

Comparative Analysis of Boron Removal by Electrocoagulation in Synthetic and Local Real Produced Waters

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**Comparative Analysis of Boron Removal by
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Produced Waters**

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Abstract

The presence of boron in oil and gas wastewater (produced waters) is a potential challenge for reuse of these waters for irrigation and agricultural uses. Boron is an essential micronutrient, but also toxic to plants at relatively low concentrations. It is also typically present as neutrally charged boric acid (H_3BO_3) in solution which is difficult to remove by conventional treatment technologies. In previous studies, electrocoagulation using an aluminum anode effectively removed boron from synthetic produced water solutions. Boron removal proceeded primarily through borate ($\text{B}(\text{OH})_4^-$) ion interactions with $\text{Al}(\text{OH})_3$, with optimal results at pH 8. The present study extends this work to examine the impacts of real produced water composition (including dissolved organic matter and high divalent cation concentrations) on boron removal by electrocoagulation and treated water quality.

Similar levels of boron removal were achieved in produced water samples from Douglas County and Reno County, Kansas. Periodically adjusting the pH of these waters was found to be a key factor in significant removal of boron. Consistent with previous studies using synthetic solutions, both increased boron removal and a faster rate of removal were observed in real produced waters with increased current loading. The presence of high concentrations of Ca and Mg in the produced water resulted in low bulk pH values throughout the process and greater formation of solid products. However, boron removal did not decrease with this lower bulk pH, as it had in the synthetic solution. This suggests there may be sorption interactions with Mg and Ca solids forming due to localized high pH conditions near the carbon electrode. The presence of organic matter from different sources (humic matter, phenol, and oilfield DOM) had minimal impact on boron removal. The removal of DOC from produced waters during the electrocoagulation process was also minimal. The use of iron as an alternative sacrificial electrode produced poor boron removal in comparison to aluminum. Further work should assess

the impact of produced water suspended solids and the integration of electrocoagulation into an integrated treatment process for produced water conditioning and desalination.

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Introduction

Increasing water demand for human use is a complex challenge the world's growing population currently faces and will continue to confront in the future. These problems are even more pressing in dryland areas trying to meet water needs. The oil and gas industry produce large volumes of water during the extraction, processing, and refining of hydrocarbons, usually called produced water¹. The total amount of oil and gas produced water generated yearly in the US is on the scale of billions of barrels and comprises 98% of the total exploration and production waste generated by the oil and gas industry². However, the majority of produced water is currently disposed of as wastewater instead of reused. A total of 83.9% of produced waters managed in the US in 2012 were disposed of following the standard industry practice, which is to re-inject it into subsurface formations³. Of these billions of barrels, only 53.7% were re-injected for enhanced oil recovery while the remaining were injected into Class II Underground Injection Control wells³. Therefore, it is crucial to discover technically feasible treatment processes that aid the beneficial reuse of produced water. This is especially true since the recent discovery of the connection between injection and increased seismic activity^{4,5}.

The disposal of large quantities of produced water is negatively impacting the environment around it. Sharp increases in seismic activity in the central US are thought to be caused by subsurface disposal of oil and gas wastewater. Evidence is still being collected to confirm the connection between the two but areas with increased seismicity seem to occur near oil and gas exploration and their disposal operations⁴. The state of Oklahoma has recorded more earthquakes in 2014 of magnitude 3 or greater than the state of California (608 vs. 270)^{5,6} which sits on tectonic plate boundaries. This increased seismic activity is thought to be anthropogenic since the earthquakes occur away from naturally occurring fault zones⁵. In south-central Kansas, earthquakes started occurring more frequently in 2013, about three years after

horizontal drilling, hydraulic fracturing, and subsequent wastewater disposal escalated in that region⁴. Again, the recorded increases in seismic activity and intensity were located near wastewater disposal sites for oil and gas operations. These large volumes of produced water must be handled properly but it is becoming clear that a route other than injection is required.

Produced water reuse could mitigate seismic issues as well as benefit human water demands. An area of great interest for produced water reuse is in agricultural irrigation. Unfortunately, the use of produced water for irrigation is hindered due to its complex, and sometimes toxic, composition. The concentrations of pollutants in produced water are much higher than the tolerable concentrations for agriculture. The quality of produced water varies significantly by region, but contaminants of interest commonly include total dissolved solids (TDS), dissolved organic matter (DOM), particularly dissolved hydrocarbons, and scale-forming cations⁷⁻⁹. The levels of some specific contaminants, such as boron (B), are especially important to agricultural reuse. For example, boron is an essential nutrient to plants up to 0.3 mg/L but can become highly toxic at concentrations that are only marginally greater¹⁰.

Boron is predominantly found in aqueous solutions as boric acid (H_3BO_3) which is a weak acid that has a pKa of 9.14 (20 °C). Due to the high pKa, aqueous boron exists as neutrally charged boric acid, in most produced waters, and it is particularly challenging to remove by most treatment processes¹¹. Boron is present in a wide range of concentrations in produced water. The USGS Produced Water Database v2.3 displays the frequency of boron concentrations present in 4,618 samples taken from national data on produced water quality¹² (Figure 1).

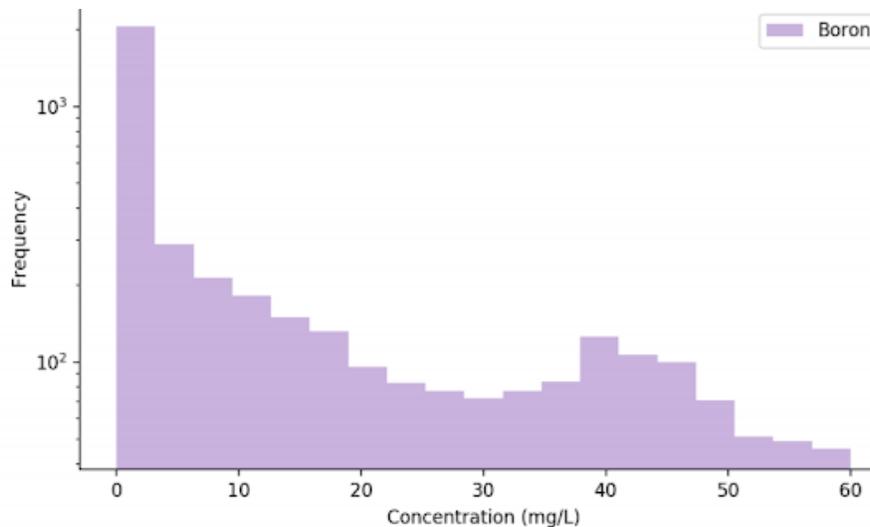


Figure 1: Occurrence of boron concentrations in USGS Produced Water Database

Electrocoagulation (EC) is an emerging pretreatment process that combines the properties of oxidation, coagulation and precipitation and may be viable for produced water treatment. The process of electrocoagulation also presents some advantages over its chemical and physical treatment counterparts. Electrocoagulation is the process of generating coagulant species in situ by electrolytic oxidation of a sacrificial anode triggered by an applied current¹³. Removal of particles is due to the destabilization/neutralization of the forces that keep particles suspended in water¹⁴. The introduction of the coagulant is able to change the surface charge of particles to a point where they can interact and aggregate. While electrocoagulation is relatively untested in full scale processes, the potential for low sludge production and low energy requirements make could it cost efficient¹⁵. More importantly, studies on synthetic produced water using multiple plate electrodes under varying pH and boron concentrations have shown significant removal^{16,17}.

The purpose of this study is to compare the performance of electrocoagulation in synthetically made and real produced water samples. Iron and aluminum sacrificial anodes will be compared under similar conditions to evaluate coagulant performance. While boron removal is the major focus of this research, the effect of removing divalent cations and organic content was also studied. The removal of organic content would be advantageous in preserving the integrity of downstream desalination processes, particularly reverse osmosis. Removal of divalent cations can reduce the potential for scaling and improve water quality, assisting in the goal of agricultural reuse. The effect of divalent cations on the effectiveness EC process was particularly important to address, as these had not been present in the synthetic produced water experiments. Current loading, pH and total dissolved solid (TDS) concentration were manipulated to understand the extent of their effect on boron removal in both types of produced water.

Literature Review

Produced Water Chemistry

Produced water has a complex and variable nature. Characteristics of produced water depend on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced⁹. Produced water properties and volume can even vary throughout the lifetime of a reservoir. Figure 2 below speaks to the variability of produced water^{18,19}. Across the US, the total dissolved concentration ranges from 100 to almost 500,000 parts per million (ppm). The state of Kansas specifically contains a large range of TDS in produced water. The produced water in north east Kansas is of lower salinity peaking at around 50,000 mg/L. In contrast, higher salinity waters are present in southern Kansas ranging from 50,000 to 460,000 mg/L.

There is also great variability in the components of these dissolved solids. Table 1 provides the ranges for major and minor dissolved constituents that are found in produced water^{19,20}.

Table 1: Concentration ranges for inorganic constituents found in produced water^{19,20}

Constituent	Concentration Range (mg/L)
Sodium	0-150,000
Chloride	0-250,000
Magnesium	0-47,000
Calcium	0-74,000
Barium	0-1,700
Strontium	0-6,200
Sulfate	0-15,000
Boron	0-250

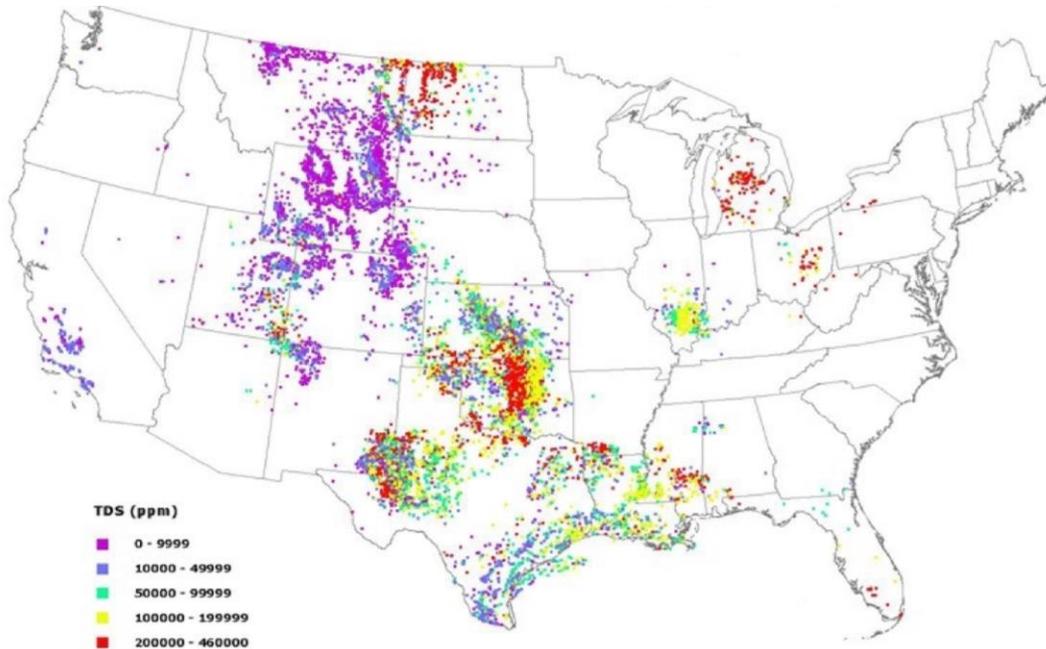


Figure 2: Regional distribution of measured salinities in produced waters across the United States

The salinity, or TDS, present in produced water can be many times greater than that present in freshwater, brackish water and even sea water. TDS values for freshwater are typically less than 500 mg/L while the average for seawater is 35,000 mg/L¹⁹. Some of the individual constituents of produced water alone can surpass these levels. The abundance of TDS in produced water can prove to be quite difficult. The presence of divalent cations, like calcium, magnesium, barium and strontium, leads to the potential of scale formation. Low solubility, supersaturation and interactions with sulfates and carbonates form precipitates that disrupt treatment processes like membrane and thermal desalination. TDS also presents toxicity issues. Produced waters contain high concentrations of metals like barium and strontium. Naturally occurring radioactive material (NORMs) can also be present depending on the geological formation⁹. These constituents need to be managed to avoid human and environmental health complications.

However, removal of these potentially hazardous constituents can be a difficult task. One constituent of interest that is particularly hard to remove is boron. Boron is usually present in water as boric acid and is neutrally charged. This means boron will not be targeted by desalination processes which employ ion exchange or ion exclusion mechanisms. Traditional methods for removing boron, like reverse osmosis, require operation at extreme pH values and boron selective exchange resins¹⁹. The costs associated with tuning these technologies to remove boron are high due to energy requirements and chemical addition.

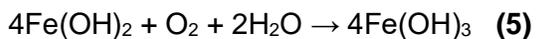
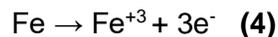
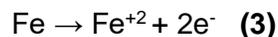
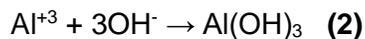
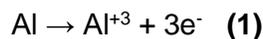
The last major contaminants present in produced water are organics. Organic constituents are normally either dispersed or dissolved in produced water⁹. A majority of the organics present are naturally occurring components of petroleum. Hydrocarbons that occur naturally in produced water include organic acids, polycyclic aromatic hydrocarbons (PAHs),

phenols, and volatiles⁹. Some of these compounds can be toxic to plants. Release of these compounds to surface waters could also lead to sheening or anoxic zones in water bodies¹⁹.

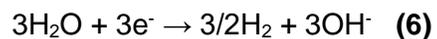
Electrocoagulation

An electrocoagulation reactor contains a cathode, an anode and an external power source. Electrodisolution of the anode and generation of the coagulant is caused by the applied current. The coagulant produced in-situ depends on the metal used during electrocoagulation. Aluminum and iron are most commonly used for this process due to their availability, low toxicity, and high valence¹³. The relevant reactions for both aluminum and iron are in Equations 1-6. Only one oxidation reaction occurs at the anode for aluminum, but monomeric and polymeric aluminum hydrolyzed species can also form in solution. Aluminum hydroxide and these hydrolyzed products are mainly responsible for floc and aggregate formation²¹. For iron, ferric and ferrous oxidation states are possible. Both Fe⁺² and Fe⁺³ can be produced directly from the anode depending on the conditions of the system. However, the iron(III) species are those that favor the coagulation-flocculation process. In particular, ferric hydroxide is the predominant species of coagulant at pH greater than 1²¹. Similar to aluminum, polymeric iron hydrolysis species can be produced as well.

Anode



Cathode



The amount and variety of produced water constituents are significant because they could affect the electro-chemical mechanisms that occur during electrocoagulation. In general the following steps occur during electrocoagulation²¹: 1) Electroodic reactions produce metal ions from anodes by electro-dissolution and H₂ gas evolution at the cathode, 2) destabilization of the pollutants, particulate suspension and breaking emulsions, 3) formation of aggregates of the coagulated, destabilized solid phases as flocs and 4) removal of coagulated and aggregated pollutants by sedimentation or by electro-flotation by evolved H₂. Any one or combination of constituents could interfere with these steps. Divalent cations, in particular, can complicate the EC process through electrode passivation due to scale formation and through solution pH changes due to bulk precipitation reactions.

Electrocoagulation is a versatile treatment process that has gained notice because it has the ability to achieve significant removal for a range of pollutants. Previously limited by the high costs of electricity¹³, electrocoagulation has now found its way into various industries. Tannery and textiles, pulp and paper, food and oil are a few of the industries that have applied electrocoagulation to their wastewater¹⁴. Studies have provided evidence that electrocoagulation can eliminate chemical oxygen demand, turbidity, organic content, dyes, heavy metals and oil-in-water emulsions²². It has been shown that the removal of these pollutants using either aluminum or iron electrodes is significant. Emamjomeh et al.²³ lists the treatment efficiencies of pollutants by electrocoagulation in water and wastewater sources. Oil wastewaters saw removal ranging from 80-99%. Removal of heavy metals like cadmium, chromium, nickel and arsenic ranged from 70-99%. The removal of boron by electrocoagulation ranged from 60-90%. Electrocoagulation also has several additional benefits compared to conventional coagulation, like eliminating the need of purchasing chemical reagents and reducing the risk of secondary pollution¹³. However, there are limitations to the process that can

easily reduce its efficiency if not managed properly. Passivation is the chemical process of increasing the thickness and protective capability of naturally occurring passive films²⁴. Passivation of an electrode is caused by the electrolytic reaction that occurs. The formation of metal hydroxides or other scales produced will inhibit these electrolytic processes²¹. Continued use consumes the sacrificial anode which means regular replacement of the electrodes is required. While electrocoagulation can reduce sludge production compared to conventional treatment¹⁵, it is still quite concentrated, and another process would be needed to handle it. Lastly, these processes are also pH sensitive. Acidic or alkaline conditions cause secondary reactions and dampen the overall efficiency of the EC process. Constant control of the bulk pH, if needed, could be a major complication that may take away from its viability as a treatment option in practice.

Although work has been done to explore electrocoagulation, its progression as a viable method for water treatment has been stagnant. The reason for this is because of how current work has been conducted. Most work done with electrocoagulation has been conducted in small volume, batch reactors and are contaminant specific²². Continued emergence of electrocoagulation will come from more work done on a larger scale and continuous flow conditions to ensure that the benefits are still obtained. More effort is also being put into combining electrocoagulation with other treatment processes. Combining electrocoagulation with biological treatment or downstream treatment processes may provide more effective preparation for specific applications. Ongoing work in this field is needed to address operational issues and to better model the behavior of electrocoagulation units as well as evaluating their performance in continuous flow²².

Previous Work

Previous work on boron electrocoagulation was done here at the University of Kansas by Orion Dollar and Dr. Ming Chen as part of the larger produced water treatment and management project¹⁵. Studies with synthetic produced water examined the impact of operating parameters and water quality on boron removal. The performance of EC to remove boron was compared against chemical coagulation with aluminum sulfate. Time, current intensity, initial B concentration, pH and TDS were explored to determine the optimal conditions for boron removal by electrocoagulation. Models were investigated in order to describe boron removal by aluminum EC. Lastly, several short experiments were done on river water and oil field water sourced from Douglas County. The optimized parameters in the synthetic water were applied to the real waters to determine if similar trends were observed. It was concluded that EC outperformed chemical coagulation under all conditions. Linear models were adequate to describe boron removal up to a concentration of 50 mg/L while the optimum pH was 8. Higher strength waters were also deemed more suitable for EC due to having a higher current limit.

Additional unpublished work done by Dr. Chen focused more on divalent cations and organic removal. Synthetic water experiments were reproduced at pH 8 and at higher applied currents ranging from 0.5 A to 2.0 A and serve as a basis for this work. Increases in removal were observed with increased applied current and longer operating times. However, there was a slight decrease in removal at the same time intervals as TDS increased. Synthetic produced water spiked with phenol saw no measurable organic removal at low concentrations (100 mg/L) and very little at high concentrations (1000 mg/L). In the real produced water, Mg and Ca had great influence on the pH of the solution during the EC process but had no effect on boron removal during pH-controlled electrocoagulation process. This work formed the basis for the current project.

Aim of Study

The work presented in this thesis was built off the knowledge gained from this previous study. In addition to aluminum, boron removal by EC with an iron sacrificial anode was investigated under similar conditions. Real produced water samples from Reno County and Douglas County, KS were used to identify how TDS and the presence of different divalent cations affect boron removal. The ability of EC to remove TOC present in the real produced waters was also investigated during these studies.

Methods and Materials

Materials

Analytical grade sodium chloride (NaCl) and boric acid (H_3BO_3), purchased from Fisher Scientific, were used to prepare synthetic produced water. Boric acid (99.8%)¹⁵ served as the boron source while NaCl was used to adjust the total dissolved solids (TDS) in synthetic experimental trials. Water samples for real produced water experimental trials were sourced from oil production sites in Reno County, KS and Douglas County, KS. Samples were collected using a combination of 5 gallon polyethylene carboys, a GeoTech Geosquirt purge pump and a GeoTech polycarbonate in-line 142mm filter holder filter apparatus with glass fiber and 0.2 micron cellulose acetate filter. Produced water quality was determined using Ion Chromatography for anions (Dionex IC-2000), a PerkinElmer Optima 2000 DV Inductively coupled plasma - optical emission spectrometry (ICP-OES) for cations and boron and a Teledyne Tekmar Torch Total Organic Carbon analyzer (TOC) for organic content. The pH values for both synthetic and real produced water samples were adjusted with 2% percent nitric acid (HNO_3) and 0.25 M sodium hydroxide (NaOH) solutions. Ultrapure water (18.2 M Ω /cm,

Milli-Q Direct 8 system) was the reagent water in the synthetic produced water. pH was measured using an AP85 Portable Waterproof pH/Conductivity Meter.

Three different electrode materials were used during experimentation to produce coagulants in situ. A 99.95% iron rod and a 99+% aluminum rod, purchased from Fisher Scientific and Strem Chemicals respectively, were used as anodes. A 99.999% graphite carbon rod, also purchased from Strem Chemicals, served as the cathode in all experiments. Before experimentation, electrodes (iron, aluminum and carbon) were sanded with sandpaper and placed in 2% HNO₃ solution to remove any form of scaling. Ultrapure water (18.2 MΩ/cm, Milli-Q Direct 8 system) was used to clean all labware in all experiments. A 150 mL Nalgene plastic beaker served as the reactor for the electrocoagulation process. The voltage was supplied by a 30 V DC Extech power source.

Produced Water

Synthetic and real produced water samples were used for comparison in this report. The synthetic water contained 50 mg/L boron and the TDS, added in the form of NaCl, ranged from 2,500-50,000 mg/L. The composition of the real produced water samples was much more complex and differed greatly between the two locations. The Reno County (RC) water had about three times more TDS than the Douglas County (DC) water. In regard to cations, the major difference between the two real produced waters was due to the presence of sulphate. The RC water contains notably more sulfate than the DC water. Since the formation of barium sulfates is favorable in these water conditions, the high sulfate RC water contains negligible amounts of barium while the DC water contains barium, but negligible sulfate. The solubility constants²⁵ of barium sulfate (BaSO₄) and strontium sulfate (SrSO₄) are extremely low (K_{sp} = 10⁻⁹ and K_{sp}= 10⁻⁷, respectively) and form when high concentrations of barium and strontium

ions are present with high sulfate concentrations. The concentrations of each ion present in both real produced waters along with total TDS and shown in Table 2.

Table 2: Concentration of major cations and anions present in produced water samples

Produced Water Ion Composition		
Constituent	Reno County (mg/L)	Douglas County (mg/L)
F^-	6	<i>bdl</i> *
Cl^-	62,294	19,111
Br^-	295	43
SO_4^{2-}	110	2
NO_2^-	17	<i>bdl</i>
NO_3^-	<i>bdl</i>	11
PO_4^{3-}	<i>bdl</i>	<i>bdl</i>
Na^+	25,690	8,691
K^+	329	128
Ca^{+2}	5,170	653
Mg^{+2}	1,422	245
Sr^{+2}	1,595	78
Ba^{+2}	<i>bdl</i>	482
TDS	96,928	29,444

**bdl* = below detection limit. Detection limits for NO_2^- , NO_3^- , PO_4^{3-} and Ba^{+2} are 0.1 mg/L, 0.1 mg/L, 0.1 mg/L and 0.04 mg/L respectively^{26,27}

Synthetic and Real Produced Water Sample Preparation

The real produced water samples required filtering before being used. These samples contained oil and other large particulate matter that either would disrupt the electrocoagulation process or cause human health complications if volatilized during the experiment. All preparations and experiments done with the real produced waters were done in the fume hood. A 0.45 micron cellulose acetate filter was used to remove these constituents. Synthetic water compositions of 50 mg/L boron and 2,500-50,000 mg/L NaCl were made by mixing the appropriate amounts of 500 mM boric acid and 2 M NaCl solutions. Previous experiments¹⁵ suggested that the optimum pH for boron removal was 8 so experiments were conducted at this pH value.

Electrocoagulation Experiments

A 150 mL Nalgene plastic beaker was filled with 150 mL of produced water with the initial pH set to 8. The electrodes were placed into solution about 2.5 cm apart and connected to the 30 V DC power source. A diagram of the setup is shown below in Figure 3. The electrocoagulation process was allowed to run for 60 minutes. Generally, 1 mL samples of the solution were collected at 0, 15, 30 and 60 minutes and diluted to 10 mL with 2% HNO₃. Electrocoagulation studies were conducted at 0.5 and 1.0 A for both synthetic and real produced waters. The desired current was achieved and maintained by changing the electrical potential applied by the DC battery. The potential had to be closely monitored as the required value changed as coagulant was produced in the reactor.

pH changes occurred during the electrocoagulation process. The production and consumption of hydrogen (H⁺) and hydroxide ions (OH⁻) occurred due to the dissociation of water molecules at the cathode and consumption of OH⁻ by the coagulant produced and

potentially by other ions present in produced water. The constant change of pH during the EC process makes it difficult to control during experimentation. In order to mimic a system held at a constant pH value, the bulk solution was adjusted to 8 before collecting samples. Samples were collected every 15 minutes. The power supply was shut off, and the pH was measured. Up to a minute was given to allow the pH to stabilize. Once the measured pH was recorded, the pH was adjusted back to 8.0 using 2% HNO₃ or 0.25 M NaOH as needed. Due to the sensitivity of the system, these reactants were added drop by drop using a pipette. Again, up to a minute was allowed to ensure the pH stabilized at 8. In other experiments, the pH was allowed to change naturally. These experiments are referred to as “unadjusted runs” in this report. After the 15-minute intervals, the pH was measured and recorded but the reactor solution was not adjusted to 8 before sampling. Smaller sampling time intervals (5 minutes) were used in several experiments to more closely monitor how the pH was changing under these unadjusted conditions.

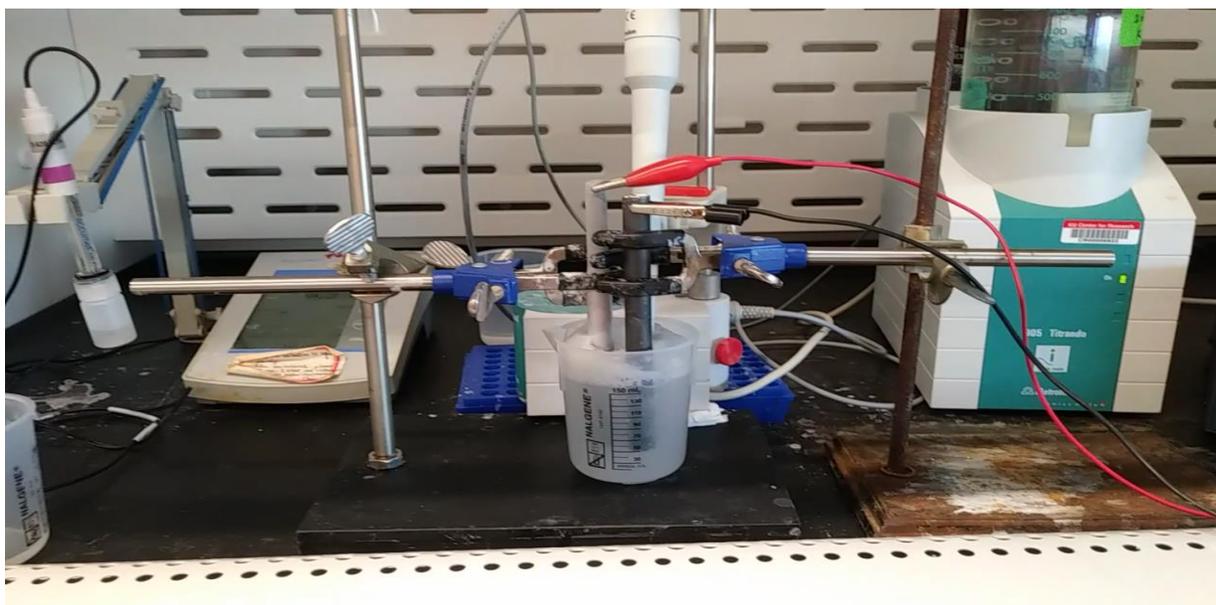


Figure 3: Reactor set up for electrocoagulation process

Sample Analysis

Cations from the samples collected from the reactor were analyzed by using Ion Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The dissolved cations of interest for this study were magnesium, calcium and barium. ICP-OES is sensitive to dissolved solids and has concentration thresholds. Based on the expected concentrations of dissolved solids in the samples, different dilution factors were used for analysis of individual constituents. A list of dilution factors for the cations of interest are displayed below in Table 3. Dilutions for Table 3 are based on the source water concentrations mentioned previously in Table 2. The dissolved aluminum concentration in acidified samples following EC can be estimated by using Faraday's Law¹⁴ of dissolution which is displayed by Equation 7.

$$m = \frac{I * t * M_w}{z * F} \quad (7)$$

I = current in amperes

t = time in seconds

M_w = molecular weight of metal

z = # of electrons involved in reaction

F = Faraday's Constant

The ICP-OES requires user made standards to create a calibration curve for sample analysis. The concentrations for the calibration curves created range from 0 to 10 parts per million (mg/L) and 2% HNO₃ serves as the solvent for these standards.

The analysis of total organic carbon in the produced water samples followed a similar method. Calibration curves were created based on estimated concentrations present in

samples. A 10 ppm Spectro Pure Organic Carbon Standard was used as the stock solution, and dilutions were done manually to create solutions that ranged from 0 to 10 ppm C. Ultrapure water (18.2 MΩ/cm, Milli-Q Direct 8 system) from the lab was used to dilute the 10 ppm Carbon Standard. This calibration curve was then applied to the analysis of the produced water samples to determine the amount of total organic carbon present before and after electrocoagulation.

Table 3: Dilution factors for elements of interest applied for ICP-OES analysis

Constituent	Reno County	Douglas County
B	10	10
Mg	1000	100
Ca	1000	100
Al	1000	1000
Ba	---	100
Fe	1000	1000

Analysis of Solid Samples

After completion of the EC process, the reactor was sealed with Parafilm and given time for the sludge settle to the bottom. The sludge was collected, and excess water was removed by vacuum filtration using a 0.45 micron filter. The wet weight of the sludge was recorded. The filtered sludge was then placed in a drying oven at 105 F overnight. Once dried, the sludge was weighed and digested with 2% HNO₃. Diluted samples of the digested sludge were analyzed by ICP-OES. Based on the recorded dry weights, the concentration values provided by the ICP-OES, the volume of 2% HNO₃ and the volume of the reactor, concentrations of the target constituents present in the reactor at the end of each EC experiment were determined.

Results

Synthetic Water Electrocoagulation

I. Aluminum Sacrificial Anode

Previous electrocoagulation experiments¹⁵ focused on Al as the sacrificial anode. Figure 4 shows boron removal data from these experiments, using NaCl to vary the TDS concentration³¹. pH was held constant at a value of 8 for these experiments. It was observed that more operating time meant more boron removal no matter the TDS concentration at a current loading of 3.33 A/L (applied current = 0.5 A, volume = 0.15 L). However, increasing the TDS concentration decreased boron removal slightly when comparing the same time interval. The percent removal of boron at 3.33 A/L after 60 minutes ranged from 53% to 58%. A similar time trend was observed in the 6.67 A/L current load (applied current = 1 A, volume = 0.15 L) except for when TDS was 2,500 mg/L NaCl. This suggests that a high current load in low TDS solutions reduces boron removal. The reduction in removal may be due to the production of solids with lower adsorptive capacity. Lower strength waters have a lower current limit which promotes the formation of more crystalline solids that have lower boron adsorption capacity than the amorphous, unstructured solids formed in high strength waters¹⁵. The percent removal of boron for 6.67 A/L current load applied for 60 minutes, for 2,500, 25,000 and 50,000 mg/L TDS were 43%, 71% and 68% respectively.

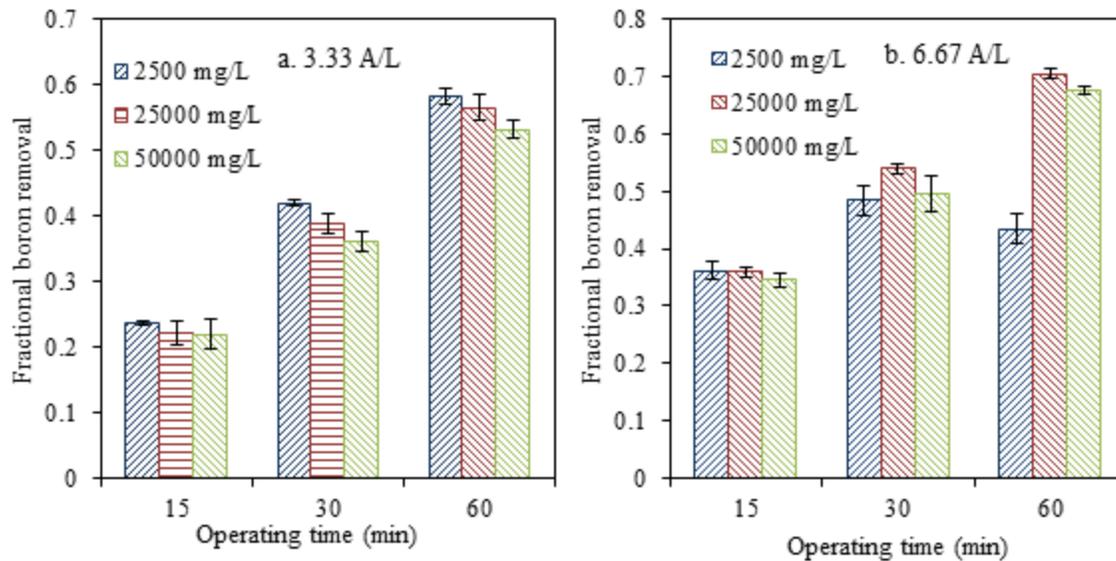


Figure 4: Boron removal with varying TDS as NaCl. *Left:* Current loading of 3.33 A/L; *Right:* Current loading of 6.67 A/L³⁰.

Present work was done at 0.5 A (or 3.33 A/L) to provide a reference point for experiments using Al as the sacrificial anode. Reproducibility of previous results were desired to ensure removal trends were consistent. While overall boron removal was generally lower than in the previous study, results still displayed the same trend for boron removal in regard to operating time (Figure 5). Percent boron removal for these experiments ranged from 42% to 55%. Present work deviates slightly from work by Chen et al. with slightly lower boron removal overall and slight increases in boron removal with TDS except at 25,000 mg/L. The synthetic water conditions may be sensitive enough to be affected by the experimenter's setup. pH was not recorded during this phase of experimentation but could have been a factor in the reduced boron removal.

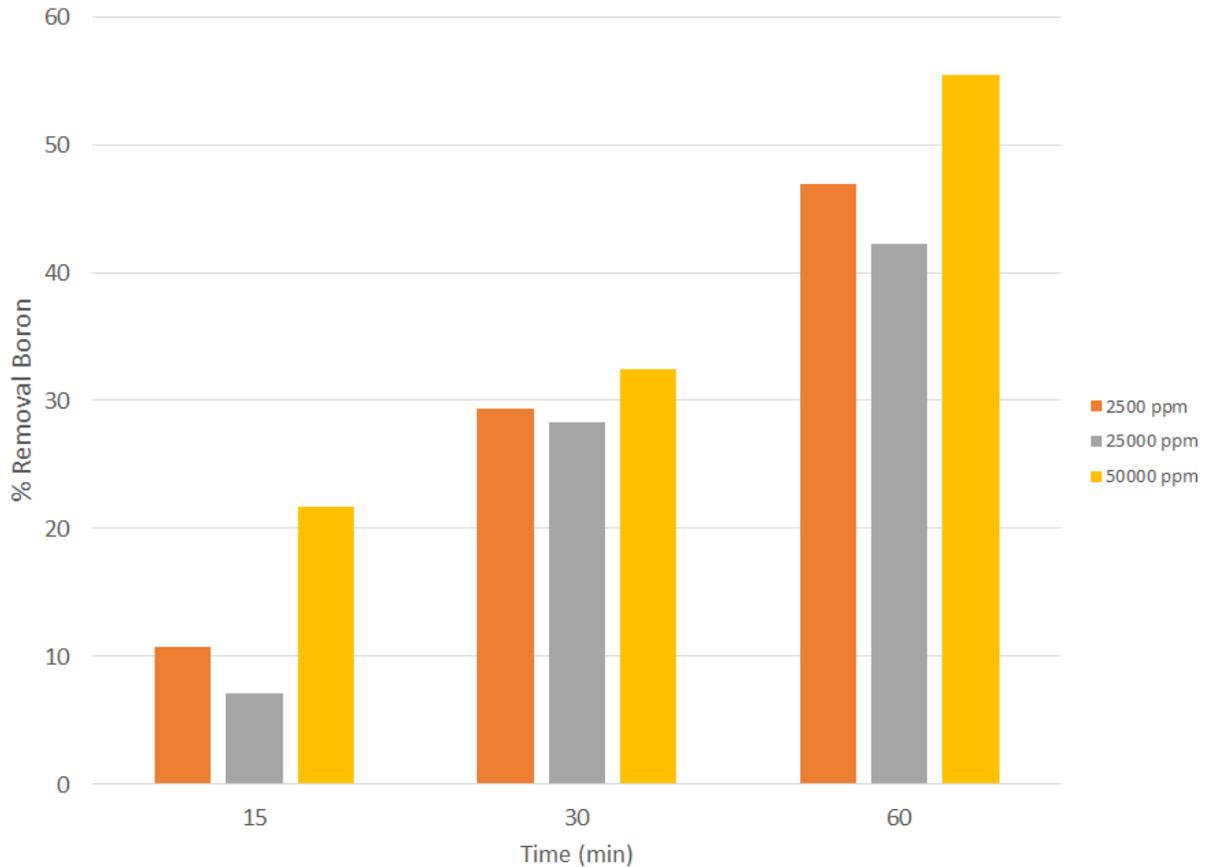


Figure 5: Percent removal of boron at varying total dissolved solid concentrations at 0.5 A

Data in Figure 6 shows the total concentration of aluminum in the electrocoagulation reactor at 15-minute intervals. All aluminum concentrations were super-Faradaic in the reactor by as much as 17%. The term super-Faradaic simply refers to dissolved metal concentrations being greater than theoretical amount calculation by Equation 7. Aluminum dissolution follows the expected pattern, with increasing levels of Al^{+3} released as the current increases. This information, paired with the increased removal seen, suggest that Al release is relatively consistent with time, leading to greater B removal as the reaction proceeds and more coagulant forms.

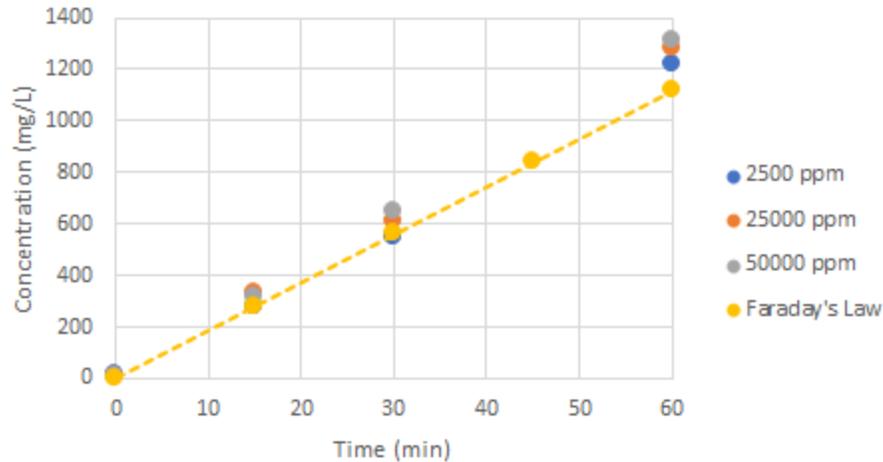


Figure 6: Dissolution of aluminum from sacrificial anode during 60 minutes of electrocoagulation at 0.5 A

II. Iron Sacrificial Anode

Experiments using iron sacrificial anodes in place of aluminum were conducted to explore the relative performance of these two metals for boron removal. The effect of total dissolved solids on boron removal was the first metric explored. As stated previously, the synthetic produced water contained 50 mg/L boron, with additional TDS composed solely of NaCl. Boron removal increases with an increase in total dissolved solids (Figure 7). At 2,500 mg/L NaCl there was a 5.7% removal of the boron present in solution. Conversely, a removal of 17.5% was observed at 50,000 mg/L NaCl. The reason for this trend can simply be explained by the relationship between TDS and conductivity.

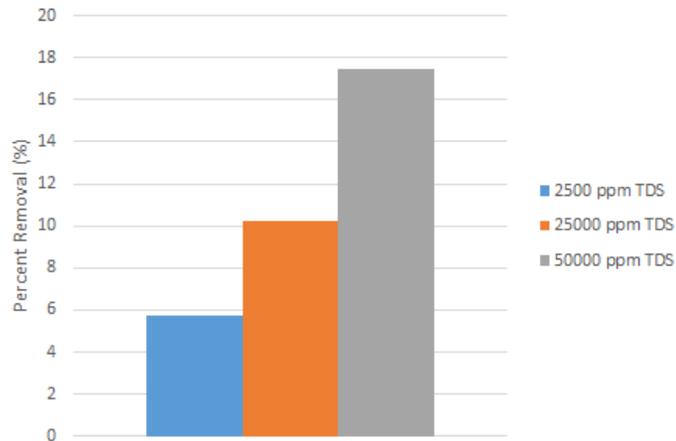


Figure 7: Percent of boron removed with varying total dissolved solids concentration

It is known that the coagulant species are generated in situ through electrodisso- lution by the current being applied to the system¹³. Referencing Equation 7 and assuming all other variables remain constant, increasing the current will increase the amount of coagulant generated. ICP-OES analysis was conducted on samples to determine the amount of iron present in solution. It was confirmed that much more coagulant was produced at 50,000 mg/L NaCl compared to the 25,000 and 2,500 mg/L solutions. The final dissolved iron concentration for 50,000 mg/L was 4,213 mg/L. The iron concentrations for TDS concentrations of 25,000 mg/L and 2,500 mg/L were 2,734 mg/L and 2,676 mg/L respectively. This can be seen in Figure 8 below. The expected amount of coagulant produced, according to Faraday’s Law, is included in Figure 8. It should be noted that the lower TDS concentration synthetic waters did not reach the theoretical amounts of coagulant.

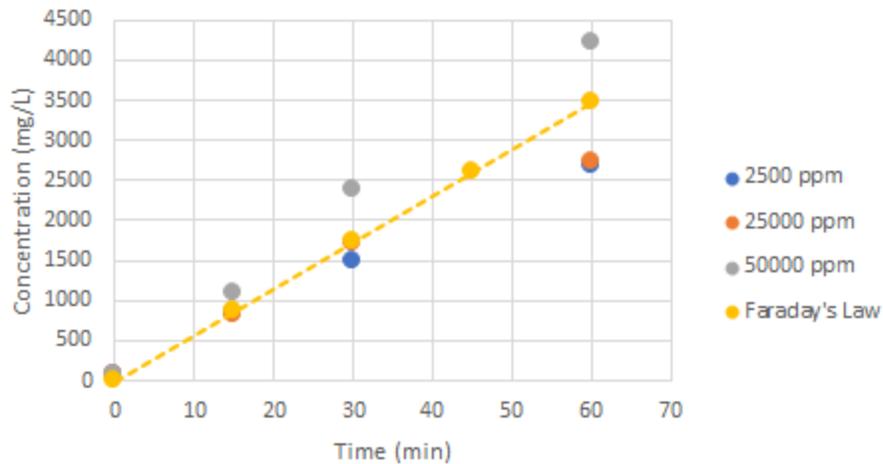
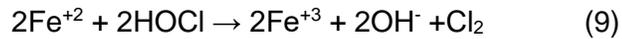
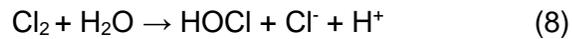


Figure 8: Dissolution of iron from sacrificial anode during 60 minutes of electrocoagulation at 0.5 A

The sub-Faradaic trends for iron are different from what was observed with the Al-EC synthetic experiments. This is believed to be due to the different nature of the metals. Current efficiency or faradaic yield is a correction factor placed on Faraday's Law to account for parallel chemical reactions that affect the dissolution of the anode¹³. The value for current efficiency is greater than one when chemical and electrolytic oxidation of the anode occur simultaneously. Aluminum anodes are known to frequently have current efficiency greater than one during electrocoagulation because of the aluminum interactions with chloride ions^{13,15}. Evidence of this is present in Figure 6 where all aluminum concentrations were greater than Faradaic calculations. Previous Al-EC work done by Dr. Chen also showed super-Faradaic behavior¹⁵. Iron, on the other hand, has more complex reaction chemistry due to iron's multiple oxidation states. Some studies have reported current efficiencies between 80% and 100% and others have reported discrepancies between the estimated theoretical amount of iron dissolved and the actual amount¹³. The iron concentrations are thought to be super-Faradaic for the 50,000 mg/L synthetic TDS because of the presence of Cl⁻. Reactions 8 & 9, below, are efficient when the Cl⁻

concentration is greater than 600 mg/L after considering the amount consumed by the current. It is possible that the 50,000 mg/L TDS solution was able to accommodate these reactions. It is uncertain how much of the Cl^- present in the synthetic water is oxidized by the current but the slight increase of iron dissolved with increasing TDS may be evidence of this. Iron (III) also forms complexes with Cl^- in solution that could further speed up iron dissolution as the chloride concentration increases.



The pH of the synthetic water was the next parameter to be adjusted during these experiments. The pH of the solution will determine the ultimate oxidation state, at equilibrium, of the iron coagulant produced during the electrocoagulation process. Fe^{+2} (ferrous) and Fe^{+3} (ferric) are the possible oxidation states for dissolved iron. Studies show that it is probable that Fe^{+2} is released from the anode¹³ however oxidation from Fe^{+2} to Fe^{+3} strongly depends on both pH and redox potential (Figure 9)^{13,14}. A suggested method for improving the oxidation rate of Fe^{+2} to Fe^{+3} in an EC reactor is to introduce another oxidant¹³, but this was not attempted in these experiments.

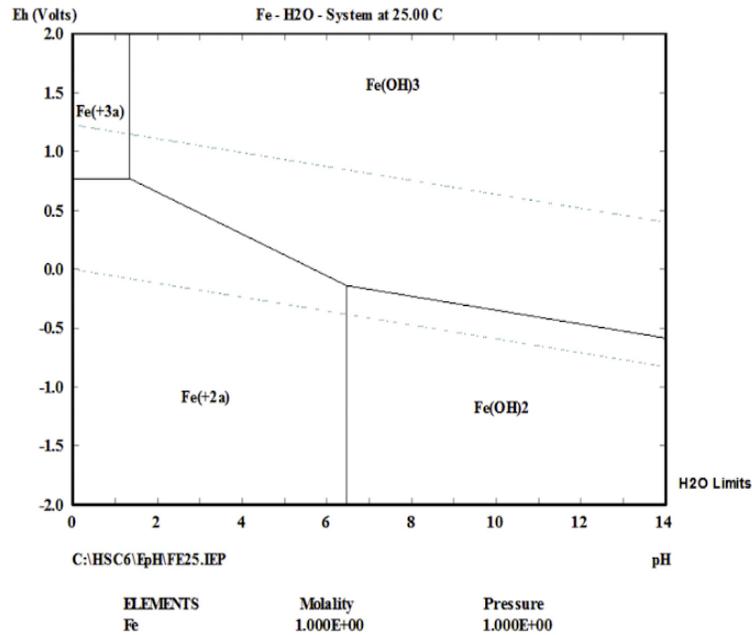


Figure 9: Pourbaix diagram of iron species at 25 C

In alkaline or neutral solutions, iron (II) (Fe^{+2}) is immediately transformed into ferrous hydroxide ($\text{Fe}(\text{OH})_2$), which is then immediately oxidized to ferric hydroxide $\text{Fe}(\text{OH})_3$ ^{0 13} if there is an adequate amount of oxygen available. $\text{Fe}(\text{OH})_3$ (s) precipitates rapidly and it is efficient for adsorbing pollutants. However, the quick oxidation of Fe^{+2} to Fe^{+3} and the precipitation of Fe^{3+} as $\text{Fe}(\text{OH})_3$ (s) reduces the total amount of iron dissolved into solution¹³. On the other hand, in acidic conditions the interaction with dissolved oxygen is slowed and more iron (II) remains dissolved in solution.

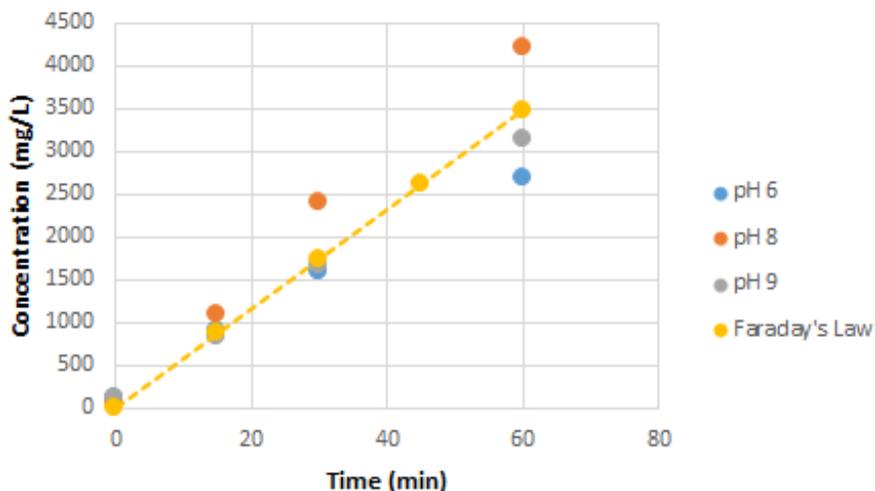


Figure 10: Dissolution of iron coagulant at 50,000 mg/L TDS as NaCl at varying pH values

Figure 10 shows the amount of iron dissolved into solution at a range of pH values. TDS was 50,000 mg/L as NaCl for each experiment. Iron concentrations are below expected concentrations at pH 6 and 9 but super-Faradaic at pH 8. Table 4 shows that boron removal decreased as the pH increased. The percent removal drops slightly from 23.7% to 17.5% when the pH increases from 6 to 8. A greater decrease in boron removal was observed at pH 9 with a value of 6.8%. Again, sub-Faradaic concentrations of iron are present in the reactor. pH 6 also yielded the best removal even though it had the lowest total iron concentrations. This pH trend can be attributed to the charge of the solids present in solution. The net surface charge of the iron hydroxide solids formed becomes more negative as the conditions become more alkaline¹⁴. This is also true of the negatively charged borate ion. Repulsive coulombic forces would lead to poor interactions between boron and iron leading to limited adsorption, thus poor boron removal.

Table 4: Percent of boron removed at varying pH values

% Removal of Boron		
pH 6	pH 8	pH 9
23.7%	17.5%	6.8%

The dissolution trends are a bit more difficult to explain. The current efficiency was expected to be greater than 1 under acidic condition and less than 1 in alkaline conditions¹³. At low pH values, corrosion reactions are thought to be the reason for current efficiencies greater than one. On the other hand, high pH values promote secondary reactions and oxygen evolution at the anode, leading to current efficiencies less than one¹³. Only the data from pH 9 agrees with these reported claims. Similar to aluminum, super-Faradaic iron concentrations would be due to chemical dissolution and electrolytic oxidation occurring simultaneously. pH adjustments for the adjusted synthetic experiments at a value of 6 should have promoted this situation. Fe⁺² oxidation occurs slowly under acidic conditions. Since dissolved iron concentrations are sub-Faradaic at pH 6, some reaction would need to occur to oxidize the abundant Fe⁺² to Fe⁺³. Fe⁺³ formation would result in a decrease in total dissolved iron concentration because the reactions requires an extra electron^{13,14}. While it is unknown what exact reaction happened, extreme pH values near the cathode may be an explanation. Under alkaline conditions, above 8.5, Fe⁺² oxidation occurs quickly, leading to the formation of Fe⁺³ and its solids. This train of thought would also support the sub-Faradaic concentrations observed at pH 9.

Real Produced Water Electrocoagulation

Experiments on real produced water used samples from wells in Reno County (RC) and Douglas County (DC), Kansas. The two waters are quite different in terms of salinity and composition. Similarly to the synthetic water experiments, the parameters of interest were total dissolved solids, pH and current. In addition to these, the impacts of divalent cation concentration and organic carbon removal were explored. All experiments were conducted using an aluminum sacrificial anode. The results in the sections below provide a better idea of how significant each of these parameters would be in practice.

I. Reno County

Current Effect on Boron Removal

Electrocoagulation experiments were conducted at 0.5 A and 1.0 A using an Al anode to be comparable to the work mentioned in previous sections. Table 5 shows results gathered from both reactors after 60 minutes of electrocoagulation. It can be observed that the trend of increasing boron removal with increasing current still holds. The total dissolved solids concentration of the RC water is about twice that of the most concentrated synthetic water experiment. However, the boron removal is comparable to that from the synthetic water (Figures 4 and 5). Compared to the 50,000 mg/L synthetic water experiment, the boron removal is only about 5% greater at 0.5 A and 4% higher at 1.0 A.

Table 5: Boron removal from Reno County produced water at varying applied currents

Current vs. Boron Removal			
0.5 A	Mass Removed (mg)	1.0 A	Mass Removed (mg)
60.8%	4.28	71.4%	5.03

pH Effect on Boron Removal

All experiments, unless specified otherwise, were conducted after initially adjusting the pH to 8. The pH was maintained at this value during the experiment by adjusting the system with either HNO₃ or NaOH. The behavior of the system was monitored by tracking the pH at different time intervals. The pH was recorded after each time interval and then adjusted back to 8 before restarting the experiment. Figure 11 displays data points from multiple experimental runs at 5 and 15-minute intervals. It can be observed that the pH of the systems decreased rather quickly, within the first 5 minutes, to values as low as 4.15. As the experiment continued the pH of the system increased to a value around 6.5-7.0. It was also observed that the pH never returns to the initial adjusted value of 8.

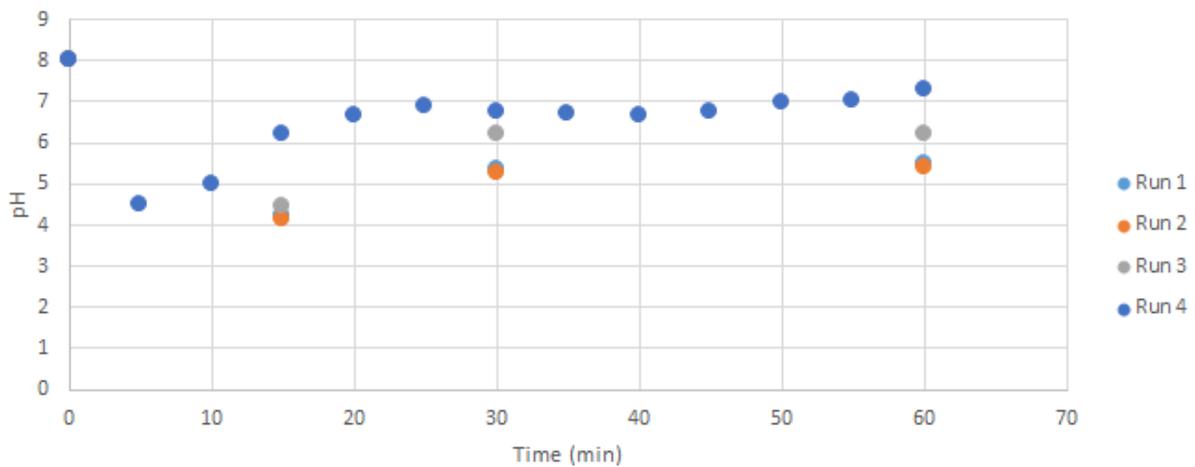


Figure 11: Bulk pH values of the reactor at 5 and 15-minute intervals

The behavior of the system was also monitored when the pH was not adjusted. Again, there was a sharp decline in pH but it did not occur as quickly. The pH in the unadjusted scenarios decreases to a value as low as 4.08 in about 15-25 minutes of electrocoagulation. As the experiment continued, the pH increased to a value of about 6 after 60 minutes (Figure 12).

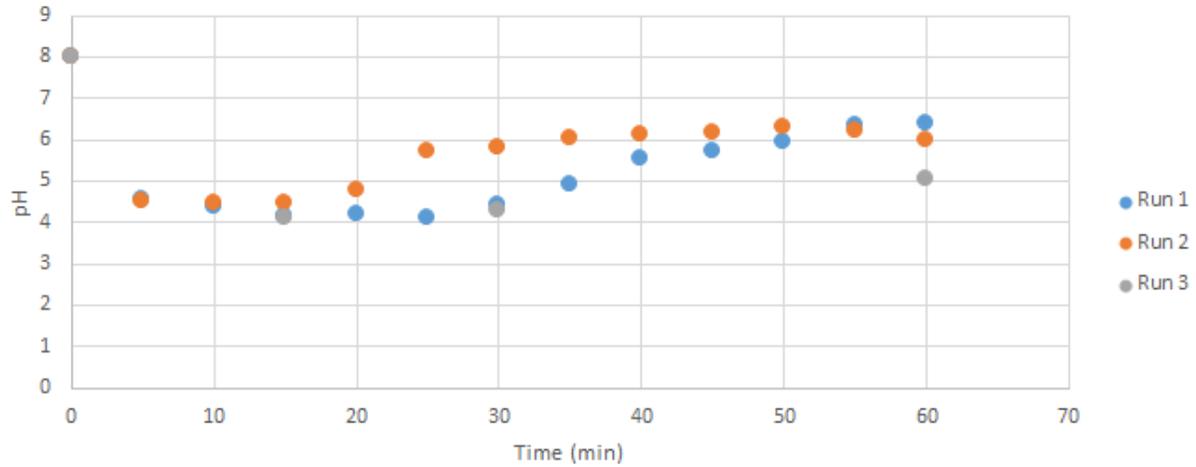


Figure 12: Bulk pH values of the reactor at 5 and 15-minute intervals when pH is not adjusted

Samples taken from both scenarios were analyzed to quantify the effect of pH on boron removal. The initial concentration of boron in the RC produced water was 8-10 mg/L. Table 6 has this data side by side and shows that boron removal decreased notably when pH was not adjusted to a value of 8. It should be noted that the initial boron concentrations from ICP analysis for adjusted Runs 1, 2 and 3 were 46.9 mg/L, 41.6 mg/L and 7.23 mg/L respectively. Initial boron concentrations in unadjusted Runs 1, 2 and 3 were 8.87 mg/L, 8.87 mg/L and 5.88 mg/L respectively. When the pH was not maintained, boron removal drops to as low as 23.6%. This removal is lower than what was observed in data collected at shorter operating times and lower applied current.

Table 6: Comparison of boron removal in adjusted and unadjusted pH conditions

Boron Removal						
	Adjusted			Unadjusted		
	Initial Concentration (mg/L)	Mass Removed (mg)	% Removal	Initial Concentration (mg/L)	Mass Removed (mg)	% Removal
Run 1	46.9	5.03	71.4	8.87	0.41	31.0
Run 2	41.6	4.59	73.6	8.87	0.31	23.6
Run 3	7.23	0.77	70.5	5.88	0.27	30.8

Divalent Cation Removal

Calcium, magnesium and strontium are the major divalent cations present in the RC produced waters. Removal of these cations was explored to further understand the water quality treatment capabilities of electrocoagulation. As was done with boron, the removal of these cations was observed in conditions where the pH was adjusted periodically and where the pH was not adjusted.

Calcium was the most abundant divalent cation with concentrations around 5,200 mg/L (Table 2). Despite its abundance, removal was poor. Percent removal for calcium was roughly 16% at best when pH was maintained at 8. This value decreased to about 5% when there was no pH control. A possible mechanism for calcium is precipitation as CaCO_3 or Ca(OH)_2 . The K_{sp} values at 25 C for these compounds are 3.36×10^{-9} and 5.02×10^{-6} respectively²⁸. Saturation calculations using Debye Huckel activity corrections to account for ionic strength (using equations 10-12) suggest that the Reno County water is saturated for CaCO_3 and undersaturated for Ca(OH)_2 . However, this approach is better suited to lower ionic-strength waters ($I \leq 0.5 \text{ M}$). Modelling done by Dr. Edward Peltier in PHREEQC using Pitzer equations to

better account for the ionic interactions in high strength solutions, however, also indicate that the solution was saturated for CaCO_3 ²⁹. In comparison to the Ca^{+2} concentration, the alkalinity in the Reno County water is small. The low percent removals of calcium are thus attributed to the low alkalinity present.

$$I = 0.5 * \Sigma([M]_i * Z_i^2) \quad (10)$$

$$\log \gamma_i = -AZ^2\sqrt{I} \quad (11)$$

$$K_{sp} = \gamma_a[A] * \gamma_b[B] \quad (12)$$

The removal of strontium was even poorer than calcium. In fact, there was no removal of strontium and this was the case in both adjusted and unadjusted pH conditions. Strontium would be removed during precipitation as either SrCO_3 or Sr(OH)_2 . Again, modelling using Pitzer corrections for ionic strength suggest that neither Sr(CO)_3 nor Sr(OH)_2 would ever be saturated under these conditions²⁹. Electrocoagulation consistently produced little or no removal of both calcium and strontium. This suggests that electrocoagulation either is not suitable for these cations or the process would need to be optimized for these cations.

Magnesium behaved differently during the electrocoagulation process. Notable removal of magnesium was observed after 60 minutes of electrocoagulation. The removal of magnesium seems to be pH dependent as well because a large decrease in removal is observed when the pH is not controlled (Table 7). Most experiments saw removals around 35% but one saw an abnormally high removal of 80%. It should be noted that removal without pH control for that experiment was also unusually high. Magnesium can be removed from solution by precipitating as Mg(OH)_2 . Precipitation of Mg from solution occurs at roughly pH 11 under freshwater conditions. This would be well above the recorded bulk pH during electrocoagulation but

possible close to the cathode where OH^- is concentrated. Saturation index calculations using the Debye Huckel method were done to evaluate the pH requirement for precipitation under these conditions. The calculations suggested that magnesium would precipitate between 9.06 and 9.15. These values are not too much higher than the adjusted pH conditions and may exist near the cathode, where the solution is H^+ deficient due to reduction to H_2 . This provides further evidence that this is the mechanism by which Mg is being removed.

Table 7: Comparison of magnesium removal in adjusted and unadjusted pH conditions

Magnesium Removal				
	Adjusted		Unadjusted	
	% Removal	Mass Removed (mg)	% Removal	Mass Removed (mg)
Run 1	34.9	86.55	4.0	9.6
Run 2	37.3	88.20	0	0
Run 3	79.7	197.55	22.5	68.55

It was expected that the removal of these divalent cations could occur due to precipitation of their hydroxide forms. To evaluate this, the blanket of sludge produced was analyzed to see if these cations were present. Settled sludge from both adjusted and unadjusted pH conditions were analyzed. Most of the sludge consisted of aluminum but it was also part magnesium and calcium. In addition, the composition of the flocculant depended on pH. Visual representations of the sludge composition are displayed in Figure 13. When the pH of the system was not controlled, aluminum made up about 87% of the sludge while magnesium and calcium comprised 6% and 7% respectively. The composition shifted when the pH was controlled. Aluminum was still the majority of the sludge at 57%. The percent of magnesium

increased greatly to 29% while the percent calcium increased slightly to 14%. Table 1 in the Appendix shows the changes from adjusted to unadjusted by mass of the shown cations.

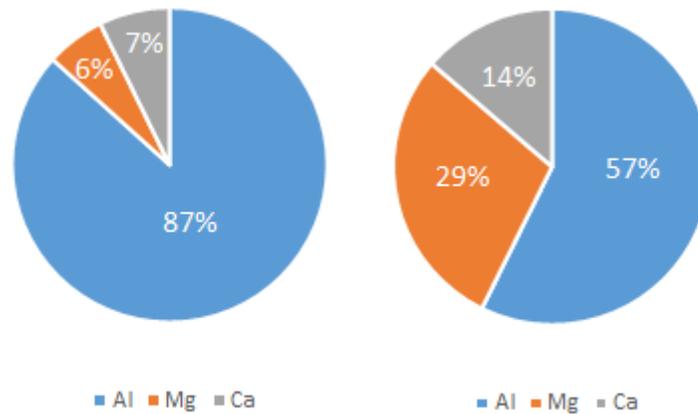


Figure 13: Composition of flocculant produced during electrocoagulation in Reno County produced water. *Left:* Unadjusted pH. *Right:* Adjusted pH.

Organics Removal

The total organic carbon (TOC) present in the RC produced water was measured at 140 mg/L prior to electrocoagulation experiments. As seen in Figure 14, electrocoagulation had only a small effect on TOC removed. The amount of TOC removed did not seem to be affected by pH adjustments. After 60 minutes of electrocoagulation 10.1% of organic carbon was removed in adjusted pH conditions and 13.9% was removed in unadjusted conditions.

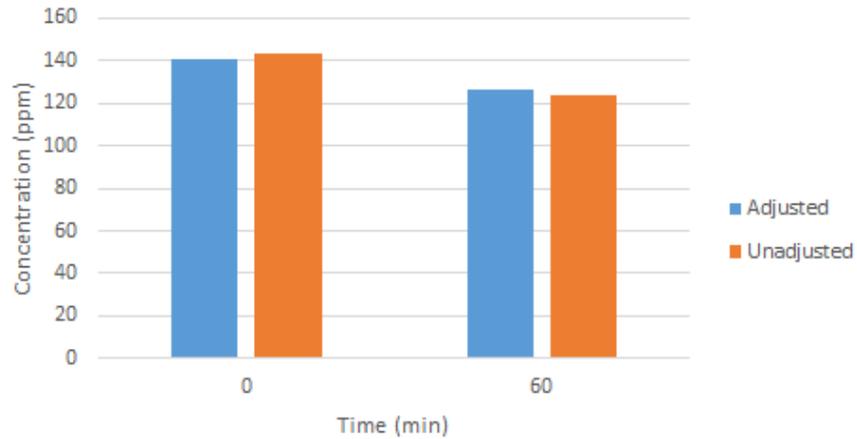


Figure 14: Total organic carbon removed during electrocoagulation process

The figure below depicts data collected in unpublished work by Dr. Chen³¹. The organic carbon present in those systems was phenol. No removal was observed when concentrations were set at 100 mg/L but 13.4% removal was observed when the concentration was increased to 1000 mg/L.

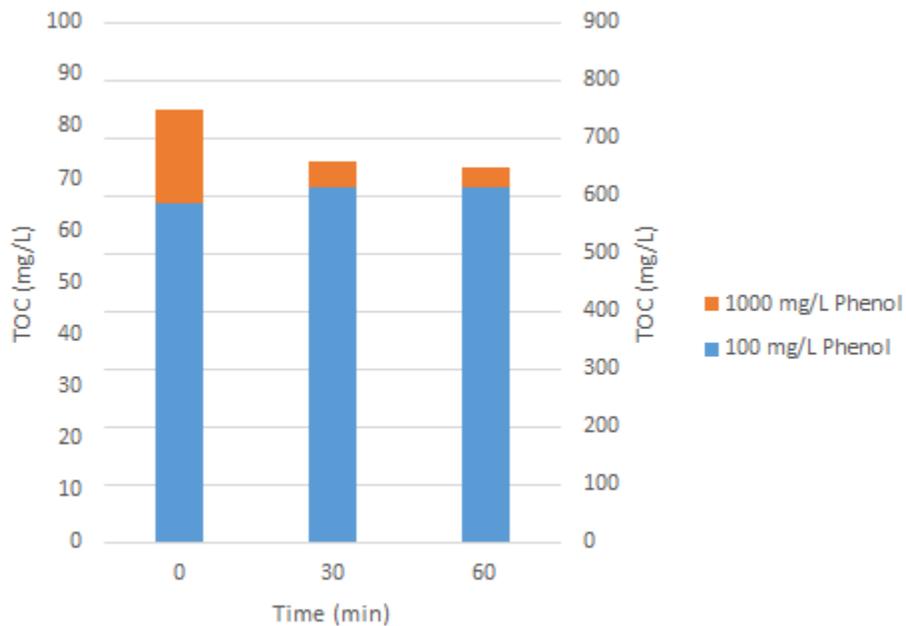


Figure 15: Change in phenol concentration during 60 minutes of electrocoagulation³¹

II. Douglas County

The DC produced water was the less saline of the two real produced waters, with a TDS measured at 29,000 mg/L (Table 2). The composition of these dissolved solids is also slightly different with barium being present and strontium concentrations being much lower than in the RC produced water. Figure 16 is a visual representation of how the composition differs in the two waters. As with the RC water, experiments on the DC produced water were conducted to observe the effects of TDS, pH, and divalent cation content on boron removal.

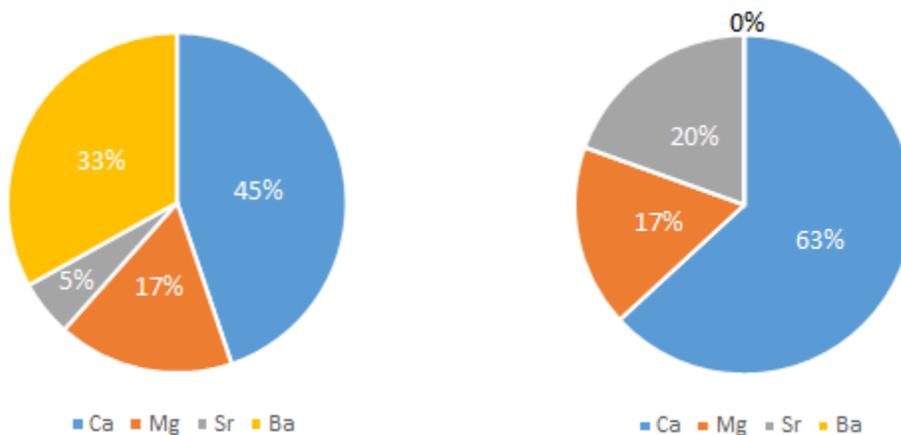


Figure 16: Composition of major cations in real produced water by percentage

pH Effect on Boron Removal

Again, manipulation of bulk pH involved adjusting the pH to a value of 8 periodically for some experiments during the electrocoagulation process, while the pH was not adjusted in other experiments. The initial pH for every experiment was adjusted to 8. Figure 17 below shows the recorded pH values for both conditions. When the pH was not adjusted during electrocoagulation the pH decreased slowly for 30 minutes to values around 6.5. After 30

minutes the pH plateaus to a value of about 7. In adjusted pH conditions, the pH decreases again to about 6.5 but does so in about 20 minutes. The pH afterward increases more than in uncontrolled pH conditions. An increase to values around 8 were observed. This was the first time where the system returned to the initial adjusted pH value. To this point, it must be mentioned that the pH of the raw produced water samples ranged from 7.00 to 7.33 and little adjustment was needed from the beginning.

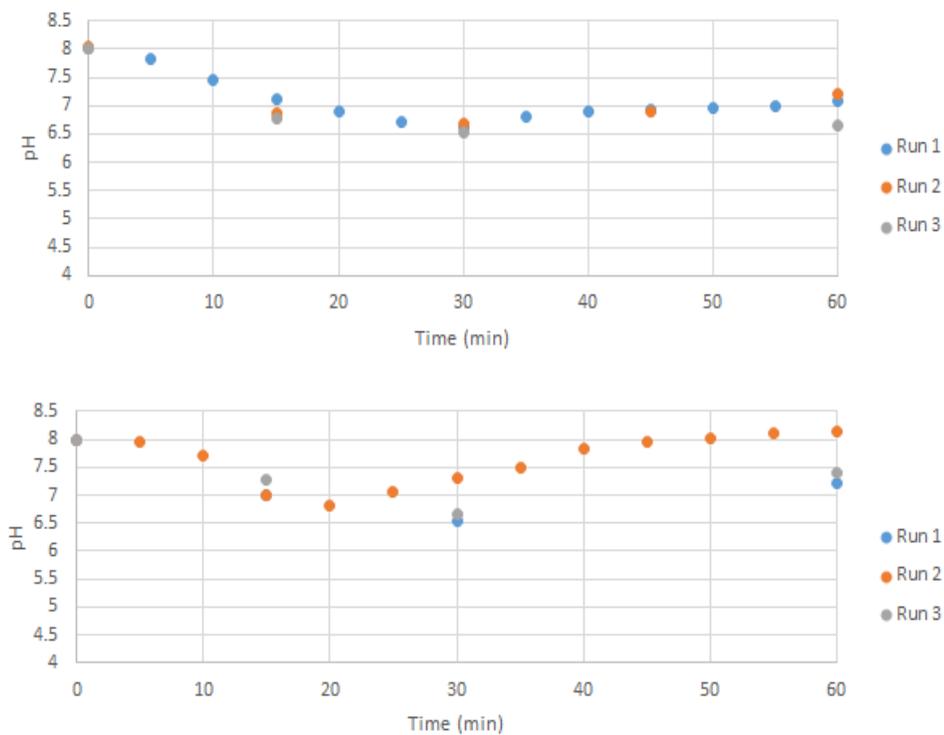


Figure 17: Bulk pH values of the reactor at 5 and 15-minute intervals. *Top:* Unadjusted pH. *Bottom:* Adjusted pH

Observing how the pH changes in Figure 17, it seems that the pH starts to stabilize after roughly 30 minutes. This trend was observed in the Reno County water too, but the stabilization occurred sooner (15-20 minutes). The fact that aluminum is known for super-Faradaic behavior

was previously mentioned. However, if aluminum production continues past 30 minutes, consumption of OH⁻ should still decrease the pH of the system. Figure 18 shows Faradaic and super-Faradaic concentrations of aluminum present in the reactor. Scale formation on the cathode during the EC process may be the culprit. The presence of scale may be reducing the rate of production of OH⁻ to the point where it matches the rate of consumption by the aluminum coagulant produced, and by magnesium and calcium present in solution. Another explanation may be chemical dissolution¹³. Secondary reactions may be occurring depending on whether or not the system is acidic or alkaline (Eq.13-16). Even if electrolytic oxidation of the anode is subpar, chemical dissolution may be occurring at a rate that stabilizes the bulk pH.

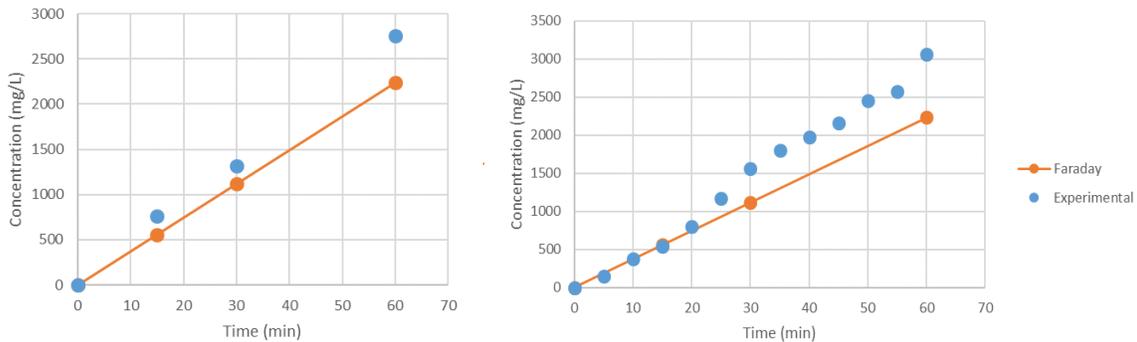
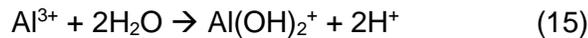


Figure 18: Dissolution of aluminum from the sacrificial anode during 60 minutes of electrocoagulation in produced water. *Left:* Adjusted pH. *Right:* Unadjusted pH

The amount of boron present in the DC produced water was roughly 3 mg/L. This value is three times lower than the amount present in the RC water. Initial boron concentrations in adjusted pH experiments 1-4 were 11.3 mg/L, 5.3 mg/L, 5.13 mg/L, and 53.91 mg/L* respectively. Unadjusted experiments 1-3 had initial boron concentrations of 2.92 mg/L, 3.44 mg/L and 3.53 mg/L respectively. The adjusted versus unadjusted pH trend continued in this produced water (Table 10). The percent of boron removed when the pH was maintained at 8 was roughly 40%. This value dropped notably to roughly 15% when the pH was not adjusted. It should be noted that the results from the adjusted pH experiment underperform when compared to the 25,000 mg/L, 1 A synthetic produced water experiments in Figure 4. To ensure this substandard performance was not affected by the initial low concentration of boron a sample of the produced water was spiked with 50 mg/L. After 60 minutes of electrocoagulation, the spiked water saw improved removal of 57%. However, this value still does not meet the expectations of the synthetic water experiments and final concentrations of boron were still higher than in the original experiment.

Table 8: Comparison of boron removal in adjusted and unadjusted pH conditions

Boron Removal						
	Adjusted			Unadjusted		
	Initial Concentration (mg/L)	% Removal	Mass Removed (mg)	Initial Concentration (mg/L)	% Removal	Mass Removed (mg)
Run 1	11.3	41.6	0.71	2.92	15.8	0.069
Run 2	5.3	42.8	0.34	3.44	12.5	0.065
Run 3	5.13	25.7	0.20	3.53	0	0
Run 4*	53.91	56.6	4.58	---	---	---

*Spiked with 50 mg/L B as boric acid

Divalent Cation Removal

Calcium, magnesium, barium and strontium are the divalent cations present in the DC produced waters. Calcium was the most abundant among the divalent cations. Percent removal for calcium averaged 23% when pH was maintained at 8. This average decreased to about 14% when there was no pH control. This further suggests that calcium removal occurs, but to a limited extent, during electrocoagulation. There was no removal of strontium which is consistent with the RC produced water experiments. Barium was the new divalent cation present, but removal was minimal. The peak removal of barium was 6.3% and averaged 3.3% removal (Table 9) under pH adjusted conditions. The removal ultimately dropped to 0% when pH was not adjusted.

Table 9: Comparison of barium removal in adjusted and unadjusted pH conditions

Barium Removal				
	Adjusted		Unadjusted	
	% Removal	Mass Removed (mg)	% Removal	Mass Removed (mg)
Run 1	6.3	5.04	0	0
Run 2	2.7	2.16	0	0
Run 3	1.0	0.71	1.7	1.35

Once again, notable magnesium removal occurred during the electrocoagulation process. Percent removal values from 60%-70% were observed in adjusted pH conditions. The pH dependency of magnesium removal continues as removal decreased essentially to zero when the pH was not controlled (Table 10).

Table 10: Comparison of magnesium removal in adjusted and unadjusted conditions

Percent Removal Magnesium				
	Adjusted		Unadjusted	
	% Removal	Mass Removed (mg)	% Removal	Mass Removed (mg)
Run 1	62.2	32.55	0	0
Run 2	70.4	34.35	0	0
Run 3	67.4	17.21	0.8	0.38

Organics Removal

The amount of total organic carbon in the DC produced water was measured to be 80 mg/L. This is close to half the concentration present in the RC waters. The removal of organics was even poorer compared the removal observed in the Reno County water. After 60 minutes of electrocoagulation, no organic carbon was removed in both adjusted and unadjusted pH conditions. The organic content present in produced water can range from dispersed oil and grease to dissolved or soluble organic compounds. Among those that are dissolved or soluble are organic acids, polycyclic aromatic hydrocarbons (PAHs) and phenols⁴. Coagulation has the ability to remove organic material, but this depends on the type of organic material present. If a large percentage of the organics present are heavy, large, positively charged NOMs, then EC would have a greater ability for removal. EC will have less ability to remove phenols and other similar hydrocarbons because of their non-polar nature. The poor removal of organics in these experiments may speak to the characteristics of the organic content present in the RC and DC produced waters.

Conclusions

Electrocoagulation of real produced water showed similar success to previous synthetic water experiments. Comparable values for percent removal of boron was recorded in the real produced waters even though initial boron concentrations were much lower. The trend of increasing removal of boron with increasing TDS was also consistent in the real produced waters. The major differences between synthetic and real produced waters originate in the composition of the water and the pH during experimentation. Over the course of each EC process, the bulk pH saw a sharp decrease followed by stabilization of the pH(a value of ~6.5 for RC and ~8 for DC). This is opposed to the increasing pH trends observed in the synthetic water. It was concluded that these trends are due to the presence of divalent cations, more specifically Mg and Ca. However, among the divalent cations present magnesium was the only one that saw significant removal. Organic material also saw little to no removal during the EC process. This leads to the conclusion that co-removal of these constituents along with boron does not occur under optimal conditions for boron removal.

Ultimately, the data collected suggest that electrocoagulation is best suited for boron removal only under conditions like those studied. This undermines the idea that electrocoagulation is generally a more viable pretreatment process than traditional processes. pH, current and TDS were monitored or controlled closely at a small scale. In practice, TDS would depend on site-specific conditions and boron removal could suffer at the extremes of low and high concentrations. It is unclear whether the complications of EC would be much better than those associated traditional treatment processes. An economical analysis of costs would aid this conclusion. If boron removal is the sole purpose of an EC process, it has to be optimized to remove other pollutants along with boron before being put into practice.

Recommended future work for electrocoagulation includes optimizing conditions for other pollutants. Organics and divalent cations need to be the focus of this optimization. Characterization of the organics in produced water would assist understanding what interactions occur during EC. Exploring the water chemistry for other divalent cations such as barium and strontium would serve the same purpose. Scaling of the cathode was an issue observed during experimentation. Investigation of the composition of the scale and how to minimize it might lead to less electrode passivation and potentially reveal what exactly is occurring near the electrode. Finally, integration of EC performance with other treatment processes should be explored to better identify and quantify its potential benefits.

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Appendix

Table 1: Dry mass composition of ions present in RC sludge after EC

Sludge Composition by Mass (mg)		
Cation	Adjusted	Unadjusted
Mg ⁺²	353	94
Ca ⁺²	167	114
Al ⁺³	699	1352
Total Floc Mass	4024	4191

Table 2: Dry mass composition of ions present in DC sludge after EC

Sludge Composition by Mass (mg)		
	Unadjusted	
Cation	Run 1	Run 2
Mg ⁺²	24	41
Ca ⁺²	12	16
Al ⁺³	336	546
Total Floc Mass	972	1436