ELECTROLYTIC METHODS AS A COST AND ENERGY EFFECTIVE ALTERNATIVE OF HARVESTING ALGAE FOR BIOFUEL

A Thesis

by

TAYLOR LEE MORRISON

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Chair of Committee, Ronald Lacey
Committee Members, Zivko Nikolov
Qi Ying
Head of Department, Stephen Searcy

December 2012

Major Subject: Biological and Agricultural Engineering

ABSTRACT

Process variables of electrolytic technology to reduce the energy consumption of harvesting *Nonnocloropsis salina* were investigated including electro-coagulation, electro-floatation, and electro-flocculation. Electro-coagulation and electro-flocculation showed significant cost savings, however electro-floatation did not. The objectives were to determine the effects of electrode material, pH adjustment and electro-polymer addition for electro-coagulation and determine the performance characteristics for electro-coagulation and electro-flocculation. Both treatments proved to be competitive with the energy consumption of a centrifuge. The best electrolytic treatments were electro-coagulation with aluminum and nickel electrodes. Energy requirements at optimum conditions were 239 and 344 kWh/ton. The best treatment combination using electro-flocculation was 432 kWh/ton with no electrode consumption, which could lead to potential cost savings.

DEDICATION

To my grandfather, Tommy E Morrison, who believed in education and paved the road for mine

ACKNOWLEDGEMENTS

The financial support for this project was from the Department of Energy through the National Alliance for Advanced Biofuels and Bioproducts. The Texas A&M campus facilities available were Dr. Ron Lacey's micro-algae lab, Dr. Nikolov's bio-separations lab and Dr. Karthi's water quality lab. The offsite facility available was the Texas AgriLife Research center in Pecos, TX. Pecos offers a pilot scale model to understand and implement scale-up parameters. Through the Texas AgriLife Research, there was access to a competent staff.

I would like to thank my committee chair, Dr. Lacey, and my committee members, Dr. Nikolov, Dr. Ying, for their guidance and support throughout the course of this research. I truly appreciate the patience and time of colleagues, Dr. Boulanger, Andrea Garzon, Taylor Weiss, Phillip Ludecke and Jarrett Lassig, who have gone above and beyond to share their understanding of algae with me.

Thanks also to my friends and colleagues, and the department faculty and staff for making my time at Texas A&M University a great experience. I also want to extend my gratitude to the influential people throughout my life who have made learning fun.

NOMENCLATURE

Min	Minute
Cm	Centimeter
#	Number
A	Amperage
V	Volts
Wh	Watt-hour
OD	Optical Density
EC	Electro-Coagulation
SS	Stainless Steel

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION: THE IMPORTANCE OF RESEARCH

There is a growing demand for alternative fuel sources as the price of conventional fuels increases. As estimated petroleum reserves decrease and demand continues to increase, compensatory fuel will be needed [1]. Many countries are in search of alternative sources of energy and considering sustainability factors such as economic feasibility and energy independence [2]. There is also growing pressure to find fuel sources with a reduced carbon footprint as the concern for global warming increases [3]. Properties of biofuel meet both of these needs and show much promise as an alternative fuel source [4].

Biofuel derived from algae has emerged as an important and competitive source of alternative fuel [5]. This is in part to its biological traits such as resilience and quick growth, the availability, abundance and the small land footprint needed to grow at an economical scale [4].

Algae as a feedstock for biofuel may be prepared to produce either gas or liquid fuels. In feedstock preparation, the varying algal products require different practices of cultivation, harvesting, and extraction [6]. Currently, harvesting systems for removing algae from water are energy intensive because of the diluted amount of algae in water, about 0.02%-0.06 total suspended solids. The standard energy input, assuming centrifuge technology, accounts for approximately forty percent of the cost associated with processing. If the cost is greatly reduced, algae will become a competitive source for biofuel [7].

The technology developed in this research will promote the renewable energy economy. The possible local impacts would be promotion of a new industry and utilization of a non-competitive resource by employing nonpotable aquifers as a water source for cultivating the algae crop [8]. This technology will be one step closer in the direction of converting algae to a biofuel where a cost effective method for harvesting algae will be a direct reduction in electricity use.

2. LITERATURE REVIEW

There are two types of liquid-solid separation technologies: liquid constrained and particle constrained systems. Either the liquid is contained and the particles are removed from solution such as settling or the particles are trapped as the liquid is removed such as a filter press. In past algae harvesting operations, centrifuge technology was used to mechanically separate the liquid and solids [9]. There are currently three technologies that are competitive: electro-coagulation, electro-floatation, and electro-flocculation [4].

Harvesting algae with centrifugation can be operated as a semi-continuous process. This method uses energy to apply centrifugal force to the separate the solids from suspension. Using a centrifuge is beneficial to separate many sizes of algae into a range of desired moisture contents [4]. However, energy requirements for centrifugation are estimated to be 3000 kWh/ton dry algal biomass [10].

Electrochemical technology is not new and has been used in wastewater treatment operations [11]; however, there are no known commercial applications for harvesting algae for biofuel [12]. The application of this technology for biofuel is unique because of considerations for downstream effects of materials used in processing. Considerations for engine operations and livestock food quality are taken when applying electrochemical process and choosing metallic electrodes

[13]. Operation and maintenance requirements of electrochemical technology are low because the metallic plates do not require frequent cleaning and the system can be operated in continuous mode. Designed to be placed-in-line at the end of the lipid production stage, ease of technology implementation into cultivation facilities is another advantage, with low environmental impacts and 98% of the water recycled. Applying a direct current across two electrodes is the common configuration for the electrochemical treatment discussed (Figure 1).

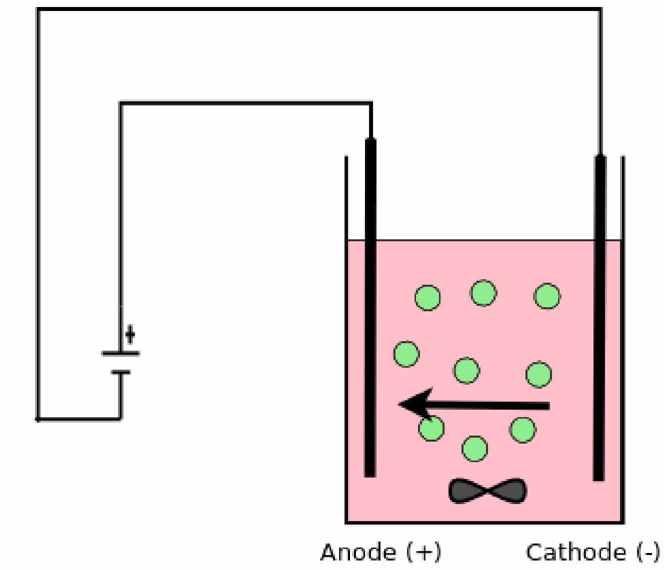

Figure 1: Conceptual drawing of electrochemical treatment cell

Algae particles have a negative surface charge as a result of surface functional group's dissociation or ionization. In order to remove the particles successfully, the surface charge must be disrupted so that the particles will not repel each other but become attracted and form large clusters, or flocs. The measurement of the repellent force is known as zeta potential, or more formally, the electric potential between two surfaces. Understanding the surface charge or zeta potential of the particles in solution determines the effectiveness of the floc formation [14].

2.1 Faraday's Law of Electrolysis

Faraday's Law of Electrolysis gives a relationship to the amount of material released from an electrode and the amount energy passed through the electrolyte [15]. The first law of electrolysis states that any material released from the electrode is proportional to the amount of electricity passed through the electrolyte. The second law of electrolysis states with the same amount of electricity passed through different electrolytes, the amount of material released is proportional to the equivalent weight of the material. A Faraday is defined as the charge on one mole of electrons. The mass of material released m, is proportional to the total electric charge passed Q, molar mass of substance M, Faraday constant F, and electrons transferred per ion, z:

$$m = \frac{Q}{F} \times \frac{M}{z} \qquad (1)$$

2.2 Electro-coagulation

Electro-coagulation (EC) is an established technology that offers greatly reduced capital and operating costs compared to harvesting with a centrifuge [16]. As with the schematic in Figure 1, a current is applied to a set of electrodes. These electrodes are made from a reactive metal that donates ions from a sacrificial electrode. The positive ions that are released and mixed into the solution attract negatively charged algae cells and create flocs. The formed flocs are then larger than individual algae cells and may then be removed more easily by floatation or sedimentation. Factors that affect the performance of EC systems include electrode material, pH and power consumption.

2.2.1 Electrode material

Metal is a commercially feasible material for donating ions, ultimately resulting in the formation of a flocculants for the algae in solution. Each electrode is tested under controlled conditions. Aluminum electrodes were utilized in the electro-coagulation process to achieve a removal as high as 99.5% [11]. Immediate spontaneous reactions will take place if iron or aluminum is used resulting in corresponding hydroxides and/or polyhydroxides [16]. Metals that are considered as possible electrodes are those with minimal downstream effects and high animal mineral tolerance. These metals include: zinc, aluminum, steel and iron.

2.2.2 pH

The initial pH affects EC performance and zeta potential and has been examined over the range of pH 4-10. The best performance then came from the pH range of 4-7 with aluminum electrodes [17]. During water treatment, lime or sodium hydroxide may be used to adjust the pH levels the treated water [4].

2.2.3 Power consumption

The water quality is dependent on the charge loading which is the product of current and duration [18]. Scale-up factors are observed to be volumetric current intensity and the chlorophyll which is a measure of cell density [19]. These parameters allow the calculation of the appropriate charge dose to relate the operating current and time to release a minimum number of aluminum ions.

2.3 Electro-floatation

Another method with competitive power requirements is electro-flotation. A sacrificial reactive metallic anode is partnered with an inert metallic cathode in a setup such as Figure 1. After applying an electric current, this pair produces complex reactions resulting in the formation of hydrogen bubbles at the cathode. Bubbles then encourage floatation of particles to the surface as the hydrogen becomes trapped under the floc or adhered by charge difference. The effectiveness of adhesions of a particle to a bubble depends on two factors: particle size and particle instability. The combination of low instability and large particle size (less than 500 µm) the higher the air-particle contact [4]. The formation of algal flocs is important for the complete removal of algae, as the mechanics of lifting individual cells is not as successful [19]. Electro-flotation alone could only achieve algae removal of 40-50 %. Mixing the ions to form flocs will also disperse gas micro-bubbles. Simultaneous flocculation-electro-flotation gives the best results [20]. A setup using aluminum anode and titanium cathode showed no clear interface between flocs and clear water. Removal potential based on zeta potential and micro-bubble size determined: the bubble and particle should be oppositely charged, maximum removal was 12% without flocculation and 98% with flocculation, and positively charged bubbles were produced by manipulating aluminum concentration and pH using $AlCl_3$ and HCl [21]. Scaling and high energy costs are the main disadvantages of an electro-floatation system [4]. After a review of electro-floatation, there is little promise of finding the most economical harvesting technique. Therefore, electro-floatation will not be tested.

2.4 Electro-flocculation

An additional method of concentrating particles is known as electrolytic flocculation (EF). Two electrodes of non-reactive metals are used in EF reactors. As a current is applied, no theoretical ions leave the electrodes. Negatively charged algae move through solution to the anode. After contact with the anode, the negative surface charge is lost which allows the algae to floc together. Effectiveness of EF is determined by how well the surface charge of the algae is changed. Flocculation is a preferred method because of its scalability and compatibility with many algal species. Because the specific gravity of flocs is approximately equal to water, flocculation alone may not achieve separation adequate for harvesting algae. EF has been shown to be more effective with a dispersed air system to create a floatation environment [7]. EF of marine species of algae is five to ten times higher energy input than freshwater, as the chemical reactivity of the cells decreases from the high salinity and reduces active sites available for flocculation [4]. Factors that affect the EF process include electrode material, electrode distance, surface area, treatment and mixing time of solution.

2.4.1 Electrode material

The material used for electrolytic flocculation is not consumed therefore reduces the constraint on mineral tolerances in downstream products. Flocculation may be performed with inert metal such as stainless steel [4].

2.4.2 Electrode distance and surface area

Another study showed that two significant design parameters were electrode surface area and distance between electrodes [22]. This also led to a change in energy consumption. Optimizing potential difference and electrode parameters leads to minimum energy consumption [4].

2.4.3 Treatment and mixing time of solution

The treatment and mixing time of the solution are factors that are not found from specific literature reviews. These are factors decidedly included intuitively after considering the distribution of particles in a solution.

3. GOAL AND OBJECTIVES

The goal of this research is to understand important parameters of electro-coagulation and electro-flocculation harvesting operations of algae for biofuel. Findings that will lead to a significant cost and energy reduction in removing algae from water will improve the economics of converting algae into a usable fuel source.

3.1 Objectives

1. Determine the effect of electrode material on algae recovery during electrocoagulation. Considerations will be taken for mineral tolerances of the metal ions in the by-product as well as costs of metals and practicality of commercially using the material.
2. Determine the effects of pre-electrocoagulation pH adjustment on algae recovery.
3. Determine the effect of post-treatment addition of an electro-polymer on electro-coagulation performance.
4. Determine the performance characteristics (power consumption and removal efficiency) versus algae recovery for electro-coagulation.
5. Determine the performance characteristics (power consumption versus removal efficiency) and significant parameters for electro-flocculation.

4. METHODOLOGY FOR ELECTRO-COAGULATION AND ELECTRO-FLOCCULATION

4.1 Electro-coagulation Methodology

Electro-coagulation is an established technology that offers greatly reduced capital and operating costs compared to harvesting with a centrifuge [16]. As with the schematic in Figure 1, a current is applied to a set of electrodes. These electrodes are a reactive metal that donate ions primarily from a sacrificial anode. The positive ions that are released and mixed into the solution attract negatively charged algae cells and create flocs. The formed flocs are then larger than individual algae cells and may then be removed easier by floatation or sedimentation.

4.1.1 Electro-coagulation Experimental Plan

Each objective had unique factors and responses that were controlled or measured during the tests:

1. The factors used to determine the effect of electrode material on algae recovery during EC were electrode material and power input. All other factors were controlled according to sections 4.3-4.4. The materials tested were aluminum, nickel and steel. The power input was controlled by setting the amperage at a value in the range of 0.01-0.125 Amps for each test. The screening was designed to take test points for each material in a range that showed a drop off in performance. The amperages of the test points for each

electrode vary within the range and were decided with observations while testing. The response that measured the recovery of algae with each factor was optical density. OD was then used to describe removal efficiency.

2. The two factors used to determine the effect of pre-electrocoagulation pH adjustment was varying the pH level with the addition of different acids. All other factors were controlled according to sections 4.3-4.4. The acids used were carbon dioxide (gas), hydrochloric acid and sulfuric acid. The range of pH tested was from pH 3 to pH 9. As a screening, one test was taken for each acid close to each whole value pH in the range 3-9. The response that measured the EC performance with each factor was optical density. OD was then used to describe removal efficiency.

3. The factor that determined the effects of post-electrocoagulation addition of an electro-polymer on algae recovery was polymer addition. All other factors were controlled according to sections 4.3-4.4. There were triplicates taken with the midpoint of a range of a calculated amount of polymer and compared to triplicates of tests without polymer addition. The triplicates were then used in a one side Student’s t-test to test for significance. The response that measured the EC performance with each factor was optical density. OD was then used to describe removal efficiency.

4. The factor used to determine the performance characteristics of EC was power consumption. All other factors were controlled according to sections 4.3-4.4. This factor was tested on the two best performing electrodes from Objective

1, aluminum and steel. The power consumption was controlled by setting the amperage for each test based on the results from Objective 1. A more detailed understanding of the minimum power input required was achieved through trial and error testing to find the range. The response that measured the EC performance with each factor was optical density. OD was then used to describe removal efficiency.

4.2 Electro-flocculation Methodology

Electro-flocculation (EF) is another method of electrolytic treatment similar to electro-coagulation. In electro-flocculation, current is applied through inert electrodes in an electrolytic cell that contains a conductive media. The mechanism that operates in EF is that the positively charged algae lose their charge after coming into contact with the anode. Theoretically, no metallic ions are donated in this process. Neutral algal cells then coagulate with other algal cells to form flocs. In electro-flocculation there is not a limited coating efficiency of an added coagulant. Formed flocs of algae cells can then be separated from solution with sedimentation or floatation.

4.2.1 Electro-flocculation Experimental Plan

This objective had unique factors and responses that were controlled or measured during the tests. Two sub-objectives were designed to address and test the most descriptive factors of the objective:

1. Sub-objective 1: The factors used to evaluate power consumption compared to removal efficiency for electro-flocculation were amperage and initial culture density. All other parameters were constant according to sections 4.3 and 4.5. Optical density was the response that measured the recovery of algae as the amperage and initial OD were varied. Final OD was then used to describe removal efficiency.

2. Sub-objective 2: The factors controlled to understand significant parameters for separating algae from the growth media were charge time, mixing time, length of electrode, and distance between electrode. All other parameters were held constant according to sections 4.3 and 4.5. High and low values were chosen based on previous experimental work and literature for the 2^4 experimental design resulting in 16 runs. The response measured throughout the experiment was optical density. OD was then used to describe removal efficiency.

4.3 Electro-coagulation and Electro-flocculation Experimental Setup

Each electrolytic test was performed with 300 mL of liquid in a 400 mL glass beaker serving as the lab scaled electrolysis unit as shown in Figure 2. A device made of PTFE hex nuts and rods was fashioned to hold the plate electrodes. Plate electrodes had submerged surface area of 60 cm^2 and small compared thicknesses (aluminum = 0.57 mm, steel = 1.54mm, nickel=0.51mm).

The electrode separation distance and surface area were measured using the same ruler as specified for each experimental design. Each anode and cathode were weighed individually using a scale (Mettler Toledo, NewClassic MF, model: ML204/03) before each test and inserted into the plastic device and submerged until a surface area of 60 cm^2 is in the solution.

Leads from the power source (Hewlett Packard, Triple Output DC Power Supply, Palo Alto, CA) were attached to the marked anode and cathode. The voltage range was adjusted to the highest potential at +25 V and the current was set as specified in the experimental design. Using an electronic timer, three voltage values were collected during the test: at time equals zero, half, and final. These values were averaged to calculate power consumption. After applying current to the solution for the specified time, the power source was turned off.

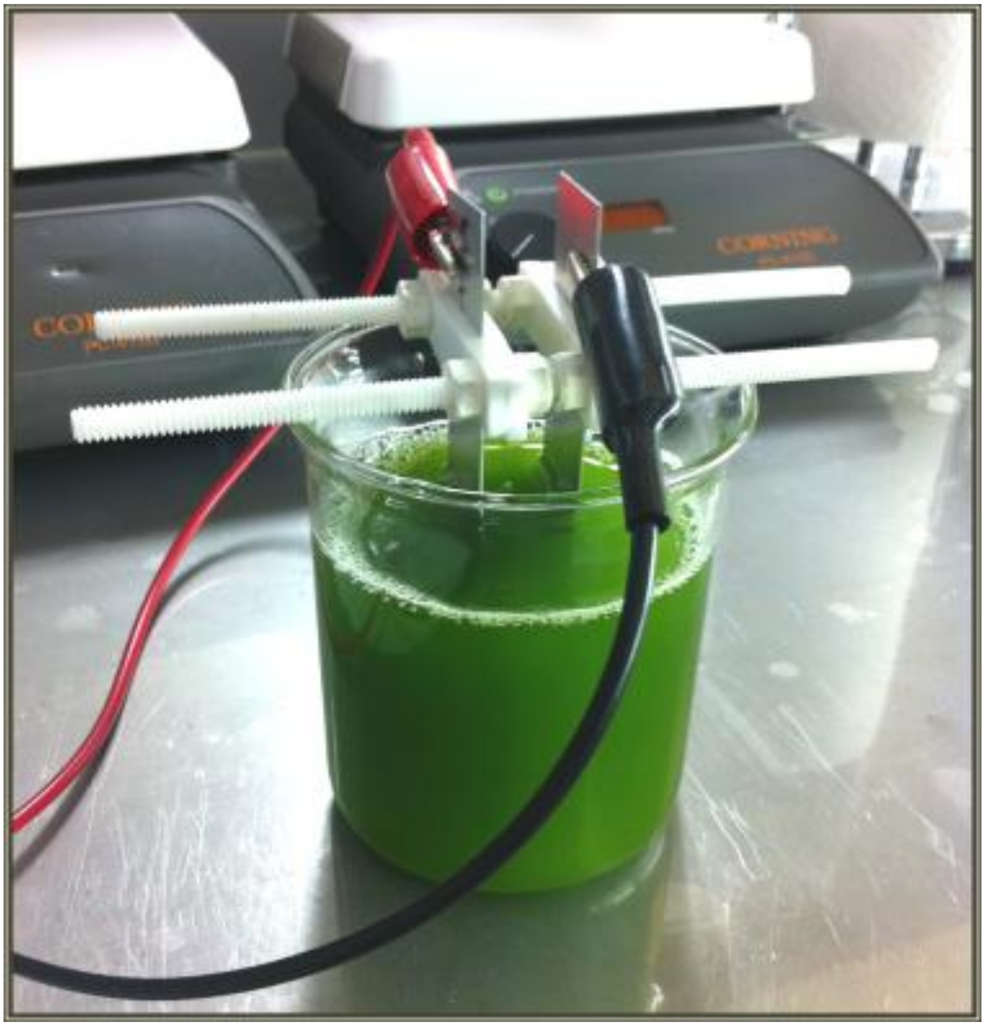

Figure 2: Lab scale (300 mL) electrolysis unit

A 2.5 cm magnetic stir bar was placed in the beaker after removing the electrodes and plastic electrode holder. Each sample was subjected to rapid mixing of 360 rpm using an electronic stirrer (Corning, model: PC-410D) for the stated mixing time. At the completion of mixing, each sample was allowed to settle *in-situ*. After the desired settling time was achieved, the final OD was measured by drawing a 1 mL sample from the same mid-point as the initial OD. The individual final weight was recorded for each dried electrode. Each OD sample was then prepared according to the OD procedures (4.2.3). The OD was used as the response of each test unless otherwise stated. The removal efficiency was calculated when the final OD was subtracted from the initial OD, divided by the initial OD, and multiplied by 100 to give the percent reduction. Removal efficiency is a descriptive term that tells the percentage of total suspended solids removed from solution.

$$Removal\ efficiency\ (\%)\ = 1 - \frac{OD_2}{OD_1} \times 100 \qquad (2)$$

The term is favored in describing recovery because it is a normalized value. Algae tested at different optical densities and efficiency requires a robust response that accommodates for the difference compared to using only the quantity of solids remaining in the treated solution (final OD).

The growth media used in all tests was a modified f/2 algae media. The recipe is given in Appendix C. The initial OD values were not significantly different. A growth curve shown in (Figure 3) demonstrates that there was no significant difference within the initial range of optical densities used in these tests.

4.3.1 Measurement of Algal Cell Concentration (OD)

The initial optical density (OD) was measured with a UV/Vis spectrophotometer (Thermo Fisher Scientific, Genesys 20, model: 4001/4) at a wavelength of 750 nm to measure the green reflected by chlorophyll. A 1 mL sample was drawn at a depth of two inches below the water surface or approximately in the middle of the sample. The 1 mL sample was then mixed with 9 mL of DI water. The 10x dilution is necessary to be within the linear range of the UV/Vis spectrophotometer.

4.3.2 Correlation of Algal Cell Concentration to OD

Optical density measures the absorbance of the material by passing a known amount of light through a cuvette and measuring the amount of light transmitted. OD measurements are quick and easy in the lab, however, an OD reading is unitless. Correlating the OD values to meaningful terms of grams of biomass per liter is useful to interpret the responses in the experiments. A growth curve was developed to have correlation between the OD, cell count and AFDW of *N. salina* in terms of both biomass (g/L) and cell counts (cells/L).

The curve was developed during an eleven day growth period. The growth curve was based on three measurements: cell count, OD and AFDW. Developing these correlations were helpful to understand the significance of the optical density. The algae used to develop this growth curve were transferred from a flask in the exponential growth phase.

One flask of algae was used for daily sampling to construct the growth curve. The flask was prepared by transferring algae to the desired initial concentration (OD ~0.40). The cell count, OD and AFDW measurements were repeated everyday for eleven days at approximately the same time following the standard operating procedure (SOP) for all procedures.

4.3.3 Standard Operating Procedure: Cell Count

Cell count of an algal culture may be used to better quantify the number of cells in solution. A 10x dilution of the algae sample was prepared and recorded. After turning on the microscope the Nikon microscope program (NMP) was opened see the live view and counting functions. The hemocytometer and slide were cleaned with alcohol and kimwipes. The live camera on the NMP was then turned on. After confirming the slide was clean by viewing under the microscope, the algae solution was carefully applied to the slide. In the NMP, the clicking order for counting was: paper symbol with a red X “Reset Data” > Count & Taxonomy > “123”. The cells were then counted by clicking on cells within the chosen count square, staying within the boundary of the middle line. The number was stored in the spreadsheet on the NMP by right clicking to apply the cell count. This was repeated twice more to have three cell counts. The screen was then cleared by selecting “Clear Screen”. This cleared the previous counts and allowed for new counts. Data recorded from NMP cell count calculations was ‘mean’ and ‘st. dev’ values for input into the AFDW spreadsheet.

4.3.4 Standard Operating Procedure: Ash Free Dry Weight

Ash Free Dry Weight (AFDW) Analysis of Organic Content Ash free dry weight was chosen instead of total dry weight to account for the presence of mineral ash. AFDW is also known as volatile suspended solids (VSS), and measures the organic material produced in algae. This was performed by filtering algae in triplicates (10 mL if OD > 1 g/L and 20 mL if OD < 1 g/L). The filter was washed with ammonium formate using 5 mL before algae was filtered and 10 mL after algae was filtered to remove any residue on the sides of the filter glass. The filters were then placed back into label aluminum trays that were weighed with the dry weight of tray and filter and placed into an oven at 100 degrees C for one hour. After the hour, the filter and trays were removed, cooled and weighed for a dry weight measurement. The trays and filters were then placed and covered with aluminum into a muffle furnace at 500 degrees C for one hour. After the hour, the filter and trays were removed, cooled and weighed for an ash free dry weight measurement. The pans and filters were washed, ashed and stored in a desiccator prior to use. AFDW is calculated as the difference of the weight of the filters after drying at 100C and after ashing at 500C. Data was recorded as g/liter AFDW and ash content as % of total dry weight.

4.3.5 Algal Growth Curve Results

The strong linear correlation of the data (Figure *3*) suggests the algae stayed in the growth phase because it grew steadily each day. It appears that during the eleven-day growth period, there was no obvious lag or stationary phase.

The OD and cell count (Figure 4) shows an increase in cell count with the increase in optical density. The data show a linear relationship; as the number of cells increase, the optical density increases proportionally. This relationship suggests that during this growth, extracellular organic matter did not skew the optical density readings.

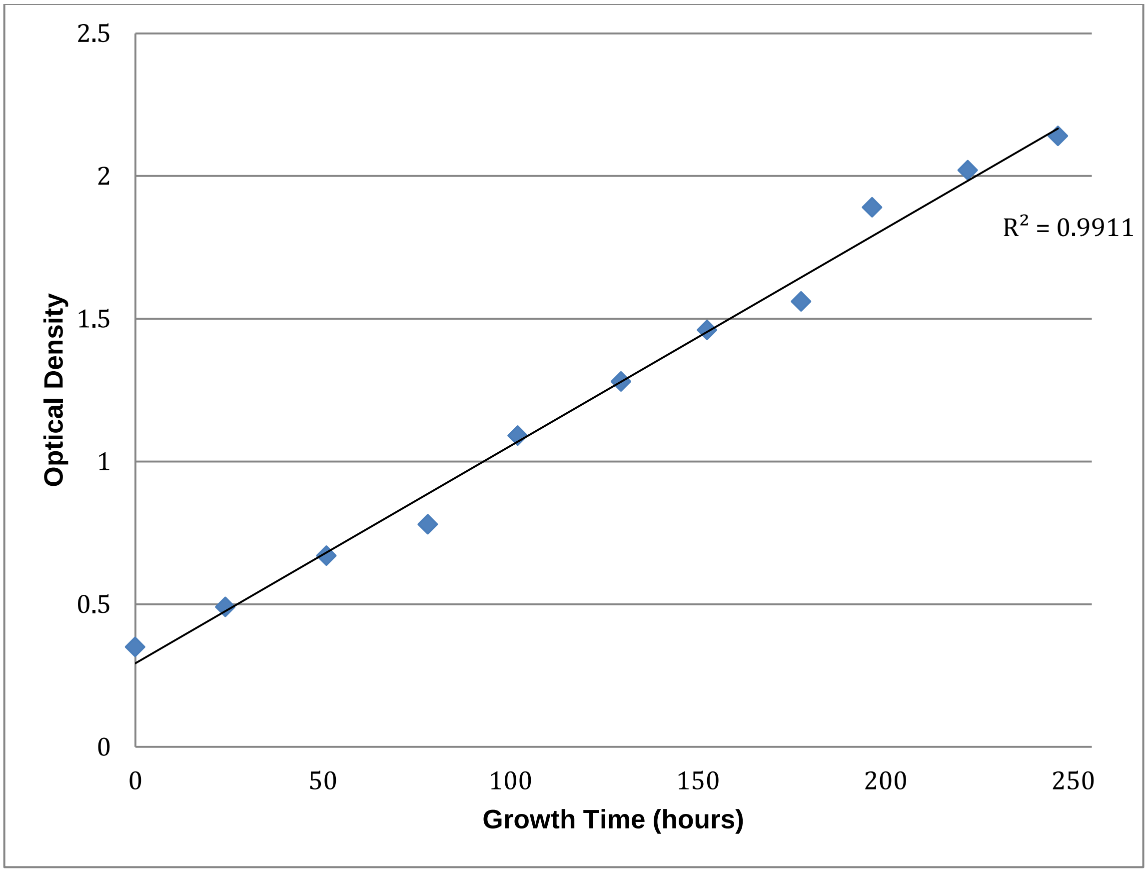

Figure 3: Optical density over 11 days of growth

The as the number of cells per liter increased, so did the amount of available dried biomass. There appears to be a variation in the biomass data (Figure 5). This was due possibly to human error in collecting the sample. Variability in biomass is also possibly in part because of environmental changes affecting the algae's behavior.

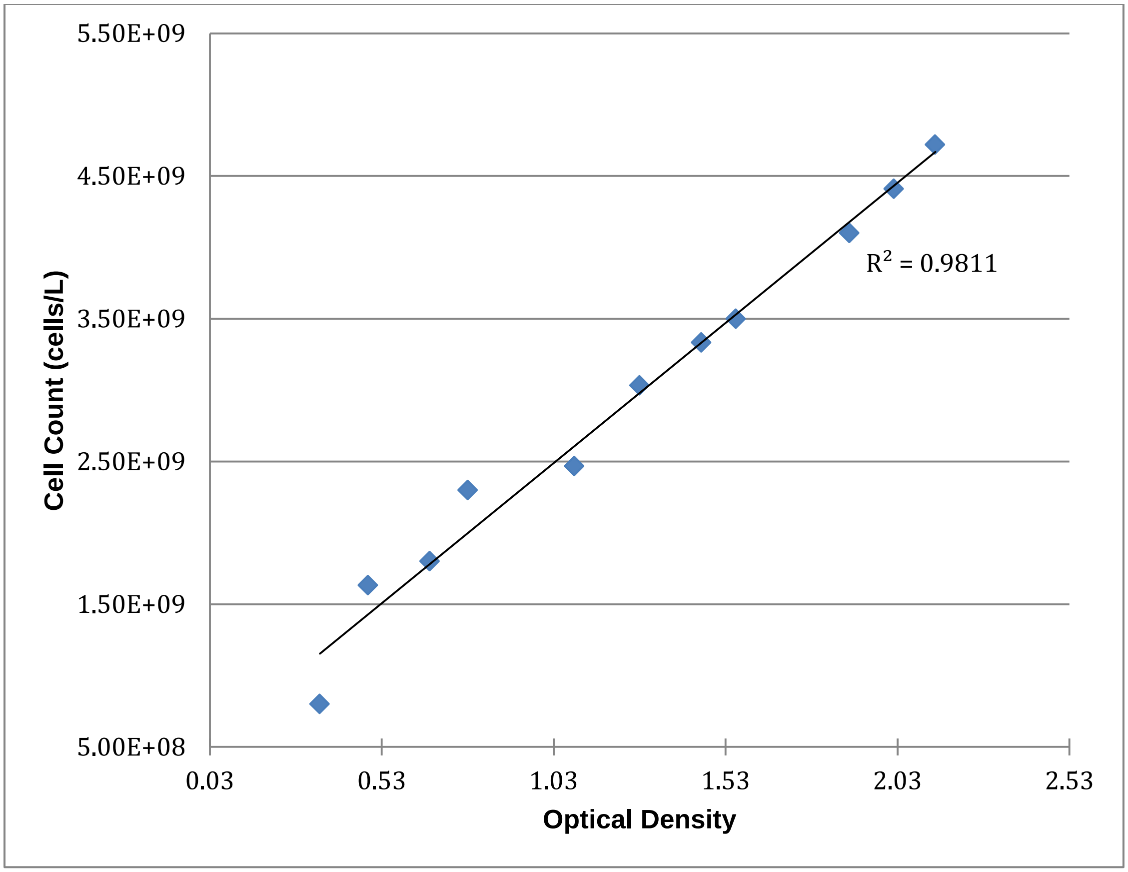

Figure 4: Growth curve shown by cell count and OD

The relationship between dry biomass and OD is shown in Figure 6. The correlation is not as strong as with the previous curves and could be in the nature of what is being measured. This graph suggests there is not a strong relationship between the mass of the total suspended solids and the amount of light the solids absorb. The variation may be caused by uncertainty error in the AFDW procedure (4.3.4) or changes in cell size because of environmental factors.

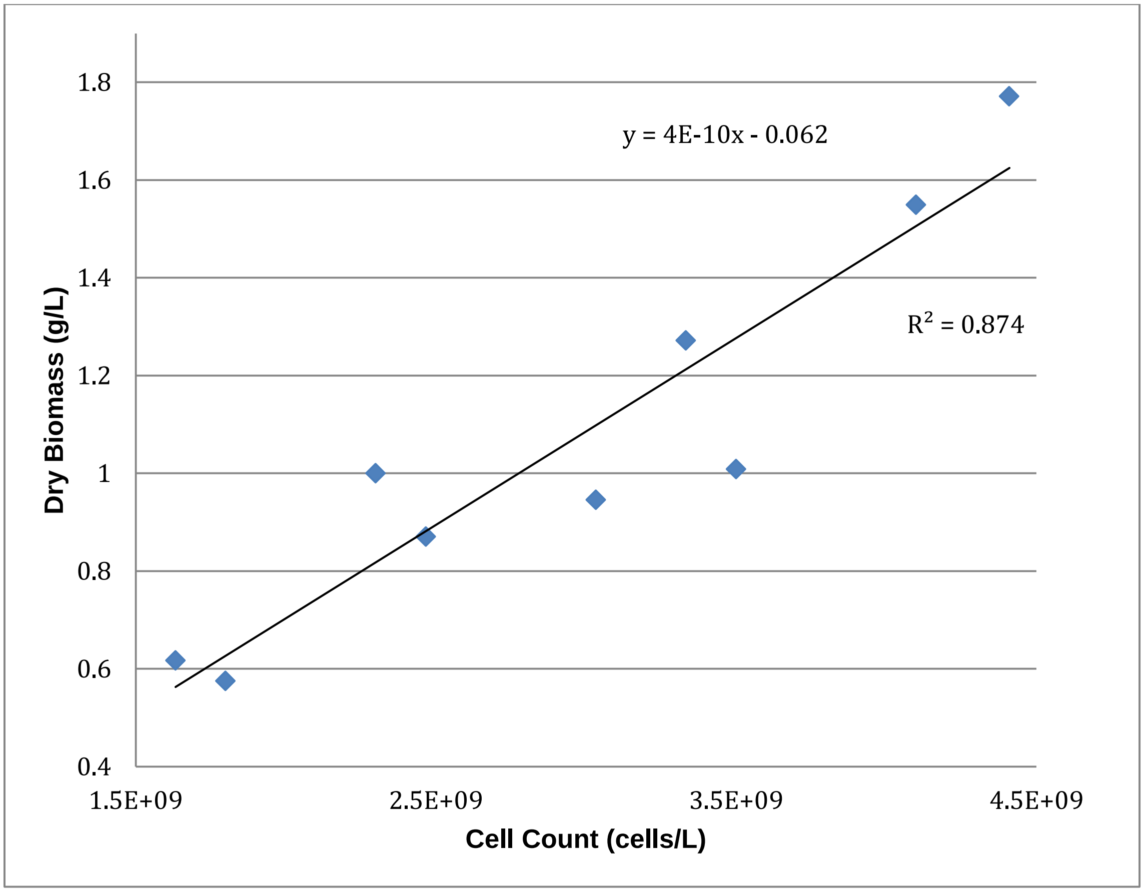

Figure 5: Number of cells per gram of biomass

The growth curve development served as a reference for the data collected in the following experiments. The dry weight data has a calculated mean of 1.2 and average standard deviation of 0.66. The cell count data has a calculated a mean of 29.2 and average standard deviation of 1.9.

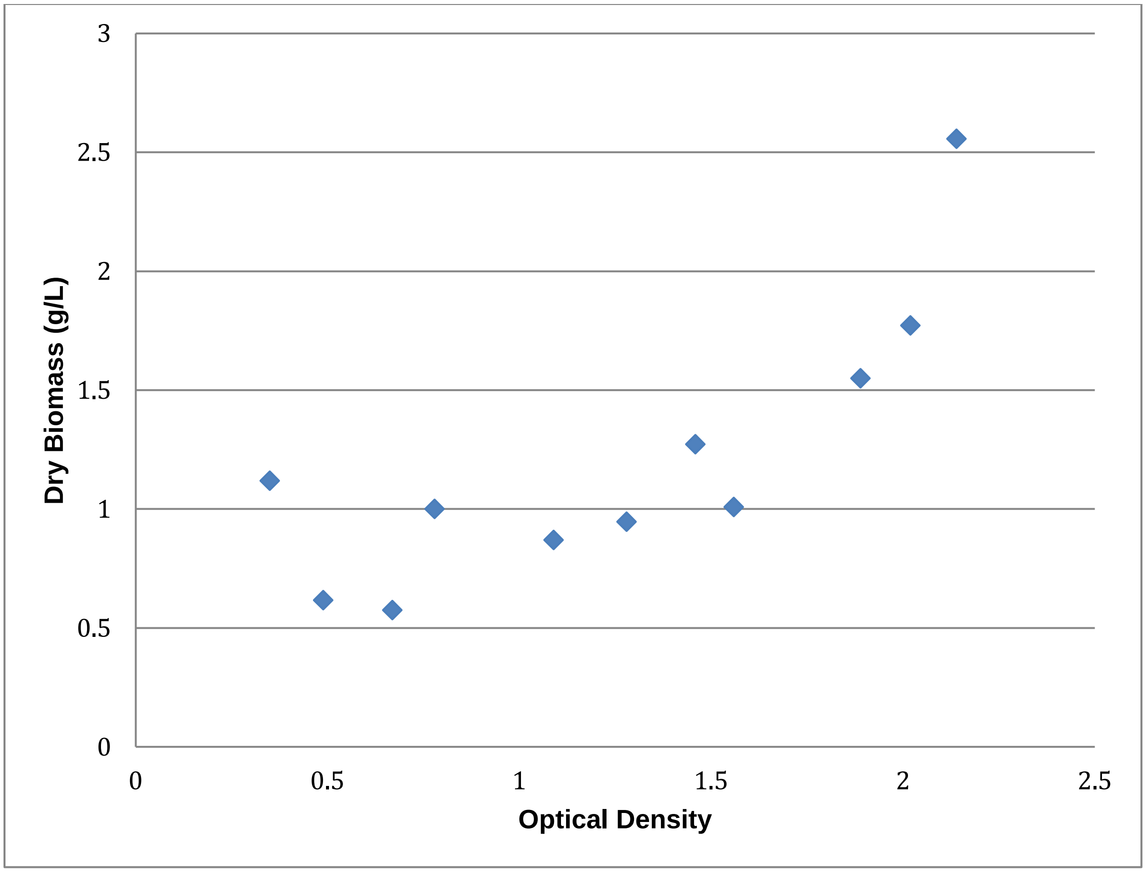

Figure 6: Optical density correlated to biomass density

4.4 Experimental Parameters for Electro-coagulation

Tests for Objective 1: Determine the effect of electrode material on algae recovery during electrocoagulation.

A screening test of electrodes showed in unpublished data (Murdoch, 2010) that the best performing and most economical electrode materials were aluminum, nickel, and steel. Each test point represents an individual electrolytic unit for each factor combination (electrode and amperage). The test points for aluminum electrodes were: 0.01, 0.03, 0.05 and 0.1 Amps. The test points for nickel electrodes were: 0.03, 0.075 and 0.1 Amps. The test points for steel electrodes were: 0.05, 0.075, 0.1 and 0.125 Amps. The removal efficiency (equation 2) was calculated when the final OD was subtracted from the initial OD, divided by the initial OD, and multiplied by 100 to give the percent reduction. The power consumption versus recovery curve was developed when the response from each test was grouped by material type and plotted.

Standard AFDW were determined on the top performing combinations (highest performance at lowest energy input for each electrode) to understand the density of the final floc material. An estimation of the distributed ions from the electrodes into the biomass was calculated (Appendix C). The ion concentrations were then checked against the maximum mineral tolerances prepared by the Donald Danforth Plant Science Center for NAABB's downstream considerations (Appendix D).

Tests for Objective 2: Determine the effects of pre-electrocoagulation pH adjustment on performance.

As literature reports, lowering the pH may be helpful in influencing zeta potential and performance of coagulation processes in algae [17]. These pH target values and chemicals were chosen based on economics and minimizing downstream effects of acid in the solution. Two screenings were performed covering three different acids.

In the first screening, the two factors used to determine the effect of pre-electrocoagulation pH adjustment were varying the pH level and electrode. Hydrochloric acid was chosen because it is relatively inexpensive and a common industrial acid. The desired pH was achieved by incrementally mixing in dosages with the electronic stirrer while reading on the pH meter (VWR SB90M5 Multiparameter Benchtop Meter). Approximately 5.5 mL of HCl was used to reduce 300 mL the algal solution to a pH of 2. One test was performed at each pH value from 2 to 8 for both aluminum and nickel. The electrolytic testing was consistent for both electrodes with surface areas of 60 cm^2 (2 cm apart) and a set current of 0.049 Amps. The response that measured the EC performance with each factor combination was the final optical density.

The second acid screening included H_2SO_4 and CO_2 tested at a range of pH 6-9 while using only aluminum electrodes. Only one electrode was used for simplicity and reduced the number of factors. The resulting experimental design was a 2^3 factorial design. This includes two levels for three factors. The factors were H_2SO_4, CO_2, and no acid addition. The levels for each factor were pH 9 (high level) and pH 6 (low level). The desired pH was achieved by incrementally adding dosages while reading on a pH meter until the desired pH of 6 was reached. The addition of 0.5 mL of H_2SO_4 was needed to lower a 300 mL flask from pH 8.45 to pH 6. The CO_2 was bubbled as a gas into a 300 mL flask and required 0.008 cfm to lower from pH 7 to pH 6. These values were compared to a test performed with no treatment and pH of 8.5. The tests were administered with an electrode surface area of 60 cm^2 set 2 cm apart and a current of 0.179 Amps. The current is higher than the first screening to insure saturation of ions in solution and eliminate the possibility of inadequate current. Optical density of the supernatant was used as the response. The response was calculated by subtracting the final OD from the initial OD, divided by the initial OD and multiplied by 100 to give a percent reduction.

Tests for Objective 3: Determine the effects of post-electrocoagulation addition of an electro-polymer on electro-coagulation recovery.

Polymer addition was added based on algal dry weight and completely mixed into the electro-coagulated solution of the lowest energy consuming and best performing electrode and pH treatments from Objective 1. This combination was aluminum electrodes at 0.1 Amps. The hypothesis was that the polymer would act as an additional flocculent to compliment the positive ion’s released into the solution from the electrodes. The first tests were performed with an available polymer from the downstream process, known as PolyDAD. A one sided t-test was used to test the null hypothesis:

Ho: The final OD of treatment with polymer additions is NOT significantly less than the final OD of treatment without polymer additions.

The amount of polymer needed after treatment was calculated based on the algal dry weight biomass treated, which was found to be 1.77 g/L. Given the polymer's density (1.09 g/cm^3) and information about optimized material covering (1-5% of dry weight), the optimum range of polymer to be tested was calculated to be between 0.006 – 0.03 mL polymer per 300 mL of algae. The median of the range, 0.017 mL of polymer, was the amount used to test the polymer treatment. The electrolytic test was performed as stated by the experimental setup with 2 cm between electrodes and a submerged surface area of 60 cm^2. The polymer was added at the beginning of the rapid mixing step. The control treatments were performed as stated by the experimental setup with no polymer addition. The removal efficiency was the response. The removal efficiency was calculated by subtracting the final OD from the initial OD, divided by the initial OD and multiplied by 100 to give a percent reduction.

Tests for Objective 4: Determine the power consumption and removal efficiency versus algae recovery for electro-coagulation comparing aluminum and steel electrodes.

All parameters were held constant in the experimental setup for the development of a, power curve of the two best performing metals from Objective 1. Standard operating procedures were used for taking OD data. No pH adjustments were made and no polymer is added during this process. Each electrode material was tested at a range of currents (0.05, 0.179, 0.50), which was held constant during each test. Using an electronic timer, three voltage values were collected during the test: at time equals zero, half, and final. These values were averaged to calculate power consumption in kW-hr. The removal efficiency was the response. The removal efficiency was calculated by subtracting the final OD from the initial OD, divided by the initial OD and multiplied by 100 to give a percent reduction. The final OD was then plotted against the average power consumption and grouped by material type to develop the power consumption versus recovery curves.

4.5 Experimental Parameters for Electro-flocculation

Tests for Objective 1: Determine the performance characteristics (power consumption and removal efficiency) for electro-flocculation.

The purpose of this experiment was to understand significant parameters for separating *N. salina* from the growth media using electro-flocculation and was tested in two subobjectives. The first subobjective was a test of the power consumption and removal efficiency over a range of cell densities. The second subobjective was to determine optimization of operating parameters with the flocculation unit.

4.5.1 Sub-objective 1

Sub-objective one determined algae recovery efficiency versus power consumption. These two parameters denote a power curve that was repeated for multiple different optical densities [0.080, 0.105, 0.140, 0.192, 0.208] and established the minimum range of power input that gives the maximum recovery efficiency. This screening was repeated for a range of cell densities to observe the performance of electro-flocculation with varying biomass concentrations. The low values for each parameter were treated as constants for sub-objective one (Table 1):

Table 1: Parameters held constant to determine algae recovery efficiency versus power consumption

Material	Current (A)	Duration (min)	Mixing (min)	Surface Area (cm)	Electrode Distance (cm)
SS and SS	Varied [0.005-0.35]	10	2	5	2

Algae was transferred from the growth flask to the test cells when the desired OD was achieved. Each test was prepared for electrolytic treatment with precedence to Table 1 and in accordance with section 4.3. At the beginning of each test, the amperage was adjusted to reflect points within the tested range

[0.005-0.035 Amps]. At the conclusion of each test, the final optical density was measured as the response.

4.5.2 Sub-objective 2

Using a two level factorial experiment design, four key operating parameters were tested in sub-objective two. Each of these parameters was chosen from literature as important to the separation process.

Table 2: Two level factorial design to determine optimum operating parameters of the flocculation unit

Test Level		Charge Time (min)	Mixing Time (min)	Length of Electrode (cm)	Surface Area (cm2) [a]	Distance between electrodes (cm)
Low	-1	10	2	5	51	2
High	1	30	10	8	81	5

[a] Suface area is calculated from length of electrode in solution. This is not an independent factor.

The 2^4 design yielded 16 tests with combinations of low and high values for each of the four parameters (Table 2). Using Design of Experiment (DOE) low and high tested values were developed to determine if a factor was significant to the response. The experimental setup generated by Design Expert © is shown in Table 3. The response (final OD) was then used to test the null hypothesis:

> *Ho: The final OD of the treatment combinations are NOT significantly different.*

If the null hypothesis failed, then a factor was significantly different from the others and could then be tested further. Other testing parameters were held constant; mixing was set at 260 rpm, the current was set at a constant amperage of 0.5, and electrodes were stainless steel. After settling for ten minutes, the final OD was measured by drawing a 1 mL sample from the same mid-point as the initial OD. The experimental response was the final OD.

Table 3: Experimental design to determine optimum operating parameters of the flocculation unit

Standard #	Run #	Charge Time (min)	Mixing Time (min)	Electrode Length (cm)	Distance between electrodes (cm)
3	1	10	10	5	2
14	2	30	2	8	5
13	3	10	2	8	5
15	4	10	10	8	5
4	5	30	10	5	2
12	6	30	10	5	5
9	7	10	2	5	5
1	8	10	2	5	2
6	9	30	2	8	2
2	10	30	2	5	2
10	11	30	2	5	5
16	12	30	10	8	5
11	13	10	10	5	5
5	14	10	2	8	2
7	15	10	10	8	2
8	16	30	10	8	2

5. ELECTRO-COAGULATION RESULTS AND DISCUSSION

5.1 Objective 1

Aluminum showed to perform better and required less energy input than steel or nickel. Electro-coagulation with aluminum electrodes had the highest percent removal with the least amount of energy consumed. The best performance for aluminum was at 0.1 Amps, which had an average voltage of 1.06. Steel and nickel averaged a much higher voltage at 0.1 Amps increasing the overall energy consumption during the tests with steel averaging 1.65 volts and nickel averaging 1.7 volts. Steel and nickel performed comparably in reduction ability and power consumption. Results for the first test are shown in Figure 7 where the percent reduction in optical density (i.e. recovery) was plotted versus power applied to the electrodes. Across the range of power tested, the aluminum electrode demonstrated greater recovery at less power than either nickel or steel.

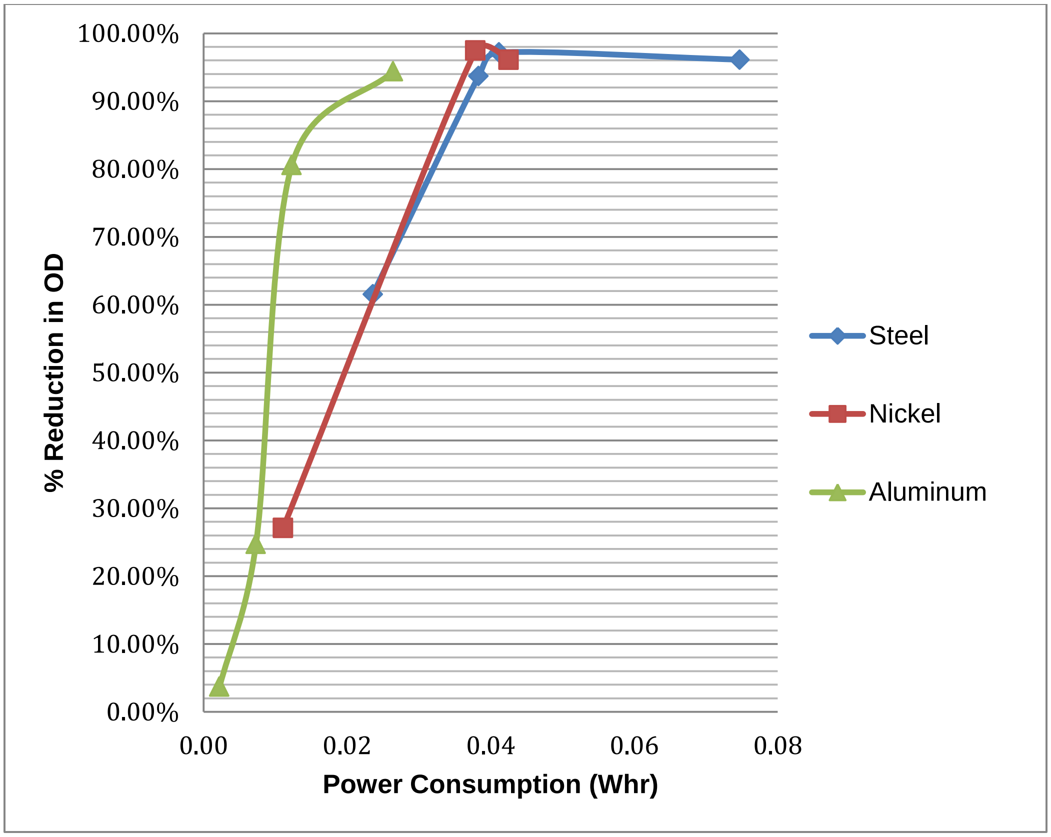

Figure 7: Performance of electrodes at lowest operable power

The results are consistent with the second law of electrolysis relating energy use and material deposited based on equivalent weight. According to the calculations using Faraday's Law of Electrolysis, there was less than half the aluminum in solution than nickel. Table 4 shows the calculated release of ions into solution (in grams) of aluminum and nickel using Faraday's Law of Electrolysis.

Table 4: Faraday's law of electrolysis ion calculations

Electrode	Atomic Wt (g)	Ions into solution (mg)[a]
Al	26.981	12.6
Ni	58.69	27.4

[a]Based on equation for the reaction that occurs at cathode of electrolysis cell.

The May 2012 price of aluminum was 1.981 USD/kg and nickel was 16.980 USD/kg [23]. The price of nickel was 8.5 times higher than aluminum, while the mineral feed tolerance in cattle for aluminum is ten times greater than nickel: 1000 mg/kg versus 100 mg/kg, respectively. Taking the price and maximum mineral tolerances into consideration, the best electrode was found to be aluminum (Table 5). Assuming that 100% of the ions are in the biomass, the amount of aluminum ions for this treatment was only 4.19% of the maximum mineral tolerance and 91.3% for nickel. Aluminum is not close to the maximum amount of ions in solution at the testing parameters used, whereas nickel is approaching the maximum allowable.

Aluminum was the best performing electrode. According to the mineral tolerance list, the amount of aluminum ions assumed to be in the algae was less than the maximum allowable for feedstock. To keep the algal byproduct marketable as livestock feed is a necessary mechanism for reducing the total cost of algae for biofuel.

Table 5: Cost and mineral tolerances of Al and Ni

Electrode	Ions in solution (mg)[a]	Maximum Mineral Tolerance (mg/kg)[b]	Biomass in Test (g)[c]	Concentration of Ions (mg/kg)	Price (USD/kg)	Cost (USD)
Al	12.59	1000	0.3	41.96	1.98	0.025
Ni	27.38	100	0.3	91.27	16.98	0.465

[a] From Table 4
[b] Appendix C
[c] Amount of biomass in test is based on the growth curve developed for *N. salina* (Figure 5). The average OD of the algae when the aluminum electrode was tested was 0.093 and 0.091 for the nickel series. The correlating amount of biomass in solution is approximately 1 gram per liter for an OD ~ 0.1.

5.2 Objective 2

As noted in the literature, there was a variation in removal efficiency of algae by electro-coagulation at different levels of pH. In comparing aluminum and nickel electrodes, only aluminum reacted favorably to pH reduction using hydrochloric acid from approximately pH 9.0 to pH 3.5 to pH 5.0. The best OD reduction with pH reduction was found with aluminum electrodes at pH 5.0 with a recovery of 94.8% (Figure 8).

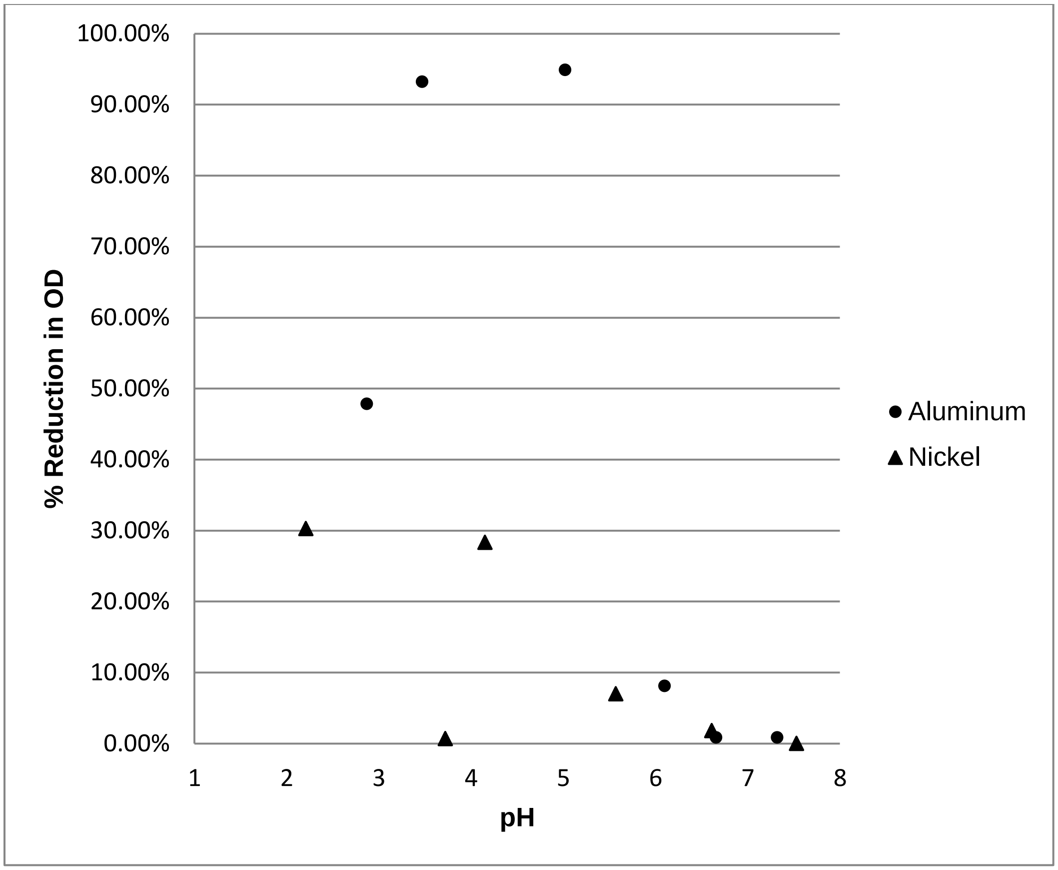

Figure 8: Screening of pH adjustments using HCl on Al and Ni electrodes

It was found that the highest removal efficiency overall was at pH 9 with 99.42% recovery (Figure 9), which was the control with no added hydrochloric acid, sulfuric acid or carbon dioxide. When carbon dioxide was used to lower the pH to 6, the percent reduction in OD was 98.32% and when sulfuric acid was used to lower the pH to 6, this resulted in the lowest recovery of 91.62% reduction in OD.

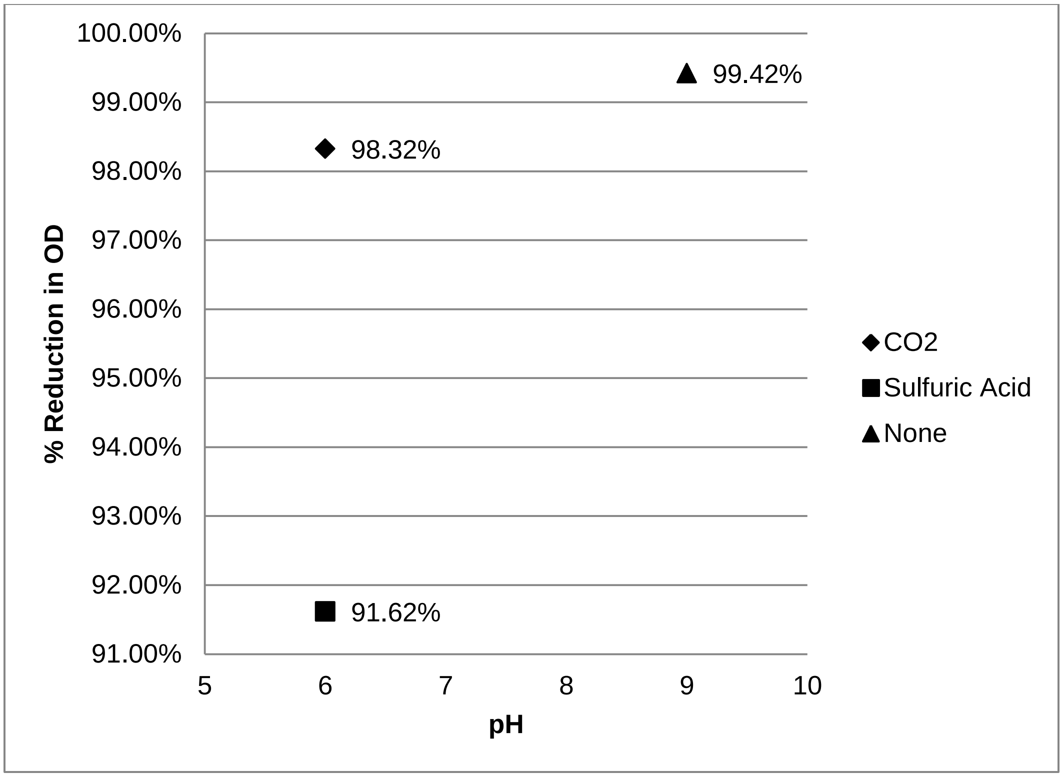

Figure 9: Screening effects of acid addition on removal efficiency

In Figure 8 it was shown that aluminum electrodes had a higher recovery potential at a pH lower than 9 using hydrochloric acid. The finding was not consistent with the acid screening with sulfuric acid or carbon dioxide in Figure 9. There are complex reactions involved in the dissociation of acids in the saline solution of the electrolytic cell. The range of responses from the three acids could be in part to the dissociation of ions from the acids and their effects on electro-coagulation. The concentration of hydrogen ions effects the ionization of the algae surface charge and the EC process as a whole [4]. The efficiency of flocculation depends on the aluminum species that form. Varying dissociation of the acids might have different reactions that interrupted the formation of positively charged aluminum species that adsorb algae during flocculation.

It was observed that the most cost effective and highest removal efficiency of electro-coagulation takes place without reducing the initial pH of the algae solution. This implied that the chemistry of adding positive hydrogen ions to lower the pH reduced the potential for electrolytic recovery. Lower recovery with lower pH was not consistent with data found in literature but could be an economic advantage if no pretreatment is required for high removal efficiency.

5.3 Objective 3

Polymer addition was calculated using an algae culture with an OD of 0.202 and biomass dry weight of 1.77 g/L. The dry weight of the untreated biomass was used as opposed to the dry weight of treated algae flocculated with aluminum ions (Table 6). This decision was rooted in the concept of the polymer's coating characteristics with untreated algae cells. The polymer had a coating efficiency of one to five percent its density. The median of this range was used to test the null hypothesis. If the addition of polymer were to have been significant, then the entire range would have been tested for optimization.

Table 6: Dry weight for polymer calculations

Sample	Note	Average DW (g/L)
Untreated Algae	OD=0.202	1.77
Algae Floc	Al electrode, 0.1 Amps	7.83

The polymer appeared to mix into the solution quickly; however, it was determined that polymer did not significantly increase the flocculation of algae (Table 7). This was likely because the electro-coagulation had effectively neutralized the negatively charged algae leaving no available bonding sites for the positively charged polymer.

Table 7: Data from polymer tests

Treatment	Average (V)	Final OD	% Reduction in OD	Average Final OD	Average % Reduction in OD	Standard Deviation
No Polymer Additions	1.06	0.008	95.77%	0.0057	97.32%	0.01
	1.15	0.005	97.66%			
	0.96	0.004	98.54%			
Polymer additions	1.08	0.025	89.84%	0.0167	93.30%	0.01
	1.05	0.013	94.49%			
	1.05	0.012	94.76%			

A 1 tailed t-test was chosen to test the statistical significance in the one direction of interest, which dedicated the complete alpha to test if 93.30% was significantly less than 97.32%. The t-test returned that the null was rejected because the mean was significantly less than 97.32% (Table 8). The result was that polymer additions returned significantly lower recovery efficiency than treatments without polymer additions.

Table 8: 1 Tailed t-test of polymer addition

	Mean	Standard Deviation	Standard Error	1-Tailed t-test
No Polymer Additions	97.32	1.42	0.82	p=0.03745
With Polymer Additions	93.03	2.77	1.6	

Figure 10 is a photo of the treatment results. Flasks 1-3 did not have polymer addition. Flasks 4-6 were treated with polymer.

Figure 10: Photo of results from polymer tests (flasks 1-3: no polymer addition, flasks 4-6: treated with polymer flocculant)

The amount of polymer needed to accurately mix with the algae was calculated based on DW of the untreated algae. After conducting experiments with aluminum electrodes at 0.1 Amps and the addition of 0.013 mL PolyDAD, the coagulation of algae after the EC treatment did not significantly increase. The addition of positive ions from the polymer failed to coagulate the remaining algae not coagulated with aluminum ions during EC treatment. The methodology of testing an amount of polymer in the middle of the functional range could contribute to the lack of significance if the polymer functions significantly better at the extremities of the range.

5.4 Objective 4

The objective was to understand the recovery curves of the two competing electrode types. The grade of steel used was 1018 Mild Steel, with low carbon (Table 9). The recovery of algae in solution varied with the current applied through electrolytic treatment (Table 10). Figure 11 shows that the comparable recovery of algae using steel electrodes required more energy input than aluminum.

One notable observation from the screening was that an orange residue coated the lab equipment when sampling solutions tested with steel. This suggests that the iron in the steel was oxidized during the electrolytic reaction and could have downstream effects.

Table 9: Properties of 1018 Mild Steel [23]

1018 Mild Steel	
Chemistry	% Composition
Iron (Fe)	98.81 - 99.26
Carbon (C)	0.18
Manganese (Mn)	0.6 - 0.9
Phosphorus (P)	0.04 max
Sulfur (S)	0.05 max

Table 10: Power consumption versus reduction in OD of Al and Steel

Material	Current (A)	Duration (min)	Average (V)	OD 1	OD 2	% Reduction in OD	Power (W)	Power Consumption (kW hr)
Al	0.05	15	0.97	0.131	0.001	99.2	0.0487	1.22E-05
Al	0.179	15	1.34	0.173	0.001	99.4	0.2399	6.00E-05
Al	0.5	15	2.22	0.143	0.001	99.3	1.1117	2.78E-04
Steel	0.05	15	0.89	0.171	0.082	52	0.0447	1.12E-05
Steel	0.179	15	1.76	0.137	0.002	98.5	0.315	7.88E-05
Steel	0.5	15	3.07	0.197	0.007	96.4	1.5367	3.84E-04

The results were plotted by material type in Figure 11, where the percent reduction in OD was plotted against the respective average power consumption.

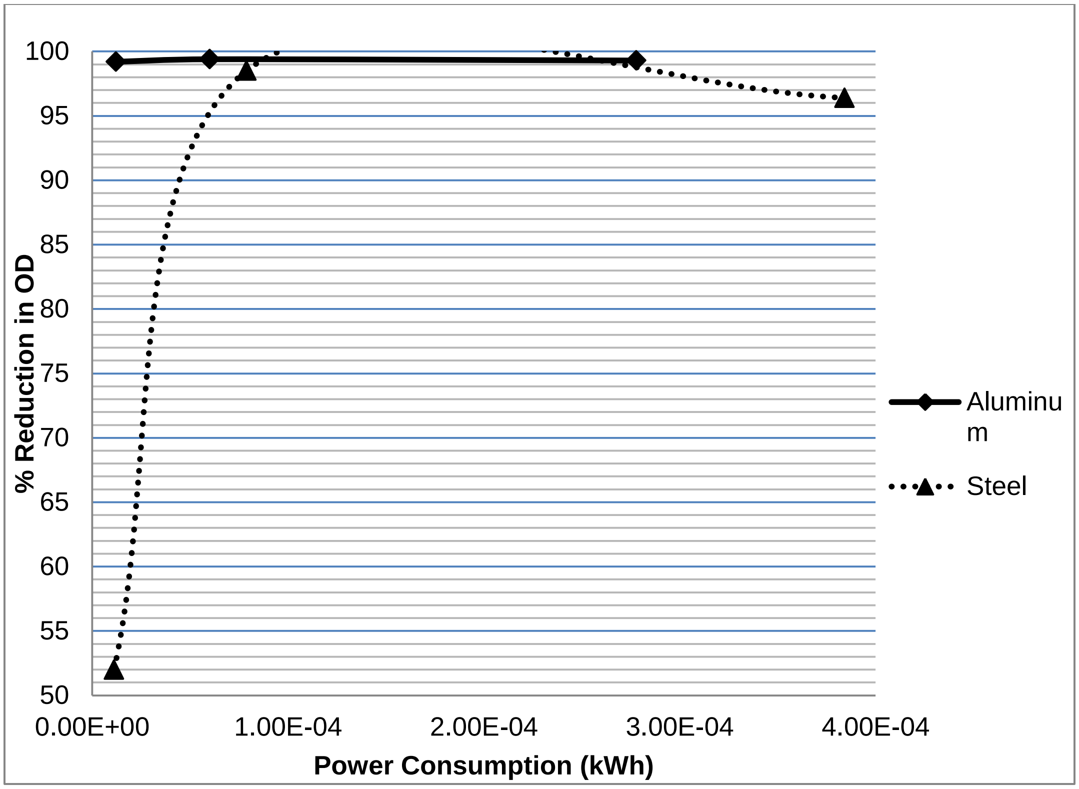

Figure 11: Recovery versus power consumption of aluminum and steel

The test indicated that the aluminum electrode maintains comparable recovery throughout the range of power tested (all recovery > 99%). The high performance at low energy inputs for aluminum suggests that operation costs lower than steel are possible. It may also be implied that the most cost effective point for aluminum was not seen in the range tested and could be at a lower energy input. The recovery varied for steel electrodes with the applied power resulting in a greater electrical demand than with aluminum electrodes while exhibiting poorer recovery.

Table 11: Faraday's calculation of Fe and Al added to algae during experiment (0.5 Amps)

Material	Amps	mol e-	Atomic Wt (g)	g into solution
Fe	0.5	4.67E-03	55.845	2.61E-01
Al	0.05	4.66E-04	26.981	1.26E-02
Al	0.5	4.67E-03	26.981	1.26E-01

Since the minimum amount of aluminum was not found in this screening, Table 11 shows the calculated and extrapolated amount of current applied and removal efficiency. The calculations were based on drop off in recovery efficiency with steel (using Fe properties). The estimate of charge from ions released into solution was calculated in Table 11, which assumes an ion of iron carries a charge of +2 and aluminum ion carries +3. Based on charge in solution, aluminum would reach the same low recovery drop to 52% as Fe at 0.033 Amps versus 0.05 Amps. There is uncertainty that is not accounted for in differences of bonding efficiencies between the two ions.

There is room for a detailed extrapolation of the power curve for aluminum. The drop off value of 0.03333 Amps for aluminum was calculated based on iron's drop off at 0.05 Amps which released a multiplier charge of -89.88. These values were found using Faraday's Law which does not removal efficiency into consideration. The extrapolated value in Table 12 is based on only two values from the steel screening. Additional iterations could be required for a detailed consumption description.

Table 12: Ion and charge calculations

Material	Amps	Removal %	Atomic Wt (g/mol)	Ions into solution (g)	Multiplier by ion charge	Multiplier by charge of e-
Al	0.03333[a]	n/a[b]	26.981	0.008	5.62E+20	-89.87
Fe	0.05	52	55.845	0.026	5.62E+20	-89.88
Al	0.05	99.2	27.981	0.013	8.43E+20	-134.82
Fe	0.179	98.5	55.845	0.093	2.01E+21	-321.76
Al	0.179	99.4	26.981	0.045	3.02E+21	-482.64

[a] 0.0333 was calculated for Al based on Fe's drop off at 0.05 Amps which released a multiplier charge of -89.88. Values were found using Faraday's Law

[b] Removal efficiency cannot be calculated.

5.5 Conclusion

In a test of aluminum, nickel, and steel electrodes, the most algae recovery was obtained with aluminum. Mineral tolerances of the metal ions in the by-product showed that aluminum was not close to the maximum allowable limit, but that nickel was. The cost of nickel was over eight times greater than aluminum as well [24]. From a commercial view, mineral allowances and cost confirm that aluminum has greater possibilities. Steel did not perform as well as nickel or aluminum.

Adjusting pH did affect electro-coagulation performance. When screening the pH with hydrochloric acid, the best performance was with aluminum electrodes between pH of 3 and 5. Screening the pH with carbon dioxide and sulfuric acid produced better results than hydrochloric acid at pH 6 with over 90% removal. Carbon dioxide addition performed the highest of any acid treatment with over 98% removal. The finding of carbon dioxide's relative success contributes to the idea that acid additions releasing hydrogen ions into the algae solution compete for aluminum flocculants such as aluminum hydroxide precipitates and monomeric-hydroxoaluminum cations [17]. The highest removal efficiency of over 99% was found with no acid treatment. There was an experimental design flaw in that the current applied to the two acid addition experiments in Objective 2 was not consistent (0.049 for Part 1 and 0.179 for Part 2) or based directly upon findings in Objective 1. The currents were chosen indirectly from a familiar range of testing.

The addition of an electro-polymer to the EC tests did not significantly improve the removal efficiency. It is assumed that the addition of positive ions into solution actually contributed to a repelling affect because the average OD with electro-polymer treatment was less than the control.

Performance characteristics versus algae recovery for EC favored aluminum electrodes. The test shows that the aluminum electrode maintains comparable recovery throughout the range of power with all recovery being above 99%. This also suggests that cost savings are possible while not sacrificing recovery of algae. The power range of aluminum was not found in this test because there was not distinct drop off in recovery. The extrapolated amperage of 0.033 is required to see a performance decline with aluminum electrodes that is paralleled to steel (52% recovery at 0.05 Amps). Recovery for steel varies greatly throughout the range of power tested. Steel electrodes never obtained recovery efficiency greater than 99% as aluminum showed consistently.

6. ELECTRO-FLOCCULATION RESULTS AND DISCUSSION

6.1 Sub-objective 1

The power consumption was calculated as the average voltage for the duration of each test. Each solution with different initial optical densities produced a similar shape performance curve. The curves display changes and distinct drop offs in removal efficiency with the variation in applied current. There is a grouping of curves (Figure 12) that have a similar performance drop off with the exception of the tests with the highest initial density (OD ~0.208). Each curve appeared to have maximum removal efficiency over 95% at values above the drop off section (0.1 Amps).

To understand how the results compared with the energy requirements for a centrifuge, the data was translated into terms of kWh/ton dry algal biomass. The energy requirements for centrifugation are estimated to be 3000 kWh/ton dry algal biomass [16]. At ~OD 0.08, the lowest density, a minimum of 0.100 Amps was required for 97.73% removal efficiency. At ~OD 0.208, the highest density, a minimum of 0.200 Amps was required for 99.89% removal efficiency. According to the Algal Growth Curve Results (4.3.5) the correlated biomass for the initial OD in the lowest and highest tested densities [OD 0.080 - OD 0.208] is 0.09 - 0.15 grams of algae per liter, respectively. The calculated energy requirements in this range are compared to energy requirements of a centrifuge.

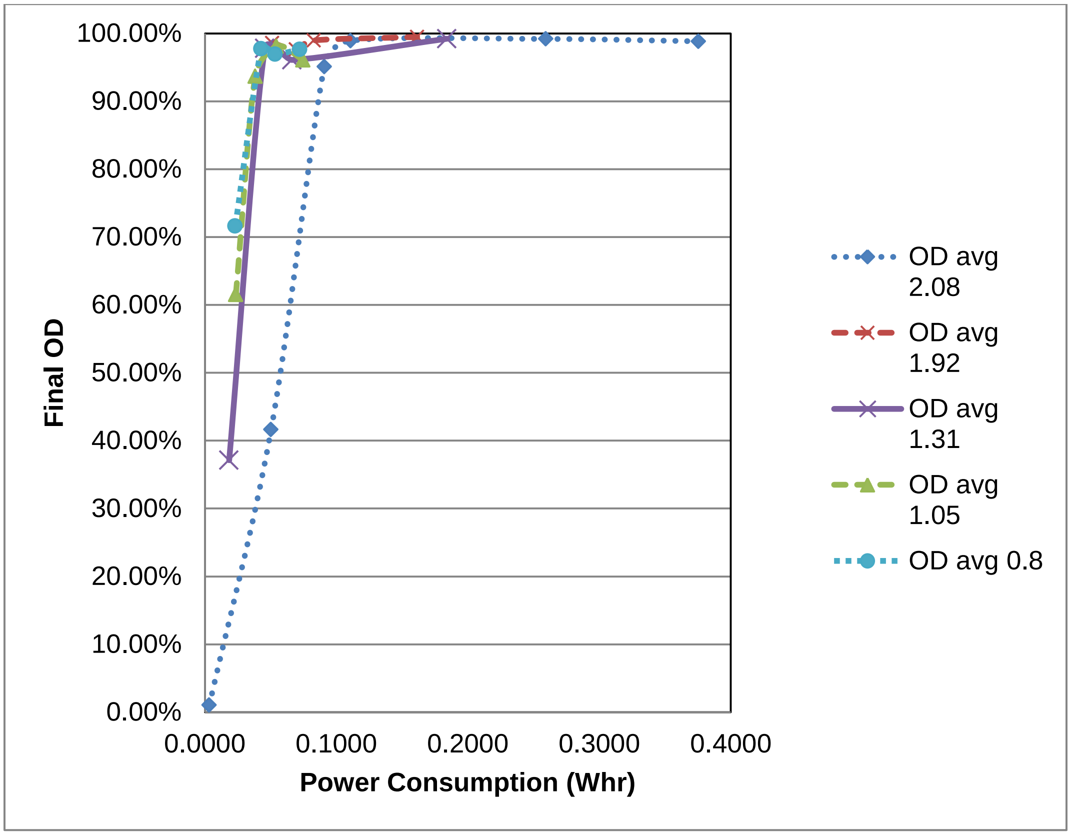

Figure 12: Power consumption versus removal efficiency for EF at OD 0.8-2.08

Table 13: Results of algae recovery efficiency and power consumption compared to centrifuge

Biomass (g/L)	kWhr	kWhr/ton	% of Centrifuge[a]
0.09	0.00009	432	14
0.15	0.00015	670	22

[a] Compared to 3000 kWh/ton dry algal biomass [10]

The minimum energy requirements for the the lowest OD curve was found to be 432 kWhr/ton and 670 kWhr/ton for the highest OD curve. The findings of these tests suggest that electro-flocculation is 4.5 - 7 times less energy intensive than a centrifuge (Table 13).

6.2 Sub-objective 2

Sub-objective 2 was designed to test dominant factors used in the electro-flocculation process (Table 14). The DOE developed for the experiment tested all combinations of factors. The current was held constant at 0.5 Amps and the final OD was the response.

Table 14: Operating parameters of the flocculation unit

2^k, k=4 parameters						Optical Density	
Material	Current (A)	Duration (min)	Mixing (min)	Surface Area (cm)	Electrode Distance (cm)	OD 1	OD 2
SS and SS	0.500	30	10	8	5	0.094	0.002
SS and SS	0.500	30	2	8	5	0.309	0.005
SS and SS	0.500	30	10	5	5	0.341	0.004
SS and SS	0.500	30	2	5	5	0.197	0.007
SS and SS	0.500	30	10	8	2	0.111	0
SS and SS	0.500	30	2	8	2	0.194	0.004
SS and SS	0.500	30	10	5	2	0.325	0.002
SS and SS	0.500	30	2	5	2	0.184	0.007
SS and SS	0.500	10	10	8	5	0.112	0.002
SS and SS	0.500	10	2	8	5	0.117	0.001
SS and SS	0.500	10	10	5	5	0.108	0.002
SS and SS	0.500	10	2	5	5	0.195	0.002
SS and SS	0.500	10	10	8	2	0.107	0.003
SS and SS	0.500	10	2	8	2	0.101	0.003
SS and SS	0.500	10	10	5	2	0.160	0.001
SS and SS	0.500	10	2	5	2	0.200	0.002

The factors found to be significant in the electrolytic process were identified for cost saving opportunities by testing the null hypothesis. An analysis of variance (ANOVA) was used for the factorial model to determine if the means of each group are equal (Table 15).

The resulting statistical analysis returned that the model was not significant. A possible flaw in the design of the experiment was the range and/or choice of values. If the high and low values tested were not exaggerated enough, then a significance will not be determined.

Table 15: ANOVA to determine optimum operating parameters of the flocculation unit (Type III)

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	6.09E-03	4	1.52E-03	0.43	7.83E-01
A-Duration	6.53E-04	1	6.53E-04	0.18	6.75E-01
B-Mixing	5.39E-03	1	5.39E-03	1.53	2.42E-01
C-Surface Area	4.98E-05	1	4.98E-05	0.014	9.08E-01
D-Electrode Distance	1.55E-06	1	1.55E-06	4.40E-04	9.84E-01

6.3 Conclusion

The findings from the electro-flocculation optimization experiments proved that the technology is competitive with centrifuge technology. The performance curves for the range of culture densities did not vary significantly. The lack of variation may offer opportunities for flexibility in design of the harvesting system as a whole when considering growth/retention time. The consistent shape of the performance curves in sub-objective 1 contributed to an understanding of electro-chemical reactions taking place in the test cell as it relates to applied current, cell density and percent removal.

7. SUMMARY

Electro-coagulation was found to offer greatly reduced capital and operating costs compared to harvesting with a centrifuge. As the objectives of Section 4 describe, there are many variables associated with optimizing the treatment process for the best quality byproduct and integration into the overall algal biofuel processing. Released ions mixed into solution have varying electro-chemistry depending on the ion species. The best treatment options found were with no initial pH reduction and no polymer addition for improved flocculation. Aluminum showed to be the favored electrode because mineral tolerances are comparatively high, the cost is lower than nickel, and the chemical reactions are better understood than steel.

The findings from the electro-flocculation optimization experiments proved the technology to be competitive with centrifugation. Electro-flocculation was also found to be comparable to electro-coagulation in energy consumption. The performance curves for the range of culture densities did not vary significantly. The lack of variation may offer opportunities for flexibility in design of the harvesting system as a whole when considering growth/retention time of an algal culture. A cost minimizing advantage of using electro-flocculation technology is that no electrode was consumed and the recovery efficiency was on par with electro-coagulation.

Table 16: Summary of proposed technology compared to centrifuge

Process	Factor	% Recovery	Amps	kWhr	kWhr/ton	% of Centrifuge Energy
Centrifuge[a]	-	100	-	-	10330	100
EC	Steel	97.17	0.100	0.00004	374	4
	Ni	97.47	0.075	0.00004	344	3
	Al	94.38	0.100	0.00003	239	2
EF	Low OD	97.73	0.100	0.00004	432	4
	High OD	95.12	0.150	0.00011	670	6

[a] [25]

Both electrolytic treatments offer robust and economic solutions to harvesting. The electrolytic methods tested in this research showed to be cost competitive with standard centrifuge technology. The best treatment combinations from the screening experiments are shown in Table 16. Electro-coagulation and electro-flocculation offer energy saving solutions equal to less than 15% of centrifuge requirements. Reduced harvesting costs could reduce the total processing costs from 40% to 3%. The energy savings implied in the findings of this work suggest direct electricity savings and progress towards a renewable energy future.

REFERENCES

[1] Energy Independence and Security Act of 2007, H.R. 6, 1st Session Cong. (2007).

[2] Ayhan, D. (2010). Use of algae as biofuel sources. *Energy Conversion and Management, 51*(12), 2738-2749. doi:10.1016/j.enconman.2010.06.010

[3] Demirbas, A., & Fatih Demirbas, M. (2011). Importance of algae oil as a source of biodiesel. *Energy Conversion and Management, 52*(1), 163-170. doi:10.1016/j.enconman.2010.06.055

[4] Uduman, N., Qi, Y., Danquah, M. K., Forde, G. M., & Hoadley, A. (2010). Dewatering of microalgal cultures: A major bottleneck to algae-based fuels. *Journal of Renewable and Sustainable Energy, 2*(1), 012701.

[5] A.L. Ahmad, N.H. Mat Yasin, C.J.C. Derek, J.K. Lim. (2010). Microalgae as a sustainable energy source for biodiesel production: A review. *Renewable and Sustainable Energy Reviews, 15*, 584-593.

[6] Wiley, Patrick, Campbell, J. Elliot, McKuin, Brandi. (2011). Production of Biodiesel and Biogas from Algae: A review of process train options. *Water Environment Research*. 83(4), 326-38. Doi: 10.2175/106143010X12780288628615

[7] Xu, L., Wang, F., Li, H., Hu, Z., Guo, C., & Liu, C. (2010). Development of an efficient electroflocculation technology integrated with dispersed-air flotation for harvesting microalgae. *Journal of Chemical Technology and Biotechnology, 85*(11), 1504-1507. doi:10.1002/jctb.2457

[8] Cherubini, F., & Stromman, A. H. (2011). Life cycle assessment of bioenergy systems: State of the art and future challenges. *Bioresource Technology, 102*(2), 437-451. doi:10.1016/j.biortech.2010.08.010

[9] Shelef, G.; Sukenik, A.; Green, M. (1984). *Microalgae Harvesting and Processing: A literature review,* SERI/STR-231-2396; Technion Research and Development Foundation Ltd.: Haifa, Israel.

[10] Schenk,P.; Thomas-Hall, S; Stephens, E; Marx, U.; Mussgnug, J.; Posten, C.; Kruse, O.; Hankamer, B. (2008) Second Generation Biofuels: High-efficiency microalgae for biodiesel production. *Bioenergy Res.* 1(1), 67-73.

[11] Azarian, G. H., Mesdaghinia, A. R., Vaezi, F., Nabizadeh, R., & Nematollahi, D. (2007). Algae removal by electro-coagulation process, application for treatment of the effluent from an industrial wastewater treatment plant. *Iranian Journal of Public Health, 36*(4), 57-64.

[12] Feng, C., Sugiura, N., Shimada, S., & Maekawa, T. (2003). Development of a high performance electrochemical wastewater treatment system. *Journal of Hazardous Materials, 103*(1-2), 65-78. doi:10.1016/S0304-3894(03)00222-X

[13] Vandamme, D., Pontes, S. C. V., Goiris, K., Foubert, I., Pinoy, L. J. J., & Muylaert, K. (2011). Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae. *Biotechnology and Bioengineering, 108*(10), 2320-2329. doi:10.1002/bit.23199

[14] Henderson, R.K., Parsons, S.A., Jefferson, B. (2008). Successful removal of algae through the control of zeta potential. *Separation Science and Technology,* 43: 1653-1666. doi: 10.1080/01496390801973771

[15] "Faraday's laws of electrolysis". *Encyclopædia Britannica. Encyclopædia Britannica Online.* Encyclopædia Britannica Inc., 2012. Web. 16 Aug. 2012 <http://www.britannica.com/EBchecked/topic/201755/Faradays-laws-of-electrolysis>.

[16] Mollah, M. Y. A., Morkovsky, P., Gomes, J. A. G., Kesmez, M., Parga, J., & Cocke, D. L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials, 114*(1-3), 199-210. doi:10.1016/j.jhazmat.2004.08.009

[17] Gao, S., Yang, J., Tian, J., Ma, F., Tu, G., & Du, M. (2010). Electro-coagulation-flotation process for algae removal. *Journal of Hazardous Materials, 177*(1-3), 336-343. doi:10.1016/j.jhazmat.2009.12.037

[18] Chen, G., & Hung, Y. (2007). Electrochemical wastewater treatment processes. *Advanced Physicochemical Treatment Technologies, 5*, 57-106.

[19] Alfafara, C., Nakano, K., Nomura, N., Igarashi, T., & Matsumura, M. (2002). Operating and scale-up factors for the electrolytic removal of algae from eutrophied lake water. *Journal of Chemical Technology and Biotechnology, 77*(8), 871-876. doi:10.1002/jctb.649

[20] Sandbank, E., Shelef, G., & Wachs, A. M. (1974). Improved electroflotation for the removal of suspended solids from algal pond effluents. *Water Research, 8*(9), 587-592. doi:10.1016/0043-1354(74)90116-X

[21] Han, M. Y., Kim, M. K., & Ahn, H. J. (2006). Effects of surface charge, micro-bubble size and particle size on removal efficiency of electro-flotation. *Water Science and Technology, 53*(7), 127-132. doi:10.2166/wst.2006.216

[22] Poelman, E., De Pauw, N., & Jeurissen, B. (1997). Potential of electrolytic flocculation for recovery of micro-algae. *Resources, Conservation and Recycling, 19*(1), 1-10. doi:10.1016/S0921-3449(96)01156-1

[23] Eagle National Steel. “Carbon Steel Grades.” 2009. Web. 5 May 2012. <http://eaglesteel.com/download/techdocs/Carbon_Steel_Grades.pdf>.

[24] MetalPrices.com. *Reports.* N.p., 2012. Web. 10 May 2012. <http://metalprices.com>.

[25] Milledge, John James. "Environment and Natural Resources Research." . N.p., 1 Dec 2011. Web. 26 Jul 2012. <http://www.ccsenet.org/journal/index.php/enrr/article/viewFile/12590/9273>.

APPENDIX A

Appendix A includes supporting data for the main results presented in Section 5 pertaining to electro-coagulation.

Table A.1: Aluminum, Nickel and Stainless Steel electrode power curve screenings (EC: Objective 1)

Date	Material	Current (A)	Avg. V	Power CONS (Whr)	RED in OD[a]	% RED in OD
27-Apr	SS	0.050	1.89	**0.0236**	0.064	61.5385
15-May	SS	0.075	2.04	**0.0383**	0.089	93.6842
16-May	SS	0.100	1.65	**0.0412**	0.103	97.1698
27-Apr	SS	0.125	2.39	**0.0747**	0.099	96.1165
15-May	Ni	0.030	1.48	**0.0111**	0.026	27.0833
15-May	Ni	0.075	2.02	**0.0379**	0.077	97.4684
15-May	Ni	0.100	1.70	**0.0425**	0.098	96.0784
15-May	Al	0.010	0.89	**0.0022**	0.003	3.7037
15-May	Al	0.030	0.97	**0.0073**	0.026	24.7619
15-May	Al	0.050	0.98	**0.0123**	0.083	80.58
16-May	Al	0.100	1.06	**0.0265**	0.084	94.38

[a] All recorded OD values were with 1/10 dilution

Table A.2: Screening of pH adjustments using HCl and Al and Ni electrodes (EC: Objective 2)

Material	Initial pH	% RED in OD
Al	2.87	0.4783
Al	3.47	0.9318
Al	5.02	0.9485
Al	6.1	0.0811
Al	6.66	0.0085
Al	7.32	0.0083
Ni	7.53	0
Ni	6.61	0.018349
Ni	5.57	0.070234
Ni	2.21	0.30303
Ni	3.72	0.007018
Ni	4.15	0.283388

Table A.3: Initial pH adjustment with electro-coagulation with Al electrodes (EC: Objective 2)

Acid	Volume (mL)	H2SO4 used (mL)	CO2 (cfm)	Desired pH	pH2	pH3	OD 1[a]	RED in OD[a]	% RED in OD
CO2	300	n/a	0.0133	6	5.76	6.02	0.179	0.176	0.983
H2SO4	300	0.5	n/a	6	6.1	6.62	0.167	0.153	0.916
None	300	n/a	n/a	9	n/a	7.15	0.173	0.172	0.99422

[a] All recorded OD values were with 1/10 dilution

Table A.4: Dry weight test results at OD of 1.92 (EC: Objective 3)

Sample Name	Volume (mL)	WT3	WT4	DW (g/L)	Average DW
100%	20	6.7768	6.8166	1.99	2.05
Dup	20	6.5573	6.5991	2.09	
Trip	20	6.8256	6.867	2.07	

Table A.5: Expected polymer range calculated based on algal dry weight (EC: Objective 3)

DW (g/L)	1% of DW	5% of DW	Units
2.05	0.0205	0.1025	g polymer/L algae
	0.0000205	0.0001025	g polymer/mL algae
	0.00615	0.03075	g polymer/300 mL algae
divided by polymer density of 1.09 g/cm3			
	0.005642202	0.028211009	mL polymer/300 mL algae

Table A.6: Performance characteristics data of Al and Steel during EC (EC: Objective 4)

Material	Current (A)	Duration (min)	Avg. V	OD 1[a]	OD 2[a]	% RED in OD	Power (Watts)	Power Cons (kW hr)
Al	0.05	15	0.97	0.131	0.001	99.2	0.0487	1.22E-05
Al	0.179	15	1.34	0.173	0.001	99.4	0.2399	6.00E-05
Al	0.5	15	2.22	0.143	0.001	99.3	1.1117	2.78E-04
Steel	0.05	15	0.89	0.171	0.082	52	0.0447	1.12E-05
Steel	0.179	15	1.76	0.137	0.002	98.5	0.315	7.88E-05
Steel	0.5	15	3.07	0.197	0.007	96.4	1.5367	3.84E-04

[a] All recorded OD values were with 1/10 dilution

APPENDIX B

Appendix B includes supporting data for the main results presented in Section 6 pertaining to electro-flocculation.

Table B.1: Recovery Efficiency versus Power Consumption at an average OD of 1.05

Current (A)	V1 (0 min)	V2 (7.5 min)	V3 (15 min)	Avg. V	Power CONS (Whr)	OD 1[a]	OD 2[a]	RED in OD	% RED in OD
0.05	2.69	1.49	1.48	1.886667	0.023583	0.104	0.04	0.064	61.54%
0.1	3.13	1.72	1.7	2.183333	0.054583	0.107	0.002	0.105	98.13%
0.15	3.35	1.92	1.9	2.39	0.074688	0.103	0.004	0.099	96.12%

[a] All recorded OD values were with 1/10 dilution

Table B.2: Recovery Efficiency versus Power Consumption at an average OD of 1.92

Current (A)	V1 (0 min)	V2 (7.5 min)	V3 (15 min)	Avg. V	Power CONS (Whr)	OD 1[a]	OD 2[a]	RED in OD	% RED in OD
0.01	2.99	1.59	1.59	2.056667	0.051417	0.211	0.003	0.208	98.58%
0.125	3.18	1.74	1.73	2.216667	0.069271	0.17	0.004	0.166	97.65%
0.15	3.19	1.73	1.71	2.21	0.082875	0.194	0.002	0.192	98.97%
0.25	3.5	2.14	2.11	2.583333	0.161458	0.192	0.001	0.191	99.48%

[a] All recorded OD values were with 1/10 dilution

Table B.3: Recovery Efficiency versus Power Consumption at an average OD of 2.08

Current (A)	V1 (0 min)	V2 (7.5 min)	V3 (15 min)	Avg. V	Power CONS (Whr)	OD 1[a]	OD 2[a]	RED in OD	% RED in OD
0.01	1.56	1.3	1.28	1.38	0.0035	0.283	0.28	0.003	1.06%
0.1	2.94	1.56	1.55	2.02	0.0504	0.264	0.154	0.11	41.67%
0.15	3.44	1.93	1.9	2.42	0.0909	0.123	0.006	0.117	95.12%
0.2	2.94	1.86	1.85	2.22	0.1108	0.282	0.003	0.279	98.94%
0.35	3.92	2.51	2.46	2.96	0.2593	0.123	0.001	0.122	99.19%
0.5	3.99	2.52	2.5	3	0.3754	0.172	0.002	0.17	98.84%

[a] All recorded OD values were with 1/10 dilution

APPENDIX C

Appendix C includes the media recipe for N. salina *grown for the studies recorded in this thesis.*

Table C.1: F/2 10x nitrates salina media recipe for all algae growth

Chemical	Weight/L	For 1L
Water		990 mL
Evaporated Sea Salt	20 g	20g
NaNO3		10mL
NaH2PO4*H2O		1mL
Trace Metals		1mL
Vitamin Solution		1mL

APPENDIX D

The maximum mineral tolerances were used throughout the research as a guide for the limits of ions released from electrolytic methods.

Table D.1: Donald Danforth Plant Sciences: Maximum mineral tolerances (prepared for NAABB by NMSU)

	Cattle	Horse	Swine	Poultry	Fish	Sheep
Aluminum mg/kg	1,000	1,000	1,000	1,000	-	1000
Arsenic mg/kg[c]	(30)	(30)	(30)	(30)	5	(30)
Barium mg/kg[c]	-	(100)	(100)	100	-	-
Bismuth mg/kg[c]	-	(500)	500	1,000	-	-
Boron mg/kg	150	(150)	(150)	(150)	-	(150)
Bromine mg/kg	200	(200)	200	2,500	-	(200)
Cadmium mg/kg[c]	10	10	10	10	10	10
Calcium %DM[d]	1.5	2	1	Growing Birds: 1.5 Laying Hens: 5	0.9	1.5
Chromium mg/kg[c] soluble Cr+++ CrO	(100) (3,000)	(100) (3,000)	(100) (3,000)	500 3,000	3,000	(100) (3,000)
Cobalt mg/kg[c]	25	(25)	100	25		25
Copper mg/kg[c]	40[h]	250	250	250[e]	100	15[h]
Fluorine mg/kg[c]	40	(40)	150	150	-	60
Iodine mg/kg[c]	50	5	400	300	-	50
Iron mg/kg[c]	500	(500)	3,000	500	-	500
Lead mg/kg[c]	100	10	10	10	10	100
Magnesium %DM	0.6	0.8	0.24	0.5 Growing Birds 0.75 Laying Hens	0.3	0.6
Manganese mg/kg	2,000	(400)	1,000	2,000	-	2,000
Mercury						

Table D.1 continued

mg/kg[c] inorganic	-	(0.2)	(0.2)	0.2	-	-
organic[f]	2	(1)	(2)	1	1	2
Molybdenum mg/kg	5	(5)	(150)	100	10	5
Nickel mg/kg	100	(50)	250	250	50	(100)
Phosphorous % DM[d]	0.7	1	1.0	1 Growing Birds 0.8 Laying Hens	1	0.6
Potassium %DM	2	1	1	1	-	2
Selenium mg/kg[c]	5	(5)	4	3	(2)	5
Silicon %DM	(0.2)	-	-	-	-	0.2
Silver mg/kg	-	-	(100)	100	>3	-
Sodium Chloride %DM	4.5 Growing Animals 3.0 Lactating Cows	6	3	1.7	-	4
Sulfur %DM	0.30 High-Concentrate Diet 0.50 High-Forage Diet	(0.5)	0.4	0.4	-	0.30 High-Concentrate Diet 0.50 High-Forage Diet
Tin mg/kg	(100)	(100)	(100)	(100)	-	(100)
Vanadium mg/kg	50	(10)	(10)	25 Growing Birds <5 Laying Hens	-	50
Zinc mg/kg	500	(500)	1000[g]	500	250	300

The mineral tolerance level (MTL) in parentheses were derived from interspecies extrapolation.

The dashes indicate that data were insufficient to set a MTL.

[c] The MTL for this nutrient is based on animal health and not human health. Lower levels are necessary to avoid excess accumulation in edible tissues.

[d] The MTL are based on diets with phosphorous levels at, but not above, the animal's requirement. Considerably higher levels can be tolerated if phosphorous levels are increased sufficiently to maintain an appropriate calcium:phosphorous ratio.

[g] Higher levels of as zinc oxide (2,000 to 3,000 mg/kg diet) are tolerated for several weeks and may provide growth promotion in weanling piglets.

[h] Assuming normal concentrations of molybdenum (1-2mg/kg diet) and sulfur (0.15-0.25%). At molybdenum and sulfur concentrations below these, copper may become toxic at lower levels.