Total dissolved solids removal by electrochemical ion exchange (EIX) process

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ABSTRACT
In the present investigation, synthetic wastewater was prepared by the addition of required amount of salts into deionized water. Their performance, on removal of Cl\(^-\), SO\(_4\)\(^{2-}\), PO\(_4\)\(^{3-}\), Ca\(^{2+}\), Fe\(^{2+}\) and Mg\(^{2+}\) in laboratory scale plate and frame type electrochemical ion exchange (EIX) cells, were evaluated under varying operating conditions. Ruthenium dioxide coated titanium plates (RuO\(_2\)/Ti) were used as anode and stainless steel plates as cathode in all the four different EIX cells used in the present investigation. All the four EIX cells were run for a maximum of 7 h. Almost complete removal of all the above ionic solids were observed within 4.5–7 h under one or more test conditions.

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1. Introduction

Rinsed water and effluents from industries such as oil field refinery, tannery, electrical, metal plating, photographic processing, nuclear and mining, etc. contain high amounts of dissolved solids that are commonly known as total dissolved solids (TDS). The major portions of such solids are inorganic and present mostly in ionic form. Nowadays, removal of dissolved solids from industrial wastewater is a challenging job for the environmental engineers. Inorganic components of dissolved solids are more difficult to remove by biological processes. There are several other treatment methods such as chemical precipitation, adsorption, electrophoresis, softening and reverse osmosis, practiced to remove dissolved solids from wastewater. However, each method has its own limitations. Although these methods are effective on removal of certain heavy metals and organics, the pollutants either get adsorbed onto the adsorbent or form complex substances with chemicals that make it difficult to recover. As for example, even though removal of various components of TDS by chemical precipitation is a proven technology [1–3], it requires an efficient solid separation system as well as appropriate solid waste disposal facility [4]. Furthermore, chemical processes produce metal ions as waste. Increasing environmental restrictions on the waste produced by chemical plants make it necessary to develop a suitable method of removing these ions from wastewater. To overcome these problems, electrochemical methods and ionic membrane technologies have proven to be successful in several cases and new applications are being studied by a growing number of researchers. Membrane separation (ultra-filtration) [5,6] or reverse-osmosis [7] and electro-dialysis [8–10] are the treatment technologies that can be employed for TDS removal. However, these methods generate significant amount of solid wastes in the form of salts [11]. Shivakumar et al. [12] analyzed and reported that none of these methods alone was sufficient or suitable for TDS removal from tanning industrial wastewater. Still, electrochemical methods have been projected to have potential applications in wastewater treatment [13,14]. Electrochemical ion exchange (EIX) process is the combination of ion exchange, electro dialysis, and elusion processes. In EIX process an electric potential in place of chemical reagents is used to elute ion exchange media [15–19]. EIX process has some specific advantages over the other methods of inorganic solids removal such as longer life of ion exchange resins in...
### Table 1
Properties of ion exchange resins Ceralite IRA 400 and Ceralite IR 120

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ceralite IRA 400</th>
<th>Ceralite IR 120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer/supplier</td>
<td>CDH, New Delhi</td>
<td>CDH, New Delhi</td>
</tr>
<tr>
<td>Ionic group</td>
<td>Cl-form strongly basic AER</td>
<td>H⁺ strongly CER</td>
</tr>
<tr>
<td>Particle size</td>
<td>0.4–0.6 (effective size) mm</td>
<td>0.45–0.6 (effective size) mm</td>
</tr>
<tr>
<td>Physical form</td>
<td>Brown resinous spherical beads</td>
<td>Yellow brown spherical beads</td>
</tr>
<tr>
<td>Density</td>
<td>0.694 g/ml</td>
<td>0.77 g/ml</td>
</tr>
<tr>
<td>Exchange capacity (fresh)</td>
<td>3–3.5 mequiv./g</td>
<td>4.5 mequiv./g</td>
</tr>
<tr>
<td>Moisture content</td>
<td>42–48 wt%</td>
<td>45–50 wt%</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>150 °C</td>
<td>120 °C</td>
</tr>
<tr>
<td>pH range</td>
<td>0–14</td>
<td>0–14</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>8% DVB</td>
<td>8% DVB</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Nominal diameter</td>
<td>0.5 mm</td>
<td>0.5 mm</td>
</tr>
</tbody>
</table>

### Table 2
Configuration of EIX cells

<table>
<thead>
<tr>
<th>EIX cell</th>
<th>Ion exchange resin in different compartments</th>
<th>Type of ion permeable membrane in between (two) compartments</th>
<th>Ions removed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cathode Middle Anode</td>
<td>Cathode and middle compartment Middle and anode compartment</td>
<td></td>
</tr>
<tr>
<td>EIX cell-1</td>
<td>No resin AER</td>
<td>No resin APM</td>
<td>Cl⁻, SO₄²⁻, PO₄³⁻, Cl⁻, SO₄²⁻</td>
</tr>
<tr>
<td>EIX cell-2</td>
<td>AER</td>
<td>No resin APM</td>
<td>Ca²⁺, Mg²⁺, Fe²⁺</td>
</tr>
<tr>
<td>EIX cell-3</td>
<td>No resin CER</td>
<td>No resin CPM</td>
<td></td>
</tr>
<tr>
<td>EIX cell-4</td>
<td>Upper compartment No resin CER AER</td>
<td>No resin CPM</td>
<td>Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, PO₄³⁻</td>
</tr>
<tr>
<td></td>
<td>Lower compartment No resin CER AER</td>
<td>No resin CPM</td>
<td></td>
</tr>
</tbody>
</table>

*a* In all the cells the left compartment is connected with cathode and right compartment is connected to anode and thereby the name cathode compartment and anode compartment are designated respectively.

*b* AER, anion exchange resin.

*c* APM, anion permeable membrane.

*d* CER, cation exchange resin.

*e* CPM, cation permeable membrane.

Comparison to that of ion exchange process; longer life of membrane in comparison to that of reverse osmosis/membrane filtration process; simpler process of regeneration of ion exchange resins; generation of target pollutant free water; and recovery of target pollutant in pure form [20]. The method is useful for the removal of both cations and anions. Recently, more than 92% textile dye, expressed as COD, removal by electrochemical techniques followed by ion exchange process is reported [21]. However, the feasibility of EIX method on the removal of TDS has not been explored so far.

The paper describes various electrochemical cell configurations combining the use of anionic and cationic membranes to remove...
chloride, sulfate, phosphate, calcium, iron and magnesium from wastewater synthetically prepared in the laboratory.

2. Materials and methods

2.1. Materials

All the chemicals used in the present study were either of analytical reagent (AR) grade or laboratory regent (LR) grade. Deionized water used to prepare synthetic wastewater was prepared by passing double distilled water through the beds of cation and then anion exchange resins. Ruthenium oxide coated titanium metal (RuO$_2$/Ti) was used as anode and stainless steel plate as cathode. The areas of the electrodes are 39.2 cm$^2$ and 49 cm$^2$, respectively. Wastewater was pumped into the electrochemical cells, and anolyte and catholyte were recirculated at controlled rate, with the help of peristaltic pumps (Model: pp10, Miclins, India). The ion exchange resins, manufactured by Central Drug House (CDH), New Delhi, India, were procured from open chemical market. The trade name of anion exchange resin (AER) and cation exchange resin (CER) used in the present investigation are Ceralite IRA 400 and Ceralite IR 150, respectively. Various properties of Ceralite IRA 400 and Ceralite IR 150 are given in Table 1. Ceralite IRA 400 is a Cl$^-$ form strongly basic AER and Ceralite IR 150 is a H$^+$ CER. Ceralite IRA 400 was treated with sodium hydroxide solution to get OH$^-$ form AER before its use. These resins do not contribute with dissolved solids to the effluent as cation exchange resins exchange hydrogen ions with the dissolved cations and (treated) anion exchange resins exchange hydroxide ions with the dissolved anions. The anion permeable
membrane (APM) and cation permeable membrane (CPM) used in the present investigation were procured from NEOSEPTA, Sweden.

### 2.2. Analytical methods

Cations and anions were measured as per the procedure suggested in Standard Methods [22]. Calcium, iron and magnesium (Cations) were measured in Atomic Absorption Spectrophotometer (Model: SPECTRAA 220, Varian) in acetylene-nitrous oxide flame at 422.7 nm, 459.4 nm and 285.2 nm wavelength, respectively. The anionic components, phosphate and sulfate, were measured by photometric method, using a spectrophotometer (Model: NOVA 60, Merck, Germany). Phosphate was measured by stannous chloride method. Phosphate was reacted, under acidic condition, with ammonium molybdate to form molybdophosphoric acid. Stannous chloride was added to develop color due to molybdenum blue. The color intensity of molybdenum blue was measured after 10 min, but before 12 min of addition of stannous chloride reagent at a temperature range of 20–30°C, and at the wavelength of 690 nm. For the measurement of sulfate, samples were reacted with barium chloride to get colloidal precipitate of barium sulfate. Concentration of barium sulfate was estimated with the help of spectrophotometer at 420 nm. Standard curves were prepared using standard solution of phosphate and sulfate before quantitative estimation of these two parameters (not shown). Chloride was determined by Argetometric titration method using chromate solution as indicator. pH

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**Fig. 4.** Schematic diagram of EIX cell-4.
of the final effluent was monitored with the help of a digital pH meter.

2.3. Experimental set-up and configuration of EIX cells

Laboratory scale four EIX cells viz., EIX cell-1, EIX cell-2, EIX cell-3 and EIX cell-4, were fabricated and operated under varying applied voltage. Each of the four electrochemical cells consisted of three compartments viz., “anode compartment”, “cathode compartment” and “middle compartment”. Anode compartment and cathode compartment were connected by electrical power but separated by the third “middle compartment”. Middle compartment was either filled up with AER or CER whereas, anode compartment was always kept empty. Cathode compartment was either filled up with AER (EIX cell-2) or kept empty (EIX cell-1, EIX cell-3 and EIX cell-4). Middle compartment was separated from the two other compartments by either cation permeable membrane or anion permeable membrane (Table 2). The dimension of each chamber was 7 cm × 7 cm × 1.5 cm. Varying voltage was applied from an Aplab D.C. Regulated power source and maintained at 5.0 V, 7.5 V and 10.0 V with the help of a voltage regulator. In all the above cell configurations, wastewater to be treated was fed at the middle compartment at constant flow rate of 12 ml/min. A constant wastewater volume of 1 l or 3 l was treated in a fed batch mode. Relevant anions and/or cations concentrations in anolytes, catholytes and final effluent were measured at regular intervals of time. Anolyte and catholyte were recirculated with the help of two peristaltic pumps. The configurations of the four EIX cells used in the present investigation are described below.

2.4. EIX cell-1

Only the middle chamber of EIX cell-1 was filled up with AER whereas, the cathode chamber and anode chamber were kept
Table 3
Performance of electrochemical ion exchange cells

<table>
<thead>
<tr>
<th>EIX cell</th>
<th>TDS component</th>
<th>Volume (l)</th>
<th>Initial concentration (mg/l)</th>
<th>Voltage (V)</th>
<th>Maximum removal (%)</th>
<th>Time (h)</th>
<th>Reference figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>EIX cell-1</td>
<td>Chloride</td>
<td>1</td>
<td>230</td>
<td>5</td>
<td>100</td>
<td>5</td>
<td>Fig. 5A</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>1</td>
<td>145</td>
<td>7.5</td>
<td>92.4</td>
<td>7</td>
<td>Fig. 5B</td>
</tr>
<tr>
<td></td>
<td>Sulphate</td>
<td>1</td>
<td>110</td>
<td>5</td>
<td>99</td>
<td>7</td>
<td>Fig. 5C</td>
</tr>
<tr>
<td>EIX cell-2</td>
<td>Chloride</td>
<td>1</td>
<td>230</td>
<td>7.5</td>
<td>99.2</td>
<td>6</td>
<td>Fig. 5D</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>3</td>
<td>230</td>
<td>7.5</td>
<td>100</td>
<td>5</td>
<td>Fig. 5E</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>3</td>
<td>145</td>
<td>5</td>
<td>100</td>
<td>7</td>
<td>Fig. 5F</td>
</tr>
<tr>
<td>EIX cell-3</td>
<td>Calcium</td>
<td>1</td>
<td>100</td>
<td>5</td>
<td>98</td>
<td>7</td>
<td>Fig. 6A</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td>1</td>
<td>60</td>
<td>7.5</td>
<td>94</td>
<td>7</td>
<td>Fig. 6B</td>
</tr>
<tr>
<td></td>
<td>Magnesium</td>
<td>1</td>
<td>100</td>
<td>5</td>
<td>95</td>
<td>7</td>
<td>Fig. 6C</td>
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<tr>
<td>EIX cell-4</td>
<td>Calcium chloride (CaCl₂)</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>1</td>
<td>130</td>
<td>5</td>
<td>95.3</td>
<td>7</td>
<td>Fig. 6D</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>1</td>
<td>230</td>
<td>7.5</td>
<td>100</td>
<td>5</td>
<td>Fig. 6E</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>3</td>
<td>110</td>
<td>7</td>
<td>100</td>
<td>7</td>
<td>Fig. 6F</td>
</tr>
<tr>
<td>Calcium sulfate (CaSO₄)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>1</td>
<td>130</td>
<td>5</td>
<td>97</td>
<td>7</td>
<td>Fig. 7A</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>1</td>
<td>310</td>
<td>7.5</td>
<td>100</td>
<td>7</td>
<td>Fig. 7B</td>
</tr>
<tr>
<td></td>
<td>Magnesium</td>
<td>1</td>
<td>65</td>
<td>5</td>
<td>95</td>
<td>7</td>
<td>Fig. 7C</td>
</tr>
<tr>
<td>Magnesium sulfate (MgSO₄)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnesium</td>
<td>1</td>
<td>65</td>
<td>7.5</td>
<td>100</td>
<td>7</td>
<td>Fig. 7D</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>1</td>
<td>250</td>
<td>7</td>
<td>100</td>
<td>7</td>
<td>Fig. 7E</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>1</td>
<td>250</td>
<td>7</td>
<td>100</td>
<td>7</td>
<td>Fig. 7F</td>
</tr>
</tbody>
</table>

empty. The middle chamber was separated from the other two chambers by APM. The purpose behind such cell configuration was to enable anion removal by ion exchange into AER in the middle compartment and to facilitate the anions to drive towards anode compartment (i.e., right compartment) to contribute to anolyte, but to prevent any anions to migrate into the cathode compartment (i.e., left compartment). Schematic diagram of EIX cell-1 is shown in Fig. 1.

2.5. EIX cell-2

Both, the cathode chamber and middle chamber of this cell were filled up with AER and the middle chamber was separated from the other two chambers by APM. Thus, the configuration of this cell was similar to that of EIX cell-1 except that the cathode chamber was filled up with AER. The purpose behind this configuration of EIX cell was to evaluate, if better performance than EIX cell-1 could be achieved by introducing AER in two chambers (i.e., in middle and cathode chambers). Schematic diagram of EIX cell-2 is shown in Fig. 2.

2.6. EIX cell-3

In this cell configuration, the middle chamber was filled up with cation exchange resin whereas the other two chambers were kept empty. The middle chamber was separated from the other two chambers by cation permeable membranes (CPM). The purpose of this EIX cell was to facilitate cations removal from wastewater. Schematic diagram of EIX cell-3 is shown in Fig. 3.

2.7. EIX cell-4

This configuration consists of two EIX cells. The middle compartments of the upper cell and lower cell were filled up with CER and AER, respectively, whereas the other two compartments of top and bottom cells were kept empty. Furthermore, the middle compartments of the upper and lower cells were separated from the other two adjacent chambers (i.e., cathode and anode chambers) by CPM and APM, respectively. The purpose of this cell was to remove cations and anions simultaneously. Schematic diagram of EIX cell-4 is shown in Fig. 4.

3. Results and discussions

Performance of EIX cell-1, EIX cell-2, EIX cell-3 and EIX cell-4 are represented in Figs. 5–8, respectively. Each of these figures is embedded with six figures to represent the performance of a specific EIX cell on removal of a pollutant from a certain volume of wastewater at certain applied voltage. As for example, there are six embedded figures viz. Fig. 5A–F in Fig. 5 to represent...
the performance of EIX cell-1 on removal of chloride, phosphate and sulfate at 5 V or 7.5 V, from 1 l of wastewater. The embedded figure number is written at the bottom of left hand corner. The texts at the top of each embedded figure gives information about the “EIX cell used”, the “pollutant considered”, the “volume of wastewater taken for treatment’ and the “voltage applied”. Overall performances of all the four EIX cells are summarized in Table 3.

3.1. Performance of EIX cell-1

EIX cell-1 was operated at 5 V and 7.5 V for removal of the anions such as chloride, phosphate and sulfate from synthetic wastewater of 1 l volume. The cell (specific area of anode is 0.39 dm$^2$) was operated at 2.5 A/dm$^2$ to get 5 V and 5.0 A/dm$^2$ to get 7.5 V. During operation current varies from 0.4 A to 1.2 A. Initial chloride, phosphate and sulfate concentrations were 230 mg/l, 145 mg/l and 110 mg/l, respectively. Complete removal of all the anions were observed within 4–7 h of operation. Fig. 5 shows the performance of EIX cell-1 under six different operating conditions mentioned in the first top line of each embedded figures. As for example, “EIX cell-1, Cl$^-$ removal, Vol. = 1 l, 5 V” written in the top of the first embedded figure (Fig. 5A), indicates “the performance of EIX cell-1 on removal of chloride from 1 l of wastewater at 5 V.” Table 3 shows the summary of performance of EIX cell-1 on removal of Chloride, phosphate and sulfate. Influence of increased applied voltage from 5 V to 7.5 V was not significant in terms of pollutant removal except on phosphate removal. About 7% increase in phosphate removal was observed after 7 h of operation, when the voltage was increased from 5 V to 7.5 V. Enhanced rate of removal of chromium due to increase in voltage from 12 V to 15 V is reported recently [23]. However, only a little effect was observed on enhancing the rate of removal of pollutant to achieve complete removal (Table 3). pH of the effluent increased from initial value of 7 to a maximum of 10.5 with due course of operation. However, the time taken to reach the maximum pH of 10.5 was faster at higher applied voltage of 7.5 V. Liberation of hydroxyl ions in exchange with anions leads to rise in pH of the solution. Removal of anions and increase in effluent pH can be explained with the following reactions [Eqs. (1)-(3)] that take place with AER.
Fig. 7. Performance of EIX cell-3. (A and B) Ca\(^{2+}\) removal from 1 l wastewater at 5 V and 7.5 V; (C and D) Fe\(^{2+}\) removal from 1 l wastewater at 5 V and 7.5 V; (E and F) Mg\(^{2+}\) removal from 1 l wastewater at 5 V and 7.5 V.

3.2. Reaction with AER

\[ \text{R}^{+} \text{OH}^{-} + \text{Cl}^{-} \rightarrow \text{RCl} + \text{OH}^{-} \]  
\[ 2\text{R}^{+} \text{OH}^{-} + \text{SO}_{4}^{2-} \rightarrow \text{R}_{2}\text{SO}_{4} + 2\text{OH}^{-} \]  
\[ 3\text{R}^{+} \text{OH}^{-} + \text{PO}_{4}^{3-} \rightarrow \text{R}_{3}\text{PO}_{4} + 3\text{OH}^{-} \]

where, \( \text{R}^{+} \) represents the cationic group attached to ion exchange resin and \( \text{OH}^{-} \) is the exchangeable part of the anion exchange resin. \( \text{Cl}^{-}, \text{SO}_{4}^{2-} \) and \( \text{PO}_{4}^{3-} \) are the anions in solution.

3.3. Performance of EIX cell-2

Operation of EIX cell-2 was started with 5 V to treat 1 l of synthetic wastewater having initial chloride concentration of 230 mg/l. The performance of the cell on removal of chloride under above mentioned conditions is shown in the embedded figure (Fig. 6A) in Fig. 6. Complete removal of chloride, from 1 l of above mentioned wastewater was observed in 5 h of operation. This showed no improvement on the rate of chloride removal in EIX cell-2 from EIX cell-1, at an applied voltage of 5 V. So, the presence of AER in the cathode compartment could not help in enhancing the cell’s performance under the above experimental condition. As mentioned earlier, the purpose behind running the EIX cell-2 was to evaluate, if the performance of EIX cell-1 would increase, in terms of rate and/or degree of removal, due to introduction of AER in two chambers viz. middle chamber and cathode chamber. Therefore, 3 l of wastewater was considered (in place of 1 l) for all subsequent experiments with EIX cell-2. To evaluate the role of additional AER, 3 l of synthetic wastewater with initial chloride concentration of 230 mg/l was treated at 7.5 V and 10 V. The performance of the cell is shown in embedded figures Fig. 6B and C, respectively. It took about 6 h for complete removal of chloride at 7.5 V. However, time taken to achieve complete removal of chloride in EIX cell-1 was 4.5 h, which was less than that of EIX cell-2 (Table 3). This might be due to higher volume (3 l) of wastewater considered for treatment in EIX cell-2 than that (1 l) in EIX cell-1. On the other hand, complete chloride removal from 3 l of wastewater was achieved at shorter period of 5 h at higher applied voltage of 10 V (Fig. 6C). The higher rate of removal in this case might be due to higher cell voltage,
as explained earlier [23]. Besides, complete removal of phosphate was observed in this cell, even at 5 V. However, it took 7 h for complete removal of phosphate or sulfate at 5 V or 7.5 V (Fig. 6D–F). Increase in effluent pH under all the operating conditions were found similar to that in EIX cell-1. Maximum pH observed was near 10.5, which was the same to that of EIX cell-1. This might be due to the same strength wastewater considered for treatment in both of the cells. The reason for increase in pH and removal of anions can be explained with the help of Eqs. (1)–(3). Thus, the performance of EIX cell-2, under various operating conditions explained, were only comparable to that of EIX cell-1. Introduction of AER in the cathode compartment could not decrease the time for complete removal of the anions. Effect of higher voltage (10 V) on chloride removal was small. Furthermore, higher cell voltage can produce more amounts of hydrogen at cathode and oxygen at anode [Eqs. (4) and (5)].

Cathode reaction:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (4)$$

Anode reaction:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (5)$$

In the present system, requirement of voltage was only to facilitate $\text{H}^+$ and $\text{OH}^-$ generations and their migration. Higher applied voltage causes higher rate of reactions on electrodes surfaces to generate more $\text{O}_2$ and $\text{H}_2$. Evolutions of these gases reduce energy efficiency of the process. Therefore, all the subsequent experiments were carried out only at 5 V and 7.5 V.

3.4. Performance of EIX cell-3

EIX cell-3 was operated at 5 V and 7.5 V, for the removal of the cations such as calcium, iron and magnesium, from synthetic wastewater of 1 l volume. Influent calcium, iron and magnesium concentrations were 100 mg/l, 60 mg/l and 100 mg/l, respectively. Although, EIX cell-3 could not completely remove any of the above mentioned cations at 5 V, complete removal of all the cations were observed at 7.5 V (Fig. 7). Furthermore, percentage increase (due to increase of applied voltage) on calcium, iron and magnesium
removal was 2%, 6% and 5%, respectively (Table 3). Enhanced performance of EIX cells on cations removal due to increase in applied voltage or current density have been reported [23,24]. pH of the effluent decreased from near 7 in the influent to a minimum of 2 with due course of operations. Liberation of hydrogen ions in exchange with cations leads to a fall in pH of the solution. Removal of cations and decrease in effluent pH can be explained with the help of following reactions [Eqs. (6)–(8)] that take place with CER:

Reactions with CER:

\[
\begin{align*}
2H^+ (R')^{-} + Ca^{2+} & \leftrightarrow Ca(R')_2 + 2H^+ \\
2H^+ (R')^{-} + Fe^{2+} & \leftrightarrow Fe(R')_2 + 2H^+ \\
2H^+ (R')^{-} + Mg^{2+} & \leftrightarrow Mg(R')_2 + 2H^+ 
\end{align*}
\]

(6) (7) (8)

where \((R')^{-}\) represents the anionic group attached to ion exchange resin and \(H^+\) is the exchangeable part of the cation exchange resin.

\(Ca^{2+}\) \(Fe^{2+}\) \(Mg^{2+}\) are the cations in solution.

3.5. Performance of EIX cell-4

EIX cell-1 and EIX cell-2 were configured to remove only anions whereas, EIX cell-3 was configured to only remove cations. However, EIX cell-4 was configured to remove both the ions. EIX cell-4 consists of two different EIX cells viz., cation removal cell (EIX cell-3) at the top and anion removal cell (EIX cell-1) at the bottom. Performance of this cell on removal of 3.25 mM of calcium chloride and calcium sulfate, and 2.6 mM of magnesium sulfate were evaluated at applied voltage of 5 V and 7.5 V (Fig. 8). More than 95% of cation (calcium) and complete removal of anion (chloride) were observed at 5 V within 7 h of operation (Fig. 8A). However, complete removal of both the components of the salts was observed at 7.5 V (Fig. 8B). Similar trends were observed on cations and anions removal during calcium sulfate and magnesium sulfate removals at 5 V and 7.5 V (Fig. 8C–F).

3.6. Regeneration and reuse of membranes and resins

In EIX process regeneration of membranes and/or resins is not required to do separately. Anions are removed from the flowing solution by the AER in the anion process compartment [Eqs. (1)–(3)]. The adsorbed anions then migrate under the influence of an electric field through an APM into the middle compartment (Figs. 1 and 2). Hydroxyl ions (OH\(^-\)) electrochemically produced at the cathode (Eq. (4)) migrates continuously to regenerate the process stream AER [backward reaction Eqs. (1)–(3)]. \(H^+\) ions produced at the anode (Eq. (5)) are excluded by the APM from entering the anion process stream. Similarly, cations are removed from the flowing solution by the cation exchange resin in the cation process compartment [Eqs. (6)–(8)]. The adsorbed cations then migrate under the influence of an electric field through CPM into the cathode compartment (Fig. 3). \(H^+\) ions electrochemically produced at the anode, migrate continuously to regenerate the process stream CER [backward reaction Eqs. (6)–(8)]. OH\(^-\) ions produced at the cathode are excluded by the CPM from entering the cation process stream (Fig. 3). In the present experimental conditions, the membranes and the resins in a particular reactor (EIX cell) were reused for next runs.

3.7. Usefulness of the EIX cells for higher strength wastewater treatment

The reactions of anions with AER (Eqs. (1)–(3)) cause an increase in pH and decrease in AER capacity with the increase in anion concentration in wastewater. Similarly, the reactions of cations with CER (Eqs. (6)–(8)) will cause a decrease in pH with the increase in cation concentration in wastewater. In both the cases, decrease in capacity of resins (AER and CER) will be more rapid with the increase in influent ion concentration. As discussed earlier, the resins get regenerated by self-regenerating mode due to the reaction with \(H^+\) and \(OH^+\) ions (backward reactions (1)–(3) and (6)–(8)) after their generation (Eqs. (4)–(5)) and migration into the middle chambers through respective ion permeable membranes. However, the rate of generation of \(H^+\) and \(OH^+\) ions (on the anode surfaces and the cathode surfaces, respectively) should be sufficient to prevent the resins from being exhausted completely. Thus, the EIX cells used in the present investigation are expected to be suitable in treating higher strength wastewater under a suitable applied voltage, flow rate, and/or quantity of resins in the middle chambers.

4. Conclusion

In the present investigation, four different configurations of EIX cells were operated under various operating conditions to evaluate their performance on removal of various ionic components from aqueous phase. Almost complete removal of all the ions was possible in one or more operating conditions tried. pH changes observed under various conditions were due to liberation of \(H^+\) or \(OH^+\) ions during ion exchange operation. Water, after treatment through EIX cell-4, was free from salts. Effects of membranes and ion exchange resins were reused without giving separate treatment for their regeneration, as the resins and membranes get regenerated by self-regeneration mode. An increase in applied voltage may help in reducing operation time to achieve complete removal of certain ions. The cells may be suitable for higher strength wastewater provided a suitable applied voltage, flow rate, and/or quantity of ion exchange resins be selected.

References