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Treatment of Oil-Sands Produced Water by Electrocoagulation

Shu, Tianpei

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Treatment of Oil-Sands Produced Water by Electrocoagulation

by

Tianpei Shu

A THESIS

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Abstract

In Alberta, the oil-sands industry plays an important role in the local economy. However, the industry consumes a large amount of water, which is not economical. Significant capital and operating costs have been invested by the oil industries in the treatment of this contaminated water every year. Our objective is to develop new treatment solutions for the removal of contaminants, particularly silica but also organics and some hardness, using electrocoagulation to enable increased water recycling while decreasing capital and operating costs.

The treatment of oil sands produced water by electrocoagulation is explored and investigated in this research. The major contaminant targeted is dissolved silica, which is the cause of the scaling problem in the steam generators in the oil-sands production process. Electrocoagulation is found to be very efficient to remove dissolved Si from approximately 60 mg/L to less than 5 mg/L, corresponding to greater than 90% Si removal. In addition, removal of 90% of the calcium present, and 60% of the magnesium could be achieved. The effect of operating parameters on electrocoagulation performance were evaluated, including the anode materials (aluminum and iron), current density, inter-electrode distance, and dissolved oxygen. Current density of 8 mA/cm$^2$ was found to be the most efficient and also economical compared to 4 and 16 mA/cm$^2$. Increasing the inter-electrode distance results in lower contaminant removal and higher energy consumption.

Dissolved oxygen is important for enhancement in Fe-EC. The current efficiencies for metal dissolution obtained with aluminum and iron electrodes materials, as well as their electrochemical behavior, was investigated. Fe-EC had current efficiencies between 90-95%, while Al-EC showed larger than 100% current efficiencies. Besides operating parameters, different electrochemical reactor designs were also tested. Experiments were carried out in system and flow recirculation systems. A novel concept of utilizing an oscillating anode in EC was tested with both batch and
recirculating flow. The combination of a batch recirculating flow reactor and anode oscillation showed the best contaminant removal performance. Investigation of the viability of EC for oil sands industry applications such as oil-sands produced water and boiler blowdown water samples have also been carried out, and the Si removal efficiency is also promising compared to the synthetic produced water. The operating cost of our EC treatments is also in the lower range compared to the general EC operating costs.
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Table of Contents
Abstract ........................................................................................................................................ i
Acknowledgments ...................................................................................................................... iii
Table of Contents ......................................................................................................................... iv
Table of Figures ............................................................................................................................. v
Table of Tables ............................................................................................................................... viii
List of Symbols and Abbreviations ............................................................................................... ix
Chapter 1. Introduction .................................................................................................................. 1
  1.1 Oil-Sands Produced Water ....................................................................................................... 1
  1.2 Common Technologies for Oil Sands Produced Water Treatment ........................................... 1
  1.3 Scaling & fouling in Steam Generation and Water Treatment Technologies .............................. 2
  1.4 Silica Chemistry and Destabilization Theory ........................................................................... 4
  1.5 Electrocoagulation Background ............................................................................................ 6
  1.6 Electrocoagulation Principles ................................................................................................ 7
      1.6.1 Potential Side Reactions .................................................................................................. 12
  1.7 EC Applications ..................................................................................................................... 13
  1.8 Factors affecting Electrocoagulation ....................................................................................... 15
  1.9 Knowledge gaps in EC .......................................................................................................... 20
  1.10 Research Objectives ............................................................................................................ 21
Chapter 2. Materials and Methodology ......................................................................................... 22
  2.1 Produced Water ...................................................................................................................... 22
  2.2 Experimental Setup .............................................................................................................. 26
  2.3 Experimental Procedure ........................................................................................................ 28
  2.4 Analytical Methods ............................................................................................................... 29
Chapter 3. Results and discussion ................................................................................................. 32
  3.1 Effect of Anode Material and Charge loading ......................................................................... 32
  3.2 Current Efficiency of Fe and Al dissolution ........................................................................... 34
  3.3 Potentiodynamic study of aluminum and mild steel anode ....................................................... 36
  3.4 Effect of dissolved oxygen ..................................................................................................... 38
      3.4.1 Effect of aeration in the batch system .............................................................................. 38
      3.4.2 Effect of dissolved oxygen in the recirculating flow reactor .......................................... 39
  3.5 Effect of current density ........................................................................................................ 42
  3.6 Effect of Inter-electrode distance ............................................................................................ 45
  3.7 Effect of Reactor Design ........................................................................................................ 46
3.7.1 Comparison of batch and recirculating flow mode ................................................. 47
3.7.2 Effect of anode oscillation in batch mode ............................................................... 50
3.7.3 Effect of current density in the oscillating anode system ....................................... 53
3.7.4 Effect of Oscillation frequency at constant Reynolds number on the oscillating anode system 55
3.7.5 Combining Oscillating anode with flow recirculation ........................................... 57
3.8 Removal of Calcium, Magnesium, and other contaminants .................................... 58
3.9 Treatment of samples of real produced water .......................................................... 62
3.9.1 Comparison of real produced water and synthetic produced water ....................... 66
3.10 Oil-sands blowdown water treatment performance ................................................ 68
3.11 Energy consumption ............................................................................................... 71
Chapter 4. Conclusions and Recommendations ............................................................ 78
4.1 Effect of operating parameters .................................................................................. 78
4.2 Effect of reactor design ............................................................................................ 80
4.3 EC for industrial applications .................................................................................. 80
4.4 Recommendations for future research ..................................................................... 81
References ...................................................................................................................... 83
Appendices .................................................................................................................... 100

Table of Figures
Figure 1-1 A schematic diagram of a typical SAGD process ............................................ 2
Figure 1-2 A schematic representation of an electrocoagulation cell .................................. 8
Figure 1-3 Pourbaix Diagram of Iron-water system at 25°C, considering Fe, Fe₂O₃ and Fe₃O₄ are the only solid substances [62] ................................................................. 10
Figure 1-4 Pourbaix Diagram of Aluminum – water system at 25°C [62] .......................... 11
Figure 2-1 A schematic diagram of the Recirculating flow EC reactor setup ................. 27
Figure 2-2 A schematic diagram of the Oscillating anode EC reactor with both batch and Recirculating flow mode ................................................................. 28
Figure 3-1 Remaining Si concentration percentage in Synthetic Produced water with iron, aluminum as anode materials. Experiments were operated at 8 mA/cm² in the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺concentration of 56 mg/L. ................................................................. 33
Figure 3-2 pH change in EC treatment with iron, aluminum as anode materials. Experiments were operated at 8 mA/cm² in the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺concentration of 56 mg/L. 34
Figure 3-3 Current Efficiency of Fe-EC and Al-EC for synthetic produced water treatment. Experiments were operated at 8 mA/cm² in the recirculating flow cell at 150 mL/min flowrate,
with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L. .............................. 36

Figure 3-4 Cyclic voltammetry study of (a) aluminum and (b) iron electrodes, with synthetic produced water effluent, scan rate 20 mV/second. ...................................................... 37

Figure 3-5 Effect of Aeration in Batch EC. Experiments were operated at 8 mA/cm² in the batch cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 39

Figure 3-6 Fe-EC with solution recirculating flow cell at an initial dissolved oxygen level of 1 mg/L, 9 mg/L, and the ambient laboratory environment. Experiments were operated at 8 mA/cm² in the recirculating flow cell (Figure 2-2) with electrolyte volume of 1.2 L, flow rate of 150 mL/min and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L. .... 41

Figure 3-7 Effect of dissolved oxygen in Al-EC on Si removal. Experiments were operated at 8 mA/cm² in the recirculating flow cell (Figure 2-2) with electrolyte volume of 1.2 L, flow rate of 150 mL/min and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L. .... 42

Figure 3-8 Synthetic Produced Water treatment by iron anode at 4, 8, 16 mA/cm². Experiments were operated with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L. .... 43

Figure 3-9 Synthetic Produced Water treatment by using aluminum anode in EC at 4, 8, 16 mA/cm². Experiments were operated with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 44

Figure 3-10 Energy consumption of Fe-EC and Al-EC for treatment of synthetic produced water at different current densities. Experiments were operated with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 44

Figure 3-11 Effect of Inter-electrode distance on Fe-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 46

Figure 3-12 Comparison of Batch and Recirculating flow mode Fe-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 49

Figure 3-13 Comparison of Batch and Recirculating flow mode Al-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 49

Figure 3-14 Fe-EC with an oscillating anode at 0.6 Hz vs. at 1.75 Hz and with a stationary anode. Experiments were operated at 8 mA/cm² with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 51

Figure 3-15 Al-EC with an oscillating anode at 0.6 Hz vs. at 1.75 Hz and with a stationary anode. Experiments were operated at 8 mA/cm² with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 52

Figure 3-16 Cell voltage of Batch EC experiments under stationary and oscillating anode system with both Fe and Al electrodes. Experiments were operated with the batch oscillating anode EC cell with 8 mA/cm² current density electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L. ...................................................... 53
Figure 3-17 Effect of Current densities in Fe-EC with Oscillation at 4 mA/cm², 8 mA/cm² and 16 mA/cm² with an oscillating frequency of 0.9 Hz and oscillation centre to peak amplitude of 6 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .................. 54
Figure 3-18 Effect of Current densities in Al-EC with Oscillation at 4 mA/cm², 8 mA/cm² and 16 mA/cm² with an oscillating frequency of 0.9 Hz and oscillation centre to peak amplitude of 6 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .................. 54
Figure 3-19 Effect of oscillation frequency at oscillatory Reynolds number of 530 on Fe-EC at 0.6 Hz and 0.9 Hz, and center-to-peak oscillation amplitudes, 6 mm and 4 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .................. 56
Figure 3-20 Effect of oscillation frequency at oscillatory Reynolds Number of 530 on Al-EC at 0.6 Hz and 0.9 Hz, and center-to-peak oscillation amplitudes, 6 mm and 4 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .................. 57
Figure 3-21 Effect of Combination of oscillation & recirculating flow on Si removal. Experiments were conducted at 8 mA/cm² with the recirculating flow reactor at flowrate of 150 mL/min with anode oscillating at 1.5 Hz. EC cell with electrolyte volume of 1.2 L and effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .............................................. 58
Figure 3-22 the removal of Mg, Ca, and Si using: a) Batch Fe-EC contaminant removal with 400 mL solution, b) Batch Fe-EC with anode oscillation contaminant removal with 400 mL solution with 0.6 Hz frequency, c) Recirculation Fe-EC contaminant removal at 150 mL/min with 1.2 L solution, d) Recirculation Fe-EC with anode oscillation at 150 mL/min with 0.6 Hz frequency with 1.2 L solution. Experiments were operated at 8 mA/cm² with effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .............................................. 58
Figure 3-23 the removal of Mg, Ca, and Si using: a) Batch Al-EC contaminant removal with 400 mL solution, b) Batch Al-EC with anode oscillation contaminant removal with 400 mL solution with 0.6 Hz frequency, c) Recirculation Al-EC contaminant removal at 150 mL/min with 1.2 L solution, d) Recirculation Al-EC with anode oscillation at 150 mL/min with 0.6 Hz frequency with 1.2 L solution. Experiments were operated at 8 mA/cm² with effective electrode area of 220 cm², initial Si⁡²⁺ concentration of 56 mg/L .............................................. 60
Figure 3-24 Real produced water contaminant removal by Batch Fe-EC. Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm² and 400 mL of real produced water was used. Effective electrode surface area is 220 cm² .............................................. 61
Figure 3-25 Real produced water treatment by batch Al-EC. Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm² and 400 mL of real produced water was used. Effective electrode surface area is 220 cm² .............................................. 63
Figure 3-26 Real produce water treatment by Recirculating flow Fe-EC. Experiments were conducted in a recirculating flow EC cell (Figure 2-2) with 8 mA/cm² and 1.2 L of real produced water at 150 mL/min. Effective electrode surface area is 220 cm² .............................................. 63
Figure 3-27 Real produce water treatment by Recirculating flow Al-EC. Experiments were conducted in a recirculating flow EC cell (Figure 2-2) with 8 mA/cm² and 1.2 L of real produced water at 150 mL/min. Effective electrode surface area is 220 cm² .............................................. 64
Figure 3-28 Real produce water treatment by batch Fe-EC with Oscillation. Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm² and 400 mL of real produced water.
Effective electrode surface area is 220 cm$^2$

Figure 3-29 Real produced water treatment by batch Al-EC with Oscillation. Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm$^2$ and 400 mL of real produced water. Effective electrode surface area is 220 cm$^2$.

Figure 3-30 Si removal from synthetic produced water and real produced water by the mild steel anode and aluminum anode. Experiments were conducted in the recirculating flow system (Figure 2-1) with 8 mA/cm$^2$ and effective electrode surface area of 320 cm$^2$, at 150 mL/min.

Figure 3-31 Cell Voltage vs. Electrolysis duration for Fe & Al EC experiments for synthetic and produced water treatment.

Figure 3-32 Contaminant Removal Efficiency for batch Fe-EC system for boiler blowdown water treatment.

Figure 3-33 Contaminant Removal Efficiency for batch Al-EC system for boiler blowdown water treatment.

Figure 3-34 Contaminant Removal Efficiency for batch Fe-EC system with anode oscillation for boiler blowdown water treatment.

Figure 3-35 Contaminant Removal Efficiency for batch Al-EC system with anode oscillation for boiler blowdown water treatment.

Figure 3-36 Energy Consumption in Recirculating flow cell for Fe-EC and Al-EC on synthetic produced water and real produced water treatment.

Figure 3-37 Operating Cost of Fe-EC and Al-EC on treatment of synthetic produced water and real produced water.

Figure 3-38 Energy Consumption of Fe-EC and Al-EC for synthetic produced water treatment at different current densities with the batch recirculating flow system shown in Figure 2-1.

Figure 3-39 Energy Consumption in batch Fe-EC and Al-EC system with anode oscillation for the treatment of synthetic produced water and real produced water at 8 mA/cm$^2$.

Figure 3-40 Energy Consumption in batch Fe-EC and Al-EC system at different current densities for the treatment of synthetic produced water with the batch system with anode oscillation in Figure 2-2.

Figure 3-41 Blowdown sample treatment by Fe-EC and Al-EC with anode oscillation in a Batch EC at 8 mA/cm$^2$.

Figure 3-42 Total operating cost of Fe-EC and Al-EC on blowdown treatment with the anode oscillation system.

### Table of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1</td>
<td>Electrocoagulation applications in industry</td>
<td>15</td>
</tr>
<tr>
<td>Table 2-1</td>
<td>Compositions of Oil Sands Produced Water obtained from the Peace River facility</td>
<td>23</td>
</tr>
<tr>
<td>Table 2-2</td>
<td>Stability of produced water composition obtained the Peace River facility</td>
<td>24</td>
</tr>
<tr>
<td>Table 2-3</td>
<td>Composition of synthetic produced water sample</td>
<td>25</td>
</tr>
<tr>
<td>Table 2-4</td>
<td>Constituents of boiler blowdown sample</td>
<td>25</td>
</tr>
</tbody>
</table>
## List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>Faraday's Constant = 96487 C/mol e-</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density, mA/cm²</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of moles of metal ion generated at the anode (mol)</td>
</tr>
<tr>
<td>$C_{Si}$</td>
<td>mg/L, Si²⁺ concentration of treated water sample</td>
</tr>
<tr>
<td>$C_{SiI}$</td>
<td>mg/L, Si²⁺ concentration of water sample before treatment</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$z$</td>
<td>The number electrons transferred per ion</td>
</tr>
<tr>
<td>$Re_o$</td>
<td>Oscillatory flow Reynolds number</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Hz, oscillation frequency</td>
</tr>
<tr>
<td>$x_0$</td>
<td>mm, centre-to-peak amplitude</td>
</tr>
<tr>
<td>$d_e$</td>
<td>mm, hydraulic diameter</td>
</tr>
<tr>
<td>$\nu$</td>
<td>mm²/s, kinematic viscosity</td>
</tr>
</tbody>
</table>

**BD**
- Blowdown water sample

**COD**
- Chemical oxygen demand

**CV**
- Cyclic Voltammetry
  - It explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through a liquid medium

**DO**
- Dissolved oxygen

**EC**
- Electrocoagulation
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDL</td>
<td>Electric Double Layer</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma - Atomic Emission Spectroscopy</td>
</tr>
<tr>
<td>SAGD</td>
<td>Steam Assisted Gravity Drainage</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1 Oil-Sands Produced Water

The oil sands in northern Alberta, have the third largest oil reserves in the world, after Venezuela and Saudi Arabia, containing an estimated 173 billion barrels of recoverable oil [1]. In Alberta, the oil-sands industry plays an important role in the local economy. However, the industry consumes a large amount of water, equivalent to the water usage of 1.7 million homes in Canada, at about 170 MMm$^3$ [2]. Of the available bitumen, only 20% can be extracted by surface mining, while the rest can only be produced by in-situ methods [3]. For in-situ methods, steam is typically injected into the reservoir to reduce the bitumen viscosity, allowing the bitumen to flow to the surface along with water. In oil sands processing, both surface mining and in-situ production methods consume huge amounts of water. For example, to produce 1 barrel of oil, usually 3 barrels of water is needed [4]. Thus, in a typical SAGD process, about 70-90% of the water has to be recycled in order for the process to be viable both economically and environmentally. Oil sands produced waters commonly contain oil, silica, hardness, and suspended solids [5]. Removal of these contaminants is necessary to make the produced waters suitable for recycling as boiler feedwater. Improved, low cost treatment of produced water will enable reduction of both boiler fresh water consumption and water disposal to rivers.

1.2 Common Technologies for Oil Sands Produced Water Treatment

The most commonly used method for in-situ oil sands production in Alberta is called steam assisted gravity drainage (SAGD). A simple schematic diagram of a typical SAGD process is shown below in Figure 1-1. In this process, steam is generated at the ground surface and is injected into the reservoir, heating and reducing the viscosity of the bitumen to allow it to drain into the horizontal production well and raised to the surface. Water is produced along with bitumen to the
surface, and this water has to be separated from the bitumen and treated before it is recycled for steam generation. After the steam generation, part of the concentrated boiler blowdown is recycled into the water treatment process. Recycling blowdown water reduces disposal water volumes and increases total water throughput in the plant to supply more boiler feedwater and steam, which improves plant efficiency. The common produced water treatment technologies used in oil sands industry can be separated into different stages, including: de-oiling, soluble organics removal, removal of suspended particles, sand, turbidity, removal of dissolved salts, and removal of hardness and silica [5]–[8]. Guirgis et al. have summarised the technologies developed to treat oil-sands produced water and their potential limitations [9]. Among the technologies stated in this review and used in Canadian oil sands industry are: chemical coagulation, warm lime softening, adsorption (by adsorbents such as activated carbon, zeolites, clays, resins, and synthetic polymers), oxidation (by chemical, photocatalytic), biological treatment and membrane processes [9].

![Figure 1-1 A schematic diagram of a typical SAGD process](image)

### 1.3 Scaling & Fouling in Steam Generation and Water Treatment Technologies

In a typical SAGD process, the presence of silica and hardness in water can create a hard scale layer in the boiler that is difficult to control or treat. The hard scale causes a reduction in the
thermal efficiency of the boiler. For example, a deposit of only 0.1 mm hard scale can reduce the heat transfer by 5% [10], [11]. Therefore, prevention of scaling, fouling, and corrosion is a major concern for oil sands extraction process operations, especially at thermal in situ operations such as the SAGD process where produced water is recycled and reused for steam generation. Scales formed in oil sands produced water steam generators typically contains mostly carbonate and silica, and may include some sulfate and phosphate [12].

Thus, from an engineering point of view, silica and hardness must be removed to increase both the recyclability of water as well as the efficacy of the SAGD process. The most common methods for removing silica and hardness from a wastewater stream are lime softening, ion exchange, and reverse osmosis [8], [13]–[17].

Lime softening is one of the most commonly used methods to remove hardness and silica from water such as make up water to cooling towers and boilers, or boiler blowdown water. In the lime softening process, lime Ca(OH)₂, soda ash (Na₂CO₃) and sodium hydroxide are added to convert soluble calcium and magnesium hardness into insoluble calcium carbonate and magnesium hydroxide for further separation. During the lime softening process, calcium is deposited as calcium carbonate while magnesium is deposited as magnesium hydroxide. Upon precipitation, Mg(OH)₂ forms large flocs that have a high affinity to silica, which is attached to the magnesium hydroxides and thus removed [18]. Ion exchange is the exchange of ions between two electrolytes or between the water being treated and the ion exchange resin. Ion exchange is very efficient in removing silica; however, the disadvantage of this process is that the resin exchangers require frequent regeneration, which adds significant operating costs to the process [19]–[22]. Reverse osmosis (RO) is a filtration method that uses a semi-permeable membrane to remove ions from solutions by applying a pressure difference across the membrane. The membrane allows small
molecules including water, such as the solvent, to pass freely, while blocking large molecules or ions to pass through the membrane [21], [23]. The use of reverse osmosis or any other membrane technology to remove silica can be operationally problematic. One of the disadvantages of this technology is that silica and other contaminants will foul the membrane, thus decreasing the efficacy of the process. Usually, membrane systems would undergo backwash to minimize fouling and damage to the membrane [8], [16], [24], [25].

1.4 Silica Chemistry and Destabilization Theory

The concentration of silica in water is generally expressed based SiO$_2$, but the exact form of dissolved silica is not yet well understood [8], [22], [24], [26]. Silica in water can be in the form of monomeric silica (silicic acid, Si(OH)$_4$(aq), a polymerized form, or in the accumulated form of silica colloids (SiO$_2$(s)). The solubility of amorphous silica in water is around 120 mg/L at neutral pH and temperature 20-25°C, the polymerization of silicic acid would likely occur for water with low silica content, whereas the accumulation of silica colloids would likely occur for high silica content. The stability of silica in water is strongly dependent on the pH and the concentration of ionic species. Solubility decreases as the pH decreases, and increases rapidly above pH 9. The increase in the total soluble silica at high pH is due to the formation of highly soluble silicate ions [27].

Colloidal silica particles exist in many natural systems. Colloidal particles stability is often evaluated based upon the repulsive forces induced by the electric charges, and attractive forces between particles. When repulsive forces are larger than attractive force, particles will remain in a dispersed state. When attractive forces dominate, the colloids will coagulate to form a larger particles, which can precipitate or settle by gravity. The repulsion needs to be minimized in order to destabilize the suspension [28]. The theory of electric double layer can be used to explain this
phenomenon. To neutralize the charge, counter charged ions can be attracted to the surface of the colloids, which forms an electric double layer. The electric double layer consists of an inner layer (the Helmholtz layer) where counter charged ions are tightly bound to the surface of the colloidal particles and an outer diffusive layer, where the ions are mobile. The zeta potential, which is defined as the electric potential at the interface of the outer limit of the inner layer (the slipping plane) and the outer layer, is an indication of the charge which leads to electrostatic repulsion between colloidal particles with the same charge [29]. The higher the value of the zeta potential, the greater the repulsion. The DLVO theory was established by Derjaguin, Landau, Verwey, and Overbeek in the 1940s gives a good explanation of the stability of colloidal particles [30]. It considers the Van der Waals force and the electrostatic repulsion are controlling the stability of colloidal particles. The net interaction energy of two particles is given by the sum of Van der Waals attraction energy and electrostatic repulsion energy. During treatment via coagulation, the coagulants destabilize the colloidal particles by reducing the repulsive energy, which allows them to agglomerate and form a floc.

There are three different mechanisms to destabilize and coagulate colloidal suspensions depending on the properties of the solution, colloid, and coagulant. The first mechanism to explain coagulation is compression of the electric double layer (EDL). The extent of repulsion can be affected by the thickness of the EDL. The lower the double layer thickness, the lower the repulsive force, which can enable particles to coagulate and form larger flocs. There are several ways to decrease the double layer thickness; one is increasing the counter ion concentration. Also, the higher the charge on each counter ion, the better the ability to destabilize the colloidal particle [31]. Another mechanism is adsorption/charge neutralization. Counter charged ions on the surface of colloidal particles can neutralize their surface charge so that van der Waals attractive forces can
dominate, particles can then come together and coagulate [28].

The third mechanism of coagulation is entrapment of silica particles in the precipitate, which is called sweep coagulation, and happens at high coagulant dosage at near neutral pH. When the coagulants alum \([\text{Al}_2(\text{SO}_4)_3]\) or FC (\(\text{FeCl}_3\)) are added in high enough concentration, they will react with water to form metal hydroxide precipitates, \(\text{Al(OH)}_3\) or \(\text{Fe}_2\text{O}_3\) respectively. The colloidal particles get entrapped in the precipitates either during the precipitate formation or just after [28], [32].

1.5 Electrocoagulation Background

Electrocoagulation (EC) is a technology that combines coagulation, flotation, and electrochemistry. It is a process that generates coagulants in-situ, using a sacrificial metal anode, usually iron or aluminum. In 1909, aluminium/iron-based electrocoagulation was first patented in the U.S. [33].

Global demand for drinking water is increasing, and the environmental regulations on wastewater discharge are getting more stringent. Thus, there is an increasing need for more effective water treatment methods to address the wide verities of pollutants in water supplies and wastewater. Over the past several decades, many studies have focused on the implementation of EC processes and their performance in treating different types of wastewater, to remove contaminants including pathogens, arsenic, iron, fluoride, nitrate, turbidity and Natural Organic Matter [34]–[42]. EC is a simple and easy to operate technology. Moreover, the remediation process can be monitored precisely by adjusting the charge loading and hence the coagulant dose. However, as sacrificial anodes are consumed throughout the process, the regular replacement of these anodes, with associated material and maintenance costs, is a disadvantage.

Moreover, other drawbacks of the process include: the possible passivation of anodes which impacts the efficiency of the process, the need to add salts if the conductivity is low, and the
coagulated solids may become soluble under certain conditions so that they can be released back into the environment [43]. Compared to chemical coagulation, however, the EC process is generally more effective at pollutant removal, produces less sludge as no pH adjustment by the addition of lime needed, avoids the addition of chemicals which eliminates secondary pollution, generates gas bubbles during the process which facilitates the removal of pollutants by flotation, and consumes less metal to reach the same level of pollutant removal [42], [44]–[46]. Researchers studied the removal of organic dyes from wastewater by EC with different operating conditions, and proposed that the EC reactor can be seen as a first-order plug flow reactor, in which the rate constant is dependent on the operating conditions controlling the anodic dissolution [47], [48]. Previous studies on the removal of humic substances by aluminum anodes reported that the production of Al(OH)_3 was not affected by initial pH, but at higher pH, a gel layer on the anode could result in decreasing pollutant removal [49], [50].

1.6 Electrocoagulation Principles

Many studies have been performed to investigate the possible EC for applications. However, the mechanism of the process for pollutant removal is not yet well understood. A schematic diagram of a simple electrocoagulation cell is shown in Figure 1-2 below:
In theory, EC is a complex process that combines the principles of electrochemistry with those of coagulation and flotation. Through the electrochemical reactions, the metal coagulant is dissolved into solution due to the external current applied to the EC cell. The dissolved metal coagulant undergoes a hydrolysis process which combines with hydroxides (formed at the cathode) to form insoluble metal hydroxides [51]. EC shares some similarities with chemical coagulation, but there are some major differences. In EC, gas bubbles are generated at the cathode, which can bring the flocs to the top of the solution. In addition the electrochemical reactions in EC can potentially oxidize some contaminant species. Thus the reactions in EC and chemical coagulation are different [42], [43], [52], [53].

A simple EC reactor consists of an electrolytic cell with metal anode and cathode electrodes connected to a DC power supply and submerged in the wastewater to be treated [54]. Iron and aluminum electrodes are the most extensively used metals for EC cells since these metals are
abundant, non-toxic, and effective [55]. Upon the application of sufficient overpotential, the anode material in an EC cell dissolves (due to oxidation) into the solution in the form of metal ions $M^{n+}$, which serve as the coagulant when they react with water to form metal hydroxides. At the cathode, water is reduced to hydrogen gas and hydroxide anions. The produced hydroxide anions can enhance the production of metal hydroxides, which can coagulate with pollutants in the water.

The rate of dissolution of the anode can be described by Faraday's law of electrolysis, Eq (1) [56]:

$$\dot{n} = \frac{\varphi I t}{zF}$$

where: $\varphi$ is the current efficiency, $I$ is the current (A), $t$ is the time of electrolysis (s), $F$ is a Faraday's constant (96,487 C/mol), $z$ is the valence of electrons and $\dot{n}$ is the rate of anode dissolution (mol).

The simplest form of anodic reactions are expressed as:

$$M(s) \rightleftharpoons M^{n+}(aq) + ze^-$$

The metal is usually iron, or aluminum. Also, if a sufficient overpotential is applied, other side reactions can take place at the anode surface, e.g., water electrolysis to produce oxygen.

The cathodic reaction is:

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$$

Generally, the electrode materials can also be iron or aluminum. However, depending on the bulk solution environment, the anode region tends to be more acidic and the cathode region to be more alkaline than the bulk solution due to oxygen evolution on the anode and hydrogen evolution on the cathode.

Considering the anode reactions, depending on the environment and operating conditions, iron can dissolve to form ferrous ($Fe^{2+}$) or ferric ($Fe^{3+}$) ions, whereas aluminum can only dissolve into the trivalent $Al^{3+}$ form. Also, depending on the pH and the cell potential, iron and aluminum can form
different hydroxide species as shown in Figure 1-3 & Figure 1-4. Figure 1-3 shows that ferric ion is effective over a wider range of pH (>3) compared to ferrous ion (>9), so oxidation of ferrous to ferric ion is desirable, preference for ferric ion formation for more effective EC.

Moreno et al. studied the types of electrochemical reactions taking place during the electrocoagulation of iron electrodes, and found that iron usually produces Fe$^{2+}$ on the anode, and in the lower pH and higher potential region, ferrous (Fe$^{2+}$) ions can be further oxidized to ferric (Fe$^{3+}$) forms [57]. There are some contradictions in the literature concerning the type of iron produced in EC reactors. Some studies suggest that both Ferrous (Fe$^{2+}$) or Ferric (Fe$^{3+}$) forms exist in the EC system, while others claim that iron is produced on the anodes mainly in Fe$^{2+}$ form [34], [38], [54], [57]–[61].
Considering, on the other hand, an EC reactor with aluminum electrodes, researchers reported current efficiencies of higher than 100%, which has been explained by aluminum dissolution at the cathode [63]. It is claimed that when the pH on the cathode increases due to the OH- formation, aluminum on the cathodes starts dissolving. Alternatively, pitting corrosion of aluminum can result in chemical (non-Faradaic) dissolution of aluminum to form additional aluminum ion production at the anode [64]. Researchers studied the cathodic dissolution for iron and aluminum, and they found that hydrogen evolution at iron cathodes followed Faraday’s law of electrolysis, whereas at aluminum cathodes the hydrogen evolution was higher due to the chemical dissolution of aluminum. The hydrogen evolution and aluminum cathode dissolution were also reported to increase with increasing current density [50], [65].

Figure 1-4 Pourbaix Diagram of Aluminum – water system at 25°C [62]
1.6.1 Potential Side Reactions

Other than the main anode and cathode reactions described above (eq. 2 and 3), many other potential reactions can occur during the EC process, including:

- Oxygen evolution on the anode

\[ H_2O \rightleftharpoons \frac{1}{2} O_2 + 2 H^+ + 2e^- \]  

(4)

- Electrodeposition of metal on the cathode

\[ M^{n+}(aq) + ze^- \rightleftharpoons M(s) \]  

(5)

- Redox reactions of other species that coexist in the water.

Studies of the iron oxidation process in EC has found that rate of the dissolution of iron at the anode can be lower than expected from Faraday’s law [60]. This observation indicates that other electrochemical reactions occur, especially under alkaline conditions.

It has been reported that when the initial pH value is less than 4 (acidic), the effluent pH increases during EC treatment, while it tends to decrease when the initial pH value is higher than 8 (basic), and the pH of the effluent changes only slightly when the initial pH value is in the neutral range (around 6–8). This situation indicates a pH buffering effect during EC, which is different from traditional chemical coagulation. This pH buffering capacity can be attributed to the balance between the production and consumption of hydroxyl ions during EC and the need for charge neutralization before the ultimate transformation of soluble aluminum compounds into aluminum hydroxides. Thus, the formation of Al(OH)$_3$ near the anode may lead to a decrease in pH (see Eq. 6). On the other hand, ultimate pH values increase rapidly during EC such that the ultimate pH values reached at the end of EC are always greater than 8–9. Similarly, in Fe-EC, the pH buffering effect is also observed by the formation of Fe(OH)$_3$ and Fe(OH)$_2$ on the anode, which decreases the pH near the anode [66].
Thus, a net increase in the pH in the bulk solution would suggest that both hydroxide ions and hydrogen evolution at the cathode are being generated at a faster rate than the hydroxide ions being consumed by hydrolysis of the metal ions generated at the anode. This phenomenon is different from the conventional chemical coagulation which has a net decrease in the pH as more of the metal salt coagulant is added. Thus, in order to maintain the pH during the chemical coagulation in the sweep flocculation stage and to prevent the pH from dropping below 6, lime should be added. Hence, the resulting volume of sludge is much larger in chemical coagulation than those found in the EC process [67]. In EC process, the required hydroxide ions are provided by the electrolysis of water at the cathodic that does not involve the addition of any metal ions, whereas in chemical coagulation larger amount of addition of alum or ferric chloride as coagulants will produce larger amount of sludge [68].

1.7 EC Applications

Many types of pollutants are observed to be removed efficiently by EC. Examples of wastewater that have been treated using EC systems are presented in Table 1-1 [1]. Experimental trials show that EC is able to remove oil from emulsions, restaurant wastewater, and refinery wastewater by dissolving ferric/aluminum ion that can destabilize the emulsion by neutralizing the charge on the

\[ Al^{3+} + nH_2O \rightarrow Al(OH)_3^- + nH^+ \]  \hspace{1cm} (6)

\[ 4Fe^{2+}(aq) + 10 H_2O + O_2(aq) \rightarrow 4Fe(OH)_3(s) + 8H^+ \]  \hspace{1cm} (7)

\[ Fe^{2+}(aq) + 2OH^- \rightarrow Fe(OH)_2(s) \]  \hspace{1cm} (8)
droplets, and by adsorption of the oil onto the ferric/aluminum hydroxide precipitates [69]–[74]. Decolourization of dye solution from textile wastewater by EC has also been demonstrated as a feasible technique. Two main mechanisms of dye removal were considered, namely precipitation and adsorption [42], [75]–[83]. The organic waste in municipal wastewater can also be removed effectively by EC. The removal of chemical oxygen demand (COD), turbidity, phenol, hydrocarbon, and grease from wastewater have also been studied, the pollutant removal process for these treatments was reported to neutralize the charge of pollutants, then generate gas bubbles and separate the coagulated flocs from the treated water [7], and the results of these studies showed that EC is an efficient technology for the treatment of industrial wastewaters. However, the capacity and efficiency strongly depend on the nature of the liquid waste and initial pollutant concentrations [84]–[87]. The removal of heavy metals (i.e., As, \( \text{Cr}^{6+} \), \( \text{Cd}^{2+} \), etc.) by EC has also been studied, and it was found that EC could successfully remove arsenic and cadmium from water or wastewater [88]–[93]. The highest removal of arsenic (over 90%) was achieved by using iron electrodes when the removal mechanism was considered to be adsorption of arsenic on hydrous ferric oxides, but there is no evidence reported to support this mechanism [53], [94]. The use of EC for nitrite and ammonia removal from aqueous solution has been investigated, and the results indicate that EC could remove about 90% of these pollutants from aqueous solution [95]. Studies were also conducted on hardness removal by electrocoagulation and observed promising removal [96], [97]. For example, the performance of fluoride removal by EC technique was also found to be effective (see Table 1-1; [39], [52], [98]–[100]).
Table 1-1 Electrocoagulation applications in industry

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>electrode material</th>
<th>Removal Efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil from refinery</td>
<td>Fe &amp; Al</td>
<td>60-99 %</td>
<td>[70]</td>
</tr>
<tr>
<td>Oil from wastewater</td>
<td>Stainless steel</td>
<td>60-99 %</td>
<td>[54]</td>
</tr>
<tr>
<td>Oil from Restaurant</td>
<td>Fe &amp; Al</td>
<td>95-99%</td>
<td>[69]</td>
</tr>
<tr>
<td>Oil in water emulsion</td>
<td>Al</td>
<td>80-99%</td>
<td>[67], [68], [71]</td>
</tr>
<tr>
<td>Dye</td>
<td>Al &amp; Fe</td>
<td>75-99%</td>
<td>[43], [72]–[80]</td>
</tr>
<tr>
<td>COD, turbidity, phenol, grease</td>
<td>Al &amp; Fe</td>
<td>75-99%</td>
<td>[81]–[84]</td>
</tr>
<tr>
<td>hardness</td>
<td>Fe &amp; Al</td>
<td>60-80%</td>
<td>[93], [94]</td>
</tr>
<tr>
<td>Nitrate &amp; Ammonia</td>
<td>Al</td>
<td>60-90%</td>
<td>[92]</td>
</tr>
<tr>
<td>Heavy metals (Cr³⁺, As, Cd²⁺,</td>
<td>Fe &amp; Al</td>
<td>70-85%</td>
<td>[85]–[90]</td>
</tr>
<tr>
<td>Pb, etc)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>Fe &amp; Al</td>
<td>70-90%</td>
<td>[40], [52], [93]–[95]</td>
</tr>
</tbody>
</table>

1.8 Factors affecting Electrocoagulation

Experimental parameters found to impact the EC performance are related to the EC electrode material, and the operating conditions such as the current density, the operation time, the design of the reactor (especially the electrode spacing), the composition of the wastewater (including the pH, and the conductivity), and the operating temperature.

Electrode material

The choice of electrode material is one of the key steps for optimizing the performance of an EC process. Several electrode materials have been tested in EC, and the most commonly used
materials are Al and Fe, while others have also tested Zn [55]. Typically, iron (or steel), or aluminum, are used as electrodes in EC process because they are able to be dissolved anodically, their hydroxides are insoluble, and they are abundantly available at low price [101], [102]. The selection of the electrode material has a large impact on the performance of the electrochemical reactor.

The surface of the electrode plays an additional role in the EC process. Plate electrodes are conventionally used; however other geometries can also be utilized. The importance of the geometry is derived from the increase the contact surface area with the electrolyte and to help regular cleaning of the surface, as any deposition of sludge on the electrode may reduce the metal cations dissolution rate and hence reduces the efficiency. Thus, although Al$^{3+}$ shows higher coagulation efficiency then iron in most applications, a passivation layer often forms on the surface aluminum electrodes (so-called fouling layer) will hinder the Al$^{3+}$ generation rate significantly. Accordingly, iron electrodes are most often used [70], [92], [103].

**Electrode separation**

The space between the electrodes also affects the reactions occurring in the EC reactor. At the cathode, if a hydrogen overpotential is reached, hydrogen gas will be generated and can partially fill the inter-electrode gap, which may increase the electrical resistance in the liquid. Although the Ohmic potential drop is proportional to the inter-electrode spacing (the smaller the gap is the lower the resistance), reducing the electrode gap can cause a problems associated with the accumulation of gases, and mass transfer of fluid and solid in the system is obstructed. Also, accumulated solid particles and gas bubbles between the electrodes can cause a higher electrical resistance [104], [105].
**Current density and charge loading**

Current density \((i, \text{A/m}^2)\) is defined as the ratio of current over electrode surface area. According to Faraday’s law (Eq. 1), the rate of metal ion dissolution per unit electrode area is directly proportional to the applied current density. Thus the current density (and the electrode area) determines the rate of coagulant dosage at the anode and the hydrogen gas evolution at the cathode. Thus, as the applied current is increased, the dissolution rate of coagulant increases, which will result in an increase in electrical energy consumption, ohmic heating the water, and a potential decrease in current efficiency if side reactions occur [35], [106], [107].

In most case the current efficiency at the anode is around 100%, so that the concentration of coagulant that is produced is proportional to the electric charge passed per volume. The dose can usually be calculated according to Faraday’s law of electrolysis when current and treatment time are given. The contaminant removal is strongly dependent on the charge loading, which is the most important parameter for the removal efficiency of the contaminants in the EC process [108].

**Current type**

Direct current (DC) supply is typically used in electrocoagulation; however, in some applications, the use of an alternating current (AC) achieved a similar performance as DC [109]. Problems associated with the application of DC are related to the formation of a fouling layer on the electrodes, which leads to higher power consumption as well as deterioration of the anode due to oxidation that leads to the loss of efficiency of the EC unit [110]. Several studies have reported using AC power supply give similar results as with DC power. For example, the use of AC power was found to extend the electrode life due to the prevention of the electrode’s passivation by
reversing the polarity [102].

**Wastewater pH**

The pH of the wastewater impacts the conductivity of the solution, the dissolution of the electrodes, speciation of hydroxides [111]. When using iron or aluminum as electrodes, a slightly acidic, neutral, and slightly alkaline pH allows the formation of hydroxide coagulants; whereas in highly alkaline conditions, the hydroxides formed remain soluble in the effluent will have a poor coagulation ability [35]. The importance of pH stems from the fact that the variation in pH can change the coagulant products and the coagulation mechanism [112]. Under high pH, the coagulation mechanism is the formation of large precipitate species that can adsorb these particles which then flocculate and form larger flocs that settle more easily. The optimum pH range for iron coagulation and aluminum coagulation are between 4.5 to 8 and 4 to 12 respectively [112].

**Dissolved oxygen**

In EC operations, the components of Fe products are very complex and the transformations of Fe(II) and Fe(III) are affected by experimental conditions, most significantly dissolved oxygen (DO) [113]. Green rust, goethite, magnetite, lepidocrocite, hematite were the most common products produced from EC in recent studies [114]. Usually, the lifetime of green rust in traditional EC is relatively short because Fe(II) compounds are sensitive to the presence of DO in solution and air and operating conditions such as aeration and agitation. Aeration promotes the transformation of green rust into magnetite, goethite and lepidocrocite, depending on the mole fraction of Fe(II) and OH\(^-\) compared to the total Fe concentration [115]. For Al-EC, there were few studies on the effect of DO. Thus, the effect of DO on the EC treatment is an important factor
and needs to be investigated.

**Reactor Design**

There have been many studies on the operating conditions of the EC process, however no systematic studies of the impact of the design of the reactor. Therefore, it is difficult to compare the performance of different reactors reported in the literature [68]. EC reactor designs range from electrochemical cells containing a simple set of anodes and cathodes to complex electrochemical assemblies. The design parameters take into account many aspects, include fluid flow pattern, floatation and precipitation, and the operating variables mentioned above (e.g., electrode materials, electrode arrangement, current density, etc.). Different applications may require different EC reactor designs.

Reactors can also be classified as continuous and batch, and batch with recirculation flow. A continuous mode reactor is dynamic in operation, and it enables monitoring the inlet and outlet concentrations of the constituents; while in a batch mode, the evaluation of pollutant, coagulant, and pH concentrations can be performed throughout the process. It is reported that for large volume processes, continuous mode operations have been found to be more economical than batch systems [47], [116]–[119].

The application of oscillatory flow has been found to offer significant enhancement on mass transfer [120]. The use of oscillatory flow has been reported in an electrochemical parallel plate reactor that it can enhance mass transport rates by a factor in excess of 10 [120]. A study also investigated the use of an oscillating anode in EC system for the treatment of turbidity due to suspended solids in kaolin and it showed that anode oscillation had a significant improvement in treatment performance compared with a stationery electrode with both Al-EC and Fe-EC.
In terms of scale-up, the surface area to volume ratio is anticipated to be an important parameter in the batch system, whereas in the continuous system the surface area to volumetric flow rate is more important. Electrode area influences the current density and the rate of coagulant dosing, as well as the rate of gas production. It was reported that as the surface area to volume ratio increases, the optimal current density decreases in batch systems [99]. The practicality of scaling up of an electrocoagulation-flotation system from laboratory to industrial size has also been evaluated [121]. The dimensionless parameters for scale-up were selected as the Reynolds number, which is a good representation of the fluid flow pattern. Geometries of reactors were kept dimensionally similar.

Other trials on enhancing the removal performance of suspended solids in wastewater were carried out using an EC reactor with iron as a sacrificial anode coupled with magnetic fields to enhance the settling velocity of the formed sludges [122].

1.9 Knowledge gaps in EC

The EC process has been widely studied for many different applications, and shown to have various advantages: simple, low-cost, efficient, and able to remove a variety of pollutants simultaneously. The process offers several advantages over conventional chemical coagulation and other water treatment methods.

Researchers have tested the performance of EC for the treatment of oil sands produced water [96], [123]. Shamaei et al studied the combination of EC and chemical coagulation on oil sands produced water treatment and they found that EC can remove 10-20 % of TOC, with the addition of chemical coagulation TOC can be removed by 39% [123]. Another study by Zhao et al investigated the hardness, COD and turbidity removals from produced water by EC and results showed that 90% of hardness and turbidity and 60% of COD are removed by EC at optimum operating conditions [96]. However, not many studies have been done on the removal of silica
from oil sands produced water. Thus, our study will investigate the effect of operating conditions and geometric designs on the EC process for the removal of silica and hardness from oil sands produced water, and aims to contribute to the development of EC as an applicable technology for this industry.

1.10 Research Objectives

The aim of this thesis is to develop an effective bench scale EC system for the treatment of oil sands produced water containing silica, hardness, and dissolved organics. The following have been investigated:

- The viability of EC for the removal of silica from oil sands produced water, which is difficult to remove by other technologies.
- The influence of the EC operating conditions on the performance for treatment of oil sands produced water, including current density, flow rate, charge loading, and the presence of dissolved oxygen.
- The influence of different reactor designs on the performance of EC, including an EC system with an oscillating anode between two cathodes and a monopolar stack design.
- The EC treatment of real oil-sands produced water, and comparison of the treatment performance with that for a synthetic produced water.
Chapter 2. Materials and Methodology

2.1 Produced Water

In this section, the composition of the synthetic and real produced water sample, the analytical methods, and the experimental procedures are discussed. Oil-sands produced water is provided from a water treatment plant located in the Peace River region of Alberta, Canada. This water is produced following the de-oiling process (the bitumen and water are separated and the oil is recovered). Usually in the oil sands industry, this produced water is de-oiled through skim tanks, filtered and then recycled through the steam generators. Since the Alberta Energy Regulator’s Directive 081 (D81) has imposed stringent disposal limit on the amount and quality of produced water that in-situ thermal facilities can produce, the facility owner must find a cost-effective way to meet D81 at their facility [124].

Samples of the de-oiled produced water were stored in sealed containers and covered by nitrogen blanket before treatment. The composition of the produced water is shown in Table 2-1, obtained using the analytical methods described in section 2.4. The concentrations of the dissolved inorganic ions, TDS, H₂S, TOC were measured by ICP-AES, Ion Chromatography, conductivity meter, and TOC Analyzer. This produced water contains elevated levels of hardness, silica, TDS, H₂S and oil, and grease.
The concentrations of major components in the produced water are analyzed and measured at the time it is received and after one month. The results are presented in Table 2-2. The analysis shows that the Si\(^{2+}\) concentration in the sample decreased from around 65 mg/L to around 56 mg/L after one month storage, and the Si\(^{2+}\) concentration of the sample after treatment decreased from 5 mg/L to 2 mg/L. The Mg\(^{2+}\) concentration in the sample before treatment remains stable in the range of 50 mg/L to 55 mg/L and 40 mg/L to 43 mg/L after treatment. The Ca\(^{2+}\) concentration remains in the range of 70 mg/L to 74 mg/L before treatment and, approximately 15 mg/L after treatment. The Cl\(^{-}\) concentration remains at approximately 4000 mg/L before treatment and 3800 mg/L after treatment. The concentration of SO\(_{4}^{2-}\) before treatment increased from approximately 48 mg/L to 140 mg/L, and increased from 25 mg/L to 53 mg/L after treatment. By atomic balance, the H\(_2\)S concentration is 150 mg/L, which is \(4.41 \times 10^{-3}\) mol/L of S\(^2-\), and the SO\(_4^{2-}\) concentration in the solution increases from 48 to 140 mg/L and 25 to 53 mg/L before and after treatment, corresponding to increases of \(9.58 \times 10^{-4}\) mol/L of SO\(_4^{2-}\) and \(2.92 \times 10^{-4}\) mol/L of SO\(_4^{2-}\) respectively, so the increase in SO\(_4^{2-}\) after one month storage before and after treatment can be totally attributed to the oxidation of S\(^2-\). The decrease of Si\(^{2+}\) before EC treatment could be due to the solubility limit of Si\(^{2+}\) under atmospheric temperature and neutral pH is around 56 mg/L, while

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Na(^{+}) (mg/L)</td>
<td>4000</td>
</tr>
<tr>
<td>Ca(^{2+}) (mg/L)</td>
<td>60</td>
</tr>
<tr>
<td>Mg(^{2+}) (mg/L)</td>
<td>20</td>
</tr>
<tr>
<td>Cl(^{-}) (mg/L)</td>
<td>2000</td>
</tr>
<tr>
<td>HCO(_3^{-}) (mg/L)</td>
<td>2000</td>
</tr>
<tr>
<td>SO(_4^{2-}) (mg/L)</td>
<td>50</td>
</tr>
<tr>
<td>H(_2)S ( @ 25°C) mg/L</td>
<td>150</td>
</tr>
<tr>
<td>Total Organic Compounds (mg/L)</td>
<td>400</td>
</tr>
<tr>
<td>Si(^{2+}) (mg/L)</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 2-1 Compositions of Oil Sands Produced Water obtained from the Peace River facility
the decrease of Si\(^{2+}\) concentration after EC could result from coagulation with the remaining Fe hydroxides after treatment.

*Table 2-2 Stability of produced water composition obtained the Peace River facility*

<table>
<thead>
<tr>
<th></th>
<th>Before treatment</th>
<th>After Treatment</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>As Received</td>
<td>After One Month</td>
<td>After One month</td>
</tr>
<tr>
<td>Si(^{2+})</td>
<td>65.0</td>
<td>56.0</td>
<td>5.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>53.3</td>
<td>52.8</td>
<td>40.9</td>
<td>41.8</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>73.5</td>
<td>74</td>
<td>15.4</td>
<td>15.6</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>4030</td>
<td>4050</td>
<td>3850</td>
<td>3830</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>48</td>
<td>140</td>
<td>25</td>
<td>53</td>
</tr>
<tr>
<td>pH</td>
<td>8.0 ± 0.2</td>
<td>8.7 ± 0.2</td>
<td>8.8 ± 0.2</td>
<td>8.7 ± 0.2</td>
</tr>
</tbody>
</table>

The characteristics of the produced water changed over time, and the composition of the water samples received at different time also varied. To ensure the reproducibility of our experiments and minimize uncertainties, we prepared synthetic produced water in our lab using similar concentrations of inorganics and salts of real produced water to mimic the composition of the produced water, but in the absence of any organics (oil and grease). Sodium bicarbonate (NaHCO\(_3\)), sodium sulfate (Na\(_2\)SO\(_4\)), sodium hydrosulfide (NaSH), sodium metasilicate (Na\(_2\)SiO\(_3\)), calcium chloride (CaCl\(_2\)), magnesium chloride (MgCl\(_2\)), and sodium chloride (NaCl) were used to prepare the synthetic produced water. Below in Table 2-3 is the composition of synthetic produced water.
Table 2-3 Composition of synthetic produced water sample

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (mg/L)</th>
<th>Concentration mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$</td>
<td>1700</td>
<td>27.861</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>40</td>
<td>0.416</td>
</tr>
<tr>
<td>Si$^{2+}$</td>
<td>56.171</td>
<td>2.000</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>65</td>
<td>1.622</td>
</tr>
<tr>
<td>SH$^-$</td>
<td>110</td>
<td>3.228</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>20</td>
<td>0.823</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1945</td>
<td>54.861</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>3800</td>
<td>165.29</td>
</tr>
</tbody>
</table>

Other than the oil-sands produced water and the synthetic produced water samples, SAGD blowdown water samples were also provided by our industrial collaborator for the testing of our EC treatment performance. This blowdown sample is the effluent stream of the steam generator following the water treatment process. Due to the lack of time for our analysis, only a selection of the concentration of the ionic species are determined by ICP-AES. From our analysis, it contains high level of Si$^{2+}$, and trace amounts of other species such as calcium, boron, and large amount of sodium salts. The constituents of the blowdown water sample are shown below in Table 2-4:

Table 2-4 Constituents of boiler blowdown sample

<table>
<thead>
<tr>
<th>Constituents of oil sands blowdown</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$ (mg/L)</td>
<td>20.5</td>
</tr>
<tr>
<td>B$^-$ (mg/L)</td>
<td>201.5</td>
</tr>
<tr>
<td>Si$^{2+}$ (mg/L)</td>
<td>170</td>
</tr>
<tr>
<td>Na$^+$ (mg/L)</td>
<td>10000</td>
</tr>
</tbody>
</table>
2.2 Experimental Setup

In order to treat this challenging water to meet the targets for boiler feedwater quality, the EC treatment was investigated.

The EC experiments were conducted in both batch mode and recirculation flow mode using either aluminum or iron (mild steel) electrodes. In our experiments, grade 1018 mild steel (Fe: 98.81-99.26 %, C: 0.14-0.20 %, Mn: 0.60-0.90%, P: ≤0.04%, and S: ≤0.05%) and grade 6061 aluminum (Al: 97.9%, Mg: 1%, Si: 0.60%, Cu: 0.28%, Cr: 0.20%) is utilized [51].

Two different cell designs were used, a recirculating flow reactor using monopolar electrode connection, and a reactor with an oscillating anode between two stationary cathodes that could be operated under either batch or recirculating flow mode. Figure 2-1 schematically illustrates the experimental setup for a recirculating flow reactor. The recirculating flow EC reactor (see Figure 2-1) was constructed using a set of 7 plates of either aluminum or mild steel as anodes (3 plates with 15 cm x 3.6 cm each) and cathodes (4 plates with 15 cm x 3.6 cm each) with a effective surface area of 320 cm² (calculated as double sided of anodes). Electrodes were assembled in parallel in a rectangular vessel (19 x 3.6 x 17 cm), with a spacing of 18 mm. The flow was arranged to follow a serpentine path, sequentially up and down between the plates. A current was applied to the electrodes using a direct current power supply (KEYSIGHT, N5766A, 40V/38A, 1520W, USA) with an anodic current density in the range of 4 to 16 mA/cm². The effluent was recirculated from the feed reservoir tank to the EC reactor at a constant flow rate of 150 mL/min with a total volume treated of 1.5 L.
The second EC reactor configuration (see Figure 2-2) used was a batch/recirculating flow reactor using an oscillating anode between two cathodes. Previous studies at the University of Calgary have shown that an oscillating anode enhances the mixing to accelerate the charge neutralization process of colloidal silica, which enhances the EC process [64]. In this experimental setup, either aluminum or mild steel were used as the electrode material. All the three electrodes are flat rectangular plates. The cathodes had dimensions of height 15.7 cm, width 10 cm, and thickness 2 mm. The anode had dimensions of height 10 cm, width 13 cm, and thickness 1.8 mm. With the solution volume of 400 mL in batch or 1.2 L in recirculating flow cell, 8.5 cm of the 10 cm height of anode is submerged in solution, results in an effective surface area to be 220 cm². The anode plate was attached to a rotating cam driven by a motor, so that as the motor rotated, the anode moved back and forth between two cathodes. The anode was oscillated at frequency in the range of 0 Hz to 1.5 Hz. The two cathodes had a gap of 2.2 cm, where the stationary anode was fixed in the middle position (frequency is 0.0 Hz.).
2.3 Experimental Procedure

The performance of the EC process was tested using a synthetic concentrate solution containing silica, sodium chloride, sodium sulfate, and sodium hydrosulfide, calcium chloride, and magnesium chloride and sodium bicarbonate. The EC treatment performance was evaluated using the synthetic produced water (see Table 2-3), designed as a model of the produced water presented in Table 2-1 and the real produced water sample and blowdown sample (see Table 2-4) from our industry collaborator. The target contaminant was silica, and no organic additives are used. EC treatment experiments were conducted under different conditions to test the performance of the reactor to remediate this synthetic effluent, the produced water and the blowdown sample.

Before each experiment, the electrode surfaces were gently polished with sand paper and rinsed with diluted HCl (1%) solutions to remove the passive oxide layers and any additional contaminants. The volume of the produced water used was 1.5 L in the recirculating flow system and 400 mL in the batch system, respectively. During each experiment, the cell voltage and the pH were monitored, 5 mL of samples were taken at 0, 200, 400, 800, 1600, 2500 C/L for monitoring the concentration change of contaminants. After each experiment, the treated sample was allowed to settle for one hour then filtered with 0.2 μm nylon filter from VWR. The treatment
efficiency of EC is evaluated by measuring the Si concentration of the sample before and after the treatment. All experiments are conducted in triplicates to ensure the results are reliable. The samples are two-fold diluted before ICP analysis. The Si percentage remaining can be calculated as follows:

\[
\frac{C}{C_0} (\%) = \frac{C_{Si_{te}}}{C_{Si_{il}}} \times 100\%
\]

where \( \frac{C}{C_0} (\%) \) is the ratio of the remaining concentration of dissolved Si\(^{2+} \) over the initial concentration of Si\(^{2+} \) in the EC process. \( C_{Si_{te}} \) and \( C_{Si_{il}} \) are the Si\(^{2+} \) concentration of treated and produced water samples before treatment.

Experimental results in Chapter 3 are shown in figures with error bars, which represent standard error (SE), can be calculated as follows:

\[
SE = \left[ \frac{1}{N(N-1)} \sum (C_i - \bar{C})^2 \right]^{1/2}
\]

Where \( N \) is the number of measurements for each sample, and \( C_i \) is the concentration of the \( i^{th} \) measurement, \( \bar{C} \) is the mean concentration.

The 95% confidence interval is used and can be calculated as:

\[
C_{95\%} = \bar{C} \pm (1.96 \times SE)
\]

Where \( C_{95\%} \) represents that there is a probability of 95% of the mean falling in between \( \bar{C} + (1.96 \times SE) \) and \( \bar{C} - (1.96 \times SE) \).

### 2.4 Analytical Methods

The following methods were utilized to analyze the water samples before treatment, during treatment and after treatment.

**Inductively coupled plasma atomic emission spectroscopy (ICP-AES):** ICP-AES (Thermo
Fischer ICAP 7200) was used to determine the concentration of metallic cations in the water samples. ICP-AES is a type of emission spectroscopy that uses inductively coupled plasma to excite atoms or ions, causing them to emit energy at wavelengths characteristic of a particular element. The atomic wavelength identifies the element and the intensity of light is indicative of the concentration of the element. The basic principle of the ICP-AES is to inject the sample into the spectrometer, where it is changed into mist. This mist is carried into the argon plasma with a stream of argon gas. The plasma produces temperatures in the range of 6000 K to 10000 K, which thermally excites the outer-shell electrons of the elements in the sample. These excited electrons emit light with an energy characteristic of the element [125].

**pH meter (Sper Scientific pH meter):** The pH of the water samples before and after treatment were determined using a pH meter.

**Hach DR 900 Colorimeter:** Sulfide concentration was determined by using the methylene blue method, which uses the reaction between N,N-dimethyl-p-phenylene diamine and H₂S, in the presence of an oxidizing agent (usually ferric iron), to form methylene blue. The concentration of methylene blue is then determined from the measured absorbance of light at wavelength 670 nm using the Hach colorimeter.

**Omega Dissolved oxygen meter:** Dissolved oxygen is measured using an Omega Dissolved oxygen meter.

**AURORA 1030C TOC analyzer:** The Aurora 1030W Total Organic Carbon (TOC) Analyzer uses the thermochemical persulfate oxidation method to analyze organic contamination levels in aqueous samples. Virtually all organic compounds dissolved in water can be oxidized by heated sodium persulfate (Na₂S₂O₈). The persulfate can effectively oxidize organic matter present in the form of colloids, macromolecules, and suspended solids in the form of CO₂. Then the NDIR
method used to directly and specifically measures the CO$_2$ generated by oxidation of the organic carbon in the oxidation reactor through the measurement of the absorption of infrared light specific to CO$_2$ flowing in and out of the detector.

**Metrohm 850 Professional Ion Chromatography Anion – MCS:** The ion chromatography instrument measures concentrations of ionic species by separating them based on their interaction with a resin. Ions will pass through the columns of the ion chromatographer at different speeds depending on their affinity for the specific resin, and they will separate from each other based upon differences in ion charge and size. Sample solutions were passed through a pressurized chromatographic column where ions are absorbed by column constituents. As the eluent runs through the column, the absorbed ions begin separating from the column. The ionic concentrations of different species in the sample were determined by their different retention time.
Chapter 3. Results and discussion

The results for experiments on the EC treatment of synthetic oil sands produced water, including the removal efficiency of the dissolved Si, and other species and the effect of operating variables are discussed in this section, as well as the treatment performance for real oil sands produced water samples.

3.1 Effect of Anode Material and Charge loading

Aluminum and iron anode materials have been studied extensively and are usually employed in EC as plate electrodes. In our experiments, aluminum (grade 6061) and iron (grade 1018), were used to evaluate the performance of EC for silica removal from both synthetic and real produced water using bench scale experiments. Experiments were carried out at a current density of 8 mA/cm$^2$ in the recirculating flow cell. Synthetic solution were prepared with the same inorganic content as the oil sands produced water received, with a Si concentration of 56 mg/L shown in Table 2-1. To evaluate the treatment performance of our experiments, the percentage of contaminant remaining was investigated as a function of the charge loading (C/L). The electrolysis charge loading can be calculated from the treatment time as follows:

$$Q = (iAt)/V$$  \hspace{1cm} (9)

where: $Q$ is charge passed into the solution (C/L), $i$ is the current density applied (mA/cm$^2$), $A$ is the surface area of electrolysis (cm$^2$), $t$ is the electrolysis time (s), $V$ is the volume of the solution (L). The results in Figure 3-1 show that both the aluminum and iron anode materials are able to achieve a Si removal of greater than 80%, correspond to the remaining concentration percentage of less than 20%, which is around 10 ppm of Si. The Si concentration was reduced from 50 ppm to the range of 2 to 10 ppm for synthetic produced water. Aluminum electrodes
showed better Si removal performance than mild steel electrodes, but with both of the electrodes, the remaining Si concentration decreased to less than 20%, which correspond to more than 80% of Si removal at around a charge loading of 2000 C/L, which can be converted to about 20 minutes of electrolysis time for these experimental conditions. The presence of hydrogen sulfide in our experiments made the experiments more difficult to interpret as dark precipitates were observed during Fe-EC and on the surface of the anode. It is speculated that the dark precipitates are the formation of iron sulfide passivation layer, which may hinder the anodic dissolution of iron coagulants [72].

Coagulant concentration in EC is directly proportional to the electric charge applied to the system and hence affects the treatment performance accordingly [126]. Results in Figure 3-1 showed that increasing the charge loading results in a higher Si removal. This is in accordance with Faraday’s law of electrolysis, since a higher the charge loading, corresponds to more coagulant dissolved
into the solution, thus removing more pollutants. In addition, the results show that aluminum electrodes were more efficient for Si removal than iron electrodes, in that they require less charge loading to achieve the same level of removal.

The initial pH was not adjusted as the change in pH will change the solubility of Si in water [127], which is not realistic as the main focus of our research is to study the effect of electrocoagulation on pollutant removal. The initial pH of the synthetic produced water is around 7.75 to mimic the pH of the real produced water. During the treatment process, the pH in iron electrocoagulation and aluminum electrocoagulation increased from 7.88 and 7.82 to 8.33 and 8.42 respectively (see Figure 3-2). The pH change in this treatment are not very significant.

![Graph showing pH change in EC treatment with iron, aluminum as anode materials. Experiments were operated at 8 mA/cm² in the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm², initial Si²⁺ concentration of 56 mg/L.](image)

**3.2 Current Efficiency of Fe and Al dissolution**

The amount of coagulant supplied in EC directly affects the removal efficiency during treatment. However, in EC process, there is a direct link between the amount of coagulant dissolved during
the reaction and the charge applied through Faraday’s Law (see Eq.1). The current efficiency is defined as the fraction of the amount of metal coagulant dissolved during EC relative to the amount theoretically dissolved based on Faraday’s law. The current efficiency is calculated based on Faraday’s law (Eq.1) for electrolysis, where $z$ (the number of moles of electrons transferred per mole of metal ion generated, equal to the valence charge of the metal ion), which is assumed to be +3 for Al and +2 for Fe electrodes, based on forming ferrous Fe$^{2+}$ ions. Some literature has reported that ferric Fe$^{3+}$ ions can be formed in EC, depending on the electrolyte [128].

Synthetic produced water was prepared and used as the electrolyte. Current was applied to the recirculating flow EC cell (see Figure 2-1) to obtain a charge loading of 400 C/L and 800 C/L at two different current density of 8 mA/cm$^2$ and 16 mA/cm$^2$, in four separate experiments. Then the entire electrolyte was collected and acidified with 4 wt% nitric acid to dissolve the metal hydroxides coagulants, and a sample was taken and analyzed with ICP-OES. The results obtained (see Figure 3-3) show that both aluminum and mild steel electrodes achieved more than 90% current efficiency, for current densities of 8 mA/cm$^2$ and 16 mA/cm$^2$. For aluminum, a current efficiency of more than 100% was observed for a charge loading of 800 C/L, indicating non-Faradaic dissolution of aluminum occurred. Previous studies have shown evidence of cathodic dissolution of aluminum in electrochemical systems [46], [74]. At the lower current density of 8 mA/cm$^2$, aluminum showed higher current efficiencies than at 16 mA/cm$^2$, which could be associated with the longer time available for cathodic dissolution duration at the lower current density, while keeping the charge loading constant. For steel electrodes, we observed around 90 % current efficiency at both 8 mA/cm$^2$ and 16 mA/cm$^2$. This may be attributed to the formation of ferrous sulfide in the presence of sulfide in the solution, forming a passivation layer on the surface of iron electrode thus decrease the faradaic efficiency or the direct formation of ferric ion or anodic
oxygen evolution.

![Graph showing current efficiency of Fe-EC and Al-EC for synthetic produced water treatment.](image)

**Figure 3-3 Current Efficiency of Fe-EC and Al-EC for synthetic produced water treatment.** Experiments were operated at 8 mA/cm$^2$ in the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm$^2$, initial Si$^{2+}$ concentration of 56 mg/L.

### 3.3 Potentiodynamic study of aluminum and mild steel anode

A Metrohm Autolab PGSTAT302N electrochemical workstation was used to control the voltage of the working electrode to change linearly with time. A volume of 25 mL synthetic produced water solution was used in a three-electrode electrochemical cell, with either aluminum or mild steel as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (3M KCl) as the reference electrode. The working electrode was 3.5 × 7.0 cm to fit the electrochemical cell and the working electrode was covered by a resin tape with a circle of approximately 2.8 cm$^2$ exposed to the electrolyte. The responding current flowing through the working electrode and counter electrode was recorded and plotted as log ($i$) vs. potential. This potentiodynamic technique was used to study the electrode kinetics, electrochemical behaviors of the electrode materials in synthetic produced water solutions.
In Fe-EC process, it is difficult to identify the speciation of iron ions dissolved from the electrode, which can be dependent on the electrolyte media and the electrode materials. In order to investigate the electrochemistry of the EC process with iron anodes and aluminum anodes, cyclic voltammetry (CV) studies were performed. This CV investigation can be helpful to understand the electrochemical behavior and the electrochemical reaction mechanism. Figure 3-4 shows voltammograms of both aluminum and steel electrodes in synthetic produced water solution using a scan rate of 20 mV/s and a potential window of -1.0 V to 0 V vs. Ag/AgCl.

The aluminum polarization curve (Figure 3-4, a) showed a corrosion potential at about -0.77 V vs. Ag/AgCl and a clear hysteresis loop was observed in the anodic scan (1-2). The anodic scan (1-2) showed a pitting loop at a potential of -0.45 V vs. Ag/AgCl layer. This polarization curve, as well as the current efficiency data, are similar to results obtained previously by Panikulam et al who used Al-EC to remove turbidity from a solution containing Kaolin and chloride [64].

The iron polarization curve (Figure 3-4, b), showed a corrosion potential at about -0.67 V vs. Ag/AgCl and a hysteresis in the anodic scan (1-2), probably due to the pitting process that occurs...
at around -0.55 V vs. Ag/AgCl. The current continued to increase as the potential increased. In the reverse anodic scan (2-3), no loop is observed and the current appears lower than that for the forward scan which may be due to the formation of hydroxide film or iron sulfide passivation layer on the electrode that lower the current density. In the cathodic scan (3-4), a hysteresis loop is observed at about -0.88 V vs. Ag/AgCl probably due to the reduction of iron oxide. This data is different from results obtained from a solution that contained no sulfide, where a higher current density was observed during the reverse anodic scan than that during the forward scan [64]. These results are consistent with the current efficiency data discussed in Section 3.2. The formation of a passive layer in Fe-EC reduces the current density in the voltammetric data, and reduces the dissolution of iron from the anode as it is used to form the passive layer and hence shows lower efficiency.

3.4 Effect of dissolved oxygen

3.4.1 Effect of aeration in the batch system

During the EC process, large amounts of metallic cations (generally Fe$^{2+}$ and Al$^{3+}$ ions) are produced by the anode dissolution and transformed into monomeric and polymeric hydroxide species [115]. In Fe–EC, components of Fe flocs are very complex and the transformations of Fe(II) and Fe(III) products are affected by experimental conditions, and in particular, impacted by the dissolved oxygen (DO) levels [34], [113], [129]. The presence of DO promotes the transformation of soluble Fe(II) products to less soluble Fe(III) product, which is a more effective coagulant. The effect of air bubbled into the system was studied in both Fe-EC and Al-EC. Synthetic produced water was used and experiments were performed in a batch reactor (Figure 2-2 with no anode oscillation). The total produced water volume was 400 mL, and the effective volume of the reactor was 500 mL. The results plotted in Figure 3-5 show higher Si removal with air injection in both
Al-EC and Fe-EC, where there is a slight enhancement for Al-EC, but significant improvement for Fe-EC. For example, after 1600 C/L charge loading, the percentage Si$^{2+}$ remaining with Al-EC decreased from 8.8% to 0.12% with aeration, which corresponds to an increase in Si removal from 90 to nearly 100%. For the same charge loading with mild steel electrodes the percentage Si remaining decreased from 63% to 27% with aeration, which is an increase of 30% Si removal, at a charge loading of 1600 coulomb/liter. Air injection can enhance agitation, thus enhance mass transfer of the dissolved coagulant species toward the bulk of the solution, which caused the enhancement in both Al-EC and Fe-EC. On the other hand, in the case of mild steel electrode, the dissolved oxygen in the solution can enhance the oxidation process of ferrous ion Fe$^{2+}$ to the better coagulant ferric ion Fe$^{3+}$, thus improved the performance of Fe-EC further. This is in agreement with previous studies, which have shown that Fe(III) products have lower solubility than ferrous hydroxide, and are therefore more favorable for coagulation [113].

![Figure 3-5 Effect of Aeration in Batch EC. Experiments were operated at 8 mA/cm$^2$ in the batch cell with electrolyte volume of 400mL and effective electrode area of 220 cm$^2$, initial Si$^{2+}$ concentration of 56 mg/L.](image)

3.4.2 Effect of dissolved oxygen in the recirculating flow reactor
The batch experiments with air injection discussed above showed that EC is efficient in removing dissolved Si from produced water, and Si removal performance of iron and aluminum anodes are enhanced by air injection. Air injection, in this case, may enhance the Si removal performance in two ways: agitation caused by air injection improves mass transfer, and the presence of dissolved oxygen by air injection enhanced the treatment process due to chemical reactions. To further understand the effect of dissolved oxygen, experiments were carried out in a recirculating flow reactor with recirculation. The air was sparged in the effluent reservoir rather than sparging in the electrolysis chamber, thus to minimize the turbulence effect by air injection. Experiments were conducted at two different initial dissolved oxygen level, 1 mg/L and 9 mg/L. To achieve these dissolved oxygen levels, nitrogen (which gave a dissolved oxygen concentration of 1 mg/L) and air (9 mg/L) were sparged into the electrolyte reservoir for 20 min before the electrocoagulation treatment starts. The flow rate was maintained at 150 mL/min and the current density was 8 mA/cm². A control experiment was conducted under ambient lab environment (5-6 mg/L of DO) at the same current density and flow rate. Previous studies have reported that iron electrocoagulation is a three-step process, in which firstly the iron material on the anode will be dissolved into the electrolyte as ferrous Fe²⁺ ions, then these ferrous ions will be oxidized to ferric Fe³⁺ ions by dissolved oxygen, which are the favored form of coagulants, and finally hydrolysis reaction with hydroxides generated at the cathode. The oxidation process of ferrous ions by oxygen has been found to be the rate-determining step in the Fe-EC process. Thus it is interesting to investigate the effect of dissolved oxygen [34], [115], [128], [130]. The results shown in Figure 3-6 show clear evidence of the impact of dissolved oxygen on the removal of Si²⁺. Fe-EC with a higher initial dissolved oxygen level achieved a higher Si²⁺ removal. For instance, Si²⁺ removal at 2500 C/L with 9 mg/L initial dissolved oxygen level reached
more than 95% removal, whereas only around 80% of Si\textsuperscript{2+} removal was achieved at 2500 Coulomb/L at 1 mg/L initial dissolved oxygen level.

![Graph showing C/C₀ vs C/L for Fe-EC with solution recirculating flow cell at 1 ppm O₂ initial, 9 ppm O₂ initial, and ambient laboratory environment. Experiments were operated at 8 mA/cm\textsuperscript{2} in the recirculating flow cell (Figure 2-2) with electrolyte volume of 1.2 L, flow rate of 150 mL/min and effective electrode area of 220 cm\textsuperscript{2}, initial Si\textsuperscript{2+} concentration of 56 mg/L.]

Al-EC experiments are also conducted at 1 mg/L and 9 mg/L initial dissolved oxygen concentration. The results shown in Figure 3-7 indicate that the initial dissolved oxygen concentration did not significantly affect the Si removal performance. Removal of Si\textsuperscript{2+} in Al-EC with air and nitrogen sparging both achieved more than 90% Si\textsuperscript{2+} removal at 800 C/L. The effect of dissolved oxygen did not lead to any enhancement in the Al-EC, which can be attributed to the fact that aluminum coagulation is a fast process and does not require oxygen to be involved.
Figure 3-7 Effect of dissolved oxygen in Al-EC on Si removal. Experiments were operated at 8 mA/cm$^2$ in the recirculating flow cell (Figure 2-2) with electrolyte volume of 1.2 L, flow rate of 150 mL/min and effective electrode area of 220 cm$^2$, initial Si$^{2+}$ concentration of 56 mg/L.

3.5 Effect of current density

Current density is an important factor in EC affecting the rate of the treatment process, or the size of the EC reactor for a continuous process with fixed charge loading. Indeed, previous studies have reported that a higher current density would achieve a higher pollutant removal [76], [89], [131]–[137]. In our work, the experiments with recirculating flow EC reactors (Figure 2-1) were conducted at different current densities, 4 mA/cm$^2$, 8 mA/cm$^2$, and 16 mA/cm$^2$ while keeping the amount of coagulant dosage constant under atmospheric environment. Electrode surface area was maintained at 320 cm$^2$ for all of the experiments, so that for a higher the current density a higher current was applied. The flow rate was kept constant at 150 mL/min for all experiments.

It was found that for synthetic produced water treatment, EC treatment with both Aluminum and mild steel electrodes was very effective for Si removal at all of the current densities studied. Figure 3-8 shows the effect of current density on Si$^{2+}$removal by Fe-EC, with about 90% Si$^{2+}$ removed
for a charge loading about of 1600 C/L at all current densities. This charge loading corresponds to 40 minutes of electrolysis time at 4 mA/cm$^2$, 20 minutes at 8 mA/cm$^2$, and 10 minutes at 16 mA/cm$^2$. EC at 4 mA/cm$^2$ showed slightly more removal at the same charge loading than higher current densities. This is probably due to the longer electrolysis duration at this current density that allows the anodically dissolved ferrous Fe$^{2+}$ to have more time to be oxidized to ferric Fe$^{3+}$ ions, leading to better coagulation.

On the other hand, Al-EC system, Figure 3-9 shows that more than 90% of Si$^{2+}$ at 4, 8, 16 mA/cm$^2$ are removed at 800 C/L, with 8 mA/cm$^2$ slightly outperforming the other current densities on Si$^{2+}$ removal. This is only half the charge dosage of Fe-EC required to remove 90% of Si$^{2+}$.

An energy consumption of EC for synthetic produced water with Fe and Al anodes at different current densities are shown below in Figure 3-10. The energy is calculated based on the charge loading required to remove 90% of Si$^{2+}$. It shows that Al-EC consumes less energy than Fe-EC, and energy consumption increases as current density increases for Al-EC and Fe-EC, due to the
increase in ohmic loss across the solution.

Figure 3-9 Synthetic Produced Water treatment by using aluminum anode in EC at 4, 8, 16 mA/cm$^2$. Experiments were operated with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm$^2$, initial Si$^{2+}$ concentration of 56 mg/L.

Figure 3-10 Energy consumption of Fe-EC and Al-EC for treatment of synthetic produced water at different current densities. Experiments were operated with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 320 cm$^2$, initial Si$^{2+}$ concentration of 56 mg/L.
3.6 Effect of Inter-electrode distance

In the literature, there are several contradictory findings in terms of the impact of inter-electrode distance on the EC process [106], [138], [139]. For example, Gatsios et al. [106] and Ghosh et al. [134] found that the inter-electrode distance in EC has an inverse effect on the pollutant removal efficiency during the treatment of toxic heavy metals that the removal is improved with decreasing gap under constant current density. However, Mohora et al. reported an improvement in the EC treatment of natural organic matter by increasing the electrode gap while maintaining current density constant[139]. In this study, to investigate the effect of the electrode spacing on the treatment of synthetic produced water by EC, two electrode separations, 1.6 cm and 3.2 cm, were tested, keeping the flow velocity and current density constant. Figure 3-11 shows the results obtaining for Fe-EC (mild steel electrodes) for a current density of 8 mA/cm². A system of 7 electrodes, consist of 4 cathode and 3 anodes, were used at $d = 1.6$ cm, whereas a system of 3 electrodes, consist of two anodes and one cathode were used at $d = 3.2$ cm. The Si removal at $d = 1.6$ cm was slightly better than that obtained at $d = 3.2$ cm. Mass transport between electrodes probably played a role in the treatment process as the increase in electrode gap caused a decrease in the mass transfer rate [140].
Figure 3-11 Effect of Inter-electrode distance on Fe-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L.

3.7 Effect of Reactor Design

When designing the EC experiments, many factors can affect pollutant removal performance. In the following experiments, the physical design of the reactor was considered, making comparisons between batch systems and recirculating flow systems, and studying the effect of a novel concept of an oscillating anode versus the commonly used stationary anode. In conventional EC treatment, the reactor usually includes parallel metal plates, and the metal ions and hydroxide ions formed at the electrodes coagulate with the contaminants, so that the rate of this process is expected to be dependent on mass transfer and mixing. The rate of transport of both metal ions and hydroxide ions from the electrode surfaces into the bulk solution can be a relatively slow process, and depends upon the flow velocity between the electrodes [64]. In order to increase the mass transfer of ions it is desirable to increase the agitation of the solution near the electrode surface, and previous study performed by Panikulam et al. has shown that the oscillation of the anode in the EC system
enhances mass transfer to accelerate the charge neutralization process which increases the rate of the initial phase of the coagulation process.

Enhancement of mass transfer in the EC system was found to enhance performance in terms of contaminant removal, and it may also affect electrode fouling. Fouling occurs due to the accumulation of precipitates on the electrode surface. During the EC process, the mass transfer of the dissolved metal cation plays a major role in electrode fouling formation. When the mass transfer of the newly dissolved ions from the electrode is slow, kinetically favored reactions, such as metal sulfide formation (iron sulfide or aluminum sulfide), or adsorption of coagulated bitumen may occur at the electrode surface. These processes at the electrode surface may enhance the formation of the fouling layer. With the enhanced mass transfer, the concentrations of accumulating species will be reduced at the electrode surface as they are mixed with the bulk solution. Thus increasing the mass transfer of the dissolved cation may help delay the formation of fouling. To date, aside from increasing the flow velocity, methods reported to enhance the mass transport through agitation have included: injection of compressed air, the use of a fluidized bed, or application of an ultrasound field [64]. In this study, mass transfer enhancement was achieved through electrode oscillation. The use of an oscillating anode in the EC reactor, effectively creating a turbulent flow that may enhance mass transfer of dissolved coagulants toward the bulk of the solution, and also leads to a variation in the current density with time on each side of the electrode, which might also affect the performance.

3.7.1 Comparison of batch and recirculating flow mode

EC reactors are usually operated in two modes: batch and continuous mode. Batch reactors are most commonly used electrochemical reactor in research literature[47]. It has a simple
configuration, but in this type of reactor the mass transfer is dependent only on the natural convection mechanisms to transport ions within the media, with the addition of magnetic stirrer as forced convection and hence the pollutant removal efficiency is usually low. Compared with batch reactors, recirculating flow reactors promotes improvement in mass transfer as forced convection mechanisms applied.

The data plotted in Figure 3-12 shows a comparison of the Si removal from synthetic produced water for recirculating flow mode and batch modes experiments. The applied current density was 8 mA/cm², the reactor contained three electrodes consisting of one anode and two cathodes, the flow rate was 150 mL/min for the recirculating mode. The results for Fe-EC (Figure 3-12) shows that recirculating flow mode achieved Si²⁺ removal by about 70% compared with 45% removal of Si²⁺ concentration in the batch system with Fe-EC at 2500 C/L. Also, another effect by mixing is the enhancement of the oxidation of Fe(II) to Fe(III) products, thus results in better Si²⁺ removal performance. For Al-EC (Figure 3-13), the effect of recirculating flow did not show any noticeable enhancement in Si²⁺ removal, and close to 100% Si²⁺ removal was obtained in both cases. This indicates that for the fast coagulation process of Al-EC the effect of mass transfer is not playing a dominant role.
Figure 3-12 Comparison of Batch and Recirculating flow mode Fe-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L.

Figure 3-13 Comparison of Batch and Recirculating flow mode Al-EC. Experiments were operated at 8 mA/cm² with the recirculating flow cell at 150 mL/min flowrate, with electrolyte volume of 1.5 L and effective electrode area of 106 cm², initial Si²⁺ concentration of 56 mg/L.
3.7.2 Effect of anode oscillation in batch mode

The electrocoagulation process requires the mass transfer of the dissolved metal cation toward the bulk solution for coagulation of contaminants (Si\textsuperscript{2+}, etc.) to take place. However, if the rate of mass transfer is low, the high concentrations and modified solutions composition at the electrode surface, including pH effects, can lead to fouling on the electrode surface [141]. The enhancement of mass transfer by electrode oscillation was evaluated using both batch and recirculating flow modes. A previous study performed in the same research group at the University of Calgary demonstrated that anode oscillation could dramatically enhance kaolin removal performance by EC compared to that of a stationary anode [64]. In conventional electrochemical reactors, to achieve a high rate of electrochemical reaction and a high rate of mass transfer, reactants transport is enhanced by the bulk flow of the electrolyte. Transport of metal ions from the anode to the bulk solution and transport of hydroxide ions from cathodes to the bulk are important and can play a significant role in the coagulation process. There are many methods to enhance mass transport, such as increasing flow velocities in flow-through reactors, agitation by compressed air injection or use of ultrasound [142]. Compared with other methods of agitation, anode oscillation is simple to set up and has demonstrated promising pollutant removal performance for EC. Anode oscillation was investigated to determine the efficacy for removal of Si from synthetic solution and produced water. Iron (mild steel) and aluminum were used as the electrode materials and the results are shown below in Figure 3-14 and Figure 3-15. Experiments were conducted in a batch cell with an oscillating anode. The electrolyte volume was 400 mL. The current density was 8 mA/cm\textsuperscript{2}, the centre to peak amplitude of the oscillation was 6 mm and the oscillation frequencies were 0.6 Hz and 1.75 Hz respectively. Similar to the batch and recirculating flow experiments, the results obtained from Al-EC at all
oscillation conditions showed better Si performance than Fe-EC. Considering Fe-EC (Figure 3-14), it was observed that with higher oscillating frequency, more Si\(^{2+}\) removal was obtained. Compared with the stationary anode, an oscillating frequency of 0.6 Hz achieved around 10% extra Si\(^{2+}\) removal (from 43% to 53%) after a charge loading of 2500 C/L. When the oscillation frequency was increased to 1.75 Hz an additional 30% - 40% Si\(^{2+}\) removal was achieved, with a final Si removal of 91% achieved after 2500 C/L.

![Graph showing Si removal with oscillation frequency](image)

*Figure 3-14 Fe-EC with an oscillating anode at 0.6 Hz vs. at 1.75 Hz and with a stationary anode. Experiments were operated at 8 mA/cm\(^2\) with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm\(^2\), initial Si\(^{2+}\) concentration of 56 mg/L.*

Using Al-EC (Figure 3-15), a higher oscillating frequency led to slightly more Si\(^{2+}\) removal, but the oscillation frequency did not significantly affect the final Si\(^{2+}\) removal achieved. In all cases, Al-EC was able to remove 90% of the Si after a charge loading of 1600 C/L. However, after 400 C/L, it was observed that with a higher the frequency, more Si\(^{2+}\) was removed. This suggests that with anode oscillation sweep coagulation occurred more rapidly than for the stationary anode system, where the sweep coagulation takes longer, consistent with the finding of Panikulam et al. [64] for kaolin removal.
Figure 3-15 Al-EC with an oscillating anode at 0.6 Hz vs. at 1.75 Hz and with a stationary anode. Experiments were operated at 8 mA/cm² with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L.

The cell voltage using oscillating anode or stationary anode with both aluminum and mild steel were monitored and are shown below in Figure 3-16. For the oscillating anode system, the cell voltage fluctuates when the anode was moving back and forth between two cathodes. The cell voltage decreases as the anode move towards each of the cathodes, and then reaches a maximum when it is in a central position. In general, the cell voltage with Al-EC is much lower than that of Fe-EC, which reflects the higher energy consumption when Fe-EC system is used to remediate this type of effluent. Considering the iron (mild steel) electrodes, the average cell voltage with the oscillating anode was lower than with stationary anode, which is probably explained by the enhanced mass transport conditions and close to each of the cathode. Whereas for aluminum electrodes, the average cell voltage with an oscillating anode is slightly higher than that with a stationary anode, which is probably attributed to more passivation with the current pulsing, leading to a slightly larger cell voltage.
3.7.3 Effect of current density in the oscillating anode system

The effect of current density was also investigated in the oscillating anode EC system. Current densities of 4 mA/cm$^2$, 8 mA/cm$^2$ and 16 mA/cm$^2$ were used with an oscillating frequency of 0.9 Hz and oscillation centre to peak amplitude of 6 mm. Figure 3-17 and Figure 3-18 show the Si$^{2+}$ removal efficiencies from synthetic produced water using Fe-EC and Al-EC systems, respectively. The duration of each experiment was adjusted to maintain the same amount of charge loading at each current density. With both Fe-EC and Al-EC the current density shows no impact on treatment performance. In Fe-EC in Figure 3-17, the change in current density did not significantly affect the Si$^{2+}$ removal performance as only around 60% of Si$^{2+}$ removal was achieved with 2500 C/L. For Al-EC in Figure 3-18, the impact of current density on the Si$^{2+}$ removal was insignificant, with around 90% of Si$^{2+}$ removal is reached at 800 C/L in all cases. However, for both Fe-EC and Al-EC, a lower current density corresponds to a longer treatment time required for the same dosage of coagulant. With higher current density less time was required and the anode oscillation helped...
to transport the dissolved ions faster, However in any case, the change in current density does not significantly affect the treatment performance.

Figure 3-17 Effect of Current densities in Fe-EC with Oscillation at 4 mA/cm^2, 8 mA/cm^2 and 16 mA/cm^2 with an oscillating frequency of 0.9 Hz and oscillation centre to peak amplitude of 6 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm^2, initial Si^{2+} concentration of 56 mg/L.

Figure 3-18 Effect of Current densities in Al-EC with Oscillation at 4 mA/cm^2, 8 mA/cm^2 and 16 mA/cm^2 with an oscillating frequency of 0.9 Hz and oscillation centre to peak amplitude of 6 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm^2, initial Si^{2+} concentration of 56 mg/L.
3.7.4 Effect of Oscillation frequency at constant Reynolds number on the oscillating anode system

In reactor design, the flow conditions can be characterized by the Reynolds number, and for an oscillating system, the flow conditions can be characterized by the oscillatory flow Reynolds number (Reo) [120]:

\[
Re_o = \frac{\omega x_0 d_e}{\nu}
\]  

(10)

where: \(\omega\) (Hz) is the oscillation frequency, \(x_0\) (cm) is the center-to-peak oscillation amplitude, \(d_e\) (cm) is the hydraulic diameter, and \(\nu\) (cm\(^2\)s\(^{-1}\)) is the kinematic viscosity of the solution.

Previous experiments showed an increase in frequency would enhance the performance, which can be attributed to the increase in Reynolds number, leading to an increase in the rate of mass transfer [64]. Figure 3-19 and Figure 3-20 showed the results of both Fe-EC and Al-EC with anode oscillation at different frequencies and amplitude while maintaining the Reynolds number constant. These conditions were obtained by keeping the product \(\omega \times x_0\) in Eq.9 constant. Thus two different frequencies, 0.6 Hz and 0.9 Hz, and center-to-peak oscillation amplitudes, 6 mm and 4 mm, were used respectively. The \(d_e\) is calculated to be 14.73 cm for the oscillating anode system shown in Figure 2-2 and the kinematic viscosity is obtained from water at 20°C to be 0.01 cm\(^2\)s\(^{-1}\). The Reynolds number was constant under these conditions at approximately 530, and the results of Si removal performance were the same for both Fe-EC and Al-EC (see Figure 3-19 & Figure 3-20). A previous study of kaolin removal by EC showed an enhancement of pollutant removal with oscillating anodes due to both the increased mass transport/mixing, and the pulsed current [64]. The pulsing of the current at the electrode surface occurs as the anode approaches each cathode, the current will preferentially be applied to the surface closest to the closer cathode. Thus even though the total current is constant, the current on each side of the anode will oscillate through a
maximum when it is close to one of the cathodes and a minimum when the distance to the cathode is a maximum. Pulsing of the current can result in periodic addition of metal ions at a higher concentration relative to a constant current, which can lead to earlier sweep coagulation due to higher metal ion concentration. However, from Figure 3-19 and Figure 3-20, the effect of current pulsation does not appear to have a significant effect on Si\(^{2+}\) removal with both Fe-EC and Al-EC.

![Graph](image)

*Figure 3-19 Effect of oscillation frequency at oscillatory Reynolds number of 530 on Fe-EC at 0.6 Hz and 0.9 Hz, and center-to-peak oscillation amplitudes, 6 mm and 4 mm. Experiments were operated with the batch oscillating anode EC cell with electrolyte volume of 400mL and effective electrode area of 220 cm\(^2\), initial Si\(^{2+}\) concentration of 56 mg/L.*
3.7.5 Combining Oscillating anode with flow recirculation

In order to further investigate the effect of enhancing mass transfer on Si$^{2+}$ removal performance, a combination of an oscillating anode with a recirculating flow reactor was tested. The geometry of this new system was the same as the batch system with an oscillating anode while the solution volume was increased to 1.2 Liter from 400 mL in order to keep the same level in the electrolysis cell. Solution was pumped from an external reservoir to an inlet that was added to the cell, and the outlet location led to flow in a direction perpendicular to the oscillation direction. The recirculation flow rate was 150 mL/min, and the current density was 8 mA/cm$^2$. Experiments were conducted at conditions of recirculation flow with oscillation and recirculation flow without oscillation with both Fe-EC and Al-EC. The anode is oscillating at a frequency of 1.5 Hz. The Si removal performance obtained for Fe-EC and Al-EC are shown in Figure 3-21. With both the Fe-EC and Al-EC systems a better Si$^{2+}$ removal was obtained with flow recirculation. The combination of recirculation flow reactor with Fe-EC shows slightly better performance (80% Si$^{2+}$ removal at
2500 C/L) with oscillation than without anode oscillation (70% at 2500 C/L). For recirculation flow reactor with Al-EC, a slightly enhanced performance was observed from anode oscillation (85% Si²⁺ removal at 800 C/L) than without anode oscillation (70% Si²⁺ removal at 800 C/L). The results suggest that anode oscillation can enhance mass transfer of metal cations and hydroxides and speed up the sweep coagulation process in the recirculation continuous flow reactor, however, the performance is only slightly better than using flow to enhance mass transport.

![Figure 3-21 Effect of Combination of oscillation & recirculating flow on Si removal. Experiments were operated at 8 mA/cm² with the recirculating flow reactor at flowrate of 150 mL/min with anode oscillating at 1.5 Hz. EC cell with electrolyte volume of 1.2 L and effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L.](image)

### 3.8 Removal of Calcium, Magnesium, and other Contaminants

EC has been reported to be effective for the removal of organics, TDS, turbidity and many other pollutants [51], [96]. The synthetic produced water contains Si, hardness, and other ionic species. Experiments conducted in previous sections were conducted to investigate the performance of EC for the treatment of synthetic produced water and the impacts of operating variables on the treatment efficiency. The results showed that EC can efficiently remove Si and Ca by around 90%
or higher, Mg by around 50% sulfate by around 50%, and has no effect on the chloride removal. The effect of EC on hardness (as CaCO₃) removal was also investigated and is discussed in this section. The Ca and Mg removal efficiencies were tested in three systems: batch, oscillating anode, and recirculating flow system with an oscillating anode. In the batch system, the total volume was 400 mL, while in the recirculating flow reactor, the total water volume was 1.2 L. The current density was 8 mA/cm² for all the experiments. The concentration of Ca, Mg, and Si were analyzed by ICP-AES, and the results are shown in Figure 3-22 & Figure 3-23. For comparison, the residual concentrations are normalized based on the initial concentration.

Using a batch Fe-EC experiment (Figure 3-22 a)), we observed that the remaining percentage of Mg was the highest (80% of the initial concentration after 2500 C/L, i.e. 20% removal) compared to Ca (60% of the initial concentration). This indicates that Mg was more difficult to remove than Ca, and 43% of the Si was removed. Combining batch Fe-EC with anode oscillation (Figure 3-22b)) enhanced the treatment performance slightly for Mg and Ca: Mg by 23%, and Ca by more than 73%. These removals can be compared with 57% removal achieved for Si under similar conditions.

Experiments are also conducted in a recirculating flow reactor, the results (Figure 3-22 c)) show that 90% of the Ca, and 35% of the Mg were removed after 2500 C/L of EC treatment. Combining recirculating flow with anode oscillation (Figure 3-22 d) gave a completely Ca removal, 80% Si removal, and 40% Mg removal, this suggests that mixing/mass transport is more important for Ca removal than for Si or Mg.
Using Al-EC, in a batch system (Figure 3-23 a)), 95% of the Si, around 40% of the Mg, and 80% of the Ca was removed after 2500 C/L. Combining the batch system with anode oscillation, in Figure 3-23 b), the performance increased slightly, with 50% Mg removal, and 90% Ca removal after 2500 C/L. Using Al-EC in the recirculation flow system (Figure 3-23 c) & d)), the additional oscillating anode enhanced the Ca removal. However, it does not show a significant enhancement.
in Mg removal. As before, the recirculating flow reactor achieved higher contaminant removal efficiencies compared with the batch system, regardless of whether the system operated with the oscillating anode or not.

Figure 3-23 the removal of Mg, Ca, and Si using: a) Batch Al-EC contaminant removal with 400 mL solution, b) Batch Al-EC with anode oscillation contaminant removal with 400 mL solution with 0.6 Hz frequency, c) Recirculation Al-EC contaminant removal at 150 mL/min with 1.2 L solution, d) Recirculation Al-EC with anode oscillation at 150 mL/min with 0.6 Hz frequency with 1.2 L solution. Experiments were operated at 8 mA/cm² with effective electrode area of 220 cm², initial Si²⁺ concentration of 56 mg/L.

Other species present include sulfate, chloride is also analyzed by the Ion Chromatography. Sulfate concentration was been reduced to around 20-25 mg/Litre from an initial concentration of 50
mg/Litre in both Al-EC and Fe-EC. However, EC showed negligible effect on chloride species in the synthetic produced water, the concentration remained at around 4000 mg/L. Sulfide in both AL-EC and Fe-EC were observed to be removed rapidly during the EC treatment, probably because sulfide can easily be converted into H₂S which would be released as a gas or it precipitates as FeS, Fe₂S₃, or Al₂S₃, where all these products have low solubility.

### 3.9 Treatment of samples of real produced water

To investigate the performance of EC for real industrial produced water, experiments were conducted using the same reactors and operating variables as used for the synthetic produced water treatment. The performance of batch and recirculating flow reactors, as well as the oscillating anode system were evaluated. Oil sands produced water and blowdown water samples are used in our study in this section.

Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm² and 400 mL of real produced water (see Table 2-1) was used. The results from batch Fe-EC are shown below in Figure 3-24. After a charge loading of 2500 C/L, 45% of the Si was removed, along with 62% of the Ca, and 22% of the Mg. With Al-EC, shown in Figure 3-25, more than 99% removal of Si was achieved, along with 92% removal of Ca, and 31% removal of Mg after 2500 C/L. The removal of organics, as TOC, was evaluated for both Fe-EC and Al-EC. In both cases only around 10% TOC removal was achieved after 2500 C/L, with the TOC concentration reduced from 400 - 450 mg/L to 370-390 mg/L.
Fe-EC with recirculation flow system (Figure 3-26) showed an enhancement in treatment efficiency compared to the batch system, with around 80% removal of both Si and Ca, and 20% removal of Mg after 2500 C/L. For Al-EC with recirculation flow (Figure 3-27), after 2500 C/L
Si removal was more than 95%, along with 80% removal of Ca, and 20% removal of Mg.

Figure 3-26 Real produce water treatment by Recirculating flow Fe-EC. Experiments were conducted in a recirculating flow EC cell (Figure 2-2) with 8 mA/cm² and 1.2 L of real produced water at 150 mL/min. Effective electrode surface area is 220 cm².

Figure 3-27 Real produce water treatment by Recirculating flow Al-EC. Experiments were conducted in a recirculating flow EC cell (Figure 2-2) with 8 mA/cm² and 1.2 L of real produced water at 150 mL/min. Effective electrode surface area is 220 cm².

The oscillating anode system was also tested with both Fe-EC and Al-EC in batch mode for the
treatment of samples of real produced water. The use of oscillating electrode with both Al and Fe electrode enhanced the removal rate of all elements studied. For example, as shown in Figure 3-28, an oscillated Fe-EC system at 2500 C/L removed 60% of the Si, 60% of the Ca, and 20% of the Mg, which is an additional 20% Si removal, and slightly more magnesium and calcium removal than the same system with no oscillation (Figure 3-24). In the case of the oscillating anode in Al-EC system at 2500 C/L, almost complete removal of Si and Ca was achieved, along with 45% removal of Mg. Compared to the removal efficiency for Al-EC with no anode oscillation (Figure 3-25), around 15% more Mg removal was achieved. More rapid initial removal of Si, Mg, and Ca was observed in Al-EC system with anode oscillation. This is probably due to the enhanced mass transfer resulted from the anode oscillation, which leads to earlier sweep coagulation than the system without oscillation.

Figure 3-28 Real produce water treatment by batch Fe-EC with Oscillation. Experiments were conducted in a batch EC cell (Figure 2-2) with 8 mA/cm² and 400 mL of real produced water. Effective electrode surface area is 220 cm².
3.9.1 Comparison of real produced water and synthetic produced water

Experiments were conducted in the recirculating flow system (Figure 2-1) with 8 mA/cm$^2$ and effective electrode surface area of 320 cm$^2$, at 150 mL/min. Figure 3-30 shows a comparison of Si removal performance between real produced water (see Table 2-1) and synthetic produced water (see Table 2-3) treatment with both aluminum and mild steel anodes. It can be seen that aluminum shows higher Si removal efficiency at the same charge dosage compared to mild steel electrodes, and the Si removal efficiency for real produced water was slightly lower than that for the synthetic produced water.
Figure 3-30: Si removal from synthetic produced water and real produced water by the mild steel anode and aluminum anode. Experiments were conducted in the recirculating flow system (Figure 2-1) with 8 mA/cm$^2$ and effective electrode surface area of 320 cm$^2$, at 150 mL/min.

Figure 3-31 compares the cell potential of both Fe-EC and Al-EC treating synthetic and real produced water samples. The cell voltage for the EC treatment of synthetic produced water were higher than those for real produced water, probably due to the high conductivity associated with the higher concentration of ions in the real produced water, which reduces the ohmic resistance of the solution. The cell voltage of Fe-EC are higher that Al-EC, from 3.9 V vs. 3.0 V for synthetic produced water treatment to 2.7 V vs. 2.2 V for real produced water treatment. The cell voltage difference between Fe-EC and Al-EC could be due to the fact that Al is a stronger reducing agent according to the standard electrode potential that it is more prone to be oxidized, thus the cell voltage of Al-EC required to drive the oxidation of Al is less than that of Fe.
3.10 Oil-sands blowdown water treatment performance

Electrocoagulation for oil-sands produced water treatment was found to be effective for removal of Si and calcium, as discussed in the previous section. The performance for treating high concentration Si in boiler blowdown was also tested and is discussed in this section. Experiments were conducted using the same EC reactors and operating conditions: a current density 8 mA/cm², a maximum charge loading of 2500 C/L as studied for produced water treatment. The blowdown water sample was produced from an evaporator following lime softening of oil sands produced water. Therefore, it contains a lower level of calcium and magnesium and a higher concentration of Si than produced water (see Table 2-4). Batch experiments with and without an oscillating anode. In Fe-EC batch treatment (Figure 3-32), after 2500C/L charge loading, only around 30% of the Si was removed, and 30% of the Ca. With Al-EC batch in (Figure 3-33), Si was almost completely removed, along with around 50% of the Ca, and 5% of the boron after 2500 C/L.
With anode oscillation, EC achieves higher contaminant removal efficiency compared to the batch system. In Fe-EC (Figure 3-34), Si removal increased to over 40%, Ca to over 40%, and boron to over 35% after 2500 C/L. In Al-EC (Figure 3-35), Si was almost completely removed, Ca removal
was around 80%, and boron removal was less than 5% after 2500 C/L.

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**Figure 3.34** Contaminant Removal Efficiency for batch Fe-EC system with anode oscillation for boiler blowdown water treatment

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**Figure 3.35** Contaminant Removal Efficiency for batch Al-EC system with anode oscillation for boiler blowdown water treatment
3.11 Energy consumption

To evaluate the feasibility of using the EC process for produced water treatment, an important parameter to evaluate is energy consumption. The energy consumption calculated for the recirculating flow cell design using Al-EC and Fe-EC for synthetic and real produced water based on 90% removal of Si, are shown below in Figure 3-36, and for a range of current densities in Figure 3-38. The electrical energy consumption was calculated by integration of the voltage data and the current applied and the electrolysis time to remove 90% of Si.

In general, the operating costs can be calculated as the sum of electrical energy and the metal consumption (electrode replacement) cost. Previous studies have shown that the operating cost and electrical energy consumption vary greatly depending on the type of contaminants being treated, and are typically 0.15 - 1.5 C$/m^3$ and 0.4 - 4.0 kWh/m$^3$ [33]. In the recirculating flow reactor (Figure 3-36), Al-EC showed lower energy consumption than Fe-EC for treatment of both synthetic and produced water, at 0.67 and 0.98 kWh/m$^3$ for Al-EC vs. 1.73 and 1.99 kWh/m$^3$ for Fe-EC, respectively. The electrical energy cost can be estimated by multiplying the electrical energy consumption by the electricity cost in Alberta (C$0.06/kWh from Alberta Utilities Commission). The metal cost can be calculated by multiplying the amount of metal consumption (in kg) by the metal price (C$1.08/kg for carbon steel from World Steel Prices and C$2.3/kg for aluminum from Markets Insider), is shown in (Figure 3-37). The operating cost for the results in Figure 3-36 were calculated to be C$0.385/m^3$ and C$0.405/m^3$ for Al-EC and C$0.600/m^3$ and C$0.616/m^3$ for Fe-EC.

For both iron and aluminum electrodes, the cell potential for produced water treatment was lower than that for synthetic produced water, probably due to the higher conductivity in the real produced water. However, the presence of organics was found to hinder the Si removal performance, which
led to a longer electrolysis duration required to remove Si.

**Figure 3-36** Energy Consumption in Recirculating flow cell for Fe-EC and Al-EC on synthetic produced water and real produced water treatment

**Figure 3-37** Operating Cost of Fe-EC and Al-EC on treatment of synthetic produced water and real produced water
From both Fe-EC and Al-EC the current density does not affect the Si removal efficiency. However, from an economic point of view, an increase in applied current results in increasing cell voltage, thus resulting in an overall increase in power consumption (Figure 3-38). Using Fe-EC system indicates that an increase in current density from 4 mA/cm², to 8 mA/cm² and 16 mA/cm² led to increasing energy consumption from 0.76 kWh/m³, to 1.29 kWh/m³ and to 2.00 kWh/m³, respectively, which corresponds to C$0.542/m³, C$0.574/m³ and C$0.617/m³ in terms of total cost. For Al-EC, the energy consumption also increased from 0.44 kWh/m³ to 0.67 kWh/m³ and 1.02 kWh/m³ at 4 mA/cm², 8 mA/cm² and 16 mA/cm² respectively, corresponding to C$0.371/m³, C$0.385/m³, and C$0.406/m³ of total cost. The increase in energy consumption is an important factor that hinders the industry from increasing the current density for industrial applications. Another factor to consider is the electrolysis time. Since the total amount of charge loading is maintained constant under different current density, the time for an experiment under 4 mA/cm² is twice the time required for 8 mA/cm², so does the experiment under 16 mA/cm². For industrial applications, a balance between current density and electrolysis time should be identified.
The mechanical energy in the oscillating anode system was not calculated as no data was recorded that could be used to determine this energy.

The energy consumption for EC with oscillating anode system was also calculated and is shown below in Figure 3-39. Al-EC showed lower energy consumption than Fe-EC for treatment of both synthetic and produced water, at 1.11 kWh/m³ and 0.499 kWh/m³ (operating cost of C$0.41/m³ and C$0.37/m³) vs. 2.78 kWh/m³ and 2.78 kWh/m³ for Fe-EC (operating cost of C$0.66/m³), respectively. For both iron and aluminum anodes, the cell potential for produced water treatment is lower than that for synthetic produced water, which can be attributed to the high conductivity in the real produced water. On the other hand, the organics present in real produced water may complex with the dissolved Si, which slows down the removal performance, leading to a longer electrolysis duration for Si removal.
For Fe-EC with anode oscillation (Figure 3-40), an increase in current density from 4 mA/cm², to 8 mA/cm² and 16 mA/cm² lead to increasing energy consumption from 2.08 kWh/m³, to 2.78 kWh/m³ and to 3.82 kWh/m³, which correspond to operating costs of C$0.62/m³, C$0.66/m³, and C$0.73/m³ respectively. For Al-EC, the energy consumption also increased from 0.82 kWh/m³ to 1.11 kWh/m³ and to 1.78 kWh/m³, which correspond to operating cost of C$0.39/m³, C$0.41/m³, and C$0.45/m³ at 4 mA/cm², 8 mA/cm² and 16 mA/cm² respectively. The operating costs in our EC experiments are in the range of C$ 0.3/m³ to C$ 0.7/m³, compared to the range of operating costs for EC reported to be 0.15- 1.5 C$/m³ [33], the costs for produced water treatment are in the low range.
The blowdown treatment was only operated with the batch system with anode oscillation, and the results are shown below in Figure 3-41. The energy consumption is 1.95 kWh/m$^3$ for Fe-EC, 0.69 kWh/m$^3$ for Al-EC. Combined with the metal cost, the total cost is C$1.64/ m^3$ for Fe-EC and C$0.59/ m^3$ for Al-EC shown in Figure 3-42.
Figure 3.42 Total operating cost of Fe-EC and Al-EC on blowdown treatment with the anode oscillation system
Chapter 4. Conclusions and Recommendations

A summary of the major findings and recommendations for future work are discussed in this chapter. The contaminant removal performance of EC treatment of oil-sands produced water has been studied at a laboratory bench scale. The target contaminant in this study was Si, which is considered to be the main cause of the scaling problem in the steam generators in oil-sands in-situ production, and significant capital and operating costs have been invested by the oil industries in the treatment of produced water for recycle to the steam generators. EC was found to be very efficient in removing dissolved Si from 56 mg/L to less than 5 mg/L, corresponds to more than 90% of Si removal, with also satisfactory removal of calcium of around 90% and magnesium removal of around 50-60%. The effect of different operating parameters was evaluated in a recirculating flow reactor, including the anode materials (Al and Fe). The current efficiencies of Al and Fe anode materials, and their electrochemical behavior was also studied. The effect of current density, inter-electrode distance, and the presence of dissolved oxygen in EC were evaluated. Besides operating parameters, different electrochemical reactor designs were also tested. A novel concept of utilizing an oscillating anode in EC was investigated with both batch system and recirculating flow system. Investigation of the viability of EC for oil sands industry applications such as produced water and boiler blowdown samples have also been carried out, and the contaminant removal efficiency was found to be promising. The operating cost of EC for the treatment of synthetic produced water, produced water and boiler blowdown were in the range C$ 0.3/m^3 to C$ 1.5/m^3.

4.1 Effect of operating parameters

The use of aluminum or iron (mild steel) as the anode material in EC was tested. The results show that aluminum outperforms mild steel based on the treatment performance, as Al-EC requires less
electrical charge than Fe-EC to remove Si from the produced water. Al-EC was found to achieve 90% Si removal at a charge dosage ranging from 400 C/L to 800 C/L for synthetic produced water, whereas Fe-EC treatment of synthetic produced water achieved 90% Si removal at around 1600 C/L. Electrochemical behaviors of the aluminum anode and the mild steel anode were also investigated. In both aluminum EC system and iron (mild steel) EC system, a passivation layer may be formed on the electrode surface that can hinder the process of electrode dissolution. The corrosion potential of mild steel occurs at -0.67 V vs. Ag/AgCl, and for aluminum at -0.77 V vs. Ag/AgCl. The current efficiencies for electrodissolution of aluminum and iron (mild steel) in the synthetic produced water were also evaluated. Aluminum anode achieved a super-Faradaic efficiency (greater than 100%) for metal dissolution, at both 8 mA/cm² and 16 mA/cm². The current efficiency of mild steel anode reached 90% - 95%, which is probably due to some dissolution of iron metal into ferric Fe³⁺ ions.

In both aluminum and mild steel EC systems, the effect of electric charge dosage was determined. The contaminant removal efficiencies increased with the electric charge dosage, which corresponds to an increase in the amount of coagulant dosage in the produced water. The effect of current density was also studied by varying the current density while changing the electrolysis duration to maintain the same charge dosage. It was found that varying current density in both aluminum EC system and iron EC systems does not affect the contaminant removal significantly.

The effect of dissolved oxygen in EC is also investigated with the synthetic produced water. In mild steel EC batch system, the presence of initial dissolved oxygen at 9 mg/L enhanced Si removal efficiency from 40% at 1 mg/L initial dissolved oxygen to 70% removal, at an charge dosage of 1600 C/L. In Al-EC batch system, the presence of 9 mg/L of initial dissolved oxygen improved Si removal efficiency from around 90% to 95% at 1600 C/L. In the recirculating flow
EC system, the Si removal efficiency in Fe-EC was enhanced from 60% to 90%. Whereas in Al-EC system, the 9 mg/L initial dissolved oxygen had little influence on the Si removal efficiency. The inter-electrode distance was also tested in the recirculating flow EC reactor with iron (mild steel) electrodes. The results showed that variation in electrode gap did not affect the Si removal efficiency significantly, but a narrower gap of 1.6 cm slightly outperformed a wider electrode gap of 3.2 cm by about 20% more Si removal at 800 C/L. The increase in electrode gap can be expected led to a decrease in the mass transfer rate, which then hindered the Si removal.

4.2 Effect of reactor design

The performance of batch EC systems and recirculating flow EC systems were compared and a novel concept of an oscillating anode was also implemented in our EC experiments. In both Fe-EC and Al-EC system, the use of recirculating flow system shows better contaminant removal efficiencies than the batch system, this is due to the enhanced mass transport of coagulants by the mixing effect induced by the flow condition. The implementation of the oscillating anode in the EC system also outperformed the system with the stationary anode in both batch EC and recirculating flow EC, although the enhancement was small for the recirculating system.

It was found that for the EC system with the oscillating anode, when the Reynolds number of the oscillating anode system was maintained constant by adjusting both the oscillation frequency and amplitude, the contaminant removal performance was not affected.

4.3 EC for industrial applications

The EC systems were also tested for the treatment of real oil-sands produced water and oil-sands boiler blowdown water. At a current density of 8 mA/cm² with less than 1600 Coulomb/Litre of charge dosage, for oil-sands produced water, a Si removal larger than 90% was achieved, from
around 60 mg/L to the range of 2 to 5 mg/L, using both Fe-EC and Al-EC; whereas for oil-sands blowdown water treatment, Fe-EC removed around 40% of the Si, Al-EC achieved almost complete Si removal.

Based on our findings above, current density of 8 mA/cm² showed less energy consumption than 16 mA/cm², while still achieved same level of Si removal; and the electrolysis duration is only half of experiments at 4 mA/cm². Dissolved oxygen does play an important role in the Fe-EC by promoting the production of insoluble Fe(III) products. The batch reactor with recirculating flow combined with anode oscillation does show the best performance compared with other reactor designs, however the mechanical energy is a factor needs to take into account. The effect of mass transport on the removal of Si, Ca, and Mg significantly enhanced Fe-EC performance, while only slightly improved Al-EC. Overall, Al-EC outperformed Fe-EC on the treatment of synthetic produced water, real produced water and blowdown sample by consuming less amount of energy, less amount of metal, to achieve higher contaminant removal.

4.4 Recommendations for future research

The viability of EC for the treatment of oil-sands produced water, and blowdown water was evaluated and shown to be effective for Si removal, calcium and partial magnesium removal. The investigation of a number of operating conditions and different reactor designs helps with the understanding of the importance of operating conditions and the engineering principles involved. However, there are still many aspects of EC treatment of produced water that need to be further investigated:

1. The particle density change and the particle size distribution during EC treatment should be monitored, as the particle size and density usually increases during EC and can identify different stages of EC;
2. The effect of current pulsation in the anode oscillation and the mechanical energy required in the anode oscillation;

3. Electrode fouling was observed in our experiments and should be studied as this can cause an increase in cell voltage and a decrease in performance, which can be problematic for large scale industrial implementation;

4. The effect of cathodic dissolution of aluminum in EC on the Faradaic efficiency, as this can enhance the coagulant dose and hence the treatment performance;

5. The effect of operating temperature at higher than 70°C to mimic the environment of real produced water on site;

6. The removal of sulfide from oil-sands produced water by EC, the effect of different anodes and operating conditions on sulfide removal;

7. Overall economic feasibility in comparison to current treatment technologies;

8. Study of continuous treatment for industrial scale-up and pilot demonstrations for industrial applications.
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102
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