate and 0.6 L/m for electrode wash. The voltage was varied from 40 to 50 V, with an increment of 5 V.

Table III.A.1. Feed Water Characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity mS/cm at 25°C</td>
<td>4.2</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
</tr>
<tr>
<td>Total dissolved solids (TDS), mg/L</td>
<td>2500</td>
</tr>
<tr>
<td>Calcium hardness as CaCO₃, mg/L</td>
<td>1380</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>1780</td>
</tr>
<tr>
<td>Calcium, mg/L</td>
<td>550</td>
</tr>
<tr>
<td>Sodium, mg/L</td>
<td>550</td>
</tr>
<tr>
<td>Nitrate, mg/L</td>
<td>420</td>
</tr>
<tr>
<td>Magnesium and potassium, mg/L</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

These values were chosen so as not to exceed the maximum values recommended by the manufacturer of the ED membranes for the electric current and flows. The current intensity was read at each stage for every value of the applied voltage. Also, 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 diluate stream; concentrates were recorded at constant time intervals, which are directly related with their respective saline concentration. Samples of the
Membrane Based Separation Processes for Effluent Treatment

solutions were collected at every 15 min of time interval for the analysis.

Table III.A.2 shows the relative elimination of ions.

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

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>NO$_3^-$ (ppm)</th>
<th>Cl$^-$ (ppm)</th>
<th>Ca$^{2+}$ (ppm)</th>
<th>Na$^+$ (ppm)</th>
<th>TDS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50v 45v 40v</td>
<td>1730 1810 1820</td>
<td>544 533 553</td>
<td>551 550 545</td>
<td>2560 2590 2550</td>
<td></td>
</tr>
<tr>
<td>15 332 310 379</td>
<td>1340 1760 1720</td>
<td>517 496 492</td>
<td>463 394 410</td>
<td>2470 2400 2380</td>
<td></td>
</tr>
<tr>
<td>30 290 271 294</td>
<td>1290 1620 1490</td>
<td>436 404 424</td>
<td>328 365 370</td>
<td>1730 2150 2170</td>
<td></td>
</tr>
<tr>
<td>45 241 226 221</td>
<td>1090 1490 1350</td>
<td>304 328 396</td>
<td>274 305 319</td>
<td>1570 1975 1940</td>
<td></td>
</tr>
<tr>
<td>60 198 190 191</td>
<td>930 1510 1140</td>
<td>252 292 384</td>
<td>231 269 286</td>
<td>1410 1799 1895</td>
<td></td>
</tr>
<tr>
<td>75 150 146 152</td>
<td>800 1230 930</td>
<td>236 252 288</td>
<td>196 236 265</td>
<td>1230 1596 1674</td>
<td></td>
</tr>
<tr>
<td>90 120 113 126</td>
<td>680 1060 810</td>
<td>188 228 252</td>
<td>159 206 231</td>
<td>1020 1430 1439</td>
<td></td>
</tr>
<tr>
<td>105 101 90 113</td>
<td>540 890 700</td>
<td>164 174 228</td>
<td>117 183 216</td>
<td>900 1282 1291</td>
<td></td>
</tr>
<tr>
<td>120 40 42 78</td>
<td>400 720 540</td>
<td>112 132 160</td>
<td>142 152 174</td>
<td>810 1101 1117</td>
<td></td>
</tr>
<tr>
<td>135 38 31 52</td>
<td>220 560 440</td>
<td>72 104 124</td>
<td>43 40 140</td>
<td>550 928 859</td>
<td></td>
</tr>
<tr>
<td>150 - - -</td>
<td>180 400 330</td>
<td>56 72 80</td>
<td>- - -</td>
<td>430 802 760</td>
<td></td>
</tr>
</tbody>
</table>

Table III.A.3. Limiting current density for different applied voltages

<table>
<thead>
<tr>
<th>Voltage (volts)</th>
<th>1/I (1/A)</th>
<th>$I_{lim}$ (A)</th>
<th>$i_{lim}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.0</td>
<td>1.11</td>
<td>11.11</td>
</tr>
<tr>
<td>45</td>
<td>1.1</td>
<td>0.9</td>
<td>9.0</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

III.A.2.1. Limiting Current Density

The limiting current density for the simulated diluate stream was determined as described before. When two straight lines are plotted for the measured data points, the intersection of these lines represents the limiting current density. For three constant voltages, the quantity, $1/I$ as a function of
resistance is shown in Figure III.A.1. 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 limiting current density. For different potentials, results of minimum found 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 III.A.3. Minimum limiting value of 9 mA/cm\(^2\) was found for an electrical potential of 45 V. However, it should be noted that LCD is not a certain value; it will change with the working conditions and operating time of the ED system.

![Graph](image)

**Figure III.A.1.** Plot of reciprocal of current vs. resistance

Changes in electrical conductivity of the diluate stream (feed, Tank 1) as a function of time at three constant applied voltages is shown in Figure III.A.2. The electrical conductivity of dilute solution decreased exponentially with time. The continuous decrease in electrical conductivity was mainly due to the deionization of dilute solution. A significant difference is observed in the electrical conductivity of dilute when operating the ED stacks at different applied voltages; a higher transfer rate of ion is observed at 50 volts.
The pH evolution in the diluate fraction during the ED experiment is shown in Figure III.A.3, as a function of time. The average starting pH was noted as 7.7; at 50 volts, the pH of diluate stream decreased more significantly than the other applied potentials. This sudden decrease in pH down to 3.1, after a linear slow decrease from 7.7 to 6.8 with time may be due to the dissociation of water molecules and liberation of hydrogen ions. Thus, the liberated hydrogen ions may involve 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 as per the chemical reaction:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (\text{III.A.1})
\]

\[
\text{NO}_3^- + 6\text{H}^+ + 5e^- \rightarrow \frac{1}{2} \text{N}_2(g) + 3\text{H}_2\text{O} \quad (\text{III.A.2})
\]
The removal of nitrate ion from diluate as a function of time is shown in Figure III.A.4. Ion exchange in the ED cells generally substitutes chloride anions for the nitrate anion without substantially changing the salinity of the feed water. Nitrate is thus preferentially removed and replaced by the chloride ions unless special nitrate selective resin is used. Since, membranes of this study are not completely selective and due to the batch nature of the process, anion composition and pH of the product will change over the service cycle. Moreover, it is observed that between 30-90 min of operation time, the nitrate removal rate at all different 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 (T2). This may be due to the osmosis (back diffusion) of water from tank T1 to tank T2 and at this voltage, the active sites of the ED membranes are taken by the anions and thus, membrane selectivity decreases due to poor mobility of the anions. However, at the lower voltage of 45 V, higher nitrate removal was achieved.
Figure III.A.4. Plot of nitrate ion concentration vs time.

Figure III.A.5. and Figure III.A.6, respectively indicate the removal path of the total dissolved solids (TDS) and chlorides as a function of time at different applied voltages. 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 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 nitrate ion concentration. 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.

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 III.A.7 shows the results of a comparative study for the separation of monovalent (Na\(^+\)) and divalent (Ca\(^{2+}\)) ions by electrodialysis. 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.
Figure III.A.5. Plot of TDS vs time.

Figure III.A.6. Plot of chloride ion concentration vs time.
Membrane Based Separation Processes for Effluent Treatment

Figure III.A.7. Plot of Na$^+$ (-•-) and Ca$^{2+}$ (-♦-) concentration vs time at different applied potentials

At the optimum LCD, the electrical energy consumption in Watts per liter (Wh/L) for the pilot plant is plotted against different potentials applied as shown in Figure III.A.8. Energy consumption calculations were made for a final concentration of NO$_3^-$ in the 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, NO$_3^-$ concentration,
Na\(^+\), Ca\(^{2+}\) concentrations as well as the Cl\(^-\) ion concentrations are all within minimum contaminant level (MCL) for drinking water.

![Figure III.A.8. Plot of energy consumption vs applied potential.](image)

**III.A.3. CONCLUSIONS**

The present study demonstrates the effective usage of electrodialysis process for the removal of nitrate from the groundwater. Optimal limiting current density of 9 A/cm\(^2\) was found for NaNO\(_3\) and CaCl\(_2\) mixture of dilute solution. At 50 volts, the removal of ions is slower due to the back diffusion of solvent (water) resulting from membrane fouling and selectivity decrease, because these ions could occupy the active sites of the membrane. More than 94 % of nitrate, 89 % of chloride and 86 % of TDS was successfully removed after 150 min of operation of the ED.
III.A.4. REFERENCES


CHAPTER-III A
POTENTIAL APPLICATION OF ELECTRODIALYSIS PILOT PLANT CONTAINING ION-EXCHANGE MEMBRANES IN CHROMIUM REMOVAL

ABSTRACT

Exploration of a new working system to investigate the removal of chromium ions in its hexavalent oxidation state singly in connection with different parameters and associated moieties in feed mixtures was performed using an indigenously built electrodialysis the (ED) pilot plant comprising a set of ion-exchange membranes. In order to check the efficacy of ED unit, parameters like applied potential, pH, initial chromium concentration of diluate and flow rates were varied. Significant results were obtained with lower initial concentrations of less than 10 ppm. Results were satisfactory in meeting the maximum contaminate level (MCL) of 0.1 ppm for chromium. Effect of working parameters on energy consumption was investigated using ion-exchange membranes (IEMs). Results of this study are useful for designing and operating different capacities of ED plants for recovering different ions. The ED plant used in this research was found to be satisfactory to produce a good quality drinking water from the simulated mixture by removing the unwanted ions.

Results of this chapter are published in Desalination (in Press, 2007)
III.B.1. INTRODUCTION

Chromium (Cr) is a naturally occurring ubiquitous element found in air, water, rocks, soil, animals, volcanic dust and gases. Cr is found in the environment in three major forms or oxidation states: trivalent Cr(III), hexavalent Cr(VI), and metallic Cr(0); of these the first two are the most important and common forms. However, its form depends upon the pH level. Cr(III) is more stable, less toxic and listed as an essential element as micronutrient to maintain good health and helps in maintaining the normal metabolism of glucose, cholesterol and fat in human bodies [1]. It is poisonous only at high concentration. Chromium hexavalent (VI) is extensively used in chemical industries such as electroplating, wood preservation, metal finishing, chrome plating and leather tanning and is highly toxic when compared to Cr(III) in biological streams. At short-term exposure levels above the MCL, chromium causes skin and stomach irritation or ulceration. Long-term exposure at levels above MCL can cause dermatitis, damage to liver, kidney circulation, nerve tissue damage and death in large doses [2,3]. Cr(VI) is highly poisonous and endangers public health and the environment. U.S. Public Health Service has adopted drinking water standards and set an acceptable limit for Cr(VI) at 0.1 mg/L, while the European Community (EC), Bureau of Indian Standards (BIS) and WHO [4,5] guidelines allow the maximum contaminant level (MLC) of 0.1 mg/L as Cr(VI).

Metallic contaminants are not easily removed without the advanced treatment. Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units and tanneries often contain metal ions at concentrations above the local discharge limits [6]. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel and copper. Groundwater around many mining, plating and processing industries, nuclear fuel
complexes and military bases often is contaminated with many toxic hazardous components. Chemical precipitation, oxidation/reduction, mechanical filtration, carbon adsorption are among the variety of traditional treatment processes that are widely used for the removal of toxic heavy metals from the waste streams [7-10]. Several researchers have studied chromium removal from water using ED membranes [11-15]. Even though, it is necessary to recover chromium in different environmental compartments collectively with its different oxidation states, hexavalent chromium salts are soluble in water, so it is considered a primary contaminant due to its ability to gain access to ground water and soil. In this study, the effect of working parameters like initial concentration, electrical potential, pH and flow rates were varied in an effort to reserve the energy consumption. The limiting current density (LCD) was calculated for different potentials to understand the efficiency of the ED process in saving electrical energy requirements.

IIIB.2. RESULTS AND DISCUSSION

It is well known in ED experiments that mobilities of the ions within a membrane depend upon external variables like concentration, pH and current density. Because of their effect in recovering both the oxidation states of chromium from an aqueous solution, an extensive study was made in the solution medium. In this route, experiments were performed at different flow rates of 0.4, 0.8 and 1.2 L/min for diluate, concentrate and a constant of 0.6 L/m for the electrode wash. Voltage was varied from 40 to 60 V, with an increment of 10 V. These values were chosen so as not to exceed the maximum values recommended by the manufacturer of the ED membranes for electric current and flow rates. The current intensity was read at each stage for every value of the applied voltage. Also, the flow rates of feed, concentrate and wash streams were determined together with
their respective electrical conductivities, pH, currents and temperatures of all solutions of the diluate stream; concentrates were recorded at constant time intervals, which are directly related with their respective saline concentrations. Samples of solutions were collected at every 15 min time interval for the analysis.

One of the most important parameters pertaining to the application of ED is electrical potential. Applied voltage and reduction in concentration of Cr(VI) with time in the ED process is summarized in Table III.B.1. 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 effluent. The elevation of current efficiency from 97 to 99.6 % is explainable by a constant voltage and the decreasing concentration of ions as shown in Figure III.B.1. 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 chromium 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.

III.B.2.1. 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. 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 presented in Table III.B.2. The minimum limiting value of 10 mA/cm² 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.

Figure III.B.1. Plot of Cr(VI) concentration vs run time for different initial concentrations.
Table III.B.1. Voltage and initial concentration dependence of Cr(VI) in dilute solution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>40 Volts</th>
<th>50 Volts</th>
<th>60 Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial concentrations (ppm)</td>
<td>Initial concentrations (ppm)</td>
<td>Initial concentrations (ppm)</td>
</tr>
<tr>
<td>30</td>
<td>48.29 19.31 8.34</td>
<td>47.38 19.39 6.93</td>
<td>42.58 17.34 6.17</td>
</tr>
<tr>
<td>60</td>
<td>41.75 16.36 6.86</td>
<td>27.38 15.82 4.11</td>
<td>30.11 14.32 3.85</td>
</tr>
<tr>
<td>90</td>
<td>29.70 14.88 4.28</td>
<td>22.40 12.93 2.96</td>
<td>20.06 11.12 1.75</td>
</tr>
<tr>
<td>120</td>
<td>24.40 10.23 2.13</td>
<td>18.43 7.40 1.39</td>
<td>13.35 6.13 0.82</td>
</tr>
<tr>
<td>150</td>
<td>18.42 6.69 1.01</td>
<td>13.79 3.37 0.49</td>
<td>9.96 1.41 0.13</td>
</tr>
<tr>
<td>165</td>
<td>15.32 3.56 0.22</td>
<td>10.39 1.11 0.08</td>
<td>10.2 0.81 0.04</td>
</tr>
</tbody>
</table>

Table III.B.2. Limiting current density for different applied voltages and pH

<table>
<thead>
<tr>
<th>Voltage (Volts)</th>
<th>1/I</th>
<th>I_{lim}</th>
<th>i_{lim} (mA/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.96</td>
<td>1.04</td>
<td>10.4</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>60</td>
<td>0.98</td>
<td>1.02</td>
<td>10.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>3</th>
<th>0.85</th>
<th>1.17</th>
<th>11.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 50 V</td>
<td>6</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.99</td>
<td>1.01</td>
<td>10.1</td>
</tr>
</tbody>
</table>

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

**III.B.2.2. Effect of Initial Concentration**

As Cr(VI) is widely used in chemical industries such as electroplating, wood preservation, metal finishing, chrome plating and leather tanning, it is found in different concentrations. 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 Figure III.B.3. 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. Efficient removal of chromium from the feed phase to a cathodic or anodic solution is essential for quantitative transport. Below pH 6.5 the dominant species is Cr(OH)₂ while the precipitate state is Cr(OH)₃, which is insoluble and dominates between pH 6.5-10.5. Therefore, the experimental conditions were specifically arranged because of the solution chemistry of chromium.

**III.B.2.3. Effect of pH**

The effect of pH on the transportation of Cr(VI) is shown in Figure III.B.4. Transfer of ion is greater at lower pH and decreases with increasing pH. The Cr(VI) can exists in several stable forms such as Cr₂O₇²⁻, HCr₂O₇²⁻, HCrO₄⁻, and CrO₄²⁻. However, the relative abundance of a particular complex depends upon the concentration of chromium ion and pH of the solution. At lower pH, Cr(VI) in its dichromate form exists mostly as an anion as per the reaction;

\[
Cr_2O_7^{2-} + H_2O \longrightarrow 2CrO_4^{2-} + 2H^+ \quad (III.B.1)
\]

As per Fig 6, the removal rate for lower level pH of 3 is elevated when compared to higher pH, leading to an effective removal of Cr(VI) even though the efficiency of the ED stack has shown nearly the same results at 165 min of ED run. Since, we have used HCl to prepare the diluate of pH 3, the process of ion exchange in ED cells substitutes the
Membrane Based Separation Processes for Effluent Treatment

chloride anions for chromium anion without substantially changing the salinity of feed water.

**Figure III.B.3.** Plot of Cr(VI) concentration vs run time for different initial concentrations.

CHAPTER-IIIB 66
The pH values of 3, 6.0 and 8.0 were investigated in order to observe the effect of pH on the removal rate and energy consumption. The removal rate and energy consumption were approximately the same at pH values of 3, 6.0 and 8.0 when a suitably high potential is applied. Chromium is thus preferentially removed and was replaced by the chloride ions unless special nitrate selective resin is used. However, due to the batch nature of the process, membranes of this study are not completely selective; the anion composition as well as pH of the solution will change over the service cycle. Figure III.B.5, supported this with a slow increase in pH from 3.1 to 5.6. The LCD were found to be 11.7, 10 and 10.1 mA/cm², respectively corresponding to pH values of 3.0, 6.0 and 8.0. By exceeding the limiting current density, water dissociation occurred as shown by the pH shift in dilute and concentrate chambers and the changes of pH value in this experiment were not remarkable.

Figure III.B.4. Plot of Cr(VI) ion concentration vs time for different pH
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. Figures III.B.6 and III.B.7 show respectively, the results of a comparative study of the separation of TDS and Na\(^+\) and K\(^+\), which are commonly encountered in hard water. Since the salts are used for regeneration of ion exchanger and to maintain the pH level, the diluate stream contains substantial amount of chloride ions.

Figure III.B.5. Plot of pH vs time.
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 ($W/l$) for the pilot plant vs. different potentials applied. The energy consumption
calculations were made for the final concentration of Cr(VI) in the diluate solution of 0.08 mg/L. When this concentration is reached, it can be assumed that water has been processed and is within the legal limits for drinking purpose. Thus, K⁺, TDS concentrations as well as Cl⁻ ion concentrations are all within the minimum contaminant level (MCL) for drinking water.

III.B.3. CONCLUSIONS

Applicability of ED technique for the removal of Cr(VI) ions from laboratory simulated solutions, which are analogous to different contaminant levels from the natural and polluted sources, has been investigated in a batch electrodialysis system to bring down to the level set by WHO from the polluted ground water. Even though membranes of this study are not completely selective for specific ions, the results of this study are satisfactory for the present ED system in removing other harmful ions from the polluted waters that causes hardness. However, the most convenient applied voltage and energy consumption values to remove the unwanted ions are reported in this work.
III.B.3. REFERENCES


