
**Investigation of Electrochemical Oxidation for Treatment of Landfill Leachate
Final Report**

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FINAL (ANNUAL) REPORT

08/21/2017 – 06/15/2019

PROJECT TITLE: Investigation of electrochemical oxidation for treatment of landfill leachate

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COMPLETION DATE: 06/15/2019

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STAKEHOLDERS:

KEY WORDS: Landfill leachate, Electrochemical Oxidation, Leachate Treatment, Response Surface Methodology

ABSTRACT: Advanced electrochemical oxidation processes have emerged as a promising method for the destruction of persistent organic material in variable waste streams. Although the process has been successfully employed for wastewater treatment applications, high energy requirements, and the risk of formation of undesirable by-products may limit its application in the field of leachate treatment. This study focuses on the investigation of the feasibility of removing organics and ammonia by electrochemical oxidation coupled with ozone, Fenton or lime. Landfill leachate was treated by two different bench scale electrochemical oxidation reactors coupled with ozone oxidation, Fenton coagulation or lime precipitation. The electrochemical oxidation was conducted using a titanium anode coated with multi-metal oxides (MMO) at three-different current densities for different durations. Treatment performance was determined based on the removal of COD, ammonium-N, and turbidity. A three-level factorial design was established, and response surface methodology (RSM) was introduced to determine the optimum process parameters. The results suggest that the process can remove appreciable

amounts of ammonium-N and COD in a very short time, demonstrating that the process is effective in rapidly degrading recalcitrant organics in leachate.

PROJECT METRICS:

1. List graduate or postdoctoral researchers **funded** by **THIS** Hinkley Center project.

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3. List research publications resulting from **THIS** Hinkley Center project.

None yet

4. List research presentations resulting from **THIS** Hinkley Center project

- Salek, Md Fahim. “Treatment of Landfill Leachate by Advanced Electrochemical Oxidation Process Coupled with Ozone or Fenton” at World Environmental and Water Resource Congress, Pittsburgh, May 2019
- Salek, Md Fahim. “Investigation of electrochemical oxidation for treatment of landfill leachate” at Joint TAG meeting in conjunction with UM, SWA of Palm Beach County, October 2018

5. List research papers that have cited any publications (or the final report) resulting from this Hinkley Center project (use format for publications as indicated in the Hinkley Center Investigators Guide)

None so far

6. List additional research funding that has been secured due to leveraging the research results from this Hinkley Center project (give project title, funding agency, amount of funding, award date, and award period)

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7. List submitted proposals which leverage the research results from this Hinkley Center project (give the proposal title, funding agency, requested funding, date submitted)

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8. What new collaborations were initiated based on **THIS** Hinkley Center project?

Magneli Materials, Origin Clear, Jay Huang, Ayush Tripathi (Application Engineer), Dr. Stephane P. Roche, Assistant Professor, Department of Chemistry and Biochemistry, FAU

9. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders in the solid waste field? Please note that the term “other stakeholders” is meant to broadly include any party or practitioner in the solid waste field. This includes county solid waste directors and their staff, municipal solid waste directors and their staff, solid waste facility design engineers, local/county/city solid waste management regulatory staff, federal solid waste regulatory staff, landfill owners and operators, waste haulers, waste to energy plant owners and operators, recyclers, composting plant owners and operators, yard waste operators, construction and demolition debris companies and organizations, county recycling coordinators, citizens and members of the academic community, etc. (1 paragraph maximum)

To date, the results have not been used by stakeholders yet.

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- October 19, 2018 (Joint TAG meeting held at SWA in conjunction with UM)

EXECUTIVE SUMMARY

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PROJECT TITLE: Investigation of electrochemical oxidation for treatment of landfill leachate

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PROJECT WEBSITE: <http://labees.civil.fau.edu/leahcate.html>

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In 2017, the Bill Hinkley Center for Solid and Hazardous Waste Management funded FAU Lab.EES to investigate the efficiency of electrochemical oxidation process using multi-metal oxide anodes (MMO) to remove selected parameters of interest (such as COD, ammonia, turbidity) from landfill leachate for safe discharge or reuse of the treated effluent. The project will also explore the generation of organo-chlorinated compounds (i.e. trihalomethanes, halo acetic acids etc.) generated as a byproduct during the treatment process.

Landfill leachate is a liquid that drains from landfill and usually contains dissolved and suspended solids. Because of its high amount of recalcitrant organic material, ammonia, chlorides, and heavy metals such as arsenic, lead, and iron, it has become a significant threat to groundwater and surface water sources. It is also challenging to treat because of its variable composition depending on its age and the type of waste dumped in the landfill. Leachate generation data shows that, in Florida approximately 2.2 billion gallons of leachate were generated in 2013 and 2.1 billion gallons in 2014 (Reinhart, 2015). And the data belongs to only half of the active landfills who have proper leachate collection system. A large number of landfills in long-term care are unlined and does not have any leachate collection and metering system.

This volume of leachate is either managed by discharging to wastewater treatment plants (WWTPs), deep-well injection, onsite treatment, offsite hauling or by combination approach. But most of the landfill operators in Florida (approximately 95%) frequently

discharge leachate to local WWTPs due to the cost and complexity associated with the onsite treatment. But in recent years electrochemical oxidation process has shown promises to remove recalcitrant organics from similar waste streams. It has been successfully implemented for treating wastewater from tanneries, (Rao, Somasekhar, Kaul, & Szpyrkowicz, 2001) textile mills, (Naumczyk, Szpyrkowicz, & Zilio-Grandi, 1996) coke plant wastewater, (L. Chiang, Chang, & Wen, 1995) and wastewater containing cyanides (Lanza & Bertazzoli, 2002). And the recent progress in the development of next generation anode materials has led FAU Lab.EES to partner with two equipment manufacturers to test the latest prototypes.

In order to investigate an efficient process to remove COD, ammonium-N and Turbidity, electrochemical oxidation was coupled with four different pretreatments (roughing EOx, ozone, Fenton, or lime). Furthermore, to compare the data obtained, a three-level factorial design was introduced, and the best treatment performance was obtained by Response Surface Methodology (RSM). The experimental data showed that, the maximum COD removal (52.1%), ammonium-N removal (51.8%), and turbidity removal (99.7%) were achieved when ozone was coupled with electrochemical oxidation. But an extended hour (7 hours) experiment with two-stage electrochemical oxidation showed better ammonium-N removal (80%). The RSM indicated a positive effect of current density and treatment duration on the responses in case of all pretreatments. From the statistical analysis, while the maximum COD removal (51%) was achieved with Fenton, maximum ammonium-N removal (51.5%) and turbidity removal (100%) were achieved with ozonation.

1 INTRODUCTION

1.1 BACKGROUND

Landfilling is a common way to dispose of municipal and industrial solid waste. However, the generation of leachate as a result of landfilling is a threat to groundwater and surface water sources (Raghab, Abd El Meguid, & Hegazi, 2013). Leachate is the liquid that percolates through the landfill. The source of the liquid in municipal solid waste (MSW) landfills can come from either precipitation (e.g. rainfall, snow, hail or sleet), moisture already present in the waste or from the metabolic water resulting from the decomposition of the waste itself (Qasim, 2017). Leachate can be characterized by elevated levels of dissolved and suspended solids, color, ammonia, chlorides, organics, and heavy metals such as arsenic, lead, and iron (Meeroff & Lakner, 2015; Mor, Ravindra, Dahiya, & Chandra, 2006; Yoshida et al., 2002). Landfills at their early stages generate leachate with high BOD/COD ratio (typically >0.6) (Deng & Englehardt, 2006a) that signifies the waste is readily biodegradable, but mature landfills produce a liquid with organics and toxic chemicals that are much more difficult to break down and are characterized by a low BOD/COD ratio (typically <0.3) (Deng & Englehardt, 2006a). Due to its variable composition that likely contains recalcitrant organic matter and bio-toxic metals, the level of purification needed typically cannot be achieved using biological processes alone (Deng & Englehardt, 2006a; Meeroff & Teegavarapu, 2010; Meeroff et al., 2012). Therefore, physical-chemical methods are more appropriate for the treatment of leachate.

Physical-chemical processes include coagulation-flocculation, activated carbon adsorption, ion exchange, membrane filtration, and advanced oxidation (such as electrochemical oxidation). Kurniawan et al. (2006) and Meeroff and Teegavarapu (2010) reviewed 118 articles and concluded that none of the physico-chemical treatment processes is universally applicable or efficient by itself to remove recalcitrant organics from landfill leachate. Since conventional methods are not capable of dealing with increasingly strict discharge limits for the various multiple constituents found in landfill leachate, it has become imperative to evaluate newer tools. Electrochemical oxidation has been successfully used for treating wastewater from tanneries (Rao, Somasekhar, Kaul, & Szpyrkowicz, 2001), textile mills (Naumczyk, Szpyrkowicz, & Zilio-Grandi, 1996), coke plant wastewater, (Chiang, Chang, & Wen, 1995), and wastewater containing cyanides (Lanza & Bertazzoli, 2002). With recent advances in anode material for electrochemical oxidation, this technique seems to show promise for the removal of pollutants typically found in landfill leachates. The focus of this study is documenting the treatment performance of electrochemical oxidation coupled with four different physico-chemical processes: A) roughing (two-stage) electrochemical oxidation, B) ozone oxidation, C) Fenton coagulation, and D) lime pretreatment for the removal of chemical oxygen

demand, ammonia, and turbidity from composite leachates sampled from an active landfill with co-disposal of MSW and ash.

However, the formation of organochlorine compounds may be a limiting issue during electrochemical oxidation of leachate with relative high chlorides, when active chlorine species are involved in indirect oxidation reactions with natural organic material (Anglada, Urtiaga, Ortiz, Mantzavinos, & Diamadopoulos, 2011). Although there is no regulation of chlorinated byproducts in treated leachate effluent, USEPA regulates total trihalomethanes (TTHMs) and haloacetic acids (HAA5) in drinking water to a maximum contaminant level (MCL) of 80 µg/L and 60 µg/L, respectively. Byproducts like TTHMs and HAA5 present a health concern when the effluent water finds its way to a drinking water source, and the downstream water is utilized as potable water supply. Studies concerning carcinogenic effects of these byproducts are insufficient, but there is epidemiological evidence of association of long-term exposure of TTHMs and bladder disorder (Villanueva, Cordier, Font-Ribera, Salas, & Levallois, 2015), reduced fertility and neurological disorder (Mohamadshafiee & Taghavi, 2012). In this study, characterization of two major disinfection byproducts: TTHMs and HAA5 are also studied.

1.2 LITERATURE REVIEW

1.2.1 Electrochemical Oxidation

Electrochemical oxidation is an oxidation process that occurs through the application of external voltage. The process involves direct oxidation of pollutants at the anode as well as indirect oxidation by mixed oxidants including chlorine and hypochlorite ion (Naumczyk et al., 1996; Vlyssides, Israilides, Loizidou, Karvouni, & Mourafeti, 1997), hydrogen peroxide (Brillas, Bastida, Llosa, & Casado, 1995) and ozone (El-Shal, Khordagui, El-Sebaie, El-Sharkawi, & Sedahmed, 1994; Stucki, Baumann, Christen, & Kötz, 1987). By direct anodic oxidation, pollutants absorbed on the anode surface may be destroyed to some extent (Li, Wang, Jiao, & Chen, 2001). However, the removal of pollutants is primarily due to the indirect oxidation by chlorine/hypochlorite generated by the oxidation of chlorine species at the anode (L. C. Chiang, Chang, & Wen, 1995).

Researchers have studied the treatment of landfill leachate by electrochemical oxidation under different conditions (Mandal, Dubey, & Gupta, 2017). Factors affecting the efficiency of electrochemical oxidation include anode material, current density, contact time, pH, type and concentration of electrolytes, and pretreatment (Mandal et al., 2017; Zhou, Li, & Hua, 2010). Several other factors that may affect the treatment performance include flow rate, inter-electrode gap between anode and cathode, ratio of anode area to

volume of effluent to be treated (A/V), temperature, reactor geometry (two dimensional or three dimensional), cathode material, and pretreatment (Mandal et al., 2017).

Feki et al. (2009) introduced membrane bioreactor (MBR) as a pretreatment of the electrochemical process for treatment of leachate from a landfill site located in Djebel Chekir (Tunisia). After more than 60% removal of organic loads by MBR, three different anode materials were tested; platinized titanium grid (Ti/Pt), PbO₂ and graphite plates all having 60 cm² surface area. The experiments were carried out in a glass beaker having a capacity of 0.25 L. They obtained the highest COD (25%), NH₄⁺ (22%) and color removal under optimal operational conditions of 1-hour reaction time and 400 Am⁻² using Ti/Pt anode alone, with an overall treatment efficiency of 85% COD, 94% NH₄⁺ and 99% color when coupled with MBR pretreatment, which reduced the power consumption from 127 kWh kg⁻¹ COD to 60 kWh kg⁻¹ COD (Feki, Aloui, Feki, & Sayadi, 2009).

Bashir et al. (2009) studied electrochemical oxidation of stabilized leachate collected from the Pulau Burung sanitary landfill in Malaysia using graphite carbon electrodes with sodium sulfate (Na₂SO₄) as an electrolyte in a 600 mL capacity batch electrochemical reactor. They observed the responses of influent COD, current density, and reaction time on BOD removal, COD removal, BOD:COD ratio, color, and pH. The optimum condition obtained by this study was 4 hours of reaction time and 799 Am⁻² current density with a removal efficiency of 70% BOD, 68% COD, and 84% color. They concluded that the method is independent of the initial COD concentration of leachate and did not increase biodegradability. An increase in color intensity was reported due to the corrosion of the carbon electrodes (Bashir et al., 2009).

Anglada et al. (2011) investigated the efficiency of Boron-doped diamond material for electrochemical oxidation of leachate. The experiments were conducted in a single compartment electrolytic cell having a capacity of 10 liters with circular Boron-doped diamond on silicon electrodes. The leachate sample was continuously recirculated in the cell using a peristaltic pump, and a cooling loop was used to release the heat from the electrolytic cell by tap water recirculation. After 8 hours of reaction time, and with 2571 Am⁻² current intensity, 51% of COD and 34% of NH₄⁺-N was achieved (Anglada et al., 2011). They also analyzed the effect of current intensity and extended electrolysis on the formation of chlorinated organic compounds. The dominant byproducts found were chloroform, dichloroacetonitrile, 1,2-dichloroethane, and 1,1-dichloroacetone (Anglada et al. 2011). The concentration of chlorinated organics was found to increase continuously with the reaction time, while the acidic condition was found to favor the formation of haloacetonitriles and haloketones (Anglada et al., 2011).

Zhang et al. (2011) investigated electrochemical oxidation of leachate samples collected from a landfill in Wuhan, China with sequencing batch reactor (SBR) pretreatment. The

electrochemical oxidation was performed in a rectangular electrolytic cell (volume = 200 mL) using anode plates made of titanium coated with iridium dioxide and ruthenium dioxide and cathode plates made of stainless steel. The treatment performance was observed at different current densities, inter-electrode gaps, and reaction times. Box-Behnken statistical experiment design and response surface methodology (RSM) were employed to investigate the effect of these variables. After oxidizing electrochemically for 60 minutes at 470 Am^{-2} , the results showed 60% ammonia nitrogen removal and 54% COD removal. However, with the increase of current density to 680 Am^{-2} and reaction time to 90 minutes, overall 98% ammonia nitrogen removal and 66% COD removal was achievable (Zhang, Ran, Wu, & Zhang, 2011). However, Zhang et al. (2011) concluded that indirect oxidation dominates during the electrochemical reaction as they observed more ammonia-nitrogen removal than COD removal. Ammonia and COD removal have different oxidation mechanisms; ammonia removal takes place when indirect oxidation is dominant, whereas COD removal is favored under direct anodic oxidation (Cabeza et al., 2007). Again, the RSM data showed that the response of current density and inter-electrode gap change is different on COD removal and ammonia removal. While ammonia removal increased with the increase of current density and inter-electrode gap; the COD removal efficiency increased with the increase of current density up to a point, and with further incremental increase, the removal efficiency started to decrease. Again, on the contrary to ammonia removal, COD removal decreased when the electrodes are placed closer (Zhang et al., 2011).

Turro et al. (2011) performed electrochemical oxidation of landfill leachate using an experimental Ti/IrO₂-RuO₂ anode. The treatment performance was investigated with different current densities (80, 160, and 320 Am^{-2}), initial pH (0.25, 3, 5, 6), temperatures (30, 60, and 80°C), reaction times up to 240 min, and the addition of electrolytes like HClO₄, NaCl and Na₂SO₄. The sample was collected from a laboratory scale bioreactor landfill operating for years. Although there was no significant change in the removal of COD with temperature change, the effect of initial pH was noticeable. At highly acidic condition (0.25), the authors achieved lower removal, and by increasing pH to 3, they were able to achieve better removal of COD (90%). Again, when NaCl concentration was increased from 20 mM to 100 mM, performance improved for instance after 240 min of reaction, the COD removal was 75% and 43% respectively for 100 mM and 20 mM externally added NaCl. Although the addition of chloride ions can improve the removal efficiency, the generation of chlorinated organic compounds may result in a final solution with a high level of ecotoxicity (Turro et al., 2012).

Table 1 summarizes treatment performance and operating conditions from the published literature cited in this section.

Table 1: Summary of treatment performance of electrochemical oxidation from published studies

Anode Material	Current Density (Am ⁻²)	Volume of Sample (L)	Time (h)	COD Removal %	Ammonia Removal %	Cl ⁻ mg/l	Authors
Ti/RuO ₂ -IrO ₂	260	0.20	1.5	44	50	831	Zhang et al. (2011)
Ti/IrO ₂ -RuO ₂	80	0.12	4.0	20	Not reported	6150	Turro et al. (2011)
	160			40			
	320			35			
Ti/RuO ₂ -IrO ₂	300	0.80	Not reported	20	35	3702	Zhang et al. (2011)
	900			10	85		
Graphite carbon	800	0.50	4.0	65	Not reported	Not reported	Bashir et al. (2009)
BDD	2571	10.00	8.0	51	34	2574	Anglada et al. (2011)
Ti/Pt	400	0.25	1.0	63	80	5500	Feki et al. (2009)

1.2.2 Ozone

Another promising treatment technique is ozone oxidation. This process involves the production of a short-lived but strong oxidizing agent, the hydroxyl radical ($\cdot\text{OH}$) to oxidize the complex leachate mixture. Hydroxyl radicals have higher oxidation potential than the ozone itself and have higher reactivity and selectivity towards organic pollutants (Chaturapruek, Visvanathan, & Ahn, 2005). Cortez (2010) studied the degradation of landfill leachate using ozone under different ozone concentrations, contact times, initial pH, and hydrogen peroxide concentrations. Ozone was produced from pure and dry oxygen using an ozone generator with corona discharge. The ozone was introduced into the reactor through a ceramic diffuser, and the reaction was allowed to continue for 60 minutes. A maximum of 23% COD removal and 14% TOC removal at 112 mg/L ozone consumption was reported with an initial pH of 3.5 for a reaction time of 60 minutes. However, a higher removal rate was observed when hydrogen peroxide was introduced. At a rate of 600 mg $\text{H}_2\text{O}_2/\text{L}$, the $\text{O}_3/\text{H}_2\text{O}_2$ system was able to remove 63% COD and 53% of TOC (Cortez, Teixeira, Oliveira, & Mota, 2010).

Bila (2004) studied a sequence of processes to treat leachate produced at the Gramacho Municipal Landfill in Rio De Janeiro, Brazil. Initially, a physicochemical treatment was used before the introduction of ozone produced via a PCI ozone generator having a capacity of 40 g/h, which uses commercial oxygen as the feed gas. A stainless-steel porous disk was used to generate oxygen bubbles. When Al_2SO_4 was used for coagulation-flocculation as a pretreatment, the total average removal levels of COD and DOC achieved by the combined process were 73% and 63% respectively for an ozone dose of 3.0 g/L (Bila, Filipe Montalvão, Silva, & Dezotti, 2005).

1.2.3 Fenton

Advanced oxidation using Fenton's reagent is another promising method to reduce organic load or toxicity from water and different waste streams (Guzzella, Feretti, & Monarca, 2002; Pérez, Torrades, Domènech, & Peral, 2002). These researchers conducted studies to optimize the key factors such as initial pH, dosage of Fenton reagents, temperature, aeration, and reagent addition mode that may affect the treatment efficiency. Deng (2007) studied COD removal efficiency in leachate by Fenton at different pH and reagent doses. Initially, pH of 200 mL prefiltered leachate was adjusted to different values ranging from 2 to 8. Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide solution (H_2O_2 , 30% w/w) was added subsequently. Finally, pH was adjusted to 8 using NaOH pellets and solution. The most favorable reported conditions were: initial pH = 3, molar ratio of reagents $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 3$, $[\text{H}_2\text{O}_2] = 240$ mM, with six dosing steps and achieved 61% COD removal (Deng, 2007).

Zhang et al. (2005) studied operating conditions such as reaction time, pH, temperature, H₂O₂ to Fe (II) molar ratio, Fenton's reagent dosage, initial COD strength, feeding mode and polymer type on the efficacy of the Fenton process. They found the process to be largely pH-dependent, and the maximum COD removal was achieved at pH 2-3. Organic removal increased with the increase of reagent dose at a favorable H₂O₂ to Fe (II) molar ratio of 1.5. They also reported stepwise addition of Fenton reagents to be more effective and found a positive effect of temperature increase (Zhang, Heung, & Huang, 2005).

1.2.4 Lime Precipitation

In 2008, Renou et al. (2008) optimized a combined process where lime precipitation was coupled with reverse osmosis. The optimum dosage of lime was obtained by jar test using lime dosage ranging from 0 to 10 g/L in a 1-liter sample. The method consists of lime addition, rapid mixing for 5 minutes, slow mixing for 30 minutes followed by a 30-minute sedimentation process. This optimized dosage was used to treat a 200-400 L sample in combination with reverse osmosis. Doses ranging from 2-6 g/L lime were shown to achieve COD removal of 20-30% by co-precipitation mechanisms, which were validated by scanning electronic microscopy (Renou, Poulain, Givaudan, & Moulin, 2008).

Preliminary experiments run by Tatsi et al. (2003) demonstrated COD removal by the addition of lime (Ca(OH)₂). At different lime dosages and pH, COD removal from 30% to 45% was achieved in both fresh and partially stabilized leachate; the maximum removal was recorded at pH 12 with a respective lime dosage of 7 g/L (Tatsi, Zouboulis, Matis, & Samaras, 2003). However, they also mentioned the production of excessive sludge as a potential drawback.

1.3 RATIONALE

According to a study by Meeroff and Teegavarapu in 2010, the amount of leachate produced from Class 1 landfills in Florida can be up to 7000 gallons per day per acre of landfill. This amount of leachate is either managed by deep well injection, onsite treatment, hauling offsite, discharge to a publicly owned treatment works (POTW), or by a combination approach (Meeroff and Lakner, 2014). However, in the case when deep-well injection is not permitted or hauling offsite is not cost effective, discharge to a POTW is preferable. However, with the current management methods available at conventional wastewater treatment plants, the proposed new treatment goals (such as USEPA emerging contaminants criteria) may not be achievable if leachate is accepted. In the foreseeable future, wastewater treatment plants may refuse to accept direct disposal of leachate or may impose excessively high surcharges. So, there is a need to develop

effective alternatives for onsite treatment of landfill leachate for safe discharge to wastewater treatment plants or the environment.

This study focuses on the effectiveness of a novel advanced electrochemical oxidation method coupled with other pretreatment methods like ozone, Fenton, dual stage EOx, and lime. Although literature review on electrochemical oxidation suggests successful removal of contaminants from industrial wastewater such as tanneries, textiles and even some landfill leachates, no published study was conducted where electrochemical oxidation was accompanied by ozone or Fenton. So, this study provides researchers with performance data on new combined approaches for treating landfill leachate.

1.4 OBJECTIVES

The main goal of this study is to investigate the treatment performance of advanced electrochemical oxidation for leachate treatment. To accomplish this goal, the study is organized into two main objectives, as follows:

1. To document the treatment performance of advanced electrochemical oxidation process with multi-metal oxide (MMO) anodes in bench scale, coupled with ozone, Fenton's reagent, dual stage EOx, or lime pretreatment to remove selected parameters of interest (specifically COD, ammonia and turbidity) from landfill leachate.
2. To assess the generation of halogenated byproducts (like TTHMs and HAA5) during the electrochemical oxidation treatment process.

2 METHODOLOGY

The first two sections of this chapter discuss the site description and how samples were collected and preserved. Later on, the procedures for determining the concentrations of selected parameters of interest, reactor development, and their details are explained. The final section of this chapter discusses the statistical analysis used to attempt to optimize the treatment process parameters.

2.1 SITE DESCRIPTION

The Solid Waste Authority of Palm Beach County provides solid waste management services to approximately 1.3 million residents of Florida's largest county (SWA End of Year Review, 2013). It owns and operates a variety of solid waste disposal units including a landfill, a 2000 ton per day Waste-to-Energy (WTE-1) facility, a 3000 ton per day mass burn Waste-to-Energy (WTE-2) plant, a recovered materials processing facility, a biosolids palletization facility, a vegetation waste processing operation, household hazardous collection facility, and six transfer stations. The waste disposed of at the landfills includes municipal solid waste (MSW) and a mixture of bottom ash and fly ash. Inert waste and rejected wastes from WTE-1 is also disposed of at the landfill. The facility started accepting waste in December 1989. More than 13,500,000 tons of waste has been disposed of in the subsequent 26 years (Meeroff & Lakner, 2015). Only MSW was disposed at the landfills in between 1989 to 1996. In 1997, SWA began operating an RDF waste to energy plant (WTE-1) on the property they own adjacent to the landfill. Waste disposed at the landfill after the WTE-1 plant came on-line was a mixture of:

- 1) Excess MSW that bypassed the WTE-1 plant
- 2) Unprocessable waste (items removed from the WTE tipping floor)
- 3) Processed residue
- 4) The mixed bottom and fly ash from the combustion of the MSW delivered to the plant

2.1.1 Class I Landfill and Cells

The facility contains a Class I and a Class III landfill. The Class I landfill accepts ash, residue from the renewable energy facilities as well as MSW and other wastes that federal and state regulations require to be disposed of in a Class I landfill. It has a total area of 262.28 acres having 4,477 feet length, oriented in north/south direction and 1,550 feet width oriented east/west direction. Currently, this landfill has sixteen separate cells (Figure 1), the first four cells (Cell 1-4) have been filled to their regulated elevation and have been capped and closed. The next six cells (Cell 5-10) have been filled to near their regulated elevation and do not receive waste regularly. Cells 11-14 are currently

operating and receive waste daily. The two remaining cells are constructed and have just started receiving waste during the project period. Table 2 summarizes the date of first waste disposal and the status of each landfill cell.

Table 2: Date of first waste disposal and status of each landfill cell

Cell No.	First Waste Disposal	Years to Date (2019)	Status
1	July, 1989	29.8	Closed
2	December, 1989	29.5	Closed
3	January, 1991	28.4	Closed
4	February, 1992	27.3	Closed
5	October, 1993	25.7	Closed
6	September, 1996	22.7	Closed
7	August, 1998	20.8	Inactive
8	April, 1998	21.2	Inactive
9	January, 2006	13.4	Inactive
10	January, 2006	13.4	Inactive
11	April, 2010	9.2	Active
12	December, 2008	10.5	Active
13	November, 2009	9.6	Active
14	February, 2013	4.3	Active

The Class III landfill accepts construction and demolition waste (C&D) and was not directly sampled in this study.

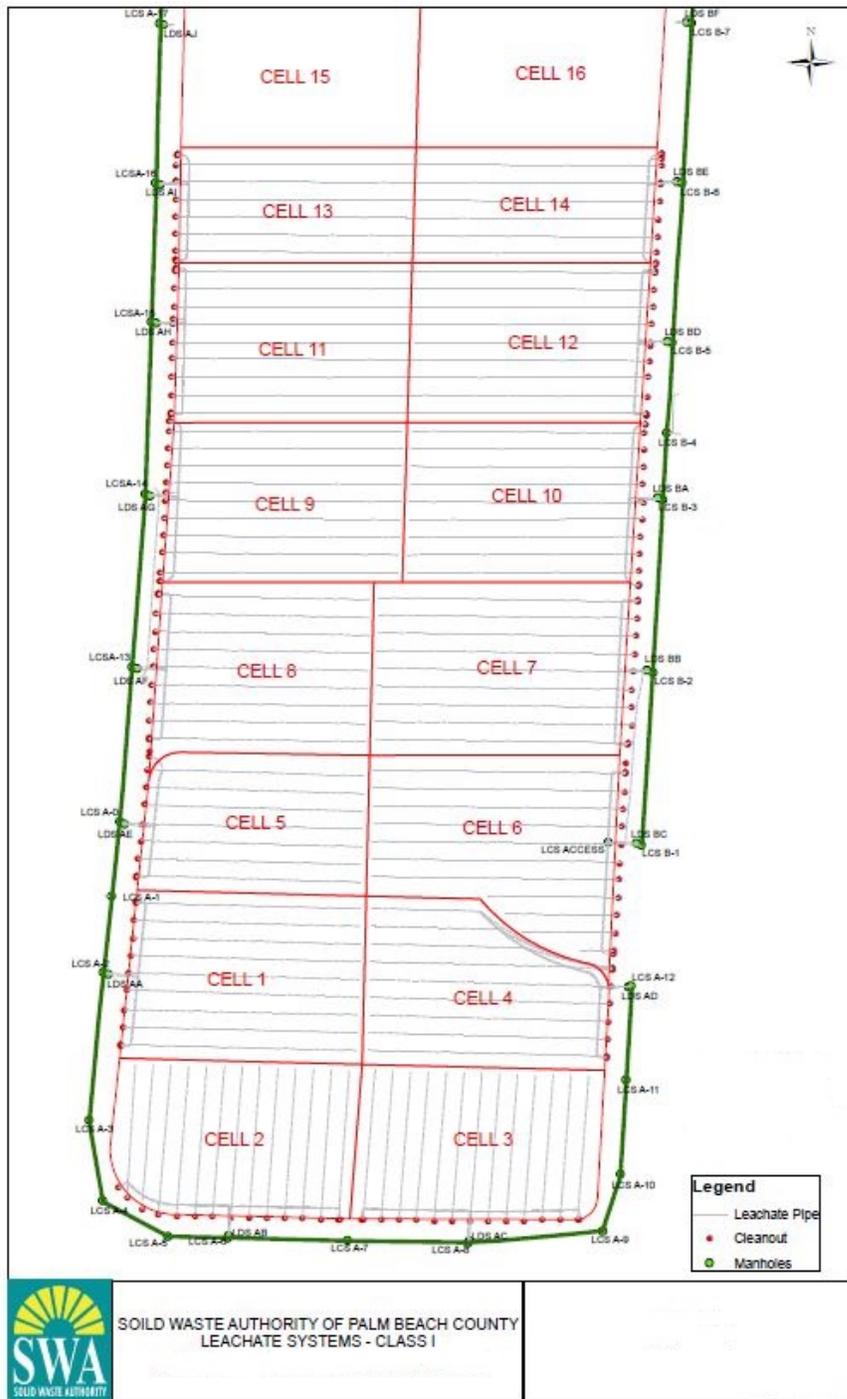


Figure 1: Landfill cells and gravity lines at SWA Class I landfill facility

2.1.2 Leachate Collection System

A raised bank surrounds the constructed landfill cells and forms the outer edge of the Class I landfill. The liner system between cells is continuous, but the leachate collection system (LCS) in each cell is independent and separated by an isolation berm as well as by the landfill bottom grades, which isolate leachate within each cell by elevation and gravity. The bottom liner of the cells is constructed with a slope of a minimum of 0.5% from a center ridge to a collection sump. Leachate flows from this elevated middle ridge to the side collection sumps located at the foot of the perimeter berm. A cross-section of the liner is shown in Figure 2.

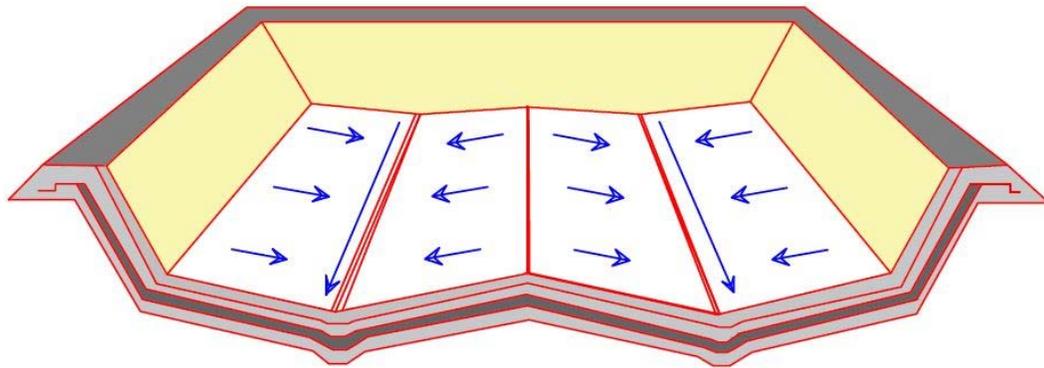


Figure 2: Landfill liner and leachate collection system design schematic (adapted from Qian, Koerner, & Gray, 2002)

Leachate collected in the sump flows by gravity through a “stub line” and discharges into a manhole located in the perimeter road. Each landfill cell has its own manhole. The manholes for the cells on the east side of the landfill are connected, and leachate flows by gravity from one manhole to the next until it reaches Pump Station B (Figure 3). The manholes for the cells along the south and west sides of the landfill are also connected and flow to Pump Station A. Leachate collected at these two pump stations is pumped into a force main around the landfill perimeter to a deep injection wet well, where the combined leachate is injected approximately 3,000 feet beneath the ground surface. Liquid from the secondary collection system (leak detection system) is also mixed with the primary leachate in manholes. Figure 3 shows a general schematic of the gravity leachate lines and location of manholes and leachate pump stations.

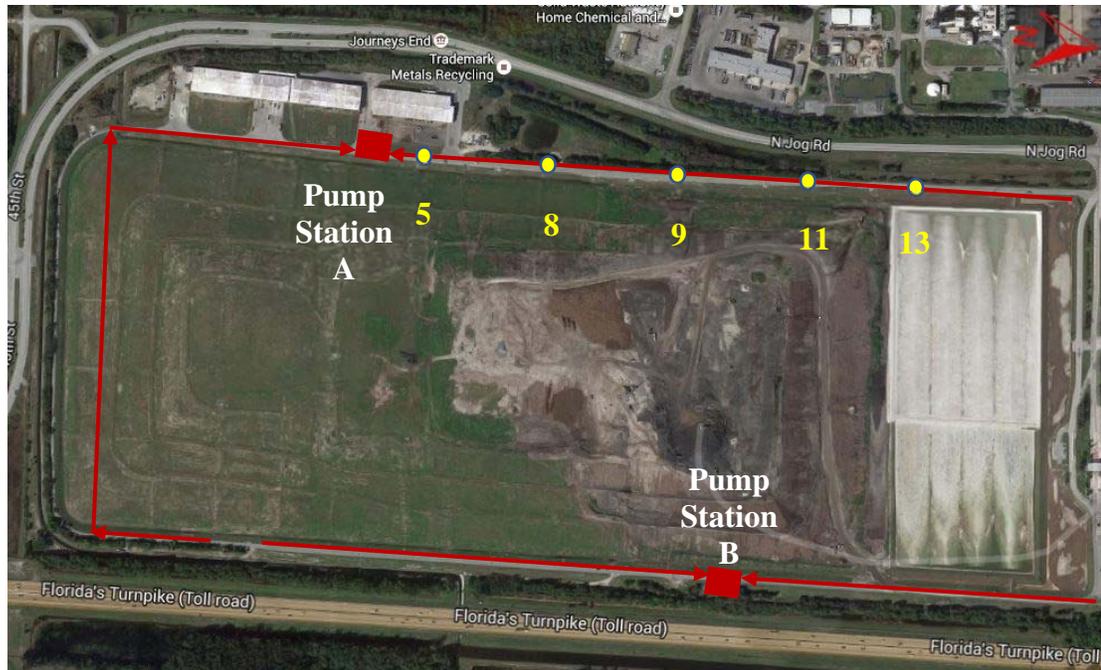


Figure 3: Schematic of gravity leachate collection line and pump station locations circa 2015. Yellow dots indicate manholes with the appropriate cell number, and the leachate flow is shown by the red arrow (Hinkley Center for Solid and Hazardous Waste Management, 2015).

2.2 RAW LEACHATE SAMPLE COLLECTION

Guidance for sample collection and preservation were obtained from:

- 1) Standard Methods 1060 Collection and Preservation of Samples (2017)
- 2) Handbook for Sampling and Sample Preservation of Water and Wastewater, USEPA, Environmental Monitoring and Support Laboratory, September 1982
- 3) Procedures for Collecting Wastewater Samples, USEPA, Region 4, Science and Ecosystem Support Division, Athens, Georgia, February 2017

All leachate samples were collected from the Solid Waste Authority (SWA) of Palm Beach County located in West Palm Beach, FL. Leachate generated in the landfills flows through drainage pipes to different manholes by gravity to one of the leachate pumping stations before it is sent to the deep injection wet well, where it is combined with other industrial wastewaters including cooling water and biosolids pelletizer wastewater. For this study, samples were collected from Manhole 9 and 11 and thus those corresponding cells containing MSW co-disposed with ash. The location of the manholes at Solid Waste Authority Landfills are shown in Figure 4.

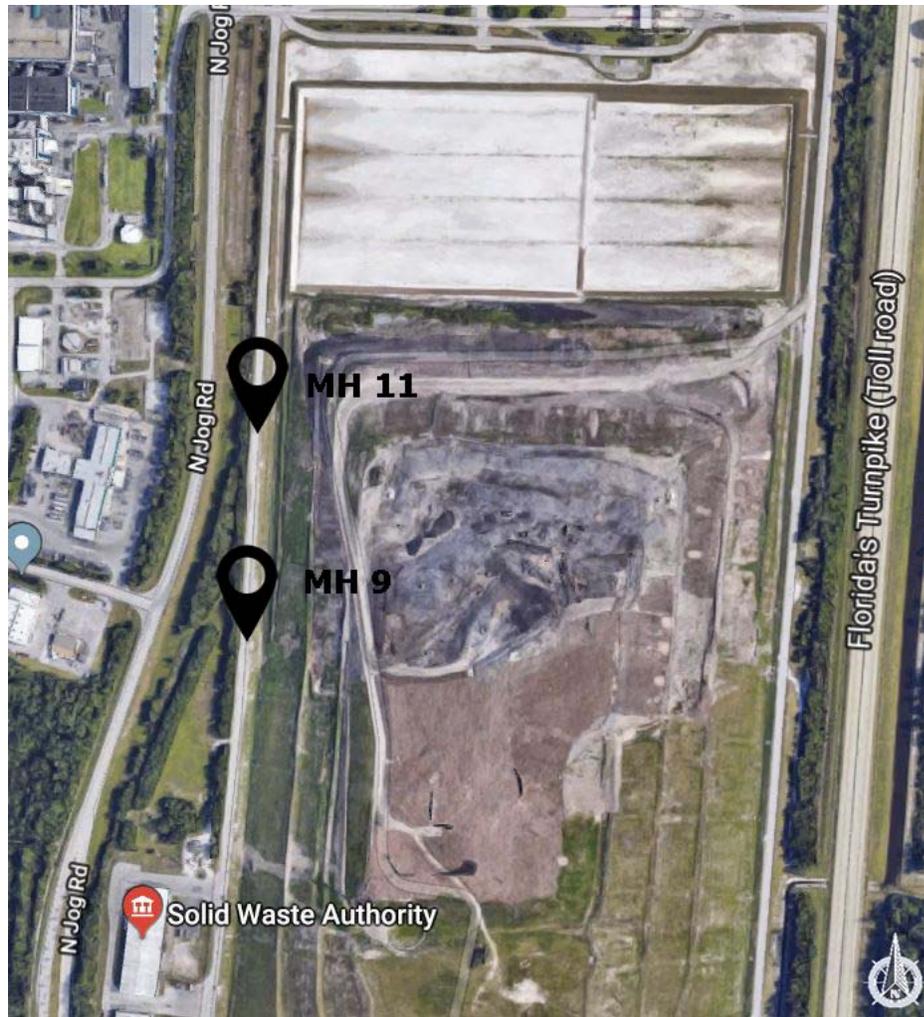


Figure 4: Sampling locations at SWA class I landfill

Samples from manholes were obtained using a clean 1-L plastic beaker tied with rope to collect liquid from the manhole, which was then transferred to a clean five-gallon plastic gasoline container with an airtight cap (Figure 5). The containers were then transported to the Lab.EES facilities in Boca Raton, FL and kept refrigerated at 4°C until needed.



Figure 5: (left) Fahim Salek collecting leachate samples from manhole 9 using a bucket tied with rope and (right) transferring to a plastic container

2.3 ANALYTICAL METHODS FOR PARAMETERS OF INTEREST

Temperature, pH, TDS, and conductivity were measured in the field during sample collection using a YSI Multiparameter System (MPS 556) that was calibrated daily per the manufacturer’s recommendations. The pH was also verified using a Hach portable pH meter (HQ40D). BOD, COD, ammonia, alkalinity, chloride, and turbidity samples were taken out at different time intervals using an appropriately sized pipette. Required dilution was conducted with double deionized water, as needed. Table 3 summarizes the different methods/devices used for measuring the parameters and their measuring limits.

Table 3: Summary of water quality analysis methods and calibration of instruments

Parameters	Method	Device	Calibration QA/QC	Method Detection Limit
pH	SM4500-H ⁺ B, Electrometric Method	YSI556 Multi-Parameter System (MPS) and Hach Portable pH Meter (HQ40D)	Calibrated with standard pH buffers of 4, 7, and 10	0-14 (± 0.01 pH)

Parameters	Method	Device	Calibration QA/QC	Method Detection Limit
Water Temperature	SM2550B	YSI556 Multi-Parameter System (MPS)	Manufacturer's calibration	1°C ± 0.1°C
Conductivity	SM2510B	YSI 556 Multi-parameter System (MPS)	Calibrated using 100 mS/cm standard solution	0.1 mS/cm ± 1%
BOD₅	Standard Methods 5210b, Dilution method	Hach Portable Meter (HQ40D) with LDO probe (LBOD101)	Using blank	Varies depending on dilution
COD	High Range Colorimetric Method	Hach DR5000 Spectrophotometer	Manufacturer's calibration	20-1500 mg/L O ₂ ± 5%
Ammonia	ASTM standard test method D1426-92, Nessler method	Hanna HI 96733C Ammonia High Range ICM	Calibrated using 25 mg/L Standard Solution	0.1 - 50 mg/L of NH ₄ ± 5%
Turbidity	Ratio turbidimetric determination using a primary nephelometric light scatter signal (90°) and transmitted light scatter signal	Hach 2100Q Turbidity meter	Calibrated using 10, 100 and 800 NTU and Validated Using 20 NTU	0.1 - 1000 NTU ± 10%
Chloride	Silver Nitrate Titration	Digital Titrator	Standard solution of 12.500 g/L Cl ⁻	2.5 to 150 g/L of Cl ⁻ ± 5%
Alkalinity	Hach Method 8203 (EPA approved, equivalent of SM2320 B)	Hach digital titrator (H ₂ SO ₄ titration method)	Manufacturer's calibration	10 - 4,000 mg/L as CaCO ₃ ± 5%

2.3.1 pH

The pH of the leachate samples was measured using SM4500-H⁺ B, Electrometric Method using a YSI556 Multi-Parameter System (MPS). The pH was also verified using Hach portable pH meter (HQ40D). The probes were calibrated using a three-point calibration before each experiment using VWR™ pH reference standard buffers (4, 7, and 10). Probes were immersed in the sample, and pH was recorded at definite time intervals during the experiments.

2.3.2 Water Temperature

The water temperature of samples was measured following SM2550B method, and readings were obtained from the display of the YSI556 Multi-Parameter System (MPS) and Hach portable pH meter (HQ40D). Like pH, the temperature was recorded at definite time intervals during the experiments.

2.3.3 Electrical Conductivity, Specific Conductance & TDS

The electrical conductivity (mS/cm) was measured following SM2510B method and was recorded at definite time intervals during the experiments using the YSI 556 MPS. The instrument was calibrated using a VWR™ 100 mS/cm standard solution. To obtain the TDS value from specific conductance, previous data suggest a constant of 1.54. Thus, the TDS is obtained by the following relationship:

$$TDS \left(\frac{g}{L} \right) = \frac{\text{Specific conductance} \left(\frac{mS}{cm} \right)}{1.54}$$

2.3.4 Biochemical Oxygen Demand

The 5-day biochemical oxygen demand (BOD₅) was measured following the Hach 8043 dilution method. Four 300 mL BOD bottles were prepared for the test. Due to the abundance of oxidizing bacteria in leachate (Zhang et al., 2011), no seed was used. The four bottles included: 1) Blank, 2) 0.5 mL sample, 3) 1 mL sample, and 4) 5 mL sample. For each dilution, the selected amount of sample was transferred to a 300 mL sterile BOD bottle using a 1 mL sterile pipette tip and then was filled with sterile dilution water containing the contents of one BOD nutrient buffer pillow pack. Using Intellical™ LBOD101 Luminescent Dissolved Oxygen (LDO) probe connected to a Hach HQ40D multimeter, the initial DO (mg/L) and the temperature (°C) was recorded. Closing the bottle with a glass stopper, the cap was wrapped with aluminum foil. Care was taken to avoid air bubbles remaining in the bottles prior to incubation for five days at 20°C in a dedicated BOD refrigerated incubator. On day 5, the DO of each sample (including the

blank) was recorded with the temperature. The unseeded BOD of the unseeded sample was calculated using the following expression

$$BOD_5 = \frac{DO_{t=0} - DO_{t=5}}{P}$$

Where P = volumetric fraction of sample used

2.3.5 Chemical Oxygen Demand

A Hach DR5000 Spectrophotometer was used to determine the chemical oxygen demand following USEPA approved high range reactor digestion method (Method 8000) that measures COD ranging between 20 to 1500 in mg/L of O₂. After homogenizing the sample by rigorous shaking, the sample was diluted (1:10) with double deionized water using a 10 mL volumetric flask. A 2 mL aliquot of the dilution was transferred to a Hach high range COD vial for digestion and colorimetric analysis. The purpose of the dilution is to lower the concentration within the detectable range while also mitigating the potential interference of chlorine at levels above 2000 mg/L (refer to Table 4). A blank was prepared by adding 2 mL of double deionized water to a Hach high range COD vial using a pipette. The vials were placed in a preheated DRB 200 reactor and kept for 120 minutes at 150°C. After 2 hours of digestion, the vials were inverted several times while they were warm and were placed in a vial stand for cooling down to room temperature in the dark.

For colorimetric determination, the 435 COD HR standard program was selected on the DR5000 Spectrophotometer display. At first, the blank was inserted into the 16 mm cell holder of the DR5000 spectrophotometer to zero the instrument. Then the sample vial was put into the instrument, and results were obtained in mg/L COD units from the display. By multiplying with the dilution factor, the final results were obtained.

The accuracy of the analysis was checked using either a 300 mg/L or 1000 mg/L Hach COD standard solution. After adding 2 mL of the standard solution into a vial, it was kept in DRB 200 digester for 2 hours, and the concentration was checked colorimetrically. The standard was checked before every full-set experiment, and the error was less than 4% each time (± 10 mg/L).

Chloride is the primary interference in this method. Each COD vials already contains mercuric sulfate to eliminate the effect of chloride present in the sample up to the level specified in Table 4. As the chloride concentration in the sample leachate was much higher than the specified limit (8-14 g/L), proper dilution (1:10) was done according to Table 4.

Table 4: Interference and Levels for COD Determination (USEPA Method 8000)

Vial Type Used	Maximum Cl⁻ concentration in sample (mg/L)	Suggested Cl⁻ concentration of diluted samples (mg/L)
Ultra-Low Range (0.7-40.0 mg/L)	2000	1000
Low Range (3-150 mg/L)	2000	1000
High Range (20-1500 mg/L)	2000	1000
High Range Plus (200-15,000 mg/L)	20,000	10,000

2.3.6 Ammonia

Ammonia was measured using a Hanna HI 96733c Ammonia High Range Ion Selective Meter following ASTM standard test method D1426-92, Nessler method. Initially, the instrument was calibrated using Hanna Cal Check™ Standards. At first, the Cal Check™ Standard HI 96733-11 Cuvette A was placed into the cuvette holder, and the instrument was zeroed. Then the Cal Check™ Standard HI 96733-11 Cuvette B was placed into the instrument, and the reading was recorded. The reading should be within the specification as reported in the Cal Check™ Standard Certificate which is 25±1 mg/L ammonium (NH₄⁺) at 25°C. If found otherwise, it was checked that the cuvettes are free of fingerprints, oil or dirt, and the validation was repeated. If results were still found out of specification, the instrument was recalibrated using the Cal Check Standard HI 96733-11 Cuvette A and B following the standard procedure mentioned in the instrument manual.

For measurement, the sample was diluted (1:10 or 1:100) with double deionized water to make the concentration detectable within the range, which is from 0.1 to 50.0 mg/L ammonium (NH₄⁺) at 25°C. For 1:100 dilution, using a calibrated pipette, 1 mL sample was transferred to a 100 mL volumetric flask and double deionized water was added up to the 100 mL mark. From the diluted sample, 1 mL was transferred to a 10 mL cuvette using a pipette and 9 mL of HI 93733B-0 ammonia reagent B was added using a pipette. The cuvette was placed into the cuvette holder of the instrument and zeroed. Then four drops of HI 93733B-0 ammonia reagent A were added to the solution, mixed gently, and the cuvette was placed again in the cuvette holder. After 3.5 minutes, the instrument directly displayed the concentration in mg/L of ammonium ion (NH₄⁺), and by multiplying with the dilution factor (100), the actual concentration of the sample was calculated.

2.3.7 Turbidity

Turbidity was measured using a Hach 2100Q Turbidity meter that uses the ratio of the primary nephelometric light scatter signal (90°) to the transmitted light scatter signal for turbidity determination. The instrument was initially calibrated using StablCal Turbidity Standard Calibration ampules of 10, 100 and 800 NTU. During calibration, the standard bottles were gently inverted, and the surface of the bottles was cleaned using a Kimwipe. After calibration, the accuracy was validated using a 20 NTU standard, which ranged between 19 to 21 NTU. For measurement, samples were transferred to a 10 mL cuvette, filled to the white mark, and then placed inside the cuvette chamber of the instrument with the lid closed. Turbidity measurements were directly recorded from the display.

2.3.8 Chloride

The initial chloride concentration was measured using the silver nitrate method. Chloride ions in the sample were titrated with silver nitrate solution in the presence of a chromate indicator (Hack Chloride 2 Indicator Powder Pillow). The sample size and the titration cartridge are chosen to correspond to the chloride (Cl^-) concentration expected using Table 5. For this analysis, 1 mL of sample was taken into a 250 mL Erlenmeyer flask using a volumetric pipette, and it was diluted to approximately 100 mL with double deionized water. Then the contents of one Hack Chloride 2 Indicator Powder Pillow were added to the solution. The sample was titrated using the 1.128 N silver nitrate (AgNO_3) titration cartridge (Table 5) until the color changed from yellow to orange-brown. The recorded reading of the digital titrator was multiplied by the appropriate multiplication factor, which is 50 in this case (Table 5) to get the actual concentration of chloride in mg/L as Cl^- of the sample.

Table 5: Sample Volume and Digit Multipliers for Chloride test

Range (mg/L as Cl^-)	Sample Volume	Titration Cartridge	Digit Multiplier
10-40	100	0.2256 N AgNO_3	0.1
25-100	40	0.2256 N AgNO_3	0.25
100-400	50	1.128 N AgNO_3	1.0
250-1,000	20	1.128 N AgNO_3	2.5
1,000-4,000	5	1.128 N AgNO_3	10.0
2,500-10,000	2	1.128 N AgNO_3	25.0
5,000-15,000	1	1.128 N AgNO_3	50.0

To validate the test procedure, reagents, apparatus, technique, and to find if there is any interference in the sample, the standard addition method (sample spike) was used. It was done by using Chloride Voluette Ampule Standard Solution of 12,500 mg/L Cl^- . At first,

the concentration of the sample was measured using the test procedure. Then using a volumetric pipette, 0.1 mL of standard solution was added to the sample. The spiked sample was titrated to the end point, and the number of digits on the counter was recorded. Again 0.1 mL of the standard solution was added, titrated to the end point, and the number of digits was recorded. The correct result for this titration should be 25 digits of the 1.128 N Silver Nitrate Titration Cartridge or 125 digits of the 0.2256 N Silver Nitrate Titration Cartridge for each 0.1 mL addition of the standard solution. In this study, 1.128 N Cartridge was used, and the digits ranged between 24 to 26, which is approximately 4% error.

Cyanide, bromide, and iodide interfere directly and are included in the results. Moreover, iron concentrations that are more than 10 mg/L prevent the color change at the end point. Again, highly buffered solution or extreme pH can prevent obtaining the correct endpoint and must be neutralized before analysis. The sample used in this study was in the neutral pH range (7.1~8.2), so there was no need to add any acid or base for neutralization.

2.3.9 Alkalinity

Alkalinity was measured following Standard Method 2320b titration method. First, 1 mL of raw sample was mixed with 99 mL of double deionized water making a dilution of 1:100. A Hach 1.600 N H₂SO₄ cartridge and digital titrator was used for the titration. The 100 mL diluted sample was transferred to a 250 mL Erlenmeyer flask. The content of one phenolphthalein indicator pouch was added to the sample. If no color change was observed, this indicated that no phenolphthalein alkalinity was present in the sample. If the color was pink, then the sample was titrated to a clear endpoint with the number of digits recorded as phenolphthalein alkalinity. Next the contents of a Bromocresol Green Methyl Red indicator pouch was added and titrated until the color turned from blue-green to light pink. The digits from the digital titrator were recorded as Bromocresol Green Methyl Red alkalinity. The total alkalinity was obtained by adding the digits from the phenolphthalein alkalinity and the Bromocresol Green Methyl Red alkalinity, multiplied by the dilution factor (100) and the digit multiplier (1) to obtain the total alkalinity in mg/L as CaCO₃ (Table 6).

Table 6: Sample Volume and Digit Multipliers for Total Alkalinity

Range (mg/L as CaCO ₃)	Sample Volume (mL)	Titration Cartridge	Digit Multiplier
10-40	100	0.1600 N H ₂ SO ₄	0.1
40-160	25	0.1600 N H ₂ SO ₄	0.4
100-400	100	1.600 N H₂SO₄	1
200-800	50	1.600 N H ₂ SO ₄	2
500-2000	20	1.600 N H ₂ SO ₄	5
1000-4000	10	1.600 N H ₂ SO ₄	10

2.4 REACTOR DEVELOPMENT

2.4.1 Laboratory Scale Electrochemical Oxidation Reactors

Experiments on electrochemical oxidation were conducted using two different laboratory scale reactors:

- 1) Roughing electrochemical oxidation reactor provided by OriginClear (Figure 6)

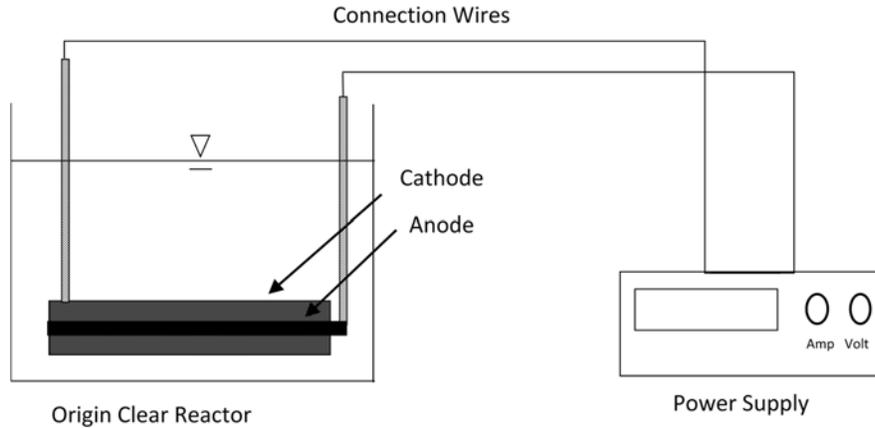


Figure 6: Schematic drawing of the roughing electrochemical oxidation reactor

- 2) Magneli reactor, provided by Magneli Materials (Figure 7)

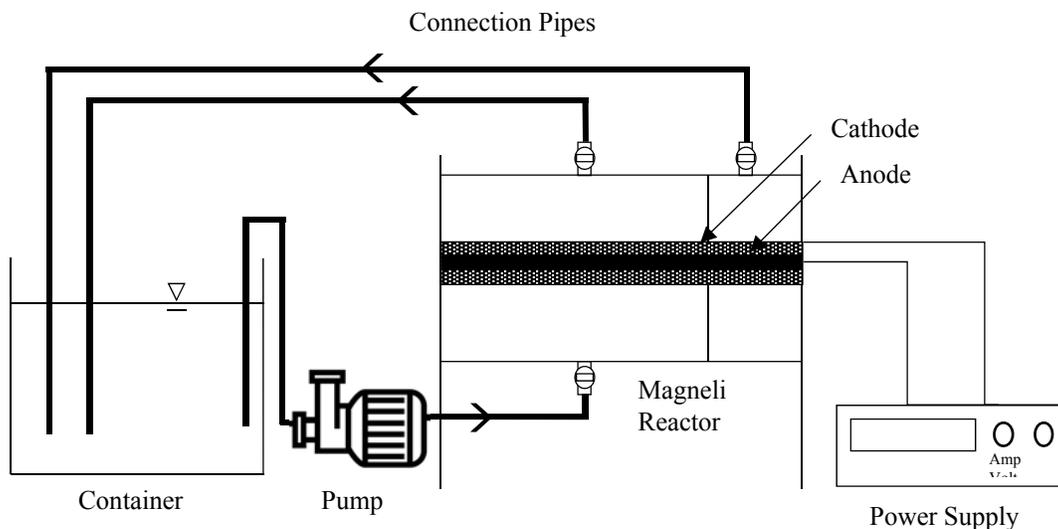


Figure 7: Schematic drawing of the Magneli reactor

For the roughing electrochemical reactor, a total of three multi-metal oxide (titanium oxide coated with iridium and ruthenium oxide) tubular anodes (Figure 8) having a total surface area of 470 cm², as measured by slide caliper, are placed inside a mesh-like cathode made of titanium.



Figure 8: MMO Anode for Roughing Unit

The required electricity is provided from a DC regulated power supply (TekPower TP1540E) with variable controls for both the current (0-40 amps) and voltage (0-15 V) outputs. The output current and voltage values can be monitored from the display of the unit. Again, the output current and voltage at the anode and the cathode were measured

manually using a multimeter (Fluke 115 RMS) to check the accuracy of the unit. The total system is placed in a Plexiglass container.

The Magneli reactor (refer to Figure 7) is a closed unit, the anode and the cathode are placed inside the chamber. The anode (Figure 9) is made of a mixture of titanium suboxide having a general formula of Ti_nO_{2n-1} ($n = 4-10$), but has a substantially higher amount of Ti_4O_7 (more than 80%) compared to the OriginClear anode. This provides higher electrical conductivity and greater chemical stability. Moreover, the 3-dimensional ceramic material provides greater surface area than traditional anodes and supports high current density operations. The cathode was made of steel. Both the electrodes were circular in geometry. The anode is placed inside the cathode and has a reported surface area of 400 cm^2 (Personal communication with Robert Sterner, manufacturer representative for Magneli Materials).



Figure 9: Anode used for the Magneli reactor

The electrodes are connected to a DC regulated power supply (TekPower TP1540E) with variable controls for both the current (0-40 amps) and voltage (0-15 V) outputs for electricity. The sample is recirculated through a piping system by a 1 gpm peristaltic pump.

2.4.2 Laboratory Scale Ozone Pretreatment Reactor Unit

The ozone unit (Figure 10) comprises of an ozone generator (OZOMAX OZO-2VTTL), custom PVC column reactor, and a mechanical mixer.

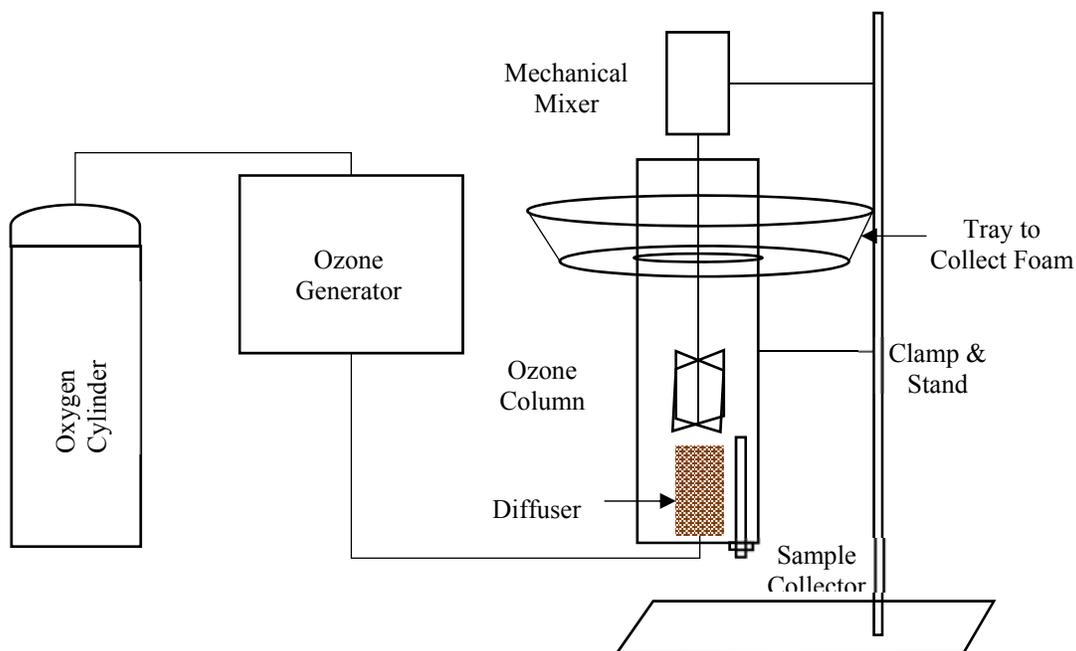


Figure 10: Schematic drawing of the ozone unit

The reactor has a height of 2 ft and an internal diameter of 4 inches (Figure 11). Ozone was produced from pure and dry oxygen by corona discharge using the ozone generator. When using dry oxygen feed, the ozone generator is capable of producing up to 20 g O_3/h . The ozone was continuously introduced into the column through a ceramic diffuser placed at the bottom. A helix mechanical mixer ensures proper mixing of ozone with the leachate by breaking down the bubbles. At different time intervals, samples were collected from the bottom of the column that contained a stopcock, which was opened to allow the sample to flow by gravity into a collection beaker (50 mL). A plate was placed at a certain height of the column to collect any foam produced during the experiment.



Figure 11: Lab-scale Ozone Reactor

2.4.3 Laboratory Scale Fenton's Reagent Pretreatment Reactor Unit

Preliminary jar tests were conducted in 1-liter glass beakers to determine the proper dose range of Fenton's Reagents. A magnetic stirrer was used for mixing. Using the appropriate dose range obtained from jar testing, final experiments were conducted in a 2-gallon plastic bucket (Figure 12). A mechanical rotator with plastic helix mixer was used to achieve complete mixing. This mechanical rotator has variable speed. A pH probe was placed into the sample for monitoring the pH during the process.



Figure 12: Experimental set up for Fenton oxidation

2.4.4 Laboratory Scale Lime Pretreatment Reactor Unit

Lime coagulation was tested as a pretreatment for electrochemical oxidation. For this purpose, lime in the form of quicklime was obtained from the Glades Road Boca Raton Water Treatment Plant and was crushed with a mortar and pestle, and then oven dried at 150°C overnight and brought to room temperature in a dessicator. A measured amount of 4.5-L of the sample was placed in a plastic 2-gallon bucket, and lime was added (98 grams) until the pH reached 12. The sample was mixed rigorously for 5 minutes and then gently for the next 30 minutes to induce coagulation. Then it was kept at quiescent conditions for at least 1 hour. After lime coagulation, the supernatant was transferred to another beaker, and the pH was adjusted to 10 using 50% H₂SO₄.

2.5 EXPERIMENTAL DESIGN AND PROCEDURE

A three-level full factorial design was introduced using Design Expert 11.0 software. The three significant process variables considered in this study were as follows: a) pretreatment (ozone, dual stage EOx, and Fenton), b) current density, and c) treatment time. The process was evaluated based on COD, ammonium-N, and turbidity removal

efficiency. Preliminary experiments were conducted to better understand the factors that affect the electrochemical oxidation. The process variables and levels are presented in

Table 7. For three-level full factorial design, a total number of 27 experiments are required, plus two additional replicates of the center point.

Table 7: Independent Variables of the Three Level Factorial Design

Level	Pretreatment	Current Density	Treatment Duration
-1	Ozone	25 mA/cm ²	30 minutes
0	Roughing EOx	50 mA/cm ²	60 minutes
+1	Fenton	75 mA/cm ²	90 minutes

For this study, the three data points of treatment duration (30, 60 and 90 minutes) for each variable were taken from a single experiment. As a result, the total number of experiments required for the analysis was reduced to 9, plus two additional replicates of the center point for a total of 11 experiments. The experiment procedure is discussed in the following sections.

2.5.1 Preliminary Experiment

To better understand the reaction conditions and factors that affect electrochemical oxidation before applying the process to real leachate, a simulated leachate sample was prepared to mimic COD and chloride of real leachate. Simulated leachate was prepared by adding 5.1 g potassium hydrogen phthalate (KHP) primary standard, (99.95-100.05%) to 4 liters of double deionized water, which was mixed thoroughly using a stirrer (Figure 13). NaHCO₃ (Arm and Hammer pure baking soda) was added to buffer the solution, and three different amounts of NaCl were added to increase the conductivity and to observe the effect of chloride ion on the process.



Figure 13: Artificial leachate preparation using KHP

The simulated leachate was tested by two-stage electrochemical oxidation where a roughing electrochemical oxidation reactor was used as pretreatment before the Magneli reactor. In both cases, the sample was treated for 60 minutes for a total reaction time of 120 minutes. A YSI 550 multiparameter probe was immersed in the sample to monitor water quality parameters including pH, water temperature, conductivity, and TDS every 15 minutes. Samples were collected from the reactor every 15 minutes to measure COD.

2.5.2 Ozone as Pretreatment

In July 2018, three different experiments were carried out where ozone was coupled with electrochemical oxidation as a pretreatment. In each case, the dose and the conditions remained the same for ozonation, but three different amperage levels (10 amps, 20 amps, and 30 amps) were used for the electrochemical oxidation. The ozonation experiments were carried out in the ozone experimental setup explained previously (2.4.2). For every experiment, the reactor was filled with 3.5 liters of leachate and was allowed to react with ozone for 45 min. Effluent samples were taken at 0, 10, 25, and 45 minutes during the reaction from the bottom of the column for measuring pH, COD, ammonium-N, turbidity. All experiments were carried out at room temperature ($22 \pm 2^\circ\text{C}$)

After ozonation pretreatment, electrochemical oxidation was performed using the electrolytic flow reactor, manufactured by Magneli Materials Incorporation, described in section 2.4.1. All experiments were carried out in batch mode and under constant amperage condition. In each run, the effluent of the ozone reactor was batch loaded in a 2-liter glass beaker and continuously recirculated in the cell using a peristaltic pump at a flow rate of 4 L/min. A YSI multiparameter probe was immersed in the sample to continuously monitor pH, temperature, conductivity, and TDS. Samples were taken at 30, 60, and 90 minutes to measure the change in COD, ammonium-N, and turbidity.

2.5.3 Fenton as Pretreatment

In April-May 2019, experiments were carried out to study Fenton as a pretreatment of electrochemical oxidation. In each case, the dose and the conditions remained the same for Fenton, but three different amperages (10 amps, 20 amps, and 30 amps) were used for the electrochemical oxidation. Preliminary experiments were conducted to optimize the reagent dosage (2.4.3). Other treatment conditions like initial pH, treatment duration, pH adjustment after treatment were set by literature review. On April 23, 2019, five different sets of experiments were conducted to find the appropriate ratio of Fenton reagent (Figure 14).



Figure 14: Experiments for optimization of iron and hydrogen peroxide molar ratio

The experiment was conducted using a 500 mL sample for each set. Keeping the amount of H_2O_2 constant (6 g/L), five different molar $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratios (1, 2, 5, 10, 20) were tested. The amount of reagents used in five sets are summarized in Table 8.

Table 8: Fenton Reagent Dose with Different Molar Ratio of Iron (II) and H_2O_2

$\text{Fe}^{2+} : \text{H}_2\text{O}_2$ (molar)	Amount of Dried FeSO_4 used in 0.5 L Sample (gm)	Amount of 30% H_2O_2 used in 0.5 L Sample (gm)	Dose of Fe^{2+} (g/L)	Dose of H_2O_2 (g/L)
1:1	13.4	10.0	9.85	6.0
1:2	6.70	10.0	4.93	6.0
1:5	2.68	10.0	1.97	6.0
1:10	1.34	10.0	0.99	6.0
1:20	0.67	10.0	0.49	6.0

Initially, the pH of the sample was adjusted to 2.5, using 50% (v/v) H_2SO_4 . Then the required amount of dried ferrous sulfate and 30% hydrogen peroxide were added in a single step. The samples were mixed rigorously at 500 rpm using a magnetic stirrer for 3

hours. Then the pH was increased to 8.0 using laboratory grade NaOH and kept for settling overnight. After 8 hours, the supernatant was decanted to another beaker without disturbing the precipitate. For COD and ammonium-N measurement, the samples were filtered using a 0.5 μm syringe filter (nylon) (Figure 15). Based on COD, ammonium-N removal, the most favorable condition observed was 1:5 molar ratio of the reagents.



Figure 15: Filtering using 0.5 μm nylon syringe filter for COD and ammonium-N analysis

Subsequently, another experiment was conducted keeping the molar ratio 1:5, but this time with an increasing amount of reagents. Four sets were prepared each having 500 mL of sample. The steps were followed exactly like the previous experiment which includes: pH adjustment with 50% (v/v) H_2SO_4 , addition of dried ferrous sulfate and 30% hydrogen peroxide, mixing for 3 hours and settling for 8 hours. After 8 hours, samples were collected for COD, ammonium-N, and turbidity measurement. The dosing details are summarized in Table 9.

Table 9: Fenton oxidation with increasing dose of iron (II) sulfate and H₂O₂ keeping constant molar ratio

Fe ²⁺ : H ₂ O ₂ (molar)	Amount of Dried FeSO ₄ used in 0.5 L (gm)	Amount of 30% H ₂ O ₂ used in 0.5 L (gm)	Dose of Fe ²⁺ (g/L)	Dose of H ₂ O ₂ (g/L)
1:5	1.12	4.17	0.82	2.5
1:5	2.23	8.33	1.64	5.0
1:5	3.35	12.50	2.46	7.5
1:5	4.47	16.67	3.28	10.0

By doing these two experiments, the most favorable conditions were achieved with a 1:5 molar ratio, and the removal efficiency increased with an increasing amount of reagents. However, a higher amount of turbidity was observed at a higher dosage of reagents without a concurrent increase in the removal of COD (only 8% increase) observed. Therefore, it was decided to use the least amount of reagent keeping the molar ratio 1:5.

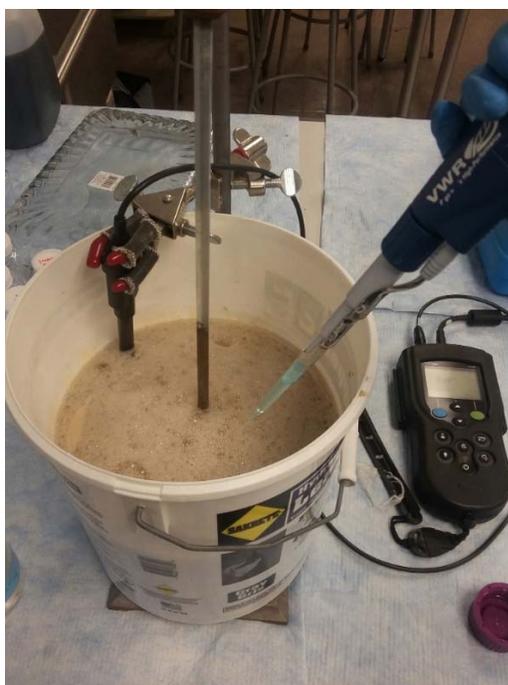


Figure 16: Adding reagents to the sample using digital pipette

On May 2-4, 2019, three different tests were performed using 5 liters of sample maintaining the same dosage of Fenton reagents and adjusting to same initial pH but coupling with electrochemical oxidation at three different amperages (10, 20 and 30 amps). Initially, the pH of the sample was adjusted to <2.5, using 50% H₂SO₄ (Figure 16). Then 11.17 grams of dried iron (II) sulfate and 41.67 grams of 30% H₂O₂ was added

in a single step. Then the solution was mixed with the leachate using a helix paint mixer. After 3 hours, the mixing was stopped, and the pH was increased to 8.05, adding laboratory grade NaOH. The solution was kept at quiescent conditions for 8 hours for settling. After 8 hours, the supernatant was decanted to another beaker, and electrochemical oxidation was carried out. The procedure is just as described in section 2.5.2.

2.5.4 Electrochemical Oxidation as Pretreatment

In March 2019, roughing electrochemical oxidation was tested as a pretreatment of the Magneli electrochemical oxidation reactor to tackle the initial organic load. For this, four liters of sample was taken to a Plexiglass container and was treated for 60 minutes at 20 amps. Samples were taken out every 20 minutes for measuring COD, ammonium-N, and turbidity. The pH, TDS, temperature, and conductivity were also recorded at these points using a YSI multiparameter probe (Figure 17).

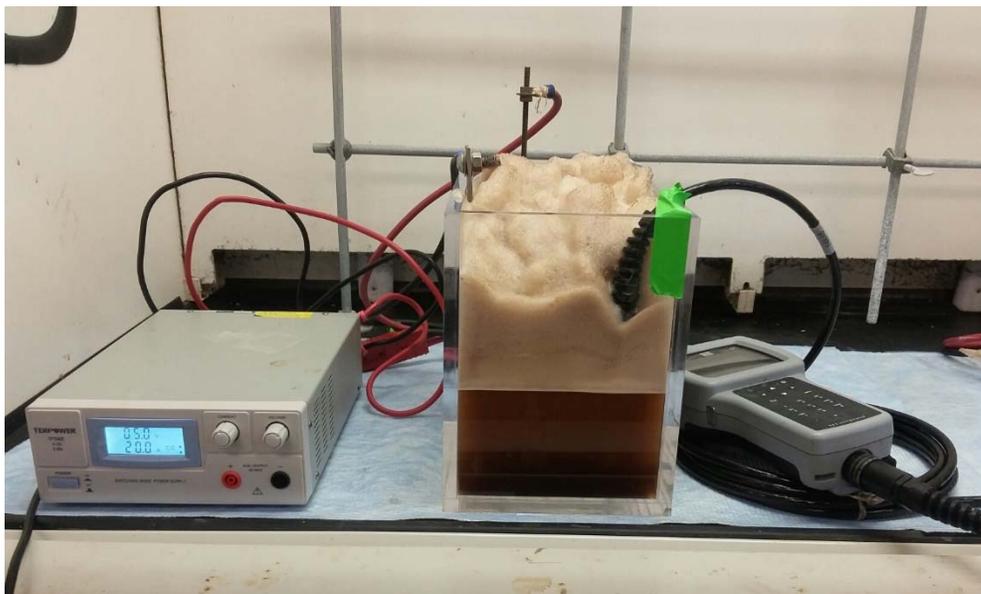


Figure 17: Experiment with the roughing electrochemical oxidation reactor

After 60 minutes, the sample was transferred to another beaker, and electrochemical oxidation was conducted for 90 minutes using the Magneli Reactor. On March 18, 20 and 22 of 2019, three separate experiments were conducted where the pretreatment condition was the same for all sets, but three different amperages were used for the Magneli reactor. The test procedure is the same as described in section 2.5.2.

On May 9, 2019, another experiment was conducted with similar conditions but for extended reaction times. Four liters of sample was initially pretreated by the roughing electrochemical oxidation reactor for 90 minutes; then it was treated by the Magneli electrochemical oxidation reactor for 7 hours. The recirculating reservoir that contains the leachate was immersed in an ice bath to keep the temperature below 40°C. Samples were collected every 30 minutes for COD, ammonium-N, and turbidity measurement.

2.5.5 Lime Coagulation as Pretreatment

On June 2, 2019, lime coagulation was tested as a pretreatment of the electrochemical oxidation. For this purpose, lime in the form of quicklime was obtained from Boca Water Treatment Plant and was crushed with a mortar and pestle, and then oven dried at 150°C. Four and a half liters of the sample was placed in a plastic 2-gallon bucket, and lime was added (98 grams) until the pH reached 12. The sample was mixed rigorously for 5 minutes and then gently for the next 30 minutes to induce coagulation. Then it was kept at quiescent conditions for at least 1 hour. After lime coagulation, the supernatant was transferred to another beaker, and the pH was decreased to 10 using 50% H₂SO₄. Then the leachate was treated by the Magneli electrochemical oxidation reactor for 90 minutes. For ammonium-N measurement, if the sample's pH was above 9.5, it was brought down to 7 using 50% H₂SO₄. Other steps are the same as the previous experiment and are described in section 2.5.2.

2.5.6 Halogenated Byproduct Determination

Samples collected after different combinations of treatment were delivered to a certified laboratory (Florida Spectrum Laboratories) for determination of halogenated byproducts (e.g. TTHMs and HAA5). The samples included were: 1) raw leachate, 2) raw leachate spiked with 100 µg/L chloroform (HPLC grade, 99.9%) and 100 µg/L monoacetic acid (from a 10 mg/L stock solution created from dry stock), 3) Fenton coupled with electrochemical oxidation (30 amps), 4) Fenton coupled with electrochemical oxidation (10 amps), 5) ozone coupled with electrochemical oxidation (20 amps), 6) lime treatment coupled with electrochemical oxidation (20 amps), 7) extended reaction time (7 hours) electrochemical oxidation (20 amps), 8) roughing electrochemical oxidation (20 amps), and 9) two-stage electrochemical oxidation (20 amps).

For QA/QC, a raw leachate sample was spiked with 100 µg/L chloroform and 100 µg/L of monoacetic acid. Both of them were diluted by serial dilution, and chloroform was dissolved in ethyl alcohol to obtain the desired concentration. For the TTHM test, samples were preserved with ascorbic acid in a 40 mL vial. Two drops of 50% hydrochloric acid were added to make the pH less than 2. For the HAA5 test, samples were transferred to a 250 mL amber bottle with the preservative ammonium chloride.

Raw leachate was filtered through 0.45 μm glass microfiber filter using a vacuum pump. All the prepared vials and bottles were kept at 4°C until delivered to the laboratory.

2.6 STATISTICAL ANALYSIS METHOD

To compare the data obtained, a three-level factorial design was introduced, and the treatment performance was analyzed by Response Surface Methodology (RSM). Factorial designs of experiments are widely accepted as the most commonly used experimental design method in manufacturing companies to study the effect of process parameters and their interactions on outcomes (Antony, 2014). It can be either full or fractional factorial design. The full factorial design is useful in the early stage of experimental design and feasible where the number of process parameters or factors is less than or equal to 4 (Antony, 2014). On the other hand, the fractional design is suggested when a limited number of experiments can be conducted due to the limitation of time and resources.

In a fractional factorial design, all the possible combinations of the levels of the factors are not required to analyze. The experimental design points are the vertices of a hypercube in the n-dimensional design space defined by the minimum and the maximum values of each of the factors (Sahoo & Barman, 2012). These points are also called factorial points. In this study, a customized and modified factorial design has been chosen to handle the complexity of the mixture of numerical and categorical variables in the same analysis. For three factors having three levels of each factor, considering customized factorial design, a total of 18 experiments have to be carried out including two replicates, required for determining a sum of squares due to error if all possible interactions are included in the analysis.

This method allows the development of mathematical equations where each response (Y) was estimated as a function of the factors and computed as the sum of a constant, linear, quadratic effects, and interaction effect according to Eq. (1). As there are only three levels for each factor, the most appropriate analysis is a quadratic relation.

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_i \sum_{<j=2}^k \beta_{ij} X_i X_j + e_i \dots\dots\dots (1)$$

where Y is the response, X_i and X_j are variables, β₀ is a constant coefficient, β_j, β_{jj}, and β_{ij} are interaction coefficients of linear, quadratic and the second order terms, respectively, k is the number of studied factors and e_i is the error.

The results for all responses are then analyzed by analysis of variance (ANOVA) to estimate the goodness of fit. A p-value of less than 0.05 was considered statistically significant. The lack of fit (LOF), F-test shows the variation of the data around the

adapted analysis, and if the analysis fits the data well, the LOF will be insignificant ($p > 0.05$). The steps followed for the analysis are demonstrated in Figure 18.

The figure consists of four screenshots from the Design Expert 11.0 software interface, illustrating the steps for setting up an Optimal (Custom) Design.

Top Left Screenshot: Shows the 'Optimal (Custom) Design' setup screen. It includes a table of factors and their levels.

Name	Units	Type	Levels	L[1]	L[2]	L[3]
A [Numeric]	Current Dens mA/cm2	Discrete	3	25	50	75
B [Numeric]	Duration min	Discrete	3	30	60	90
C [Categorical]	Pretreatment	Nominal	3	EOx	Ozone	Fenton

Top Right Screenshot: Shows the search criteria for the 'Optimal (Custom) Design'. The search is set to 'Best' with 'Optimality' set to 'I'. The 'Runs' section shows 12 required model points, 0 additional model points, 3 lack-of-fit points, 3 replicate points, and 0 additional center points, for a total of 18 runs.

Bottom Left Screenshot: Shows the 'Responses' section of the 'Optimal (Custom) Design' setup. Three responses are listed: COD % Removal, Ammonium-N % Removal, and Turbidity % Removal.

Bottom Right Screenshot: Shows the 'Design (Actual)' table, which is a table of 18 runs with columns for factors and responses.

Run	Factor 1 A:Current Density mA/cm2	Factor 2 B:Duration min	Factor 3 C:Pretreatment	Response 1 COD % Removal	Response 2 Ammonium-N % Removal	Response 3 Turbidity % Removal
1	25	30	EOx	15.01	14.34	69.77
2	50	60	EOx	21.55	28.07	81.28
3	25	90	EOx	19.17	30.07	83.12
4	75	60	Fenton	39.01	23.81	56.4
5	25	30	Fenton	26.67	5.82	17.39
6	75	30	EOx	18.4	22.61	77.9
7	75	90	EOx	37.12	47.7	96.17
8	25	30	Ozone	19.56	17.31	92.2
9	50	90	Ozone	43.22	43.14	98.9
10	50	30	Ozone	22.35	23.53	93.5
11	25	60	Ozone	28.32	26.54	95.3
12	75	60	Fenton	36.01	23.81	58.4
13	75	60	Ozone	42.34	42.23	99.68
14	50	30	Fenton	32.81	12.24	19.12
15	50	30	EOx	18.25	20.35	70.34
16	50	60	EOx	18.9	27.48	81.34
17	25	90	Fenton	37.3	19.41	28.26
18	50	60	EOx	21.83	29.9	86.71

Figure 18: Steps for statistical analysis in Design Expert 11.0

3 RESULTS AND DISCUSSION

This chapter discusses the experimental results obtained from preliminary testing and experiments conducted using the laboratory scale reactors over the study period. Raw data of the tests are included in Appendix 1 for reference. In the preliminary stage, a laboratory prepared artificial leachate sample was tested to observe the treatment performance and the factors affecting the electrochemical oxidation (EOx). Then for the first set of experiments, leachate was treated by two-stage electrochemical oxidation comprised of two successive electrochemical oxidation units: 1) OriginClear “roughing” reactor and 2) Magneli reactor. In the second set of experiments, the roughing reactor pretreatment was replaced by ozone oxidation, and in the third set, Fenton coagulation was used as a pretreatment of electrochemical oxidation. Additionally, lime coagulation was also tested as a pretreatment of EOx. The samples after different treatment combinations were further analyzed for chlorinated byproducts like TTHM and HAA5. In the last section, a preliminary cost estimate for each treatment scheme is presented.

3.1 LEACHATE CHARACTERISTICS

Characteristics of leachate vary depending on the type and moisture content of the waste, composition of waste, age of landfill, amount of rainfall, seasonal weather conditions and degree of decomposition (Abbas, Jingsong, Ping, Ya, & Al-Rekabi, 2009; Chu, Cheung, & Wong, 1994; Fatta, Papadopoulos, & Loizidou, 1999; Han et al., 2016; Panizza & Martinez-Huitle, 2013; Shehzad, Bashir, Sethupathi, & Lim, 2015). Table 10 summarizes the general characteristics of the leachate sample collected from manholes 9 and 11 from the SWA facility for this study.

Table 10: Leachate Characteristics

Parameters	Concentration Range
pH	7.2 – 8.1
COD	5,500 – 10,000 mg/L O ₂
Ammonium-N	2200 – 3200 mg/L
BOD ₅	500 – 700 mg/L O ₂
Turbidity	230 – 1000+ NTU
Conductivity	30 – 80 mS/cm
TDS	23 – 54 g/L
Field Water Temperature	29 – 40°C
Chloride	8 – 14 g/L

These manholes receive leachate from cells 9,11 and 13, which is representative of waste placed up to 12 years ago at the latest. Based on the age of the landfill, leachate can be classified in three categories: a) young (<5 years), b) intermediate (5-10 years), and c) mature (>10 years) (Ahmed & Lan, 2012; Hassan, Zhao, & Xie, 2016). According to this classification, the sample used in this study generally falls into the category of intermediate age. The high amount of COD (5,500-10,000 mg/L O₂) and low BOD₅/COD ratio (<0.1~0.15), falls within the intermediate range (4,000-10,000 mg/L COD and COD/BOD₅ of 0.1~0.5) (Peng, 2017; Zhou et al., 2010), which is expected since the waste that generated the leachate is a mixture from up to 12 years old. Again, the low BOD₅/COD ratio also indicates the presence of recalcitrant organics. During the initial phase of a landfill, an important amount of the readily biodegradable compounds break down, and the BOD₅/COD ratio rapidly decreases over time (Mandal et al., 2017). The leachate collected at this age shows substantial amounts of bio-refractory organics, which cannot be treated by biological processes (Calace, Liberatori, Petronio, & Pietroletti, 2001).

3.2 PRELIMINARY TESTING WITH ARTIFICIAL LEACHATE

The COD removal at different chloride levels is shown in Figure 19.

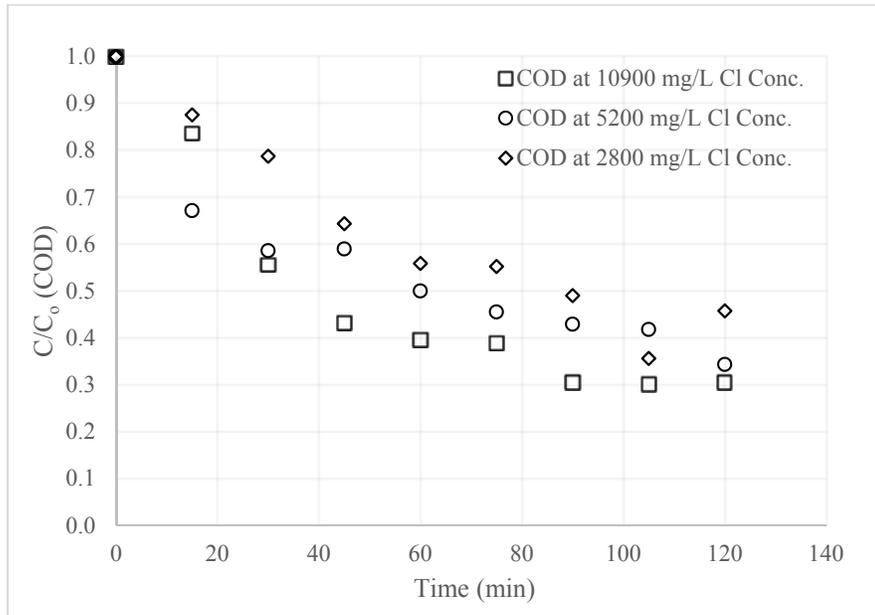


Figure 19: COD removal at different chloride ion concentrations

It is evident from Figure 19 that chloride ion has a positive effect on electrochemical oxidation. For each concentration (2800, 5200, 10900 mg/L Cl⁻ concentration), the COD removal efficiency increased with time, and the maximum removal was observed at

10900 mg/L Cl⁻ concentration. Figure 20 shows the relationship of chloride ion with specific conductance.

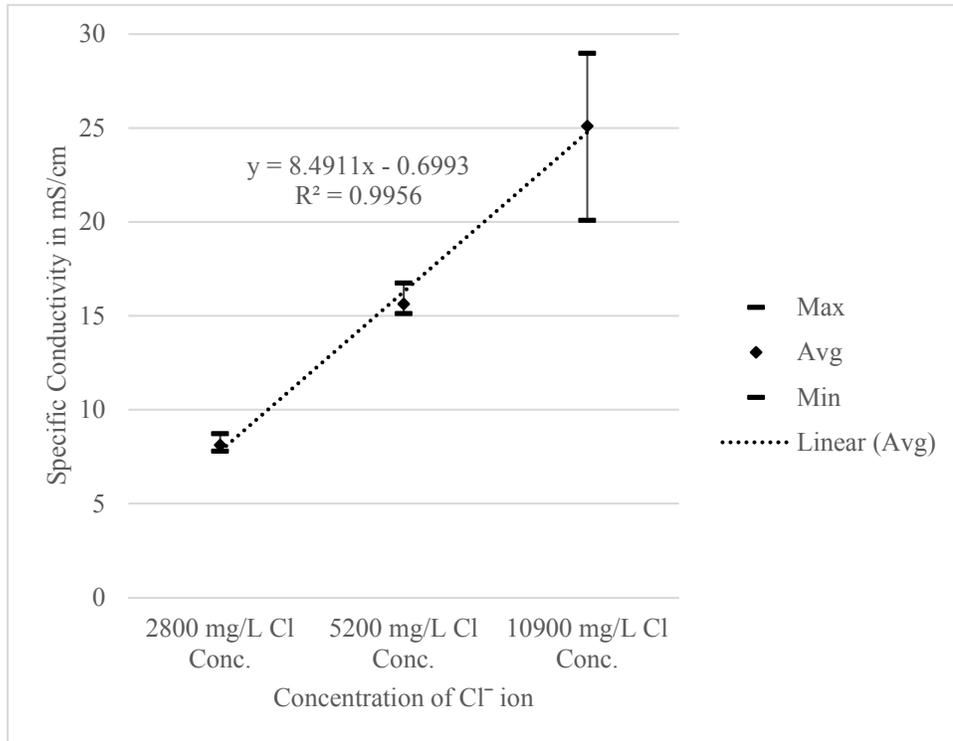


Figure 20: Effect of chloride ion concentration on specific conductivity

The solution that has more free ions can conduct electricity more easily because of the charge. In this experiment, the specific conductance changed over time with average values of 8.1, 15.6, and 25.1 mS/cm for 2800, 5200, 10900 mg/L Cl⁻ concentration, which depicts the positive relationship between chloride ion concentration and specific conductance. This higher specific conductance favors the electrochemical oxidation process, and less amperage is then required to maintain the same voltage where the chloride ion concentration was high (10,900 mg/L Cl⁻). Details of this data are presented in Appendix 1.

3.3 OZONE AS PRETREATMENT

Figure 21 shows the effect of current density (25, 50, and 75 mA/cm²) on COD removal efficiency when ozone was used as a pretreatment. After 90 minutes of electrochemical oxidation, a maximum 52% COD removal was achieved with 75 mA/cm² current density. Figure 22 and Figure 23 illustrate the ammonium-N and turbidity removal over time. Ammonium-N removal was higher, with 75 mA/cm² (52%). However, more than 80% of turbidity was removed by the ozonation initially, and it became clearer by electrochemical oxidation up to a maximum 99% removal.

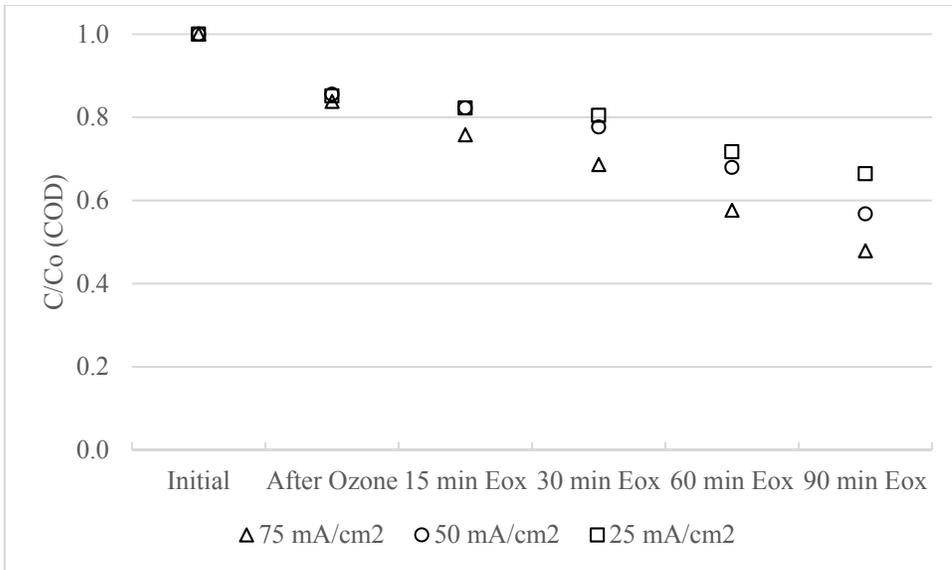


Figure 21: COD removal by electrochemical oxidation coupled with ozone

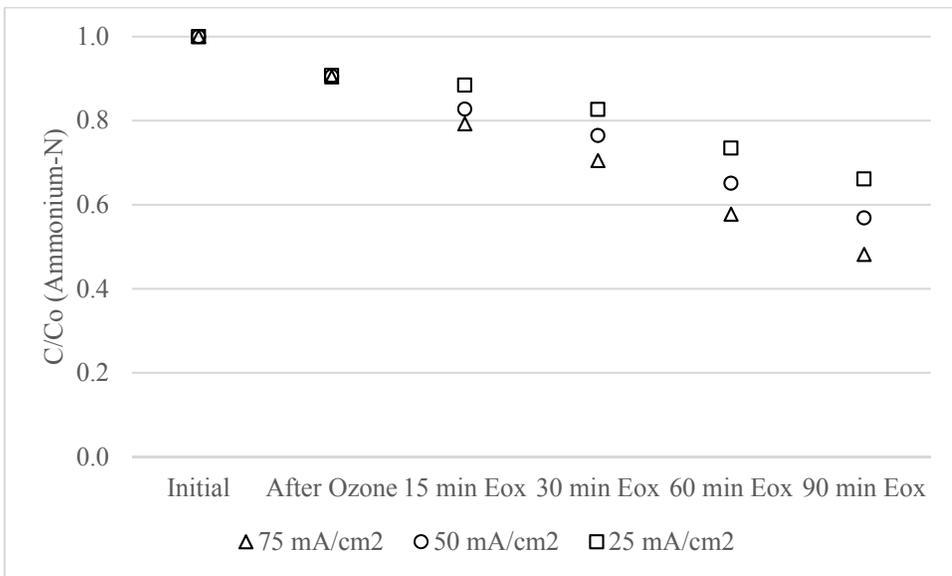


Figure 22: Ammonium-N removal by electrochemical oxidation coupled with ozone

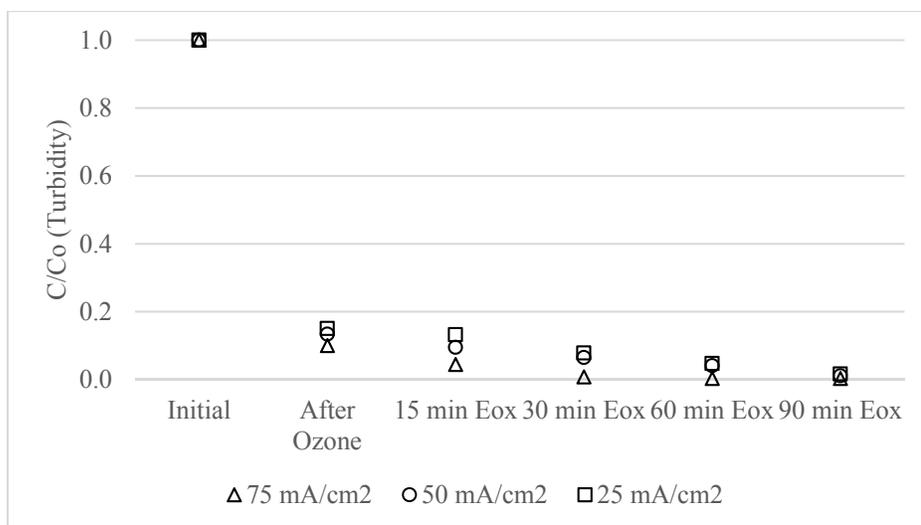


Figure 23: Turbidity removal by electrochemical oxidation coupled with ozone

3.4 FENTON'S REAGENT PRETREATMENT

In order to investigate the optimum molar ratio of $H_2O_2/Fe(II)$, five different molar ratios (1:1, 1:2, 1:5, 1:10, 1:20) were tested maintaining a constant amount of H_2O_2 of 6000 mg/L based on the initial COD value (5800 mg/L O_2) (Trujillo, Font, & Sánchez, 2006). The COD and ammonia-N removal efficiency increased with the increase of $H_2O_2/Fe(II)$ molar ratio until it reaches the peak at 1:5 molar ratio (Figure 24). Further increase in $H_2O_2/Fe(II)$ molar ratio decreased the removal efficiency. This may be because the Fenton reaction rate follows second order when the molar ratio is low, but when the $H_2O_2/Fe(II)$ molar ratio is high, other scavenging side reactions occur, and the reaction becomes zero-order becoming independent of hydrogen peroxide (Lopez, Pagano, Volpe, & Di Pinto, 2004; H. Zhang et al., 2005). Moreover, sludge settling becomes difficult at lower molar ratios, so a molar ratio of 1:5 was used for subsequent experiments. This ratio is consistent with previous studies where researchers used an optimum ratio in the range of 1:3 to 1:12. (Deng & Englehardt, 2006b; Umar, Aziz, & Yusoff, 2010).

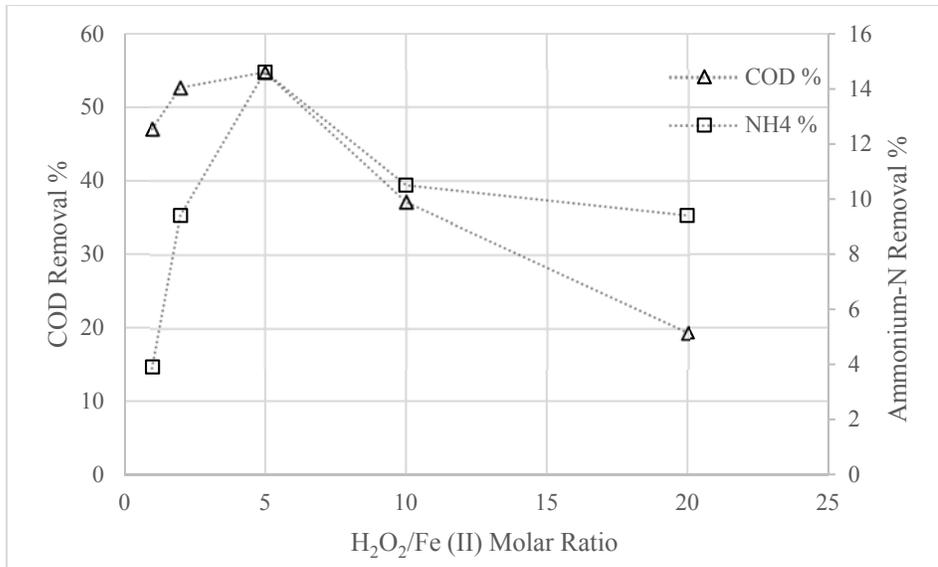


Figure 24: COD & ammonium-N removal at different H₂O₂/Fe(II) molar ratios

To determine the appropriate reagent dosage at a constant molar ratio (1:5), another set of experiments were conducted. COD and ammonium-N removal efficiency increased with the increase in dosage of the reagents (Figure 25), but the slope became asymptotic at the higher dosage. Also, the sludge settling becomes poor at a higher dosage. Since minimal improvement in removal efficiency was gained with higher doses, a lower dosage of 2.5 g/L H₂O₂ and 1.1 g/L of FeSO₄ was used for subsequent experiments.

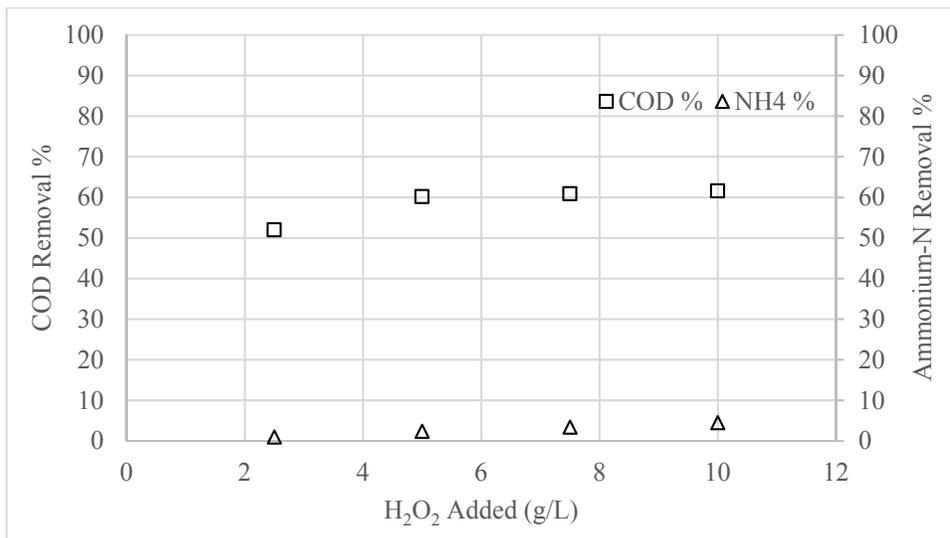


Figure 25: COD and ammonium-N removal efficiency at different dosage with constant (1:5) H₂O₂/Fe(II) molar ratio

Figure 26 shows the COD removal efficiency by electrochemical oxidation coupled with Fenton coagulation at three different current densities.

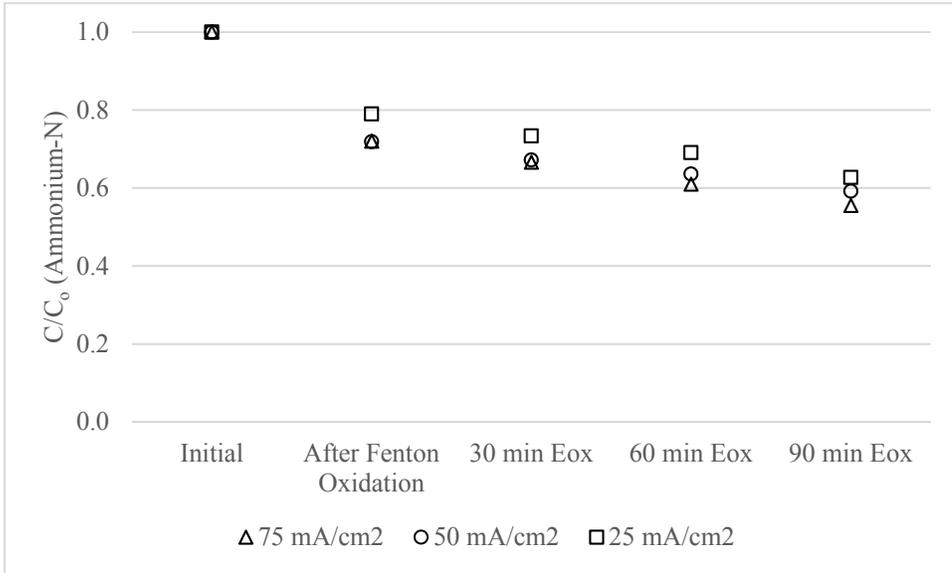


Figure 26: COD removal by electrochemical oxidation coupled with Fenton

Initially treated by Fenton, 90 minutes of electrochemical oxidation provided 45% COD removal. However, Fenton could not remove appreciable amounts of ammonium-N resulting in low ammonium-N removal by the combined process (32%, 29% and 19% at 75 mA/cm², 50 mA/cm² and 25 mA/cm², respectively) (Figure 27).

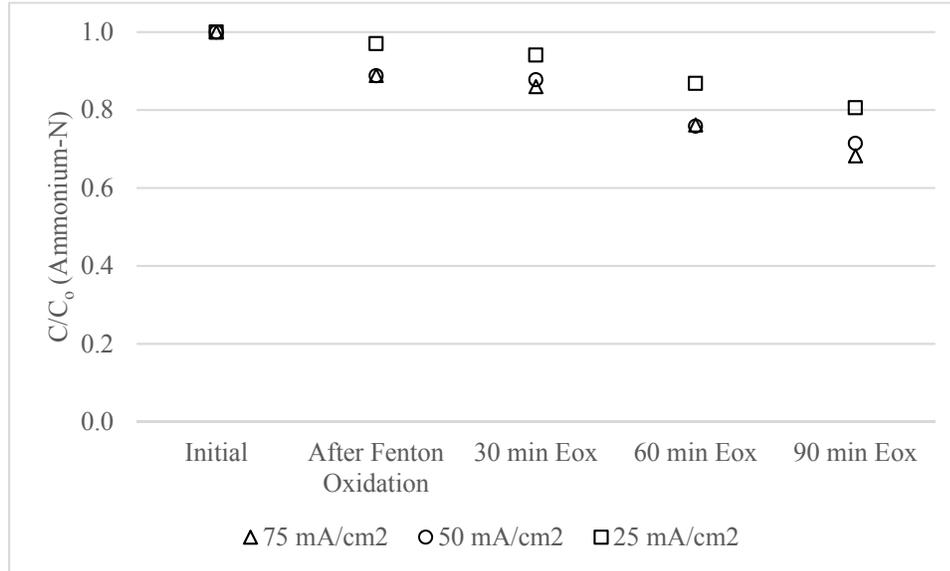


Figure 27: Ammonium-N removal by electrochemical oxidation coupled with Fenton

In Figure 28, turbidity removal is presented; it did not follow any definite pattern, even for 75 mA/cm², the turbidity increased due to the color generated by the Fenton reagents.

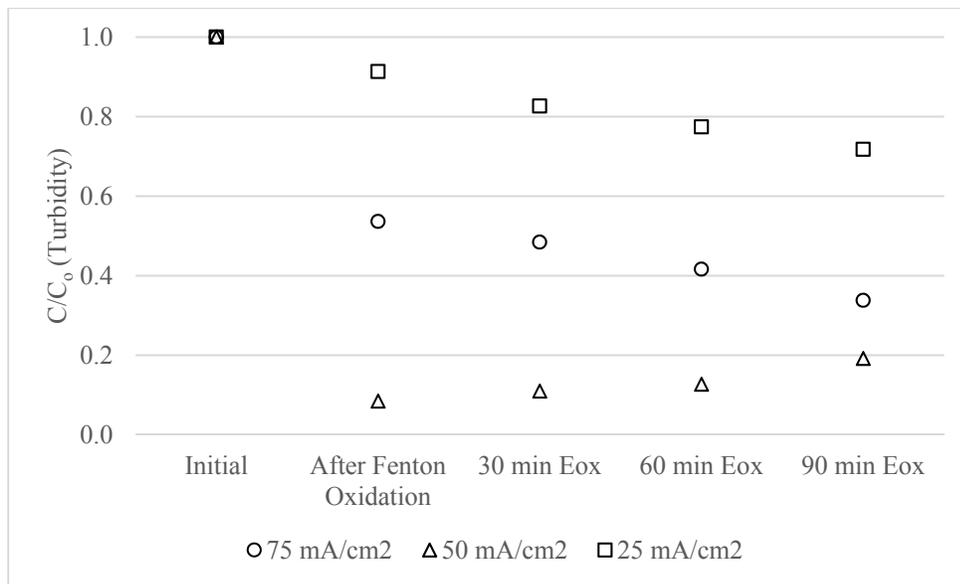


Figure 28: Turbidity removal by electrochemical oxidation coupled with Fenton

3.5 TWO STAGE ELECTROCHEMICAL OXIDATION

The two-stage electrochemical oxidation includes 60 minutes of electrochemical oxidation by the roughing reactor and subsequent treatment by the Magneli reactor up to 90 minutes. Maximum COD, ammonium-N, and turbidity removal achieved was 37%, 48%, and 96%, respectively (Figure 29, Figure 30, Figure 31).

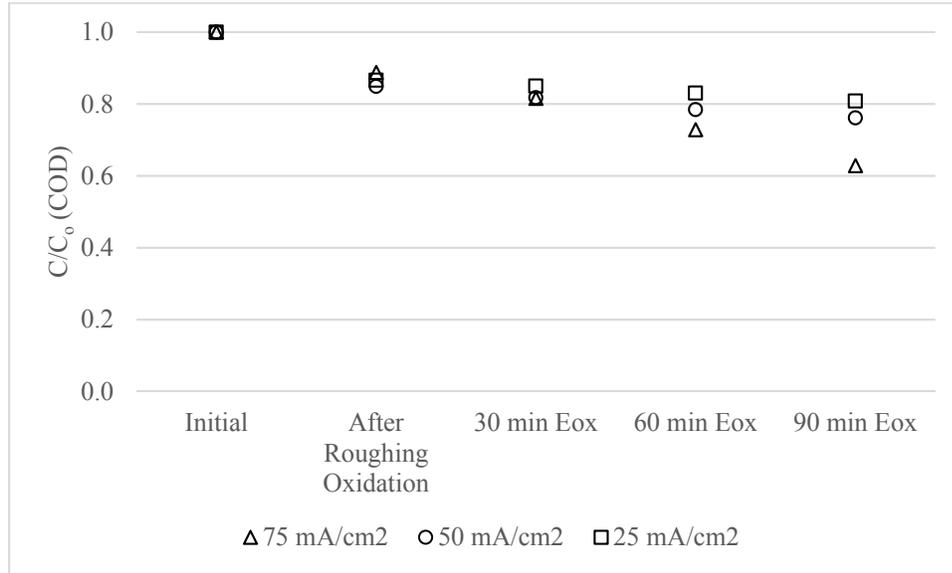


Figure 29: COD removal by two-stage electrochemical oxidation

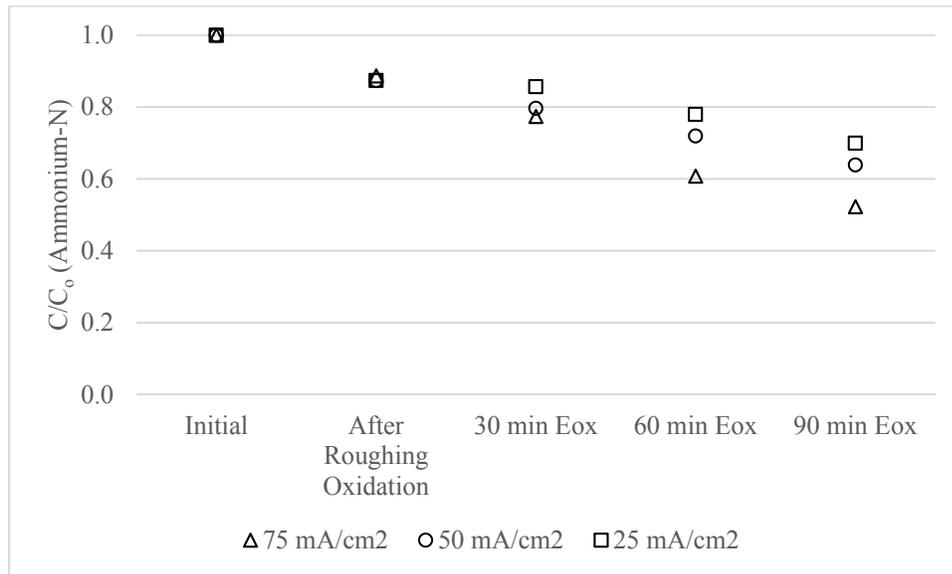


Figure 30: Ammonium-N removal by two-stage electrochemical oxidation

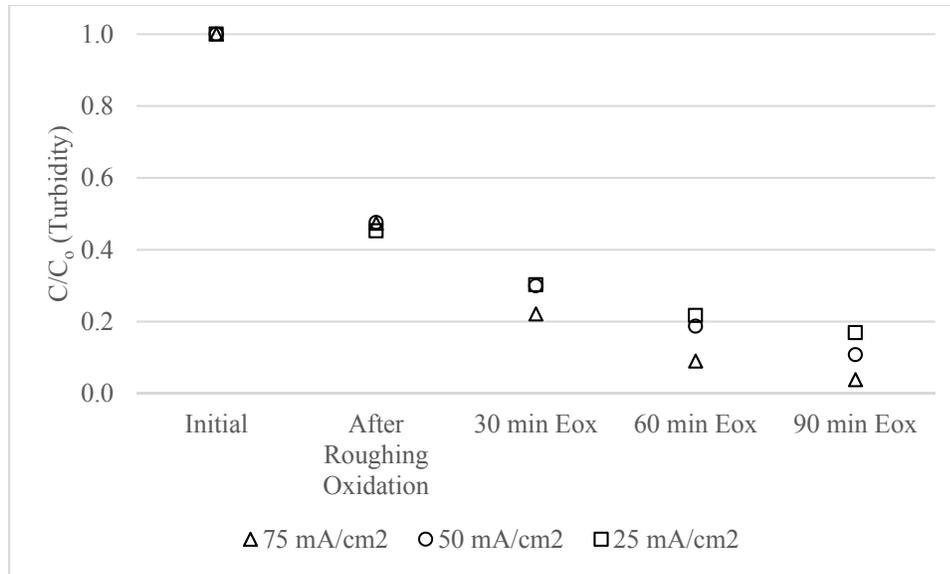


Figure 31: Turbidity removal by two-stage electrochemical oxidation

3.6 STATISTICAL ANALYSIS

The experimental design, mathematical analysis, and optimization were done using Design Expert 11.0 software. A three-level factorial design was employed to optimize the three independent variables in the experimental design: a) current density, b) treatment duration, and c) pretreatment. The three levels and types of the independent variables are listed in Table 11.

Table 11: Independent Variable and Their Ranges for Three Level Factorial Design

Variables	Current Density (mA/cm ²)	Treatment Duration (min)	Pretreatment
Type	Numerical (Discrete)	Numerical (Discrete)	Categoric (Nominal)
Low Level	25	30	Fenton
Mid-Level	50	60	Roughing EOx
High Level	75	90	Ozone

The experimental results of COD removal, ammonium-N removal, and turbidity removal at different levels of the factor for the development of the analysis are summarized in Table 12. The total number of experiments required for the analysis was 15 individual experiments plus three additional replicates.

Table 12: Experimental Responses at Different Levels of the Factors

Run	Factor 1 Current Density (mA/cm ²)	Factor 2 Time (min)	Factor 3 PreTrt	Response 1 COD (% Removal)	Response 2 NH ₄ ⁺ -N (% Removal)	Response 3 Turbidity (% Removal)
1	25	30	EOx	15	14	70
2	50	60	EOx	22	28	81
3	25	90	EOx	19	30	83
4	75	60	Fenton	39	24	58
5	25	30	Fenton	27	6	17
6	75	30	EOx	18	23	78
7	75	90	EOx	37	48	96
8	25	30	Ozone	20	17	92
9	50	90	Ozone	43	43	99
10	50	30	Ozone	22	24	94
11	25	60	Ozone	28	27	95
12	75	60	Fenton	39	24	58
13	75	60	Ozone	42	42	99
14	50	30	Fenton	33	12	19
15	50	30	EOx	18	20	70
16	50	60	EOx	19	27	81
17	25	90	Fenton	37	19	28
18	50	60	EOx	22	30	87

3.6.1 COD Removal

The analysis of variance was conducted to see the goodness of fit for all responses. The results of the ANOVA for COD removal are summarized in Table 13.

Table 13: ANOVA Results for COD Removal

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p-value	
Analysis	1458.25	5	291.65	30.39	< 0.0001	significant
A-Current Density	287.59	1	287.59	29.97	0.0001	
B-Duration	426.33	1	426.33	44.43	< 0.0001	
C-Pretrt	727.35	2	363.67	37.90	< 0.0001	
AB	34.38	1	34.38	3.58	0.0827	
Residual	115.15	12	9.60			
Lack of Fit	109.92	9	12.21	7.01	0.0682	not significant
Pure Error	5.23	3	1.74			
Cor Total	1573.40	17				

The F-value of 30.39 implies the analysis is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate terms are significant. In this case, A, B, C are significant. Values greater than 0.1000 indicate the analysis terms are not significant and hence are discarded. If there are many insignificant analysis terms (not counting those required to support hierarchy), model reduction may improve the analysis. The lack of fit F-value of 7.01 implies there is a 6.82% chance that a lack of fit F-value this large could occur due to noise.

Table 14: Fit Statistics for COD Removal

Std. Dev.	Mean	C.V. %	R ²	Adjusted R ²	Predicted R ²	Adequate Precision
3.10	27.82	11.13	0.93	0.90	0.84	16.47

The predicted correlation coefficient (R²) of 0.842 is in reasonable agreement with the adjusted R² of 0.896; i.e., the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 16.47 indicates an adequate signal. This analysis can be used to navigate the design space.

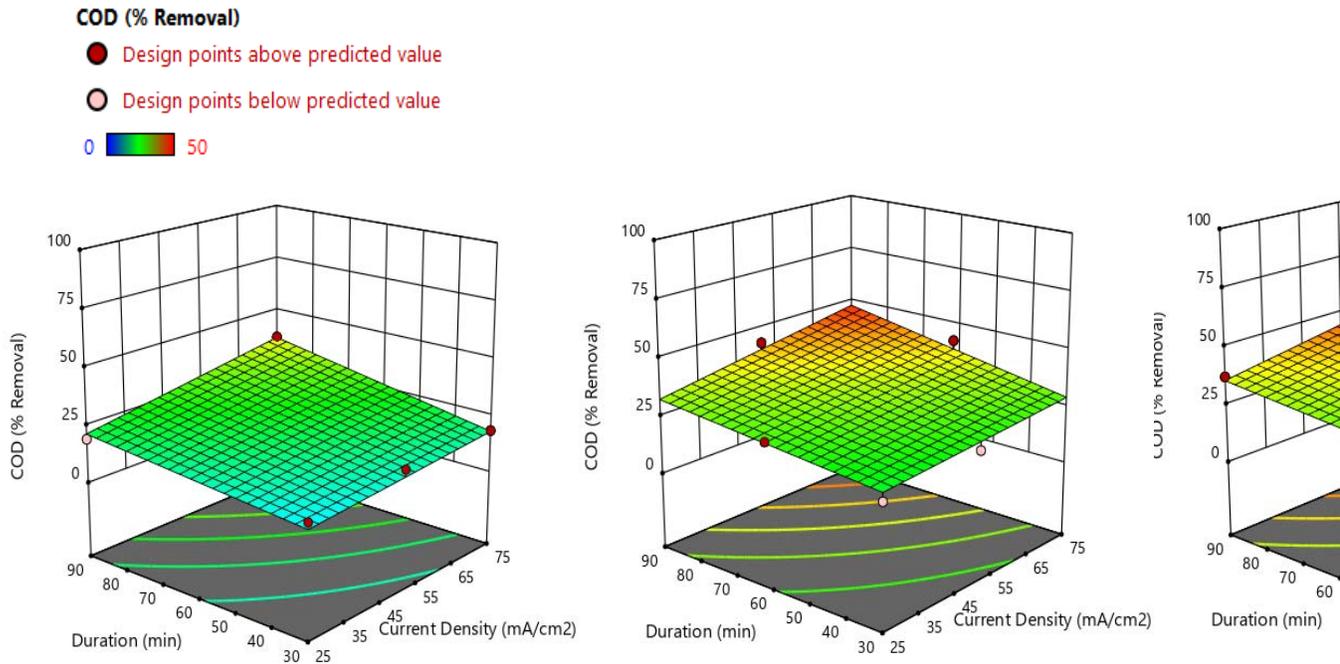


Figure 32 illustrates the three-dimensional surface plots for COD removal efficiency for three different pretreatment methods: a) roughing EOX, b) ozone, and c) Fenton. For all the three pretreatments, the shape is approximately similar, having a flat surface. All plots show clear peaks at extremities indicating that the optimum conditions for maximum values of the response may not lie within the design boundary. The plots also indicate a positive effect of current density and treatment duration on the response in case of all pretreatments. Within the design boundary of this study, the maximum removal was achieved at 75 mA/cm² and 90 minutes treatment duration, and Fenton pretreatment was found to be more effective (51%) than the other two pretreatment methods, roughing EOX (36.5%) and ozone (47.5%). The experimental value at 75 mA/cm² and 90 minutes with roughing EOX is 37.12%, which indicates less than 1% error from the predicted result from the analysis.

COD (% Removal)

● Design points above predicted value

○ Design points below predicted value

0  50

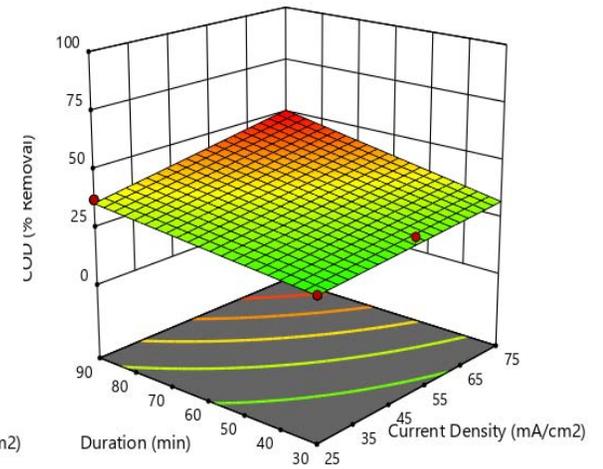
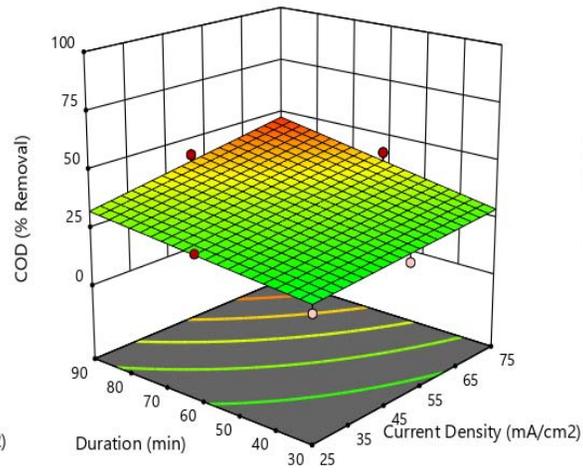
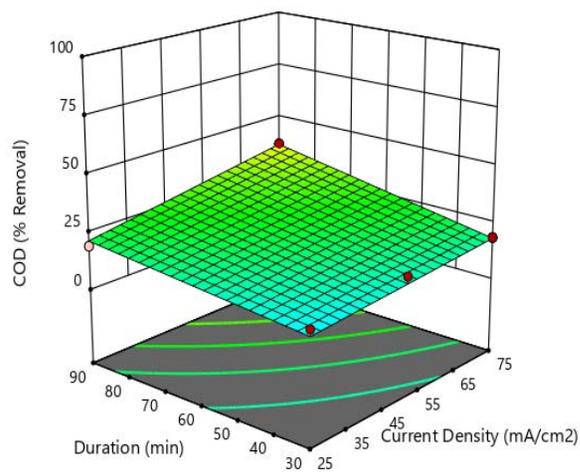


Figure 32: Three-dimensional surface plots for COD removal efficiency for roughing EOX (left), ozone (middle), and Fenton (right)

3.6.2 Ammonium-N Removal

The results of the ANOVA for ammonium-N removal are summarized in Table 15.

Table 15: ANOVA Results for Ammonium-N Removal

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p-value	
Analysis	1936.75	5	387.35	148.16	< 0.0001	significant
A- Current Density	450.38	1	450.38	172.27	< 0.0001	
B- Duration	838.62	1	838.62	320.78	< 0.0001	
C- Pretrt	539.64	2	269.82	103.21	< 0.0001	
AB	27.80	1	27.80	10.63	0.0068	
Residual	31.37	12	2.61			
Lack of Fit	28.19	9	3.13	2.95	0.2021	not significant
Pure Error	3.18	3	1.06			
Cor Total	1968.12	17				

The F-value of 148.16 implies that the analysis is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate analysis terms are significant. In this case, A, B, C, and AB are significant. Values greater than 0.1000 indicate the analysis terms are not significant and are discarded from the analysis. If there are many insignificant analysis terms (not counting those required to support hierarchy), model reduction may improve the analysis. The lack of fit F-value of 2.95 implies the lack of fit is not significant relative to the pure error. There is a 20.21% chance that a lack of fit F-value this large could occur due to noise. Non-significant lack of fit is preferable.

Table 16: Fit Statistics for Ammonium-N Removal

Std. Dev.	Mean	C.V. %	R²	Adjusted R²	Predicted R²	Adequate Precision
1.62	25.47	6.35	0.98	0.98	0.96	45.07

The predicted R² of 0.96 is in reasonable agreement with the adjusted R² of 0.98; i.e., the difference is 0.2. The adequate precision ratio is 45.07, which is greater than 4, indicating the analysis can be used to navigate the design space.

The 3-D surface plots in Figure 33 demonstrate the effect of current density and duration on ammonium-N removal with three different pretreatment methods: a) roughing EOx, b) ozone, and c) Fenton, respectively. In each case, the 3-D plot is flat and inclined towards the peak value. The removal efficiency increases with increasing treatment time and current density. Moreover, the maximum removal was achieved with ozone pretreatment (51.5%) at the most favorable condition of 75 mA/cm² current density and 90 minutes treatment time.

Ammonium-N (% Removal)

● Design points above predicted value

○ Design points below predicted value

0  50

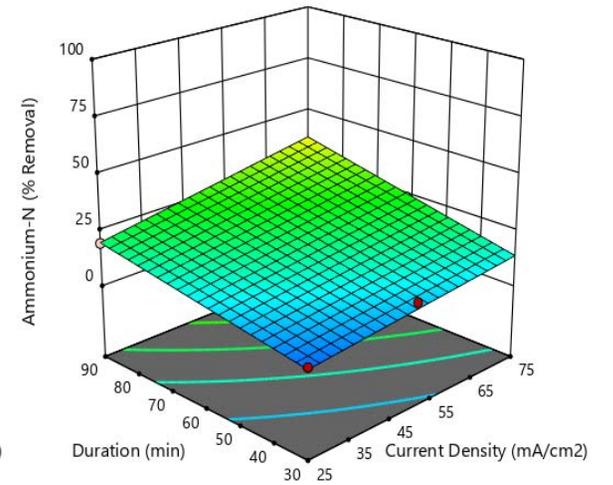
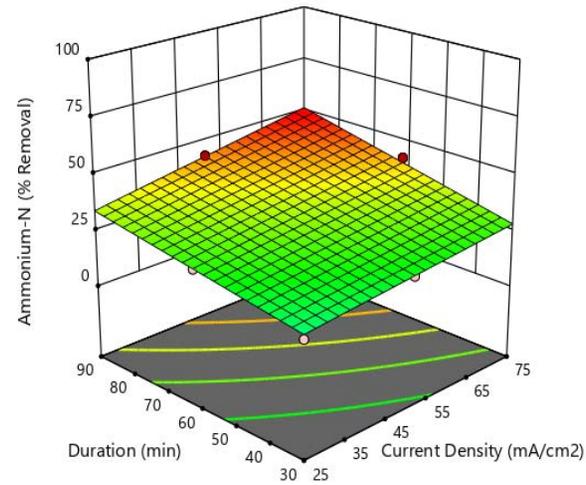
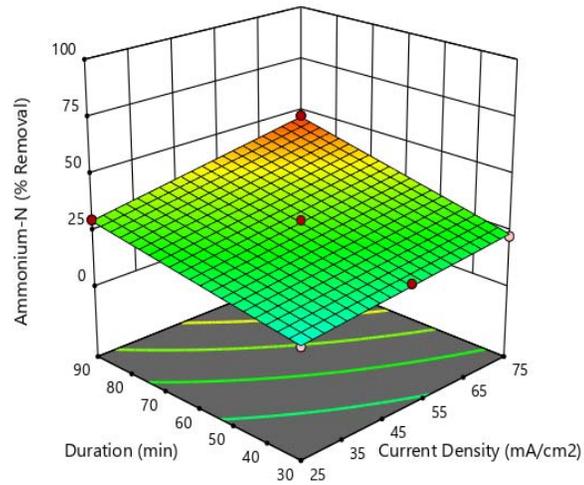


Figure 33: Three-dimensional surface plots for Ammonium-N removal efficiency for roughing EOX (left), ozone (middle), and Fenton (right)

3.6.3 Turbidity Removal

The results of the ANOVA for turbidity removal are summarized in Table 17.

Table 17: ANOVA Results for Turbidity Removal

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p-value	
Analysis	11822.61	6	1970.43	78.98	< 0.0001	significant
A- Current Density	829.30	1	829.30	33.24	0.0001	
B- Duration	578.27	1	578.27	23.18	0.0005	
C- Pretrt	10140.89	2	5070.45	203.24	< 0.0001	
AC	549.95	2	274.97	11.02	0.0024	
Residual	274.43	11	24.95			
Lack of Fit	254.99	8	31.87	4.92	0.1087	not significant
Pure Error	19.44	3	6.48			
Cor Total	12097.04	17				

The F-value of 78.98 implies the analysis is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. In this case, A, B, C, and AC are significant. Values greater than 0.1000 indicate the analysis terms are not significant. The lack of fit F-value of 4.92 implies the lack of fit is not significant relative to the pure error. There is a 10.87% chance that a lack of fit F-value this large could occur due to noise.

Table 18: Fit Statistics for Turbidity Removal

Std. Dev.	Mean	C.V. %	R ²	Adjusted R ²	Predicted R ²	Adequate Precision
4.99	72.65	6.87	0.98	0.96	0.97	29.72

The predicted R² of 0.97 is in reasonable agreement with the adjusted R² of 0.96; i.e., the difference is less than 0.2. Adequate precision of 29.72 indicates an adequate signal (>4.0). This analysis can be used to navigate the design space.

The relationship between turbidity removal with the factors, current density, and treatment time is plotted in 3D in Figure 34. Comparatively less removal was observed when Fenton was coupled with the electrochemical oxidation due to the color and turbidity coming from the Fenton's reagent. However, when ozone was introduced as a pretreatment, even with the low values of the factors (25 mA/cm² current density and 30 minutes treatment time), more than 90% removal was achieved, and 100% removal was achieved before the high values of the factor according to the analysis. On the other hand, with roughing EOX, the predicted maximum response is 94.5%, which is approximately 2% lower than the experimental value (96.17%).

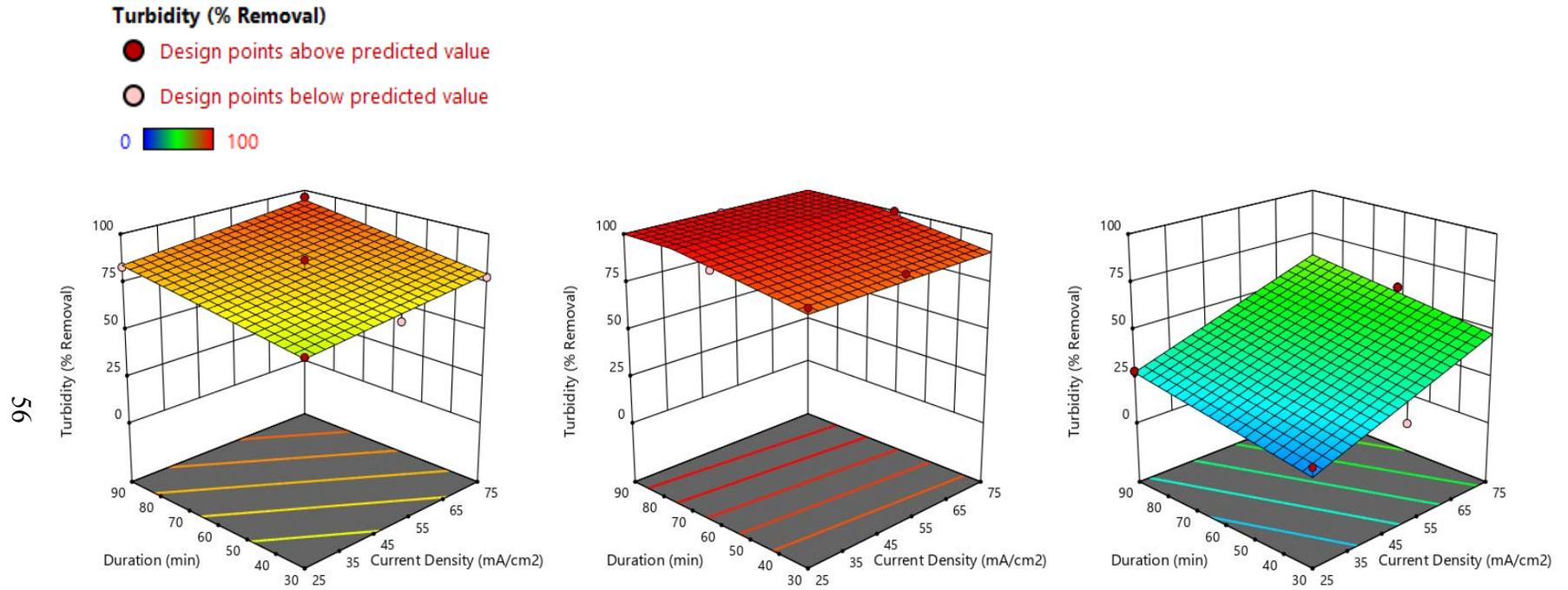


Figure 34: Three-dimensional Surface Plots for Turbidity Removal Efficiency for Roughing EOx (left), Ozone (middle), and Fenton (right)

3.7 ELECTROCHEMICAL OXIDATION FOR EXTENDED HOURS

After conducting the statistical analysis, it was decided to perform a series of experiments designed to improve treatment efficiency or at least determine the factors that control treatment efficiency. The first experiment in this series was conducted for extended time with the coupled electrochemical oxidation (roughing EOx + Magneli). An initial linear increase in water temperature was noticed in the first 90 minutes of reaction. Therefore, whenever the temperature reached 40°C, the sample was cooled down by placing the recirculating reservoir beaker in an ice-water bath. At the peak points, the system was cooled down, but the temperature increased again. The crests and troughs of Figure 35 document continuous heat generation from the system due to the relatively small volume of water treated in the pilot reactors, and without any cooling measures, the temperature continuously rises.

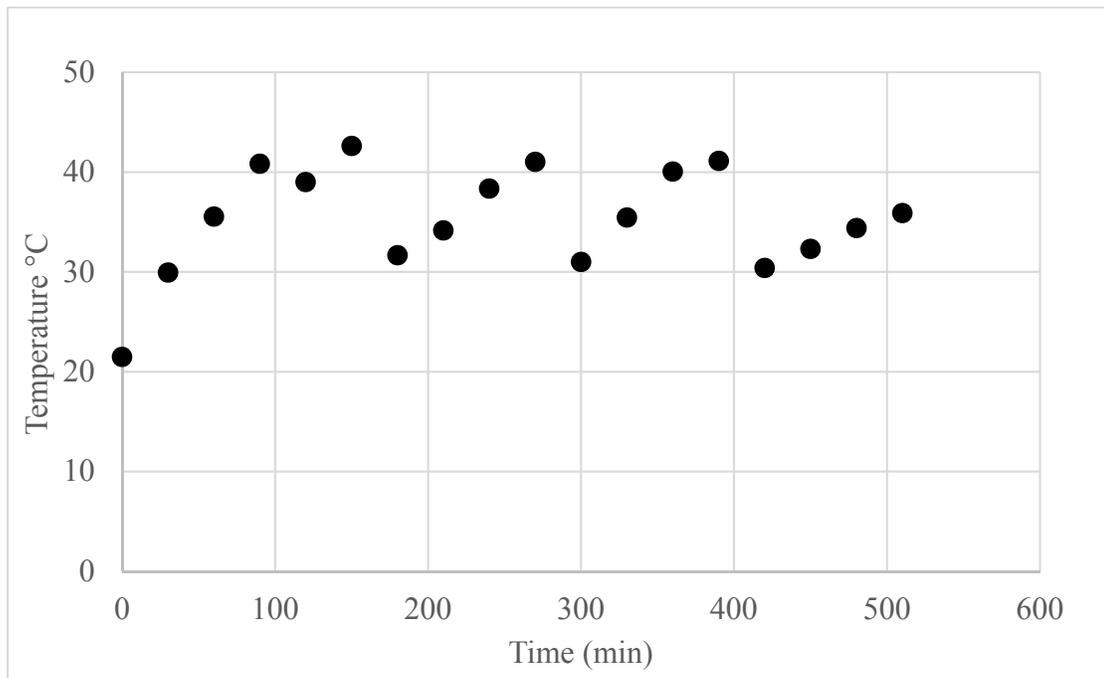


Figure 35: Temperature change over the time during electrochemical oxidation

The results of the COD and ammonium-N removal for this extended experiment is shown in Figure 36. The ammonium-N removal (80%) was higher than COD removal (51%) efficiency. According to a study by Deng and Englehardt (2006), in the competition between ammonium-N and organic oxidation, removal of ammonium-N is greater than the COD removal when indirect oxidation dominates. The greater ammonium-N removal of this experiment indicates that indirect oxidation was dominant in the electrochemical oxidation reactor. It is also noticeable that after 450 minutes, the trend line for ammonium-N removal started to flatten, which indicates a decrease in the rate of

removal. Moreover, COD and ammonium-N removal for the 90 minutes experiment was plotted in the same graph. Slightly higher removal is observed with the regular experiment for both COD and ammonium-N.

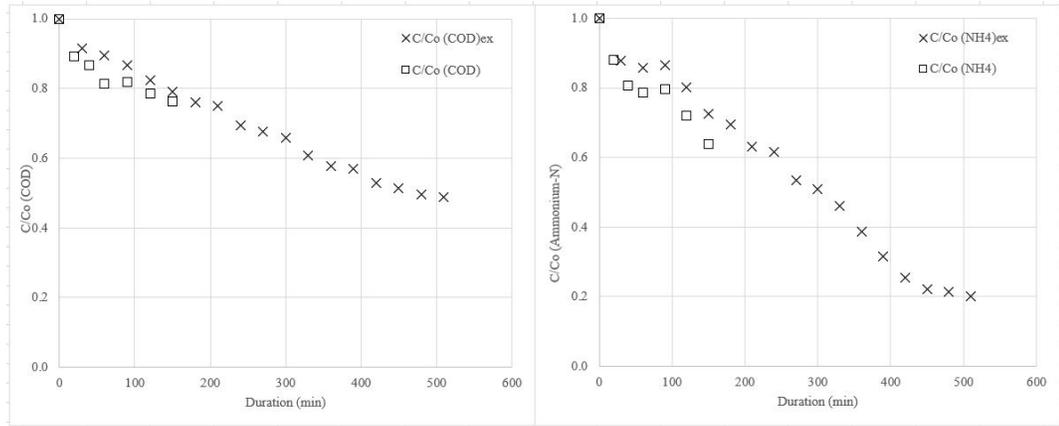


Figure 36: COD (left) and ammonium-N (right) removal by two stage electrochemical oxidation

3.8 LIME PRETREATMENT

An experiment was conducted to observe the performance of lime as a pretreatment for electrochemical oxidation. The results are shown in Figure 37. The results were unexpected as the amount of ammonium-N and turbidity increased with time. This increment indicates that at high pH with lime addition, the ammonium-N converted to nitrate-nitrogen, which was trapped in the solution, but subsequent decrease of pH during the electrochemical oxidation converted the nitrate-nitrogen back to ammonium-N again. However, the COD decreased over time with the electrochemical oxidation

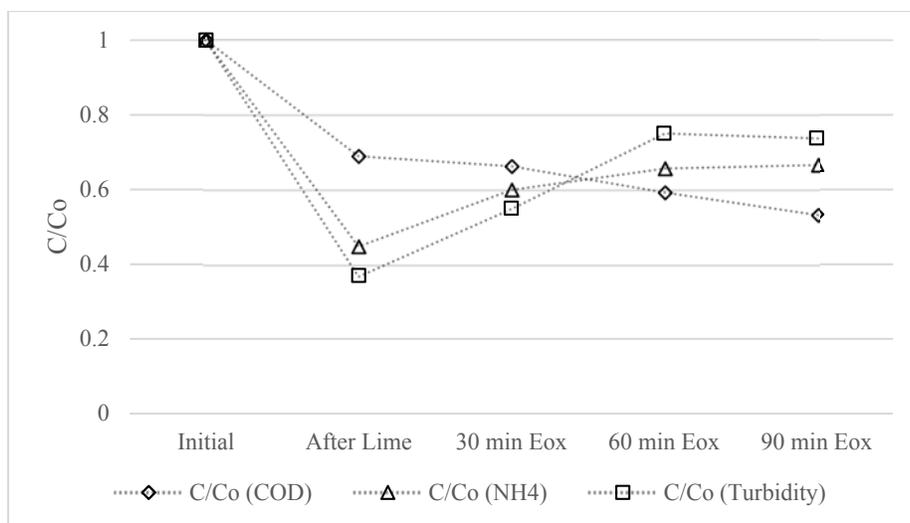


Figure 37: COD, ammonium-N, and turbidity removal by lime coupled with electrochemical oxidation

3.9 HALOGENATED BYPRODUCT DETECTION

Undesirable halogenated byproducts such as TTHMs and HAA5 were detected using liquid chromatography-mass spectroscopy (LC/MS). The speciation of the compounds is presented in Figure 38 and Figure 39. It is noticeable that all the TTHMs were below the detection limit and a very low amount of dichloroacetic acid (95 µg/L) and trichloroacetic acid (32 µg/L) were detected in the raw leachate. Again, a higher concentration of total trihalomethane (TTHM) was observed when the amperage was increased from 10 to 30 amps, indicating a positive effect of current density on the formation of TTHMs. The least amount of TTHMs and HAA5 were detected for the lime pretreatment. However, a significant amount of bromodichloromethane, bromoform, dibromochloromethane, dibromoacetic acid and monobromoacetic acid were detected for all of the combined treatment processes, indicating active bromine presence in the raw leachate.

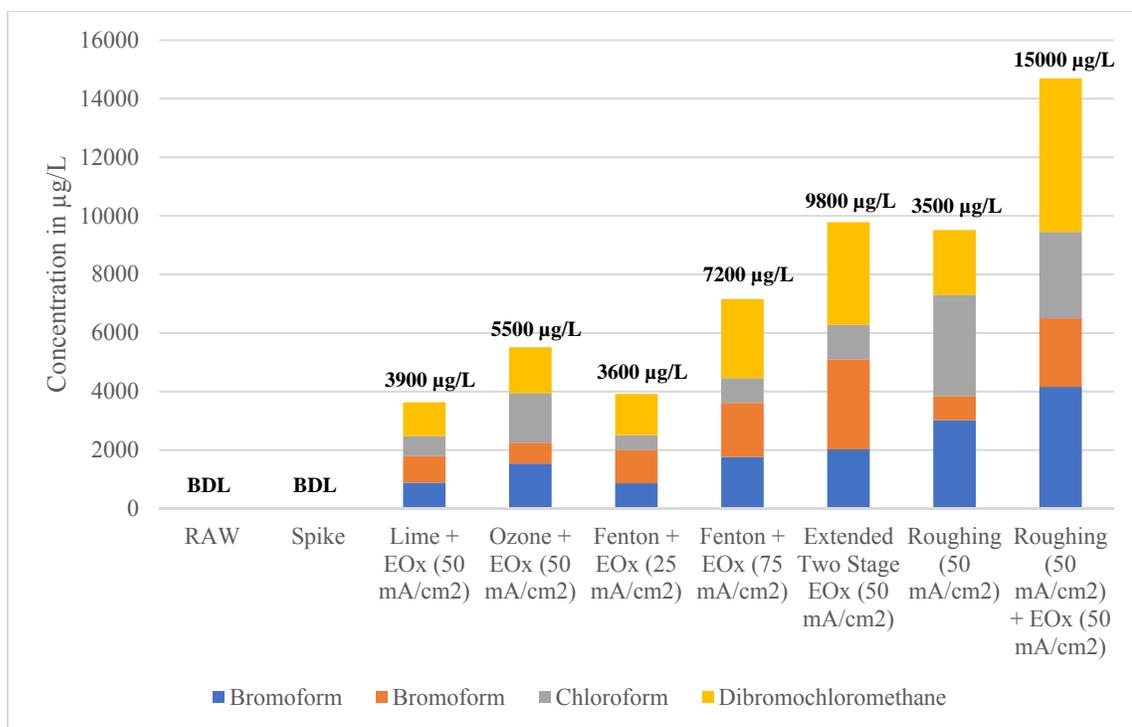


Figure 38: TTHM detection after different combination of treatment

In the case of HAA5 detection, a different behavior is observed (Figure 39). In comparison with the 10-amp EOX with Fenton, a lower amount of HAA5 was observed for higher amperage (30 amps). Moreover, a greater amount of HAA5 was detected in between roughing and Magneli EOX, which was unexpected. Again, a noticeable amount of monochloroacetic acid was detected when only the roughing reactor was used.

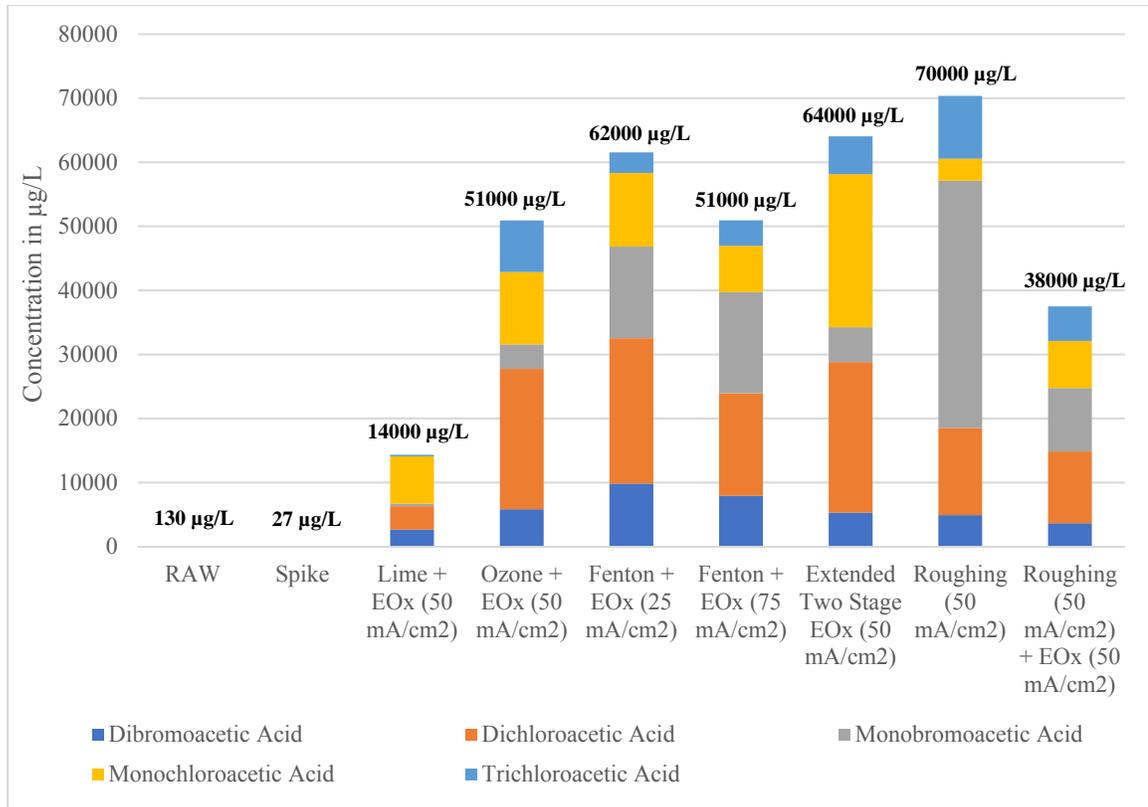


Figure 39: HAA5 detection after different combination of treatment

3.10 PRELIMINARY COST ANALYSIS

In this section, the preliminary costs of the different treatment process configurations studied in this thesis are presented, including the following:

1. Magneli reactor
2. Roughing electrochemical oxidation reactor
3. Ozone pretreatment
4. Fenton pretreatment
5. Lime pretreatment

The analysis is conducted for a theoretical design flow of 0.5 MGD, which is the average flow of the landfill leachate collection system generated from monthly reports from the Solid Waste Authority of Palm Beach County over the period of 2017-2018, which was generated from an average of 3.1 million tons MSW discarded, annually. The electricity required is scaled up from the laboratory scale treatment unit to the designed unit. Table 19 summarizes the approximate cost of the treatment using a field scale Magneli reactor for 90 minutes at 30 amps and 8 volts. From this data, calculated electricity requirements for each unit would be 5,375 kWh per day. The cost of each treatment unit having

capacity of 2.5 tons/hour is considered \$10,000 (provided by the manufacturer). In total 36 units are required working 325 days a year with 10% downtime and including 4 units for redundancy. The capital cost is amortized for 16 years at an interest rate of 4%. The operational cost includes the cost of the electricity to run each unit for 325 days and the technician labor cost. The cost of treatment by this configuration would be approximately \$39 per 1000 gallons with the electricity cost being the main driver.

Table 19: Cost Analysis: Magneli Electrochemical Oxidation

Item	Quantity	Unit Cost	Total Cost
<i>Capital Cost Breakdown</i>			
EOx Unit, Pumps, Wiring	36	10,000	\$360,000
<i>Operational Cost Breakdown</i>			
Electricity (\$0.12/kWh)	325 days	\$0.12/kWh	\$7,546,500
Labor	12 months	\$8000	\$96,000
<i>Total O&M</i>			\$7,642,500
<i>Summary Breakdown</i>			
Annualized (4%, 16 Years)			\$30,895
Total Annual Cost			\$7,673,395
Volume Treated per year			195,000 kgal
Cost per 1000 Gal			\$39.35

Table **20** is the preliminary cost analysis for the roughing pretreatment for 60 minutes at 20 amps. Thus, the electricity required for each unit of 0.2 MGD would be 20,000 kWh per day. The capital cost is calculated from the manufacturer's estimate. The cost of electricity is scaled up from the 4-liter laboratory scale unit to three 0.2 MGD industrial units. Although a leachate treatment plant should run without any interruption, a 10% downtime is considered. A batch process with adequate on-site storage is suggested to manage the minor downtime. This capital cost is annualized over 10 year at an interest rate of 4% and then added to the annual operational cost. The cost to treat leachate by this process configuration is \$13 per 1000 gallons approximately. Again the main driver is the electricity cost.

Table 20: Cost Analysis: Roughing Electrochemical Oxidation

Item	Quantity	Unit Cost	Total Cost
<i>Capital Cost Breakdown</i>			
EOx Unit, Wiring	3	\$350,000	\$1,050,000
<i>Operational Cost Breakdown</i>			
Electricity (\$0.12/kWh)	325 day/year	\$0.12/kWh	\$2,340,000
Employee	12 months	\$8,000	\$96,000
<i>Total O&M</i>			\$2,436,000
<i>Summary Breakdown</i>			
Annualized (4%, 10 Years)			\$129,455
Total Annual Cost			\$2,565,455
Volume Treated per year			195,000 kgal
Cost per 1000 Gal			\$13.16

In this case, the primary driver is the acquisition cost of the ozone treatment units.

Table 21, the cost analysis of ozone pretreatment is presented. The capital cost includes three treatment units, each having 0.2 MGD capacity and one ozone generator. Additionally, an approximate amount is assumed with the employee cost for maintenance. Compared to electrochemical oxidation, the preliminary cost of ozone pretreatment is very low (\$2.5 per 1000 gallon). In this case, the primary driver is the acquisition cost of the ozone treatment units.

Table 21: Cost Analysis: Ozone Pretreatment

Item	Quantity	Unit Cost	Total Cost
<i>Capital Cost Breakdown</i>			
Ozone Treatment Unit	3	\$585,000	\$1,755,000
Ozone Generator	1	\$290,000	\$290,000
<i>Total Capital Cost</i>			\$2,045,000
<i>Operational Cost Breakdown</i>			
Electricity			\$100,000
Employee & Maintenance			\$135,000
<i>Total O&M</i>			\$235,000
<i>Summary Breakdown</i>			
Annualized (4%, 10 Years)			\$184,936
Total Annual Cost			\$487,130
Volume Treated per year			195,000 kgal
Cost per 1000 Gal			\$2.50

Table 22 is the preliminary cost analysis for Fenton pretreatment. The cost of the treatment unit is estimated by personal communication with Dr. Bloetscher (Professor, CECE, FAU). The amount of chemicals needed is scaled up from the laboratory scale experiments, and the costs are calculated from the manufacturer's website (Brenntag Connect). The capital cost is annualized and added to the annual operational and maintenance cost. Comparing all the treatment process studied here, Fenton pretreatment requires the maximum cost at \$55 per 1000 gallons, with the main driver being the chemical costs.

Table 22: Cost Analysis: Fenton Pretreatment

Item	Quantity	Unit Cost	Total Cost
<i>Capital Cost Breakdown</i>			
Mixing basin, settling tank, pumps & piping	3	\$500,000	\$1,500,000
<i>Operational Cost Breakdown</i>			
Chemical Cost			
30% H ₂ O ₂	6320 kg/0.2 MGD	\$0.46/lb	\$6,235,944
Dry FeSO ₄	1700 kg/0.2 MGD	\$1.16/lb	\$4,229,940
Employee & Maintenance			\$125,000
<i>Total O&M</i>			\$10,590,884
<i>Summary Breakdown</i>			
Annualized (4%, 10 Years)			\$184,936
Total Annual Cost			\$10,775,820
Volume Treated per year			195,000 kgal
Cost per 1000 Gal			\$55.26

Table 23 shows the preliminary cost analysis of lime pretreatment. The capital cost and the operational cost is estimated by personal communication with Dr. Bloetscher. The capital cost includes the cost of the slaker, reactor, clarifier, required pumps, and piping. A total of three units is selected including one as redundant. Assuming \$0.80/1000 gallons for chemicals and employee labor costs, the total operational and maintenance cost is obtained considering three units running for 325 days a year. The lime pretreatment is the least expensive treatment process studied here (\$1.97 per 1000 gallon).

Table 23: Cost Analysis: Lime Pretreatment

Item	Quantity	Unit Cost	Total Cost
<i>Capital Cost Breakdown</i>			
Slaker, Reactor, Clarifier, Pumps and Piping	3	\$615,000	\$1,845,000
<i>Operational Cost Breakdown</i>			
Chemical & Employee	200 k/day/unit	\$0.80/1000 Gal	\$156,000
<i>Total O&M</i>			\$156,000
<i>Summary Breakdown</i>			
Annualized (4%, 10 Years)			\$227,472
Total Annual Cost			\$383,472
Volume Treated per year			195,000 kgal
Cost per 1000 Gal			\$1.97

Tables 19 through 23 summarize the individual costs of the various treatment processes investigated in this study. When the pretreatments are coupled with electrochemical oxidation there may be some additional costs for equalization tanks, pumps and plumbing that are not considered in this analysis. The preliminary cost of the coupled treatment processes could likely be reduced even more, if the cost of a larger field scale Magneli reactor is known. Again, a large percentage (at \$0.12/kWh, 96% of the total annual cost) of the annual cost is for electricity, so a lower rate of electricity could reduce the cost of the process for example at \$0.06/kWh the cost would be reduced to only \$20 per 1000 gallons. When the roughing EOx reactor is coupled with Magneli reactor (2-stage EOx process), the preliminary cost is \$52.5 per 1000 gallons approximately. In this case, the cost is mainly governed by the price of electricity (at \$0.12/kWh, electricity is 91% of the total annual cost). If electricity can be managed at a lower rate, the cost of this pretreatment will be reduced substantially, for example at \$0.06/kWh, the cost decreases from \$14 to \$7.16 per thousand gallons. The Fenton-Magneli EOx coupled process costs approximately \$95 per thousand gallons. However, for Fenton, this study did not attempt to optimize chemical usage, therefore, it is likely that a scaled-up unit would probably require less chemicals than anticipated, which would in turn drive down the cost substantially since 97% of the cost is driven by chemical dosage. On the other hand, the approximate cost of lime pretreatment with the Magneli reactor is \$41 per 1000 gallons, which is comparatively lower than the other coupled processes studied. The most efficient in terms of performance was ozone-Magneli EOx, which also happened to have the lowest cost (\$41 per 1000 gallons).

4 CONCLUSIONS AND RECOMMENDATION

4.1 SUMMARY OF FINDINGS

The preliminary experiments using artificial leachate demonstrated that the two-stage electrochemical oxidation process (OriginClear followed by Magneli) is effective in reducing COD (54%) and can be applied to raw leachate. The tests also demonstrated that higher levels of electrolytes (chlorides > 10,900 mg/L) yielded a higher removal rate of COD and ammonium-N.

In order to investigate more efficient removal of COD and ammonium-N, electrochemical oxidation was coupled with four different pretreatments (roughing EOx, ozone, Fenton, or lime). A three-level factorial design of experiments was implemented, and response surface methodology was developed to analyze the results and optimize the process parameters. The ANOVA analysis showed that all the terms included in the analysis are significant at 95% confidence level with all the p values less than 0.05 and insignificant values for lack of fit. The higher values of determination coefficient R^2 (0.93 for COD removal, 0.98 for ammonium-N removal, and 0.98 for turbidity removal) also indicate a strong relation. Again, the close values of the adjusted determination coefficient (R^2_{adj}) to the R^2 show high significance. From the statistical analysis, the maximum removal was obtained at 75 mA/cm² current density and 90 minutes of treatment time. While the maximum COD removal (51%) was achieved with Fenton, maximum ammonium-N removal (51.5%) and turbidity removal (100%) were achieved with ozonation. However, from experiments, the maximum COD removal (52.1%), ammonium-N removal (51.8%), and turbidity removal (99.7%) were achieved from ozonation. A better result (51% COD removal, 80% ammonium-N removal, and 99.5%) was obtained by the two-stage electrochemical oxidation conducted for extended hours (7 hours) but discouraged due to the high amount of energy requirement and potential generation of halogenated byproducts.

Lime treatment showed noticeable results when implemented alone, but not suggested with electrochemical oxidation due to the regeneration of ammonium-N over time. Lime treatment removed more than 50% ammonia alone, but when coupled with electrochemical oxidation, the final effluent had more ammonium-N than it was in between the two processes. Byproducts analysis demonstrated elevated levels of TTHMs and HAA5. The maximum amount of TTHM and HAA5 were observed for the two-stage electrochemical oxidation configuration (15,000 µg/L) and by roughing reactor (70,000 µg/L), respectively. Bromodichloromethane, dichlorobromoethane, dichloroacetic acid, monochloroacetic acid were the main halogenated organic byproducts detected. A noticeable amount of brominated organic byproducts were detected, indicating the likely presence of a high amount of bromine in the raw leachate.

From the cost analysis of different treatment processes, the least expensive coupled process observed was lime pretreatment with electrochemical oxidation (\$41 per 1000 gallons). On the other hand, the most feasible combination was ozone coupled with electrochemical oxidation having a cost of \$41 for every 1000 gallons with the maximum removal efficiency. Fenton

pretreatment shows an excessively high cost of \$95 per 1000 gallons, which is associated with the cost of relatively expensive chemicals required for this process.

Overall, this study has shown that the electrochemical oxidation using MMO anode is capable of removing an appreciable amount of contaminants (COD and ammonium-N) from leachate but not enough for safe discharge to the environment. However, improvement has been made by coupling other pretreatments with electrochemical oxidation, and hence, further research can make it possible to achieve the discharge goal.

4.2 RECOMMENDATIONS

The main limitation of this study is the variability of the leachate characteristics due to the variability of rainfall, waste disposed at the landfill, decomposition rate and temperature (Calace et al., 2001; Chu et al., 1994). These changes significantly limit the reproducibility of the experiments. Controlled lab experiments by diluting the sample to a constant concentration may help to overcome the constraint.

In this study, maximum removal was obtained at the boundary points (75 mA/cm² and 90 minutes), which is another limitation of this study. Although a positive effect of current density increment was observed, the amperage used in this study was limited by the capacity of the power supply used. Again, the temperature increase over time restricts its use for longer period. An experiment for extended hours was conducted by controlling the temperature using an ice-water bath, but experiments conducted in a temperature-controlled environment at a higher current density from a stronger power supply should be studied to see the effect.

For lime treatment, the dosage was chosen to the amount that was required to increase the pH to 12 to achieve co-precipitation. However, no experiment was conducted to optimize the lime dosage. A set of experiments with different lime doses and at different final pH values can be studied to find out the optimum dosage. Moreover, sludge settlement could be improved by using multiple containers in series having a larger surface area.

For halogenated byproducts generation, the concentration used for the matrix spike was 100 µg/L chloroform, and 100 µg/L monochloroacetic acid in this study. However, the practical quantitation limits for TTHMs and HAA5 in leachate were found to be 4.58 and 90 µg/L. Thus at a 100-fold dilution, the results obtained for the matrix spikes in leachate were below the detection limit of the LC/MS. For future study of halogenated byproducts, a higher concentration for matrix spiking should be used. The sample in-between two processes should also be tested to observe the effect of the individual process on byproduct generation.

An inherent limitation of RSM is, the model is invalid out of the range of the factor studied. That means the model cannot be used to predict removal efficiency at extended points of the

parameters. Again, for this analysis, three replicates only with roughing EOX were used. More replicates with other pretreatments would make the analysis more accurate.

Finally, although an appreciable amount of COD and ammonium-N removal was achieved by coupling electrochemical oxidation with other pretreatments (ozone, Fenton and lime), the process can be improved if a substantial amount of contaminants can be removed by any alternative pretreatment. Researchers have found struvite to be effective in removing ammonium-N from similar waste streams (Ryu, Kim, & Lee, 2008; Yu, Geng, Ren, Wang, & Xu, 2013). Application of struvite as a pretreatment before electrochemical oxidation could show improved performance and should be investigated.

5 APPENDIX

A) Two stage Electrochemical Oxidation with 2800mg/L Cl

Date:

Sample Volume: 4 liters Chloride: 2800 mg/L

Electrochemical Oxidation with Roughing Eox

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O2	Turbidity (NTU)
0	6.2	20	19.5	5.67	8.72	7.49	1340	0.31
15	6.2	20.5	22.6	5.39	8.3	8.62	900	0.53
30	6.2	21.1	25.75	5.12	7.88	9.15	785	0.54
45	6.2	21.7	28.58	5.06	7.79	9.36	790	0.98
60	5.9	20.6	30.9	5.15	7.93	9.49	670	1.05

Electrochemical Oxidation with Magneli Reactor

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O2	Turbidity (NTU)
15	8.8	19.8	31.5	5.27	8.12	8.8	620	1.7
30	5.6	19.6	32.9	5.33	8.2	8.8	610	2.34
45	5.7	21.3	34.6	5.19	7.99	8.8	575	1.49
60	5.7	21.1	35.3	5.28	8.13	8.8	560	1.93

B) Two stage Electrochemical Oxidation with 5200 mg/L cl

Date:

Sample Volume: 4 liters Chloride: 5200 mg/L

Electrochemical Oxidation with Roughing Eox

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O ₂	Turbidity (NTU)
0	5.1	20.4	19.1	10.88	16.74	6.66	1375	0.65
15	5.1	20.6	21.4	10.4	16	8.38	1150	1.82
30	5.1	21	23.7	10.12	15.57	8.95	765	1.84
45	5	20.5	25.8	9.9	15.37	9.24	595	2.04
60	4.9	20.6	27.6	9.8	15.118	9.68	545	2.46

Electrochemical Oxidation with Magneli Reactor

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O ₂	Turbidity (NTU)
15	5.2	25.5	29.3	9.97	15.35	9.18	535	4.81
30	5.1	25.5	31.6	10.01	15.41	9.12	420	4.88
45	5	25.5	33.3	10.05	15.47	8.97	415	5.53
60	5.1	25.5	34.79	10.17	15.65	9.16	420	5.6

C) Two stage Electrochemical Oxidation with 10900 mg/L Cl

Date:

Sample Volume: 4 liters Chloride: 10900 mg/L

Electrochemical Oxidation with Roughing Eox

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O ₂	Turbidity (NTU)
0	4.3	20.6	20.73	18.83	28.97	6.58	1530	0.38
15	4.4	20.7	22.72	17.68	27.2	8.43	1340	0.36
30	4.3	20.7	24.46	13.05	20.08	8.96	1205	0.23
45	4.3	20.7	26.19	9.34	14.37	9.15	985	0.25
60	4.3	20.7	27.79	9.39	14.37	9.32	855	0.4

Electrochemical Oxidation with Magneli Reactor

Time (min)	Voltage (V)	Current (A)	Temp (C)	TDS (mg/l)	Sp. Cond (ms/cm)	pH	COD mg/L O ₂	Turbidity (NTU)
15	3.9	20.7	29.21	18.03	27.74	8.88	845	1.95
30	3.9	20.7	30.46	18.12	27.88	8.9	750	0.97
45	4	20.7	31.5	18.28	28.12	8.8	545	1.21
60	3.9	20.7	32.37	18.2	28	8.74	700	1.11

D) Ozone Coupled with Electrochemical Oxidation at 10 Amps

Date 6/10/2

: 018

Sample 3.5 Chlorid

Volume: Liters e: 13.325 g/L

Ozonation

Time	pH	COD (mg/L)	NH ₄ (mg/L)	Turbidity (NTU)
0	7.9	6850	2600	1000
10	7.45	6410	2530	1000
25	7.3	6310	2460	1000
45	7.1	5830	2360	1000

Electrochemical Oxidation

Time	Volts (V)	Amps (A)	pH	Temp (°C)	Cond (mS/cm)	COD (mg/L)	NH ₄ (mg/L)	TDS	Turbidity (NTU)
0	3.9	10	7.61	23.1	78.5	5830	2360	53.1	150
15	4.1	10	7.72	24.9	64.1	5630	2300	45.1	132
30	4.1	10.1	7.53	25.3	62.1	5510	2150	42.8	78
60	4.2	10	7.02	28.1	54.1	4910	1910	38.4	47
90	4.1	9.9	6.78	30.1	50.3	4550	1720	35.2	16

E) Ozone Coupled with Electrochemical Oxidation at 20 Amps

Date: 6/16/2018

Sample Volume: 3.5 Liters Chloride: 13.325 g/L

Ozonation

Time	pH	COD (mg/L)	NH4 (mg/L)	Turbidity (NTU)
0	7.52	6710	2550	1000
10	7.6	6340	2470	1000
25	7.81	6250	2390	1000
45	7.7	5740	2310	1000

Electrochemical Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turb (NTU)
0	4.7	20	7.81	22.3	79.3	5740	2310	49.3	13
15	4.9	19.9	7.73	26.2	48.84	5520	2110	26.87	9
30	4.7	20	6.92	28.1	48.53	5210	1950	24.68	6
60	4.7	20	5.75	32.9	50.1	4560	1660	24.7	4
90	4.8	20	5.4	37.1	46.3	3810	1450	23.1	1

F) Ozone Coupled with Electrochemical Oxidation at 30 Amps

Date: 6/28/2018

Sample Volume: 3.5 Liters Chloride: 13.325 g/L

Ozonation

Time	pH	COD (mg/L)	NH4 (mg/L)	Turbidity (NTU)
0	7.2	6850	2510	1000
10	7.5	6310	2400	1000
25	7.9	6260	2290	1000
45	7.1	5740	2270	1000

Electrochemical Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turb (NT)
0	6.1	30	7.41	26	78.5	5740	2270	50.06	1
15	6.2	30	7.71	34.5	60.1	5190	1990	36.1	4
30	6.1	30	6.24	39.6	56.3	4700	1770	34.4	7
60	6	30	5.12	41.6	54.1	3950	1450	33.9	3
90	6.3	30	4.8	43.7	52.1	3280	1210	31.3	2

G) Two stage Electrochemical Oxidation at 10 Amps

Date: 3/20/2019

Sample Volume: 4 liters Chloride: 8.6 g/L

Origin Clear Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turb (NT)
0	4.8	20	7.72	20.81	34.51	6730	2860	24.38	218
20	5.1	19.9	7.67	25.71	36.24	6320	2820	23.25	143
40	5.2	20	7.27	29.05	38	5940	2520	23.34	93
60	5.4	20	7.1	33.39	40.98	5710	2390	22.97	66
Break	5.4	10	7.4	31.33	39.43	5830	2500	22.86	98

Electrochemical Oxidation with Magneli Reactor

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turb (NT)
30	5.8	10.2	7.42	32.04	37.79	5720	2450	21.64	65
60	5.8	10.3	7.48	33.6	37.89	5590	2230	21.09	47
90	5.8	10.5	7.52	34.41	39.08	5440	2000	21.54	36

H) Two stage Electrochemical Oxidation at 20 Amps

Date: 3/18/2019

Sample Volume: 4 liters Chloride: 8.6 g/L

Origin Clear Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turbid (NTU)
0	4.9	20	8.03	20.63	32.98	6960	2850	23.39	227.0
20	5.1	20	7.3	25.83	34.73	6210	2510	22.21	326.0
40	5.1	20	7.3	29.79	37.48	6040	2300	22.32	155.0
60	5	20	7.07	34.02	39.5	5660	2240	21.89	71.8
Break	6.2	20	7.37	3.84	37.83	5910	2490	21.75	108.0

Electrochemical Oxidation with Magneli Reactor

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turbid (NTU)
30	6.3	20.1	7.21	38.58	40.96	5690	2270	21.14	68.0
60	6.4	20.1	7.57	42.52	42.02	5460	2050	20.45	42.5
90	6.3	20	7.08	42.88	42.88	5300	1820	19.96	24.5

I) Two stage Electrochemical Oxidation at 30 Amps

Date: 3/22/2019

Sample Volume: 4 liters Chloride: 8.6 g/L

Origin Clear Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turbid (NTU)
0	5.4	20	7.72	20.83	34.86	6520	2830	24.62	186.0
20	5.4	20	7.57	26.25	37.73	6200	2540	23.96	129.0
40	5	20	7.32	30.15	39.77	5690	2490	23.53	80.0
60	5	20	7.28	33.69	41.79	5700	2380	23.3	54.0
Break	8.2	30	7.46	31.49	36.23	5790	2510	2096	88.0

Electrochemical Oxidation with Magneli Reactor

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS	Turbid (NTU)
30	8.3	30.1	7.43	43.75	46.41	5320	2190	22.15	41.0
60	7.9	30	7.41	53	47.4	4750	1720	16.80	16.0
90	7.9	30	7.57	51.63	47.15	4100	1480	20.32	7.1

J) Fenton Optimization

Date: 4/23/2019

Sample Volume: 0.5 Liters Chloride: 8.6 g/L

Test with different molar ratio of reagent with constant H₂O₂

Fe ⁺⁺ :H ₂ O ₂ (molar)		1:1	1:2	1:5	1:10	1:20
FeSO ₄ :H ₂ O ₂ (gm)		13.4:10	6.7:10	2.68:10	1.34:10	0.67:10
Dosage	Fe ²⁺		4.93	1.97	0.99	0.49
	H ₂ O ₂ (mg/L)	6,000	6,000	6,000	6,000	6,000
Initial	Temp (°C)	20.6	20.5	20.5	20.4	20.5
	pH	7.71	7.67	7.77	7.67	7.72
	Turbidity (NTU)	217	217	217	217	217
	NH ₄ (mg/L)	3090	3090	3090	3090	3090
	COD (mg/L)	5800	5800	5800	5800	5800
pH adjustment	Temp (°C)	21.1	21.3	21.2	22.3	21.3
	pH	2.47	2.46	2.5	2.48	2.46
pH adjustment	Temp (°C)	25.3	24.4	25.9	26.1	24.2
	pH	7.92	7.94	7.95	7.97	7.97
Final	Turbidity (NTU)	196	71.6	283	110	97.5
	NH ₄ (mg/L)	2970	2800	2640	2765	2800
	COD (mg/L)	3075	2750	2625	3650	4675

K) Fenton Optimization

Date: 4/24/2019

Sample Volume: 0.5 Liters Chloride: 8.6 g/L

Test with different molar ratio maintaining same molar ratio

Fe ⁺⁺ :H ₂ O ₂ (molar)	1:5	1:5	1:5	1:5
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FeSO4:H2O2 (mg)		1117:4167	2234:8333	3351:12500	4468:16667
Dosage	Fe2+	0.821241	1.642483	2.463724	3.284965
	H2O2 (mg/L)	2500	5000	7500	10000
Initial	Temp (°C)	21	20.9	21	21.1
	pH	8.1	8.07	8.15	8.14
	Turbidity (NTU)	194	194	194	194
	NH4(mg/L)	2910	2910	2910	2910
	COD (mg/L)	6975	6975	6975	6975
pH adjustment	Temp (°C)	21.9	21.7	21.8	22.1
	pH	2.5	2.49	2.49	2.51
pH adjustment	Temp (°C)	24.5	25.6	24.5	24.2
	pH	7.97	7.95	8.01	8.05
Final	Turbidity (NTU)	278	478	296	516
	NH4(mg/L)	2880	2840	2810	2780
	COD (mg/L)	3350	2775	2730	2675

L) Fenton Coupled with Electrochemical Oxidation at 10 Amps

Date 5/4/2019

Sample Volume: 5 Liters Chloride 8.6 g/L

Fe⁺⁺:H₂O₂ (molar): 1:5 FeSO₄: 11170 gm H₂O₂: 41667 gm

Fenton

	Temp (°C)	pH	Turbidity (NTU)	NH4 (mg/L)	COD (mg/L)
Initial	20	7.58	230	3040	6300
Final	22	8.03	210	2950	4975

Magneli Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	TDS	COD (mg/L)	NH4 (mg/L)	Tu (NTU)
0	5.4	10	7.4	31.33	39.43	22.86	4975	2950	204
30	5.8	10.2	7.42	32.04	37.79	21.64	4620	2860	204
60	5.8	10.3	7.48	33.6	37.89	21.09	4350	2640	174
90	5.8	10.5	7.52	34.41	39.08	21.54	3950	2450	174

M) Fenton Coupled with Electrochemical Oxidation at 20 Amps

Date 5/2/2019

Sample Volume: 5 Liters Chloride: 8.6 g/L

Fe⁺⁺:H₂O₂ (molar): 1:5 FeSO₄: 11170 gm H₂O₂: 41667 gm

Fenton

	Temp (°C)	pH	Turbidity (NTU)	NH4 (mg/L)	COD (mg/L)
Initial	18.1	7.64	204	2940	5425
Final	22.4	8.05	174	2610	3900

Magneli Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	TDS	Sp Cond (mS/cm)	COD (mg/L)	Tu (NTU)
0	5.3	20	6.87	21.17	37.51	26.31	40.47	3900	204
30	5.4	20.1	5.86	28.77	42.53	25.79	39.68	3645	204
60	5.2	20	3.84	34.09	45.95	25.45	39.15	3450	174
90	4.9	20	2.89	38.33	47.46	24.59	37.83	3210	174

N) Fenton Coupled with Electrochemical Oxidation at 30 Amps

Date 5/3/2019

Sample Volume: 5 Liters Chloride: 8.6 g/L

Fe⁺⁺:H₂O₂ (molar): 1:5 FeSO₄: 11170 gm H₂O₂: 41667 gm

Fenton

	Temp (°C)	pH	Turbidity (NTU)	NH4 (mg/L)	COD (mg/L)
Initial	18.5	7.96	250	3150	6575
Final	22	8.08	134	2800	4734

Magneli Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	TDS	Sp Cond (mS/cm)	COD (mg/L)	
0	6.7	29.9	7.15	21.35	44.84	31.33	48.19	4735	
30	6.2	30.1	5.22	34.19	55.38	30.62	47.11	4380	
60	6.1	30	4.35	42.65	61.72	30	46.16	4010	
90	5.6	30	3.65	49.29	46.41	20.6	31.78	3650	

O) Two stage Electrochemical Oxidation for Extended hours

Date 5/9/2019 Sample Vol 4 liters Chloride 8.6 g/L

Origin Clear Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	Sp Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS
0	5.9	20.1	7.88	21.49	43.11	46.21	7100	3420	30.04
30	5.8	19.9	7.77	29.93	49.19	44.96	6500	3000	29.22
60	5.7	19.9	7.63	35.54	53.53	44.95	6350	2930	28.96
90	5.7	20	7.61	40.84	57.65	44.26	6150	2960	28.77

Magneli Advanced Oxidation

Time	Volts (v)	Amps (A)	pH	Temp (C)	Cond (mS/cm)	Sp Cond (mS/cm)	COD (mg/L)	NH4 (mg/L)	TDS
0	5.5	20.1	7.59	34.7	52.08	43.94	6180	3060	28.56
30	6.2	20	7.71	39	53.45	42.17	5855	2740	27.41
60	6.2	19.9	7.68	42.62	55.21	41.31	5610	2480	26.85
90	6.5	19.9	8.09	31.67	45.38	40.25	5405	2380	26.16
120	6.3	20	8.1	34.15	46.36	39.46	5330	2160	25.65
150	6.5	20	8.02	38.35	48.84	38.19	4920	2110	25.29
180	6.4	19.9	7.98	41.02	50.2	38.44	4805	1830	24.98
210	6.6	19.9	8.2	31	42.2	37.69	4680	1740	24.51
240	6.4	20	7.73	35.45	44.82	37.37	4320	1580	24.29
270	6.2	20.3	7.66	40.05	47.14	36.61	4100	1320	23.8
300	6.2	20.4	7.54	41.12	46.87	35.83	4040	1080	23.29
330	6.1	20.1	7.43	30.4	45.1	34.7	3750	870	22.55
360	6.1	20.2	7.23	32.3	45.3	35.1	3640	760	22.81
390	6.2	19.9	6.9	34.4	44.8	34.62	3520	730	22.51
420	6.3	20.2	6.23	35.9	43.1	34.45	3470	690	22.39

P) THMs and HAA5 Results from LC/MS

THM analyzed on 06/17/19

Haloacetic acid analyzed on 06/18/19

Sample	Bromodichloromethane	Bromoform	Chloroform	Dibromochloromethane	Total Trihalomethane	Dibromoacetic Acid	Dichloroacetic Acid	Monobromoacetic Acid	Monochloroacetic Acid	Trichloroacetic Acid
RAW	<4.58	<3.24	<5.20	<6.48	-	<60	95	<90	<90	32.2
Spike	<4.58	<3.24	<5.20	<6.48	-	<60	27.1	<90	<90	<30
Fenton + 10-amp EOx	863	1140	509	1400	3900	9830	22700	14300	11500	3210
Fenton + 30-amp EOx	1760	1850	844	2700	7200	7920	16000	15800	7240	3960
Ozone + 20-amp Eox	1540	708	1700	1560	5500	5820	21900	3840	11300	8030
Lime + 20-amp Eox	887	908	678	1160	3600	2640	3650	413	7360	249
Extended Two Stage Eox (20 amps)	2020	3080	1170	3510	9800	5300	23500	5430	23900	5900
Only Roughing	3020	825	3450	2220	9500	4920	13600	38600	3430	9790
Roughing + 20-amp Eox	4160	2340	2950	5240	15000	3650	11200	9890	7350	5400

* all are in µg

6 REFERENCES

- Abbas, A. A., Jingsong, G., Ping, L. Z., Ya, P. Y., & Al-Rekabi, W. S. (2009). Review on landfill leachate treatments. *American Journal of Applied Sciences*.
<https://doi.org/10.3844/ajas.2009.672.684>
- Ahmed, F. N., & Lan, C. Q. (2012). Treatment of landfill leachate using membrane bioreactors: A review. *Desalination*. <https://doi.org/10.1016/j.desal.2011.12.012>
- Anglada, Á., Urtiaga, A., Ortiz, I., Mantzavinos, D., & Diamadopoulos, E. (2011). Boron-doped diamond anodic treatment of landfill leachate: Evaluation of operating variables and formation of oxidation by-products. *Water Research*, *45*(2), 828–838.
<https://doi.org/10.1016/j.watres.2010.09.017>
- Antony, J. (2014). *6 - Full Factorial Designs* (J. B. T.-D. of E. for E. and S. (Second E. Antony, ed.). <https://doi.org/https://doi.org/10.1016/B978-0-08-099417-8.00006-7>
- Bashir, M. J. K., Isa, M. H., Kutty, S. R. M., Awang, Z. Bin, Aziz, H. A., Mohajeri, S., & Farooqi, I. H. (2009). Landfill leachate treatment by electrochemical oxidation. *Waste Management*, *29*(9), 2534–2541. <https://doi.org/10.1016/j.wasman.2009.05.004>
- Bila, D. M., Filipe Montalvão, A., Silva, A. C., & Dezotti, M. (2005). Ozonation of a landfill leachate: Evaluation of toxicity removal and biodegradability improvement. *Journal of Hazardous Materials*, *117*(2–3), 235–242. <https://doi.org/10.1016/j.jhazmat.2004.09.022>
- Brillas, E., Bastida, R. M., Llosa, E., & Casado, J. (1995). Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O₂-fed cathode. *Journal of the Electrochemical Society*, *142*(6), 1733–1741.
- Calace, N., Liberatori, A., Petronio, B. M., & Pietroletti, M. (2001). Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals. *Environmental Pollution*. [https://doi.org/10.1016/S0269-7491\(00\)00186-X](https://doi.org/10.1016/S0269-7491(00)00186-X)
- Chaturapruek, A., Visvanathan, C., & Ahn, K. H. (2005). Ozonation of membrane bioreactor effluent for landfill leachate treatment. *Environmental Technology*.
<https://doi.org/10.1080/09593332608618583>
- Chiang, L. C., Chang, J. E., & Wen, T. C. (1995). Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. *Water Research*, *29*(2), 671–678.
[https://doi.org/10.1016/0043-1354\(94\)00146-X](https://doi.org/10.1016/0043-1354(94)00146-X)

- Chiang, L., Chang, J., & Wen, T. (1995). Electrochemical oxidation process for the treatment of coke plant wastewater. *Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology*, 30(4), 753–771.
<https://doi.org/10.1080/10934529509376231>
- Chu, L. M., Cheung, K. C., & Wong, M. H. (1994). Variations in the chemical properties of landfill leachate. *Environmental Management*. <https://doi.org/10.1007/BF02393753>
- Cortez, S., Teixeira, P., Oliveira, R., & Mota, M. (2010). Ozonation as polishing treatment of mature landfill leachate. *Journal of Hazardous Materials*, 182(1–3), 730–734.
<https://doi.org/10.1016/j.jhazmat.2010.06.095>
- Deng, Y. (2007). Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *Journal of Hazardous Materials*, 146(1–2), 334–340.
<https://doi.org/10.1016/j.jhazmat.2006.12.026>
- Deng, Y., & Englehardt, J. D. (2006a). Treatment of landfill leachate by the Fenton process. *Water Research*, 40(20), 3683–3694. <https://doi.org/10.1016/J.WATRES.2006.08.009>
- Deng, Y., & Englehardt, J. D. (2006b). Treatment of landfill leachate by the Fenton process. *Water Research*, 40(20), 3683–3694. <https://doi.org/10.1016/j.watres.2006.08.009>
- El-Shal, W., Khordagui, H., El-Sebaie, O., El-Sharkawi, F., & Sedahmed, G. H. (1994). Electrochemical generation of ozone for water treatment using a cell operating under natural convection. *Desalination*. [https://doi.org/10.1016/0011-9164\(94\)00124-3](https://doi.org/10.1016/0011-9164(94)00124-3)
- Fatta, D., Papadopoulou, A., & Loizidou, M. (1999). A study on the landfill leachate and its impact on the groundwater quality of the greater area. *Environmental Geochemistry and Health*. <https://doi.org/10.1023/A:1006613530137>
- Feki, F., Aloui, F., Feki, M., & Sayadi, S. (2009). Electrochemical oxidation post-treatment of landfill leachates treated with membrane bioreactor. *Chemosphere*, 75(2), 256–260.
<https://doi.org/10.1016/j.chemosphere.2008.12.013>
- Guzzella, L., Feretti, D., & Monarca, S. (2002). Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply. *Water Research*. [https://doi.org/10.1016/S0043-1354\(02\)00145-8](https://doi.org/10.1016/S0043-1354(02)00145-8)
- Han, Z., Ma, H., Shi, G., He, L., Wei, L., & Shi, Q. (2016). A review of groundwater contamination near municipal solid waste landfill sites in China. *Science of the Total Environment*. <https://doi.org/10.1016/j.scitotenv.2016.06.201>

- Hassan, M., Zhao, Y., & Xie, B. (2016). Employing TiO₂ photocatalysis to deal with landfill leachate: Current status and development. *Chemical Engineering Journal*.
<https://doi.org/10.1016/j.cej.2015.09.093>
- Kurniawan, T. A., Lo, W. H., & Chan, G. Y. S. (2006). Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials*, 129(1–3), 80–100. <https://doi.org/10.1016/j.jhazmat.2005.08.010>
- Lanza, M. R. V., & Bertazzoli, R. (2002). Cyanide oxidation from wastewater in a flow electrochemical reactor. *Industrial and Engineering Chemistry Research*, 41(1), 22–26.
<https://doi.org/10.1021/ie010363n>
- Li, X. M., Wang, M., Jiao, Z. K., & Chen, Z. Y. (2001). Study on electrolytic oxidation for landfill leachate treatment. *China Water and Wastewater*, 17(8), 14–17.
- Lopez, A., Pagano, M., Volpe, A., & Di Pinto, A. C. (2004). Fenton's pre-treatment of mature landfill leachate. *Chemosphere*, 54(7), 1005–1010.
<https://doi.org/10.1016/j.chemosphere.2003.09.015>
- Mandal, P., Dubey, B. K., & Gupta, A. K. (2017). Review on landfill leachate treatment by electrochemical oxidation: Drawbacks, challenges and future scope. *Waste Management*, 69, 250–273. <https://doi.org/10.1016/j.wasman.2017.08.034>
- Meeroff, D. E., Bloetscher, F., Reddy, D. V., Gasnier, F., Jain, S., McBarnette, A., & Hamaguchi, H. (2012). Application of photochemical technologies for treatment of landfill leachate. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2012.01.028>
- Meeroff, D. E., & Lakner, J. (2015). *Safe Discharge of Landfill Leachate to the Environment Co-Author*. (March).
- Meeroff, D. E., & Teegavarapu, R. (2010). *Interactive decision support tool for leachate management*. Gainesville, FL.
- Mohamadshafiee, M. R., & Taghavi, L. (2012). Health Effects of Trihalomethanes as Chlorinated Disinfection by Products : A Review Article. *International Journal of Environmental and Ecological Engineering*.
- Mor, S., Ravindra, K., Dahiya, R. P., & Chandra, A. (2006). Leachate Characterization and Assessment of Groundwater Pollution Near Municipal Solid Waste Landfill Site. *Environmental Monitoring and Assessment*, 118(1–3), 435–456.
- Naumczyk, J., Szpyrkowicz, L., & Zilio-Grandi, F. (1996). Electrochemical treatment of textile

- wastewater. *Water Science and Technology*, 34(11), 17–24.
[https://doi.org/https://doi.org/10.1016/S0273-1223\(96\)00816-5](https://doi.org/https://doi.org/10.1016/S0273-1223(96)00816-5)
- Panizza, M., & Martinez-Huitle, C. A. (2013). Role of electrode materials for the anodic oxidation of a real landfill leachate - Comparison between Ti-Ru-Sn ternary oxide, PbO₂ and boron-doped diamond anode. *Chemosphere*.
<https://doi.org/10.1016/j.chemosphere.2012.09.006>
- Peng, Y. (2017). Perspectives on technology for landfill leachate treatment. *Arabian Journal of Chemistry*. <https://doi.org/10.1016/j.arabjc.2013.09.031>
- Pérez, M., Torrades, F., Domènech, X., & Peral, J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water Research*. [https://doi.org/10.1016/S0043-1354\(01\)00506-1](https://doi.org/10.1016/S0043-1354(01)00506-1)
- Qasim, S. R. (2017). *Sanitary landfill leachate: generation, control and treatment*. Routledge.
- Qian, X., Koerner, R. M., & Gray, D. H. (2002). Geotechnical aspects of landfill design and construction. In *Prentice Hall*.
- Raghab, S. M., Abd El Meguid, A. M., & Hegazi, H. A. (2013). Treatment of leachate from municipal solid waste landfill. *HBRC Journal*, 9(2), 187–192.
<https://doi.org/10.1016/j.hbrcj.2013.05.007>
- Rao, N. N., Somasekhar, K. M., Kaul, S. N., & Szpyrkowicz, L. (2001). Electrochemical oxidation of tannery wastewater. *Journal of Chemical Technology and Biotechnology*, 76(11), 1124–1131. <https://doi.org/10.1002/jctb.493>
- Renou, S., Poulain, S., Givaudan, J. G., & Moulin, P. (2008). Treatment process adapted to stabilized leachates: Lime precipitation-prefiltration-reverse osmosis. *Journal of Membrane Science*, 313(1–2), 9–22. <https://doi.org/10.1016/j.memsci.2007.11.023>
- Sahoo, P., & Barman, T. K. (2012). 5 - ANN modelling of fractal dimension in machining. In J. P. B. T.-M. and M. E. Davim (Ed.), *Woodhead Publishing Reviews: Mechanical Engineering Series* (pp. 159–226).
<https://doi.org/https://doi.org/10.1533/9780857095893.159>
- Shehzad, A., Bashir, M. J. K., Sethupathi, S., & Lim, J. W. (2015). An overview of heavily polluted landfill leachate treatment using food waste as an alternative and renewable source of activated carbon. *Process Safety and Environmental Protection*.
<https://doi.org/10.1016/j.psep.2015.09.005>
- Stucki, S., Baumann, H., Christen, H. J., & Kötz, R. (1987). Performance of a pressurized

electrochemical ozone generator. *Journal of Applied Electrochemistry*.
<https://doi.org/10.1007/BF01007814>

SWA End of Year Review. (2013). West Palm Beach.

Tatsi, A. A., Zouboulis, A. I., Matis, K. A., & Samaras, P. (2003). Coagulation-flocculation pretreatment of sanitary landfill leachates. *Chemosphere*, *53*(7), 737–744.
[https://doi.org/10.1016/S0045-6535\(03\)00513-7](https://doi.org/10.1016/S0045-6535(03)00513-7)

Trujillo, D., Font, X., & Sánchez, A. (2006). Use of Fenton reaction for the treatment of leachate from composting of different wastes. *Journal of Hazardous Materials*, *138*(1), 201–204.
<https://doi.org/10.1016/j.jhazmat.2006.05.053>

Turro, E., Giannis, A., Cossu, R., Gidarakos, E., Mantzavinos, D., & Katsaounis, A. (2012). Reprint of: Electrochemical oxidation of stabilized landfill leachate on DSA electrodes. *Journal of Hazardous Materials*, *207–208*(1–3), 73–78.
<https://doi.org/10.1016/j.jhazmat.2012.01.083>

Umar, M., Aziz, H. A., & Yusoff, M. S. (2010). Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste Management*, *30*(11), 2113–2121.
<https://doi.org/10.1016/j.wasman.2010.07.003>

Villanueva, C. M., Cordier, S., Font-Ribera, L., Salas, L. A., & Levallois, P. (2015). Overview of Disinfection By-products and Associated Health Effects. *Current Environmental Health Reports*. <https://doi.org/10.1007/s40572-014-0032-x>

Vlyssides, A. G., Israilides, C. J., Loizidou, M., Karvouni, G., & Mourafeti, V. (1997). Electrochemical treatment of vinasse from beet molasses. *Water Science and Technology*.
[https://doi.org/10.1016/S0273-1223\(97\)00398-3](https://doi.org/10.1016/S0273-1223(97)00398-3)

Yoshida, M., Sothom, A., Souissi, N., Bousselmi, L., Jedidi, N., Ghrabi, A., & Ferchichi, M. (2002). *Characterization of leachate from Henchir El Yahoudia closed landfill*.

Zhang, H., Heung, J. C., & Huang, C. P. (2005). Optimization of Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials*, *125*(1–3), 166–174.
<https://doi.org/10.1016/j.jhazmat.2005.05.025>

Zhang, H., Ran, X., Wu, X., & Zhang, D. (2011). Evaluation of electro-oxidation of biologically treated landfill leachate using response surface methodology. *Journal of Hazardous Materials*, *188*(1–3), 261–268. <https://doi.org/10.1016/j.jhazmat.2011.01.097>

Zhang, W., Yue, B., Wang, Q., Huang, Z., Huang, Q., & Zhang, Z. (2011). Bacterial community

composition and abundance in leachate of semi-aerobic and anaerobic landfills. *Journal of Environmental Sciences*. [https://doi.org/10.1016/S1001-0742\(10\)60613-4](https://doi.org/10.1016/S1001-0742(10)60613-4)

Zhou, Q., Li, W., & Hua, T. (2010). Removal of organic matter from landfill leachate by advanced oxidation processes: A review. *International Journal of Chemical Engineering*, 2010. <https://doi.org/10.1155/2010/270532>