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Electrocoagulation for the Treatment of Oilsands Tailings Water

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Electrocoagulation for the Treatment of Oilsands Tailings Water

by

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A THESIS

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Abstract

The treatment of tailings water, a major environmental challenge facing the oil sands industry is explored in this research. The focus was on the removal of very fine solids, a very difficult to treat contaminant in tailings water. Electrocoagulation, an electrochemical method of water treatment was tested to assess the performance in removal of fines. Synthetic wastewater samples with kaolin clay dispersed was used as a model. Different electrochemical reactor designs were tested to assess the contaminants removal performance. The results show that electrocoagulation is very effective at removal of fines. Turbidity removals of over 95 % were achieved in 20 minutes settling time versus a control experiment that achieved removals of only 10% for the same settling time.

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List of Symbols and Abbreviations

<i>A</i>	Amperes of Current
<i>AES</i>	Atomic Emissions Spectroscopy
<i>Al</i>	Aluminum
<i>e⁻</i>	Electron
<i>EC</i>	Electrocoagulation
<i>F</i>	Faraday's Constant = 96500 C/mole e ⁻
<i>Fe</i>	Iron
<i>I</i>	Current (A)
<i>ICP</i>	Inductively Coupled Plasma
<i>K</i>	Kelvin
<i>n</i>	number of moles of metal ion generated at the anode (mol)
<i>NTU</i>	Nephelometric Turbidity Units
<i>SS</i>	Stainless Steel
<i>t</i>	Electrolysis Duration (s)
<i>T</i>	Temperature (°C or K)
<i>z</i>	From Faraday's Law; i.e. number of moles of electrons involved in the electrochemical reaction per mole of ion generated or consumed

Chapter 1. Introduction

1.1 Background on tailings water

A major criticism of the oil sands industry on environmental issues is its use of water resources. A common process to recover the valuable bitumen from the oil sands is surface mining. This process requires large volumes of water (Canadian Association of Petroleum Producers, 2013).

A by-product of mining operations is large volumes of toxic water (Masliyah et al., 2008; Canadian Association of Petroleum Producers, 2013) which are stored in large ponds, the infamous 'tailings ponds'. These have led to significant environmental damage because of land displacement, the contamination of natural waters, and impact on wildlife such as waterfowl that land into the surface water. Moreover,

Typically about 70 % of the tailings water from the top three meters of tailings ponds is recycled (Mikula et al., 2008). However, on average three to four barrels of fresh water is withdrawn from surface water sources per barrel of bitumen produced (Mikula et al., 2008). The primary source of fresh water is the Athabasca River. The local communities and stakeholders have expressed concerns about the large volume of fresh water being withdrawn, potentially creating water shortage issues (Mikula et al., 2008).

The nature of contaminants in oil sands tailings water makes the treatment costly in order to minimize environmental damage. A major contributor to the necessity of this form of water storage is the presence of very fine clay particles (particle size less than 44 microns) that take a long time to settle. Therefore the water needs to be stored for many years to allow the particle

separation by settling (Mikula et al., 2008). Currently, tailings ponds and dykes combined occupy land area of over 175 sq. km (Canadian Association of Petroleum Producers, 2013).

Furthermore, these waters contain toxic matter such as residual oil, naphthenic acids, polycyclic aromatic hydrocarbons (PAH's), benzene, and heavy metals such as lead, arsenic, and mercury (Husein et al., 2011; Nix and Martin, 1992). Tailings ponds have been used since the first mining operations in 1967, and the practice has yet to be discontinued. The storage of large volumes of water in tailings ponds is having an immense environmental impact and is a very primitive approach to the treatment of slow settling solids. There is an urgent need for the development of new technologies that can alleviate these issues.

1.2 Background on Electrocoagulation

Electrocoagulation (EC) is one technology that could address these challenges. Prior research has shown that EC can simultaneously remove several contaminants in wastewaters including fine suspended solids, toxic organic matter, silica, and heavy metals (Emamjomeh and Sivakumar, 2009; Mollah et al., 2001), all of which are common contaminants in oil sands wastewaters. Contaminant removals have been shown to be well over 90 % in each case.

EC uses an electrochemical cell to generate coagulating agents in the wastewater by electrochemical reactions, resulting in flocculation of contaminated particles which separate out by settling or flotation. Conventionally, coagulation and flocculation are performed by the addition of chemicals including metal salts or polymeric flocculants. However, EC has many advantages over the chemical method. The electric field used in EC enhances the flocculation process by setting the charged colloidal particles in motion resulting in the coagulation of even very fine suspended solids (Harif and Adin, 2007). This will be advantageous when applied to

tailings water because the difficulty in treating tailings water as mentioned is the presence of very fine, slow settling clay particles. In addition, EC simultaneously removes heavy metals by precipitation as the pH increases during the process. Furthermore, hydrogen gas bubbles generated by reduction of water at the cathode ($2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$) will lead to floatation of the flocculated particles to the water surface thus providing better separation of contaminants. Another major advantage is that no chemicals are required, minimizing secondary pollution. The tailings water is electrolytically conductive due to the presence of sufficient dissolved ions (Allen, 2008), which is beneficial because it will provide low electrolytic solution resistance, leading to low energy requirement. Increased contaminants removal rates, the avoidance of chemical addition, and lower energy consumption suggest that EC could reduce the environmental impact and cost of water treatment for these applications.

The process makes use of an electrochemical cell with two electrode plates, an iron or aluminum anode and a cathode also usually made of iron or aluminum (Liu et al., 2010). Other anode materials have also been reported in literature such as copper (Ali et al., 2013), zinc (Ali et al., 2013; Fajardo et al., 2015), and magnesium (Vasudevan et al., 2010). The wastewater stream is the electrolytic solution.

When current is passed, the anodic material is oxidized to its respective cations which dissolve into the water stream. These metal cations will hydrolyze to form metal hydroxy cations or metal hydroxide precipitates which are excellent coagulating agents. The cationic coagulants generated will neutralize the negative surface charge present on the colloidal matter such as suspended solids or emulsified oil droplets. Hence the electrostatic repulsion among the colloidal particles which hinder separation by settling is eliminated leading to predominantly Van der

Waals attraction among the particles which causes coagulation (Liu et al., 2010). The neutral metal precipitates can also coagulate colloidal particles and other contaminants by adsorption of onto the precipitates. The larger aggregates then flocculate and separate out by settling or flotation. Figure 1 illustrates this process.

Figure 1: Electrocoagulation Illustration

At the cathode, water is reduced generating hydrogen gas and hydroxide ions. The hydroxide ions will increase the pH of the water. The hydrogen gas bubbles will float the lighter flocculated particles such as oil to the water surface. The increase in pH by the generation of hydroxide ions will cause the precipitation of other cations present such as heavy metals and calcium and magnesium which reduces hardness. Silica will also precipitate and removal of

silica can also occur by adsorption onto the iron or aluminum hydroxide precipitates. Due to the presence of chlorides in tailings water, oil removal can occur not only by flocculation and flotation but also by oxidation due to free chlorine generation at the anode. The free chlorine generated will also have a disinfecting effect on the water.

Disadvantages of electrocoagulation include passivation in aluminum electrodes that inhibit the electrodisolution and the replacement of the anode metal once it is consumed (Mollah et al., 2004).

For the EC process, the electrical current is typically fixed because the amount of metal to be electrodissovled from the anode for coagulation depends on the current passed based on Faraday's Law of electrolysis. The relation is described by the equation below:

$$n = \frac{I t}{z F} \quad (\text{Equation 1})$$

where:

- n is the number of moles of metal ion generated at the anode (mol)
- I is the current passed (A, C s^{-1})
- t is the electrolysis duration (s)
- z is the number of moles of electrons involved in the electrochemical reaction per mole of ion generated or consumed. For the aluminum oxidation reaction, $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$, $z = 3$.

For the iron oxidation reaction, $\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^-$, $z = 3$.

- F is Faraday's constant (96500 C/mole e^-)

Figure 2: Schematic diagram of an Electrocoagulation Cell

Figure 2 shows a schematic diagram of an EC cell. It is shown with two cathodes, but an EC cell can also be operated with a single cathode. However, a three electrode setup or a stack of electrochemical cells is more representative of a full scale system than a two electrode arrangement, because this makes effective use of the anode surface as it allows current to flow to both sides. As discussed above, the anode is typically either aluminum or steel and the wastewater will be the electrolytic solution, provided it has sufficient conductivity. Pure water will allow current to pass, but will require significantly higher voltage and thus the energy consumption will also be significantly higher.

1.3 Coagulation theory

Fine colloidal particles don't separate easily; due to the small diameter (1-1000 nm), they settle very slowly. Moreover, the presence of negative surface charges that arise from ion exchange between the silica and aluminum in the clay crystal lattice with monovalent ions in

water such as hydrogen ions and sodium ions (Canizares et al., 2007), the particles repel each other electrostatically. Thus, the particles don't aggregate easily which further hinders settling.

Therefore the main objective of coagulation is to form positively charge species that can neutralize the negative surface charges on these particles. Once neutralized, the particles will flocculate by van-Der Waal's attraction forces and settle faster. This mechanism is charge neutralization coagulation/flocculation. Another major mechanism is the formation of large precipitate species that adsorb these fine solids which then flocculate and form larger species that settle more easily. This mechanism is known as sweep coagulation/flocculation. These coagulating agents are typically generated by dissolving iron or aluminum based metal salts such as alum, ferric chloride, ferric sulfate, etc. at high pH because the pH decreases after dissolution as the metal ions consume the hydroxide ions in water. This results in the formation of their respective metal hydroxyl cations and precipitates which are excellent coagulating agents. pH is a very important factor in coagulation. For aluminum based coagulation, the optimum pH is typically between 4.5 and 8 (Reynolds and Richards, 1996). For iron based coagulation, the optimum pH is between 4 and 12 (Reynolds and Richards, 1996). These pH ranges are considered optimum in order to generate high concentrations of metal hydroxide precipitates (Reynolds and Richards, 1996), so that the predominant contaminant removal mechanism is by sweep flocculation. A diagram that best illustrates the fact that iron is more effective than aluminum at a wider range of pH because it forms higher concentrations of precipitates at a wider range is a Pourbaix diagram. Figures 3 and 4 are Pourbaix Diagrams for aluminum and iron respectively. Comparing figure 4 to 3, iron hydroxide precipitates are more thermodynamically stable than aluminum over a wider range of pH. The same coagulating agents can be generated electrochemically by electrocoagulation.

Figure 3: Pourbaix Diagram for Aluminum; obtained with permission from (Micro Magazine.com, 2007)

Figure 4: Pourbaix Diagram for Iron; no copyright permission required from (Wikimedia Commons, 2006)

1.4 Contaminant removal mechanisms and analysis

The literature on the use of electrocoagulation for the treatment of the three main contaminants in tailings water; fine suspended solids, oils and dissolved organics, and heavy metals, will be discussed in this section.

Reports on the ability of EC to remove petroleum contaminated wastewaters are scarce. Of the few that are available, EC has been tested on reservoir produced water (Ahmadun et al., 2009), flow back water from fracking operations (Bryant and Haggstrom, 2012), and wastewaters from refineries/petrochemical plants (Mossavi et al., 2011). The well cited review paper on various technologies for the treatment of oil and gas produced water (Ahmadun et al., 2009) reported only one instance of an electrocoagulation application for oilfield produced water, reporting results of a pilot plant study done in China (Ma and Wang, 2006) on the treatment of oil field produced water for reinjection. However, the anode featured was not a simple iron anode, but included an undisclosed catalytic coating. This treatment process used not only electrocoagulation but also electrochemical oxidation to oxidize organics by free radical formation. Therefore, the results reported would have the benefits of both electrocoagulation and electro-oxidation. The authors report that just by this treatment step method, they were able to meet the standards required for re-injection.

A conference paper has reported the treatment of reservoir produced water in Canada (Younker et al., 2011). The treatment of synthetic wastewater prepared in the lab, which had crude oil emulsified in brine water, was studied. The authors claimed that electrocoagulation yielded better COD removals over chemical coagulation, removals of more than 70 %, suggesting that EC can improve oil removal.

Another study was performed examining the treatment of petroleum contaminated ground water due to a refinery (Moussavi et al., 2011). In this study the total petroleum hydrocarbons (TPH) was used as the water quality parameter rather than COD, therefore the amount of petroleum hydrocarbons being removed was measured directly. Removal levels as high as 95 % were achieved by the use of iron anode.

Oils and organics removal has been analyzed by (Canizares et al., 2007). In this study, treatment of both emulsified oil (motor oil) and dissolved organics (used a dye) was considered. The authors reported high removals for oils (greater than 80 %). The authors studied the speciation after metal hydrolysis and reported that both flocculation mechanisms occurred, charge neutralization and sweep flocculation. For emulsified oils, the charged hydroxyl cations produced will neutralize the surface active groups on the anionic surfactant such that no bridging by the surfactant can occur between the water molecules and the oil droplets. Oils also get adsorbed on the precipitates. All of this is enhanced in EC when compared to chemical coagulation due to the presence of the electric field. For dyes, removal mechanism is similar. The hydroxyl ions preferentially gets bound to polar groups in the dyes in the presence of the electric field, hence the interaction between the organic phase and the water molecule was reduced. The dye is also removed by adsorption onto precipitates. The same study reported similar removal for the fine suspended solids, in the form of dispersed kaolin in water, which is the type of clay found in tailings water, and the most burdensome of all the contaminants. Suspended solids removals were reported to be well over 90 %. (Harif and Adin, 2007) also stated that kaolin particles are set in motion by the electric field and hence can form bigger flocs than chemical coagulation yielding better separation.

1.5 Electrocoagulation reactor design

Common cell designs in literature for electrocoagulation experiments would have two electrodes, an anode and cathode in a lab stirred beaker or vessel. There is a lack of studies on the effect of mass transfer on EC and methods to enhance mass transfer to improve contaminant removals. During electrolysis, the metal ions electrodisolved are adjacent to the anode, while the hydroxide ions are adjacent to the cathode. Mixing by stirring causes a non-uniform distribution of these two important ions for the coagulation process. If an anode is to oscillate between two cathodes, the problem of non-uniform charge distribution can be minimized, as in this case of mixing the charge distribution is more uniform, and so it is expected that mass transfer will be enhanced. Oscillations are also expected to induce current pulsation as the anode moves back and forth from a cathode, current will preferentially flow from the side that is closer to the cathode (as this side has less ohmic resistance), while the other side of the which is much further from the other cathode will have less current flow (as this side as higher ohmic resistance). Pulse current in EC by other methods in literature was shown to improve contaminant removals (Keshmirizadeh et al., 2011; Chen et al., 2011). Literature (Carpenter and Roberts, 1999) on mass transport characteristics for another electrochemical application reports that with oscillatory flow, there was an increase in overall mass transfer coefficient in excess of 10. (Khamelsky et al., 2000) a US patent reported better contaminant removals for EC with a “mobile electrode”, though no systematic studies of this effect were done. Moreover, this patent was about the treatment of heavy metals as the contaminants and not fine solid particles. It is expected that the cell voltage can be lowered by oscillating the anode because when the anode moves closer to either of the two cathodes, the net cell potential will be lowered compared to a stationary anode in the middle.

In industry, electrochemical reactor designs often use multiple pairs of electrodes for a workable rate metal dissolution (Mollah et al., 2004), as multiple electrodes provide a larger surface area. Often, the configuration to polarize these electrodes is bipolar instead of monopolar, as for a given amount of charge passed, the bipolar case will provide it at higher potential and lower current, while the monopolar case will provide it at lower potential and higher current. On an industrial scale, it is easier to provide electrical power at higher potential and lower current. Moreover, the monopolar configuration requires very complex circuitry of many wires which further increases the favourability of bipolar configuration over the monopolar case. It is hypothesized that for the case with multiple plates, the oscillating case will improve contaminant removals and lower cell voltage. Another major hypothesis tested in this research that will be discussed in the following sections, is that the use of multiple electrodes that are corrugated in shape with oscillations will lower cell energy when compared to oscillating flat plates. The corrugation will allow the oscillating plate to approach the stationary plates at a closer proximity than stationary electrodes.

1.6 Project Objectives

With the aim of finding an effective method for the treatment of oil sands tailings water and to develop innovative electrochemical reactor designs, the following objectives were developed:

- To test the effectiveness of electrocoagulation in the removal of fine suspended particles through accelerated settling, which is a very difficult to treat contaminant in tailings water.

- To develop innovative electrochemical reactor design technologies that could have a major impact on not just oilsands tailings water, but water treatment by electrocoagulation in general. The design should improve water contaminant removals and simultaneously lower energy requirements.
- The reactor designs to be tested are a cell with an anode oscillating between two cathodes, and another cell with multiple electrodes, with both monopolar and bipolar configurations tested.

1.7 Outline of the Thesis

This thesis has 4 chapters. The background on tailings water and electrocoagulation is described in Chapter 1. The objectives of this research are also mentioned in Chapter 1. Chapter 2 discusses the methodology of the research. The experimental apparatus and the analytical methods are described. Chapter 3 discusses the findings of the research. Chapter 4 discusses the conclusions and the original contributions to knowledge from this research.

Chapter 2. Methodology

In this section, the apparatus used for the experiments, the instruments used, and the experimental procedure are discussed.

2.1 Electrocoagulation cells description

Two different EC cell designs were used in this study, a cell using flat plate electrodes and an alternative design using corrugated electrodes. These two cell designs are described below.

2.1.1 Flat plate cell

This cell, illustrated in Figures 4 and 5, makes use of three flat plates. The cathodes are made of stainless steel to prevent corrosion. The anode used was either aluminum (grade 6061) or mild carbon steel (grade 1018), as typically used for electrocoagulation. The cell was constructed in order to allow the anode to oscillate between the cathodes as illustrated in Figure 5.

Figure 5: Model of Plates in the Flat Plates Cell

All the three plates were rectangular with necks adjoining the plates in order to connect wires. 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. The difference in thickness for the anode and the cathodes was based on the materials that were available at the Engineering building's machine shop, as the cell was constructed there. The anode had a different height compared to the cathodes because its bottom could not touch the base of the vessel (the bottom of the cathodes were touching the base of the vessel) in order to allow oscillations. The greater width of the anode compared to the cathodes allowed more contact with the water during oscillations, thus better convection. The volume of water treated was 400 mL. The anode plate was thus suspended on a bar, which was adjacent to a disc attached to a motor. The disc attached has a slight offset such that as it rotates, the bar and the anode plate will oscillate back and forth. The stationary plates had a gap of 2.2 cm, between which was suspended the anode. The full model is as shown in Figure 6. The vessel is made of plexi glass because any metallic material is not appropriate for electrolysis. This cell was used with monopolar configuration.

Figure 6: Full model of the Flat Plates Cell

2.1.2 Corrugated plate cell

A cell with 13 V-shaped plates was constructed to test the performance of a novel oscillating plate electrocoagulation cell which can also be used with bipolar configuration. With a flat plate cell the cell voltage will not be reduced by oscillation (in the direction of current flow) in the bipolar configuration. With the corrugated design combined with oscillation perpendicular to the direction of current flow, in principle a reduction of cell voltage should be possible. The cell could be connected in either monopolar or bipolar configuration. Figure 7 shows a cross sectional view of the cell design.

Figure 7: Cross Sectional View of the Corrugated Plates Cell

As shown in Figure 7, there are 7 plates that are fixed into slots in the sides of the vessel. Also there are 6 plates which can be oscillated between the seven stationary plates. Similar to the flat plate cell, the plates that can be oscillated are suspended on a horizontal bar that is adjacent to a disc, which on rotation, will oscillate the plates. The volume of the water treated in this cell is also 400 mL. Both the stationary and the oscillating plates were bent at 49° . The stationary and the oscillating plates were symmetrical. For the stationary plates, each plate had a height of 13.5 cm and the width beside the bend was 3.6 cm (i.e. distance from the outer edge to the bend). The thickness of the stationary plate was 1.8 mm. For the oscillating plate, the height was 13.2 cm, and the width beside the bend was also 3.6 cm. The distance (in the oscillating direction shown in Figure 6) between two stationary plates was 7.3 mm. The full 3D model of this cell with the plates and the vessel is illustrated in Figure 8.

Figure 8: Full Model of the Corrugated Plates Cell

2.2 Analytical Methods

The following instruments were used to analyse samples of water before and after treatment.

Turbidity meter: Turbidity is a measure of the clarity of the water. Water loses clarity or becomes cloudy due to the presence of colloidal particles such as clay, silt, microbial organisms, organics, etc. These cause the passage of light to be scattered as it travels through the water. A turbidity meter is a nephelometric instrument which measures the degree of the reduction in light

transmitted through the sample as compared to a clear blank standard (Reynolds and Richards, 1996). The turbidity meter used for the analysis was VWR 800. The instrument was calibrated using triple filtered reverse osmosis (RO) water as the blank standard. Detection limit is 0-199.9 NTU and accuracy $\pm 2\%$ or 0.50 NTU (whichever is greater).

Inductively Coupled Plasma- Atomic Emissions Spectroscopy (ICP-AES): ICP was utilized to determine the metal concentration of the iron or aluminum electrodisolved. ICP utilizes a plasma generated at 6000 K to 8000 K (America Water Works Association, 1998), temperatures at which the elements in the sample gets converted to ions and is excited, producing an emission spectra. The metal concentration is then determined from the intensity of the emission (America Water Works Association, 1998).

The ICP used for the analysis was an IRIS Intrepid IIXDL, ThermoInstruments Canada Inc. For calibration, a solution was prepared with 30 ppm aluminum and 100 ppm iron using ICP standard solutions of 1000 ppm (from Sigma Aldrich) by diluting with RO water.

2.3 Experimental Procedure

The experimental procedure for the fine solids removal and ICP measurements will be discussed in this section.

2.3.1 Fines removal experiments

For the fines removal experiments, EC was performed to test the removal of kaolin clay as the model for the fine suspended solids in tailings water. Kaolin clay (Sigma Aldrich) at a concentration of 1g/L was dispersed in tap water to simulate the fine clay particles in tailings water. Tap water was used due to its higher conductivity and because it provides better dispersion of the clay particles. To further increase the dispersion in order to make the test more

rigorous, the dispersant poly acrylic acid sodium salt was added at 60 mg/L. It was determined that the solids settle significantly slower with the dispersant added, hence the experiments are rigorous because if there is significant settling after electrocoagulation, it is predominantly due to the treatment process and not natural settling. Sodium chloride at 3 g/L was added to increase the conductivity of the solution to lower ohmic resistance of the cell. A fixed current was applied for a timed electrolysis duration to achieve the EC treatment. The volume of the sample treated for each electrolysis experiment was 400 mL. Following electrolysis, the sample was allowed to settle for 20 minutes in a 1000 mL beaker. The turbidity of a sample of the clarified liquid following settling was determined to measure the solids removal. Figure 9 is an illustration of the experimental procedure.

Figure 9: Experimental Procedure for Turbidity Removal by EC

2.3.2 ICP measurements to determine metal concentrations

In order to determine the rate of dissolution of metal into the treated water, electrolysis experiments were carried out in the absence of kaolin, and the concentration of metal in solution was measured as a function of the electrolysis time. Kaolin was not added because the ICP-AES requires the absence of any solids within the liquid and the precipitates have to be dissolved by the

addition of an acid (typically nitric acid is used for the digestion). As clay is difficult to dissolve, it wasn't included. Hence the initial water prior to electrolysis was composed of 400 mL RO water and sodium chloride at 3 g/L. It is assumed that without kaolin in the water, the amount of metal electrodisolved would be the same as with kaolin in water. Following electrolysis, 2 mL conc. nitric acid was added. For aluminum, the precipitates were fully dissolved. However for the iron, precipitates were still present, but was well dispersed after acid addition (prior to acid addition the precipitates were large clumps). Therefore, 5 mL of the dispersed iron in water mixture was added to 15 mL conc. nitric acid, which formed a clear solution. The sample was then analyzed for metal (Fe or Al) concentrations using the ICP-AES.

Chapter 3. Results and Discussion

The results for the experiments conducted on suspended solids removal, cell energy requirement, and metal concentration determination by ICP analysis will be discussed in this chapter.

3.1 Flat plates cell results

Experiments were conducted with the flat plates cell discussed in the Chapter 2 to test the removal of the fine suspended solids. Kaolin was used to simulate the fine clay particles in tailings water. Turbidity was used to characterise the water quality and the removal of suspended solids. Several types of experiments were conducted to determine the best experimental conditions. Two different anode materials were tested aluminum and iron (as steel) and the respective performances were compared. For the two anode materials, the performance of the cell using an oscillating anode was compared to the performance with a stationary anode. In addition, the turbidity removal performance was investigated at two different current densities while maintaining the charged passed by proportionally adjusting the electrolysis duration. Experiments were also conducted with the flat plates cell to test the impact of initial pH on turbidity removal. These experiments were conducted with both aluminum and iron anodes.

3.1.1 Electrode material

This section includes results comparing the performance of aluminum anode and steel anode to determine whether aluminum or iron based electrocoagulation is more effective for removal of fine clay particles. Experiments were conducted with the synthetic wastewater with compositions described in Chapter 2. The initial pH of the wastewater was set at 4.5. The electrolysis was carried out at a current density of 0.5 mA cm^{-2} . These two parameters were selected as they were seen in the literature (Canizares et al., 2007), which also looked at treating

kaolin contaminated water. This stage was the starting point of the research, hence, this literature was selected to prepare an appropriate wastewater sample and also to select a current density. The synthetic wastewater prepared had the same concentrations of kaolin and sodium chloride as (Canizares et al., 2007), however, the synthetic wastewater sample they prepared did not have any dispersants present. As discussed in Chapter 2, following electrolysis, the flocculated sample was allowed to settle for 20 minutes (this duration was also selected from Canizares, et al., 2007). The pH of the sample was also measured following electrolysis.

Figure 10 compares the treatment performance of electrocoagulation using a stationary aluminum and steel (iron) electrode with repeat experiments for some conditions to demonstrate reproducibility. Figure 11 compares the pH after electrolysis for the two anode materials for the same set of experiments in Figure 10. The results of the repeated experiments shown in Figures 10 and 11 show that the removal and the pH was reproducible on an average of 6 % for turbidity removals and 2 % for pH after electrolysis. In Figure 10, data is also plotted for a control experiment performed to validate the effect of electrolysis on the flocculation of suspended solids after settling for 20 minutes. For this control experiment, the wastewater sample prepared did not undergo electrolysis in the electrocoagulation cell, but was allowed to settle for 20 minutes. The settling took place in the 1 L beaker that was used for the settling of the samples after electrocoagulation. This control experiment is shown in Figure 10 as the turbidity removal for an electrolysis duration of zero minutes. The solids removal in this case was about 10 %. Each point in Figure 10 is a separate experiment.

Clearly from Figure 10 with increasing electrolysis durations, the turbidity removals of the flocculated sample following electrolysis increased. At 0 minutes of electrolysis of the control sample, the turbidity removal was only about 10 %, while at the highest electrolysis

duration tested of approximately 20 minutes, the turbidity removal after 20 minutes settling was over 95 %. This indicated that EC had an effect on turbidity removals because it led to the destabilization of the suspended kaolin particles, so they could be readily settled from the treated water. As the duration of current increases, more metal is electrodissoved and more hydroxide ions generated at the cathode, thus more coagulant is added by hydrolysis, explaining the increased turbidity removals.

Figure 10: Effect of electrolysis duration and electrode material on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, initial pH 4.5, average initial turbidity range 290 NTU, current density 0.5 mA cm^{-2} . Turbidity removal was determined by measuring the turbidity of the treated water after allowing 20 minutes settling. Repeat experiments for some conditions demonstrate the reproducibility of the experiments.

Figure 11: Effect of electrolysis duration on the pH for Figure 10. Solution volume 400 mL, initial pH 4.5, current density 0.5 mA cm^{-2} . pH was measured after electrolysis. Repeat experiments for some conditions demonstrate the reproducibility of the experiments.

Another important observation is that the pH of the samples after electrolysis shown in Figure 11, at electrolysis durations of over 5 minutes, which showed rapidly increasing turbidity removals (Figure 10), the pH after electrolysis was greater than 6.5 and less than 8.0. This indicates that for these conditions, the predominant coagulation/flocculation mechanism was sweep flocculation as mentioned in the “Introduction” section.

Comparing the removal performance between iron and aluminum anodes shown in Figure 10, both electrode materials exhibited maximum removals after 20 minutes of electrolysis. However, in most cases aluminum was observed to generate better turbidity removal

performance at the sweep flocculation stage of electrolysis durations over 5 minutes. One explanation is that aluminum hydroxides have better adsorption capacity than iron based. However from Figure 10, the turbidity removal with a steel anode caught up with aluminum after approximately 17 minutes of electrolysis.

For pH less than 6, the predominant coagulation mechanism is normally considered to be by charge neutralization (Reynolds and Richards, 1996) followed by aggregation by van der Waal's forces as discussed in Chapter 1. The pH after electrolysis for electrolysis durations less than 5 minutes in Figure 11 suggests that the removal mechanism at this stage is charge neutralization. This is because at pH less than 6, the metal hydroxy cations formed will neutralize the surface charges and destabilize the suspension. However, with continuous addition of metal ions, there will be an excess of positive charges on the colloidal particles, thus re-stabilizing the suspension. When this happens, the removals will decrease from the initial peak in removals. This is clearly seen in Figure 10, with the case of aluminum being more evident. When the charges are neutralized completely, the zeta potential which is a parameter that quantifies the charges present will be 0, unlike when the suspension is stable with negative charges, at which the zeta potential will have significantly negative values (Reynolds and Richards, 1996).

For EC using both aluminum and iron anodes, the pH increased with increase in electrolysis durations. Hydrolysis reaction of the metal ion generated at the anode would decrease the pH. However, a net increase in the pH would suggest that hydroxide ions from 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 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 in the sweep flocculation stage and to prevent the pH

from dropping below 6, more lime has to be added. Hence, the resulting volume of sludge is much larger. This could possibly explain the previous studies that have indicated that EC produces lower sludge volumes than chemical coagulation (Liu et al., 2010; Zhu et al., 2005). The hydroxide ions/alkalinity required in EC is provided by a cathodic reduction reaction that does not involve the generation of any metal ions, in contrast to chemical coagulation where the calcium added with the lime contributes to the sludge produced.

3.1.2 Comparing oscillating anode v's stationary anode

The concept of an oscillating anode in electrocoagulation is a novel one. Though, there is a patent (Khamelsky et al., 2000) describing it with data that shows improved performance, there have been no published studies of this effect. Besides, this patent looked at examining heavy metal removal. The concept of an oscillating anode for the removal of fine particles has not been tested. It is proposed that an oscillating anode could improve fine solids removals by EC. All the experiments discussed in section 3.1 were carried out with stationary anodes. For the same set of electrolysis durations, the performance of oscillating anodes was tested and compared. The composition of the wastewater prepared was the same. The current density was also set at 0.5 mA cm^{-2} . The initial pH of the sample was 4.5. EC using both an aluminum and a steel anode were tested. Following electrolysis, the sample was allowed to settle for 20 minutes. The pH of the sample was measured just after electrolysis, similar to the procedure for the stationary case. The oscillation of the anode was at a frequency of 0.23 Hz (the disc was rotating at 14 RPM) and the peak to peak amplitude was 16.2 mm (the stationary cathodes had a distance of 21.6 mm, and so this amplitude allowed the anode to approach either of the cathodes at a close proximity while avoid touching each other and short circuiting).

The results of the turbidity removals by EC for the case of a stationary and oscillating aluminum anode are plotted as a function of electrolysis duration in Figure 12. The pH measured after electrolysis for the same experiments is plotted in Figure 13. Clearly, from Figure 12, for the case of oscillations, turbidity removals increased with increasing electrolysis durations. However, the main conclusion from the results is that oscillations were able to significantly reduce the treatment duration. It took only 11 minutes for the case with an oscillating anode to achieve the highest turbidity removal of over 96 % while for the case with a stationary anode it took 20 minutes to reach the maximum removal.

Figure 12: Effect of electrolysis duration and stationary vs oscillations with aluminum anode on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, initial pH 4.5, average initial turbidity 290 NTU, current density 0.5 mA cm^{-2} . Turbidity removal was measured after treated sample was allowed to settle for 20 minutes.

Figure 13: Effect of electrolysis duration on the pH for figure 12, Solution volume 400 mL, initial pH 4.5, current density 0.5 mA cm^{-2} . pH was measured after electrolysis.

Oscillations thus reduced the treatment duration by 44 % for the case of aluminum anode at constant current density. By reducing the treatment duration, if this technology is to be implemented for a continuous treatment operation, the retention time can be reduced. Moreover, by introducing oscillations to reduced treatment duration, the cell's electrochemical energy can be reduced, as electrical energy consumed $= \int V I dt$, where V is the cell potential (V), I is the cell current passed (A), and t is electrolysis duration (s).

Therefore, the hypothesis that the use of an oscillating anode will improve turbidity removal by EC has been demonstrated. As mentioned earlier, this concept has not previously been the subject of a systematic experimental study, however, the underlying mechanisms that explain why oscillations improve turbidity removal is not available.

It is expected that oscillations improve the mass transport conditions as the convection would lead to faster hydrolysis of ions, aggregation of the metal hydroxy cations, metal hydroxyl precipitates, and the contaminants, in this case the colloidal clay particles. Moreover, the

influence of the electric field is important. By allowing the anode plate to approach closer to one of the cathode plates, the electric field at this stage between the pair of plates is stronger than the case with the anode stationary with greater distance between the anode-cathode pair. With stronger electric field, there will be greater transport of colloidal particles by electrophoresis, and the hydroxide production will occur close to the anode where metal ions are dissolving.

From Figure 12, for both cases, the stationary as well as the oscillating anode, at first there is a gradual increase in the turbidity removals followed by a dip before the turbidity removals increase dramatically to the maximum removals. This can be attributed to the removal mechanism which follows the sequence of charge neutralization followed by destabilization of the suspension, which is followed by re-stabilization of the suspension, and finally the last step which is removal by sweep flocculation. For both the stationary and the oscillating case, the initial peak occurs under 3 minutes. From Figure 13, the pH for this is under 6, clearly indicating that charge neutralization is the main mechanism up to this point. However, with the continuous addition of the metal, there will be the excess of positive charges on the particles, and this causes the suspension to be re-stabilized and the particles once again will start repelling each other and thus preventing aggregation, hence the removal started to decrease after the peak in Figure 12. With further addition of the metal and with the simultaneous increase in pH due to the generation of the hydroxide ions at the cathode, the conditions were favorable for the generation of aluminum hydroxide precipitates. With electrolysis durations over 5 minutes, the pH was well over 6 in Figure 13, indicating the formation of precipitates, which would cause sweep flocculation. After this stage the turbidity removals started to increase dramatically. The mentioned literature which utilized the similar suspension (Canizares et al., 2007), also had two

peaks in the turbidity removal plots clearly indicating charge neutralization and sweep flocculation , although the removal by charge neutralization was much higher in that literature.

Another theory is the oscillating nature of the current from the anode. As the anode electrode moves closer to one of the two cathodes, the ohmic resistance between that pair lowers while the ohmic resistance between the anode and the other cathode will increase significantly. Hence most of the current will originate from the faces closer to each other, causing larger electrodissoolution of the metal ion between that anode-cathode pair, while significantly lower electrodissoolution from the other face. When the anode swings the other way, the face closer to the other electrode will experience more electrodissoolution. Therefore, as this process continues, there is a continuous dynamic pulsing of current with greater concentrations of metal ions being generated at one anode-cathode pair in one cycle which may intensify the coagulation/flocculation process.

From the data plotted in Figure 13, the pH after electrolysis plot shows that in most cases for the oscillating anode a pH greater than 6 was obtained especially at the higher electrolysis durations that yielded the highest turbidity removals, indicating that sweep flocculation or aggregation onto aluminum hydroxide precipitates is the main removal mechanism as with the stationary electrodes. In the oscillating case, for electrolysis durations of 7 minutes and greater, a lower pH was observed compared to that obtained for the stationary case, which could perhaps indicate oscillations lead to faster hydrolysis reactions. In fact, the pH plot also showed that at about the 5 minute mark and beyond, the pH for the oscillating case started to decrease compared to the cases at lower electrolysis durations. From the turbidity removals plot, at the mentioned electrolysis durations of 5 minutes and beyond, the turbidity removals started to increase dramatically. This indicates as well that oscillations lead to faster hydrolysis reactions because of

the decrease in pH. The turbidity removals shown in Figure 12 under these conditions (electrolysis durations of 7 minutes and greater), show an enhanced removal compared to the stationary case, further strengthening the argument that oscillations lead to faster hydrolysis, and so flocculating at a faster rate.

For the case of steel, experiments with an oscillating anode were conducted to compare to the case of a stationary anode. Experiments were carried out with the same set of electrolysis durations conducted at 0.5 mA/cm^2 as described above for an aluminium anode. The turbidity removal is plotted as a function of electrolysis duration in Figure 14, comparing the oscillating and stationary cases, and the pH measured after electrolysis is shown in Figure 15.

Unlike aluminum which formed a clear suspension following electrolysis, the steel electrode was observed to introduce color into the solution, either orange or blue, depending on the operating conditions. It was noticed that at lower electrolysis durations, the color was orange, suggesting the presence of ferric iron, Fe(III).

Figure 14: Effect of electrolysis duration and stationary vs oscillations with steel anode on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, initial pH 4.5, average initial turbidity 290 NTU, current density 0.5 mA cm^{-2} . Turbidity removal was measured after treated sample was allowed to settle for 20 minutes.

Figure 15: Effect of electrolysis duration on the pH for figure 14, Solution volume 400 mL, initial pH 4.5, current density 0.5 mA cm^{-2} . pH was measured after electrolysis.

For long electrolysis durations, especially the case with the oscillations, the color generated was dark blue, suggestive of ferrous iron, Fe (II). It can be speculated that the orange color forms due to predominantly ferric ions while the blue color is due to ferrous ions.

As with the aluminium anode, the turbidity removal observed with an oscillating iron anode was higher than that observed with a stationary iron anode. For the case of iron, the oscillating anode reduced the treatment duration by 33 %, from around 20 min to 13 min for ca. 95 % turbidity removal. Therefore, the hypothesis that oscillations would improve turbidity removal by EC has been demonstrated for an iron anode as well as for aluminium. Hence, for the case of iron, the reduced treatment duration is likely to yield lower electrochemical energy requirement as well as reduced retention time, if implemented on a large scale as a continuous treatment process. The explanation for the improved performance with oscillations may be the enhanced mixing and pulsed current as with the aluminum anode. By oscillating the anode, the electric field between an anode-cathode pair is significantly stronger, and by electrophoresis, the flocculation process is significantly improved. As discussed earlier, the dynamic pulsing of current from the two faces of the anode plate changing in each cycle, causing significantly more electrodisolution from one face per cycle, thus intensifying the flocculation process.

From the pH after electrolysis, most of the experiments, especially those which showed very high removal rates, show a pH after electrolysis between 6 and 8, indicating that most of the removals occur by sweep flocculation, i.e. turbidity removals by adsorption onto iron hydroxide precipitates. However, unlike the case with the aluminum, for this case, the trend in pH increase with increasing electrolysis duration was quite similar for both the oscillating and the stationary case. For aluminum, the pH after electrolysis typically was lower for the oscillating case, for a given duration, suggesting that hydrolysis was occurring at a faster rate for the oscillating case.

Another major result is that if figures 12 and 14 are to be compared, the stationary anode case of both metals show that the highest removals of ca. 95 % occurred at about 20 minutes. However, if the oscillating cases are compared, clearly the aluminum anode performs better than the iron/steel anode. The aluminum anode was able to achieve a removal of ca. 95% at about 11 minutes of electrolysis, while the steel anode only achieved ca. 95% removal after 13 minutes of electrolysis. A possible explanation for this difference could be that for this particular contaminant, kaolin, aluminum hydroxides have better adsorptive capacity for kaolin, thus explaining the higher rates of removals. In fact, even for the case of stationary, though the maximum removals take place at similar durations between the materials, for most part, the aluminum anode had better removals than the steel. From the literature (Canizares et al., 2007) discussed earlier that was used to prepare the synthetic wastewater, it was reported that with the case of aluminum, the suspension after electrolysis achieved a zeta potential of zero faster than the case with the iron. Zeta potential signifies the stability of a colloidal suspension, with more negative the zeta potential, the more stable the colloidal suspension. (Canizares et al., 2007) also reported that the kaolin contaminated sample is one with a negative zeta potential. If the case with iron achieves zeta potential of zero after aluminum, it could also explain the reason why iron is slower at destabilizing the kaolin contaminated suspension.

3.1.3 Test of equivalent dosage at higher current densities

The previous two subsections in this chapter discussed the differences in performance between iron and aluminum based anodes, and also evaluated the hypothesis that an oscillating anode would yield better contaminant removals than a stationary anode. This study was carried out by determining the turbidity removals at a fixed current density of 0.5 mA/cm^2 by varying the electrolysis durations from under 1 minute to about 20 minutes.

Nevertheless, it would be interesting to explore whether the electrolysis duration could be further decreased while maintaining the same turbidity removals for the same charge passed by increasing the current density. Therefore, a new hypothesis was developed that by maintaining the same charge passed, if the electrolysis duration is reduced while proportionally increasing the current density, the turbidity removals will remain the same. This hypothesis assumes that the turbidity removal is only a function of the amount of metal coagulant dissolved. If all of the current at the anode is used for metal dissolution, then the turbidity removal should be purely a function of the charge passed.

Therefore, in order to test this hypothesis four experiments were selected with the oscillating case in figures 12 and 14 to investigate the effect of current density. For the selected four points, experiments were conducted such that the current density was four times the case in figures 12 and 14 while the electrolysis durations for these points were proportionally decreased by a factor of 4, therefore maintaining the same amount of metal electrodisolved based on Faraday's Law of Electrolysis. For the case of aluminum from figure 12, the cases of electrolysis durations of 8.77 minutes, 11.00 minutes, 13.16 minutes, and 17.55 minutes were tested which corresponds to 0.50 mmol/L, 0.63 mmol/L, 0.75 mmol/L, and 1.00 mmol/L respectively of aluminum electrodisolved assuming 100 % current efficiency at the anode. In order to maintain the dose of metal electrodisolved using a current density of 2.0 mA/cm², the electrolysis durations tested were 2.20 minutes, 2.75 minutes, 3.30 minutes, and 4.38 minutes.

For the case of the steel anode, the set of electrolysis durations tested were 11 minutes, 13.16 minutes, 17.55 minutes, and 19.74 minutes. These durations correspond to 0.63 mmol/L, 0.75 mmol/L, 1.00 mmol/L, and 1.13 mmol/L of iron electrodisolved, assuming 100 % current efficiency based on Fe³⁺. To discharge the same amount of metal at the current density of 2.0

mA/cm², the electrolysis durations tested were proportionally reduced by a fourth and were 2.75 minutes, 3.30 minutes, 4.38 minutes, and 4.88 minutes.

For all the tested cases, the sample prepared had the same composition as in the cases with the lower current density and longer electrolysis durations. The initial pH of the sample was set at 4.5 as before. Following electrolysis, the suspension was allowed to settle for 20 minutes and then the turbidity was measured. Following electrolysis, the pH of the sample was also measured.

Figure 16 shows a plot of the turbidity removals obtained for the aluminum anode as a function of aluminium dose, calculated assuming 100% current efficiency, based on Faraday's Law (equation 1 in "Introduction" chapter). The turbidity removals are compared for the two current densities using an oscillating anode. Figure 17 shows the corresponding pH after electrolysis for the data in Figure 16. For the steel anode, Figure 18 shows a plot of the turbidity removal as a function of the electrolysis duration, and Figure 19 shows the data for the pH after electrolysis.

As seen from the mentioned figures, for both aluminum and iron, the turbidity removal values are very close for the case with the higher current density and proportionally lower electrolysis durations. Therefore, if required, the treatment time can be reduced by a desired factor to meet the required turbidity removals, provided the current density is increased by the same factor. However, the cell voltage will increase as well if the current density is increased, and so the energy consumption increases. On an industrial scale, a reduction in process time could mean lower operating costs. The pH after electrolysis for both iron and aluminum indicate that sweep flocculation is the predominant mechanism. Another major inference is that despite significantly lesser time available for the hydrolysis reaction and flocculation for the higher

current density and proportionally lower electrolysis duration, the turbidity removals remained the same. Hence these electrolysis durations and the settling time are sufficient for the flocculation to come to completion. Perhaps, this indicates that hydrolysis and flocculation reactions are not the rate limiting steps.

Therefore, in order to not be limited by time and to quicken the pace of the experiments, the rest of the experiments in this research were conducted at 2 mA/cm^2 .

Figure 16: Comparing turbidity removals aluminum anode- two different current densities and electrolysis durations (4 X current means 2 mAcm⁻² and 1/4th current means 0.5 mA cm⁻²).

Figure 17: pH after electrolysis aluminum anode- two different current densities and electrolysis durations for figure 16 (4 X current means 2 mAcm⁻² and 1/4th current means 0.5 mA cm⁻²).

Figure 18: Comparing turbidity removals steel anode- two different current densities and electrolysis durations (4 X current means 2 mA cm^{-2} and $1/4^{\text{th}}$ current means 0.5 mA cm^{-2}).

Figure 19: pH after electrolysis steel anode based on figure 18- two different current densities and electrolysis durations (4 X current means 2 mA cm^{-2} and $1/4^{\text{th}}$ current means 0.5 mA cm^{-2}).

3.1.4 Effect of initial pH

The initial pH of the sample is a very important parameter in treatment by electrocoagulation. As discussed earlier, the pH of the sample determines the type of flocculation that will be predominant. Moreover, for the treatment of real tailings water, the initial pH of the sample is alkaline with a pH of over 7 (Saidi-Mehrabad et al., 2013). The initial pH of the sample in the prior cases were all at 4.5. The formation of sweep flocs would require the pH to be between 6 and 8. However, if the initial pH of real tailings water is basic, tests need to be done to determine the performance of EC at varying pH values, so as to determine whether adjustment of pH is required to optimize the performance.

The effect of initial pH on treatment performance was tested for both aluminum and iron/steel anodes. The current density used was 2 mA/cm^2 , to carry out the electrolysis at short durations. Five different initial pH were analyzed; 3.0, 4.5, 6.0, 7.5, and 9.0, and all cases used an oscillating anode. The electrolysis duration selected for the aluminum anode was 2.75 minutes, because it is the smallest duration at 2 mA/cm^2 at pH 4.5 that yields maximum (>90%) turbidity removal (Figure 16). Similarly for the case with the iron/steel electrode, Figure 18, the case with oscillation at 2 mA/cm^2 achieved the maximum (>90%) removal at a lowest electrolysis duration of 4.38 minutes. The turbidity removal obtained is plotted as a function of initial pH for the case with aluminum in Figure 20 and the pH after electrolysis is plotted in Figure 21. For the case with steel electrode, the turbidity removal as a function of initial pH is as seen in Figure 22 and the pH after electrolysis is plotted in Figure 23.

From Figure 20, it is clear that the aluminum based EC is effective at only a narrow range of pH. In fact only two points, initial pH of 4.5 and 6 achieved a turbidity removal of >90%. Even the case with the initial pH of 3 did not provide the highest possible removal. For pH

greater than 6, the turbidity removal performance decreased dramatically. At an initial pH of 9.0, very low turbidity removal was obtained, similar to the removal achieved in the control experiment with no EC (Figure 10).

From the plot of pH after electrolysis, it is clear that the two points with the maximum removals are within the pH range for sweep flocculation range of 6 to 8, and this perhaps indicates the maximum removal rates. All the other points are outside this pH range. For an initial pH of 3.0, the final pH was only 4.5, suggesting that the removal mechanism in this case was predominantly charge neutralization. The last two points which are well above pH 8, indicating that the aluminum hydroxide precipitates have further hydrolyzed to form aluminum hydroxyl anions which re-stabilize the colloidal suspension and thus hinders flocculation.

Iron on the other hand demonstrated to be very effective at a wider range of pH. All five cases had very high removals, with the middle points 4.5, 6.0, and 7.5 all demonstrating maximum removals. The first point had only slightly lower removals. All these points are within the sweep flocculation range pH of between 6 and 8, based on the plot in figure 23. Moreover, even the last point which had a final pH of over 9 had very high removals. This indicates that with iron, even at higher, more basic pH, it is possible to have high concentrations of precipitates that allow more sweep flocculation. Aluminum at the same pH of 9 would have had significantly lower concentrations of precipitates, thus explaining the very low turbidity removals. This is consistent with literature reports of iron being more effective at coagulation over a wider range of pH (Reynolds and Richards, 1996).

Figure 20: Effect of initial pH with aluminum anode on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, electrolysis duration 2.75 minutes, average initial turbidity 290 NTU, current density 2.0 mA cm^{-2} . Turbidity removal was measured after treated sample was allowed to settle for 20 minutes.

Figure 21: pH after electrolysis aluminum anode based on Figure 20

Figure 22: Effect of initial pH with steel anode on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, electrolysis duration 4.38 minutes, average initial turbidity 290 NTU, current density 2.0 mA cm^{-2} . Turbidity removal was measured after treated sample was allowed to settle for 20 minutes.

Figure 23: pH after electrolysis steel aluminum based on figure 22

3.2 Corrugated plates cell results; turbidity removal performance

It is hypothesized that for the case with corrugated plates, the oscillating anode will improve turbidity removals, as with the flat plate cell. Moreover, by the use of multiple number of these plates, bipolar mode of contaminant removals can be tested, and compared against the monopolar case. By the use of multiple electrodes, it is hypothesized that for a given current density, the electrolysis duration for maximum turbidity removal can be further decreased.

As discussed in the “Methodology” section, for the experiments conducted with the corrugated plates, the cell had 13 plates. All the plates in this case were made of mild carbon steel. Due to time constraint, only carbon steel material/iron was tested for this cell design and not aluminum. The first set of experiments were conducted with bipolar mode with both oscillating and stationary configurations tested.

For the previous case with the flat plates cell, two different current densities were tested, 0.5 mA/cm^2 and 2.0 mA/cm^2 . For the case with the corrugated plates, due to the bipolar mode of operation and the small area of the end plates, only 2.0 mA/cm^2 was tested as with 0.5 mA/cm^2 , the current to be generated is so small that it could not be set by the power supply in use.

Apart from the very different electrochemical reactor design, the sample preparation and the treatment procedure was the same. The sample prepared had the same composition as the prior cases, i.e. 1 g/L of kaolin dispersed in water, with 60 mg/L of poly acrylic acid sodium salt. As before, 3 g/L sodium chloride was added to increase the conductivity of the water and to simulate the saline tailings water. The initial pH of the sample was 4.5. Following electrolysis in the corrugated plates cell, the sample was allowed to settle for 20 minutes before determining the turbidity removals. The results of the turbidity removal performance of the corrugated plate cell in bipolar and monopolar modes are discussed below.

3.2.1 Bipolar cell test results; Oscillating and Stationary

Experiments were conducted to compare whether for the case with a cell of multiple electrodes in bipolar configuration, oscillations would improve turbidity removals. The first set of experiments were conducted with oscillating anodes at current density of 2 mA/cm^2 . From figure 17, the concentrations of 1.00 mmol/L and 1.16 mmol/L were selected and the corresponding electrolysis durations for the case of bipolar corrugated plates were determined based on Faraday's Law assuming 100 % current efficiency and the absence of bypass currents. At concentrations under 1.00 mmol/L from figure 17, the electrolysis durations were determined to be very low for the bipolar cell and hence were not selected to perform experiments. The electrolysis durations at 1.00 mmol/L and 1.16 mmol/L for the corrugated plates cell in bipolar configuration were 75 and 84 seconds respectively assuming 100 % current efficiency and no bypass currents.

At these two theoretical coagulant doses, the turbidity removals obtained at 2.0 mA/cm^2 for the case of bipolar corrugated configuration, the turbidity removals were significantly lower than that of the flat plate cell. The comparison between these two theoretical points is shown in Figure 24. As seen in Figure 24, for the case of the bipolar corrugated plate cell, a significantly higher metal concentration was required to achieve high turbidity removal. At coagulant doses of greater than 6.22 mmol/L , the turbidity removals decreased. This can be explained based on

Figure 24: Turbidity removals for oscillating electrodes: Comparing bipolar case of corrugated cell with the flat plates cell at the two different current densities, but equal dosage based on Equation1. Initial pH 4.5. Volume of water treated 400 mL.

the pH after electrolysis plot as seen in figure 25. For iron doses of greater than 6.22 mmol/L, the pH was well above the range of 6 to 8, which is the sweep flocculation range. Therefore, due to the dissolution of some of the precipitates and slight increase in stability of the colloidal

suspension, turbidity removals decrease. This is similar to the case in figure 22, where for the flat plates steel cell, at higher pH, turbidity removals decreased.

Figure 25: pH after electrolysis plot for oscillating electrodes for data in figure 24: Comparing bipolar case of corrugated cell with the flat plates cell at the two different current densities.

For Fe doses less than 6.22 mmol/L, a gradual increase in turbidity removal with Fe dose was observed up to the maximum turbidity removal of around 95%. For these sets of electrolysis durations, the performance of both oscillating and stationary electrodes with bipolar configuration was compared and is illustrated by figure 26. The difference in turbidity removal

performance was more significant for this case than all the previous cases that compared stationary and oscillating electrodes. Oscillations for this cell design and mode of operation decreased the electrolysis duration required for maximum (>90%) turbidity removal by approximately 67 %. Figure 27 compares the pH after electrolysis.

Figure 26: Effect of electrolysis duration and stationary vs oscillations on turbidity removal by electrocoagulation, for a kaolin suspension. Bipolar corrugated cell, solution volume 400 mL, initial pH 4.5, average initial turbidity range 290 NTU, current density 2 mA cm^{-2} . Turbidity removal was determined by measuring the turbidity of the treated after allowing 20 minutes settling.

Figure 27: pH after electrolysis for the set of data in figure 26.

From the pH after electrolysis plot, it is clear that the removals are within the sweep flocculation range. The pH values between the oscillating and stationary case are close.

3.2.2 Monopolar cell test results

For the monopolar case, experiments were carried out an electrolysis durations corresponding to the same theoretical iron dosage as for the bipolar experiments, at a monopolar current density of 2 mA/cm^2 . The turbidity removals of monopolar oscillating corrugated plates is compared to bipolar oscillating corrugated plates in Figure 28. An issue with the bipolar configuration when compared to monopolar is the presence of bypass current. Bypass current is a phenomenon whereby there is current leakage from the series of redox pairs and therefore, the net electrode reaction produced is lower than what is expected theoretically. Hence, due to

bypass current, the amount of metal electrodisolved could be lower in the case of bipolar than the monopolar case, for which there is a parallel connection, and so bypass currents are avoided. However, based on the turbidity removals plot in figure 28, the turbidity removal performance is very similar. If bypass currents were significant, the monopolar would be expected to have significantly outperformed the bipolar case in turbidity removals. Since this is not the case, it can be concluded that for this case, bypass current is very low.

Figure 28: Effect of iron dosage determined based on Equation 1 and bipolar vs monopolar case with oscillations on turbidity removal by electrocoagulation, for a kaolin suspension. Solution volume 400 mL, initial pH 4.5, average initial turbidity range 290 NTU, current density 2 mA cm^{-2} . Turbidity removal was determined by measuring the turbidity of the treated after allowing 20 minutes settling.

The pH obtained after electrolysis (Figure 29), for the monopolar case was found to be similar to that of the bipolar case. This could also suggest that bypass current in the bipolar

oscillating case is insignificant. From the pH range, most of the contaminant removals are in the sweep flocculation stage.

Figure 29: Comparing bipolar and monopolar pH after electrolysis based on data in figure 28

The comparison between the turbidity removal as a function of electrolysis duration for oscillating and stationary cases for monopolar configuration is shown in figure 30.

Surprisingly, for this case, oscillations had very little impact on the turbidity removal. The turbidity removal profile is quite similar for both the cases. Experiments were conducted at lower current density to examine whether, the observation that there was no significant impact due to oscillation was due to passivation effects. However, even at the lower current density, the removal profiles are similar. With the available data it is possible to give an

Figure 30: Effect of electrolysis duration and stationary vs oscillations on turbidity removal by electrocoagulation, for a kaolin suspension. Monopolar corrugated cell, solution volume 400 mL, initial pH 4.5, average initial turbidity range 290 NTU, current density 2 mA cm⁻². Turbidity removal was determined by measuring the turbidity of the treated after allowing 20 minutes settling.

Figure 31: pH after electrolysis for the set of data in figure 30

explanation as to why the turbidity removal profiles with oscillations was similar to the turbidity removals with stationary electrodes. One reason could be that as the cell was designed such that the electrodes were very close, at a perpendicular distance of 3 mm between the oscillating plate and the adjacent plate. Due to the close proximity between the two electrodes, perhaps oscillation didn't have a significant impact on improving the hydrolysis and flocculation reactions.

Moreover, the pH after electrolysis profiles as seen in figure 31 are nearly identical. Perhaps, this too confirms that reasoning. However, this is not consistent with the observation of a significant improvement in turbidity removal performance with oscillating electrodes for the corrugated electrodes with bipolar operation.

Another set of comparison was made between bipolar stationary and monopolar stationary for the same set of dosage in the previous figures with monopolar configuration. It is as shown in Figure 32. Comparing the turbidity removals for the two configurations with stationary anodes, it is clear that the monopolar significantly outperforms the bipolar configuration. Hence, one can conclude that bypass currents are significant in the stationary case. This is very different from the oscillating case, where there was no significant difference between the monopolar and bipolar configuration with regards to turbidity removals and thus had no significant bypass currents. As the electrodes move closer together, the bypass current will be significantly lower. The pH after electrolysis plot in figure 33 comparing bipolar vs monopolar for the stationary case shows the two pH profiles to be quite similar. The pH range shows that most of the turbidity removals are in the sweep flocculation stage.

Figure 32: Effect of iron dosage determined based on Equation1 and bipolar vs monopolar case with stationary electrodes on turbidity removal by electrocoagulation, for a kaolin suspension. Corrugated cell, solution volume 400 mL, initial pH 4.5, average initial turbidity range 290 NTU, current density 2 mA cm⁻². Turbidity removal was determined by measuring the turbidity of the treated after allowing 20 minutes settling.

Figure 33: Comparing bipolar and monopolar pH after electrolysis based on data in Figure 32.

This concludes the subsection on comparing turbidity removals with the corrugated plates cell.

3.3 Voltage measurements and energy requirement

For the earlier cases of turbidity removal performance, the voltage could not be clearly measured with the power supply. Therefore, a Metrohm potentiostat (Votalab PGstat) was utilized to accurately monitor the cell voltage, from which the energy requirement can be subsequently determined. Focus was given to the impact of oscillations on voltage and electrochemical energy requirements.

Samples prepared were identical to the samples used for the turbidity removal tests. Kaolin of 1 g/L was dispersed in tap water in the presence of the dispersant poly-acrylic acid sodium salt of 60 mg/L. Sodium chloride was added at a concentration of 3 g/L. The pH of the sample was set at 4.5. All the experiments were carried out at 2 mA/cm² current density.

The first set of experiments were conducted using the flat plates cell with the aluminum anode. Both oscillation and stationary cases were tested. For the case of the aluminum, duration of 263 seconds or 4.38 minutes, the maximum duration from figure 16 show the highest current density with the highest dosage. For these conditions, the turbidity removals were ca, 95%, chosen to compare the electrochemical energy required for effective treatment for the stationary and oscillating cases. Figure 34 compares the cell potentials of aluminum oscillating and stationary electrodes for the flat plate cell. From this plot, oscillations significantly lowered the cell potential when compared to stationary. There was a reduction in cell potential from not just mass transport effects in the presence of oscillations, but also by bringing the anode closer to one of the cathodes, the cell potential gets lowered even further. Thus electrochemical energy savings can be achieved from both reduced treatment duration for maximum removal and from lowered

cell potential. The data shown in Figure 34 was integrated numerically (using the Trapezoidal Rule) to determine the electrical energy consumption, for a duration of 263 seconds, the cell energy was 320 J/L for the oscillating case and 375 J/L for the stationary case.

Figure 34: Comparing the cell potentials between stationary and oscillating anode anode at 2 mA/cm² current density for kaolin suspensions, initial pH 4.5, and electrolysis duration 263 s.

Similar procedure was performed for the steel anode to compare the cell potentials between stationary and oscillating cases. The comparison is illustrated by figure 35. From this plot, it is clear that for steel as well, oscillations had an impact by significantly lowering the cell potentials. For steel, the duration of 296 seconds was selected. The electrochemical energy required for this case is 468 J/L for the oscillations case and 522 J/L for the stationary case.

Figure 35: Comparing the cell potentials between stationary and oscillating steel anode at 2 mA/cm² current density for kaolin suspensions, initial pH 4.5, and electrolysis duration 296 s.

Using similar procedure, the potentials of oscillating versus stationary electrodes for the bipolar corrugated case was tested. The current was set at 2 mA/cm² and the electrolysis duration selected was 180 seconds as it is at this duration based on figure 26, that the maximum removal is first observed for the case of oscillating anode. Figure 36 compares the cell voltages obtained from the stationary and oscillating electrodes. Again, the potential for the oscillating case is lower than the potential for the stationary plates. The amplitude of the oscillations in the oscillating case is smaller due to the fact that the amplitude of the oscillations of the plates is lower. For the bipolar case as well, based on figure 26, there was electrochemical energy savings from reduced treatment time. However from figure 36, there is also electrical energy saved from reduced cell potential.

Figure 36: Comparing the cell potentials between stationary and oscillations steel bipolar corrugated electrodes at 2 mA/cm^2 current density for kaolin suspensions, initial pH 4.5, and electrolysis duration of 180 s.

Based on figure 36, at a total duration of 180 seconds, the energy calculated from the integral for the oscillation case is 515 J/L and for the stationary case is 535 J/L.

Similarly for the monopolar case, from a duration of 207 seconds selected based on figure 29 at which point, the turbidity removals just hit maximum. The plot comparing the potentials is as shown by figure 37. Strangely, for the oscillating case with monopolar cell, the oscillating case yielded greater potentials than the stationary case. Tests were conducted to evaluate the possibility of passivation in causing this to occur. Hence, a case of lowered current density was tested. For this case, the oscillating case yielded lower potentials than the stationary

case. Thus, one of the possible explanations for the higher potentials observed in figure 37 could be attributed to passivation.

Figure 37: Comparing the cell potentials between stationary and oscillations steel monopolar corrugated electrodes at 2 mA/cm^2 current density for kaolin suspensions, initial pH 4.5, and electrolysis duration of 207 s.

Based on the above plot, for the duration of 207 seconds, the energy requirement for the oscillating case is 731 J/L and for the stationary case is 694 J/L. Thus, more electrochemical energy is required for the oscillating case. This concludes this set of experiments.

3.4 ICP analysis

3.4.1 Experiments with the flat plates cell

In order to determine the metal concentration of the sample to evaluate the current efficiency and confirm the metal coagulant dose, as discussed in Chapter 2, the ICP instrument was utilized. In order to prepare the samples, RO water was used with sodium chloride of 3 g/L concentration and the pH was adjusted to 4.5. Kaolin was not added because the ICP requires all solids in the sample to be digested prior to being fed to chamber. After electrolysis, the metal precipitates formed were digested using concentrated nitric acid. The sample was then injected into the ICP for determination of the metal concentration in solution.

For the case with aluminum three durations at 2 mA/cm² were selected. These durations are 132 s, 165 s, and 198 s based on the durations represented by the dosage plots in figure 16. All these experiments were carried out using stationary electrodes. One experiment with an oscillating anode was carried out at 198 s to compare it to the stationary in order to determine whether oscillations could differ in current efficiency for electrodisolution. As discussed in the Chapter 2, Faraday's Law was used as the model for the theoretical concentrations (Equation 1 in "Introduction Section").

As shown in figure 38, the measured aluminum concentrations were found to be close to the theoretical concentrations. In fact, the current efficiency was found to be over 100 %. The greater than expected aluminium concentrations could be due to corrosion effects. Some corrosion experiments were conducted by operating the cell at pH 4.5 with no current and the solution aluminium concentrations were determined. Some small concentrations of aluminum were observed without electrolysis. However with electrolysis, the corrosion effects are even more significant because as the anode is oxidized, the ions generated hydrolyze immediately thus

lowering the pH at the electrode surface. The pH at the surface of the anode will be the lowest, and this will generate even greater corrosion.

Figure 38: Comparing experimental concentrations of aluminum with theoretical concentrations for flat plates cell, stationary anode, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

Based on figure 39, comparing the effect of oscillation on electrodisolution, the values of aluminum dissolved with oscillation is nearly identical to that of the case with stationary anode. Thus oscillations appear to have no significant effect on the rate of metal concentration when compared to the stationary case.

Figure 39: Comparing stationary vs oscillating anode concentrations of aluminum with theoretical concentrations for flat plates cell, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

Similar procedure was conducted for the steel anode, also flat plates. From figure 18, for the iron dosage at 2 mA/cm^2 , three durations were selected. These durations are 165 s, 198 s, and 263 s. All these cases were tested with stationary anode. Figure 40 compares the experimental concentrations with the theoretical values based on Faraday's Law.

Figure 40: Comparing experimental concentrations of iron with theoretical concentrations for flat plates cell, stationary steel anode, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

Figure 40 illustrates that for the case with iron, the experimental concentrations are very close to the theoretical concentrations. Hence, the current efficiency is nearly 100 %. For the case with 263 s, a trial was conducted with an oscillating anode to compare with the stationary case of 263 s in figure 40. The result is as seen in figure 41.

Figure 41: Comparing stationary vs oscillating anode concentrations of iron with theoretical concentrations for steel flat plates cell, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

Figure 41 shows that the oscillating case generated an iron dosage close to the stationary case and both values are close to the theoretical concentration.

The fact that for both the aluminum and iron anodes, the experimental concentrations were close to the theoretical concentrations could suggest that the anode material for both cases is of high purity. If there were other metals present, the concentrations of iron or aluminum would be lower because part of the current would be consumed for the oxidation of those metals.

3.4.2 Experiments with the corrugated plates cell

For the case with the corrugated plates cell, the cases of bipolar and monopolar were both tested. Comparing the concentrations will help determine if there were bypass effects or not. For both cases, the theoretical concentrations as determined by Faraday's law (assuming 100 % current efficiency and no bypass current) and the current density was 2 mA/cm². Theoretical

concentrations of 43.3 mg/L and 57.5 mg/L were the basis for comparison. Figure 42 compares the experimental concentrations in bipolar configuration for stationary and oscillating to the theoretical concentration.

Figure 42: Comparing experimental concentrations of iron and stationary vs oscillating plates with theoretical concentrations for corrugated plates bipolar cell, steel anode, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

For the stationary and the oscillating case, the experimental concentrations were significantly lower than the theoretical concentrations. This could suggest that bypass current was present. Moreover, the oscillating case concentration was greater than the stationary case. This confirmed the expectation that oscillations would lower bypass currents.

Figure 43 compares monopolar stationary vs oscillating for the same set of theoretical concentrations of 43.3 mg/L and 57.5 mg/L seen in figure 42. The corresponding electrolysis durations were determined based on Faraday's Law.

Figure 43: Comparing experimental concentrations of iron and stationary vs oscillating plates with theoretical concentrations for corrugated plates monopolar cell, steel anode, initial pH 4.5, NaCl (3000 ppm) in RO water solution, 400 mL volume during electrolysis.

For figure 43 on the other hand, both the oscillating and the stationary cases had concentrations greater than the theoretical expectations. As the same theoretical concentration was compared in Figure 42, it is clear that the monopolar concentrations were significantly higher than the bipolar concentrations for a given theoretical concentration. Hence, one can conclude that bypass currents are significant for this cell. However, a major finding is that bypass currents can be reduced in a bipolar cell by introducing oscillations.

Chapter 4: Conclusions

A summary of the major findings, contributions to knowledge, and recommendations for future work are discussed in this chapter.

4.1 Summary of major findings

In this research, the potential of EC for the removal of fine clay particles has been explored. Model synthetic wastewaters were prepared to simulate water contaminated heavily with fine clay particles, which was dispersed using a strong dispersant, sodium poly acrylate.

Different electrochemical reactor designs were tested. Two different anode materials, aluminum and iron from mild carbon steel were tested. Aluminum outperformed steel in terms of turbidity removal, which was the water quality parameter used to test the removal of the fines. The novel concept of an oscillating anode was evaluated. For the case with aluminum flat plates, oscillating the anode reduced the treatment duration by 44 % when compared to a current density of 0.5 mA/cm^2 . Oscillating the steel anode reduced the treatment time by 33 %. It was observed that to further decrease the treatment time, the current density could be increased, with a proportional decrease in the required treatment time. Sweep flocculation was found to be the predominant mechanism by which the maximum amount of fines can be removed. Experiments demonstrated that EC with iron is more effective at a wider range of pH. Aluminum was found to be most effective only between initial pH of 3 to 6, due to its amphoteric nature.

For a cell with multiple corrugated electrodes, oscillating the bipolar configuration was found to be significantly better than stationary bipolar. The treatment time required was reduced by 67 % by oscillating the electrodes. For monopolar configuration however, oscillation did not have any significant benefit in terms of treatment performance.

Another major important result is that oscillations reduced the cell potential. By moving the anode closer to one of the nearby electrodes, the potential at a fixed current is reduced. Therefore, there is a net electrochemical energy saving from both reduced treatment time for maximum removals as well as reduced cell potential.

Electrochemical energy consumption, an important parameter was seen to be lowered with oscillations for most of the tests when compared with the stationary anodes, except for the monopolar corrugated plates oscillating case. There was a net reduction in the electrochemical energy from reduced treatment time as well as with lowered cell potential as the anode moves closer to the one of the cathodes. To compare with data available from literature, the highly cited literature (Chen, 2004) that review electrochemical technologies for wastewater treatment was used. For this literature which discussed electrocoagulation technologies, the energy consumption was seen to be in the range of 20-40 W h/m³ for turbidity removal for metal dissolved within the range of 0.15-0.2 mg. From this research, for the case which had the highest energy consumption being the oscillating monopolar cell, the energy consumption to generate between 0.15-0.2 mg of metal would require energy in the range of 19.06-25.41 W h/m³, which is closer to the lower limits reported in the literature.

Finally, experiments were conducted using an ICP to determine whether rate of metal dissolution during EC corresponded to 100 % current efficiency. For the flat plates cell, the current efficiency was nearly 100 %. However for the corrugated plates, depending on the configuration, the current efficiency varied. For the bipolar case, the current efficiency was well below 100 %. However for the monopolar case, the current efficiency was greater than 100 %. The difference in the concentrations between the monopolar and bipolar case indicates that bypass currents are significant for this cell.

4.2 Contributions to knowledge

Contributions to knowledge from this research are numerous, and include:

- To the best of author's knowledge, this is the first time electrocoagulation has been tested extensively to potentially treat oil sands tailings water.
- This the first detailed study of the novel concept of using an oscillating anode in EC, comparing the difference in performance between oscillating flat anode versus stationary flat plate in colloidal clay removal.
- The removal of fine clay particles was studied with the use of a strong dispersant, poly acrylic acid sodium salt; this made the test rigorous because it indicated that EC is very effective at improving the settling of the fine solids when compared to removal by free settling alone.
- This study has introduced the concept of an oscillating bipolar electrode. This is an innovative concept and a patent application is in preparation.
- The results demonstrated that oscillating plates reduced the cell voltage for many different EC cell configurations.

4.3 Recommendations for future work

As this is only the beginning in the research of EC as an effective method for treating tailings water, there are numerous recommendations:

- Testing EC on real tailings water to examine suspended solids removals, organic removals, heavy metals, and silica.

- The fundamental electrochemistry principles and water chemistry merit further investigation. The pH distribution in solution and the behaviour of colloidal particles in the electric field should be investigated.
- The effect of current density should be investigated over a wider range.
- Electrode passivation and fouling is one of the potential drawbacks of EC. This must be further analyzed for the application in real tailings water.
- For the case with an oscillating steel anode, after electrolysis the treated sample developed a deep blue- green color, suggesting that ferrous ions were formed rather than ferric. Further research is needed to characterize the precipitates formed as a function of the treatment conditions. However, this may be difficult to study as ferrous compounds are readily oxidized in air to ferric species.
- As the oscillating anode is a new concept, the various aspects of oscillations such as amplitude and frequency in treatment performance should be studied.
- Further research should be conducted on the monopolar oscillating system to examine why there wasn't a significant difference between turbidity removals when compared to the stationary case.
- The performance of continuous, flow-through EC treatment processes with oscillating anodes should be investigated.

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Kind regards,

Paul Panikulam

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