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Evaluating Chemical and Electrocoagulation for the Treatment of Hydraulic Fracturing Wastewater

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EVALUATING CHEMICAL AND ELECTROCOAGULATION FOR THE TREATMENT OF HYDRAULIC FRACTURING WASTEWATER

by

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This thesis entitled:

EVALUATING CHEMICAL AND ELECTROCOAGULATION FOR THE TREATMENT OF HYDRAULIC FRACTURING WASTEWATER

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has been approved for the Department of Environmental Engineering

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

ABSTRACT

Sitterley, Kurban Andrew (M.S., Environmental Engineering)

Evaluating Chemical and Electrocoagulation for the Treatment of Hydraulic Fracturing Wastewater
Thesis directed by Professor Karl Linden

Hydraulic fracturing (HF) for oil and gas extraction is helping to meet worldwide changes in energy demand, but uses up to 13 million gallons of water per well, and generates a significant amount of high strength wastewater (HFWW). Onsite reuse of the wastewater can reduce the water intensity of HF through a combination of treatment and dilution. This type of reuse typically requires a reduction of suspended and colloidal material (turbidity), which can be accomplished with chemical coagulation (CC) and electrocoagulation (EC). In this study, EC was evaluated as a pretreatment option for a treatment train that could be used for onsite reuse of HFWW with a treatment goal of 90% reduction in turbidity and optimized reductions of the chemical oxygen demand (COD) and dissolved organic carbon (DOC). Design of experiments was employed to execute 32 experiments on a produced water sample that varied EC process control factors. Additionally, a dose-response curve was generated for CC with doses from 5 – 1,500 mg/L $FeCl_3$ and $AlCl_3$ as coagulants. The study evaluated the EC treatment impact on turbidity, COD, and DOC reduction. In addition, the treated water from four experiments was fractionated with membranes (10 kD, 5 kD, 1 kD) to evaluate the size of OM removed during EC and to compare them to chemically coagulated samples of the same water. For EC, turbidity reductions ranged from 74.6 – 97.3%, COD reductions ranged from 7.1 – 37.4%, and DOC reductions ranged from 5.7 – 54.0%; EC samples generally outperformed chemically coagulated samples, however, the dose-response curve indicates a high level of turbidity reduction with doses as low as 5 mg/L. Analysis of Variance (ANOVA) on experiments with the same electrode material revealed that the number of electrodes and amperage impacted treatment with EC most. The middle fraction (5 – 10 kD) saw the highest reductions in organic material and the smallest fraction (<1 kD) contained the most organic material but saw the smallest reductions. Electrocoagulation proved to be a suitable technology for turbidity reduction in a potential reuse scenario while achieving modest reductions in organic concentration that could be enhanced with another treatment technology after EC.

DEDICATION

This thesis is dedicated to my endlessly supportive parents, Buzz and Carol. With everything you have provided for me, I have been fortunate enough to enjoy experiences and opportunities that have enriched my life and opened new doors.

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My advisor, Dr. Karl Linden, deserves acknowledgement for giving me the freedom and autonomy to take this project where I wanted while also providing excellent guidance and advice and encouraging critical thinking. I also must acknowledge the Postdoc for this research project, Dr. James Rosenblum, for being a great resource and companion in the laboratory and giving me confidence to pursue research and my education at the next level. Finally, I must acknowledge my funding source, the Sustainability Research Network and National Science Foundation, and the community of researchers involved with the project.

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Introduction

Water is a precious natural resource, once thought to be infinite in supply and free of cost. However, as populations and industries grew, water started to have an increased and varied role in human society and industry. Water has been used in industry as a reactant, solvent, cleaning agent, and in a cooling or heating capacity [1]. It plays an intrinsic role in the energy industry, both in generating the energy (e.g. power plant cooling towers) and obtaining the raw materials used as fuel sources (e.g. oil and natural gas). The Energy-Water nexus considers the energy required to move, collect, treat, and store water and the water required to generate and transmit energy. These relationships are integral to the quality of life enjoyed by the much of the developed and developing world and will be a force that shapes the future.

Easily accessible conventional sources of oil and gas (O&G) have largely been exploited and will eventually be exhausted. With the demand for energy rising, industry is continually looking for efficient ways to extract O&G from new, unconventional sources such as methane hydrates, tar sands, coal bed methane, and shale oil/gas. Though these sources of O&G have been known for a while, it only recently became an economically viable way to obtain energy. It is estimated that these unconventional natural gas sources contain in excess of 730,000 trillion cubic feet (TCF) of natural gas, compared to the 6,600 TCF attributable to conventional sources [2]. Similarly, unconventional sources of oil have combined to total 70% of the world's 9 to 13 trillion barrels of oil resources and of that 70%, 6 to 8 trillion barrels are estimated to be from shale-based sources [2]. The development of two technologies has made exploiting unconventional sources more popular: directional drilling and hydraulic fracturing (HF).

Introduced by Stanolind Oil in 1949, initial HF wells saw production increase by 75% and used 750 gallons of HF fluid and 400 lb of sand [2]. Today, the average HF operation uses 60,000 gallons of fracturing fluid and 100,000 lb of propping agent; the largest operations exceed 1 million gallons of fluid and 5 million lb of proppant [2]. Recently, technological advances in horizontal drilling have made it economically feasible for energy companies to withdraw more oil and natural gas from tight, low-permeability geologic formations that previously would have been too expensive to exploit. These advances, including HF, have allowed production from tight formations to increase from <1 million barrels per day (MMbbl/d) in 2010 to >3 MMbbl/d in 2013 [3]. Overall, this has lead to an increase in natural gas production by 30% between 2010 and 2013 [4]. Assuming that oil and natural gas continue as a primary fuel source, some projections indicate that production could reach 13 MMbbl/d by 2035 and cause net oil imports to decline to zero by 2037 [3].

Water in Hydraulic Fracturing

While there is an obvious advantage to eliminating the need to import O&G, the increase in HF has led to an increase in the amount of produced water generated. Using data from 2007, Clark and Veil estimated that about 872 billion gallons of wastewater are generated from conventional and unconventional oil and gas sources in the United States each year [5]. The characteristics of this wastewater is highly variable and formation dependent, but is typically characterized by high levels of total dissolved solids (TDS), total suspended solids (TSS), hardness, bacteria, and naturally occurring radioactive material (NORM) [6].

The life of an oil and natural gas well has two phases: the development phase and the production phase. Depending on the target formation, each well requires between 2 and 13 million gallons of water to produce [4]. Wells drilled in the Wattenburg field, located in the Denver-Julesberg Basin northeast of Denver, CO, require between 1.4 and 7.5 million gallons per well for the development phase [7], with an average of 2.8 million gallons, much of which flows back to the surface and becomes wastewater (termed "flowback water") [8]. During the production phase, water flows to the surface that was previously contained in the formation and only is released during oil and natural gas production (termed "produced water"). The sum of these two wastewater sources is all the wastewater generated from HF operations. Controversy between O&G producers, local communities, and environmental activists surrounds the methods for disposing of hydraulic fracturing waste water (HFWW). Currently, the primary methods of disposal are: (1) injection into Class II injection disposal wells, (2) environmental discharge, (3) discharge to a treatment facility for eventual environmental discharge, and (4) on-site treatment and reuse [9].

Environmental Concern

Hydraulic fracturing is a practice that uses and generates toxic materials. Contamination of surface and ground water sources is a primary concern, but there are also impacts regarding air pollution, greenhouse gas emissions, and NORM.

The water used in HF can contaminate shallow drinking water aquifers through unintended perforations in the well casing, along existing geologic faults/fractures in the formation, or by way of an abandoned well that is no longer monitored or maintained [4]. As an example, analysis of wells in northeastern PA that were <1 km from HF operations found levels of short-chain hydrocarbons (i.e. methane and ethane) in proportions that were consistent with gas from the Marcellus formation at levels seventeen times higher than those wells not close to HF operations [10].

In addition to product oil and/or gas, there is also concern that the fracturing fluid itself or the produced water can contaminate drinking water aquifers. A controversial study by the EPA in Pavilion, WY suggested that elevated conductivity, pH, methane, ethane, and propane were a result of HF operations in the area [11], though the exact mechanism was not determined. Drinking wells in Garfield County, CO were found to have increasing chloride and methane concentrations over time that corresponded to an increase in O&G wells in the area from 200 to more than 1,300 [12]. There are several other examples of similar potential groundwater contamination occurring as a result of HF, well-summarized in [4].

HF can also have a negative affect on the air surrounding fracturing operations. Releases of NO_X, SO_X, volatile organic carbon (VOCs), particulate material (PM), ozone, and radioactive material (e.g. radon) can come from leaks at the well head, volatilization during unsealed storage, and unintentional releases during transport [13, 14]. Concentrations of ^{222}Ra were found to be ten times background levels in a study that sampled several HF sites in northeastern Colorado [15]. Perhaps the greatest concern is that fugitive emissions of methane during HF operations potentially negate any greenhouse gas emission reductions that are seen by burning natural gas instead of coal for energy, since methane contributes more to global warming that CO_2 on a mass basis [13]. A widely publicized study found that an average of 5.8% of the total methane flowing out of a shale gas well was lost to the environment throughout the whole process (i.e. production and upstream/downstream processes) [13]. A separate study that sampled air around HF operations in western Colorado found elevated levels of methane, methylene chloride, ethane, methanol, acetone, formaldehyde, and acetaldehyde [16]. Some of these chemicals are known to be toxic to humans and wildlife, and could especially impact young children or the elderly over long, chronic exposure times, or have synergistic effects when mixed with other toxic chemicals [16].

Another source of environmental concern that is not obvious is how treated produced water impacts the water bodies to which the effluent is discharged. Certain inorganic contaminants, like bromide, iodide, chloride, and ammonium, can pass through the treatment plant and impact downstream formation of disinfection by-products, which are known carcinogens [17]. Indeed, researchers have found that treated produced water effluent promoted the formation of haloaceto-nitriles (HANs), N-nitrosodimethylamine (NDMA), bromate, and trihalomethanes (THMs), as well as their iodated analogues (iodo-THMs) [18]. Treatment of produced water by three facilities in Pennsylvania that accepted produced water increased concentrations of Cl, Br, Sr, and Ba in the receiving water body to levels that exceeded the EPA's published maximum concentrations, and these levels were seen to decrease after the Pennsylvania Department of Environmental Protection requested that treatment facilities stop accepting produced water [19]. Warner, Christie [20] found that ^{226}Ra levels in sediments near the point of discharge were 200 times higher than background and concentrations of Cl, Br, Ca, Na, and Sr were 6,700 times higher than upstream concentrations at some sampling times. Among other trends, they found that the treated produced water effluent contributes 78% of the total downstream chloride flux despite contributing only 0.1% of the total flow. These types of results highlight how HF can truly impact the surrounding environment and why a membrane-based technology would be necessary in any treatment process if environmental discharge is to be a realistic disposal option for HFWW.

Regulations

Despite the increase in HF in the past decade, there is still little regulatory oversight of the practice at both the state and federal level compared to other industries. At the federal level, the Clean Water Act (CWA, 1972) regulates discharges of wastewater into “navigable waters” and established the National Pollutant Discharge Elimination System (NPDES), which requires permits for stormwater and wastewater discharge into surface waters. Additionally, the Safe Drinking Water Act (SDWA, 1976) implemented an Underground Injection Control (UIC) program intending to regulate subsurface storage of fluids and injections [21]. Seemingly, these two acts would provide authority for regulation of either surface storage ponds or underground disposal of HFWW, but the Energy Policy Act of 2005 exempted the “underground injection of fluids or propping agents … pursuant to hydraulic fracturing operations related to oil, gas, or geothermal production activities” [22]. The Energy Policy Act also gave categorical exclusion of O&G related activities to the National Environmental Policy Act (NEPA) of 1969, which intended to require government to consider the environmental impact of any federal action, unless the public can prove “extraordinary circumstances in which a normally excluded action may have a significant environmental effect” [21]. Hydraulic fracturing was further exempted from other federal hazardous waste regulations including those under the Subtitle C (HF waste is instead subject to the less stringent Subtitle D, which does not require surface storage pits to be lined) of the Resource Conservation and Recovery Act (RCRA) and regulations pertaining to the cleanup of accidental spills, leaks, and problems associated with underground disposal implemented by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, 1980) [21].

Most recently, on March 26, 2015 the Federal government released a Final Rule for HF on Federal and Indian Lands (40 CFR Part 3160). This was an update to regulations that were in place for 25-30 years and gave the BLM the authority to enforce monitoring and reporting requirements for the well casing on a hydraulically fractured well [23]. It also included a provision that requires operators to "manage recovered fluids in a rigid, enclosed, covered or netted and screened above-ground storage tank" and provides for very limited situations in which a lined pit may be used. However, on September 30, 2015, the U.S. District Court of Wyoming issued a preliminary injunction blocking this new rule from taking effect, contending that since the Energy Policy Act of 2005 eliminated the authority of the EPA to regulate HF on public land, Congress cannot now give this authority to the BLM [24]. Nevertheless, neither the existing Federal rules nor the new rules provide any specific guidance regarding how to dispose of HFWW, but mention that it could be injected, stored, taken to an off-site treatment facility, or re-used [23].

At the state level, states are allowed to impose regulations on HF, provided they meet the minimum requirements established at the federal level [21]. In some cases, states have imposed regulations specific to HF as a separate practice from general oil and gas operations, while in other cases constructing specific policies related to HF. For example, in Colorado oil and gas drillers must apply to the Colorado Oil and Gas Conservation Commission (COGCC) for a permit-to-drill that includes considerations of water sources up to 400 ft from the wellhead. If an operator wants to engage in "enhanced recovery operations" (e.g. hydraulic fracturing) they must apply for additional authorization and include details of the well-casing construction, the type and composition of fluids to be injected, as well as a description of the "stimulation program" they will use. When the composition of the injected fluid is considered to be a trade secret, operators are only required to acknowledge and record its identity, but must disclose it in the event of an occurrence (e.g. spill) that impacts public health, welfare, safety, or the environment and they must disclose it on FracFocus.org. The COGCC also requires operators to apply for an Earthen Pit Permit if they intend to use a pit to store wastewater, and also requires these pits to be lined, which is more strict than Federal regulations under RCRA Subtitle D that do not require a lining for storage pits of HF waste [21].

The State of New York has taken a more extreme position on HF, as it has completely banned the practice since 2010 until their Department of Environmental Conservation (DEC) had time to review the practice to certify that it is safe and develop "rigorous and effective controls" [21]. The DEC released their proposed regulations in 2011 and, among other considerations, they propose imposing setback limits for a well's proximity to drinking water sources, requiring three well casings on the borehole, requiring full disclosure of any chemicals used to the DEC, instituting a monitoring program for wastewater generated, and requiring a plan for disposal of flowback water that must be approved by the DEC. Additionally, several towns in New York have banned HF through zoning ordinances [21].

Texas, Wyoming, Pennsylvania, and Louisiana have also implemented their own regulations for HF operations in their state. The regulations are all similar, as operators in these states are required to apply for a permit and are responsible for disclosing what is in their fracturing fluid as well as for properly disposing of waste materials. All these states allow operators to store the waste generated onsite in lined pits, and Texas allows certain low-Chloride wastes to be disposed of by spreading it on the site where it was generated or by burying. All of these states require disclosure of chemicals used in HF to FracFocus.org [21].

Water Reuse In Hydraulic Fracturing

Reuse of HFWW is dependent on several factors: (1) how much HFWW is produced, (2) the time span over which HFWW is produced, (3) the rate at which HFWW is produced and how this rate changes over the life of the well, (4) the proximity of the well to a facility that is capable of treating the water for reuse, and (5) the quality of the HFWW generated [25]. Wells that produce a lot of water during the initial flowback are more ideal for reuse options because of the logistics associated with transporting and storing the water for reuse.

For operators producing water in the Marcellus Shale (and Pennsylvania in particular), reuse of HFWW increased significantly from 2009 to 2011, from <10% of all wastewater being reused in 2008, to almost 80% being reused in the latter half of 2011 [9]. Operators will commonly reuse HFWW by mixing it with freshwater in proportions that would sufficiently lower the TDS to allow for successful mixing of a fracturing fluid [26]. In addition, this same time period corresponded to a 30% dip in the average distance travelled per unit of wastewater disposed, indicating an increase in capacity and infrastructure required to treat and reuse this wastewater [9]. However, this increase in reuse may be unique to the Marcellus Shale and Pennsylvania, since there are only eight approved Class II injection disposal wells in Pennsylvania (thus having a much lower capacity to dispose of waste via injection) and the properties of the Marcellus Shale allow it to retain fluids through physiochemical interactions in a much higher capacity than other plays [9, 25]. The opposite is true in Texas, where only 5% of all water used is recycled due to the abundance of suitable injection wells [27]. Nationally, the rate of reuse for produced water is very small, and remains the lowest of all the disposal options used, as only 2% is estimated to go towards a beneficial reuse [5, 28].

It is estimated that 25% of the cost of a well is attributable to the act of fracturing the well, which is inclusive of the cost of water to fracture the well, and the cost to hydraulically fracture a well rose almost 500% between 2000 and 2007 due to more directional drilling and the requirement for more advanced drilling equipment [29]. Additionally, between 2000 and 2014, the median amount of water used to fracture wells rose from 177,000 gallons to 5.1 million gallons [30]. Considering these factors and the volatile nature of oil and gas prices, increasing reuse would reduce operators' costs, help improve their standing with the public, and reduce the amount of water withdrawn from the water cycle for HF [25]. Developing a suitable method for onsite reuse would not only reduce the cost of obtaining water to perform the hydraulic fracturing, but it would cut down on the financial and environmental cost attributable to transporting and disposing of the HFWW generated at each well. Range Resources, a company operating in the Marcellus Shale, attempts to reuse 100% of its HFWW, and the only "technology" it uses to do so is settling and dilution (i.e. blending with freshwater). They have found that they get the same result by using diluted HFWW as they would by using a fresh water source. In 2009, they completed 44 wells using 158 million gallons of fracturing fluid, 28% of which was recycled water, and estimate they saved $3.2 million in disposal fees, water cost, and trucking costs [26].

Water Quality for Hydraulic Fracturing Reuse

The water quality plays a huge role in determining the suitability of a water for reuse, as HFWW is typically high in TDS, TSS, hardness, and bacteria, all of which can impact the potential for that water to be reused as fracturing fluid [25]. Suspended solids and particulates can cause the well to clog as well as decrease the effectiveness of biocides present in the fracturing fluids. The concentration of organics in a water source will impact the fluid's stability under elevated temperature and pressure [31]. High TDS in a fracturing fluid will increase friction and cause mechanical problems for the drilling and pumping equipment [25]. Similarly, hardness and bacteria can cause scaling and fouling of the equipment used and the well bore itself, which would build up over time and cause damage that would cost the operator money (due to less productive well). Ideally, HFWW intended for reuse would have low TDS, low TSS, and minimal hardness and bacteria [25].

There is not consensus in the community of operators or the literature as to the water quality required for a water source to produce a successful fracturing fluid. Some operators insist on using a low-TDS source water while others have reportedly considered reusing waters with TDS approaching 120,000 ppm [31]. The range of TDS concentrations is similarly reflected in the acceptable range for other constituents, summarized in Table 1. This table reflects a combination of data from [31] that was acquired from two operators, Range Resources and Halliburton/XTO Energy, operating in the Marcellus Shale.

Table 1: Potential Water Quality Requirements for Frac Water Reuse

Parameter	Units	Source		
		Fresh	Clarified	Blended
TDS	mg/L	<500	<35,000 to 50,000	~26,000
TSS	mg/L	<2 to 10	<50	~1,500
Turbidity	NTU	<4	<100	NR
Hardness*	mg/L as $CaCO_3$	<150	<2,500	<5,000
Alkalinity	mg.L	~50	<600	NR
Soluble Organics	mg/L	<10 to 25	<50	<5
Bacteria Count	#/100 mL	<100	<100	10^6
Chloride	mg/L	<50	NR	~26,000
Iron	mg/L	<20	<3.5 to 10	~15
Sulfate	mg/L	<25	<125	NR
pH	---	6.0 to 8.0	6.5 to 8.5	>8

Table 1: Water quality parameters for a fresh, clarified for reuse, and blended water source for fracturing fluid. Taken from multiple sources so data many not be consistent. * : Hardness may include concentrations of Ca, Ba, Fe, Al, Mg, Mn, Sr, SO_4, CO_3

It is unknown how these water quality requirements would apply to source waters for different shale plays and fracturing fluid compositions.

The amount of treatment required for on-site reuse is extremely variable and is largely dependent on the method of hydraulic fracturing the operator is using as well as the geologic formation of interest. There are a wide variety of technologies capable of adequately treating the wastewater. Depending on the end-use goal, any treatment train developed for HFWW treatment would likely require multiple steps, with each step removing a different constituent of the wastewater (e.g. particulates, organics, salinity). Typically, a membrane technology such as reverse osmosis (RO) or nanofiltration (NF) or thermal distillation would be used for salinity reduction/removal (if blending with freshwater is not sufficient), and other physical, chemical, or biological treatment technologies would be used alone or in conjunction with one another as a pretreatment to reduce fouling on the membrane. A common physiochemical option for suspended and colloidal solids reduction before a membrane-based process is coagulation.

Coagulation as Treatment Process

In a water treatment process, coagulation is generally a pretreatment technology used before other technologies primarily to enable the removal of turbidity and suspended particles that may harbor pathogens [32]. It has also proven to be an efficient and economic method to reduce the organic concentration of water [33]. In coagulation, inorganic metal salts (generally based around Al(III) and Fe(III)) are added to water where they dissociate to their cationic metal species and then rapidly form a wide range of positively charged complexes. Negatively charged suspended colloids have their surface charge distribution destabilized by these complexes. These small, destabilized particles aggregate together (flocculation) to form larger particles, known as flocs, which are then settled and disposed. Colloids and organic matter (OM) is removed by coagulation by one of four mechanisms: (1) becoming enmeshed in the flocs, (2) sorption to flocs, (3) forming complexes and hydrolyzed species with the flocs, or (4) destabilization due to the flocs [33].

For all of these removal mechanisms, the speciation of aluminum and iron is important in determining the type and properties of the flocculant formed, which is largely based on the solution pH. The pH of minimum solubility is 6.3 for aluminum chloride and is 5.8 for iron chloride [32]. Higher molar mass polymer complexes are formed at pH values greater than the minimum solubility of the coagulants, while lower mass complexes, medium polymers, and monomers are formed at pH values less than this value. In general, the medium polymers are considered to be the most efficient for DOC removal, primarily because they are able to undergo complexation, adsorption, charge neutralization, and coprecipitation with OM [33].

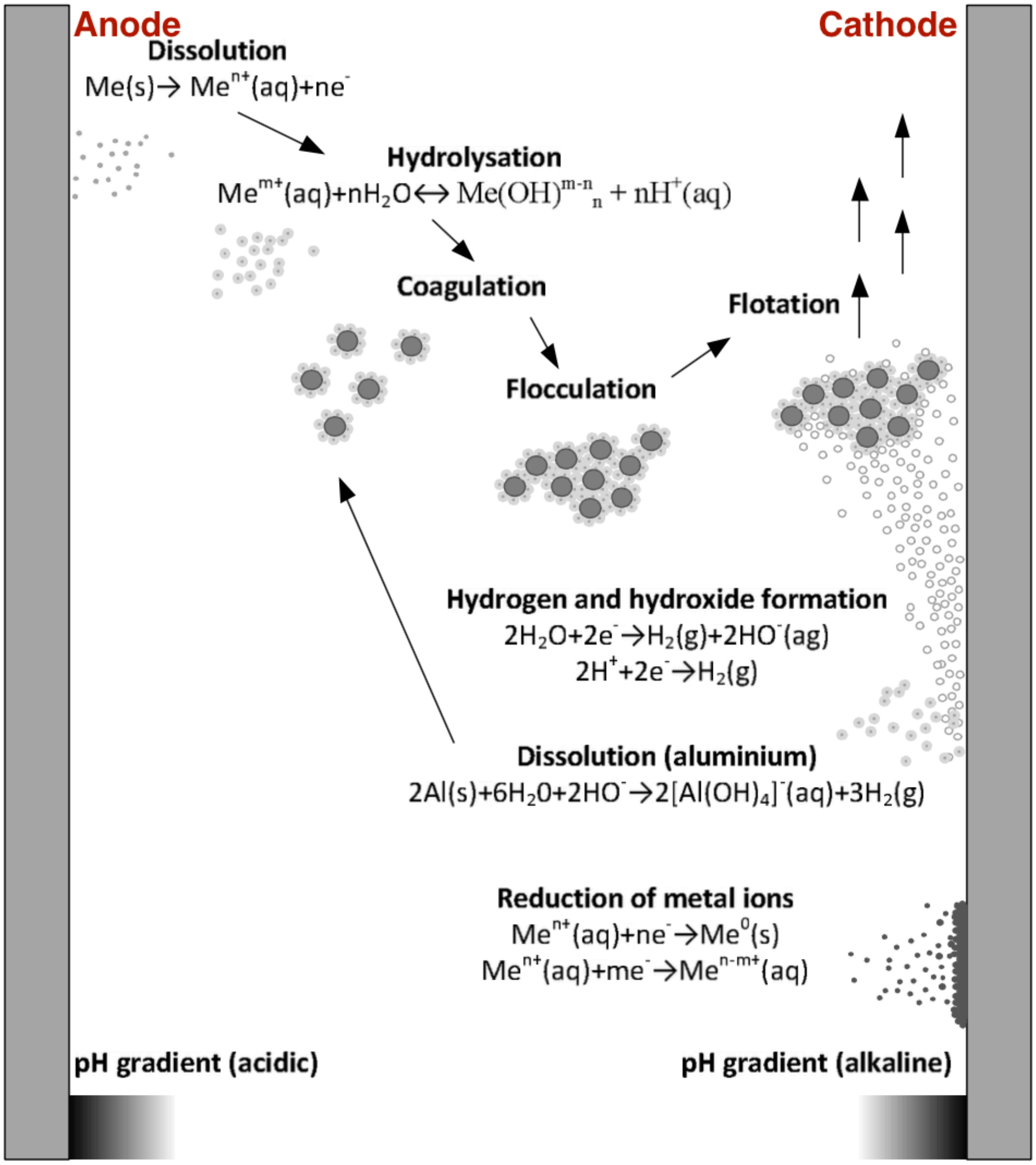
The efficacy of coagulation as a treatment technology relies on several factors: coagulant type, coagulant dose, mixing conditions, temperature, particle and OM properties, pH, and the ionic strength of the water. Optimizing and understanding these conditions for a particular water matrix is a popular research topic. In general, the inorganic metal salts are added as a solution ("chemical coagulation") but it is also possible to add them through electrocoagulation.

Electrocoagulation

Electrocoagulation (EC) is a physical-chemical water treatment technology that has been practiced for much of the 20th century and most recently used primarily for industrial wastewater applications [34]. EC works by passing an electric current through two (or more) electrodes that are immersed in the water to be treated. The electric current causes chemical reactions to occur at the cathode (positive electrode) and anode (negative electrode) that produce positively charged metal species to dissolve into the water. These species precipitate into solids that serve to destabilize particles and neutralize the electric charge on particles in the water, which then aggregate and settle [35].

There are a myriad of chemical reactions occurring simultaneously at the cathode and electrode that impact EC performance, illustrated in Figure 1 (adapted from [36]):

Figure 1: Electrocoagulation Illustration



Cations dissolve from the anode according to:

$$Fe_{(s)} \rightarrow Fe^{n+}_{(aq)} + ne^-$$

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$$

The speciation of iron is dependent on pH, but can be either +2 (Fe(II)) or +3 (Fe(III)). At the cathode, water is reduced to hydrogen gas and hydroxide:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$$

This reaction reveals one of the major differences between chemical coagulation (CC) and electrocoagulation: in chemical coagulation, addition of the coagulants results in a drop in pH, whereas in electrocoagulation, the pH increases over the duration of the process.

After the cationic metal ions are released into the water, they begin to react with constituents in the water to form precipitates and complexes that are responsible for pollutant removal. These complexes are largely dependent on the bulk characteristics of the water. These can be mononuclear (containing one metal atom) or polynuclear (containing multiple metal atoms). The mononuclear speciation for aluminum and iron is presented in Figure 2 and 3 as a function of pH and electrode potential (V) vs. Standard Hydrogen Electrode (SHE) (from [37]). These diagrams are important to consider when evaluating the different precipitates and complexes that could be present in an EC system as well as the potential for passivating conditions to exist. Passivation occurs when a thin metal oxide forms on the surface of the anode, restricting the ability to dissolve into the bulk solution [37].

Figure 2: Pourbaix Diagram – Iron

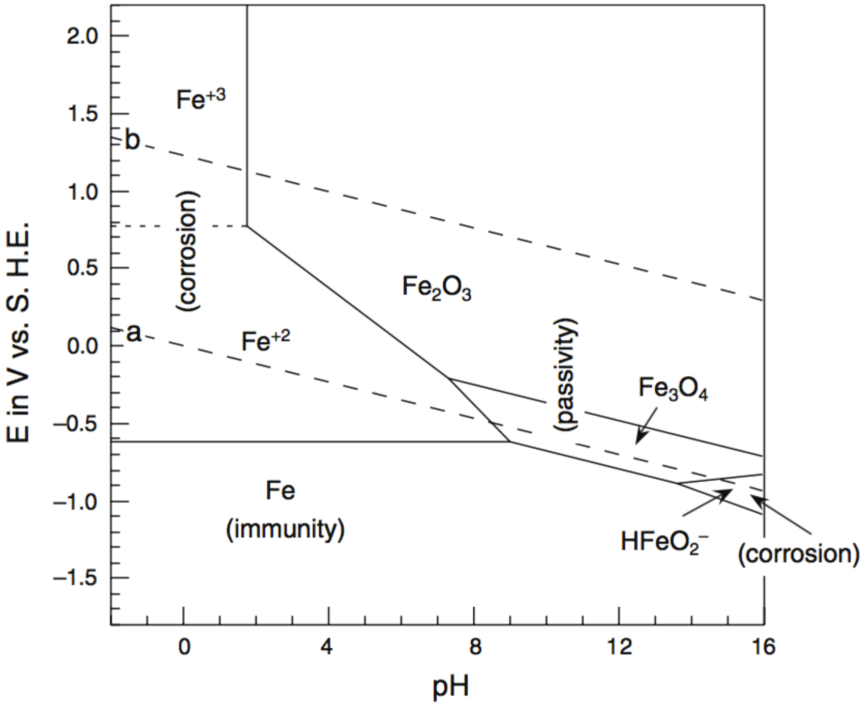
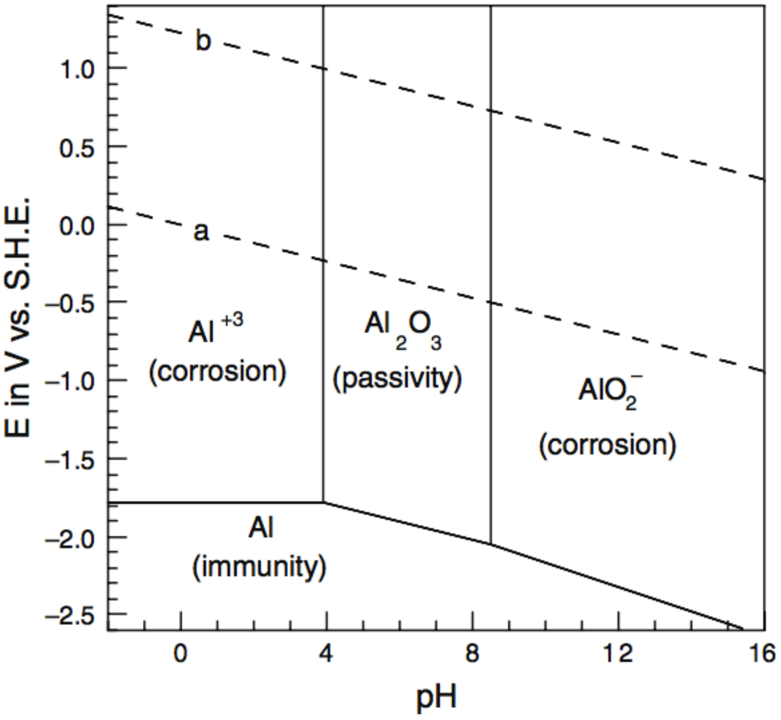


Figure 3: Pourbaix Diagram – Aluminum



There are several factors that can influence treatment with electrocoagulation [36]:

- *Electrode material*: typically iron or aluminum, but can be an inert material.
- *pH of the bulk water*: influences metal speciation and zeta potential of suspended particles.
- *Current density*: influences the amount of metal dissolved into the water over time.
- *Treatment time*: also influences the amount of metal dissolved into the water.
- *Electrode potential*: defines the reactions occurring at the electrode surface.
- *Bulk water quality*: affects removal efficiency and which pollutants are removed.
- *Concentration of anions*: influences the power necessary for treatment and the composition of complexes and precipitates formed.
- *Temperature*: impacts floc formation, reaction rates, conductivity, and removal efficiency.

Varying these parameters can have a significant impact on removal.

The electrical current affects EC mainly by controlling the charge loading (also called current density in some publications, units of Ah/m^3) in the system, which, for a batch system, is described by Eq. (1) [38]:

$$Q_e = \frac{nIt}{V} \qquad (1)$$

Where Q_e is the charge loading in the EC system (Ah/m^3), n is the number of EC cells in the system (two electrodes = one cell), I is the current through the cells (A), t is the residence time (h), and V is the volume of the batch of water treated (m^3). Charge loading has been shown to impact removal of turbidity [39, 40], COD [40-42], TOC [41, 42], oil and grease [43], and elemental pollutants [38, 44-46]. The charge loading controls the amount of cationic metal species that are dissolved in the water and are available to flocculate [47]. The amount of metal dissolved from the anode is described by Eq. (2) [48]:

$$w = \frac{ItM}{zF} \qquad (2)$$

Where w is the amount of metal dissolved (g), I is the current through the EC cell (A), t is the contact time (s), M is the molar mass of the anode material (g/mol, M = 55.85 g/mol for iron and 26.98 g/mol for aluminum), z is the number of electrons involved in the redox reaction (dimensionless), and F is Faraday's constant (96,500 C/mol, 1 C = 1 A*s). M, z, and F are constant (for the same electrode material), so the mass of ions dissolved into the water would increase with increasing current and time.

The initial pH of the wastewater has previously been shown to be a significant factor affecting performance of EC for removal of turbidity [40, 49-51], COD [40, 42, 50-52], TOC [50], oil [53], phosphate [54], hardness [51, 55, 56], and elemental pollutants [38, 57-59]. Differing pH impacts the metal precipitates and complexes formed for both aluminum and iron electrodes, and so would affect removal of suspended material and organics.

All of these factors would impact treatment of produced water from a HF operation. Electrocoagulation was thought to be a good pretreatment technology option for HFWW since (1) HFWW generally has a high conductivity, (2) EC has found success as a treatment technology for other high strength industrial wastewaters, and (3) EC can have a smaller footprint than other technology options [36].

Literature Review

Electrocoagulation is a physical-chemical water treatment technology that has been practiced for much of the 20th century and so there has been considerable research done on EC in a wide range of applications. The miniature review here is not comprehensive. A very comprehensive review can be found in [41].

Application for Industrial Wastewater

Organic Concentration Reduction

The effect of various parameters (reaction time, current density, pH) on COD and color removal were investigated using response surface methodology (RSM) by Davarnejad, Mohammadi [60]. Their results indicate current density to be the most significant factor for removal, and achieved 53.9% COD and 67.4% color reduction using aluminum electrodes, and 67.3% COD and 71.6% color reduction using iron electrodes, concluding that iron was a more effective electrode material in the treatment of petrochemical wastewater [60]. Similarly, RSM was used to optimize operational parameters (current density, pH, reaction time) of EC for turbidity reduction of a surface water prior to RO filtration by Moulai-Mostefa, Ladjelat [49] and determined the reaction time to be the most significant single factor affecting performance, and turbidity reduction increased with increasing pH and increasing current density [49]. RSM and central composite design (CCD) were used as statistical methods to analyze the turbidity, COD, and TOC removal for textile dyeing wastewater treated with EC under varying conditions by Kobya, Gengec [50]. Their experimental conditions included varying current density from 30 – 100 A m^{-2}, an initial pH between 4 – 8, and an operating time of 10 – 40 minutes for both aluminum and iron electrodes. Maximum removal of turbidity, COD, and TOC for aluminum electrodes was 94%, 82%, and 77% and for the iron electrodes was 99%, 69%, and 68%, respectively [50]. Zodi, Potier [61] evaluated the efficiency of the EC process for treatment of textile wastewater using RSM. They varied the current density (60 – 140 A m^{-2}), initial pH (3 – 11), and reaction time (30 – 90 minutes) to determine the optimum conditions for COD, turbidity, and total solids (TS) removal. Results show a maximum reduction of 73.3% COD reduction, 64.4% TS reduction, and 98.0% turbidity reduction and that optimum conditions for treatment are a current density of 85 A m^{-2} for 80 minutes at an initial pH of 7 [61].

EC operational parameters have also been optimized for phosphorous and COD removal from medical waste sterilization plant wastewater [54]. Using the Taguchi experimental method, experimenters varied the initial wastewater concentration, pH, current density, and the contact time and found that the initial wastewater concentration and pH had the greatest influence on removal, achieving 52% reduction in COD and complete phosphorous removal [54]. Similar research was done on synthetic dairy effluent wastewater and the results were compared to chemical coagulation with aluminum sulfate (Alum). Synthetic wastewaters of varying strengths were treated with a pair of aluminum electrodes and then samples were collected to determine the COD, phosphorous, and nitrogen concentrations. Results give an 89% reduction in phosphorous, 81% reduction in nitrogen, and a 61% reduction in COD [62]. Phosphorous and COD removal from municipal wastewater was also investigated using cylindrical aluminum electrodes and was found to increase with increasing salt content and applied electrical potential, up to 99% reduction of phosphorous and 75% reduction of COD [63]. Yavuz, Koparal [64] applied several electrochemical methods to a petroleum refinery wastewater to evaluate phenol and COD reduction potential. In this study, electrocoagulation was found to be ineffective for the treatment of petroleum refinery wastewater as they only achieved a 6.3% and 2.3% phenol and COD reduction, respectively, at a current density of 1 mA/cm^2 and 120 minute contact time with iron electrodes [64]. EC has been applied to potato chip manufacturing wastewater, which is high in COD, BOD, and suspended solids. Kobya, Hiz [40] performed experiments intended to determine the optimized operating conditions for the system. Electrode type (aluminum and iron), pH (2 – 8), current density (25 – 300 A m^{-2}), and residence time (5 – 40 min) were all varied to investigate their effect on COD and turbidity removal. They were able to achieve up to a 65% reduction in COD, a 98% reduction in turbidity, and a 95% reduction in TSS [40].

Hardness/Ion reduction

EC has also been investigated for its potential to reduce the hardness and concentration of inorganic ions in various types of wastewater. The operational conditions that affect phosphate reduction from synthetic wastewater using EC with aluminum electrodes was thoroughly studied by Attour, Touati [65]. Electrode spacing, current density, initial pH, conductivity, and temperature were all considered as potential factors affecting phosphate removal, with the best operating conditions found to be at a smaller electrode spacing, lower initial pH, higher current density, higher conductivity, and higher temperature [65]. Schulz, Baygents [66] explored the potential for EC to reduce concentrations of calcium, silica, and magnesium from cooling tower and reverse osmosis reject waters. Using a range of current densities, hydraulic residence times, and both aluminum and iron electrodes, researchers demonstrated a 80% reduction in silica and a 20 to 40% reduction in calcium and magnesium concentrations [66]. Hardness removal of up to 90% from was reported to be a function of initial pH (5.3, 7.2, and 10.1), voltage (5, 10, and 20), and retention time (20, 40, and 60 minutes) using aluminum electrodes [56]. A similar study was conducted using iron electrodes that determined the maximum hardness removal (98.2% for calcium hardness, 97.4% for total hardness) was obtained at a pH of 10, voltage of 12 V, and 60-minute reaction time [55]. EC treatment of chemical mechanical polishing wastewater was found to achieve a significant reduction in conductivity due to a 77% reduction in fluoride and 99% reduction of metallic ions as determined by x-ray fluorescence. The same study with the same water found a 75% reduction in COD [67]. Additionally, EC has been shown to reduce iron concentrations in tap water up to 99.2%. Ghosh, Solanki [59] found that a higher charge loading and closer electrodes gave a higher reduction in iron concentrations than other conditions tested. Using aluminum electrodes and increasing the contact time up to 60 s, EC was found to achieve high removal of ionic metal species responsible for scaling and fouling of membranes, such as calcium (100%), magnesium (87.9%), strontium (99.3%), barium (100%), and silicates (98.3%) [46].

Boron removal from wastewater using EC has also been demonstrated. Over a range of conditions tested, a neutral pH, higher charge loading, tighter electrode spacing, and longer residence time produced a lower Boron residual. At optimum conditions, 98% boron removal was obtained. [38]. EC aided by curcumin, the main curcuminoid in the spice turmeric, removed 20% more Boron from solution than EC alone. Boron removal increased when researchers increased the charge density of the EC cell and dropped the pH to 4.0 with a curcumin dose of 0.05 g [57].

Application for Produced Water

EC has shown promise as a technology to adequately treat produced water. Zhao, Huang [51] investigated EC removal of hardness, COD, and turbidity as a pretreatment for reverse osmosis (RO) membranes in the treatment of produced water and were able to achieve 85.81% reduction of hardness, 93.8% reduction of turbidity, and 66.6% reduction of COD under optimized conditions [51]. Similarly, using batch experiments of varying current density with lead dioxide and boron-doped diamond electrodes, COD was reduced by 96% using the boron-doped diamond electrode, and 84% using the lead dioxide anode. Total Petroleum Hydrocarbons (TPH) was reduced by 97% with the boron-doped diamond electrode and 84% with the lead dioxide electrode [68]. Gomes, Cocke [69] treated produced water from an oilfield in Texas with both aluminum and iron electrodes in a continuous flow cell and varied the residence time, initial pH, and added chemicals intended to serve as alkalinity boosters. The highest COD removal efficiency was 74.1% with the alkalinity booster and 82.9% without the alkalinity booster.

Goals

This study is one of several that are being done at the University of Colorado Boulder (CU) as part of the AirWaterGas Sustainability Research Network (SRN) funded by the National Science Foundation. From the program website, AirWaterGas.org:

> "The mission of the Sustainability Research Network is to provide a logical, science-based framework for evaluating the environmental, economic, and social trade-offs between development of natural gas resources and protection of water and air resources … Our goal is to find the balance between maximizing the development of natural gas and oil resources – for the benefits of short-term reduction of carbon dioxide emissions from power generation and transportation, national energy independence, and national job growth – and minimizing damage to water and air resources and risks to human health."

Considering this, the research presented here is intended to increase the knowledge of coagulation-based technologies and their application to HFWW as well as evaluate their potential in a reuse scenario or as a pretreatment for subsequent treatment technologies. This research is in addition to other research done on the efficacy of biological, Ultraviolet (UV), Advanced Oxidation Processes (AOPs), and membrane-based technologies as treatment options for HFWW. Each of these technologies can provide a different level of treatment that could enable the reuse of HFWW for different end-use options that require different levels of treatment. Essentially, the goal is to convert an otherwise worthless high strength wastewater to a water resource for operators. If the end-use goal were onsite reuse, the treated water would be used to mix hydraulic fracturing fluid to stimulate a HF well.

Objectives

The primary objective of this research is to evaluate the reduction in the suspended and colloidal fraction of solid material of HFWW through coagulation-based technologies. As there are no known water quality requirements for the fracturing fluid source water, a treatment goal of 90% reduction in turbidity was set. This was thought to represent a robust but achievable treatment level that could contribute to the general goals of this research.

A secondary objective of this research was to determine the reduction in COD and DOC that could be achieved with electrocoagulation and evaluate the size distribution of OM in the raw and treated sample. There was not a quantitative goal set for organic concentration reduction, only the maximum reduction associated with achieving the primary objective. The organic concentration would likely impact the potential for this water to be reused as a base for fracturing fluid, and OM size distribution could also influence the selection and operation of another treatment technology that could follow pretreatment in a treatment train.

A tertiary objective of this research is to determine the impact that different process variables have on the efficacy of electrocoagulation as a treatment option and determine which factors are statistically significant. This could help the optimization of treatment conditions in a reuse scenario. It should be noted that effectively modeling treatment outcomes is not an objective of this research.

Approach

The approach taken to evaluate CC and EC as treatment technologies was to determine the treatment outcome for each technology under conditions that are known to impact their performance. For CC, the only condition that was varied was the coagulant type and dosing. Dosing ranged from 5 – 1,500 mg/L for CC to replicate as closely as possible the dosing for EC experiments. It should be noted, however, that the research done in this work is supplemental to a more comprehensive study on CC for HFWW (publication under development).

Factors affecting EC are evaluated in this research. Five separate factors known to impact treatment were considered. Their impact on treatment was evaluated with a statistical method known as Design of Experiments (DoE) to determine optimum conditions and analyze the combined effects between different factors. This can be a powerful tool for efficient process optimization and model development. DoE involves randomized trials of examining a high (+1) and low (-1) input level for each factor and then evaluating the output with Analysis of Variance (ANOVA). All input levels for all factors are matched with each other in an experiment. Since there are two levels per factor, the total number of experimental condition combinations to examine all factors is 2^n, where n is the number of factors to be examined.

Methods

Water Sample

The produced water sample used for this analysis was collected 30 days after flowback from a horizontally drilled and hydraulically fractured well in Weld County, CO. The well was drilled in the Denver-Julesberg basin (Wattenburg Field) to access the Niobrara Shale. The sample was collected from a storage tank onsite and stored at 4°C prior to analysis. A partial summary of the water quality characteristics for this sample is provided in Table 2.

Table 2: Water Quality of Produced Water Sample

Constituent	Value
DOC	790 mg/L
COD	2,120 mg/L
TDS	24,700 mg/L
TSS	850 mg/L
Alkalinity	390 mg/L
Turbidity	390 NTU
pH	6.65
Ca	543.0 mg/L
Fe	0.5 mg/L
Si	26.6 mg/L
Na	9,440 mg/L
Cl	14,400 mg/L
Br	224 mg/L

Electrocoagulation Experimental Conditions

In this research, four input factors (X_i) were examined: (1) the applied current to the system (one or two amps), (2) the initial pH of the water (unchanged or adjusted to 10), (3) the contact time (i.e. the residence time, either 10 or 20 minutes), and (4) the number of electrodes (either 2 or 4). All of these factors were examined for both aluminum and iron electrodes. Three output factors (Y_i) were examined for each combination of factors: (1)

Turbidity reduction, (2) COD reduction, and (3) DOC reduction. Reduction was calculated according to Eq. (3):

$$\%R = \frac{Y_o - Y_i}{Y_0} \quad (3)$$

Where $\%R$ is the percent reduction of any parameter Y, Y_0 is the initial value for turbidity, COD, or DOC, and Y_i is the value of turbidity, COD, or DOC for experiment i. With four factors, 16 experiments were carried out for each electrode material, for a total of 32 experiments. The specific conditions for each experiment are summarized in Table 3. To assess the reproducibility of the experiments and to facilitate further analysis of the organics leftover from treatment, duplicates on some were carried out at a later date.

Table 3: Experimental Conditions

Identifier	Electrode Material	Amperage (A)	pH adj.	Res. Time (Minutes)	Number Electrodes
EC1	Al	1	---	10	2
EC2	Al	1	---	10	4
EC3	Al	1	---	20	2
EC4	Al	1	---	20	4
EC5	Al	1	10	10	2
EC6	Al	1	10	10	4
EC7	Al	1	10	20	2
EC8	Al	1	10	20	4
EC9	Al	2	---	10	2
EC10	Al	2	---	10	4
EC11	Al	2	---	20	2
EC12	Al	2	---	20	4
EC13	Al	2	10	10	2
EC14	Al	2	10	10	4
EC15	Al	2	10	20	2
EC16	Al	2	10	20	4
EC17	Fe	1	---	10	2
EC18	Fe	1	---	10	4
EC19	Fe	1	---	20	2
EC20	Fe	1	---	20	4
EC21	Fe	1	10	10	2
EC22	Fe	1	10	10	4
EC23	Fe	1	10	20	2
EC24	Fe	1	10	20	4
EC25	Fe	2	---	10	2
EC26	Fe	2	---	10	4
EC27	Fe	2	---	20	2
EC28	Fe	2	---	20	4
EC29	Fe	2	10	10	2
EC30	Fe	2	10	10	4
EC31	Fe	2	10	20	2
EC32	Fe	2	10	20	4

Design of Experiments Analysis

ANOVA for the DoE was carried out with Minitab (Minitab Inc.; State College, PA).

The input factors were: amperage (X_1), pH (X_2), residence time (X_3), and number of electrodes (X_4). The output factors were: turbidity reduction (Y_1), COD reduction (Y_2), and DOC reduction (Y_3). The analysis was done to give a linear model that include two-way interactions of the form:

$$Y_i = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_{ij} + \varepsilon$$

Where Y_i is the removal efficiency for an output factor, β_0, β_i. and β_{ij}, are the regression coefficients for the intercept, linear, and interaction terms, respectively, and X_i and X_{ij} are the input variables that correspond to factor levels.

Based on the literature review, it was expected that the electrode material would be a significant factor, so the ANOVA was initially analyzed as two separate groups of 16 experiments based on electrode material. That is, electrode material was not initially included as a factor for the ANOVA analysis. This was done to better understand how the other factors impacted treatment.

Because the object of this study was not to effectively model these constituent reductions with different factors (but rather to identify which factors most significantly affect removal), models were not optimized to give the highest possible R-squared values. Adding or removing factors and factor interactions from a model would affect the relative significance for included terms. By leaving all first and second-order terms in all models, factor significance could effectively be compared from one model to the next.

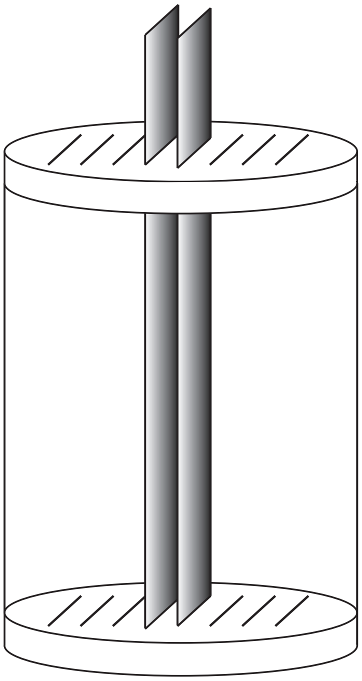
Experimental Procedures

Electrocoagulation

The vessel used to conduct the electrocoagulation experiments was a cylinder with a height of 10.5 cm and a diameter of 6.25 cm. It was designed with a lid that had slits spaced

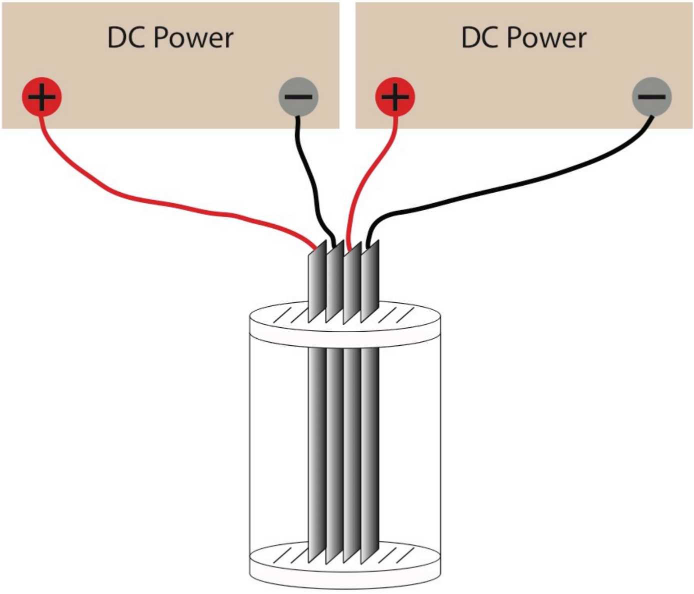
0.5 cm apart to facilitate variable spacing of electrodes. These slits were designed so that the experimenter could insert the electrodes into the lid and the electrodes would then sit in identically spaced grooves in the bottom of the cylinder. This was done to ensure that the desired electrode spacing would be preserved throughout the experiment. The height of the vessel was chosen as to allow for 0.5 cm of the electrode to protrude from the top of the lid when in place to allow for attachment of the alligator clips from the DC power source. Figure 4 is a schematic of the electrocoagulation reactor (not to scale).

Figure 4: Electrocoagulation Reactor



The electrodes were strips of metal with dimensions of 12.7 cm x 2.2 cm and made of either iron or aluminum (VWR Intl.; Radnor, PA). The total area of electrodes that was submerged was 20 cm^2 and electrode spacing was kept constant at 1 cm. The electrodes were connected in series with the DC power supply capable of maintaining constant amperage through the circuit. Each pair of electrodes was connected to its own power supply (i.e. two power supplies were used for the experiments run with four electrodes) and electrodes were connected in an alternating cathode/anode fashion (see Figure 5).

Figure 5: Electrode Configuration – Four Electrodes



Each experiment was conducted in 250 mL batches. Prior to any experimental run, the vessel and electrodes were rinsed thoroughly with Milli-Q water. The raw water was measured using a graduated cylinder and then placed in the EC vessel. Electrode spacing was 1 cm for all experiments. After setting the proper amperage on the power supply, the electrodes were connected and the power was turned on. At the end of the predetermined contact time, the power was shut off and the electrodes were carefully removed from the vessel before allowing the sample to settle for 30 minutes. Used electrodes were soaked in acetone for 10 minutes and then scrubbed and rinsed with Milli-Q water to remove solid residues and set aside to dry. At the end of the settling period, a 55 mL aliquot was taken from the middle of the reactor. Approximately 25 mL of this sample was immediately put in a turbidity cell and analyzed for turbidity, while the other 30 mL was filtered through 0.45 µm nylon filters (flushed with 30 mL of Milli-Q) and set aside for COD and DOC analysis.

Samples were diluted 1:10 prior to COD and DOC analysis in order to stay in the accepted range for the instruments. DOC was analyzed using a Shimadzu TOC-V CSH. COD was analyzed using Hach COD HR 21259 (Hach Co.; Loveland, CO). Turbidity was analyzed with a Hach 2100N Turbidimeter.

Chemical Coagulation

The coagulants used were iron chloride ($FeCl_3$) and aluminum chloride ($AlCl_3$). $FeCl_3$ was added pre-hydrolyzed as Ferric Chloride Hexahydrate ($FeCl_3*6H_2O$; Fisher Scientific; Fair Lawn, NJ) and $AlCl_3$ was added pre-hydrolyzed as Aluminum Chlorohydrate ($Al_2ClH_5O_5*2H_2O$; Spectrum Chemical Mfg. Corp.; Gardena, CA). Samples treated with doses of 5, 15, 30, 45, 60, 90, 120, 240, 500, 1000, and 1,500 mg/L of both coagulants were prepared through a series of jar tests. The samples were analyzed for turbidity to generate a dose-response curve.

Chemical coagulation samples were prepared using a Jar Tester (Phipps & Bird, Model 7790-400). One liter of raw water was placed into each jar. An appropriate amount of coagulant was added and mixed at 300 rpm for 1 minute. Then the jars were set to a three-stage tapered floc of 55 rpm, 35 rpm, and 15 rpm, each stage for 10 minutes. Finally, the mixers were turned off and the jar was left to settle for 30 minutes.

Fractionations

Samples generated from EC and CC tests were fractionated to roughly determine the size distribution of organic material that remained after treatment. The experiments chosen for fractionation corresponded to those performed with the lower levels of each factor for each electrode material (EC1/EC17) and those done with the higher levels of each factor (EC16/EC32) as well as two chemically coagulated samples that achieved a

90% reduction in turbidity (45 mg/L $FeCl_3$ and 30 mg/L $AlCl_3$). The raw water was also fractionated as a control for comparison. The fractionated samples were then evaluated against each other.

Fractionations were done using regenerated cellulose membranes Ultracel Ultrafiltration Discs (EMD Millipore Corporation, Billerica, MA) with pore sizes of 10,000 Daltons (kD), 5 kD, and 1 kD. The membrane was first soaked in one liter of DI water with slow stirring for one hour, changing water every 15 minutes. Then, the membrane was placed in the 300 mL fractionation cell and flushed with a minimum of 50 mL of DI.

A total of four mass fractions were calculated for each sample: >10 kD, 5 kD to 10 kD, 1 kD to 5 kD, and <1 kD. Three dilutions (1:50) of each sample were fractionated through each membrane rather than serially fractionating one dilution. That is, one dilution was fractionated with a 10 kD membrane, one dilution was fractionated with a 5 kD membrane, and one dilution was fractionated through a 1 kD membrane.

After fractionating, the water that passed through the membrane and that didn't pass through the membrane was captured and their volume measured. The volume of diluted sample that entered the fractionation cell was measured by weighing the dilution vessel before and after placing the sample in the dilution vessel and taking the difference, with the assumption that 1 g of water was equivalent to 1 mL of water. The volume of the recovered water was measured in an identical way. Then, the recovered water and the initial dilution were analyzed for DOC.

Results

A series of tests were carried out based on the DoE and results were compiled and summarized. Table 4 summarizes reductions overall, as well as reductions for experiments carried out with aluminum electrodes and iron electrodes separately. The primary treatment objective of the study was to achieve a 90% reduction in turbidity, as clarification is generally the primary goal of a pretreatment technology, with reductions in organic concentration (i.e. COD and DOC) being a secondary treatment objective for EC.

In the following sections, results are first presented for EC reductions of turbidity, COD, and DOC, and how the ANOVA analysis informed the significance of each factor to treatment. Then, the results of the jar tests for each coagulant are presented. Finally, the results from the mass fractionation are shown as the size distribution in the raw and treated samples as well as changes to each fraction when compared to the raw sample.

For ease of presentation, models are referred to as "electrode material/output factor," so the model for DOC removal with aluminum electrodes would be "aluminum/DOC". The p-values for the factors and interactions for each model generated are summarized in Table 5 (for aluminum electrodes) and Table 6 (for iron electrodes), and the model summaries are in Table 7 and 8. The models themselves are available in the Appendix. Significance was determined by having a p-value less than the predetermined significance level of 95% (α = 0.05) in the ANOVA analysis.

The effects plots presented (Figures 6, 9, and 11) are intended to show how the reduction changed with a change in factor level. The vertical axis is the average reduction at that factor level, and the horizontal axis is the value of each factor level. Lines with a positive slope indicate that reduction of that constituent increased with increasing factor levels, while lines with a negative slope indicate that reduction of that constituent decreased with increasing factor levels. The average reductions for each constituent at the different factor levels are available in tables in the Appendix. Supplemental material regarding the modeling aspect of this research, as well as the models themselves, can also be found in the Appendix.

Table 4: Constituent Reduction Summary

Electrode Material	**% Turbidity Reduction**				**% COD Reduction**				**% DOC Reduction**			
	Min.	*Max.*	*Avg.*	*SD*	*Min.*	*Max.*	*Avg.*	*SD*	*Min.*	*Max.*	*Avg.*	*SD*
Overall	74.6%	97.3%	87.4%	6.7%	7.1%	37.4%	22.2%	8.3%	5.7%	54.0%	28.8%	14.0%
Aluminum	80.6%	97.3%	93.0%	3.9%	7.1%	34.8%	22.4%	7.2%	13.2%	47.8%	30.4%	10.7%
Iron	74.6%	87.8%	81.9%	3.5%	9.5%	37.4%	22.1%	9.6%	5.7%	54.0%	27.2%	16.9%

Table 5: P-values for Aluminum Models

Source	**P-value (Turbidity)**	**P-value (COD)**	**P-value (DOC)**
Amps	0.036	0.003	0.001
pH	0.011	0.436	0.115
Residence Time	0.155	0.033	0.012
Number of Electrodes	0.024	0.006	0.001
Amps*pH	0.185	0.240	0.580
Amps*Residence Time	0.512	0.282	0.641
Amps*Number of Electrodes	0.691	0.053	0.911
pH*Residence Time	0.218	0.339	0.836
pH*Number of Electrodes	0.251	0.357	0.222
Residence Time*Number of Electrodes	0.292	0.167	0.600

Table 6: P-values for Iron Models

Source	P-value (Turbidity)	P-value (COD)	P-value (DOC)
Amps	0.391	0.004	0.007
pH	0.226	0.073	0.092
Residence Time	0.149	0.023	0.513
Number of Electrodes	0.478	0.000	0.000
Amps*pH	0.318	0.892	0.652
Amps*Residence Time	0.453	0.471	0.500
Amps*Number of Electrodes	0.192	0.026	0.004
pH*Residence Time	0.618	0.535	0.540
pH*Number of Electrodes	0.739	0.026	0.285
Residence Time*Number of Electrodes	0.935	0.054	0.090

Table 7: Model Summary for Aluminum Models

Parameter	Turbidity	COD	DOC
S	0.0240	0.0315	0.0358
R-sq	90.0%	93.6%	96.3%
R-sq (adj.)	70.0%	80.7%	88.8%
R-sq (pred.)	0.0%	34.2%	61.8%

Table 8: Model Summary for Iron Models

Parameter	Turbidity	COD	DOC
S	0.0343	0.0226	0.0364
R-sq	68.5%	98.1%	98.5%
R-sq (adj.)	5.4%	94.4%	95.4%
R-sq (pred.)	0.0%	80.8%	84.1%

Treatment Outcomes

Turbidity

Of all of the different combinations of factors that were tested, only those that used aluminum electrodes were able to achieve the primary objective of a 90% reduction in turbidity. In general, turbidity reduction did not appear to be a function of any of the four factors considered in these experiments, as the average reduction showed minimal difference between factor levels. Figure 3 describes how each factor level for both electrode materials impacted turbidity reduction.

Turbidity reduction for all experiments is summarized in Table 9, and the first two columns summarize turbidity reductions for experiments done with aluminum electrodes. Of the those carried out with aluminum electrodes, fifteen achieved a reduction of 90% or greater. The only combination of factors that did not achieve the 90% reduction target was EC12, with a reduction of 80.6%. The average turbidity reduction with aluminum electrodes did not change much between factors and factor levels, but generally decreased with increasing factor levels. Table 4 shows the p-values for the aluminum/turbidity model, which found that amperage, pH, and the number of electrodes were all significant.

The right two columns of Table 9 summarize turbidity reductions for experiments done with iron electrodes. None of the experiments carried out with iron electrodes achieved the stated goal of 90% reduction in turbidity. Figure 6 indicates that, similar to those experiments done with aluminum electrodes, turbidity reduction was not markedly affected by a change in factor levels. The iron/turbidity model was the worst fit model, and none of the factors or factor interactions were found to be significant.

Figure 7 is a contour plot showing how turbidity reduction was affected by the number of electrodes (vertical axis) and the pH (horizontal axis) for both aluminum (left plot) and iron (right plot) electrodes. Figure 8 is a similar contour plot, except with residence time (vertical axis) and pH (horizontal axis). Darker greens correspond to higher reductions and light green/darker blue corresponds to lower reductions. These two figures intend to highlight how, under identical conditions, the turbidity reduction trend for iron electrodes was the opposite of that for aluminum electrodes with respect to the initial pH of the water.

Table 9: Turbidity Reduction Summary

Identifier (Al electrodes)	Turbidity Reduction	Identifier (Fe electrodes)	Turbidity Reduction
EC1	94.9%	EC17	79.9%
EC2	91.2%	EC18	86.0%
EC3	93.1%	EC19	84.5%
EC4	90.1%	EC20	81.5%
EC5	97.3%	EC21	87.8%
EC6	94.1%	EC22	80.3%
EC7	96.0%	EC23	81.3%
EC8	93.0%	EC24	80.6%
EC9	94.1%	EC25	85.1%
EC10	90.7%	EC26	85.5%
EC11	94.2%	EC27	79.1%
EC12	80.6%	EC28	83.3%
EC13	96.1%	EC29	77.8%
EC14	93.4%	EC30	84.7%
EC15	92.5%	EC31	74.6%
EC16	96.1%	EC32	78.8%

Figure 6: Effects Plot – Turbidity

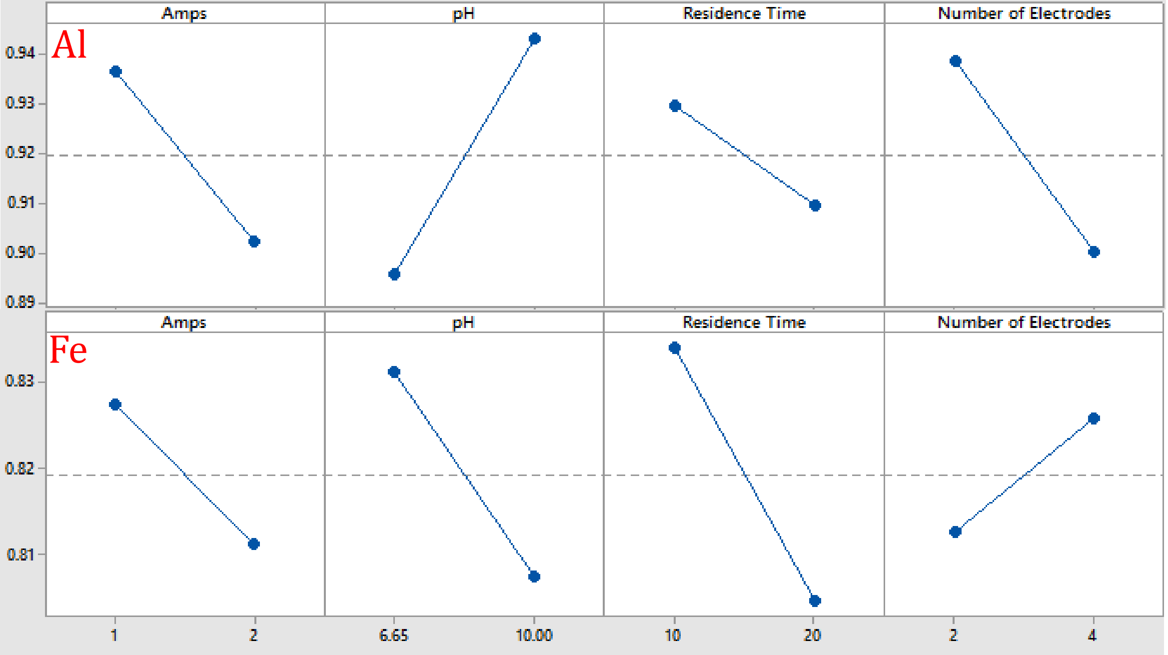


Figure 7: Turbidity Reduction Contour Plot – Number of Electrodes vs. pH

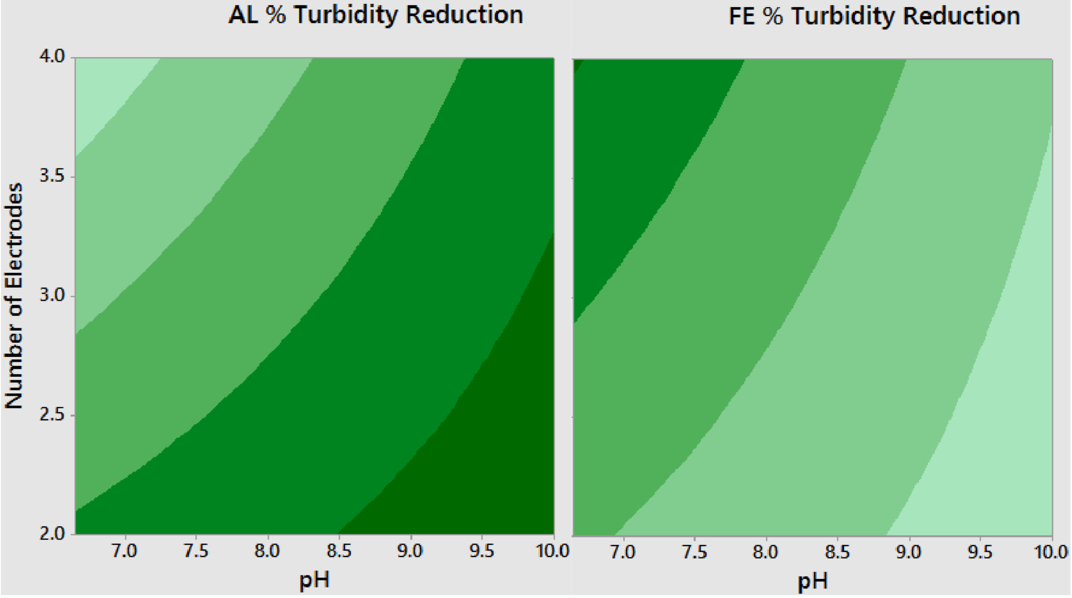
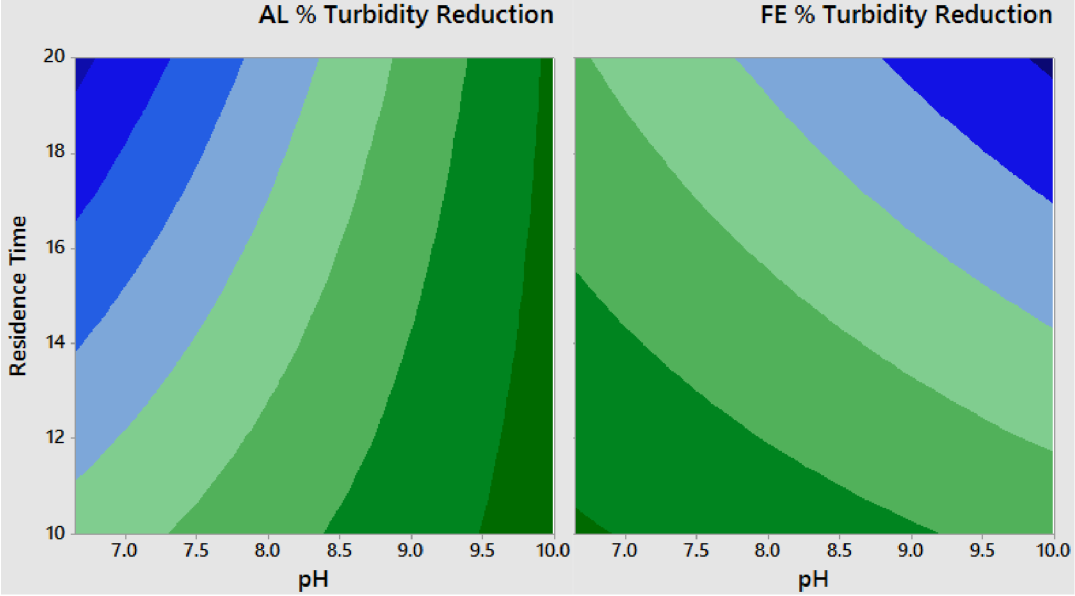


Figure 8: Turbidity Reduction Contour Plot – Residence Time vs. pH



COD

In this study, COD reduction was not an objective, but considered an ancillary benefit to turbidity reduction. In general, COD reduction increased with increasing factor levels, described by Figure 9. Increasing the number of electrodes and the amperage caused the most drastic increases in COD reduction. The highest overall COD reduction (37.4%, EC28) was achieved with the iron electrodes.

COD reduction for each experiment is summarized in Table 10, and the left two columns summarize reductions with aluminum electrodes. In general, COD reduction increased when each factor level is increased, and was most pronounced when the number of electrodes and amperage were increased. P-values for this model (Table 5) show amperage, residence time, and the number of electrodes as significant factors for COD reduction with aluminum electrodes. No factor interactions were found to be significant.

The right two columns of Table 10 present COD reductions for experiments with iron electrodes. Increasing the number of electrodes had the most prominent increase in COD reduction, while increasing the amperage had a less pronounced effect on COD reduction when compared to the reduction with aluminum electrodes. Similar to aluminum electrodes, amperage, residence time, and number of electrodes were all found to be significant in the iron/COD model. However, unlike aluminum electrodes, the interaction of amperage/number of electrodes and pH/number of electrodes was found to be significant.

Figure 10 is a contour plot that shows the COD reduction as a function of residence time (vertical axis) and pH (horizontal axis) and intends to highlight the impact that pH had in COD reductions for the two electrode materials (aluminum on left, iron on right). Experiments done with aluminum electrodes had higher COD reductions at higher pH, while iron electrodes had higher reductions at lower pH.

Table 10: COD Reduction Summary

Identifier (Al electrodes)	COD Reduction	Identifier (Fe electrodes)	COD Reduction
EC1	7.1%	EC17	13.8%
EC2	23.8%	EC18	21.2%
EC3	19.0%	EC19	18.1%
EC4	24.6%	EC20	29.6%
EC5	8.7%	EC21	11.3%
EC6	20.5%	EC22	21.8%
EC7	15.7%	EC23	9.5%
EC8	26.7%	EC24	29.2%
EC9	22.4%	EC25	19.8%
EC10	27.8%	EC26	29.8%
EC11	27.0%	EC27	17.2%
EC12	22.2%	EC28	37.4%
EC13	22.6%	EC29	10.1%
EC14	28.1%	EC30	34.2%
EC15	27.6%	EC31	13.6%
EC16	34.8%	EC32	36.8%

Figure 9: Effects Plot – COD

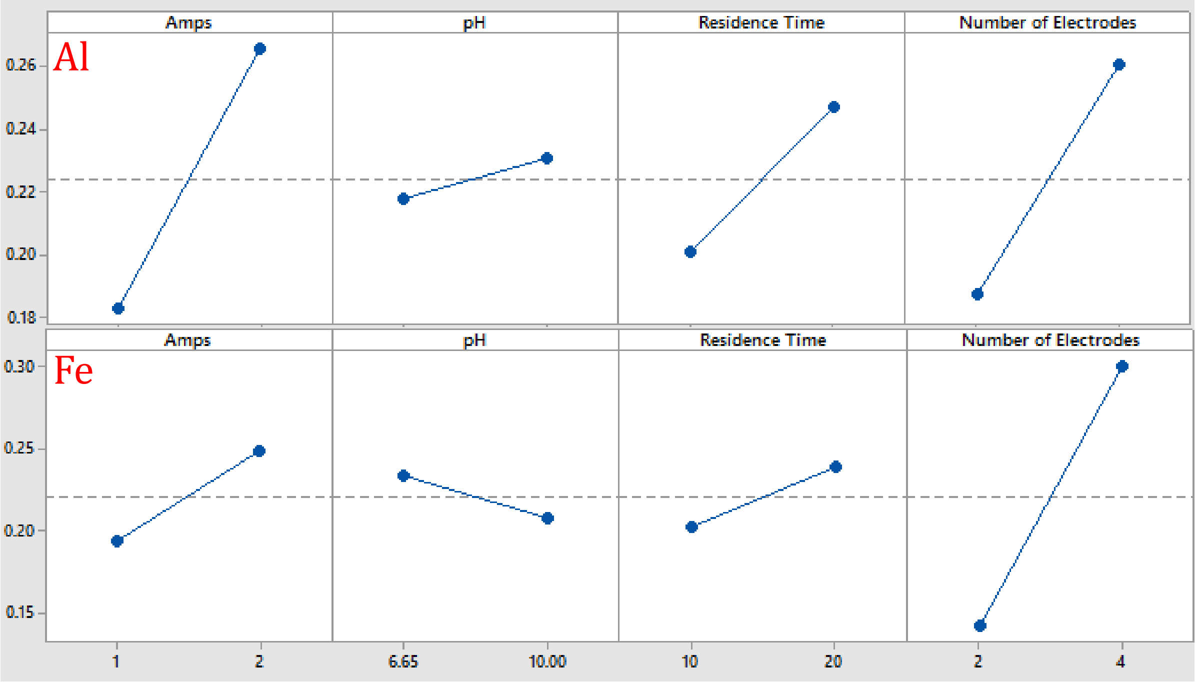
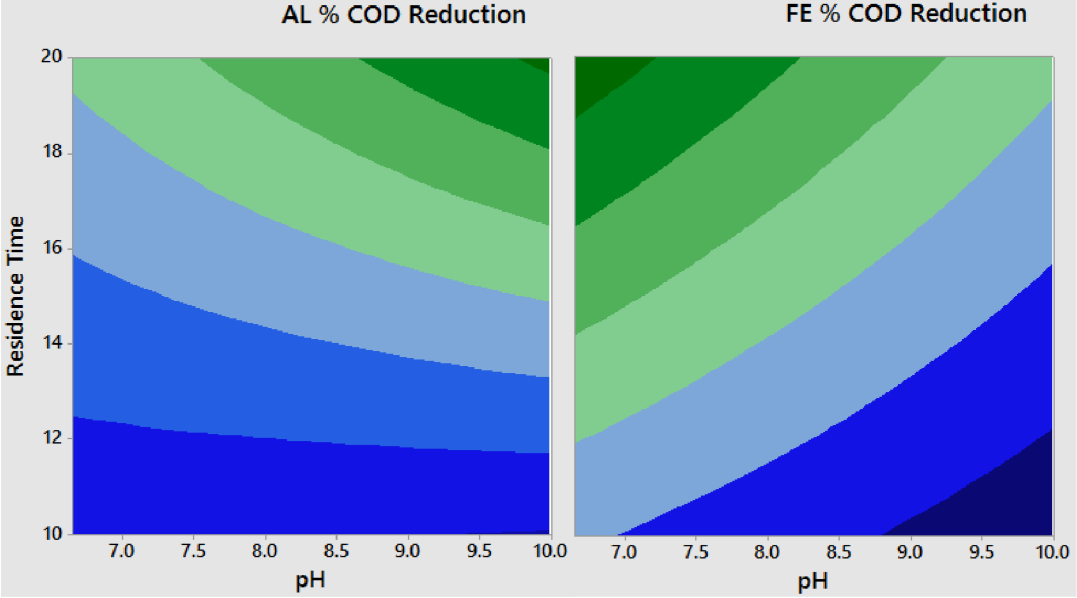


Figure 10: COD Reduction Contour Plot – Residence Time vs. pH



DOC

Like COD reduction, DOC reduction was not considered a primary goal of this study, but was evaluated as a secondary benefit to downstream water treatment processes. DOC reduction increased with increasing residence time, number of electrodes, and amperage, while increasing the pH had almost no effect, described by Figure 8. The highest overall DOC (54.0%, EC28) reduction was achieved with iron electrodes.

DOC reduction is summarized in Table 11, with the left two columns presenting DOC reductions for aluminum electrode experiments. In general, DOC reduction increased as factor levels increased, with increasing amperage causing the highest increase and increasing pH causing the smallest increase. Again all factors except for pH were found to be significant in the aluminum/DOC model, and no factor interactions were significant.

The right two columns of Table 11 summarize DOC reductions with iron electrodes. These results showed slightly different trends than aluminum electrodes. DOC reduction increased with an increase in all factors except pH, which showed a decrease. Increasing the number of electrodes showed the most marked increase in DOC reduction, while an increase in amperage gave a smaller increase in DOC reduction than those done with aluminum electrodes under identical conditions. Amperage and number of electrodes as well as the interaction between amperage/number of electrodes were found to be significant factors in the iron/DOC model (p-values summarized in Table 6).

Figure 12 is a contour plot reflecting DOC reductions at varying pH (vertical axis) and amperage (horizontal axis) based on the model generated. Figure 13 is a similar plot except with residence time (vertical axis) and pH (horizontal axis). Again, these plots aim to inform how differing the initial pH impacted treatment between electrode materials. Similar to the iron COD residence time/pH contour plot (Figure 10), the highest reduction for DOC with iron electrodes was seen at a higher residence time and lower initial pH, while the highest reduction in DOC with aluminum electrodes was seen at a higher residence time but lower initial pH.

Table 11: DOC Reduction Summary

Identifier (Al electrodes)	DOC Reduction	Identifier (Fe electrodes)	DOC Reduction
EC1	15.9%	EC17	17.9%
EC2	21.4%	EC18	28.8%
EC3	18.4%	EC19	13.2%
EC4	34.7%	EC20	38.7%
EC5	13.2%	EC21	15.8%
EC6	28.9%	EC22	30.4%
EC7	22.0%	EC23	5.7%
EC8	35.7%	EC24	35.1%
EC9	24.3%	EC25	15.5%
EC10	38.4%	EC26	49.3%
EC11	35.1%	EC27	15.5%
EC12	41.2%	EC28	54.0%
EC13	26.2%	EC29	6.0%
EC14	47.0%	EC30	48.9%
EC15	36.0%	EC31	10.6%
EC16	47.8%	EC32	50.1%

Figure 11: Effects Plot – DOC

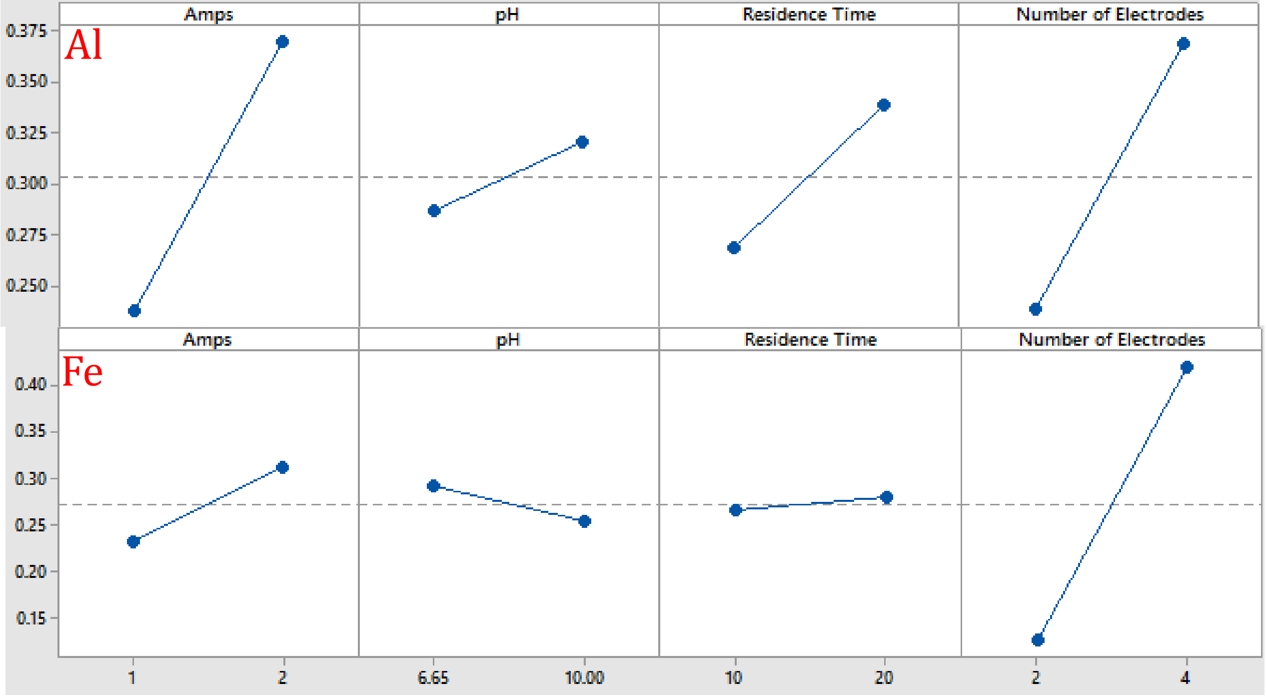


Figure 12: DOC Reduction Contour Plot – pH vs. Amperage

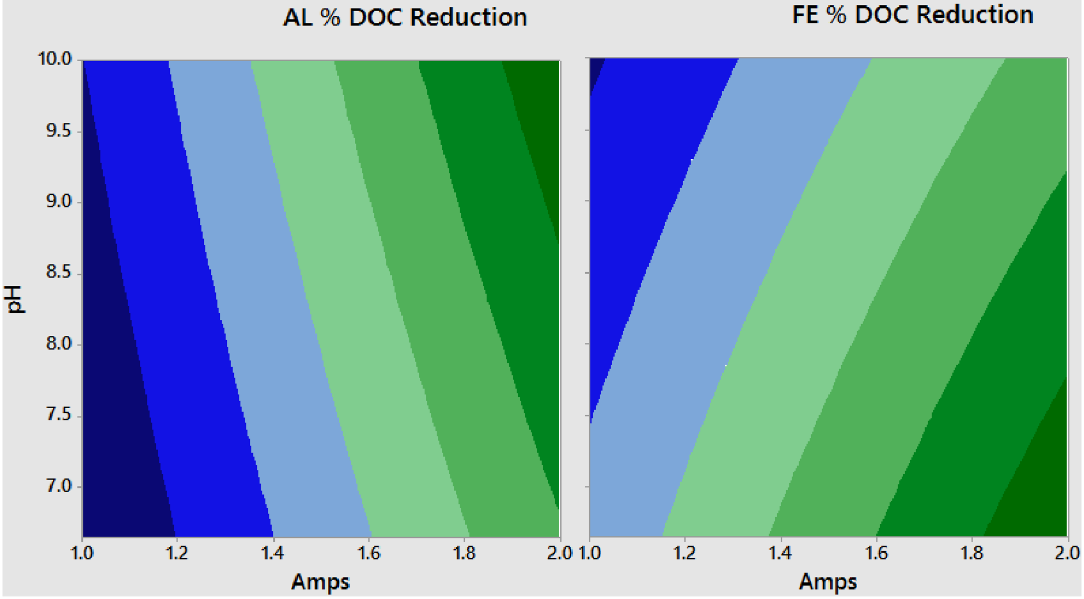
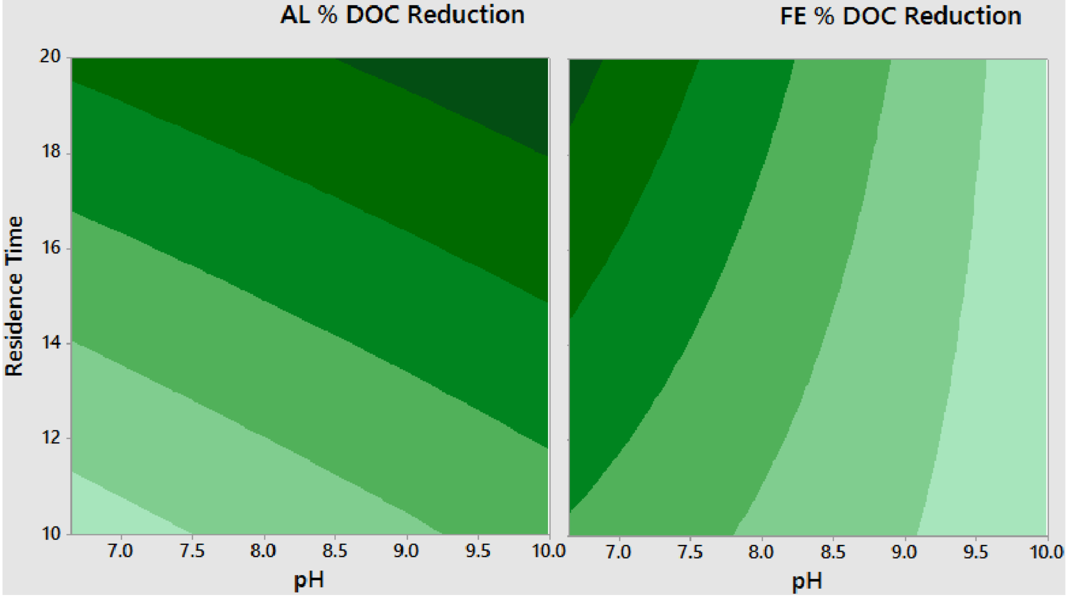


Figure 13: DOC Reduction Contour Plot – Residence Time vs. pH



Optimization

The optimum EC conditions for the treatment goals can be developed based on the models described in the previous section and are presented in Table 12. Optimization was centered on a 90% reduction in turbidity while maximizing the reduction potential for COD and DOC.

Table 12: Optimization of Treatment Factors

Material	Amperage (A)	pH	Residence Time (min)	Number of Electrodes	Turbidity Reduction	COD Reduction	DOC Reduction
Aluminum	2	9.2	20	4	90.0%	30.1%	47.8%
Iron	2	6.7	17.9	4	84.4%	35.8%	54.0%

As expected, the optimized parameters were not able to achieve the 90% reduction in turbidity for iron electrodes, since no experiments done with iron electrodes achieved a 90% reduction in turbidity. The optimized parameters almost exactly correspond to experiments conducted. Those for aluminum correspond to experiment EC16, and those for iron correspond to experiment EC28. With the exception of the pH for the optimized iron conditions, these optimized factors correspond to the higher levels tested for each factor.

Chemically Coagulated Samples

The dose response curve for chemically coagulated samples is shown in Figure 14. The figure exhibits classic dose-response characteristics – increasing dose cause increased turbidity reduction to certain point. After this point, turbidity increases.

A 90% reduction in turbidity was achieved at low doses – 15 mg/L for $AlCl_3$ and 5 mg/L for $FeCl_3$ – and this reduction was maintained for $AlCl_3$ for all the dosing up to 1,500 mg/L. $FeCl_3$ was able to achieve a 90% reduction in turbidity up through a dose of 500 mg/L. Starting at 240 mg/L $FeCl_3$, the samples were seen to have a reddish hue, which impacted turbidity. In addition to the dose-response curve, the samples chosen for fractionation were analyzed for COD and DOC, and the results are in Table 13.

Figure 14: Chemical Coagulation Dose-Response Curve

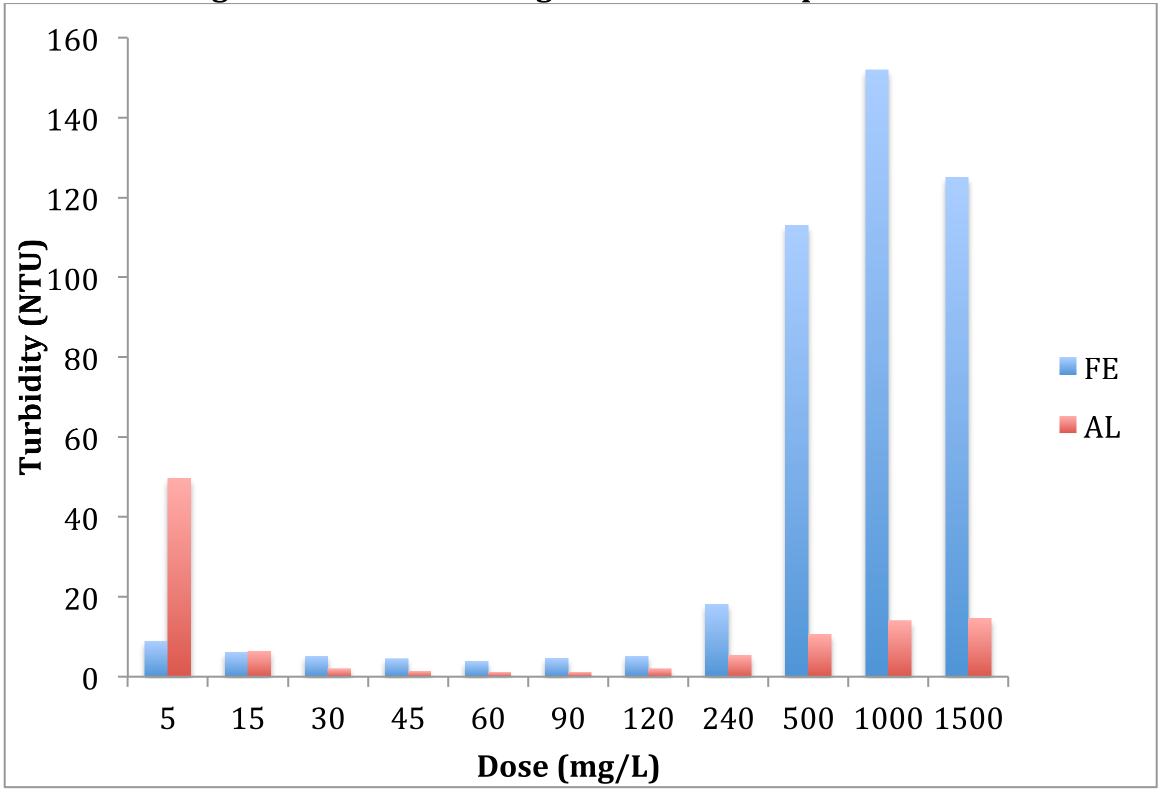


Table 13: Chemical Coagulation Organic Concentration Reduction

Sample	Turbidity Reduction	COD Reduction	DOC Reduction
45 FE	99.4%	5.2%	7.8%
30 AL	96.4%	4.7%	11.2%

Mass Fractionations

The mass of the carbon in each sample was calculated according to:

$$m_{sample} = [DOC]_{sample}V_{sample}$$

Where m_{sample} is the mass of carbon in the sample (mg), $[DOC]_{sample}$ is the DOC of the sample (mg/L), and V_{sample} is the volume of the sample (L). Determining the mass in each fraction was straightforward. The fractions on the high and low end of the cut-off (i.e. >10 kD and

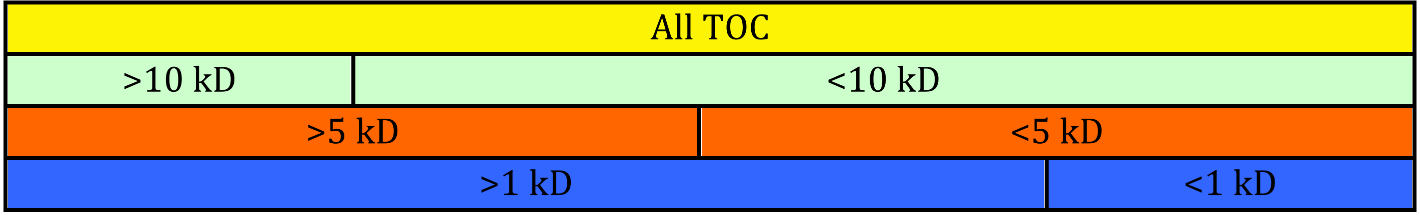
<1 kD) were simply calculated according to the above equation. The two fractions in the middle of the spectrum (i.e 5 kD – 10 kD and 1 kD – 5 kD) required manipulation:

$$m_{5kD:10kD} = m_{>5kD} - m_{>10kD}$$

$$m_{1kD:5kD} = m_{>1kD} - m_{>5kD}$$

This is perhaps best represented visually by Figure 15.

Figure 15: Representation of Mass Fractions



All TOC

>10 kD | <10 kD

>5 kD | <5 kD

>1 kD | <1 kD

The result of fractionating the raw sample is presented in Table 14. Results reflect a 1:50 dilution. After determining the mass fractions for each sample, the percent change of each fraction was determined by comparing it to the same fraction of the raw water. The changes for each fraction are summarized in Table 15, and the proportion of mass in each fraction is in Figure 15.

Table 14: Mass Fractions of Raw Sample

Fraction	Mass C (mg)	% of Total
Total	4.43	---
>10kD	0.25	5.6%
5kD-10kD	1.22	27.5%
1kD-5kD	0.47	10.6%
<1kD	2.41	54.3%

Table 15: Percent Change in Mass Fractions for Treated Samples

Sample	Fraction	Mass C (mg)	% Change
EC1	Whole	3.67	-17.2%
	>10kD	0.26	4.7%
	5kD-10kD	0.92	-24.5%
	1kD-5kD	0.32	-31.6%
	<1kD	2.21	-8.3%
EC16	Whole	2.48	-44.0%
	>10kD	0.14	-43.1%
	5kD-10kD	0.24	-80.6%
	1kD-5kD	0.25	-47.2%
	<1kD	2.04	-15.2%
EC17	Whole	3.68	-17.1%
	>10kD	0.15	-40.9%
	5kD-10kD	0.31	-74.6%
	1kD-5kD	1.08	129.7%
	<1kD	2.54	5.5%
EC32	Whole	2.32	-47.6%
	>10kD	0.15	-40.3%
	5kD-10kD	0.08	-93.2%
	1kD-5kD	0.18	-62.4%
	<1kD	2.19	-8.9%
45 FE	Whole	4.17	-5.9%
	>10kD	0.29	16.9%
	5kD-10kD	0.82	-32.9%
	1kD-5kD	0.65	36.9%
	<1kD	2.20	-8.6%
30 AL	Whole	4.16	-6.2%
	>10kD	0.25	0.9%
	5kD-10kD	1.05	-14.1%
	1kD-5kD	0.70	49.2%
	<1kD	2.60	8.0%

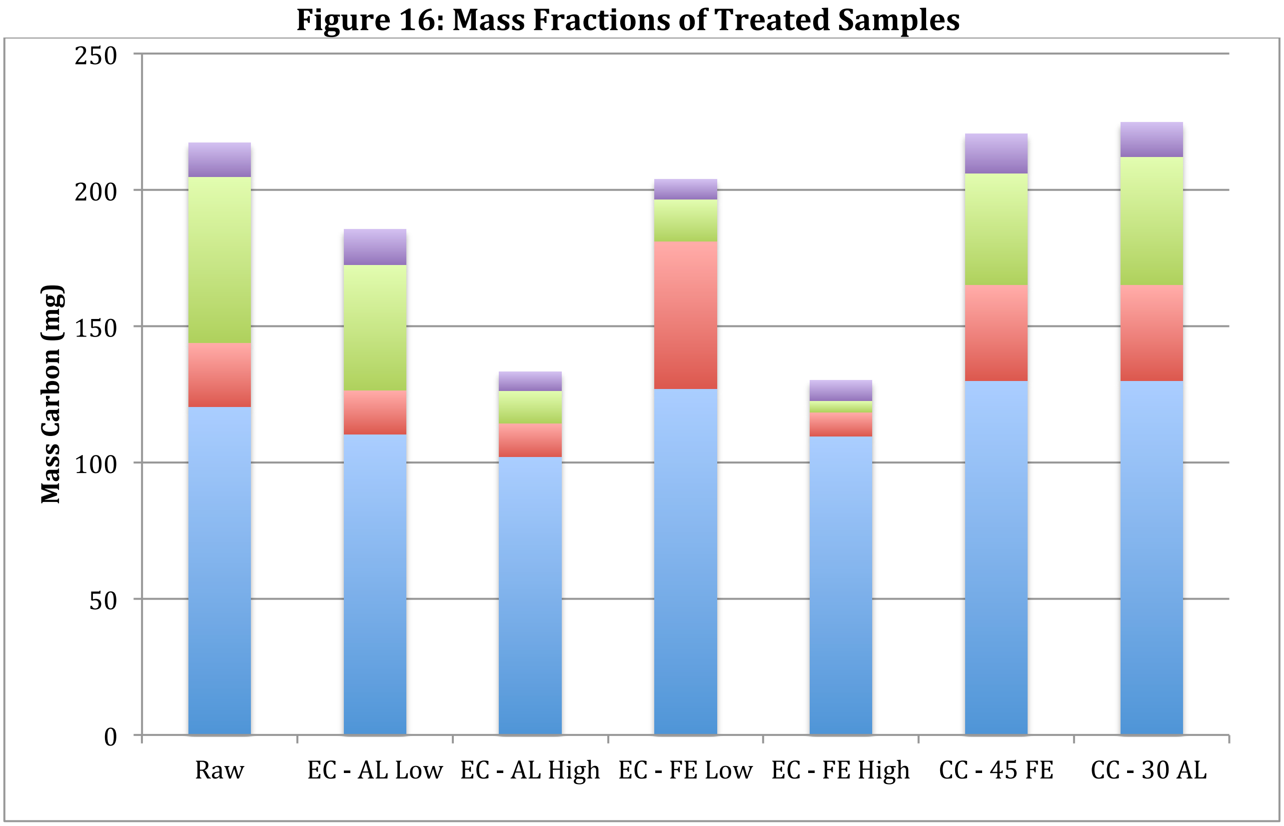


Figure 16: Mass of carbon in 300 mL raw and treated samples amplified by dilution factor of 50x to reflect true nature of samples; blue is <1 kD, red is 1 – 5 kD, green is 5 – 10 kD, purple is >10 kD.

Removal percentages for the whole fraction were similar to what was seen for those samples generated for the DoE analysis. Samples that were subject to the higher levels of treatment (EC16/EC32) saw higher DOC removals than those subject to lower levels of treatment (EC1/EC17), and all electrocoagulated samples outperformed the chemically coagulated samples.

>10 kD Fraction

This fraction contains the smallest amount of mass of the four fractions analyzed. From Table 14, only 5% of all mass in the raw sample was found to be >10 kD. From Table 15, EC16, EC17, and EC32 all experienced reductions in mass of this fraction, with EC16 having the maximum reduction of 43.1%. All other samples did not experience any appreciable reduction for this fraction. Any increase in mass of this fraction was minimal and assumed to be within the error of the analysis.

5 kD – 10 kD Fraction

The mass of carbon that fell into this range represented 27.5% of the total mass found in the raw sample (Table 14). Table 15 shows that all analyzed samples experienced a reduction in DOC of this fraction, and reductions were wide ranging, from a maximum of 93.2% reduction (EC32) to the minimum of 14.1% (30 AL). The highest reductions were seen with the higher factor level samples (EC16/EC32) and iron-based samples (EC17/EC32/45 FE) outperformed the aluminum-based samples (EC1/EC17/30 AL). The iron-based chemically coagulated sample saw a higher reduction in this fraction (45 FE, -32.9%) than the lower factor level aluminum sample (EC1, -24.5%).

1kD – 5 kD Fraction

The 1kD – 5kD fraction represented the second smallest fraction analyzed, with 10.6% of the carbon mass of the raw sample falling into this fraction (Table 14). The highest reductions were again achieved by the higher factor level samples (EC16, -47.2%; EC32, -62.4%), which was reflective of the removal efficiencies overall. This was the only fraction analyzed that had a significant increase in the mass of carbon compared to the raw water, as EC17 saw the mass of carbon more than double for an increase of 129.7%, 45 FE had an increase of 36.9%, and 30 AL had an increase of 49.2%. This may be a result of error in the experiment, but the mass balance is consistent for these samples and it is not unreasonable to consider that some of the larger OM was transformed into smaller molecules by some other process not considered. For the EC17 sample it is possible that this occurred via hydroxyl radicals, which have been shown to be generated in electrocoagulation experiments [60, 70], though under different conditions. Nevertheless, performing a mass balance on the fractionations determined that all the mass was accounted for and that if this fraction of EC17 were to have a mass similar to that of another electrocoagulated sample, the mass balance would not be consistent (data not shown).

<1 kD Fraction

The smallest fraction accounts for 54.3% of the OM in the raw sample and the smallest reduction of any mass fraction analyzed (Table 15). DOC reductions were minimal or non-existent across all samples analyzed, as the maximum reduction realized was -15.2% for EC16.

Discussion

The reduction of each constituent performed as expected with regards to organics reduction: increases in amperage, residence time, and number of electrodes resulted in an increase in reduction of COD and DOC, likely due to an increase in flocculated material. However, variations in pH had the opposite effect on removal for each electrode material – increasing the pH with aluminum electrodes had the opposite effect on constituent removal as it did with iron electrodes.

Impact of Factors

Overall, the higher levels of amperage, residence time, and number of electrodes produced higher reductions. Considering that the maximum and average reductions for COD and DOC using different electrode materials were very similar, an additional ANOVA analysis was done to determine how significant of a factor the electrode material was (data available in Appendix). Rather than analyzing the 16 experiments for each electrode material separately, the ANOVA was done this time to include electrode material as a factor and analyze all 32 experiments. Results from this separate analysis show that electrode material was not a significant factor for COD and DOC removal, but was a significant factor for turbidity removal. Additionally, this analysis showed that the interaction of pH and electrode material was significant, which may be a result of the different metal speciation and complex formation that occurs at different pH for each metal. Also, passivation of each electrode material occurs at different pH, which would reduce the amount of flocculated material generated at that pH.

Turbidity

In contrast to COD and DOC, turbidity did not always show increasing reduction with increasing factor levels of electrodes, current, and residence time. For aluminum electrodes, turbidity reduction increased only with pH, and decreased with an increase of all other factors. For iron electrodes, turbidity reduction increased with the number of electrodes, and decreased with an increase of all other factors. When comparing turbidity reduction between electrode materials, pH makes a significant difference, as the trends are the opposite (see Figure 7 and 8, higher reductions are dark green, lower reductions are light green to darker blue). Aluminum electrodes gave higher turbidity reduction at higher pH, whereas iron electrodes gave higher reduction at lower pH, while holding other factors to be the same. The overall ability of aluminum to give better turbidity reductions agrees with previous research that found the same, though the percent reductions were lower [71, 72]. However, this research is in contrast to previous research that determined electrocoagulation is more effective for turbidity removal than chemical coagulation [72], though some combinations of factors in this study with aluminum electrodes gave similar reductions. It is though that these anomalies are the result of different bulk water characteristics, since different water will respond differently to identical treatments.

Higher amperage, residence time, and number of electrodes corresponded to an increase in material that was in the reaction vessel. Some of this material was not able to sufficiently settle in the 30 minute allotted time at the end of each experiment, as there were still noticeable suspended flocs in the sampled material - this is thought to contribute to the general decrease in turbidity removal with increases in these factors.

During EC runs using iron electrodes, the resulting water was always visibly dirtier than those done with aluminum electrodes. Greenish, orangeish, and blackish flocs were observed during EC runs but not with iron-based chemical coagulants, and only white flocs were observed with aluminum electrodes. Since iron has more than one oxidation state, it is able to form a much wider variety of solid materials that are responsible for these colors. Inspection of the Pourbaix diagram for iron (Figure 1), Fe(II) is the predominant form of iron available for reactions under the conditions of these experiments. Notably, green rust forms from Fe(II), which was noted to be present around the cathode in most iron EC experiments [73, 74]. Additionally, some of these complexes that include Fe(II) are insoluble at the pH values in this study, and so would be ineffective at forming flocs and reducing turbidity [75]. This could explain why iron-based chemical coagulants are more effective than iron-based electrocoagulation at turbidity reduction, since the dosing involves adding Fe(III) in solution directly to the bulk water rather than relying on the *in situ* oxidation of Fe(II) to Fe(III), as is the case with electrocoagulation.

COD

The COD strength in any wastewater includes an organic and inorganic portion. For the organic portion, the mechanism of COD removal with electrocoagulation is thought to be a function of: (1) the electrode material, (2) the formation and type of floc formed, (3) the initial and final pH, (4) the reactivity of the OM in the water with metal species present, and (5) the solubility of the compounds formed with these metal species [73]. The compounds in the wastewater react with metal species to form either soluble or insoluble compounds, and the insoluble compounds are removed with the flocculant.

The amount of COD reduction found in this study was comparable to that of other studies. For iron electrodes, an analysis of 65 experiments performed by KASELCO Co., a private manufacturer for EC reactors, found a minimum reduction of 0.5% and a maximum of 86.40% with an average of 38.9%, which is higher than the 22.2% average observed in this study but similar to the maximum achieved with iron electrodes of 37.4% [73]. COD reductions using aluminum electrodes range from 61% [62] from dairy effluents to 89% [43] with restaurant effluent, both higher than the average of 22.4% and maximum of 34.8% achieved with aluminum electrodes in this study. With the exception of pH, COD removal increased by increasing the factor levels for both electrode materials, and most dramatically with increased current and number of electrodes. The average COD reduction for iron and aluminum electrodes is almost identical (22.1% and 22.4%, respectively) to the overall average of the 32 experiments (22.2%). Since reduction was generally increased with all factors besides pH, this lends itself to the idea that COD removal was mostly dictated by the amount of flocculated material. The initial pH was important to consider when looking at the two electrode materials separately, and could be important when designing an EC reactor for a reuse application.

For iron electrodes, the EC process generates both Fe(II) and Fe(III) depending on pH. The ratio of Fe(III)/Fe(II) is expected to be lower at neutral pH values and higher at higher pH values (see Figure 2: Iron Pourbaix Diagram). In this study, we saw higher COD reductions at lower pH with the highest COD reduction overall coming from EC28, which took place with a neutral pH, four electrodes, two A of current, and a 20 minute residence time. This is the combination of factors in this study that would be expected to generate the maximum amount of Fe(II), indicating that there could be more compounds present in the raw water that formed insoluble compounds with Fe(II) than Fe(III). Small organic acids such as citric acid, salicylic acid, tartaric acid, and oxalic acid have been shown to form insoluble products with Fe(II) but not with Fe(III) [73]. This could explain the increased reductions at lower pH, except that molecules of this size (< 1 kD) were hardly removed by iron-based electrocoagulation. A better explanation for this deviation relates to the ability of iron-based coagulants to remove humic and fulvic acid OM, however this was not considered in this research and the abundance of these materials is thought to be low in produced water samples when compared to other OM present [76].

It is possible that the nature of the OM exhibiting COD on the water changes at higher pH such that it will not as readily react with the flocs generated at higher pH, since the amount of Fe(II) and Fe(III) is different at neutral and high pH. This difference in metal speciation would affect the characteristics of the complexes/precipitates formed that are responsible for COD removal. Another possibility is that at higher pH, the iron electrodes can become passive and release less metal from the anode, thus reducing the amount of floc generated. Also at higher pH, the anode was seen to be coated with a dark substance. This may have been some sort of mineral formed as a result of the oxidation conditions present, as the Pourbaix diagram indicates that it is possible for Hematite and Magnetite to form under these conditions. This coating, could have limited release of Fe from the anode and further reduced the amount of floc and may have occurred as a result of passivation.

With aluminum electrodes, the trend with pH is the opposite: lower reduction at lower pH values and higher reduction at higher pH values (see Figure 10). Aluminum only has one oxidation state (Al^{+3}), so the nature of the reactive species generated by EC with aluminum electrodes is less variable and pH dependent [77]. At the lower pH values considered in this study, aluminum is passive, meaning that aluminum is less reactive and that there is a "protective" film that forms on the metal and reduces the amount of cationic metal species available to react [37]. At high pH values, more reactive aluminum complexes are present (e.g. $Al(OH)_4^{-,}$ $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{+2}$, $Al(H_2O)_4OH^{+1}$) [55, 77]. The increased reactivity of aluminum and aluminum complexes at higher pH informs the increase in COD removal within the aluminum experiments when compared to the iron experiments. The largest COD reduction for aluminum electrodes was found under these conditions (34.8%, EC16).

DOC

OM removal using electrocoagulation has been extensively studied in the literature [33]. With iron electrodes, reduction ranged between 70 and 80%, while aluminum electrodes gave reductions of up to 98%. However, all of these studies used either natural water or synthetic water, and none used a high strength industrial wastewater. Like COD reduction, average DOC reductions in this study for both iron and aluminum electrodes (27.2% and 30.4%, respectively) were similar to each other and the overall reductions (28.8%). This, along with how DOC reduction increased with increasing current, residence time, and number of electrodes, is similar to trends in COD reduction and supports the hypothesis that DOC reduction increased simply by increasing the amount of flocculated material in the system.

In general, the mechanism of DOC removal with coagulation is a combination of charge neutralization, entrapment, adsorption, and aggregation of insoluble complexes with metal ions [32]. DOC removal increased with increasing residence time, amperage, and number of electrodes for both aluminum and iron EC coagulation experiments.

However, DOC removal increased with aluminum electrodes with increasing pH and had an opposite trend for iron electrodes, further suggesting the impact pH has on metal speciation and reduction of organic strength in this application.

The OM in this study was not thoroughly characterized, so interactions of OM and coagulant can only be postulated based off of previous work with HFWW. Lester, Y., et al performed a characterization of the OM in a flowback sample from the Denver-Julesberg basin, the same basin from which the water for this study was sampled [76]. Their analysis detected VOCs, semi-volatile organic compounds (SVOCs), as well as trace organic compounds. Low molecular weight hydrophilic compounds (HPI) were found to account for over 60% of the OM present, with hydrophobic organic acids (HPOA, ~10%), transphilic organic acids (TPIA, ~10%), and hydrophobic organic neutrals (HPON, ~3%) accounting for the rest. The high level of HPIs agreed with the high level of acetic acid found in this sample, and the HPON fraction may include linear alkyl ethoxylates that were also detected and are used in fracturing fluid composition [76]. However, the HPOA, which are typically associated with humic materials, were found to more resemble phenolic compounds based on fluorescence spectroscopy analysis performed. This means, for this research, that humic substances may be minimally present in the HFWW sample used, which would have implications for mechanisms of OM removal with coagulation-based technologies. Electrocoagulation has been shown to be effective at removing phenolic compounds. Under similar conditions of current density and electrolysis time, Adhoum and Monser used aluminum and iron electrodes to reduce polyphenols up to 78% [78] from olive mill wastewater, and found this was most efficient at an acidic to neutral pH.

DOC reduction is also influenced by iron speciation and the potential for OM to form insoluble material with the iron cations. It is only possible for the electrodes to release Fe(II) at the lower pH, and previous research has shown that Fe(II) forms complexes with organic material that are soluble and therefore not removable [75]. In the same study, increasing pH was found to be responsible for oxidation of Fe(II) to Fe(III), which forms more favorable complexes for removal; therefore, a higher pH would be expected to give higher DOC removal with all other factors constant, which is not the case in this study [75]. A possible explanation for this deviation is how the pH changes over the course of an electrocoagulation treatment. Natural organic material has also been found to quickly complex with Fe(II), preventing it from oxidizing to the less soluble Fe(III) and inhibiting DOC removal [79]. These previous analyses lead to the hypothesis that the highest DOC removal in this study would correspond to the conditions that generated the highest concentration of Fe(III) and suppressed Fe(II) production.

Similar to iron, DOC removal with aluminum electrodes is increased by increasing the amount of flocculant, forming aluminum hydroxide precipitates which then sorb and entrap DOM on their surfaces, or form insoluble complexes with aluminum [80]. However, unlike iron, aluminum only has one oxidation state (Al^{+3}), so the difference in removal may be a function of the type of complexes that aluminum forms at different pH values, the corresponding zeta potential, [81] and the physio-chemical interactions of the wastewater with the aluminum electrodes [82]. Cañizares, Martinez [81] studied the aluminum speciation formed in electrocoagulation over a range of pH values and found that at neutral pH, the predominant form of aluminum is of aluminum hydroxide precipitates, which are not as effective at OM removal as the polymeric complex forms. Additionally, they found that the zeta potential is strongly positive at neutral pH (as high as +35 mV), and became more negative with increasing pH. Previous research has shown that maximum organic removal is achieved in a zeta potential between -10 and +5 mV [32]. The authors postulate that the variation of zeta potential with pH is due to the adsorption of cations to the hydroxide precipitate at neutral pH while at higher pH, the predominant form of aluminum is the negatively charged hydroxoaluminum ($Al(OH)_4$), thus changing the zeta potential from positive to negative. The increased DOC removal at higher pH could be a function of the OM present in the sample in that it is more likely to sorb to hydroxoaluminum complexes than the solid $Al(OH)_{3(s)}$ precipitate. In addition, aluminum electrodes in the EC system experience passivation at neutral pH (4 – 8), meaning there is potentially less cationic aluminum available to form any kind of precipitate or complex.

Chemical Coagulation

Chemical coagulation showed a 90% turbidity reduction at low coagulant values. The approximate range of metal dosing from EC was 150 – 650 mg/L for aluminum electrodes, and 500 – 2000 mg/L for iron electrodes. A 90% reduction was achievable for both aluminum-based coagulants (i.e. CC and EC) for the overlapping dose ranges studied, but was not possible with iron-based coagulants. This may be related to the dual speciation of iron present in EC and the destabilization of particles that occurs in CC at sufficiently high doses. The two CC samples that were selected for fractionation were also analyzed for COD and DOC and showed much lower reductions than for EC. However the two technologies are not comparable at these low doses, so no conclusion can be drawn on the utility of one over the other for COD and DOC reduction. Similarly, the range of CC doses that corresponded to EC doses did not give adequate turbidity reduction, but EC was not evaluated at the lower doses. It is unclear if increasing CC dose to the EC range would give added reduction in organics with a sacrifice to increased turbidity.

The advantage to using chemically based iron coagulants versus electrocoagulated cationic iron species is that with chemical coagulants, Fe(III) is added directly to the bulk water as a solution whereas with electrocoagulation, Fe(II) is released from the anode and must be oxidized *in situ* to Fe(III), which is more useful for floc formation than Fe(II) [75]. The increased organics removal with EC is not surprising. Calculating the mass of metal dissolved off the anode (Eq. (2)) in any of the EC experiments would show that the coagulant dosing on a mass basis in EC is significantly higher than in chemical coagulation. More cationic metal species means more floc will form, positively impacting DOC and COD reduction, but not necessarily turbidity reduction.

Mass Fractionation

Iron-based coagulants have been shown to be more effective at removing OM in the middle fraction (1 kD – 5 kD) possibly because of the higher charge density associated with them [33, 83]. In this study, iron-based coagulants were shown to remove a higher amount of DOC in this weight fraction than with aluminum electrodes, and EC32 (carried out at higher pH) was shown to almost completely remove the DOC in this range. Bratskaya, Golikov [84] demonstrated that as pH increases, the charge density of humic and fulvic acids also increases and so would be more attracted to the electro-precipitated iron complexes at a higher pH vs. at a lower pH. However, as previously discussed, it is possible that humic substances only represent a maximum of 10% of the OM in this study, though it is likely less [76]. Additionally, the previous research by Lester, et al supports the finding in this study that the largest fraction of OM is < 1 kD. In their study, they found the largest fraction of OM (>61%) to be low molecular weight hydrophilic compounds, including a large concentration of acetic acid [76]. The lower charge density of aluminum-based coagulants could explain for a similar pattern of removal with respect to pH (i.e. lower removal overall but still higher removal at higher pH).

A phenomenon that was not considered in the fractionation work done for this research is the transformation of OM from one mass fraction to another as a result of treatment. This phenomenon was observed with the fractionation of EC17. EC17 was carried out with iron electrodes at 1 A, 10 minute residence time, 2 electrodes, and a neutral pH (low factor levels with iron electrodes). The amount of carbon in the 5 kD – 10 kD fraction decreased significantly while the mass of the 1 kD – 5kD fraction increased over what was present in the raw water by 130%. This could be interpreted as an error in analytical procedures (e.g. outside contamination), but the mass balance was within 10% of the expected mass. This phenomenon could be explained by an electro-chemical advanced oxidation process that generates hydroxyl radicals (OH•) based on the Fenton reaction [85]:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH\bullet$$

Radicals are also generated at the anode due to the oxidation of water:

$$H_2O \rightarrow H^+ + OH\bullet + e^-$$

Then Fe(III) can be reduced to Fe(II) at the cathode, which are then destroyed by hydroxyl radicals:

$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$

$$Fe^{+2} + OH\bullet \rightarrow Fe^{+3} + OH^-$$

Hydroxyl radicals react with organic material to break it down to smaller pieces and potential mineralization. They are produced most effectively at a pH < 5 and not produced at all at basic pH, but could be produced *in situ* locally around the anode due to the oxidation of water, since the region around the anode has been shown to be very acidic [36]. This process also requires the addition of H_2O_2 to the wastewater, which did not occur for these experiments, though peroxide is sometimes used in hydraulic fracturing operations and so may be present at trace levels [86]. However, it is possible to generate H_2O_2 *in situ* with electrocoagulation under certain conditions [87].

Utility for Pretreatment and Reuse

The primary purpose of any pretreatment technology is to clarify the water, with secondary benefits being organics removal. Therefore, the next step in the treatment process would be responsible for additional organics removal. Depending on what the next step in a treatment train would be, electrocoagulation could be an excellent pretreatment technology. If a filtration technology (sand, activated carbon) were to be the next step, then pretreatment clarification is very important since suspended material and colloids can quickly clog filters, reducing the efficiency of the operation. In this case, electrocoagulation with aluminum electrodes would be the best option, since turbidity reduction was maximized. Biological treatment is also a possible treatment technology, and has been effective at achieving increased reduction in organic loads when combined with electrocoagulation in both aerobic and anaerobic reactors [41]. Electrocoagulation can also serve to remove toxic substances from the water that could kill off the microorganisms used in biological treatment [36].

Lester et al saw a reduction in DOC of only 50% over 6 hours using biological treatment for HFWW, and minimal reductions with advanced oxidation processes (AOPs), indicating there could be a fraction of the OM that is biologically recalcitrant [76]. Additionally, research on biological treatment of HFWW as a pretreatment for membrane treatment showed that elevated TDS is inhibitory [88]. For this reason TDS may impact the treatment with these technologies and a reduction may give more favorable results.

The size of the remaining OM after pretreatment can impact biological treatment processes. Waters with OM in the 5 kD – 10 kD weight range are typically assumed to be good candidates for coagulation [83], and this was observed in this study. OM with a lower molecular weight (<5 kD) is more difficult to remove with biological treatment, so the gains in organic reduction as a result of biological treatment could be minimal, and a more suitable technology (e.g. activated carbon filtration or powder activated carbon) may be necessary to reduce this fraction.

However, it is important to consider that, based on the anecdotal evidence of reuse in hydraulic fracturing, the organic concentration of the wastewater does not necessarily impact the potential for reuse of this water. In this study (and others) EC has been shown to effectively remove turbidity with aluminum electrodes, and in other studies it has been shown to remove some hardness [51, 55, 56, 66, 89], so EC could be an attractive option for onsite reuse or as a pretreatment for other processes if blending is considered.

Conclusion

This study was intended to investigate the ability of coagulation-based pretreatment technologies to reduce turbidity in HFWW as well as factors affecting turbidity, COD, and DOC reduction of a produced water with EC. The goal of 90% reduction in turbidity was only achieved with aluminum electrodes and was achieved in fifteen of the sixteen experiments done with aluminum electrodes. Iron electrodes achieved less turbidity reduction and produced a less visually appealing product water, but saw a greater reduction in organic concentration of the water over aluminum electrodes. However, electrode material was not statistically significant for COD and DOC reduction, but was for turbidity reduction. Similar to other studies, increases in residence time, electrodes, and amperage were shown to generally increase organics removal, as increases in these factors increase the amount of floc generated and therefore increase the potential for OM to sorb or form complexes with the floc. The optimized parameters for treatment from this study reflect this, as they include most of the higher levels for each factor. pH is also a very important factor to consider for electrocoagulation when deciding upon the material of the electrodes, though a neutral or basic pH was not shown to significantly impact constituent reduction. Increasing pH did not always lead to increased removal, perhaps due to the different metal speciation, complexing, and OM behavior that occurs at basic and neutral pH. pH can also cause passivating conditions to be present in the system, which may limit the amount of coagulant generated. Additionally, chemical coagulation was able to achieve a 90% turbidity reduction over a wide range of doses for both coagulants considered.

There are several advantages to EC over CC and choosing one over the other requires evaluation of several factors. First, EC can generally achieve a higher level of overall treatment than CC, as was the case in this study, though CC is effective at turbidity reduction at lower doses. EC can have a smaller footprint and be more energy efficient than CC. EC will increase the pH of the water over the course of treatment, which is the opposite of CC. This could be important if the effluent needs to be at a certain level either for the next treatment technology or discharge requirements. If the pH of the raw water needs to be raised, EC could provide *in situ* base addition; if it needs to be lowered, CC may be a better option. However, CC has the advantage of being able to directly add the preferred metal speciation to the bulk water (i.e. Fe(III) over Fe(II)), rather than relying on *in situ* oxidation, which is the case with EC. It is also possible to add pre-hydrolyzed coagulants with CC, which could help with pH control and alkalinity consumption. Finally, the amount of coagulant added with EC on a mass basis is much higher than CC, so an operator could have more solids to dispose of with EC, which would add cost.

EC was shown to most significantly reduce the organic carbon in the 5 kD – 10 kD weight fraction. The effect was more pronounced with iron electrodes than with aluminum electrodes, but a higher pH gave a larger reduction of organics in this fraction, potentially due to variable OM characteristics at high pH. The lower molecular weight fractions saw very little decrease due to coagulation, and one fractionated sample studied showed an increase in mass in this fraction over the raw water, which could be due to the presence of hydroxyl radicals generated during the EC process or other transformational processes not considered. This phenomenon warrants more research, as it could be a useful aspect of this technology to exploit.

The most important consideration when evaluating EC as a pretreatment technology is the treatment goals. Electrocoagulation could be used as a stand-alone pretreatment technology for the reuse of hydraulic fracturing wastewater if the operator is blending with a fresh source and the only treatment requirement is a reduction in turbidity and colloidal material. If clarification is the goal, aluminum electrodes are more effective. If reduction in organic concentration is the goal, iron electrodes could give a higher reduction; but, for this water sample, electrode material was not shown to be a significant factor in subsequent ANOVA analysis. CC is a good option over a wide range of doses for turbidity reduction. Achieving additional reductions in organic concentration will require subsequent treatments by another treatment technology.

Electrocoagulation as a pretreatment for another technology in a treatment train intended for reuse would be better than chemical coagulation, if only considering the reductions in constituents (and not operational and cost considerations, which were not evaluated in this study). Any subsequent technology benefits from clarification, and EC with aluminum electrodes was shown to be at least as good as CC in this study. If the next technology in the treatment train were biological, then the microorganisms in the biological process could benefit from a reduction in dissolved solids, which was not evaluated in this study but which EC has been shown to accomplish with varying levels of success in previous studies. Membrane-based technologies would benefit from a reduction in suspended solids and organic material to reduce the potential for fouling.

Any advanced oxidation process (AOP) using UV light would require that suspended materials be significantly removed to allow for the UV light to effectively travel through the bulk water. Additionally, it would seriously benefit from a reduction in scavenging ions (e.g. Cl^- and Br^-), as the hydroxyl radicals generated during UV/AOP preferentially react with these ions and reduce their capacity to oxidize OM. Reduction of these ions was not evaluated in this study, so it is unclear if EC would be an effective pretreatment for an AOP process.

The next steps to increase reuse of HFWW would be to truly identify the treatment goals. Since fracturing fluid is a trade secret, it would be very difficult for researchers to identify the minimum water quality conditions required to allow for successful reuse, so this would undoubtedly require greater cooperation between researchers and operators. There is no doubt that the technology exists to treat the water effectively, but if there is no definite treatment goal, it is difficult to direct research in a useful direction. It is also important to evaluate the value of water in the HF process and if onsite reuse could give an economic and/or social benefit, as they are unlikely to adopt a reuse scheme without incentive.

The water quality of hydraulic fracturing wastewater is extremely variable. It is likely that the optimized parameters for this water sample would not produce similar results for another well in a different part of the country that used a different method for hydraulic fracturing. Dissolved solids, suspended solids, natural pH, organic characteristics of the water, and treatment goals would all play a role in the utility of electrocoagulation or chemical coagulation as a treatment technology. However, EC is capable of removing most suspended solids and some dissolved solids, which could allow the treated water to be reused onsite if it is blended with freshwater. Continuing research in this area is valuable since it is beneficial for the operators, the public, and the environment to increase water reuse in HF and other human endeavors.

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Appendix

Average Constituent Reduction at Factor Levels

Average Constituent Reduction – Amperage

Conditions (Electrode Material/Amperage)	Turbidity	COD	DOC
Overall/1 A	88.2%	18.8%	23.5%
Overall/2 A	86.7%	25.7%	34.1%
Al/1 A	93.7%	18.3%	23.8%
Al/2 A	92.2%	26.5%	37.0%
Fe/1 A	82.7%	19.3%	23.2%
Fe/2 A	81.1%	24.9%	31.3%

Average Constituent Reduction – pH

Conditions (Electrode Material/pH)	Turbidity	COD	DOC
Overall/6.6	87.1%	22.6%	28.9%
Overall/10	87.8%	21.9%	28.7%
Al/6.6	91.1%	21.7%	28.7%
Al/10	94.8%	23.1%	32.1%
Fe/6.6	83.1%	23.4%	29.1%
Fe/10	80.7%	20.8%	25.3%

Average Constituent Reduction – Residence Time

Conditions (Electrode Material/Residence Time)	Turbidity	COD	DOC
Overall/10 min.	88.7%	20.2%	26.8%
Overall/20 min.	86.2%	24.3%	30.9%
Al/10 min.	94.0%	20.1%	26.9%
Al/20 min.	92.0%	24.7%	33.9%
Fe/10 min.	83.4%	20.2%	26.6%
Fe/20 min.	80.5%	23.9%	27.9%

Average Constituent Reduction – Number of Electrodes

Conditions (Electrode Material/Number of Electrodes)	**Turbidity**	**COD**	**DOC**
Overall/2	88.0%	16.5%	18.2%
Overall/4	86.9%	28.0%	39.4%
Al/2	94.8%	18.8%	23.9%
Al/4	91.1%	26.1%	36.9%
Fe/2	81.3%	14.2%	12.5%
Fe/4	82.6%	30.0%	41.9%

Components of ANOVA Results

DF (Degrees of Freedom) – Determined by the number of observations in the data set. Since each experiment output (Y_i) was only assigned one value for each of the factors evaluated, the DF for each of the linear and two-way interactions is one. Similarly, since there are four linear and six two-way interactions modeled, the DF for each of these sources is four and six, respectively. Increasing the number of observations increases the sample size and provides more information about the sample population, which increases the DF and the robustness of the model.

Adj SS (Adjusted Sum of Squares) – In general, sum of squares (SS) is a measure of how the model output deviates from the observed mean by summing the squares of the differences from the mean. The adjusted SS for each factor only considers how much of the total model variation that particular factor accounts for. In ANOVA analysis, Adj SS is used to calculate the p-value and R^2, which are better metrics for interpreting regression analysis.

Adj MS (Adjusted Mean Squares) – Calculated by dividing the Adj SS by the DF. In these models, Adj MS = Adj SS for all individual sources except for the linear and two-way interactions, which are simply the sum of the Adj MS for each factor or combination of factors divided by the total number of sources (i.e. Linear Adj MS is the sum of the Adj MS for X_1, X_2, X_3, and X_4 divided by four, or an average of the Adj MS for the linear portion of the model).

F-value – In essence, the F-Value for a particular factor (or combination of factors) can be thought of a ratio of how much the factor contributes to variations in the model to how much general error contributes to variations in the model. So, if the factor's contribution to variations in the model were greater than that of pure error, the factor's contribution to the model would be considered significant. Conversely, if the factor's contribution to variations in the model were equal to or less than that of pure error, the factor is not significant. Therefore, the larger the F-value, the more significant the factor, and F-values equal to or less than one indicate that the factor is not significant. It can be calculated a few different ways, but for this ANOVA, the F-value is the ratio of the Adj MS for the individual factor to the Adj MS associated with the error term for the entire regression. F-values are used to calculate the p-value, which indicates the significance of the terms and the model.

p-value – Used to determine whether or not each factor or factor interaction is statistically significant by comparing the evidence for each against the null hypothesis (the hypothesis that there is no relationship between the effect or effect interaction and the outcome). A significance level (α) is chosen before the ANOVA analysis as a threshold for evaluating factor significant. For example, $\alpha = 0.05$ (the level chosen for this analysis) indicates that there is a 5% risk of determining that a factor effect exists when there really is no effect. A p-value less than α indicates that the factor effect is statistically significant, while a p-value greater than α indicates that the factor effect is not statistically significant.

S – The standard deviation of how much the observed data differs from the fitted data. This statistic is presented in the units of the observed data. If comparing models, a model with a lower S better describes the observed data and is a better fit.

R-squared - Intended to describe the percentage of response variation that is explained by the model. Calculated by subtracting the ratio of the error Adj SS (the variation not explained by the model) to the total Adj SS (the total variation of the model) from one. It is always between 0 and 100%. A higher R-squared value is one indication that the model is a good fit for the data, but it should be considered in conjunction with other statistical information about the model (e.g. residual plots, F-values, p-values).

R-squared adjusted - This value is always less than R-squared, and is "adjusted" because it changes based on the number of factor effects included in the model. Increasing factor effects will always increase R-squared, so R-squared adjusted increases if an added factor effect improves the model's ability to describe response variation in the model, and decreases if the added factor improves the model less than would be expected by chance. R-squared adjusted is not intended to be used as a measure of fit for the model and observations, but rather a measure of how the current model compares to alternative models that include more or less factor effects. The closer that R-squared adjusted is to R-squared, the better.

R-squared predicted – This value is also always lower than R-squared and intends to determine how well the current model would be at predicting new observations. It is calculated by removing a particular observation from the data set, generating a model, and then determining how well the new model is able to predict the removed observation. Even if the model will not be used to make future predictions, R-squared predicted can provide valuable information. A low (or zero) value for R-squared predicted indicates that the model may include terms that are not relevant (over-fit). A model that has a R-squared predicted that is close to R-squared is better at predicting new observations.

Detailed ANOVA Results

ANOVA Analysis for Aluminum, %Turbidity Reduction (Y_1)

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	10	0.025876	0.002588	4.50	0.055
Linear	4	0.021228	0.005307	9.24	0.016
X_1	1	0.00467	0.00467	8.13	0.036
X_2	1	0.009037	0.009037	15.73	0.011
X_3	1	0.00161	0.00161	2.80	0.155
X_4	1	0.005912	0.005912	10.29	0.024
2-Way Interactions	6	0.004648	0.000775	1.35	0.38
X_1*X_2	1	0.001353	0.001353	2.36	0.185
X_1*X_3	1	0.000286	0.000286	0.50	0.512
X_1*X_4	1	0.000102	0.000102	0.18	0.691
X_2*X_3	1	0.00114	0.00114	1.98	0.218
X_1*X_4	1	0.000969	0.000969	1.69	0.251
X_3*X_4	1	0.000798	0.000798	1.39	0.292
Error	5	0.002872	0.00057		
Total	15	0.028748			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0239665	90.01%	70.03%	0.00%

ANOVA Analysis for Aluminum, %Turbidity Reduction (Y_2)

% Turb. red. AL = 1.322 -0.0851*X1 -0.0313*X2 -0.01210*X3-0.0715*X4 +0.01098*X1*X2-0.00169*X1*X3 -0.0051*X1*X4+0.001008*X2*X3 +0.00465*X2*X4+0.00141*X3*X4

ANOVA Analysis for Aluminum, %COD Reduction (Y_2)

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	10	0.072162	0.007216	7.28	0.020
Linear	4	0.057911	0.014478	14.61	0.006
X_1	1	0.027351	0.027351	27.60	0.003
X_2	1	0.000709	0.000709	0.72	0.436
X_3	1	0.008515	0.008515	8.59	0.033
X_4	1	0.021336	0.021336	21.53	0.006
2-Way Interactions	6	0.014251	0.002375	2.40	0.178
X_1*X_2	1	0.001765	0.001765	1.78	0.240
X_1*X_3	1	0.001438	0.001438	1.45	0.282
X_1*X_4	1	0.006335	0.006335	6.39	0.053
X_2*X_3	1	0.001108	0.001108	1.12	0.339
X_1*X_4	1	0.001017	0.001017	1.03	0.357
X_3*X_4	1	0.002590	0.002590	2.61	0.167
Error	5	0.004950	0.000990		
Total	15	0.077120			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0314775	93.58%	80.73%	34.22%

% COD red. AL = -0.091 +0.155*X1 -0.0440*X2 +0.0097*X3+0.0947*X4 +0.01254*X1*X2-0.00379*X1*X3-0.0398*X1* X4 +*0.000994*X2*X3+0.00476*X2*X4-0.00254*X3*X4

ANOVA Analysis for Aluminum, %DOC Reduction (Y_3)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	10	0.165233	0.016523	12.90	0.006
Linear	4	0.161502	0.040376	31.51	0.001
X_1	1	0.070202	0.070202	54.79	0.001
X_2	1	0.004657	0.004657	3.63	0.115
X_3	1	0.019227	0.019227	15.01	0.012
X_4	1	0.067417	0.067417	52.62	0.001
2-Way Interactions	6	0.003730	0.000622	0.49	0.798
X_1*X_2	1	0.000447	0.000447	0.35	0.580
X_1*X_3	1	0.000315	0.000315	0.25	0.641
X_1*X_4	1	0.000018	0.000018	0.01	0.911
X_2*X_3	1	0.000061	0.000061	0.05	0.836
X_1*X_4	1	0.002487	0.002487	1.94	0.222
X_3*X_4	1	0.000401	0.000401	0.31	0.600
Error	5	0.006406	0.001281		
Total	15	0.171639			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0357943	96.27%	88.80%	61.78%

% DOC red. AL = -0.118 +0.100*X1 -0.0181*X2 +0.0145*X3+0.0148*X4 +0.0063*X1*X2 - 0.00178*X1*X3 +0.0021*X1*X4-0.00023*X2*X3+0.00744*X2*X4-0.00100*X3*X4

ANOVA Analysis for Iron, %Turbidity Reduction (Y_1)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	10	0.01276	0.001276	1.09	0.494
Linear	4	0.007388	0.001847	1.57	0.313
X_1	1	0.001036	0.001036	0.88	0.391
X_2	1	0.002238	0.002238	1.90	0.226
X_3	1	0.003422	0.003422	2.91	0.149
X_4	1	0.000691	0.000691	0.59	0.478
2-Way Interactions	6	0.005372	0.000895	0.76	0.630
X_1*X_2	1	0.001445	0.001445	1.23	0.318
X_1*X_3	1	0.000776	0.000776	0.66	0.453
X_1*X_4	1	0.002666	0.002666	2.27	0.192
X_2*X_3	1	0.000331	0.000331	0.28	0.618
X_1*X_4	1	0.000146	0.000146	0.12	0.739
X_3*X_4	1	0.000009	0.000009	0.01	0.935
Error	5	0.005876	0.001175		
Total	15	0.018636			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0342813	68.47%	5.41%	0.00%

% Turb. red. FE = 0.719 +0.043*X1 +0.0235*X2 +0.0062*X3-0.0149*X4 -0.0113*X1*X2-0.00279*X1*X3 +0.0258*X1*X4-0.00054*X2*X3 -0.00180*X2*X4-0.00015*X3*X4

ANOVA Analysis for Iron, %COD Reduction (Y_2)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	10	0.134353	0.013435	26.21	0.001
Linear	4	0.120492	0.030123	58.77	0.000
X_1	1	0.01229	0.01229	23.98	0.004
X_2	1	0.002616	0.002616	5.10	0.073
X_3	1	0.005406	0.005406	10.55	0.023
X_4	1	0.10018	0.10018	195.45	0.000
2-Way Interactions	6	0.01386	0.00231	4.51	0.060
X_1*X_2	1	0.000011	0.000011	0.02	0.892
X_1*X_3	1	0.000312	0.000312	0.61	0.471
X_1*X_4	1	0.005023	0.005023	9.80	0.026
X_2*X_3	1	0.000227	0.000227	0.44	0.535
X_1*X_4	1	0.005059	0.005059	9.87	0.026
X_3*X_4	1	0.003229	0.003229	6.30	0.054
Error	5	0.002563	0.000513		
Total	15	0.428441			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0226396	98.13%	94.38%	80.83%

% DOC red. FE = 0.443-0.195*X1-0.0123*X2-0.0082*X3-0.1039*X4-0.0052*X1*X2+0.00265*X1*X3+0.0929*X1*X4-0.00071*X2*X3+0.00651*X2*X4 +0.00382X3*X4

ANOVA Analysis for Iron, %DOC Reduction (Y_3)

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	10	0.421804	0.04218	31.78	0.001
Linear	4	0.377983	0.094496	71.19	0.000
X_1	1	0.025862	0.025862	19.48	0.007
X_2	1	0.005735	0.005735	4.32	0.092
X_3	1	0.000657	0.000657	0.50	0.513
X_4	1	0.345729	0.345729	260.45	0.000
2-Way Interactions	6	0.043821	0.007303	5.50	0.041
X_1*X_2	1	0.000305	0.000305	0.23	0.652
X_1*X_3	1	0.000701	0.000701	0.53	0.500
X_1*X_4	1	0.034489	0.034489	25.98	0.004
X_2*X_3	1	0.000573	0.000573	0.43	0.540
X_1*X_4	1	0.001904	0.001904	1.43	0.285
X_3*X_4	1	0.005848	0.005848	4.41	0.090
Error	5	0.006637	0.001327		
Total	15	0.428441			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0364339	98.45%	95.35%	84.14%

% DOC red. FE = 0.443-0.195*X1-0.0123*X2-0.0082*X3-0.1039*X4-0.0052*X1*X2+0.00265*X1*X3+0.0929*X1*X4-0.00071*X1*X3+0.00651*X1*X4+0.00382*X3*X4

ANOVA Analysis for Combination, %Turbidity Reduction (Y_1)

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	15	0.120568	0.008038	7.21	0.000
Linear	5	0.105511	0.021102	18.92	0.000
X_5	1	0.097300	0.09730	87.22	0.000
X_1	1	0.001955	0.001955	1.75	0.204
X_2	1	0.000356	0.000356	0.32	0.580
X_3	1	0.004850	0.004850	4.35	0.053
X_4	1	0.001050	0.001050	0.94	0.346
2-Way Interactions	10	0.015057	0.001506	1.35	0.286
X_5*X_1	1	0.000002	0.000002	0.00	0.969
X_5*X_2	1	0.007359	0.007359	6.60	0.021
X_5*X_3	1	0.000171	0.000171	0.15	0.700
X_5*X_4	1	0.004843	0.004843	4.34	0.054
X_1*X_2	1	0.000196	0.000196	0.18	0.681
X_1*X_3	1	0.000888	0.000888	0.80	0.386
X_1*X_4	1	0.000959	0.000959	0.86	0.368
X_2*X_3	1	0.000017	0.000017	0.02	0.904
X_2*X_4	1	0.000569	0.000569	0.51	0.485
X_3*X_4	1	0.000053	0.000053	0.05	0.830
Error	16	0.017849	0.001116		
Total	31	0.138417			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0334005	87.10%	75.02%	48.42%

%Turbidity Reduction = 0.963 -*0.0077*X5 +0.0082*X1 -0.0025*X2 +0.00074*X3 -0.0396*X4-0.0005*X5*X1 -0.00919*X5*X2-0.00046*X5*X3+0.01230*X5*X4 -0.00300*X1*X2-0.00211*X1*X3 +0.0109*X1*X4+0.000088*X2*X3 +0.00256*X2*X4-0.00026*X3*X4

ANOVA Analysis for Combination, %COD Reduction (Y_2)

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	15	0.18658	0.01244	7.23	0.000
Linear	5	0.15928	0.03186	18.51	0.000
X_5	1	0.00008	0.00008	0.05	0.828
X_1	1	0.03816	0.03816	22.17	0.000
X_2	1	0.00030	0.00030	0.17	0.681
X_3	1	0.01375	0.01375	7.99	0.012
X_4	1	0.10699	0.10699	62.18	0.000
2-Way Interactions	10	0.02731	0.00273	1.59	0.198
X_5*X_1	1	0.00149	0.00149	0.86	0.367
X_5*X_2	1	0.00302	0.00302	1.76	0.204
X_5*X_3	1	0.00018	0.00018	0.10	0.753
X_5*X_4	1	0.01453	0.01453	8.44	0.010
X_1*X_2	1	0.00102	0.00102	0.60	0.452
X_1*X_3	1	0.00154	0.00154	0.90	0.358
X_1*X_4	1	0.00004	0.00004	0.02	0.884
X_2*X_3	1	0.00017	0.00017	0.10	0.760
X_2*X_4	1	0.00531	0.00531	3.08	0.098
X_3*X_4	1	0.00002	0.00002	0.01	0.921
Error	16	0.02753	0.00172		
Total	31	0.21412			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.041482	87.14%	75.09%	48.57%

%COD Reduction = 0.149 +0.0111*X5 +0.0600*X1 -0.0397*X2+0.00556*X3 -0.0063*X4-0.0136*X5*X1 -0.00589*X5*X2-0.00047*X5*X3+0.02131*X5*X4 +0.00686*X1*X2-0.00278*X1*X3 -0.0022*X1*X4+0.000276*X2*X3 +0.00780*X2*X4+0.00015*X3*X4

ANOVA Analysis for Combination, %DOC Reduction (Y_3)

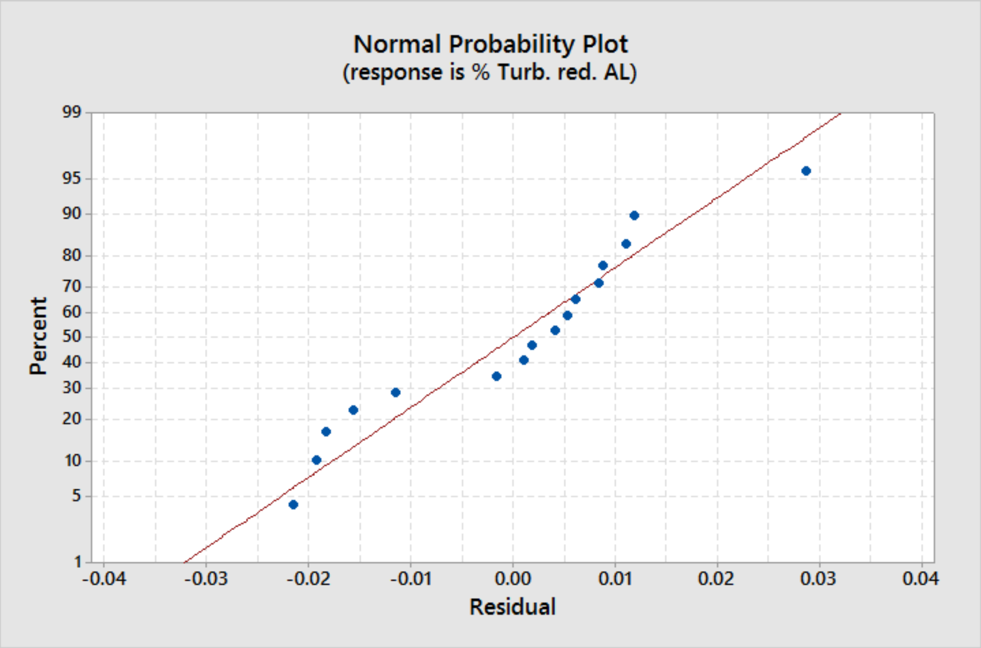
Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	15	0.57201	0.03813	16.93	0.000
Linear	5	0.47139	0.09428	41.85	0.000
X_5	1	0.00798	0.00798	3.54	0.078
X_1	1	0.09064	0.09064	40.23	0.000
X_2	1	0.00003	0.00003	0.01	0.913
X_3	1	0.01350	0.01350	5.99	0.026
X_4	1	0.35924	0.35924	159.46	0.000
2-Way Interactions	10	0.10062	0.01006	4.47	0.004
X_5*X_1	1	0.00542	0.00542	2.41	0.140
X_5*X_2	1	0.01036	0.01036	4.60	0.048
X_5*X_3	1	0.00639	0.00639	2.83	0.112
X_5*X_4	1	0.05390	0.05390	23.93	0.000
X_1*X_2	1	0.00001	0.00001	0.00	0.957
X_1*X_3	1	0.00004	0.00004	0.02	0.898
X_1*X_4	1	0.01803	0.01803	8.00	0.012
X_2*X_3	1	0.00050	0.00050	0.22	0.643
X_2*X_4	1	0.00437	0.00437	1.94	0.183
X_3*X_4	1	0.00159	0.00159	0.71	0.413
Error	16	0.03605	0.00225		
Total	31	0.60806			

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.047465	94.07%	88.51%	76.29%

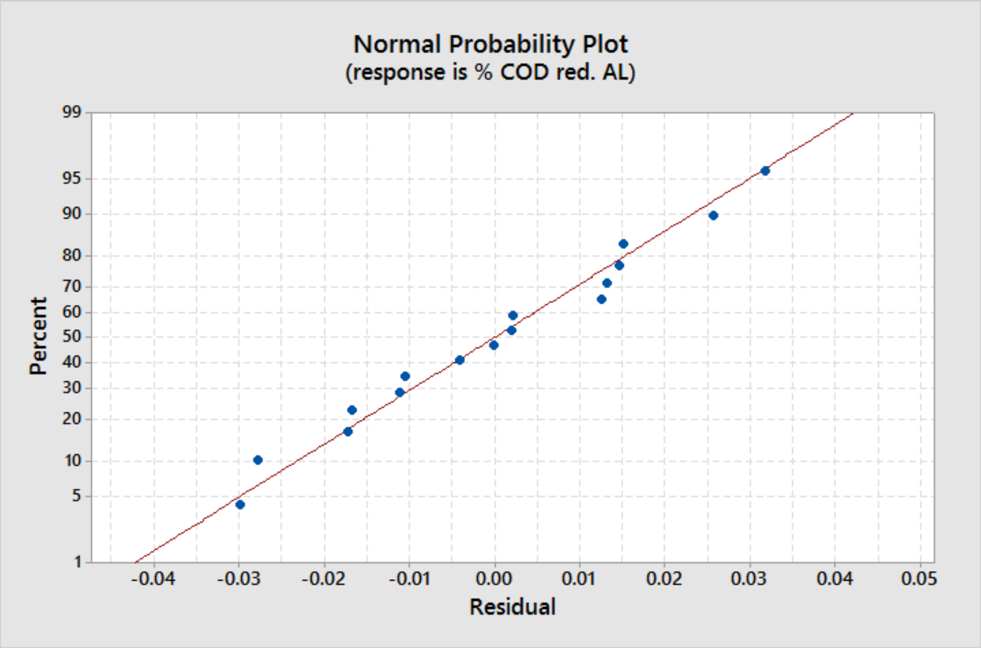
%DOC Reduction = 0.165 +0.0336*X5 -0.047*X1 -0.0154*X2+0.0032*X3 -0.0456*X4-0.0260*X5*X1 -0.01091*X5*X2-0.00283*X5*X3+0.04104*X5*X4 +0.0006*X1*X2+0.00044*X1*X3 +0.0475*X1*X4-0.00048*X2*X3 +0.00708*X2*X4+0.00141*X3*X4

Additional ANOVA Plots

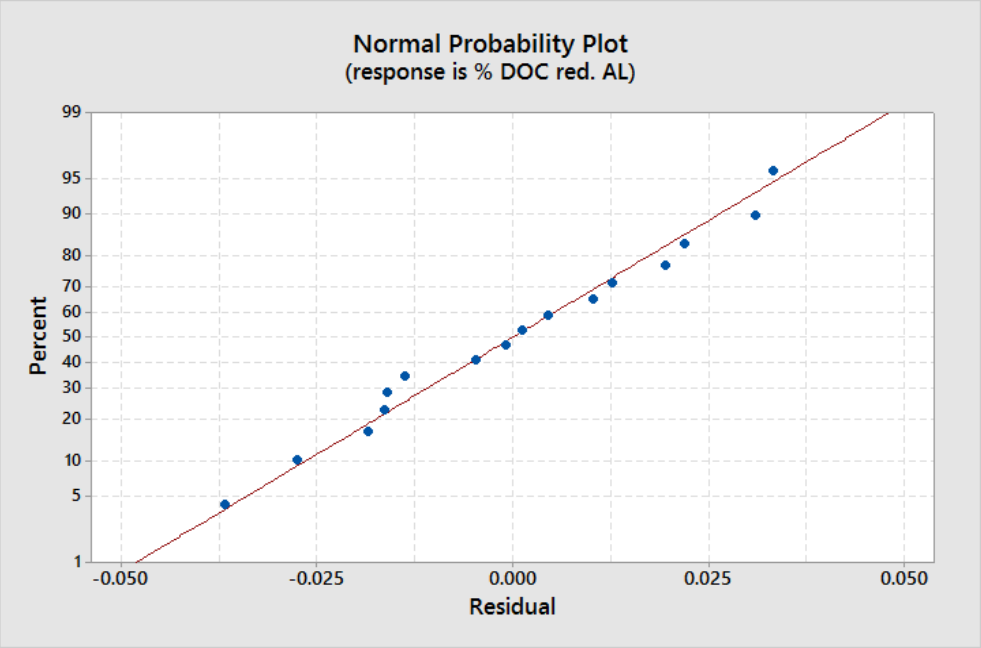
Normal Probability Plot – Aluminum/Turbidity



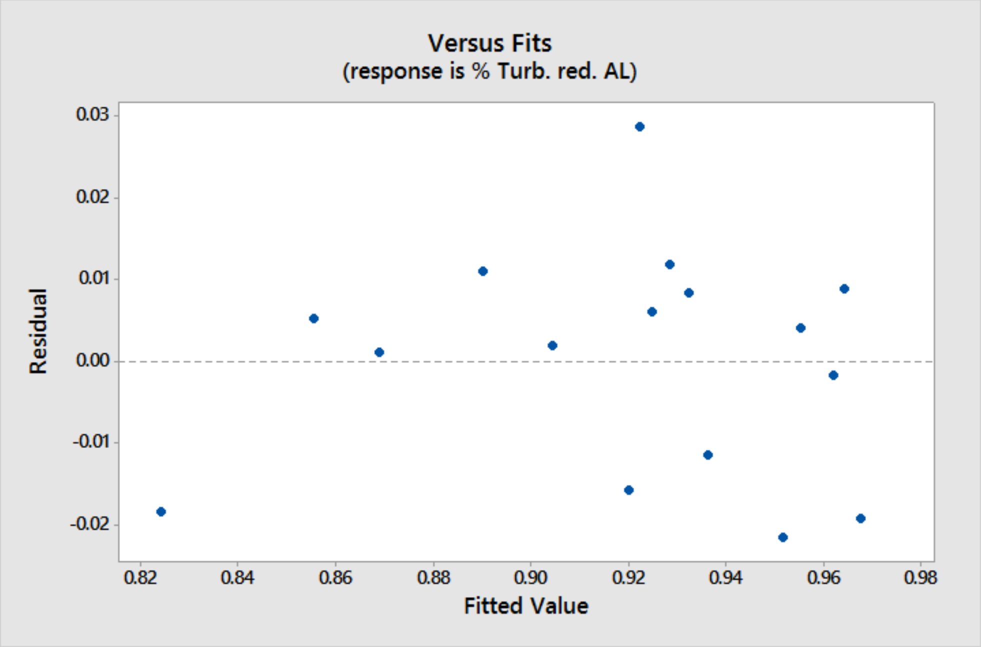
Normal Probability Plot – Aluminum/COD



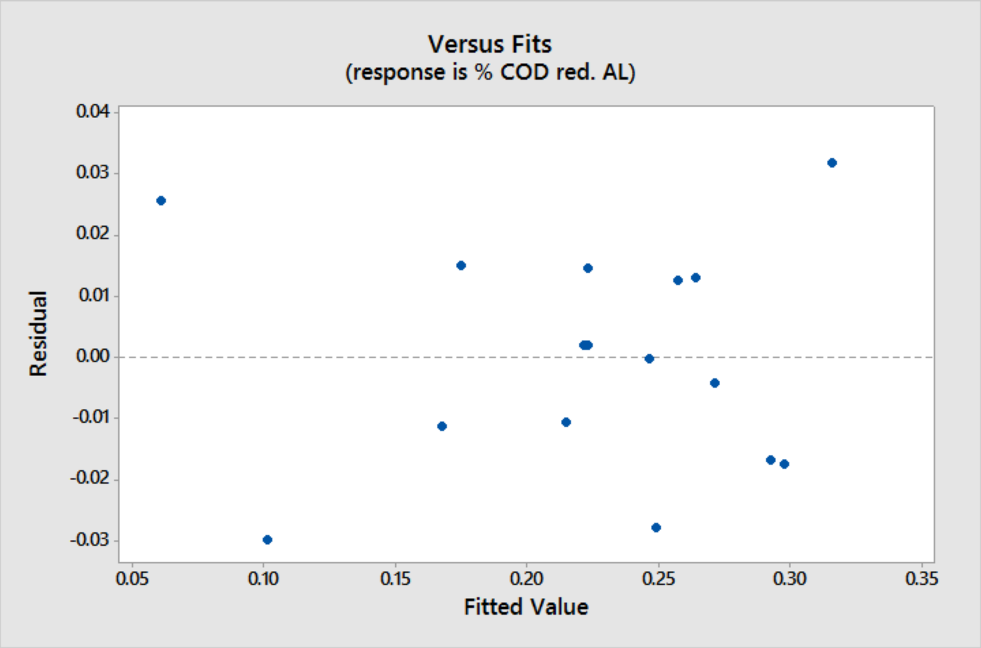
Normal Probability Plot – Aluminum/DOC



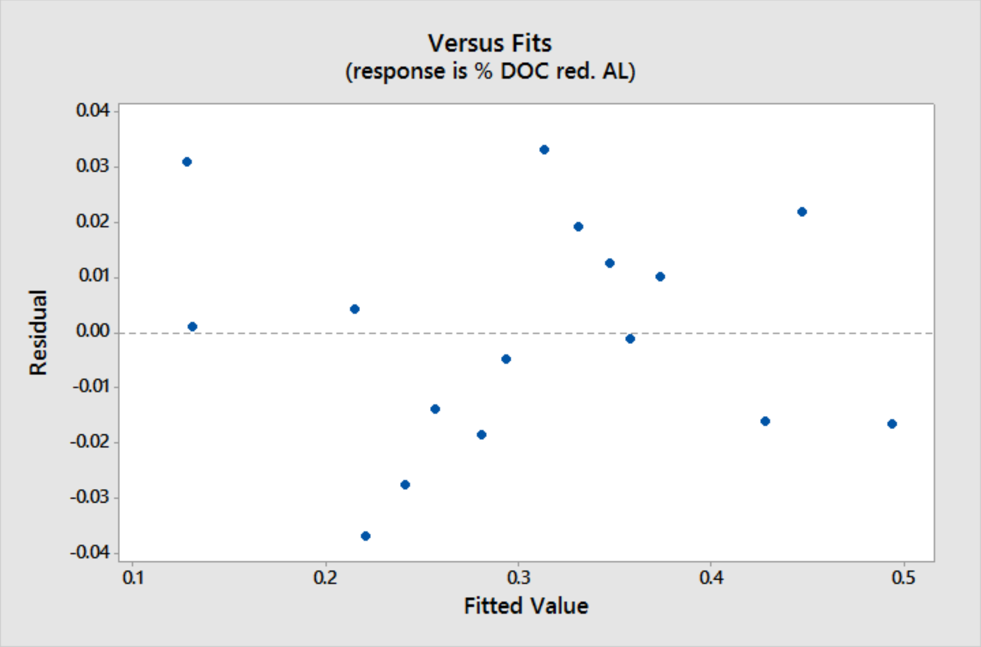
Residuals vs. Fits – Aluminum/Turbidity



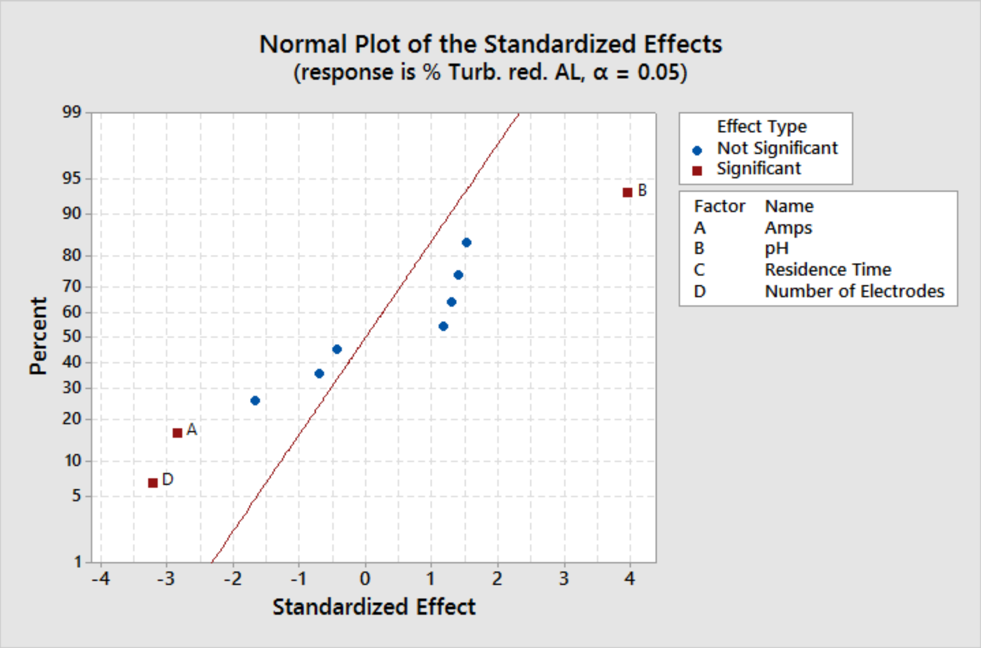
Residuals vs. Fits – Aluminum/COD



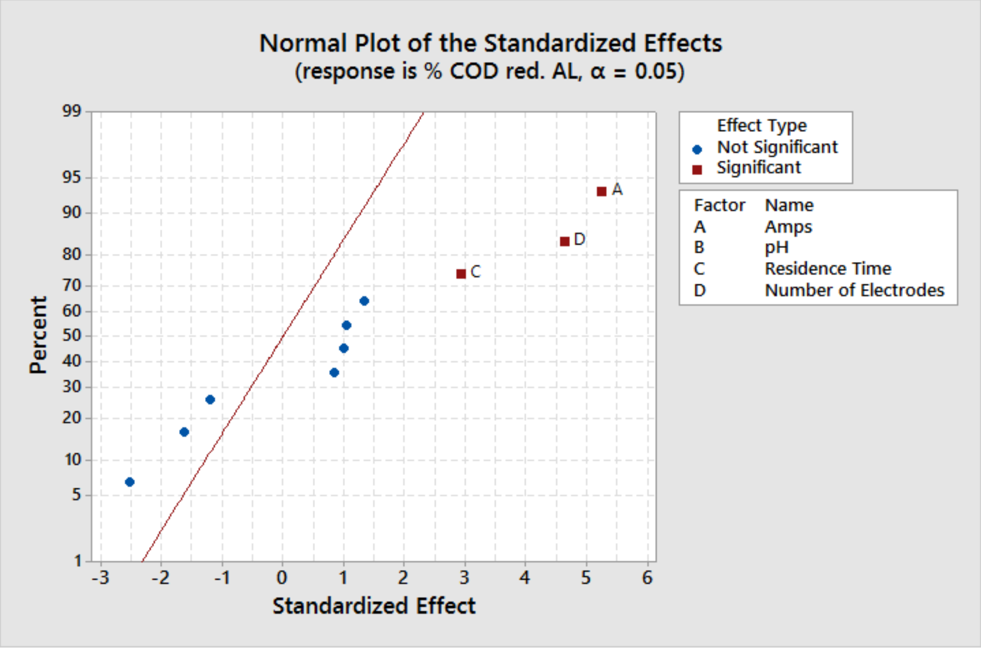
Residuals vs. Fits – Aluminum/DOC



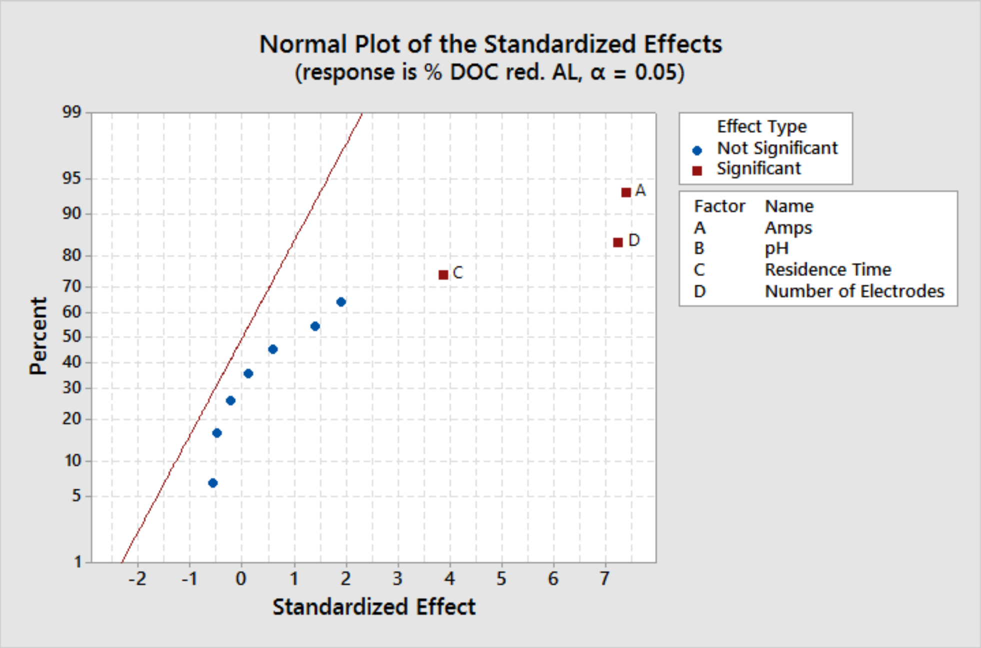
Normal Plot of Standardized Effects – Aluminum/Turbidity



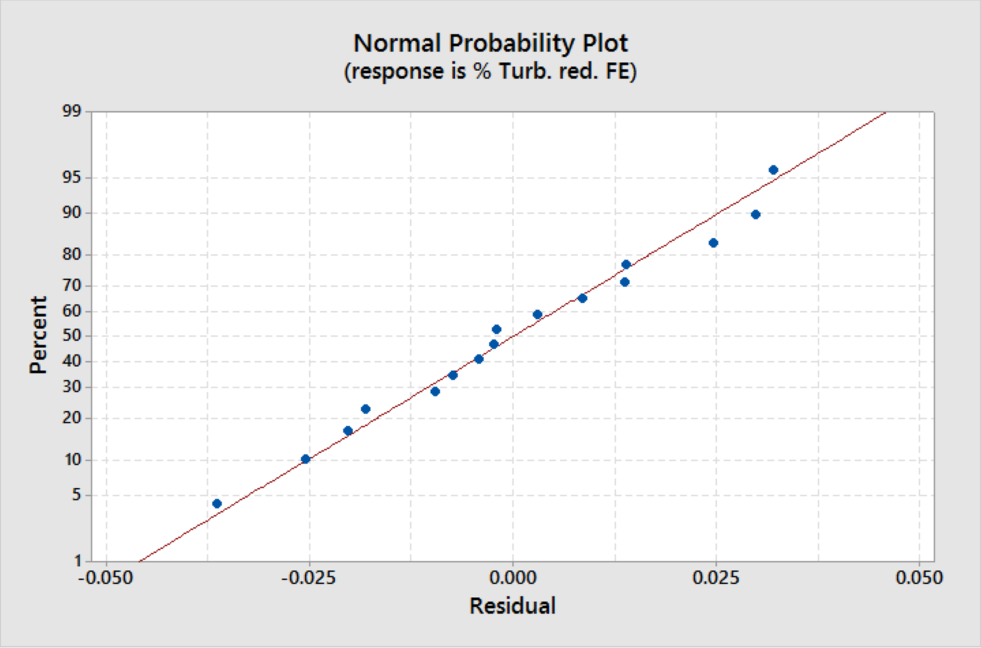
Normal Plot of Standardized Effects – Aluminum/COD



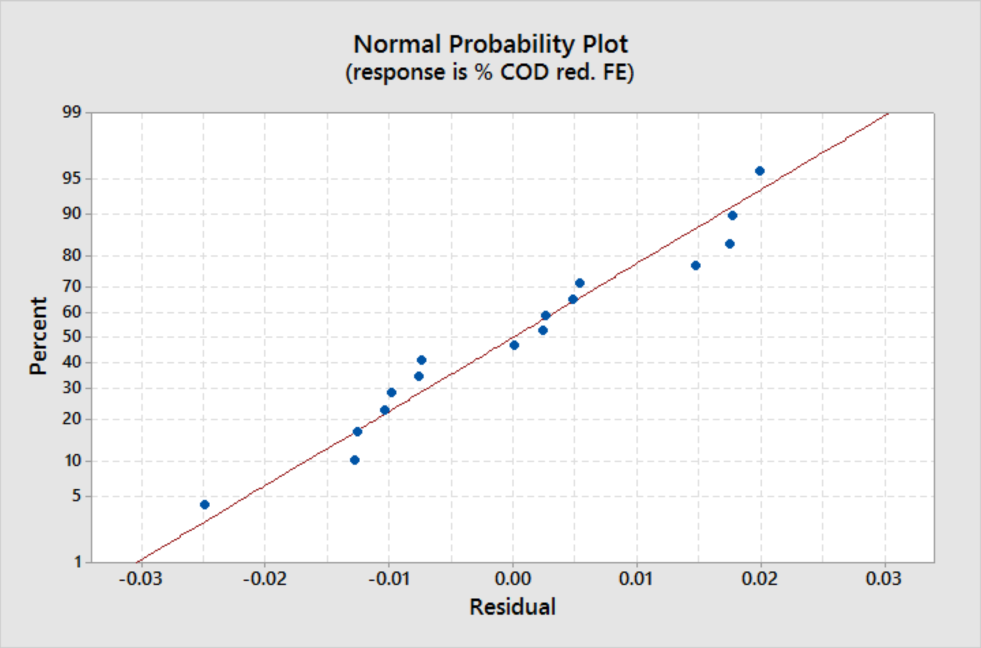
Normal Plot of Standardized Effects – Aluminum/DOC



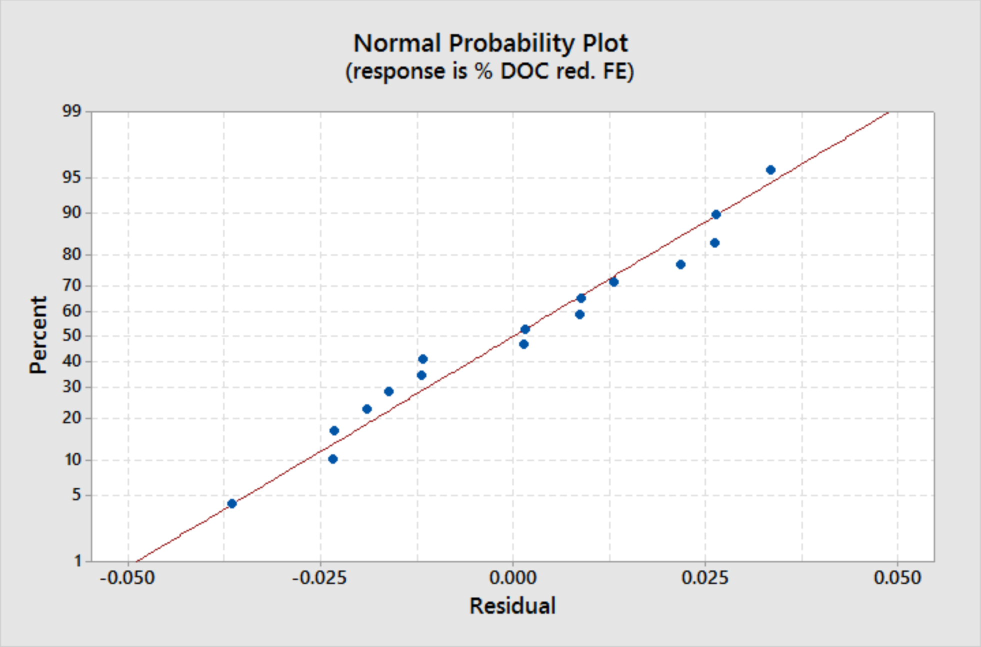
Normal Probability Plot – Iron/Turbidity



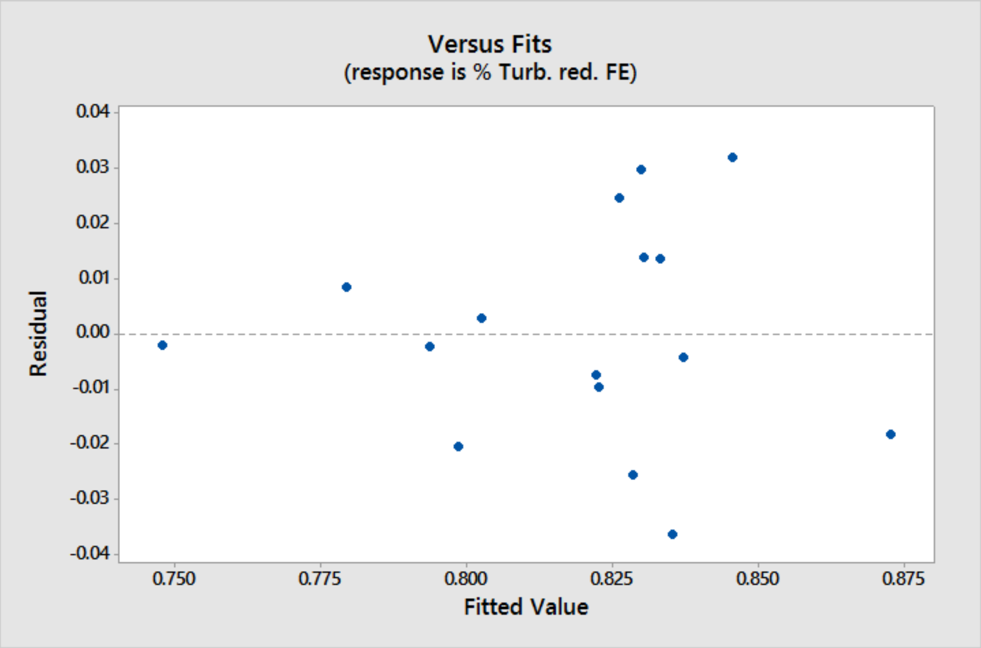
Normal Probability Plot – Iron/COD



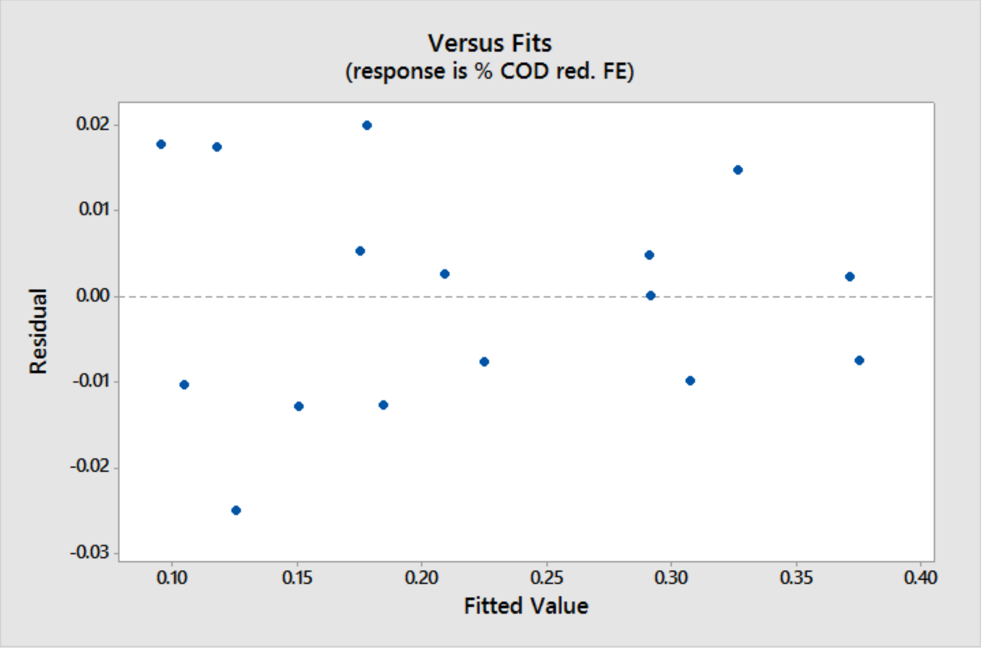
Normal Probability Plot – Iron/DOC



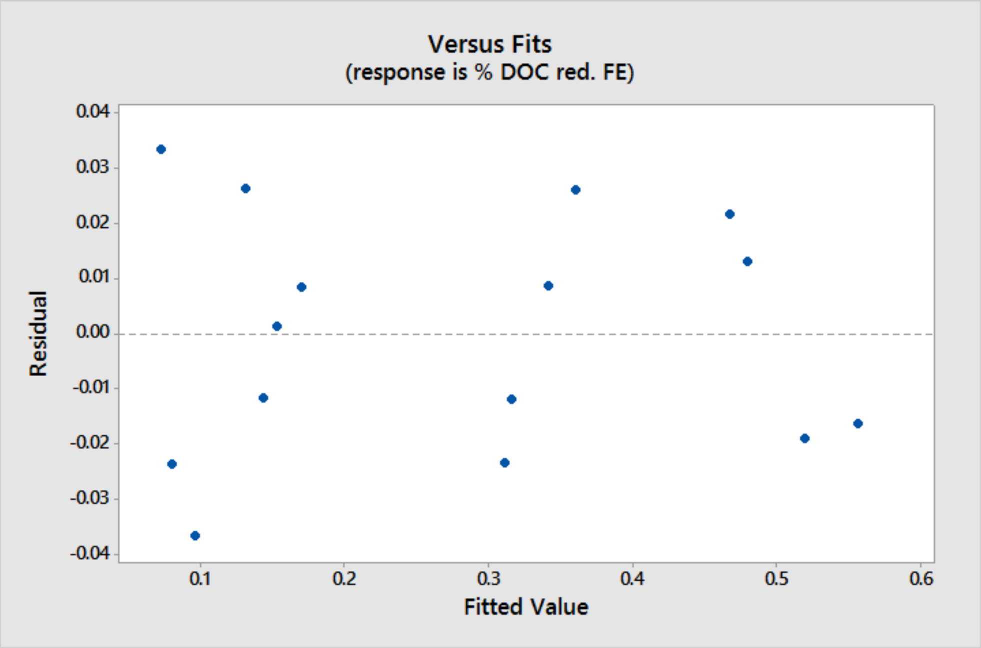
Residuals vs. Fits – Iron/Turbidity



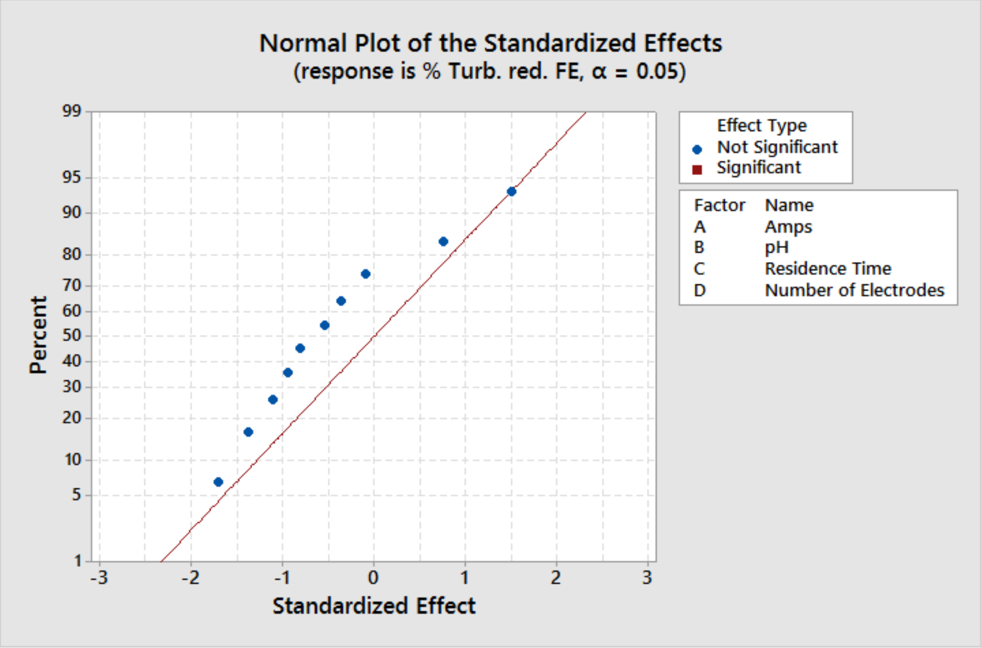
Residuals vs. Fits – Iron/COD



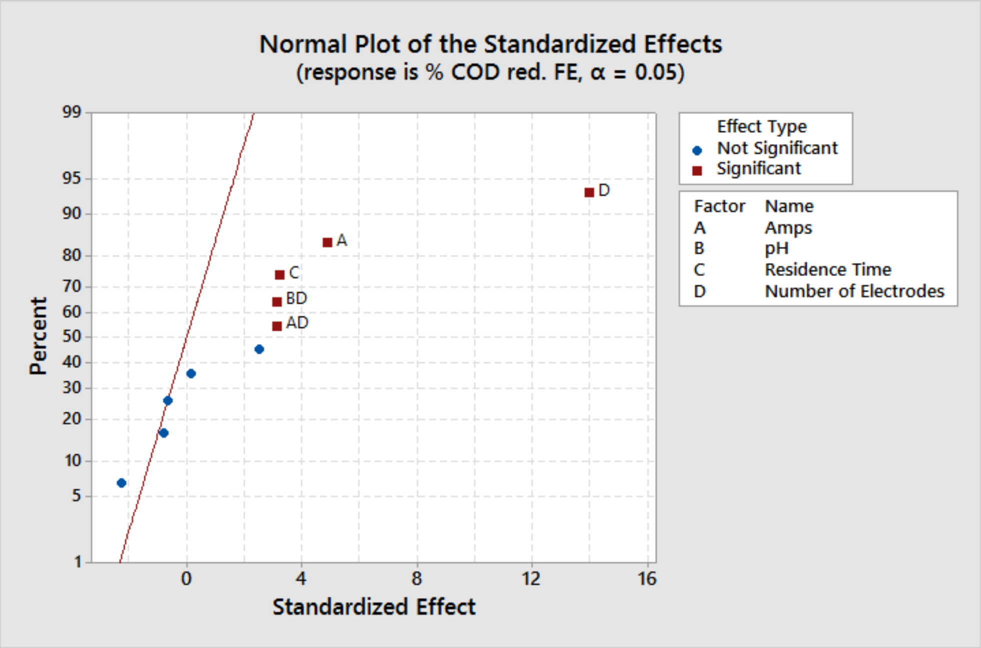
Residuals vs. Fits – Iron/DOC



Normal Plot of Standardized Effects – Iron/Turbidity



Normal Plot of Standardized Effects – Iron/COD



Normal Plot of Standardized Effects – Iron/DOC