Research Article

Selection of the Best Process Stream to Remove Ca\(^{2+}\) Ion Using Electrodialysis from Sugar Solution

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Electrodialytic removal of calcium chloride (CaCl\(_2\), 25–50 mol m\(^{-3}\)) from 5% sugar solution was executed in batch recirculation mode. Calcium ion removal rate was monitored with (i) applied potential, (ii) feed flow rate, (iii) solution viscosity and conductivity, and (iv) catholyte streams (NaOH or sodium salt of ethylene diamine tetraacetic acid-acetic acid, Na\(_2\)EDTA-AA). Unsteady state model for ion concentration change was written for the ED cell used. Linearized Nernst-Planck equation instead of Ohm’s law was applied to closely obtain the current density and concentration change theoretically. The model developed could closely predict the experimental observation. Mass transfer coefficients and specific energy densities were estimated for each combination of catholyte stream used. NaOH showed better performance for a short duration over Na\(_2\)EDTA-acetic acid combination.

1. Introduction

In cane based sugar industry the sugar concentration in the extracted juice after lime (CaO + H\(_2\)O) treatment and color removal (clarification step) usually reaches around 5% (mass basis). This stream subsequently enters into series of evaporators to get concentrated. Presence of excess calcium in the postfloculation and precipitation stage of clarified sugar juice creates series of nuisance [1] to the subsequent stages (evaporators, etc.) in sugar industries affecting product quality as follows.

1. Scale formation in the evaporators.
2. Improper crystallization.
3. Molasses percentage may increase due to inversion of sugar in alkaline medium.
4. Storage is hampered because of hygroscopic nature of these metals ions.
5. Excess calcium is not hygienic as well.

Therefore, removal of it at appropriate stage would drastically reduce operation and maintenance (evaporator scaling) cost and improve product quality. Electrodialysis (ED) was chosen to remove CaCl\(_2\) from its sugar solution. ED was applied earlier in sugar industry to recover tartrate and malate from grape sugar [2] and in demineralisation of beet sugar syrup, juice, and molasses [3, 4]. The technological difficulties arise due to fouling of ion exchange membranes mainly due to deposition of organic/inorganic molecules (sugars, proteins, Ca\(^{2+}\), Mg\(^{2+}\), etc.). With increase in solution viscosity fouling becomes even severe and affects the current efficiency and ion removal rate. The concentration polarization occurs around membrane surface leading to increase in ion resistance, and this is minimized with the help of suitable spacer design, temperature, pH, and flow rates applied [5–11].

A batch recirculation ED process having a single diluate channel was performed to remove the CaCl\(_2\) from sugar solution. As reported elsewhere [5] during ED process concentration polarization arises around the membrane which limits
the net salt transport. This issue was taken up and sorted out using different combination of anolyte and catholyte streams. Different electrolyte streams (NaOH, acetic acid-Na$_2$EDTA mixture) were selected as catholyte keeping anolyte as HCl solution.

In a batch mode electrodialysis with continuous recirculation of feed stream, properties like electrolyte concentration of diluate (feed tank), concentration profiles around that membrane, and all physical properties of the solution change with time. The effect of all these parameters is reflected in ion removal rate and current density of the ED cell. Therefore, an unsteady state model that can closely predict the ion removal rate and overall current density will be quite relevant in application point of view. Nernst-Planck equation (purely based on first principles) and irreversible thermodynamics were used to estimate current density and ion concentration [12].

2. Materials and Methods

2.1. Equipment

2.1.1. Electrodialysis Setup. The experimental setup used for ED application is shown in the Figure 1 [13]. The ED cell and setup were from Berghof, Germany. The electric field was applied across the cell stack by a built-in D.C. source. Voltage and current between the two electrodes were measured by a built-in digital voltmeter and ammeter, respectively. The ED cell consisted of three compartments as shown in the figure. Membranes used were obtained from Permeonics, Gujarat, and cross-linked styrene and di-vinyl benzene gel was used as base material. Cation exchange membrane (CEM) separates the cathode compartment and anion exchange membrane (AEM) separates the anode compartment from the feed chamber. The effective membrane area for the cell, $A_m$, was 0.0037 m$^2$ and the feed compartment thickness, $h$, was 0.002 m.

2.1.2. Power Supply. The power supply was provided through a voltage stabilizer of 110/220 V A.C. with 50–80 Hz frequency. The same gave an output voltage 0–49.9 V DC and current 0–3.99 A. Four centrifugal pumps were inbuilt with the system for pumping the solution.

2.1.3. Conductivity Meter. Solution conductivity was noted at regular interval through an offline conductivity meter (Systronics India) of 200 mMho with 5 ranges (accuracy ±1%).

2.1.4. ED Cell Compartments and Solutions Used. 1000 mL solutions of each stream (feed, catholyte, and anolyte) were taken in three chambers (Figure 1), respectively. Each chamber was connected with the respective three compartments of the ED cell through flexi tubing. Solutions were circulated at a constant rate by three centrifugal pumps and the solution flow rates were measured using rotameters connected to each stream. Table 1 indicates membrane parameters obtained from Permeonics India Ltd. The composition and flow rates of three streams used are reported in Table 2.

Synthetic solution of 5% sugar and calcium chloride (CaCl$_2$) was prepared in distilled water. The concentration of sugar was kept unchanged but that of CaCl$_2$ was varied. The synthetic solution having CaCl$_2$ with initial concentrations of 25 mol·m$^{-3}$ and 50 mol·m$^{-3}$ were used in the diluate channel of ED cell. Dilute solution of HCl (100 mol·m$^{-3}$) was used as anolyte in all experiments while NaOH (100 mol·m$^{-3}$) was used as catholyte in experiment 1 and equimolar mixtures of acetic acid (AA) and Na$_2$EDTA (25 mol·m$^{-3}$ and 50 mol·m$^{-3}$) were, respectively, used as catholyte in experiments 2 and 3 (Table 2).

2.1.5. Viscosity Measurement. Viscosity measurement was carried out using Ubbelholz viscometer always fitted in a constant temperature bath to nullify any temperature effect on capillary flow.

2.2. Procedure. The chambers of the ED cell and membranes were washed thoroughly before each experiment was carried out. Initially, the feed solution containing 5% sugar and CaCl$_2$
was used and was circulated at a constant rate (130 mL/min) 
through the feed compartment. The feed solution, anolyte, 
and catholyte were continuously recycled through the ED cell 
and that caused a continuous change in salt concentration 
of feed solution. The concentration was measured at regular 
intervals. For a fixed applied voltage (V), variation of current 
("I"") through the membrane stack and concentration of salt 
(Ca2+ ions) was estimated from conductivity measurement 
and using standard calibration chart (mass concentration 
versus conductance) and was recorded with time (t).

ED cell was dismantled; membranes were taken out, 
checked visually to find any deposition over the surfaces after 
each experiment. Membranes were then washed with distilled 
water and oven dried at 100°C for 24 hours and weighed to 
find any gain or loss in mass of membrane.

3. Modeling of Ion Transport

Current density and limiting current density (LCD) of an 
ED cell is a function of a series of parameters, for example, 
physical (cell geometry, flow dynamics, spacer spacing, 
solution density, and viscosity) and chemical (ion concen-
tration, transport number, and diffusivity) for a given set 
of membrane pairs. Precise estimate of these parameters 
and application of Nernst-Planck equation (assuming zero 
ion concentration on the membrane surface) would give a 
theoretical estimate of LCD which can also be determined 
experimentally from plot of I versus V characteristics of the 
electrolyte in the ED cell [7, 9].

3.1. Determination of Bulk Concentration of Diluate Com-
partment. Concentration of ions was obtained through unsteady 
state mass balance over diluate, catholyte, and anolyte compart-
ments. The following assumptions were made [18].

(i) The ED cell and the feed tank are approximated to be 
a perfectly mixed flow reactor.

(ii) Back diffusion of ions was ignored.

(iii) Electroneutrality condition is always maintained.

The mass balance equation of diluate compartment in the ED 
cell can be expressed as

\[ V_{dil} \frac{dC^{\text{dil}}_j}{dt} = Q^{\text{dil}} \left( C^{\text{dil}}_j - C^{\text{dil}}_j \right) - \eta \frac{A_m}{zF}, \]  

where \( V_{dil} \) is the volume of the diluate compartment (m³) 
and \( t \) is time (s), \( C^{\text{dil}}_j \) and \( C^{\text{dil}}_j \) represent diluate concentrations 
leaving feed tank and leaving cell compartment (mol⁻³), 
\( Q^{\text{dil}} \) is the diluate volumetric flow rate (m³/s), \( \eta \) is the current 
efficiency, \( i \) is the current density (A·m⁻²), and \( A_m \) is the effective membrane area (m²).

\( \eta \) can be obtained from the following equation [18, 19]:

\[ \eta = t_{+,CEM} + t_{-,AEM} - 1, \]  

where \( t_{+,CEM} \) is the transport number of cation in cation exchange membranes and \( t_{-,AEM} \) is the transport number of anion in anion exchange membrane.

Similarly, unsteady state mass balance around feed tank 
can be written as

\[ \frac{d}{dt} \left( V_f C_{f,\text{feed}} \right) = Q_{f,\text{feed}} \left( C_{f,\text{feed}}^{\text{dil}} - C_{f,\text{feed}}^{\text{C}} \right), \]

where \( V_f \) is the volume of feed tank (m³). During electro-
dialysis water transport occurs across the membranes due 
to electroosmosis and osmosis [19]. Volume change (due to 
water transport) was ignored as there was no net volume 
change noted experimentally.

3.2. Determination of the Current Density

3.2.1. Overall Flux Equation. A pictorial representation of 
different concentration profiles possibly developed around 
the membrane is described in Figure 2. The flux of ions passing 
through the membrane can be expressed by generalized 
Nernst Planck equation as [7]

\[ N_j = -D_j \frac{\partial C_j}{\partial x} - z_j C_j F D_j \frac{\partial \psi}{RT} \frac{\partial x}{\partial x}, \]  

where \( x \) is the distance measured from boundary layer in 
contact with the bulk solution in diluate channel towards 
the membrane, \( D_j \) is the diffusivity of ion (m²·s⁻¹), \( C_j \) is 
the concentration of ion \( j \) (mol·m⁻³), \( R \) is the universal gas 
constant (8.314 J·mol⁻¹·K⁻¹), \( T \) is the temperature (K), \( z_j \) is 
the charge of diffusing species \( j \), and \( \partial \psi/\partial x \) is the potential 
gradient (V·m⁻¹) and \( F \) is the Faraday constant (C·geqv⁻¹).
The total molar flux of ion "j" through the ion exchange membrane, $N_{j,m}$, can be related to the current density, $i$, as [7]

$$N_{j,m} = \frac{t_{j,m}i}{z_jF}, \quad (5)$$

where $t_{j,m}$ is the transport number of ion $j$ in the membrane, $i$ is current per unit area of membrane or current density ($A\cdot m^{-2}$), and $z_j$ is the charge of the ion.

At steady state $N_j$ and $N_{j,m}$ are equal; that is,

$$\frac{t_{j,m}i}{z_jF} = -D_j \frac{\partial C_j}{\partial x} - \frac{z_jC_jF\xi}{RT} \frac{\partial \psi}{\partial x}. \quad (6)$$

Assuming that a linear profile of the concentration distribution exists along the boundary layer, the linearized Nernst-Planck equation could be used instead of (6). Expression for the linearized Nernst-Planck equation when applied in the dilute chamber is [7]

$$\frac{t_{j,m1}}{z_jF} = \frac{D_j(C_{j,b}^{dl} - C_{j,m}^{dl})}{\delta} - \frac{z_jD_jF\xi C_{j,m}^{dl}}{RT}, \quad (7)$$

where $\delta$ is the boundary layer thickness (m), $C_{j,b}^{dl}$ and $C_{j,m}^{dl}$ are concentrations of ions in bulk and at the membrane surface, respectively, of the dilute compartment, and $\xi$ is the potential gradient ($V\cdot m^{-1}$) and is expressed as

$$\xi = \frac{\psi}{\delta}. \quad (8)$$

In (7) the first part, that is, $D_j(C_{j,b}^{dl} - C_{j,m}^{dl})/\delta$, denotes flux due to molecular diffusion flux of ion arising out of concentration variation between solution bulk and boundary layer over membrane surface. The second part, that is, $z_jD_jF\xi C_{j,m}^{dl}/RT$, shows flux due to externally applied potential over the membrane.

3.2.2. Boundary Layer Thickness, $\delta$ Estimation. $\delta$ is estimated using film theory (equation (9)) and salt mass-transfer coefficient [7, 20]. Salt mass-transfer coefficient is usually determined based on salt diffusivity and suitable mass-transfer correlation, which in-turn is dependent on flow profile and physical properties of the fluids, cell geometry, and surface morphology of membranes used in ED cell [7, 9, 21, 22]:

$$\delta = \frac{D_j}{k}, \quad (9)$$

where, $D_j$ and $k$ are diffusivity and mass transfer coefficient of diffusing species in solution. Each of these parameters was separately estimated using standard correlations. The mass transfer coefficient was obtained from Sherwood number [7, 20, 21] as:

$$Sh = \frac{k \cdot l}{D_j}, \quad (10)$$

where $l$ is the characteristic length (m). Sherwood number, Sh, is expressed as a function of Reynolds number, Re, and Schmidt number, Sc [7, 20]. The empirical expression of Sherwood number is based on cell geometry and spacer configuration chosen for the present cell as indicated in the following [17, 20, 23]:

$$Sh = a \cdot Re^b \cdot Sc^c, \quad (11)$$

where Sc (Schmidt number, $\mu/p\rho D_j$) is estimated from physical properties (viscosity and density) of the medium while Reynolds number ($\rho V/\mu$) indicates flow characteristics of the medium and channel spacing as "l" and $a$, $b$, $c$ are the empirical constants, which are determined by fitting the data ($Sh/Sc^c$ versus Re) for experiments where flow rate is varied. In this work, the values of $a$, $b$, and $c$ are taken from literature [17] and are given in Table 3.

Ionic diffusivity is entirely dependent on the size of hydrodynamic diameter of ions. Assuming infinite dilution this ionic diffusivity is estimated using the Nernst-Haskel equation (12) [14] as

$$D^* = \frac{RT \cdot \left[ (1/z_+) + (1/z_-) \right]}{F^2 \cdot \left[ (1/\lambda_+) + (1/\lambda_-) \right]}, \quad (12)$$

where $z_+$ and $z_-$ denote charges of cation and anion, respectively, while $\lambda_+$ and $\lambda_-$ denote limiting ionic conductance in the solvent. Other parameters bearing meaning and units are as reported in the nomenclature.
Table 3: Values of different physical parameters used in the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, T</td>
<td>298 K</td>
<td>This work</td>
</tr>
<tr>
<td>Transport number of the cation in CEM, (t_{*,\text{CEM}})</td>
<td>0.91</td>
<td>Table 1</td>
</tr>
<tr>
<td>Transport number of the anion in AEM, (t_{*,\text{AEM}})</td>
<td>0.9</td>
<td>Table 1</td>
</tr>
<tr>
<td>Transport number of anion in the solution, (t_{\text{Ca}^{2+},s})</td>
<td>0.4387</td>
<td>This work [7]</td>
</tr>
<tr>
<td>Diffusivity of CaCl(<em>2) in 5% sugar solution at 25°C, (D</em>{\text{CaCl}_2})</td>
<td>(1.98 \times 10^{-10} \text{ m}^2\text{s}^{-1})</td>
<td>This work [14, 15]</td>
</tr>
<tr>
<td>Diffusivity of Ca(^{2+}) ions at infinite dilution and at 25°C, (D_{\text{Ca}^{2+}})</td>
<td>(7.92 \times 10^{-10} \text{ m}^2\text{s}^{-1})</td>
<td>This work [14]</td>
</tr>
<tr>
<td>Diffusivity of Ca(^{2+}) ions in 5% sugar solutions at 25°C, (D_{\text{Ca}^{2+}})</td>
<td>(7.11 \times 10^{-10} \text{ m}^2\text{s}^{-1})</td>
<td>This work [14, 15]</td>
</tr>
<tr>
<td>Diffusivity of Cl(^-) ions in 5% sugar solutions at 25°C, (D_{\text{Cl}^-})</td>
<td>(18.2 \times 10^{-10} \text{ m}^2\text{s}^{-1})</td>
<td>This work [14, 15]</td>
</tr>
<tr>
<td>Distance between adjacent membranes, (l)</td>
<td>(2 \times 10^{-3} \text{ m})</td>
<td>This work</td>
</tr>
<tr>
<td>Area of the membrane, (A_m)</td>
<td>(3.7 \times 10^{-3} \text{ m}^2)</td>
<td>This work</td>
</tr>
<tr>
<td>Charge on the calcium ion, (z_{\text{Ca}^{2+}})</td>
<td>+2</td>
<td>This work</td>
</tr>
<tr>
<td>Viscosity of 5% sugar solution, (\mu)</td>
<td>(9.92 \times 10^{-4} \text{ Pa s})</td>
<td>[16]</td>
</tr>
<tr>
<td>Velocity of the feed stream, (v)</td>
<td>(3.1 \times 10^{3} \text{ m}^2\text{s}^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>Applied voltage, (E_{\text{int}})</td>
<td>(4 \text{ V})</td>
<td>This work</td>
</tr>
<tr>
<td>Current density initial value, (i(0))</td>
<td>(122 \text{ A.m}^{-2})</td>
<td>This work</td>
</tr>
<tr>
<td>Current efficiency, (\eta)</td>
<td>0.81</td>
<td>This work</td>
</tr>
<tr>
<td>Sh number empirical equation constant, (a)</td>
<td>0.46 for catholyte NaOH</td>
<td>[17]</td>
</tr>
<tr>
<td>Sh number empirical equation constant, (b)</td>
<td>0.25 ± 0.03 for catholyte AA-Na_2EDTA</td>
<td>This work</td>
</tr>
<tr>
<td>Sh number empirical equation constant, (c)</td>
<td>0.63 for any anolyte and catholyte</td>
<td>[17]</td>
</tr>
<tr>
<td>Diffusivity is a strong function of viscosity which was corrected using equation proposed by Yuan-Hui and Gregory [15]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{D}{D^*} = \frac{\mu^*}{\mu}.
\]  

(13)

3.2.3. Estimation of Membrane Surface Concentration. The membrane surface concentration of ions is dependent on current density under an applied voltage. As long as the ED operation is executed below limiting current (surface concentration becomes zero), the surface concentration on either side can be estimated from bulk concentration measurement (diluate/concentrate), current density, and limiting current density using (14) and (15) [19, 24]:

\[
C_{j,m}^{\text{conc}} = C_{j,b}^{\text{conc}} \left(1 + \frac{i}{i_{\text{lim}}}\right),
\]  

(14)

\[
C_{j,m}^{\text{dil}} = C_{j,b}^{\text{dil}} \left(1 - \frac{i}{i_{\text{lim}}}\right),
\]  

(15)

where \(C_{j,m}^{\text{conc}}\) and \(C_{j,b}^{\text{conc}}\) are the concentrations of ion \(j\) on the membrane surface and in bulk of the concentrate compartment, respectively, in the ED cell. \(C_{j,m}^{\text{dil}}\) and \(C_{j,b}^{\text{dil}}\) are the concentrations of ion \(j\) on the membrane surface and in the bulk of the diluate side, respectively, in the ED cell.

3.2.4. Estimation of Current Density and Limiting Current Density (\(i\) and \(i_{\text{lim}}\)). LCD (of a single electrolyte) is estimated using the following equation [5, 9]:

\[
i_{\text{lim}} = \frac{C_{j,b}^{\text{dil}} D_j z_j F}{\delta (t_{j,m} - t_{j,b})},
\]  

(16)

where \(t_{j,m}\) and \(t_{j,b}\) are transport numbers of ion \(j\) in membrane and electrolyte solution, respectively. Considering ion flux in the diluate side of the IEM, (15) is used to calculate concentration of ion \(j\) at the membrane surface of diluate side \(C_{j,m}^{\text{dil}}\).

The current density can be expressed by (17) after substitution of (15) and (16) in (6):

\[
i = \left(C_{j,b}^{\text{dil}} D_j z_j F \frac{\xi F}{RT}\right) \times \left(\frac{t_{j,m} - t_{j,b}}{z_j F} + \frac{\xi \delta (t_{j,m} - t_{j,b})}{RT} - \frac{t_{j,m} z_j}{F}\right)^{-1},
\]  

(17)

where \(\xi\) the potential gradient can be estimated from Nernst equation given as follows [18, 19]:

\[
\xi = -(2t_{j,m} - 1) \frac{RT}{\delta F} \ln \left(\frac{\gamma_{j,b}^{\text{dil}} C_{j,b}^{\text{dil}}}{\gamma_{j,m}^{\text{dil}} C_{j,m}^{\text{dil}}}\right),
\]  

(18)

where \(\gamma_{j,m}^{\text{dil}}\) and \(\gamma_{j,b}^{\text{dil}}\) are the mean ionic activity coefficients corresponding to the ions at the wall of IEM and in the bulk.
of solution, respectively, within the diluate channel and they can be estimated using Debye-Hückel limiting law [25].

4. Numerical Estimation of Parameters

The sequence of steps followed to obtain theoretical estimate of concentration variation is described using flow chart (Figure 3). The differential equations (1) and (3) were integrated using Euler method with 1s time step. Few crucial parameters and their evaluation method are presented below.

4.1. Determination of Transport Number of Ion in Solution

Bulk transport number \( t_{j,b} \) is the fraction of total current carried by the ion type which is a function of diffusion coefficient and ionic mobility of hydrated species. Ions in solution get hydrated with solvent molecules and difference in hydration ability causes variation in size, diffusivity, and mobility of such species. Thus, ions do not transport current appreciably but carry by the ion type which is a function of diffusion coefficient and ionic mobility of hydrated species. Ions in solution get hydrated with solvent molecules and difference in hydration ability causes variation in size, diffusivity, and mobility of such species. Thus, ions do not transport current appreciably but carry by the ion type which is a function of diffusion coefficient and ionic mobility of hydrated species.

4.2. Determination of Current from Resistance Measurement

Initial current density estimation is essential to obtain salt concentration at membrane surface and start numerical integration which may be evaluated either experimentally or from applied potential and solution resistance using Ohm’s law. The potential applied may be expressed as

\[
E_{\text{tot}} - E_a = R_{\text{tot}} \cdot J,
\]

where \( E_a \) is the potential drop near the electrodes, \( R_{\text{tot}} \) is the overall resistance (ohm) of the ED cell, and \( J \) is the current (A). The overall resistance is the sum of resistances of individual chambers:

\[
R_{\text{tot}} = R_{\text{anolyte}} + R_{\text{diluate}} + R_{\text{catholyte}},
\]

where resistance of anolyte, catholyte, and diluate channel are determined either directly from conductivity measurement or from extended Kohlrausch-equation [19, 25]. The conductivity and the resistance are related as

\[
\text{Resistance} = \frac{1}{\Lambda A_m}.
\]

where \( \Lambda \) is the conductivity of solution (mho-m\(^{-1}\)), \( L \) is the gap between membranes or the compartment thickness (m), and \( A_m \) is the effective membrane area (m\(^2\)).

4.3. Determination of Specific Energy Consumption

The specific energy consumption, \( E_{sp} \) (kWh-kg\(^{-1}\)), was obtained using the following equation:

\[
E_{sp} = \frac{\int_{t_1}^{t_2} \varepsilon A_m i(t) \, dt}{M_{\text{CaCl}_2} n_{\text{CaCl}_2}(t)},
\]

where \( \varepsilon \) is the applied potential in V, \( A_m \) is the area of the membrane in m\(^2\), \( i(t) \) is the current density as a function of time in A/m\(^2\), \( M_{\text{CaCl}_2} = 111.02 \text{ g/mol} \), and \( \Delta n_{\text{CaCl}_2}(t) \) is the number of moles of \( \text{CaCl}_2 \) removed from the feed solution at various time intervals.

5. Results and Discussions

5.1. Role of Sugar and \( \text{CaCl}_2 \) Concentration on Solution Viscosity and Influence of Temperature

Sugar solution viscosity increases nonlinearly (Figure 4) with increase in sugar concentration (5 to 20 wt%). Viscosity values range between 0.72 and 1.5 mPa-s with increase in sugar concentration. These values were very much comparable with the literature reported data [16]. Solution viscosity does not show any appreciable change with \( \text{CaCl}_2 \) concentration (0–50 mol/m\(^3\)) (Figure 5). Influence of temperature on \( \text{CaCl}_2 \) solution viscosity was recorded at 20, 25, 32, 37, and 42°C and viscosity decreases between 1.22 and 0.7 mPa-s. Nearly ~43% lowering in solution viscosity with temperature rise between 20 and 42°C is noted in Figure 5.

5.2. Role of Sugar and \( \text{CaCl}_2 \) Concentration on Electrical Conductivity of Electrolyte

Figure 6 shows plot of \( \text{CaCl}_2 \) concentration on the electrical conductivity, which was estimated in presence and absence of sugar. Electrical conductivity increases almost linearly with rise in \( \text{CaCl}_2 \) concentration (5 to 50 mol·m\(^{-3}\)). The \( \text{CaCl}_2 \) being a strong electrolyte, dissociates completely in solution, thus increasing number of ions per unit volume available for ionic conductance. On the contrary, sugar addition dampens the conductivity value. This is possibly because sugar is a water soluble nonelectrolyte which does not change the number of ionic species responsible for current carriage; thus, presence of inert sugar molecules basically increases crowding in solution.

5.3. Effect of Applied Potential on Ion-Removal Rate

The applied potential is a crucial parameter to define removal
rate and efficiency. With increased potential, ion removal rate increases causing rapid lowering of batch time [26]. In a batch operation, with gradual lowering of ion concentration the current density keeps dropping. Once, the concentration reaches below limiting value the solution resistance becomes very high and heating starts. At this increased temperature electrolysis of water starts and a major portion of applied potential gets consumed without much gain in ion removal. Thus, overall energy consumption increases affecting process efficiency [5, 22].

Three different voltages (4 V, 8 V, and 12 V) were applied keeping other process parameters unchanged. Figure 7 shows effect of applied potential on Ca\(^{2+}\) ion removal rate. With higher potential, the ion removal rate increases. This is quite obvious because with increased electrical driving force (potential), more current passes through the solution as long as resistance remains unchanged. It is interesting to note that at lower potential, the ion removal rate remains linear for a long duration (>240 min) indicating Ohm's law might be applicable. This is not observed with higher potentials. With ~8 V, the nonlinearity appears at time ~180 min while the same happens at time ~120 min for ~12 V. Possibly unwanted electrode reactions (water splitting) initiate at early stages with increased potential. This certainly influences the ion removal rate showing variation in slope of the concentration
drop curve. This indicates that at higher voltage rapid depletion of ions and a nonlinear rise in resistance occurs. Rapid nonlinear rise in solution resistance was also observed earlier by different scientists [8, 9].

5.4. Effect of Flow Rate on Ion Removal Rate. Change in ion removal rate with variation in feed flow rate, without disturbing catholyte and anolyte streams conditions (flow rate, components, concentration, etc.), was analyzed and reported in Figure 8. Feed flow rates were varied as 80, 130, and 180 mL/min and change in ion removal rate was noted after nearly 60 min of ED operation. A slow rise in removal rate with increased flow rate was observed. Increased flow rate possibly increased turbulence which reduced thickness of stationary boundary film over membrane surface. This lowered the overall ion transfer resistance and increased ion removal rate.

5.5. Model Prediction of Experimental “i” and Ca\(^{2+}\) Ion Concentration. The batch mode of electrodialysis with continuous recirculation under an applied potential becomes an unsteady state process. The electrolyte concentration of diluate (feed tank) and concentrate streams, solution resistance (conductivity), concentration profile around membrane, and bulk physical properties of the solution become time dependent. The cumulative effects of all these parameters are reflected in diluate (feed tank) concentration and overall current density of the ED cell. Therefore, the mathematical model emphasizes two crucial parameters: (i) electrolyte (CaCl\(_2\)) concentration of the diluate stream (feed tank) and (ii) overall current density of the cell. Unsteady state mass balance around the diluate channel/tank is written in terms of important process variables, for example, vessel volume, flow rate, concentration, current density, current efficiency, and membrane area. Nernst Planck equation and irreversible thermodynamics are used to estimate the ionic flux through the boundary layer over the membrane. The model proposed closely predicts experimental data between the chosen range of process condition of Ca\(^{2+}\) ion (Figures 9 and 10) and current density with time (Figure 9) in the ED cell.

Molar concentration of the recirculating feed solution was obtained by solving coupled differential equations. Equations (1) and (3) and physical process parameters values are listed in Table 3. Solution steps (using MATLAB code) are discussed in Figure 3. The concentration estimates so obtained were used to estimate current density, \(i\) (17). The theoretical model could closely predict the experimental data (Experiments 1, 2, and 3) of concentration variation (Figures 9 and 10). Experiments 2 and 3, performed with two different concentrations of CaCl\(_2\) (25 and 50 mol·m\(^{-3}\)) in feed solution, behaved in the same manner (Figure 10). This supports the fact that the method adopted in concentration estimation was correct and reproducible.

Initially solute concentration (25 mol·m\(^{-3}\)) of the feed solution drops steadily in experiment 1, the rate of which slows down after nearly 200 min (Figure 9). The experimental current density also follows same trend (Figure 9). A steady drop in current density from 120 A·m\(^{-2}\) to 40 A·m\(^{-2}\) during first 200 min was recorded possibly due to rapid lowering in ionic concentration in the diluate under applied potential of 4 V.
5.6. Role of Catholyte Composition and a Probable Mechanism for Smooth Operation of ED. CaCl₂ is a strong electrolyte and preferentially exists in ionized (Ca²⁺ and 2Cl⁻) state in the aqueous solution containing sugar (5%). Water molecules form a hydration sphere around each dissociated ion and stabilize it. On application of external potential these hydrated species start crossing polar membranes charged with counter ions and cause concentration polarization buildup across the polar membrane.

The approach adopted here is to minimize the concentration polarization. Ca²⁺ ion crosses the cation exchange membrane. This was accomplished by either (i) precipitating out the ions or by (ii) complexing out before a back diffusion sets in. Two different catholyte streams were chosen with a concentration ratio of 1:1 (discrete data points) versus time (min) for specified ED operating conditions: (i) experiment 2 (feed flow rate = 130 mL min⁻¹; anolyte = 100 mol m⁻³ HCl; catholyte = 25 mol m⁻³ Na₂EDTA + 25 mol m⁻³ AA; applied voltage = 4 V), (ii) Experiment 3 (feed flow rate = 130 mL min⁻¹; anolyte = 100 mol m⁻³ HCl; catholyte = 50 mol m⁻³ Na₂EDTA + 50 mol m⁻³ AA; applied voltage = 4 V) [13].

Figure 10: Close resemblance of theory (continuous line) with experimental molar concentration of CaCl₂ of the dilute tank (mol m⁻³) (discrete data points) versus time (min) for specified ED operating conditions: (i) experiment 2 (feed flow rate = 130 mL min⁻¹; anolyte = 100 mol m⁻³ HCl; catholyte = 25 mol m⁻³ Na₂EDTA + 25 mol m⁻³ AA; applied voltage = 4 V). (ii) Experiment 3 (feed flow rate = 130 mL min⁻¹; anolyte = 100 mol m⁻³ HCl; catholyte = 50 mol m⁻³ Na₂EDTA + 50 mol m⁻³ AA; applied voltage = 4 V) [13].

As the solubility product of Ca(OH)₂ in water is very low (∼10⁻¹²), it experiences high probability of precipitation over membrane surface facing higher pH. Once this precipitate comes in contact with electrolyte containing Na₂EDTA, it reacts and forms a stable complex, CaNa₂EDTA, which washes out the precipitate formed and cleans the membrane surface. The scheme of overall reaction is presented as follows:

\[
\text{Ca}^{2+} + 2 (\text{OH}^-) \rightarrow \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (24)
\]

\[
\text{Ca}^{2+} + \text{Na}_2\text{EDTA} \rightarrow \text{CaNa}_2\text{EDTA} + 2\text{H}^+ \quad (25)
\]

Bivalent cation are well known for their low solubility at high pH and often precipitate out as metal hydroxides [27]. This precipitation problem was also observed with calcium ion reported here when NaOH was used in catholyte stream. Figure II shows NaOH (100 mol m⁻³) as catholyte streams although increases ion removal rate initially, but vigorous fouling prevented the process from running for long duration. With NaOH as catholyte, Ca(OH)₂ precipitation was extensive which turned the membrane color from brownish yellow to white and probably blocked the swollen membrane pores on the rare side. Although this approach completely arrested the reverse transport of Ca²⁺ ions but continuous operation was limited due to membrane fouling, increased resistance, and drop in current density. Frequent acid wash helped in improving the membrane performance but continuous operation was not feasible.

Formation of white solid powder was noted over the membrane (CEM) surface facing catholyte stream (NaOH, higher pH) in experiment 1 and experiment 3. The white powder over membrane was investigated further to have better understanding of the problem which arose after ED operation for specified duration. Quantitative estimations of the fouled membrane were made by gravimetric method. The CEM membrane after ED experimentation was taken out, washed, and weighed, after drying and equilibration. The used membrane (equilibrated 24 hours at 100°C) was found to increase in mass over its initial mass (equilibrated) before ED. Gain of mass in used membrane is reported in Table 4.

The white deposit on the membrane surface could be removed by immersing the membrane in a dilute HCl (10%) in water) solution. Immediately after immersion bubbling from the fouled surface of the membrane was observed. For complete dissolution of the white deposit, the membrane was left immersed in the solution for ~30 minutes until bubbling stopped. Subsequently the membrane was removed, washed repeatedly with deionized water, and dried in oven (100°C for 24 hours) and weighed. A blank test was simultaneously performed using a fresh membrane to record the difference between used and fresh membrane. For an applied potential the dry mass of the used membrane was found to be dependent on its duration of application, electrolyte concentration, and electrolyte stream pH.

Multiple samples of the used membrane were tested and formation of bubbles was confirmed. Once the bubbling stopped after immersing the membrane in dilute HCl solution, the piece was taken out, washed, dried, and equilibrated before weighing. Mass of the membrane did not deviate much from its initial value. This indicated possibility of CO₂ evolution from the reaction of HCl with CaCO₃. The most probable sequence of the overall reaction occurring over the
mixed electrolyte only but of course energy consumption will be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing.

Removal rate between two different techniques adopted. Case 1: membrane surface and its subsequent cleaning with dilute HCl may be explained by the following scheme:

$$\text{CO}_2 \text{ (air)} + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$  

(26)

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 \text{ (s)} + \text{H}_2\text{O}$$  

(27)

$$\text{CaCO}_3 \text{ (s)} + \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 \text{ (g)} + \text{H}_2\text{O}$$  

(28)

At higher pH, solubility of CO$_2$ (air) increases in NaOH solution (catholyte stream) which results in formation of HCO$_3^{-}$/CO$_3^{2-}$. These ions subsequently react with NaOH to form Na$_2$CO$_3$ providing the source for CaCO$_3$ precipitation from Ca(OH)$_2$. Conversion of Ca(OH)$_2$ to CO$_3^{2-}$ is (27) is thermodynamically favorable and moves forward. Nearly 1000 times higher value of solubility product of Ca(OH)$_2$ [5.5 × 10$^{-6}$] over CaCO$_3$ [3.39 × 10$^{-9}$] [28] drives the process faster.

Formation of CaCO$_3$ not only increased membrane resistance to ion transport but also made the ED operation discontinuous. The process was made uninterrupted by changing the electrolyte composition of the catholyte stream. Here we report application of Na$_2$EDTA-acetic acid solution as catholyte stream; the chelating agent continuously complexes with the precipitated CaCO$_3$ and formed corresponding salt CaNa$_2$EDTA. The pH of catholyte stream was adjusted between 3.5–5.0 (Table 2) and the anolyte was maintained as HCl (100 mol·m$^{-3}$). This combination showed negligible fouling even after long (240 min) operation time (Table 4).

The mass transfer coefficients estimated from Sherwood number correlation (II) showed higher values while NaOH (100 mol·m$^{-3}$) was used as catholyte stream compared to Na$_2$EDTA-acetic acid (AA) combination (Table 4). Reduced mass transfer coefficient with Na$_2$EDTA-acetic acid stream may be attributed to higher solution resistance arising possibly due to weak dissociation of acetic acid of Na$_2$EDTA + AA combination than that of NaOH. The dissociation constant can get further affected due to Na$_2$EDTA (a bulky diffusing species). Thus, reduction in mass transfer coefficient lowered Ca$^{2+}$ ion removal rate.

As of now, we have understood that chemical composition and concentration of anolyte/catholyte streams play crucial role in controlling overall resistance and ion removal rate. The specific energy consumption, $E_{sp}$, estimated from (23) (Table 4) shows lower value with NaOH compared to the streams containing Na$_2$EDTA + AA.

The average running cost to remove unit mass of CaCl$_2$ is reported in Table 4. The cost is dependent on concentration of the electrolyte stream and time of ED operation. Cost is inversely proportional to initial concentration of the stream and directly proportional to operation time. Energy due to pumping is the major contribution to the overall costs estimate in a batch ED operation for a given time.

### 6. Conclusions

Calcium ion (CaCl$_2$, 25 mol·m$^{-3}$) removal rate depends on feed flow rates, electrolyte (anolyte/catholyte) components, concentrations, applied potential, and so forth. NaOH as catholyte showed higher removal rate and increased mass transfer coefficient over mixed electrolyte (AA-Na$_2$EDTA). Specific energy consumption ($E_{sp}$, kWh·kg$^{-1}$) estimates for three typical set of experiments (Table 4) also support the above observation of easy ion removal rate. Based on this it may be concluded that although NaOH shows better performance for the duration chosen in this report, but an uninterrupted mode ED operation would be feasible with mixed electrolyte only but of course energy consumption will be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing. The unsteady state model used could be partly increasing.
effectively predict the current density and concentration change with an accuracy of 95%.

Appendix

Density values of 5% sugar solution with varying concentration of CaCl$_2$ were estimated from the fitted equation (Density (kg·m$^{-3}$) = 0.323 × Concentration (mol·m$^{-3}$) + 1017.5; $R^2 = .98$) obtained from the experimental data of density versus concentration of CaCl$_2$ in 5% sugar solution (Figure 12).

Nomenclature

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Sh number empirical equation constant</td>
</tr>
<tr>
<td>$A_m$</td>
<td>Area of the membrane, m$^2$</td>
</tr>
<tr>
<td>$b$</td>
<td>Sh number empirical equation constant</td>
</tr>
<tr>
<td>$c$</td>
<td>Sh number empirical equation constant</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration, mol·m$^{-3}$</td>
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<tr>
<td>$D_0$</td>
<td>Diffusivity of the salt or ion in the solution at temperature, $T$</td>
</tr>
<tr>
<td>$D_0^*$</td>
<td>Diffusivity of the salt or ion at infinite dilution at temperature, $T$</td>
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<tr>
<td>$D_j$</td>
<td>Diffusivity of ion “$j$”</td>
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<tr>
<td>$E_{el}$</td>
<td>Electrode potential, V</td>
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<tr>
<td>$E_{tot}$</td>
<td>Total electric potential applied, V</td>
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<tr>
<td>$E_{sp}$</td>
<td>Specific energy consumption, kWh·kg$^{-1}$</td>
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<tr>
<td>$F$</td>
<td>Faraday constant, C·gm-eq$^{-1}$</td>
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<tr>
<td>$i$</td>
<td>Current density, A·m$^{-2}$</td>
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<tr>
<td>$i_{j,lim}$</td>
<td>Limiting current density of ion “$j$”</td>
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<tr>
<td>$I$</td>
<td>Ionic strength</td>
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<td>$J$</td>
<td>Current, A</td>
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<td>$k$</td>
<td>Mass transfer coefficient, m/s</td>
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<td>$L$</td>
<td>Characteristic length, m</td>
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<td>$m_j$</td>
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<td>$Q$</td>
<td>Volumetric flow rate, m$^3$·s$^{-1}$</td>
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<tr>
<td>$R$</td>
<td>Gas constant, J·kg$^{-1}$·K$^{-1}$</td>
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<tr>
<td>$R_{anolyte}$</td>
<td>Resistance of anolyte chamber</td>
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<td>$R_{catholyte}$</td>
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<td>$R_{diluate}$</td>
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<td>$T$</td>
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<td>$t_{+,CEM}$</td>
<td>Transport number of cation in cation exchange membrane</td>
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<td>$t_{-,AEM}$</td>
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<td>$t_{j,b}$</td>
<td>Transport number of ion “$j$” in the bulk solution</td>
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<td>Velocity, m/s</td>
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<td>$V$</td>
<td>Volume, m$^3$</td>
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<td>$z$</td>
<td>Ion charge</td>
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Subscripts

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<td>AEM</td>
<td>Anion exchange membrane</td>
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<td>Bulk solution</td>
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<tr>
<td>CEM</td>
<td>Cation exchange membrane</td>
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<tr>
<td>C</td>
<td>Compartment</td>
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<tr>
<td>$j$</td>
<td>Ion, “$j$”</td>
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<td>$T$</td>
<td>Feed tank</td>
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<tr>
<td>$±$</td>
<td>Cation or anion</td>
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Superscripts

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<td>Conc</td>
<td>Concentrate</td>
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<tr>
<td>dil</td>
<td>Diluate</td>
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<tr>
<td>lim</td>
<td>Limiting</td>
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Greek Symbols

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<tr>
<td>$\eta$</td>
<td>Current efficiency</td>
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<tr>
<td>$\epsilon$</td>
<td>Applied voltage, V</td>
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<tr>
<td>$\mu$</td>
<td>Viscosity of the solution at the same temperature $T$, Pa·s</td>
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<tr>
<td>$\mu'$</td>
<td>Viscosity of the pure water at a temperature $T$, Pa·s</td>
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<tr>
<td>$\Lambda$</td>
<td>Conductivity, S</td>
</tr>
<tr>
<td>$\lambda_+\lambda_-$: Limiting (zero concentration) ionic conductance, (A·cm$^{-2}$)·(V·cm$^{-1}$)(g-equiv·cm$^{-3}$)</td>
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<tr>
<td>$\rho$</td>
<td>Density, kg·m$^{-3}$</td>
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<tr>
<td>$\delta$</td>
<td>Diffusion boundary layer thickness, m</td>
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<tr>
<td>$\xi$</td>
<td>Potential gradient, V·m$^{-1}$</td>
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<td>$\psi$</td>
<td>Potential drop in the diffusion boundary layer, V</td>
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<td>$\gamma_z$</td>
<td>Mean ionic activity coefficient.</td>
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Conflict of Interests

The authors declare that there is no conflict of interests regarding to the publication of this paper.

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