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EFFECTS OF COAGULATION AND FENTON'S OXIDATION ON THE REMOVAL OF UV-QUENCHING SUBTANCES IN LANDFILL LEACHATE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Earth Sciences

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by
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Accepted by
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ABSTRACT

Landfills are the primary method to dispose of municipal solid waste, and the water leaching from landfills contains products of physiochemical and biochemical reactions, presenting an important environmental challenge. In many cases, leachate is diverted to publicly owned treatment works (POTWs) for treatment. However, even if leachate contributes less than 1% of the total wastewater flow, recalcitrant dissolved organic matter (DOM) containing ultraviolet-quenching substances (UVQs) remains in the leachate after biological treatment, contributing to a low UV transmittance, thus also decreasing the effectiveness of UV disinfection. To analyze the removal of UVQS of landfill leachate before sent to POTWs, this study researches and compares coagulation/flocculation and Fenton's oxidation, an advanced oxidation process, to remove UVQS in landfill leachate by analyzing the differences in soluble chemical oxygen demand (sCOD), dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}), specific UV absorbance at 254 nm ($SUVA_{254}$) and tryptophan, fulvic acid, tyrosine, and marine humic acid-like fluorescent intensities with an excitation emission matrix (EEM) and functional groups with Fourier-transform infrared spectroscopy (FTIR) to better understand the removal mechanisms. This study also evaluates a Fenton's dimensionless oxidant dose (DOD) of 0.7 for three different leachates to analyze trends in treatment levels. DOD is a normalization of the reactive oxygen present to the initial sCOD. During coagulation studies, three initial pH values (5.5, 6.5, and 8.2) and $FeCl_3$ dosages (1 g/L, 5 g/L, 10 g/L) were studied. Initial pH of 6.5 and 10 g/L $FeCl_3$ dosage reached the maximum DOC removal, and UVA_{254} and $SUVA_{254}$ reduction, reaching 65.1%, 2.6 cm^{-1} (from 22.4 cm^{-1}), and 0.62 L/mg-M (from 1.86 L/mg-M), respectively. This treatment also had large DOM removals with an affinity toward fulvic acids, however it was not effective in removing carboxylic acid functional groups. For Fenton's oxidation, first, two leachate samples taken from a landfill in Greenville County, SC, at different times, treated with a 24-hour reaction time at a DOD from 0.07-0.72 with a molar ratio of 5:2 for H_2O_2:$FeCl_2$ at pH 4, were studied. The 0.72 DOD dose led to the highest decrease in UVA_{254} to 4.2 cm^{-1} and $SUVA_{254}$ to 0.63 L/mg-M, with a DOC removal of 48.8%. All treatments targeted fulvic acids above other DOM. The higher the DOD, the more DOM removed, and the better able Fenton's oxidation was at breaking down the C=C in aromatics and COO^- in carboxylic acids. From analyzing the precipitate formed during Fenton's treatment, it was also found that at lower DOD doses the treatment is partially due to coagulation only, whereas at higher concentrations the treatment oxidation accounted for all DOC removal. When comparing these results to a leachate taken from a landfill in Orange County, FL treated with a 0.7 DOD, the removal trends of DOC, $UVA_{254,}$ and $SUVA_{254}$ were not consistent, suggesting normalizing treatment requirements for UVQS removal may be better with $SUVA_{254}$ instead of sCOD This research successfully shows that coagulation/flocculation and Fenton's oxidation can remove UVQS, but due to the complex nature of the UVQS, neither treatment removes all constituents. The results indicate coagulation/flocculation will result in better treatment, but it is likely Fenton's oxidation will result in a larger number of biodegradable organics that can be removed during biological treatment at a POTW.

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LIST OF ABBREVIATIONS

Aluminum sulphate	Alum.
Artificial neutral networks	ANN.
Biochemical oxygen demand	BOD.
Chemical oxygen demand	COD.
Code of Federal Regulations	CFR.
Deionized	DI.
Dimensionless oxidant dose	DOD.
Dissolved organic carbon	DOC.
Dissolved organic matter	DOM.
Environmental Protection Agency	EPA.
Excitation emission matrix	EEM.
Fulvic acid	FA.
Fourier-transform infrared	FTIR.
Gas chromatography-mass spectroscopy	GC-MS.
Hydrophilic	Hpi.
Humic acid	HA.
Hydroxyl radical	·OH.
Isoelectric point	IEP.
Molecular weight cut-off filtration	MWCO.
Municipal solid waste	MSW.
National Pollution Discharge Elimination System	NPDES.
Nuclear magnetic resonance	NMR.

LIST OF ABBREVATIONS (CONTINUED)

Orange County leachate sample 1	OC-1.
Orange County leachate sample 2	OC-2.
Parallel factor analysis	PARAFAC.
Publicly owned treatment work	POTW.
Renewable Water Resources	ReWa.
Resource Conservation and Recovery Act	RCRA.
Response Surface Methodology	RSM.
Self-organizing maps	SOM.
Sequencing batch reactor	SBR.
Sludge volume index	SVI.
Soluble chemical oxygen demand	sCOD.
Specific UV absorbance at 254 nm	SUVA254.
Scanning electron microscope-energy dispersive X-ray spectroscopy	SEM-EDS.
Two-dimensional correlation spectroscopy	2D-COS.
Twin Chimney's February 2019 leachate	TC-2019.
Twin Chimney's July 2018 leachate	TC-2018.
Ultraviolet-quenching substances	UVQS.
Ultraviolent	UV.
UV absorbance at 254 nm	UVA254.
UV transmittance	UVT.
UV- visible spectroscopy	UV-VIS.
UV at 254 nm	UV254.
Volatile organic acid	VOA.

1 INTRODUCTION

In the United States, during 2015, roughly 137 million tons of municipal solid waste (MSW) was disposed of in landfills [1]. Due to the magnitude of waste being discarded by consumers, the Environmental Protection Agency (EPA), regulates non-hazardous waste under Subtitle D of the Resource Conservation and Recovery Act (RCRA) and Title 40 of the Code of Federal Regulations (CFR) Part 258. A large portion of these regulations include; constructing liners to prevent leachate releases, leachate collection and removal systems, groundwater monitoring for leachate releases, and corrective actions if leachate has been released. Leachate is produced during precipitation events when the water infiltrates uncapped, or poorly capped, landfills causing the water to take up the constituents from the decomposing waste it encounters. Aside from uptake of harmful compounds from the waste as the leachate migrates, there can also be several reactions taking place changing the composition of the water. These include physical changes by dispersion or filtration, chemical changes by oxidation-reduction (redox) reactions or hydrolysis, or biological changes by biodegradation [2], [3]. With one ton of MSW producing roughly 0.2 m^3 of leachate, 27.4 million m^3 of leachate was generated from landfills in 2015 alone in the United States [4].

Since landfills are a mixture of nonhazardous wastes from residents, industries, and commercial entities, there is a wide variety of objects being disposed of. In 2015, food, plastics, rubber, metal, and paper/cardboard made up 74.5% of the total MSW landfilled. The complete item break down for 2015 can be found in **Appendix A, Table A-1** [1]. Since the infiltrating water reacts with the chemicals released during each waste's decomposition, leachate can contain many harmful substances, including halogenated organics, polychlorinated biphenyls, and heavy metals. Also due to the anaerobic biological processes of waste decomposition, leachate can contain high concentrations of ammonia, chlorides, dissolved organic matter (DOM), and sulfates [5]. If untreated leachate is discharged to surface water, it can deplete the oxygen disrupting the stream bottom fauna, flora, and cause ammonia toxicity, in turn affecting recreational activities and possibly drinking water supplies [6]. It can also seep into the groundwater from breaks in the landfill liner or if leachate holding ponds are used. Studies have shown when this occurs the chloride, sulfates, metals, and nitrate levels in the nearby groundwater wells are above the recommended values from the World Health Organization and the regulated maximum contaminant levels from the EPA [7]–[11]. Since untreated leachate is full of constituents harmful to ecosystems and human health, untreated leachate presents a variety of environmental problems.

To avoid receiving water pollution, landfills are often lined with a geo-membrane over compacted clay with a leachate collection system installed [2]. The collected leachate can then either be treated on-site or off-site. When treated on-site, the facility must abide by a National Pollution Discharge Elimination System (NPDES) permit with 40 CFR Part 445 regulations [12]. To minimize cost for treatment and the complexity of an entire onsite system, leachate is often sent to be treated at publicly owned treatment works (POTWs). According the EPA, landfill leachate wastewater flows are often less than one percent of the total POTW flow [13], [14]. Due to leachate's high chemical oxygen demand (COD) concentrations ranging from 2,000-10,000 mg/L, initial leachate treatment studies looked at optimizing COD removal, to minimizing any shock loading to the wastewater plant [15]. Sequencing batch reactors (SBRs) are often used for biological pretreatment on site at the landfills if the BOD (biochemical oxygen demand)/COD is high enough, and have been found to remove 62-95% of COD [16]–[19]. Membranes have also been studied to treat leachate, with microfiltration reaching 25-35% COD removal, ultrafiltration from 10-98% (highly dependent on the material used), and reverse osmosis above 98% [20]–[23].

Physio-chemical methods are also used, with coagulation-flocculation able to remove 25-80% COD (depending on landfill age and coagulant used) and adsorption 50-80% (depending on material used) [24]–[26]. Chemical oxidation has also been researched, using ozonation, peroxone, Fenton's oxidation, and photochemical methods. These processes have ranged from 40-90% COD removal [27], [28]. As mentioned, the treatment used is highly dependent on the landfill age. As will be discussed in **Section 2.1**, the younger the landfill, the more biodegradable the organics within the leachate are, making a biological process more applicable. Whereas, when a landfill ages, the organics are dominated by more recalcitrant molecules that are often larger and can be easier to remove by a physical means. Or a chemical oxidation process can be used to break down the larger organics to be more biodegradable.

Many POTWs have started using ultraviolent (UV) disinfection since it can inactivate pathogens without leaving a residual and provide a safer work environment than chlorination. However, even after biological treatment, leachate contains a large amount of UV-quenching substances (UVQS) that can interfere with UV disinfection. The UVQS are recalcitrant DOM that can absorb UV light and cause a low UV transmittance (UVT), threatening the facility's ability to meet its NPDES permit if not enough pathogens are removed. Or, to meet permit limits, wastewater facilities can increase the intensity of their lamps to meet the dosage required. Facilities with medium-pressure lamps can have 15-20 times the UV intensity of low-pressure ones, but increased intensity means a higher energy demand and higher cost for the replacement of lamps. The recalcitrant DOM is primarily from the high concentration of humic substances in the decomposing paper, yard trimmings, and wood products, releasing lignin unable to be removed during pretreatment [4], [29]–[33].

Most UV systems need a 65% UVT of water to be considered effective at a UV wavelength of 254 nm (UV_{254}). As wastewater leaves secondary clarification at POTWs, the UVT can range from 66-72% [34], [35]. Landfill leachate can range from $1.9\text{x}10^{-3}$ % to even $1.6\text{x}10^{-33}$ % UVT, depending on the landfill's age and composition. This means that UV disinfection needs a maximum UV_{254} absorbance (UVA_{254}) of roughly 0.19 cm^{-1}, and untreated leachate can range from 4.7 cm^{-1} to 34.8 cm^{-1} [36], [37]. Although there is no requirement for the UVT of leachate, with such a low initial UVT, it still has a significant impact on the overall UVT once mixed with domestic wastewater. Due to the increase in popularity of UV disinfection and the issues leachate poses to its effectiveness, it is important to research methods to reduce these impacts.

1.1 LITERATURE REVIEW

This research studies the effects two treatments - coagulation/flocculation and Fenton's oxidation - on the removal of UVQS in landfill leachate. The current research on these topics has one large unknown; a lack of understanding about what the effect of treatment on the transformation of UVQS is. This research aims to answer the questions. What DOM is being removed by coagulation or oxidation? What DOM is likely being transformed into simpler compounds? What in the leachate is being broken down from treatment and what still contributes to a lower UVT despite treatment? Is this trend consistent with different leachates? What is the best way to determine the dosage required to treat varying leachates?

Former research on Fenton's oxidation treatment of landfill leachate has focused heavily on optimizing the H_2O_2:Fe^{2+} dosing ratio and initial solution pH. Optimization success was primarily based on COD removal. A breakdown of the research conducted on landfill leachate using Fenton's oxidation can be found in **Table 1** and includes the landfill age, pretreatment, optimization parameters, mixing/reaction time, characteristics measured, and analytical methods used.

Table 1: Research conducted on landfill leachate with treatment by Fenton's oxidation.

Landfill Age (yrs)	Leachate Pretreatment	H_2O_2:Fe^{2+} Ratio	pH	Mixing and Reaction Time	Characteristics Measured	Analytic Methods	Ref. and Year
26	0.7 µm Filter	3-9 molar	3-9, 9 after reaction	60 min reaction, pH change, 20 min at 20 rpm 120 min 30°C water bath	UVA_{254}, DOC	FTIR 2D-COS, EEM-PARAFAC	[38] 2018
N/A	N/A	2-10 molar	3-9, 7.5 after reaction	80 sec at 250 rpm, 50 rpm for 5-60 min, 1 hr settling	COD	ANN	[39] 2018
27	SBR, 0.45 µm filter	1.5-16 molar	3-9, 8 after reaction	60 min at 100 rpm, 20 min at 20 rpm, then 30 min settling, 30 min 50°C water bath	DOC, sCOD, UVA_{254}, $SUVA_{254}$	EEM-PARAFAC, DOM fractions, MWCO	[32] 2017
Synthetic Waste	Anaerobic Bioreactor	2.5 molar	4, 7 after reaction	60 min reaction, centrifuge for 10 min and 1.5 µm filter	COD, DOC, $SUVA_{254}$	FTIR, NMR, DOM fraction	[36] 2016
14	Untreated	192	3	96 hr reaction	COD	None	[40] 2015
>20	N/A	1.8 mass	2.5-6, 7 after reaction	10 min reaction, 5 min of increased pH at 100 rpm, 15 min at 30 rpm, 45 min settling	COD	EDS	[41] 2013
N/A and 16	SBR & none	1.6 & 2.4 molar	3-5	5 min at 100 rpm, 25 min at 40 rpm, 1 hr settling	UVA_{254}	DOM fractions, MWCO	[37] 2014

Table 1: Research conducted on landfill leachate with treatment by Fenton's oxidation continued.

Landfill Age (yrs)	Leachate Pretreatment	H_2O_2:Fe^{2+} Ratio	pH	Mixing and Reaction Time	Characteristics Measured	Analytic Methods	Ref. and Year
N/A	N/A	16.7-40 mass	2-8	5-100 min with 0.2min/L air agitator mixing	COD	None	[42] 2011
N/A	Centrifuged	1-5 molar	2-4, 7.5 after reaction	10-20 min at 1,750 rpm, 20 min settling, centrifuged for 10 min	COD	None	[43] 2005
"Old"	N/A	6.3-63 mass	3, 8.5 after reaction	2 hr reaction, pH change, cationic polyelectrolyte coagulant addition, settling	COD	None	[44] 2004

As it can be seen, only recently have studies began looking at changes in UVA_{254} due to Fenton's oxidation. Out of the ten studies listed, only three evaluated changes in UVA_{254} and four used methods that would show changes in the DOM. Fourier-transform infrared spectroscopy (FTIR), which can show the functional groups present, was used alone, but also in conjunction with two-dimensional correlation spectroscopy (2D-COS) to help illustrate the changes in functional groups. Excitation emission matrix (EEM) and parallel factor analysis (PARAFAC) were also used in two studies to show the change in fluorescent DOM. Two studies also separated the DOM by size with molecular weight cut-off filtration (MWCO) to see if the larger or smaller organics were being removed. The last two analytical methods used, DOM fractionation into humic acids (HA), fulvic acids (FA), and hydrophilic (Hpi) compounds and nuclear magnetic resonance (NMR) on HA, may have caused unintended and unwanted changes to the DOM. To separate the DOM, one must do a series of pH changes and filtrations to remove each component. It has been found and will be discussed in **Section 4.2.1**, that adjusting the pH causes irreversible changes to the DOM and can affect COD and DOC measurements. Therefore, it is very likely that during the pH changes, samples were comprised.

Even so, it has been reported that Fenton's oxidation can remove 46-97% of landfill leachate COD and can result in up to a 91% increase in UVA_{254}. EEM showed that humic-like substances had the largest removals. However, even though Hpi was still contributing a significant amount to the DOM, it was not classified using EEM, suggesting a limitation when using EEM alone. FTIR showed that aromatic functional groups were broken down first during oxidation, and MWCO showed that the larger organics were first to degrade. Optimum results were found with $H_2O_2:Fe^{3+}$ molar ratios from 2-4 and initial pH values from 2-6 [13], [32], [48]–[50], [36], [38]–[40], [44]–[47].

At the end of the Fenton's oxidation reaction, the pH is increased to a neutral value to remove any residual iron, forming $Fe(OH)_3$ causing an coagulation effect that can also remove organic matter by physical means. Few studies have researched the effects of treatment by oxidation versus physical removal during Fenton's oxidation. One study found that landfill leachate DOC and sCOD removals were 30% and 40%, respectively, before Fenton's coagulation, and reached 60% and 75%, respectively, after Fenton's coagulation [51]. However, another study on a simulated industrial wastewater found that after Fenton's coagulation and the addition of polyaluminum chloride and a polymer to help facilitate the coagulation, the largest removal increase for COD was from 80.6% to 82.9% [52]. Some studies have even compared Fenton's oxidation treatment to coagulation by itself on the same landfill leachate. They found that they both have an affinity for larger organics (above a molecular weight of 500), reaching 73% removal for both, with Fenton's oxidation resulting in slightly better removal of smaller organics, reaching 43% removal versus coagulation removing 18% [53]. However, COD removals have been found to be very similar, reaching 64.2% for coagulation alone and 63.2% for Fenton's oxidation alone [54]. However, these studies have not focused on UVQS.

Landfill leachate coagulation and flocculation experiments have been focused on optimizing COD removal, with some emphasis on color and turbidity. The optimization tests have been done based on coagulant type, coagulant dosage, and initial solution pH. A breakdown of the research conducted on landfill leachate using coagulation and flocculation can be found in **Table 2** with the landfill age, pretreatment, optimization treatment parameters, mixing/reaction time, characteristics measured, and analytical methods used listed. Out of the twelve studies listed, only three used analytical methods that would help characterize the organic matter being removed; EEM-PARAFAC, FTIR, and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS). SEM-EDS can image the surface of the sludge and measure the elements present on the surface. However, it cannot do this to the entire sample, so one can only analyze a point on the sludge. Nonetheless, these experiments have shown that iron-based coagulation/flocculation can remove 25-80% of COD in leachate, as mostly large humic and fulvic acids. These studies showed optimum results with a pH of 5-8 and 0.7-10 g/L $FeCl_3$ dosage [40], [55], [64], [65], [56]–[63].

Overall, for coagulation, there is very little emphasis on changes in UVA_{254} and an in-depth analysis of the organics removed after treatment so far. For Fenton’s oxidation, it been shown to decrease UVQS by the increase in UVA_{254}, but there are still several unknowns about the treatment levels. For example, some analytical methods have been shown to have limitations when looking at DOM alone and require another method to be used in conjunction. Also, there has been little focus on what is being removed via oxidation versus coagulation with Fenton’s oxidation. Determining the dominating mechanism at varying doses of Fenton’s reagent can help understand the leachate treatment. Studies also use a dimensionless oxidant dose (DOD) for Fenton’s reagent, normalizing the oxidant dose to the initial concentration of COD, but this may not be the most effective method for determining the oxidant dose required for effective treatment. Therefore, with the lack of pertinent information on coagulation/flocculation and Fenton’s oxidation treatment of landfill leachate, this research focuses on the unknowns to gain a better understanding of removing UVQS in landfill leachate.

Table 2: Research conducted on landfill leachate with treatment by coagulation and flocculation with an iron-based-coagulant.

Landfill age (yrs)	Leachate Pretreatment	Dosage (Fe^{3+})	pH range	Mixing and Reaction Time	Characteristics Measured	Analytic Methods	Ref. & Year
"Mature" & "young" from lysimeter	SBR, 0.45 µm filter	0.01-0.60 mol/L	4-9	1 min at 150 rpm, 30 min at 20 rpm, 30 min settling	UVA_{254}, Mixing ratio	DOM fractions, MWCO	[50] 2018
14	N/A	3.4-54.4 mg/L	pH 7	2 min at 250 rpm, 20 min at 70 rpm, and 30 min settling	DOC, DOM fractions	EEM/PARAFAC	[55] 2017
N/A	Untreated	7 g/L	8.1	1 min at 200 rpm, 20 at 40 rpm, 30 min settling	COD	EEM-PARAFAC-SOM	[60] 2017
N/A	N/A	1-13 g/L	2-12	3 min at 150 rpm, 20 min at 40 rpm, 30 min settling	COD	None	[61] 2016
22	Untreated	2-3 g/L	8-12	30-150 minutes at 140 rpm, 60 min settling	COD	RSM	[66] 2015
N/A	N/A	3-4 g/L	4-9	Rapid, flocculation, and sedimentation stage	COD	FTIR (of $FeCl_3$), SVI, IEP	[59] 2014
14	Untreated	0.8-4 g/L	6-11	3 min at 120 rpm, 20 min at 20 rpm, 60 min settling	COD, DOC	None	[40] 2015
> 3 years & <2 years	Untreated	0.2- 1 g/L	7.4	3 min at 160 rpm, 17 min 40 rpm, 60 min settling	COD	None	[58] 2013

Table 2: Research conducted on landfill leachate with treatment by coagulation and flocculation with an iron-based-coagulant continued.

Landfill age (yrs)	Leachate Pretreatment	Dosage (Fe^{3+})	pH range	Mixing and Reaction Time	Characteristics Measured	Analytic Methods	Ref. & Year
10	N/A	2-20 g/L	2-11	5 min at 200 rpm, 25 min at 60 rpm, 30 min settling	COD, HA	SEM-EDS, RSM	[56] 2012
19, 11-7, 5-15 (mixed)	Recirculation	3.7-37 mmol/L	None	5 min at 100 rpm, 25 min at 35 rpm, 30 min settling	DOC, $SUVA_{254}$	EEM	[64] 2011
N/A	N/A	0.1-1 g/L	2-6	5 min at200 rpm, 55 min at 60 rpm	COD	None	[62]2006
"Old", "fresh"	Untreated	<1 g/L - ~5 g/L	9-12	5 min at 200 rpm, 55 min at 60 rpm, 1 hr settling	COD	None	[65] 2003

2 BACKGROUND

2.1 LEACHATE CHARACTERISTICS

To understand landfill leachate composition and characteristics, it is important to know the reactions occurring within the landfill. The first stage of landfill stabilization is aerobic decomposition. The oxygen present in the pores of the freshly added waste is used by aerobic microbes to begin breaking down the easier biodegradable waste, like food, into carbon dioxide. As the oxygen is depleted, other electron acceptors are used, likely nitrate or sulfate and the COD, volatile organic acids (VOAs), and BOD concentrations in the leachate begin to increase. The pH will also decrease from the acids being produced, which can mobilize any metals within the system. Next hydrolysis will occur where polymers, like carbohydrates, fats, and proteins, are converted into less complex organic compounds, like sugars, amino acids, carboxylic acids and glycerol. Fermentation at this time will also use the organic substrates to produces VOAs, ketones, alcohols, hydrogen, and carbon dioxide. Due to products of these reactions, the BOD and COD will dramatically increase, and from the accumulation of acids the pH will continue to decrease, risking more metal contamination. Acetogenesis is the next phase, where the acids and alcohols are oxidized into hydrogen, carbon dioxide, and acetate. The hydrogen concentration present in the system must be low enough for this conversion to take place, or else the reaction will not be thermodynamically favorable. However, as acetogenesis occurs, methanogens can begin to convert the hydrogen and acetate into methane. As methanogenesis dominates the system, the pH will increase, and the BOD and COD in the leachate will decrease. The pH increase can then decrease the mobility of the metals from precipitation [6], [67]–[69].

Landfill age plays an important role in the composition of leachate and how treatable it is. From the analysis on landfill stabilization stages, one can predict that the leachate of younger landfills will have a higher BOD/COD ratio due to the larger number of biodegradable compounds within the beginning stages. Then, as the landfill begins to age, the BOD/COD ratio will decrease as the landfill reaches the methanogenesis decomposition stage and the biodegradable matter decreases. Typically, younger landfills (within the acetogenesis phase) have a BOD/COD ratio from 0.40 to 0.75, while older landfills (far within the methanogenesis phase) often fall below 0.10. Therefore, the organic matter present in older landfills is recalcitrant and can be more difficult to treat [6], [70], [71].

It has also been found that as a landfill matures, the amount of total organic carbon (TOC) contributed from DOM (HA, FA, and Hpi) in leachate decreases from upwards of 19,000 mg/L to 400 mg/L, but Hpi usually dominates the TOC concentration for all ages. In younger landfills, Hpi contributes 60-75% of the total TOC in leachate and it only decreases to 37-70% in older landfills. However, there have been studies that have shown that HA will become more dominant as the landfill ages, increasing to above 44% of the total TOC concentration. [4], [37], [71], [72].

It has also been found that the larger the molecular size of a compound, the more it will absorb UV_{254}. For fractions 3 kDa and larger, the UVA_{254} can reach above 10 cm^{-1} with little to no decrease after biological treatment [4], [29], [32], [73]. HA and FA in landfill leachate have both shown that 50-85% of their structures have a molecular size of 3 kDa or larger and that this size range contributes 50-73% to their individual UVA_{254} [74], [75]. Hpi fractions have also shown to have a similar molecular size composition as HA and FA, but their molecules above 3 kDa only account for 20-25% of their UVA_{254}. However, when looking at the total UVA_{254} of leachate, even though the larger Hpi structures are not as impactful, the Hpi fraction often makes up the largest percent of DOM. Therefore, their smaller fractions can contribute more to the overall UVA_{254} than HA or FA individually. This means that younger landfills still within the acetogenesis phase will have smaller Hpi size fractions that largely influence the total UVA_{254} of untreated leachate. This corresponds with the findings that the younger a landfill, the higher the UVA_{254}. But, as a landfill ages and the BOD/COD ratio decreases, even with Hpi likely still being the largest DOM fraction, the smaller molecules within all the DOM will be removed via biodegradation leaving only larger molecules. The causes the UVA_{254} to decrease with age, but the remaining UVQS are recalcitrant, leaving the leachate well above the 0.19 cm^{-1} UVA_{254} required [4], [32], [37], [72], [76].

The FTIR studies on untreated leachate have found that the functional groups present are mostly a mix of aromatic, carboxylic, amide, methyl, phenolic, alkene, and aliphatic ether groups. It has also been shown that as a landfill stabilizes, there will be an increase in C=O and N-H amide functional groups, suggesting there is likely decomposition of larger proteins, equivalent with the reactions taking place during hydrolysis and fermentation. A higher concentration of phenolic and aromatic functional groups were also seen in older landfills, coinciding with the pervious conclusion that as a landfill ages, the larger, more recalcitrant organic matter is more relevant [4], [77], [78].

Some research has included EEM results on untreated leachate. In younger leachate, the largest peaks were associated with tyrosine-like and tryptophan-like materials likely bonded to amino acids or proteins. While in older leachate, the humic-like and fulvic-like peaks were dominant, which coincided with the larger humifaction degree found. It was also found that EEM was unsuccessful in showing any Hpi peaks, despite having a high concentration within the leachate [55], [70], [79], [80].

Due to the complexities that come with landfill leachate composition, it shows the importance of having a deeper analysis on the functional groups present, how old the landfill is, and if the samples were taken before or after any pretreatment.

2.2 COAGULATION AND FLOCCULATION

Coagulation and flocculation are often used in water treatment to reduce turbidity and color by removing constituents that are suspended, large DOM, or absorbed to colloidal matter. This matter can be incredibly small, on the scale of 10^{-5} to 10^{-9} m, so Brownian motion is one of their primary methods of movement. Normally, Brownian motion can cause matter to collide forcing some settling. However, there are two primary concepts that help keep them stable in suspension and unable to settle out by gravity during a reasonable timeframe for water treatment. First, since this matter is so small it can surround itself by a layer of water molecules causing gravitational forces to be minute. Second, they often have a large surface area and negative surface charge, which repels other colloids by repulsive forces, decreasing the likelihood of particle collisions. Colloids can be anything from viruses to clays and can take up to two years to settle by gravity. Luckily, coagulation and flocculation allow for the removal of these constituents in a timelier manner [81], [82].

Coagulation uses the addition of a coagulant, or chemical, to destabilize the particulate, dissolved, or colloidal matter within the water. The coagulant, usually a metal compound or polymer, is added in a flash mixer to rapidly distribute the coagulant within the water stream. The water then goes into the flocculation stage where it moves from compartment to compartment with slower mixing within each. This allows aggregates to form, knowns as flocs, and become larger with collisions. These flocs are then removed out by gravity settling or filtration. The flocculation stage mixing speed, intensity, and time are important parameters, because if the mixing speed or intensity is too high, the flocs will break apart. If the mixing time is too little, the flocs may not have developed to be large enough and not completely settle out. Mixing time usually ranges from 20 to 45 minutes and paddle tip speed up to 4 m/s, depending on the paddle type used, water quality, and destabilization method [83].

Destabilization can occur by four mechanisms. The first is double layer compression to increase the likelihood of collisions. This method increases the solution's ionic strength to decrease the size of the electron cloud around the particle. That in turn, decreases the diffusion required to reach the particle. However, this is not a primary destabilization method in water treatment. The second is inter-particle bridging, where a polymer or organic binds to two particles causing the two to be linked, increasing their size and allowing a floc to form [83].

The third destabilization method is surface charge neutralization, which takes advantage of the fact that particles are often negatively charged in a neutral pH range via surface group ionization, isomorphous replacement, or specific ion adsorption. Since a metal coagulant is in a positive oxidation state (often the +3-oxidation state) and the organic matter has a negative surface charge, they become attracted to each other via electrostatic interaction. This can destabilize the particle when the coagulant hydrolyzes and absorbs to the negative surface of the organic matter allowing a precipitate to form. Once the water moves into the flocculation stage it takes advantage of the reduced repulsive forces of the destabilized particles for increased particle collision and aggregate production [83].

The last method of destabilization is sweep flocculation. Sweep flocculation occurs when a coagulant is overdosed to form metal coagulant precipitates in the form of hydroxide compounds. These compounds produce a large floc that can entrap organic matter by some absorption, but mostly by capturing the matter and forcing it to move with the precipitate as it settles. Therefore, sweep flocculation is less about particle destabilization and more about physical removal [80], [83], [84].

Hydrolyzing metallic salts, like alum (aluminum sulphate), ferric chloride, or ferric sulphate, are the most common coagulants used, as they have been shown to decrease turbidity and color, have high solubility, form precipitates that are heavy enough for settling, and are cheaper than using polymers alone. When these salts are added to water, several reactions occur that allow coagulation to take place. For example, when ferric chloride ($FeCl_3$) is added to water, it will initially dissociate, but after interacting with the water molecules around it, it will then become hydrated to form numerous complexes until the hydroxide precipitate is formed in the overall reaction seen in **Eq. 1**.

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3HCl \qquad \textbf{Eq. 1}$$

But there are several factors that can determine its effectiveness. For example, the pH of the water will control the speciation and solubility of the metal coagulant. Therefore, hydrolyzing metallic salts are pH sensitive with ferric compounds between 5.5 and 8.5. Metal coagulants also decrease the pH of the solution, as can be seen in **Eq. 1** with the addition of 3 moles of HCl, so alkalinity can affect the buffering capacity to reach an ideal solution pH and maintain it. Lower temperatures also cause more viscous waters, which can decrease hydrolysis and settling speeds [83].

Therefore, it is not surprising that source water can control what kind of coagulant and destabilization method is used. In drinking water treatment, the source water turbidity is a primary factor when deciding between charge neutralization and sweep flocculation. In wastewater treatment, coagulants can be used help clarifier performance or remove phosphorus. However, if used during primary clarification, special attention needs to be kept so the coagulant does not affect the alkalinity or remove too much phosphorus before biological treatment. Due to the high amount of turbidity and color, sweep flocculation is most often used for wastewater treatment [81].

In general, coagulation and flocculation are a fairly simple way to treat water, requiring only a coagulant (possibly a coagulant aid too) to be added before a flash mixer and then flocculation and sedimentation tanks. Operators do not need to worry about aeration, UV intensity, pressurized systems, or a lot of complex moving parts. Primary concerns include pH/alkalinity adjustments, coagulant dosage, and flocculation mixing speeds. Coagulation also has a low capital and operation and maintenance costs. Sweep flocculation produces the most sludge, so it has a higher operation and maintenance cost. But, sweep flocculation is easier for operators, because charge neutralization is very dosage dependent, whereas sweep flocculation has less strict of a range. There can be some areas of concerns depending on the water flow rate, since flocculation tanks need to be followed by sedimentation or filtration [81].

2.3 FENTON'S OXIDATION

Fenton's oxidation is the reaction between hydrogen peroxide (H_2O_2) and iron in the +2-oxidation state (Fe^{2+}), often in the form of iron chloride ($FeCl_2$) or iron sulfate ($FeSO_4$). When these two compounds are added together, the iron acts as a catalyst in the production of hydroxyl radicals (·OH) from H_2O_2, as seen in **Eq. 2**. One can also get similar reactions when using iron in the +3-oxidiaton state (Fe^{3+}), but the reaction is less effective and produces less ·OH [85].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad \textbf{Eq. 2}$$

These radicals are highly reactive and unstable with a redox potential of 2.73 V at standard state (only behind free fluorine at 2.87 V which can degrade glass or metal [86]), giving them the ability to oxidize organic matter and synthetic dyes [87], [88]. Degradation of these compounds in an aqueous environment via ·OH occurs primarily by combing with carbon-carbon unsaturated bonds or breaking aromatic rings by attacking hydrogen atoms [85]. If the reaction goes to completion, these organics are mineralized into carbon dioxide and water. However, if carbon double bonds, amino, or nitro compounds are present, they are often attacked and degraded into simpler compounds. It is important to note that $\cdot OH$ during Fenton's oxidation is unable to attack saturated carbon-carbon bonds or some organics like acetone or acetic acid. As mentioned, $\cdot OH$ are highly reactive and generally nonselective, but they do gravitate towards phenols and petroleum hydrocarbons [89].

Since an iron compound is being used during Fenton's reaction, an acidic solution pH must be used for optimum results. At a neutral pH, the dominant Fe^{2+} species will be $Fe(OH)_{2(s)}$ which means the reaction will not proceed, because iron will be in a solid form [90]. H_2O_2 can also be partially decomposed into water and oxygen with a pH level above 9 [91]. On the other side, too low of a pH can increase H^+ scavenging on $\cdot OH$. Therefore, the optimum pH for COD and DOC removal has been found to be from 3-5 [32]. When the pH is lowered, there is also the possibility to recycle Fe^{3+} back into Fe^{2+} for further treatment, which is shown by the possible set of reactions in **Eq. 3 – Eq. 6.** But, **Eq. 2** is faster than **Eq. 5** and **Eq. 6** where the iron is recycled, so the speed of the overall reaction will decrease as Fe^{2+} is used [85]. The reactions taking place in **Eq. 5** and **Eq. 6** are pH dependent. For the iron to be recycled from Fe^{3+} back into Fe^{2+}, Fe^{3+} must be the dominant species, which occurs when the pH of the solution falls below 3 [92].

$$H_2O_2 + \cdot OH \rightarrow \cdot O_2H + H_2O \qquad \textbf{Eq. 3}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad \textbf{Eq. 4}$$

$$Fe^{3+} + \cdot O_2H \rightarrow Fe^{2+} + O_2 + H_2O \qquad \textbf{Eq. 5}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot O_2H + H_2O \qquad \textbf{Eq. 6}$$

It can also be seen from **Eq. 4**, that if iron is overdosed it will also scavenge for $\cdot OH$, causing the reaction efficiency to decrease. Therefore, when adding Fe^{2+} and H_2O_2 to a system, the initial

H_2O_2 concentration should be larger to ensure the continual production of ·OH until all the H_2O_2 is used [85]. In previous Fenton's reagent experiments seen in **Table 1**, the H_2O_2:Fe^{2+} molar ratio ranges from 0.5 to 10. It should also be noted that ·OH is not the only compound during these reactions that can oxidize compounds. H_2O_2 alone has some oxidizing power with a reduction potential of 1.78 V and the prehydroxyl radical (·O_2H) has a reduction potential of 1.70 V [90], [93]. However, these potentials are less than ·OH, leaving it as the dominant oxidant.

Reaction time can also affect the success of Fenton's oxidation, but this parameter is very wastewater specific. If a sample is comprised of smaller organics or phenols, the reaction can be completed in less than an hour. But, if more complex organics are present, like lignin derivatives, the reaction can take longer. As seen in **Table 1**, reaction times are typically within the 60-minute range. At the end of the reaction, the pH of the solution must be increased. Even with the initial solution pH being acidic, an even lower pH is possible after the reaction. Not shown in **Eq. 2**, is the initial iron compound reacting with water, which is seen in **Eq. 7** with $FeCl_2$. From this, one can see that as $FeCl_2$ is dissolved in water, HCl is formed and can further decrease the solution pH causing some leachates to reach below pH 3. [94]. As mentioned, this is the pH range required for iron recycling.

$$FeCl_2 + H_2O \rightarrow Fe^{2+} + 2HCl \qquad \textbf{Eq. 7}$$

As seen in **Eq. 2** and previously discussed, the iron will be in the Fe^{3+} form when the pH is readjusted at the end of a reaction into a neutral range. Therefore, the iron will be converted into $Fe(OH)_{3(s)}$ causing a sweep coagulation effect on the solution [90]. This is followed by a flocculation period often around 60-minutes, producing a large amount of sludge to be disposed of.

Advanced oxidation is growing in popularity for water treatment, because it can reduce formation of disinfection by-products, does not require special temperature or pressure conditions, is capable of complete oxidation, can degrade recalcitrant compounds, can decrease the issues causing unfavorable taste and order in drinking water, and H_2O_2 is stable when stored properly [95]. However, when using Fenton's oxidation in industry, there are some concerns. As mentioned, pH plays an important role. H_2O_2 is expensive and if stored improperly can decompose producing oxygen and heat. Sludge disposal costs can be high, and the ·OH cannot target specific compounds. Some research has been done on minimizing these issues by producing H_2O_2 in-situ without requiring mixing hydrogen and oxygen, which are explosive. Electrochemical methods have become a popular area of research for in-situ H_2O_2 production using electrodes as surface catalysts, but these methods have not been able to produce H_2O_2 on a large enough scale and require aerated conditions, expensive apparatus, or a high energy demand [87], [96]–[98]. Therefore, most often industrial wastewater applications of Fenton's reagent have been performed in a batch mode, followed by flocculation and sedimentation. It is primarily used as a pretreatment to degrade larger compounds before biological treatment, or toxic compounds before discharge [99], [100].

3 OBJECTIVES, HYPOTHESIS, MATERIALS, AND METHODS

3.1 RESEARCH OBJECTIVES

The goal of this research is to identify the treatment level of coagulation/flocculation and Fenton's oxidation on removing UVQS in landfill leachate and the mechanisms by which the organic matter is removed to better understand how to decrease the negative impacts on POTWs when treating the wastewater. For both treatments, previous research has focused on optimizing parameters for COD removal, without an in-depth analysis of what leachate constituents have been mineralized, adsorbed, or degraded into simpler compounds at varying treatment concentrations which would give a better indication of why or why not a treatment is reaching desired results. Since Fenton's oxidation is capable of coagulation/flocculation, coagulation/flocculation alone will be used to help compare which mechanism during Fenton's oxidation, physical or chemical processes, is more dominant. The Fenton's oxidation results are compared between leachates from two different landfills, to understand if treatment trends are consistent. To meet the overall objective, the following are the sub-objectives of this research:

- ***Identify ways to accelerate residual H_2O_2 decomposition without compromising the sample.*** To decrease the interference on sCOD and UVA_{254} measurements, heating, increasing the pH, and adding catalase to the solution was analyzed for H_2O_2 degradation over time and then applied to leachate to ensure no constituent changes.

- ***Conduct coagulation and flocculation studies at three different pH values and $FeCl_3$ coagulant doses.*** Jar tests were conducted with pH solutions at 5.5, 6.5, and unchanged (8.2) with $FeCl_3$ coagulant doses of 1 g/L, 5 g/L, and 10 g/L. The supernatant and precipitate were collected for further analysis.
- ***Conduct Fenton's oxidation studies with four different chemical dosages.*** At a solution pH of 4 and $[H_2O_2]:[Fe^{2+}]$ molar ratio of 5:2, experiments with 0.10%, 0.20%, 0.50%, 1.0% H_2O_2 concentrations (0.07-0.72 DOD) were done and the supernatant and precipitate were collected for further analysis.
- ***Compare supernatant constituents to each other, untreated leachate, and required treatment levels.*** DOC, sCOD, UV_{254}, and $SUVA_{254}$ were measured on all supernatant samples to identify differences in physical treatment (coagulation) and chemical treatment (Fenton's oxidation).
- ***Analyze the dominant DOM and functional groups present before and after treatment for all supernatants.*** Perform FTIR and EEM measurements on the supernatant of the treated and untreated leachate to evaluate DOM and functional groups present.
- ***Evaluated the functional groups adsorbed to the precipitate of treated samples.*** FTIR was used on the dried precipitate of all samples to understand the functional groups that adhered to the precipitates.
- ***Compare treatment trends with the most effective Fenton's oxidant dose on different leachates.*** Leachate taken from Greenville County, SC and Orange County, FL were subject to a 0.7 DOD to compare if treatment removals were consistent when looking at sCOD, DOC, UVA_{254}, $SUVA_{254}$, and EEM.

3.2 RESEARCH HYPOTHESIS

The overall hypothesis of the research was that Fenton's oxidation combined with coagulation/flocculation will result in better treatment than coagulation/flocculation alone, due to the additional treatment by oxidation. However, based on previous research, it was assumed that these treatments will greatly reduce the DOC and sCOD, but will not remove all the UVQS. It was hypothesized that this would be due to large organic matter being degraded into smaller compounds instead of complete mineralization, when using Fenton's oxidation, and that smaller organics are less likely to be removed during a coagulation/flocculation process. This research used the objectives listed in **Section 3.1** to either confirm or disprove this hypothesis.

3.3 EXPERIMENTAL DESIGN

3.3.1 REAGENTS AND LEACHATE SAMPLES

All reagents used were analytical grade. One set of landfill leachate samples was collected from Renewable Water Resources (ReWa) in Greenville, South Carolina, which collects leachate from the Greenville County Twin Chimneys Landfill. Samples were taken in July 2018 and February 2019. Twin Chimneys is a 1,155-acre, Subtitle B landfill holding MSW since 2007. The leachate is pretreated by aeration before being sent to ReWa. A photograph of this leachate can be seen in **Appendix B, Figure B-1**. Landfill leachate was also collected from Orange County Utilities Laboratory in Orange County, Florida during September 2018. This landfill is considered mature and there was no leachate pretreatment. Once collected, the leachate was stored in a 4 °C refrigerator.

The leachate samples taken were measured for pH, COD, UV- visible spectroscopy (UV-VIS), DOC, and $SUVA_{254}$ and analyzed with fluorescence EEM. The leachate was also dried at 100°C for 24 hours and the powdered residual was analyzed with an FTIR.

3.3.2 COAGULATION AND FLOCCULATION

All coagulation/flocculation experiments were carried out in duplicate using a Phipps & Bird jar tester at room temperature. Each leachate solution was 1 L and the initial solution pH was adjusted to the desired value using 12 M HCl or 1 M HCl. Leachate was not filled to the jar volume capacity to allow room for any foaming than may occur after adding the coagulant. The required amount of crystalline ferric chloride ($FeCl_3$, Alfa Aesar, Ward Hill, MA) was then added to the solution and rapidly mixed for 5 min at 200 rpm, followed by 30 min at 60 rpm, 10 min at 20 rpm, and then settling for 60 min. $FeCl_3$ was used in this study, because it is applicable at a wider range of pH values and has been found to be more effective when treating landfill leachate (references shown in **Table 2**). Three initial pH values used were 5.5, 6.5, and unchanged (8.2). There were also three different coagulant doses studied, 1 g/L, 5 g/L, and 10 g/L of $FeCl_3$.

The pH of each sample was increased to 8.2 (the initial leachate pH) to precipitate any soluble iron. If there was still turbidity or interference with UV-VIS analysis, the sample pH was further increased and centrifuged with a Sorvall Evolution at 15,000 rpm for 7 min. This was only done for the UV-VIS analysis, because it was found that increased pH and centrifuging did not affect UV-VIS, as will be discussed in **Section 4.2.1**. At least 150 mL of each sample supernatant and 60 mL of the sludge were removed. A portion of the supernatant was filtered through a 0.45 μm membrane filter for sCOD and DOC analysis. Unfiltered supernatant was used for UV-VIS and EEM analysis. Each sample analysis and measurement were carried out in duplicate, as well. Unfiltered supernatant (20 mL) from each sample and 20 mL of sludge from each sample was then dried at 100 °C for 24 hours. The dried residue of the supernatant and sludge were used for FTIR analysis.

3.3.3 FENTON’S OXIDATION

Fenton’s oxidation experiments were carried out in duplicate using a New Brunswick Scientific E24 shaker table at room temperature. Experiments were carried out in 250 or 500 mL beakers and each leachate solution was 125 mL, allowing extra room for any foaming that may occur during the reaction. The initial solution pH was adjusted to 4 using 12 M HCl or 1 M HCl and the required amount of granular ferric chloride ($FeCl_2 \cdot 4H_2O$, Acros Organics, New Jersey, USA) and liquid hydrogen peroxide (35% H_2O_2 w/w, VWR Analytical, Radnor, PA) was then added to the solution and mixed for 24 hours at 125 rpm, to ensure the reaction had reached completion. After, the solution pH was increased using 5M and 1M NaOH until pH 8.2 was reached. Lyophilized powder catalase (Sigma-Aldrich Co. St. Louis, MO) was also added to the solution to degrade any residual H_2O_2 into water and oxygen, because H_2O_2 can interfere with UV-VIS and sCOD measurements [122]. Catalase was chosen to initiate H_2O_2 decomposition to avoid irreversible damage from further pH adjustments and after finding heating the H_2O_2 had little effect on degradation. These results will be discussed in **Section 4.2.1**. The amount of catalase added was calculated based on 0.06 mg catalase/mg H_2O_2 [96]. The leachate was then mixed at 125 rpm for 3 minutes to ensure full decomposition. The solution then settled for 60 min and the supernatant was removed to 1 cm above the sludge. A portion of the supernatant was filtered through a 0.45 µm membrane filter for sCOD and DOC. Unfiltered supernatant was used for UV-VIS and EEM analysis. Each sample analysis and measurement were carried out in duplicate, as well. Unfiltered supernatant (20 mL) from each sample was dried at 100 °C for 24 hours. The remainder of the solution was then centrifuged with a Sorvall Evolution at 15,000 rpm for 7 min. The sludge was then collected and dried at 100 °C for 24 hours. The dried residue of the supernatant and sludge were used for FTIR analysis.

For the Fenton's oxidation experiments, DOD was used to compare the oxidant dose to amount of organic matter present. DOD is a ratio of the available reactive oxygen within H_2O_2 to the amount of initial sCOD ($sCOD_O$). In this case, in 1 mg/L of H_2O_2 there is 0.471 mg/L of reactive oxygen in the form of ·OH [32], [41]. The DOD equation can be seen in **Eq. 8** where H_2O_2 and sCOD are in units of mg/L.

$$DOD = \frac{0.471 H_2O_2}{sCOD_O} \qquad \textbf{Eq. 8}$$

3.4 SAMPLE ANALYSIS

For control H_2O_2 degradation experiments, H_2O_2 concentrations were measured as outlined in *Murawski 2018* [96]. The sCOD was measured in accordance with the 5220D standard method via spectrophotometer with a HACH DRB 200 (250-15,000 mg/L range, Loveland, CO) with readings from a HACH DRB 3900. UV absorbance was measured from 300 nm to 220 nm with a Varian Cary 50 Bio UV scan spectrophotometer at 0.50 cm^{-1} increments (equivalent to the slowest scan control). Quartz cuvettes were used for the UV-VIS and deionized (DI) water was used for a baseline correction. Samples were 15-40 times diluted with DI water, depending on the UVA_{254}. DOC was analyzed with a Shimadzu TOC-V with DOC calibration done with crystal potassium hydrogen phthalate (KHP, EMD Millipore Co., Billerica, MA). An example of the calibration curve used can be found in **Appendix C, Figure C-1.** $SUVA_{254}$ was found with **Eq. 9**, where UVA_{254} has units of cm^{-1} and DOC of mg/L.

$$SUVA_{254} = \frac{UV_{254}}{DOC} * 100\frac{cm}{m} \qquad \textbf{Eq. 9}$$

For FTIR analysis, the dried supernatant and sludge residuals were analyzed with a Thermo Nicolet 6700 FTIR spectrometer with a diamond ATR cell (64 scans at 0.2 cm^{-1} resolution). Between samples, the cell was cleaned with acetone and the background was collected.

EEM analysis was conducted on the liquid supernatant with a Schimadzu spectrofluorometer RF5301. The instrument warmed up for one hour, and a lamp adjustment was done to ensure the signal-to-noise ratio was above 150. Due to the sensitivity of the instrument, quartz cuvettes were cleaned in methanol to ensure there was not any contamination. Each sample was diluted with DI water to below a UVA_{254} of 0.15 cm^{-1} and then scanned with a 5 nm slit in emission from 220 to 450 nm and 1 nm slit in excitation from 280 to 550 nm. A DI water sample was used for a baseline correction.

4 RESULTS AND DISCUSSION

4.1 COAGULATION AND FLOCCULATION PROCESS

4.1.1 SUPERNATANT

Photos of the coagulation experiments can be seen in **Appendix B, Figures B-2** and **B-3**. There was increased foaming with increased coagulant dosage in the jar testers. Visibly the supernatant looked clearer with increased dosage and decreased pH, as well. The 5 g/L and 10 g/l $FeCl_3$ dosages for pH 5.5 and 10 g/L $FeCl_3$ dosage for 6.5 were subject to increased pH after these photos were taken to precipitate any more soluble iron for the UV-VIS analysis, since there was some interference from soluble iron still present, and this increased the visible color even more.

The untreated leachate characteristics can be seen in **Table 3.**

Table 3: Untreated Twin Chimney's February 2019 characteristics.

Parameter	Average ± Standard Deviation
UVA_{254} (cm^{-1})	22.4 ± 0.01
UVT_{254} (%)	$4.0x10^{-23} \pm 5.8x10^{-22}$
sCOD (mg/L)	6,570 ± 30
DOC (mg/L)	1,208 ± 13
$SUVA_{254}$ (L/mg*M)	1.86 ± 0.02

The effect of pH and coagulant dose on sCOD and DOC removal on Twin Chimney's leachate collected in February 2019 is shown in **Figure 1**. When considering sCOD removal, the samples had little differences between them. All samples ranged from 20.4-33.3% sCOD removal, with pH 5.5 and 6.5 at 5 g/L reaching 33.2 and 33.3% removal, respectively. These numbers are on the lower end of previous removals reported by most studies that achieved 25-80% COD removal. This may be because the optimal parameters for sCOD removal were not met for this experiment [40], [56], [59]–[62], [101]. Although there is little difference between pH and coagulant dosage for sCOD removal, they do play a larger role in DOC removal. The pH 5.5 treatment worked better at the lower dosages with 39.4% and 64.7% removal for 1 g/L and 5 g/L $FeCl_3$, respectively. However, when increasing the dosage to 10 g/L $FeCl_3$, pH 5.5 and pH 6.5 had 62.5% and 65.1% removal, respectively, whereas pH 8.2 only reached 21.4%. These removal rates are on par with other leachate studies that ranged from 50-71% DOC removal [40], [55], [64].

The decreased removal efficiency at pH 8.2 is expected, because as the solution pH increases, it also increases the amount of negatively charged iron hydrolysis species that form. Also, the DOC will begin to ionize at higher pH values from the carboxyl groups, making them more negative. Since the minimum solubility of iron occurs around pH 8.0 at 25°C, at higher pH values the iron species are less effective at destabilizing the organic matter via charge neutralization and rely on sweep coagulation [83]. Therefore, at pH 8.2, the DOC removal mechanism is by a physical means rather than destabilization. This is proven by the 1 g/L $FeCl_3$ sample which does not have enough iron to cause sweep flocculation, and therefore has poor removals. However, the decreased efficiency at a 10 g/L $FeCl_3$ dosage for pH 8.2 may be attributed to colloidal destabilization. The dosage is too high and moved past the zone of effective destabilization, but too low for sweep coagulation. This in-between zone is when the concentration of the positively charged coagulant converts the particles that were neutralized, into positively charged particles that are now stable again. This causes the organic matter to become repulsed by each other, preventing adsorption. However, these turn into insoluble particulates, but colloids can range anywhere from 10^{-5}-10^{-9} m, so they may not be removed by a 0.45 μm filter used for DOC, resulting in lower DOC removal at 10 g/L $FeCl_3$ [81], [83], [102].

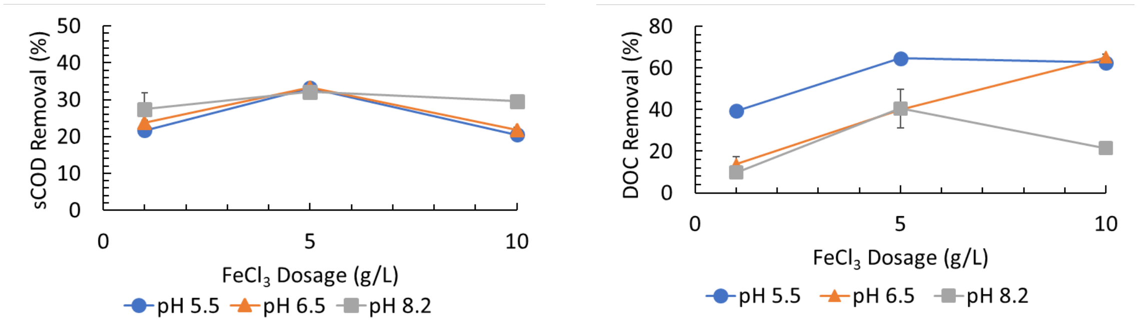


Figure 1: Coagulation treated Twin Chimney's leachate (February 2019) sCOD (left) and DOC (right) removal percentage at different FeCl$_3$ dosages and initial pH values. Leachate initial characteristics: sCOD 6,570 mg/L and DOC 1,208 mg/L.

The effect of pH and coagulant dose on UV$_{254}$ and SUVA$_{254}$ are shown in **Figure 2**. The changes in UVA$_{254}$ follow the same pattern as DOC removal, with increased removal for pH 5.5 and pH 6.5 as dosage is increased and pH 6.5 10 g/L FeCl$_3$ having the highest reduction with a final UV$_{254}$ of 2.6 cm^{-1}, resulting in an 88.4% decrease. This is on par with the study by *Jung et al.* which showed 84% decrease UVA$_{254}$ with FeCl$_3$ [50]. The pH 8.2 samples also follow the same the pattern as the DOC removal, with a UVA$_{254}$ decrease at 1 g/L, further decrease at 5 g/L, but then back to a lower decrease at 10 g/L FeCl$_3$. This correlation between UV$_{254}$ and DOC levels corresponds with previous research [13], [103].

As for SUVA$_{254}$, the initial value of 1.86 L/mg-M indicates more hydrophilic fractions and lower molecular weight compounds are present [104]. The pH 8.2 and pH 5.5 had an increased SUVA$_{254}$ at 1 g/L FeCl$_3$ dosage but lowered at the other dosages. So, at 1 g/L FeCl$_3$ dosage there is not an affinity for the aromatic compounds present. This is likely from the dosage not being large enough to destabilize the larger organics that correspond with aromatic compounds. Therefore, the removal that occurred was likely smaller, aliphatic compounds [105]. At low SUVA$_{254}$ levels, such as this leachate, coagulation is often not very effective since there is not a large amount of humic substances [106]. However, at 5 g/L and 10 g/L FeCl$_3$, each sample decreases in SUVA$_{254}$. The pH 6.5 10 g/L FeCl$_3$ dose treatment had the largest decrease to 0.62

L/mg-M. The $SUVA_{254}$ decrease indicates that at higher dosages, there is a higher removal of aromatic and any hydrophobic compounds present from better charge neutralization or sweep flocculation. The $SUVA_{254}$ values (from pH5.5, 5 g/L $FeCl_3$ dose and pH 8.2, 10 g/L $FeCl_3$ dose) that had little decreases may indicate that the organic compounds that were removed were equal parts simple aliphatic organics and complex aromatic compounds, having no bias towards either.

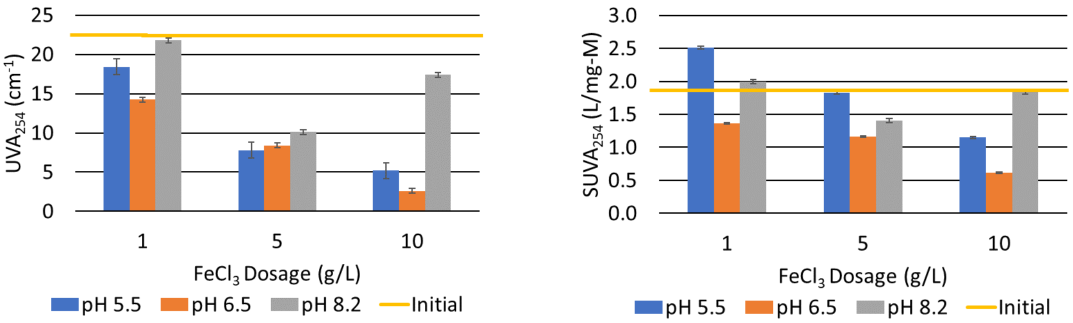


Figure 2: Coagulation treated Twin Chimney's leachate (February 2019) UVA_{254} (left) and $SUVA_{254}$ (right) at different $FeCl_3$ dosages and initial pH values. Leachate initial characteristics: $SUVA_{254}$ 1.86 mg/L, UVA_{254} 22.4 cm^{-1}, and DOC 1,208 mg/L.

EEM for the untreated leachate can be found in **Figure 3** and coagulation treated samples can be found in **Figure 4**. Note the untreated leachate has a fluorescence intensity scale of 60 RU and the treated samples 30 RU to better distinguish the treatment between each. Visually one can see there is little difference between the pH 8.2 samples. However, with the pH 5.5 and 6.5 samples, increased dosage decreases the fluorescent DOM. Four EEM peaks were analyzed for each pH and coagulant dosage combination. These peak positions and their corresponding components can be seen **Table 4**. The fluorescence intensities of each peak for the untreated leachate and coagulation treated leachate are shown in **Table** 5. Each treatment was able to decrease all peaks. There were little changes for all pH 8.2 treatments, but 5 g/L $FeCl_3$ dose had slightly better removal than the others, which corresponds with the DOC, UV_{254}, and $SUVA_{254}$ changes. The pH 6.5 and pH 5.5 10 g/L $FeCl_3$ dose treatments had the largest decreases, also following DOC, UV_{254}, and $SUVA_{254}$ changes. Note that sCOD and DOC removal percentages for the two samples were close (**Figure 1**), as are the EEM peak intensities. However, pH 6.5 10 g/L $FeCl_3$ dose had a more significant $SUVA_{254}$ and UV_{254} decrease, but Peak B is the only component with a lower intensity than pH 5.5 and 10 g/L $FeCl_3$ dose. Therefore, for this leachate, the fulvic acids are likely the fluorescent DOM fraction contributing most to UV-quenching. In previous studies, there was a higher removal of the humic acid peaks, followed by fulvic acid and then protein peaks for coagulation. These studies had lower DOC or COD concentrations than this leachate, which may attribute to the difference in DOM removal preference [55], [60].

Table 4: EEM peak positions and corresponding components.

Peak	Position		Component	Ref.
	Excitation (nm)	Emission (nm)		
A	240	350	Tryptophan-like	[107], [108]
B	255	460	Fulvic acid-like	[107], [108], [109]
C	285	367	Tyrosine-like	[107], [108]
D	320	410	Marine humic-like	[107], [108], [110]

Table 5: EEM fluorescence intensities for each peak of untreated and coagulation treated (different $FeCl_3$ dosage and initial pH values).

pH	Treatment ($FeCl_3$ g/L)	Fluorescence Intensities (RU)			
		Peak A	Peak B	Peak C	Peak D
8.2	0	10	48	15	28
8.2	1	9	46	14	23
	5	8	33	11	18
	10	9	34	12	18
6.5	1	7	34	10	17
	5	4	27	6	8
	10	3	5	4	3
5.5	1	5	29	8	11
	5	3	15	4	5
	10	2	7	3	3

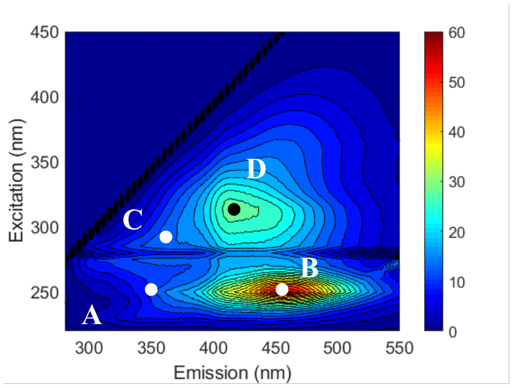


Figure 3: EEM of Twin Chimneys (February 2019) untreated leachate.

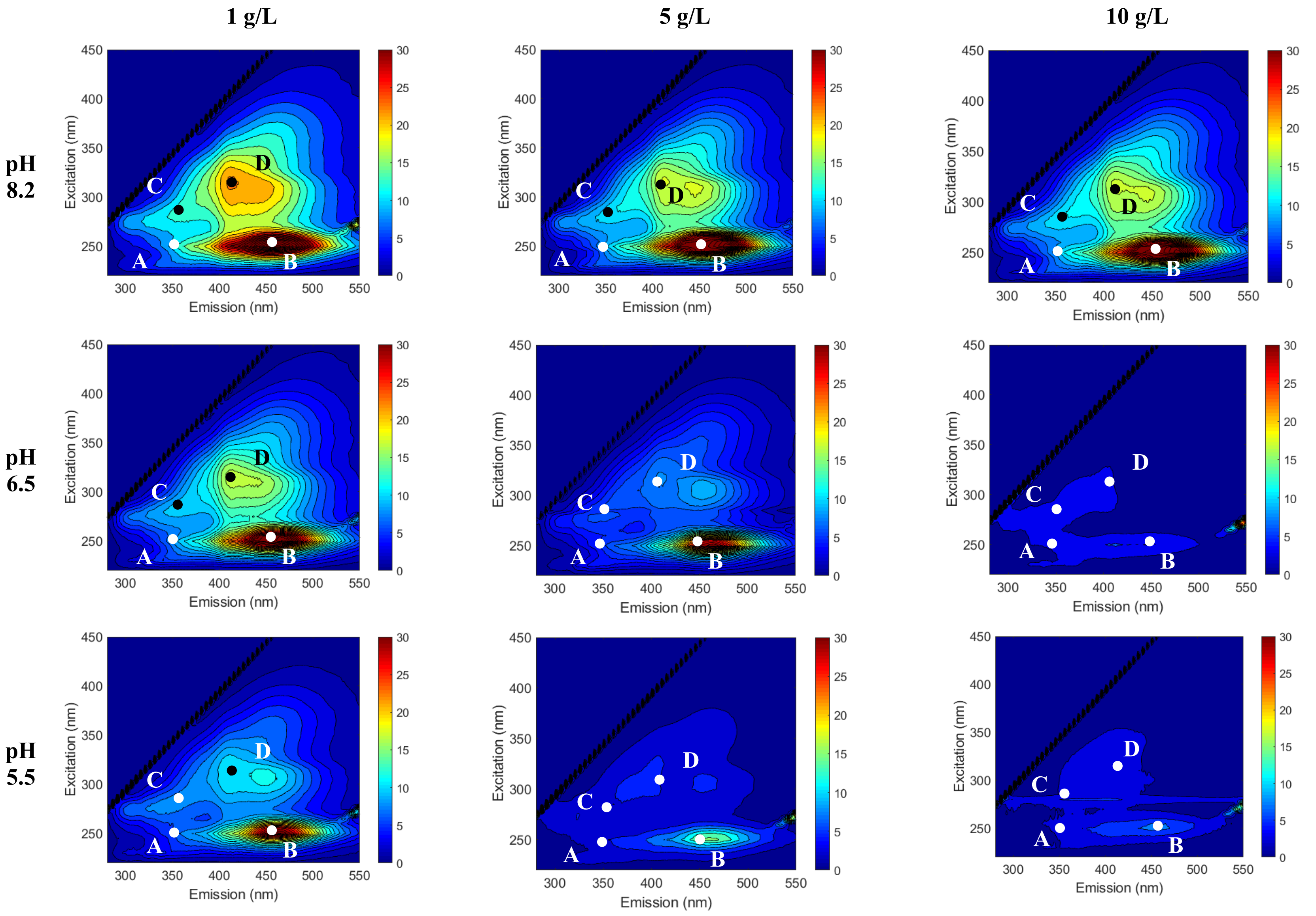


Figure 4: EEM of Twin Chimneys (February 2019) coagulation treated leachate at varying initial pH values and $FeCl_3$ dosages.

The FTIR spectrums of the untreated and coagulation treated samples are presented In **Figure 5**. The region below 1,500 cm^{-1} is considered the fingerprint region, where many bands overlap making it difficult to make conclusive prediction on what each band represents. So, they were not evaluated during this study [111]. **Table 6** shows what each band absorption represents. The pH 8.2 treatment samples have minimal changes to the spectrum. This is expected, since they had minor treatment effects. The most significant changes are seen in the 5 g/L and 10 g/L $FeCl_3$ dose samples, where there is an increase at 3,112 and 3,027 cm^{-1}, representing C-H bonds in aromatics, and a broadening of 1,558 cm^{-1}, likely meaning an exchange of protons on COO^- bonds. The pH 8.2 and pH 6.5 1 g/L $FeCl_3$ spectrum closely mirror each other, as did their DOC removals.

As for 5 g/L and 10 g/L $FeCl_3$ doses, pH 5.5 and pH 6.5 were similar, and the major changes for these samples are as follows:

- Shift of C-H bond locations in aromatic compounds (changing the location where bond is present on the compound)
- Increase in C-H bonds in aliphatic structures
- Increase in COO^-
- Decrease in N-H absorption intensity

The decrease in N-H can be predicted by the aromatic protein peak intensities decrease in the EEM. The 5 g/L and 10 g/L $FeCl_3$ dose, pH 5.5 and pH 6.5 treatments all shifted the C-H bonds in the aromatics, which may indicate that the heavier atoms within the aromatic compounds are being removed because the bonds shift to a higher wavenumber. The increased intensity in the 3,000 cm^{-1} regions may be attributed to interference by the iron complexes. With a large iron dosage, there is a lot of $Fe(OH)_3$ and these O-H bonds can interfere with the FTIR [113]. Previous research also found that coagulation by $FeCl_3$ is less effective at removing carboxylic acids, which may explain the band increase at 1,400 cm^{-1} [114]. However, FTIR indicates coagulation was able to remove some aromatics, possibly the larger aromatic proteins, and some bonds associated with other aromatics as well. Other than this, there are little changes that indicate treatment improvement. This shows a weakness when using FTIR alone.

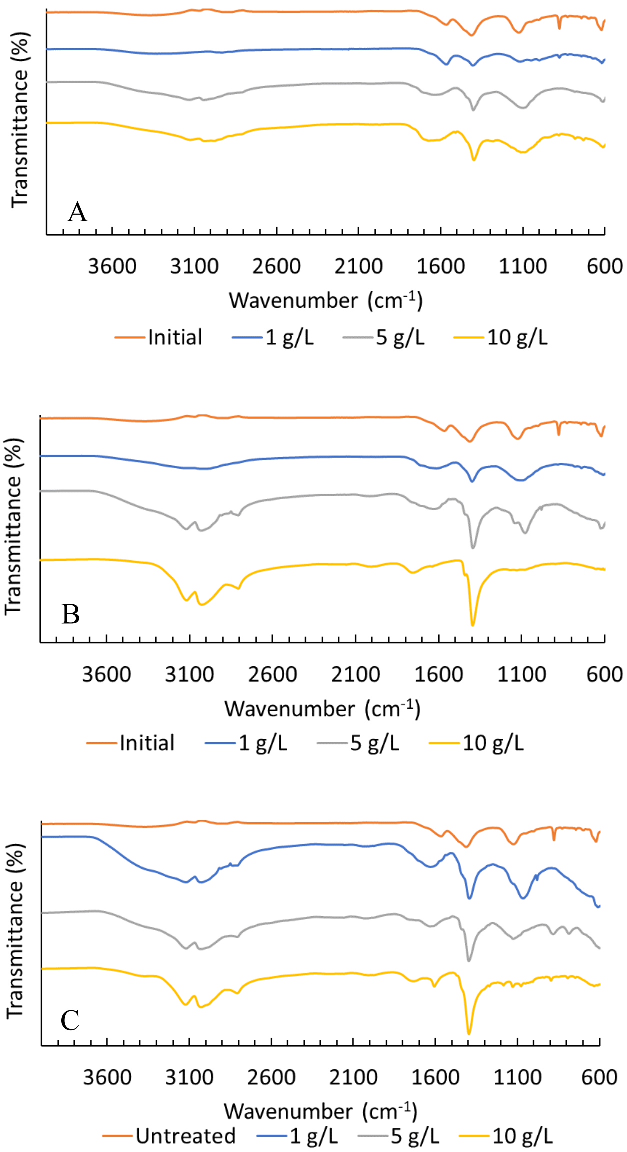


Figure 5: FTIR of untreated and pH 8.2 (A), pH 6.5 (B), and pH 5.5 (C) coagulation treated leachate at varying $FeCl_3$ dosages.

Table 6: FTIR absorption band definitions for untreated and coagulation treated Twin Chimney's leachate.

Wavenumber (cm^{-1})	Vibration	Functional Group	Ref.
3570-3200	O-H Stretching	Hydroxyl group	[115], [116]
3200-3050	C-H stretching, NH_2 stretching	Aromatic, primary amides	[115], [117]
3120	C-H stretch	Aromatic	[115], [118]
3030	C-H stretch	Aromatic	[79], [117], [119]
2940	C-H Stretching	Methylene, Aliphatic Structures	[115], [118], [120]
2870	C-H Stretching	Methylene, aliphatic	[115], [117], [119]
2810	C-H stretching	Aliphatic	[119]–[121]
1690-1640	C=O, C=C stretching	Carboxylic acid, aromatic	[116], [117], [121]
1570-1560	N-H in Plane	Secondary Amides	[116], [117], [119]
1400-1390	COO- stretch	Carboxylic acids	[4], [71]

4.1.2 SLUDGE

The sludge of the coagulation experiments was also analyzed to gain a better understanding of the functional groups removed The FTIR spectrum for each coagulation sample sludge can be seen in **Figure 6**. The sludge FTIR spectrums closely mirror their corresponding supernatant spectrums. This can tell us one of two things. First, it could confirm that the iron complexes are interfering with the FTIR. To test this hypothesis, a set of samples were centrifuged as a control to see if there would be any changes in the supernatant and sludge FTIR. It was assumed that when the samples were centrifuged, if there was any liquid still within the sludge that could interfere with FTIR, it would be removed. But, the spectra for the supernatant and sludge were the same for the centrifuged and uncentrifuged samples. This can be seen in **Appendix C, Figure C-2.** The absorption band intensities change between centrifuging and settling, however the peaks out of the fingerprint region are the same. Peak intensities may be different from the heterogeneity of the samples being used. One could have increased the pH further to precipitate any residual iron complexes, but, as will be discussed in **Section 4.2.1**, that causes irreversible changes to the DOM. The second thing it may suggest is that coagulation is still removing the function groups discussed above, but it is not very efficient at doing so. Therefore, those functional groups are still present within the supernatant.

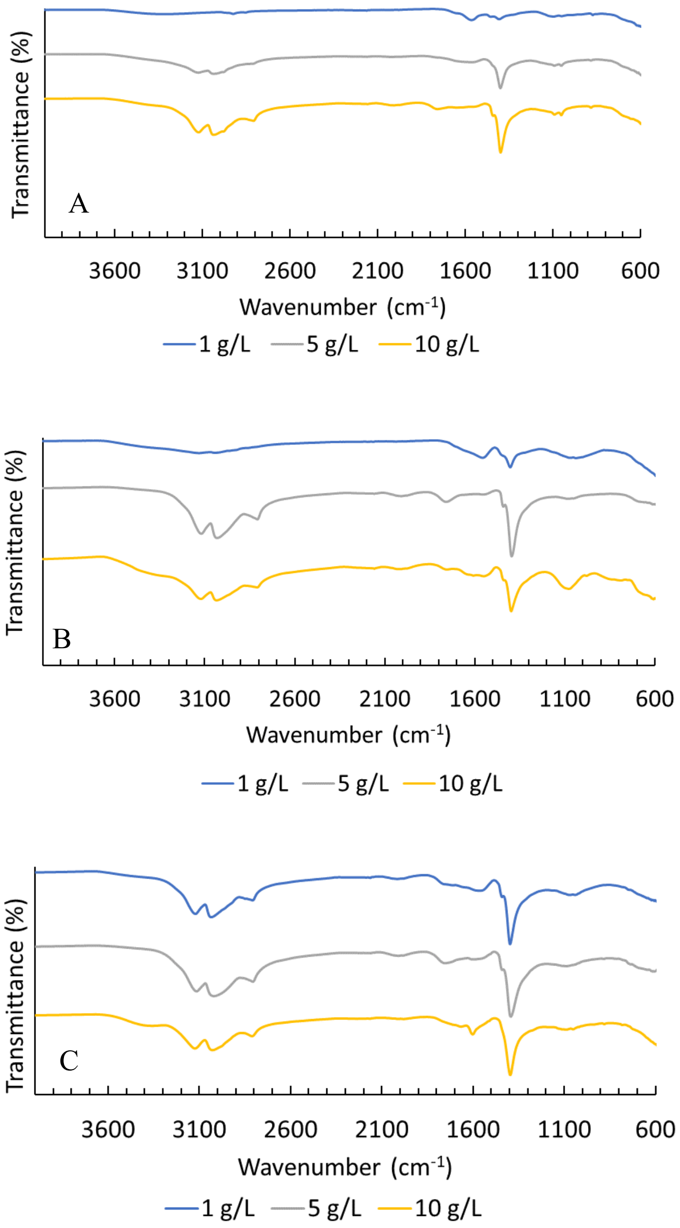


Figure 6: FTIR of the sludge of pH 8.2 (A), pH 6.5 (B), and pH 5.5 (C) coagulation treated leachate at varying $FeCl_3$ dosages.

4.2 FENTON’S REAGENT PRCOESS AT VARYING OXIDANT DOSAGES

4.2.1 CONTROL

Control experiments were first conducted to find the most effective means to degrade any residual H_2O_2. Residual H_2O_2 in water can contribute to UV absorbance and, therefore, decrease UVT. At the visual light spectrum (400 nm to 700 nm), the absorbance is, as expected, low since the solution is clear. However, in the ultraviolet spectrum (400 to 10 nm), the absorbance increases [122]. H_2O_2 also contributes two electrons when oxidized, so it can also contribute to the COD of the solution, so a method to destroy the residual concentration was studied to get a true analysis. Previous studies heated samples at 50˚C for 30 minutes or raised the solution pH to accelerate decomposition [32], [91]. These methods alone were not successful, but a combination of raising the solution pH to 12 and heating the sample at 80 °C for 1 hour was able to sufficiently remove, at the minimum, 87% of the residual H_2O_2, seen in **Appendix C, Table C-1**. For this method, the sCOD, DOC, UVA_{254}, and FTIR of the untreated leachate were analyzed when subject to this treatment, including a final pH readjustment back to pH 8. The sCOD, DOC, and UV_{254} values are seen in **Appendix C, Table C-2** and the FTIR in **Figure C-3.** The UV_{254} is relatively unchanged, but the sCOD, DOC, and functional groups within the FTIR are altered.

When further analyzing the FTIR graphs, the samples at pH 12 no longer had an absorption above 3,000 cm^{-1}. Lignin is a source for humic substances and contains phenolic compounds. It has been found that caffeic acid, chlorogenic acid, and gallic acid, all monocyclic polyphenolic compounds and intermediates of lignin, are unstable at pH values above 10. It was also found that when lowering the pH back to 8 that the changes were nonreversible. The multi-ring aromatic phenols, like catechin and rutin, were unstable at a higher pH, but due to their strong bonds the changes from pH were more reversible. It is likely that when introduced to a higher pH these phenols form quinone intermediates and become oxidized shortly thereafter. As for the reversible phenol degradation, they may be reacting with the NaOH to form soluble salts. Therefore, according to our FTIR results, from the irreversible O-H bond degradation occurring the leachate samples may contain lignin monomers present in the sample that are not as strong. This would correspond with why we are seeing a decrease in DOC but not UVA_{254}. There are still lignin polymers present that have not been broken down to increase the UVA_{254}, but the lignin monomers that were broken down do decrease the DOC [123]–[126]. This breakdown of bonds is further confirmed by the disappearance or decrease at higher a pH of the C-H methylene aliphatic bonds around 2,940 cm^{-1}, the C=O, COO^{-}, or C=C in a primary amide, carboxylate, or aromatic ring, respectively, at 1,620 cm^{-1}, the N-H in secondary amides at 1,560 cm^{-1}, or the COO- in carboxylic acids at 1,420 cm^{-1}.

Due to these changes, the use of catalase was studied instead. Catalase is an enzyme that, when added to a H_2O_2 solution increase the rate of its degradation to oxygen. Due to the quick speed of this conversion, this reaction normally takes two minutes [127]. The catalase was able to sufficiently remove the residual H_2O_2, seen in **Appendix C, Table C-3**. The sCOD, DOC, and UVA_{254} are seen in **Appendix C, Table C-4** and the FTIR in **Figure C-4.** Note, these experiments were not done on the leachate used for the control experiment when increasing the pH and heating the solution, so the untreated results are different.

With the little changes to the leachate constituents when using catalase, it was chosen for all Fenton's oxidation experiments as a method to remove residual H_2O_2. Further controls for Fenton's oxidation experiments were done with the catalase to analyze if there were any unintended removals during the treatment process. One experiment included leachate with the pH adjusted to 4, back to 8, and then catalase addition and centrifuged (**Table C-5**). The other controls were done on leachate with a DOD of 0.07, 0.13, and 0.33 without iron addition and a DOD of 0.33 with the pH initially lowered to 4, then readjusted to 8 without iron addition (**Table C-6**). All samples were mixed at 125 rpm for 24 hours, catalase was added, and centrifuging was undertaken at the end of the reaction. The controls without H_2O_2 addition caused little changes to the leachate characteristics. However, when looking at the FTIR, there were some changes, seen in **Figure C-5.** The controls with H_2O_2 addition did have some changes, with the initial pH 4 sample having the largest removals. This tells us that there is some iron present in the leachate that results in Fenton's oxidation. However, there is not enough iron present to make the reaction cause significant removals. When looking at the FTIR, **Figure C-6**, the unchanged pH sample had little to no changes in the FTIR. However, after the pH changes there were some differences. As it can be seen, the C-H bonds from aromatic and aliphatic bonds increase in the lower 3,000 cm^{-1} region and the C=C bonds in aromatics at 1,670 cm^{-1} decrease, which happened similarly at the pH-adjusted catalase control. This increase is also observed in the coagulation and Fenton's FTIR. Therefore, it may be that this increase is from the organics reacting with the soluble iron. Since we did see some removals with just the H_2O_2 added at a lower pH, it suggests there is some iron. So, when the pH is decreased the iron that is present can cause some treatment of the organics, shown by aromatic functional group changes.

4.2.2 SUPERNATANT

Photos of the Fenton's oxidation treated leachate from February 2019 can be seen in **Appendix B, Figure B-4.** With increased DOD, there is visibly better color removal, but there is little difference between the 0.36 and 0.72 DODs.

The Fenton's oxidation treatments were done on two leachate samples taken at different times, July 2018 (TC-2018) and February 2019 (TC-2019), from Twin Chimney's. TC-2018 was tested with three DOD values and TC-2019 with four. TC-2019 untreated characteristics are seen in **Table 3** and TC-2018 in **Table 7**.

Table 7: Untreated Twin Chimney's July 2018 characteristics.

Parameter	Average ± Standard Deviation
UVA_{254} (cm^{-1})	35.7 ± 0.01
UVT_{254} (%)	$1.9 \times 10^{-36} \pm 2.9 \times 10^{-35}$
sCOD (mg/L)	$7{,}208 \pm 53$
DOC (mg/L)	$1{,}407 \pm 59$
$SUVA_{254}$ (L/mg*M)	2.54 ± 0.07

The effect of DOD on sCOD and DOC removal for the two leachates is shown in **Figure 7**. Even with differing initial concentrations, the sCOD and DOC removal follow the same trend for both leachates. As the DOD increases, the amount of sCOD removal begins to plateau. TC-2018 maximum sCOD removal was 42.3% (0.33 DOD) and TC-2019 was 25.9% (0.72 DOD, 0.36 DOD had a 21.5% removal). The lower TC-2019 sCOD removals may have been be attributed to TC-2019 coming from a different cell within the landfill, meaning it had a different landfill age. TC-2019 had a lower UVA_{254}, indicting it was more stabilized. If this was the case, part of the sCOD may be comprised of constituents that are not a part of DOC, like hydrogen, nitrogen, or sulfur compounds that are more difficult for Fenton's reagent to remove with the molar concentrations used in this study [128]–[130]. Similarly, to the coagulation studies, the sCOD removals are lower than the COD removals from the literature, which were able to remove 39-98% COD with Fenton's oxidation [32], [39], [40], [43], [46].

However, the DOC removals were very similar for both leachates, and follow more a linear trend. Therefore, even with a higher oxidant dose, one may not get proportionally higher removals of sCOD but could for DOC. *Jung et al.* found similar trends with COD quickly plateauing before 0.6 DOD, while DOC does not until after 1.0 DOD [32]. TC-2018 maximum DOC removal was 44.6% (0.33 DOD) and TC-2019 was 48.8% (0.72 DOD, 0.36 DOD had a

36.2% removal). Previous studies reached a DOC removal from 48-84%, so this experiment is on the lower end of removals [32], [38]

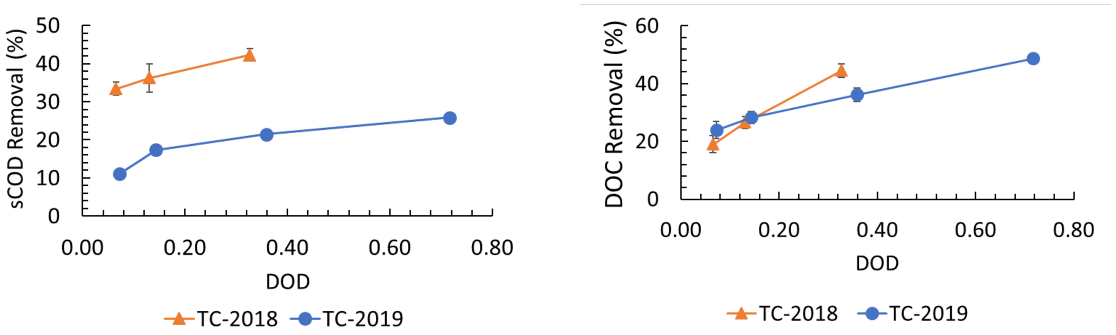


Figure 7: Fenton's reagent treated leachate sCOD (left) and DOC (right) removal percentage at different DODs for leachate taken in July 2018 and February 2019. Leachate initial characteristics: sCOD 7,208 mg/L and DOC 1,407 mg/L for TC-2018 and sCOD 6,570 mg/L and DOC 1,208 mg/L for TC-2019.

The effect of DOD on UV_{254} and $SUVA_{254}$ for the two leachates is shown in **Figure 8**. TC-2018 had a higher UV_{254} (35.7 cm^{-1} versus 22.4 cm^{-1}) and $SUVA_{254}$ (2.54 L/mg-M versus 1.86 L/mg-M), meaning there were more UVQS present that were likely larger and more aromatic, hydrophobic, and recalcitrant. With increased DOD, there were higher UV_{254} and $SUVA_{254}$ removals. The UV_{254} of TC-2018 decreased to 10.4 cm^{-1} (70.8% reduction) and the $SUVA_{254}$ to 1.33 L/mg-M (0.33 DOD). The UVA_{254} of TC-2019 decreased to 4.2 cm^{-1} (81.3% reduction) and the $SUVA_{254}$ to 0.63 L/mg-M (0.72 DOD, 0.36 DOD reached a UVA_{254} of 8.3 cm^{-1}, and $SUVA_{254}$ of 1.00). Previous studies had a 84-94% UVA_{254} reduction and were able to reach a $SUVA_{254}$ of 0.45 L/mg-M from 2.54 L/mg-M [13], [32], [38] The UVA_{254} and $SUVA_{254}$ decrease suggests the hydroxyl radical has an affinity for the larger aromatic compounds, indicating Fenton's oxidation can successfully remove UVQS.

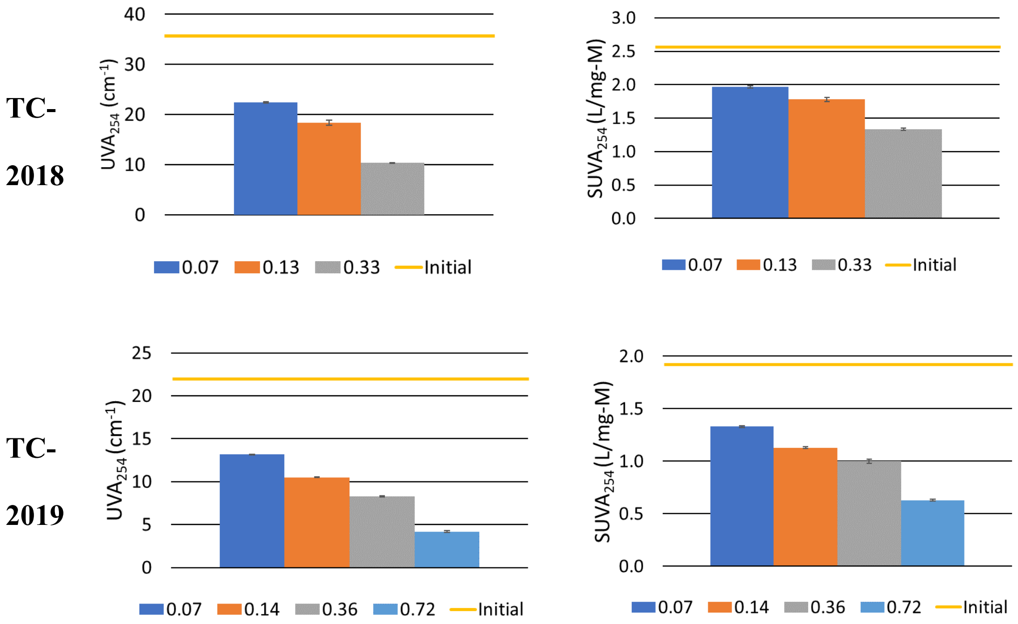


Figure 8: Fenton's reagent treated leachate UVA_{254} (left) and $SUVA_{254}$ (right) at different DODs for leachate taken in July 2018 and February 2019. Leachate initial characteristics: $SUVA_{254}$ 2.54 mg/L, UVA_{254} 35.7 cm^{-1}, and DOC 1,407 mg/L for TC-2018 and $SUVA_{254}$ 1.86 mg/L, UVA_{254} 22.4 cm^{-1}, and DOC 1,208 mg/L for TC-2019.

The same four EEM peaks in **Table 4** were evaluated in the two untreated leachates and the Fenton's reagent treated samples at varying DODs. The untreated EEM for both leachates can be seen in **Figure 9** (fluorescence intensity 500 RU for TC-2018, 60 RU for TC-2019) and the treated leachate with Fenton's for TC-2018 in **Figure 10** (fluorescence intensity 200 RU) and TC-2019 in **Figure 11** (fluorescence intensity 15 RU). Visually one can see that with increased DOD there is more peak removals. However, for TC-2019 the removal does seem to plateau at the higher DODs. The fluorescence peak intensities for TC-2018 can be found in **Table 8** and TC-2019 in **Table 9**. TC-2018 had much higher intensities, corresponding with the higher UV_{254}. However, in both leachates Peak B and Peak D (marine humic acid-like and fulvic acid-like, respectively) are the most dominant. After treatment, each sample had the same shift of which Peak became the highest intensity, changing from Peak B > D > A > C before treatment to Peak D > B > C > A after treatment (until a 0.72 DOD in TC-2019 where Peak B=D>A=C). Therefore, for the Twin Chimneys leachate, Fenton's can consistently and effectively remove fulvic acids, and as was concluded in **Section 4.1.1**, fulvic acids contribute a higher degree to the UVQS in this leachate. *Aftab et al.* found that differing oxidant doses, removed different DOM fractions, unlike this study in which the removal trend was consistent between dosages [38].

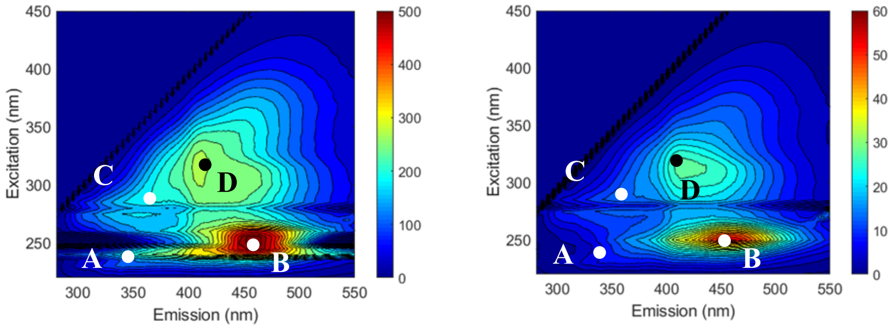
The peak intensity removal between DODs follow the DOC, UVA_{254}, and $SUVA_{254}$ treatment level changes, with increasing removals with increased DOD. After 0.33 DOD, TC-2018 had peak intensities in range with the untreated TC-2019, while the DODs above 0.13 for TC-2019 almost completely removed all peak intensities. Even though the peaks were almost gone with a 0.72 DOD, the sCOD and DOC removal only reached 26% and 49%, respectively, but the UVA_{254} decreased by 81%. The same pattern follows with TC-2018, where 0.33 DOD had a 42% and 45% sCOD and DOC removal, respectively, but UVA_{254} decreased by 71%. Therefore, EEM analysis has shown to be an appropriate representation of the treatment of UVQS since the peak removals correspond better with the UVA_{254}.

Table 8: EEM fluorescence intensities for each peak of untreated and Fenton's reagent treated Twin Chimney's leachate (July 2018) at varying DODs.

DOD	Fluorescence Intensities (RU)			
	Peak A	Peak B	Peak C	Peak D
0	198	501	192	268
0.07	49	123	60	157
0.13	42	102	49	145
0.33	22	42	26	59

Table 9: EEM fluorescence intensities for each peak of untreated and Fenton's reagent treated Twin Chimney's leachate (February 2019) at varying DODs.

DOD	Fluorescence Intensities Averages (RU)			
	Peak A	Peak B	Peak C	Peak D
0	10	48	15	28
0.07	2	10	3	13
0.13	1	5	3	7
0.36	1	4	2	5
0.72	1	2	1	2



TC-2018 TC-2019

Figure 9: EEM of untreated Twin Chimneys leachate taken in July 2018 and February 2019.

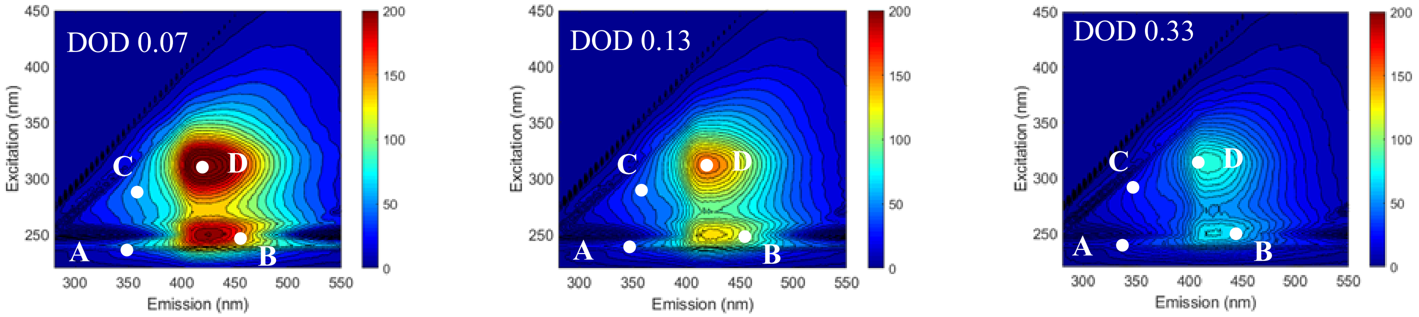


Figure 10: EEM of Fenton's oxidation treated Twin Chimneys leachate taken in July 2018.

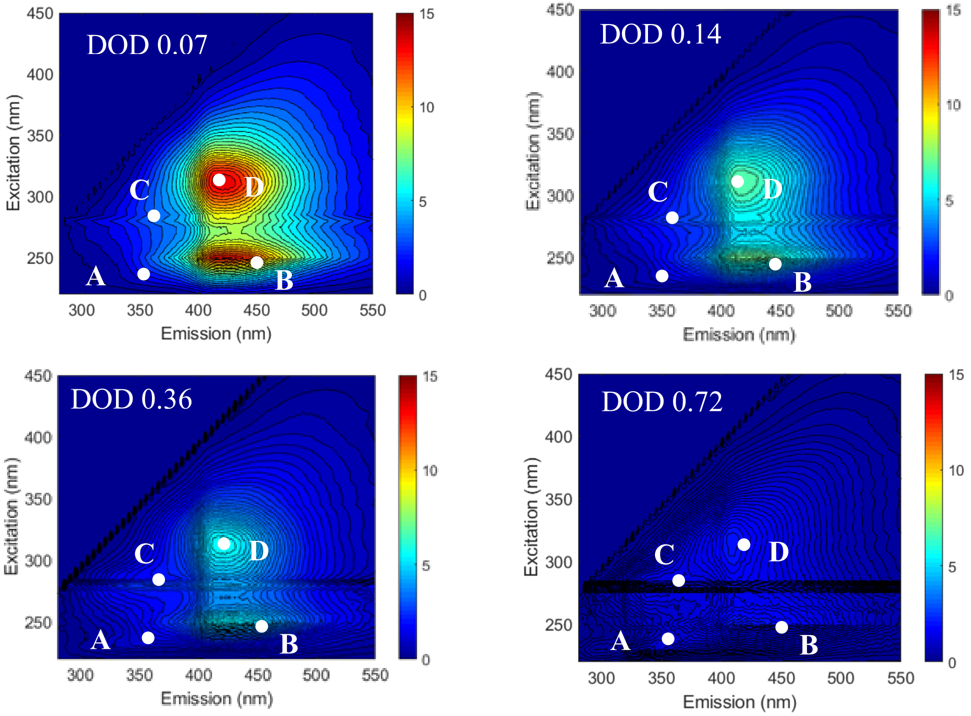


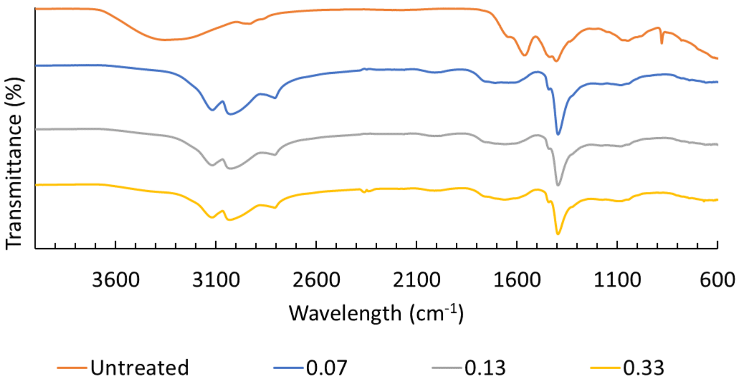
Figure 11: EEM of treated Fenton's oxidation treated Twin Chimneys leachate taken in February 2019.

The FTIR spectrum for the two untreated and Fenton's reagent treated leachate at varying DODs is shown in **Figure 12.** The absorption band assignments can be found in **Table 10.** One can see differences in the untreated leachate spectra, with the TC-2018 being more complex with more O-H phenol, C-H aliphatic, and COO- carboxylic bonds. This aligns with the initial leachate characteristics having higher concentrations of sCOD and DOC. However, when looking at the Fenton's oxidation treated samples, the spectrum for both leachates mirror each other. The spectra are also like the coagulation spectra in **Figure 5**. The major changes in the Fenton's treated samples are as follows:

- Decrease of phenolic compounds (TC-2018), likely from breaking down the humic substances derived from lignin
- Shift of C-H bond locations in aromatic compounds (changing the location where bond is present on the compound) to a higher wavelength, indicating atom mass decrease [112]
- Increase in C-H bonds in aliphatic structures, likely from hydroxyl radicals attacking unsaturated compounds from cyclic or aromatic compounds
- Increase in COO^-
- Decrease in N-H absorption intensity, which can be predicted by the aromatic protein peak intensities decrease in EEM

As dosage increased, the C=C peaks disappeared in the aromatic compounds. All treatments shift the C-H bonds in the aromatics, which may indicate that the heavier atoms within the aromatic compounds are being removed from the bonds causing the shift to a higher wavenumber. The breakdown of aromatics also corresponds with the increase in C-H bonds with an increase in aliphatic compounds. *Aftab et al.* also found that aromatic compounds were the first to degrade when using Fenton's oxidation [38].

TC-2018



TC-2019

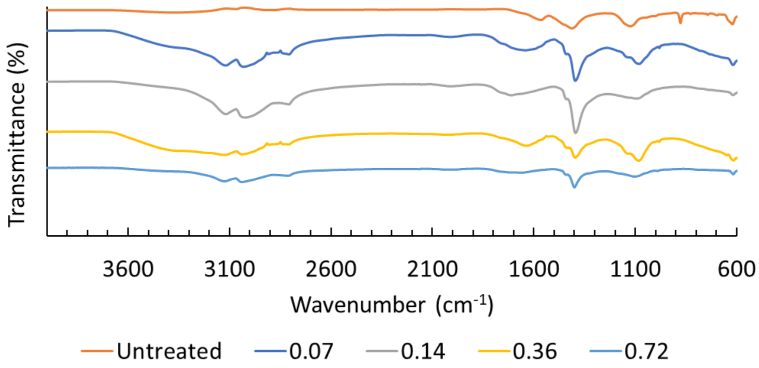


Figure 12: FTIR of untreated and Fenton's reagent treated (varying DOD values) supernatant of leachate taken on July 2018, top, and February 2019, bottom.

Table 10: FTIR absorption band definitions for untreated and Fenton's reagent treated Twin Chimney's leachate.

Wavenumber (cm^{-1})	Vibration	Functional Group	Ref.
3630-3200	O-H Stretching	Phenols	[115]–[117]
3200-3050	C-H stretching, NH_2 stretching	Aromatic, primary amides	[115], [117]
3120	C-H stretch	Aromatic	[115], [118]
3030	C-H stretch	Aromatic	[79], [117], [119]
2940	C-H Stretching	Methylene, Aliphatic Structures	[115], [118], [120]
2870	C-H Stretching	Methylene, aliphatic	[115], [117], [119]
2810	C-H stretching	Aliphatic	[119]–[121]
1690-1640	C=O, C=C stretching	Carboxylic acid, aromatic	[116], [117], [121]
1570-1560	N-H in Plane	Secondary Amides	[116], [117], [119]
1400-1390	COO- stretch	Carboxylic acids	[4], [71]

4.2.3 SLUDGE

To understand the removal occurring from oxidation versus coagulation at the end of the reaction, an FTIR of the sludge was analyzed, and can be seen in **Figure 13**. The transmittance scale is the same for both figures to show spectrum intensity. With increased DOD, there is less bonds present on the sludge. TC-2018 likely has lower intensity either from a heterogenous sample used, or since the sCOD removal was higher, more was being oxidized and less removal by a physical means. However, TC-2018 and TC-2019 have the same bonds present. The broad absorption in the higher wavelength is likely the O-H bonds from $Fe(OH)_3$ forming. The peak at 1,540 cm^{-1} is likely N-H in secondary amides [116], [117], [119]. As one can see, this band does not disappear with increased dosage. If the N-H bonds are a part of a saturated compound, this could explain why they do not decrease. As mentioned, Fenton's does not have an affinity for saturated compounds, so their primary method for removal is by coagulation. However, the peak at 1,420 cm^{-1} does nearly disappear at higher dosage. This band represents C-H bonds in aliphatic structures [117]–[119]. This decrease in absorption corresponds with the increase in the supernatant, suggesting as these form aromatic compounds, they are decreasing in size, making them harder to be removed, or, instead, these compounds are being mineralized at higher oxidant dosage.

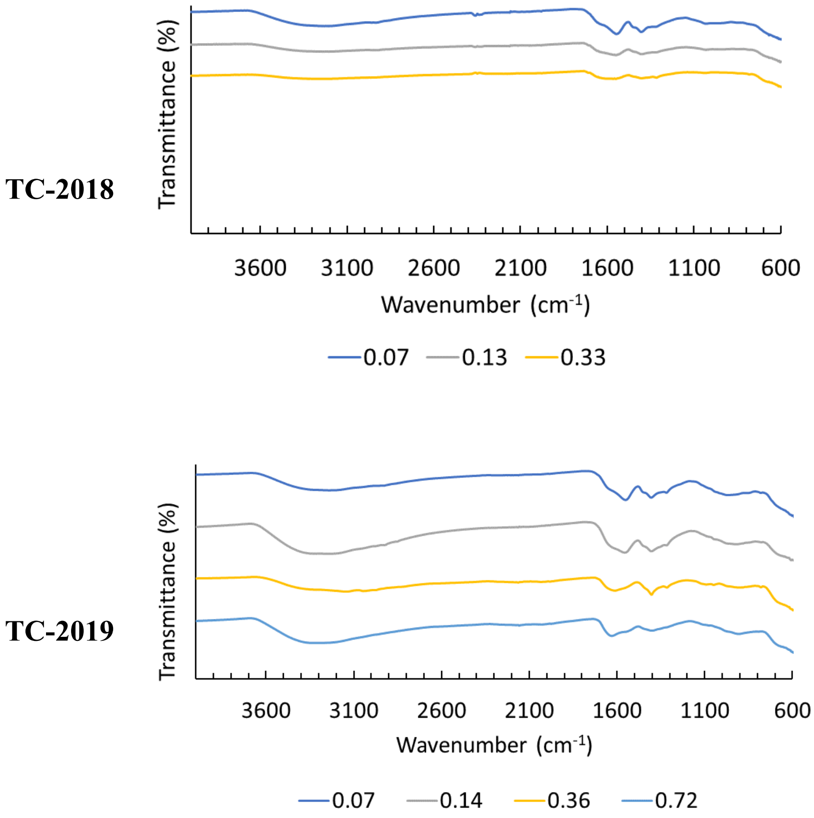


Figure 13: Sludge FTIR of Fenton's reagent treated (varying DOD values) leachate taken on July 2018, top, and February 2019, bottom.

4.3 FENTON'S REAGENT ON DIFFERENT LEACHATES AT THE SAME OXIDANT DOSAGE

From the analysis of the leachates taken at varying times from the same location, it was concluded they follow the same treatment trend, even with differing initial characteristics. To see if the same trend would occur with leachates at a different location, the higher oxidant dosage (0.72 DOD) experiment was done on two other leachates collected from a different landfill at different times. These samples were taken from Orange County in Florida and are labeled OC-1 and OC-2. The UVA_{254}, sCOD, DOC, and $SUVA_{254}$ before and after Fenton's oxidation treatment of ~0.7 DOD, compared to TC-2019 leachate are shown in **Figure 14**. The OC samples had a higher UVA_{254} (43.6 cm^{-1} and 53.0 cm^{-1} for OC-1 and OC-2, respectively) than TC-2019, but a lower sCOD (3,471 mg/L and 3,893 mg/L for OC-1 and OC-2, respectively) and slightly lower DOC (1,080 mg/L and 952 mg/L for OC-1 and OC-2, respectively). This tells us that the organic matter present in the OC leachate contains a larger amount of UVQS than TC-2019. This can be seen by the high initial $SUVA_{254}$ values of the OC leachate, with OC-1 reaching 4.04 L/mg-M and OC-2 5.57 L/mg-M.

Similarly to the other experiments, the sCOD removals were low compared to the literature, ranging from 18.8% to 25.9% removal for each leachate [32], [39], [40], [43], [46]. However, DOC, UV_{254}, $SUVA_{254}$ reduction removals did not show similar treatment patterns. For example, Fenton's oxidation on TC-2019 was able to decrease UVA_{254} by 81.3% while with OC-1 and OC-2 UVA_{254} was reduced by 69.5% and 64.7%, respectively. DOC changes were also not consistent, with TC-2019 Fenton's oxidation removing 48.8%, but OC-1 only removed 64.2% and OC-2 40.8%. However, both OC leachates end at a similar $SUVA_{254}$, reaching 3.44 L/mg-M and 3.32 L/mg-M for OC-1 and OC-2, respectively. The decrease indicates some hydrophobic and larger organics are being removed, but the plateau confirms that the DOC present within the OC leachates is more difficult to remove via oxidation or coagulation. The DOC left over is likely too large for significant oxidation and the coagulation at the end of the reaction does not have significant effects. Or, the DOC removed or broken down consisted of aromatic compounds and there is a larger amount of smaller organics and hydrophilic compounds left over that Fenton's oxidation does not have an affinity for and are harder to be removed by Fenton's coagulation.

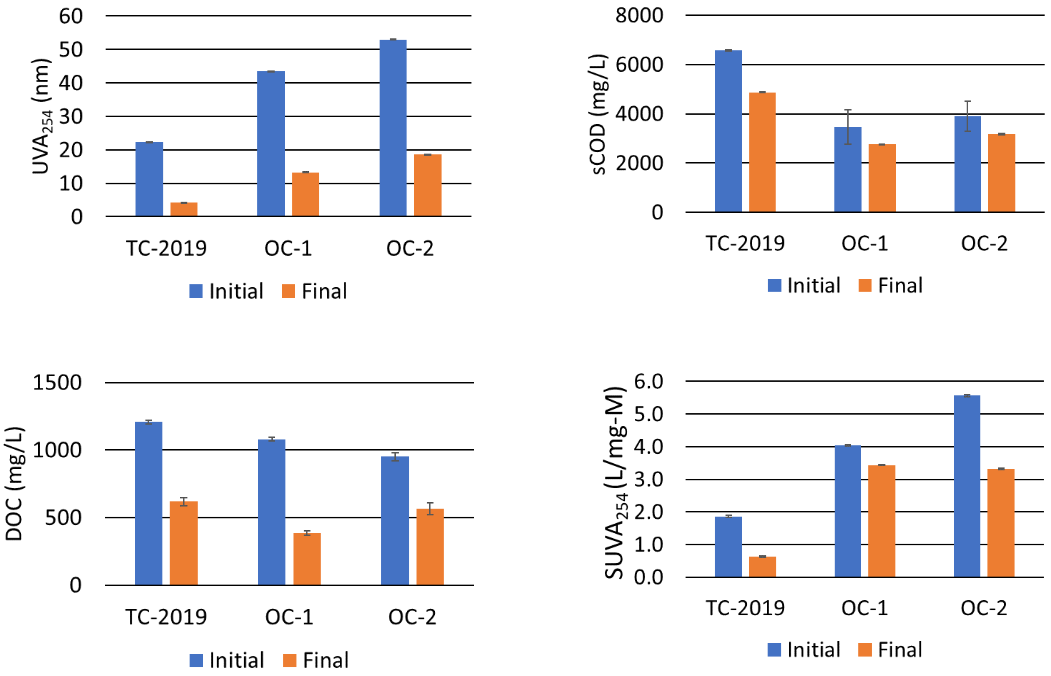


Figure 14: The UVA_{254} (top left), sCOD (top right), DOC (bottom left), and $SUVA_{254}$ (bottom right) of three untreated and treated leachates by Fenton's reagent at a ~0.7 DOD.

The EEM of the three untreated leachates and Fenton's oxidation treated leachate at a DOD ~0.7 can be found in **Figure 15.** Note the differences in fluorescence intensity scale for each. **Table 11** compares the EEM fluorescence peak intensities that were listed in **Table 4**. Like the initial sCOD and DOC concentrations versus the untreated UVA_{254}, these peak intensities do not match the pattern one would expect from the larger UVA_{254}. TC-2019 has a higher peak intensity than both OC leachates (minus Peak D in OC-2) even though it has a lower UVA_{254}. Also, after Fenton's treatment, the peak intensities of all samples were within range of each other. As mentioned, it has been found that EEM cannot successfully show the magnitude of the Hpi DOM fraction within a sample [32]. It has also been mentioned that the Hpi makes up the largest fraction of the TOC and the smaller organics within Hpi account for the largest individual

UVA_{254} fraction. Therefore, the EEM peaks represent the hydrophobic DOM removal, and the decrease in DOC and $SUVA_{254}$ is represented by these changes. However, the remaining DOC and high $SUVA_{254}$ for OC leachates are likely the Hpi fraction.

Table 11: EEM fluorescence intensities for each peak of untreated and Fenton's reagent treated TC and OC leachate at ~0.7 DOD.

	Fluorescence Intensities (RU)			
	Peak A	**Peak B**	**Peak C**	**Peak D**
TC-2019	10	48	15	28
DOD 0.72	1	2	1	2
OC-1	6	26	11	26
OC-1 DOD 0.70	1	2	1	3
OC-2	8	34	15	36
OC-2 DOD 0.67	1	5	2	6

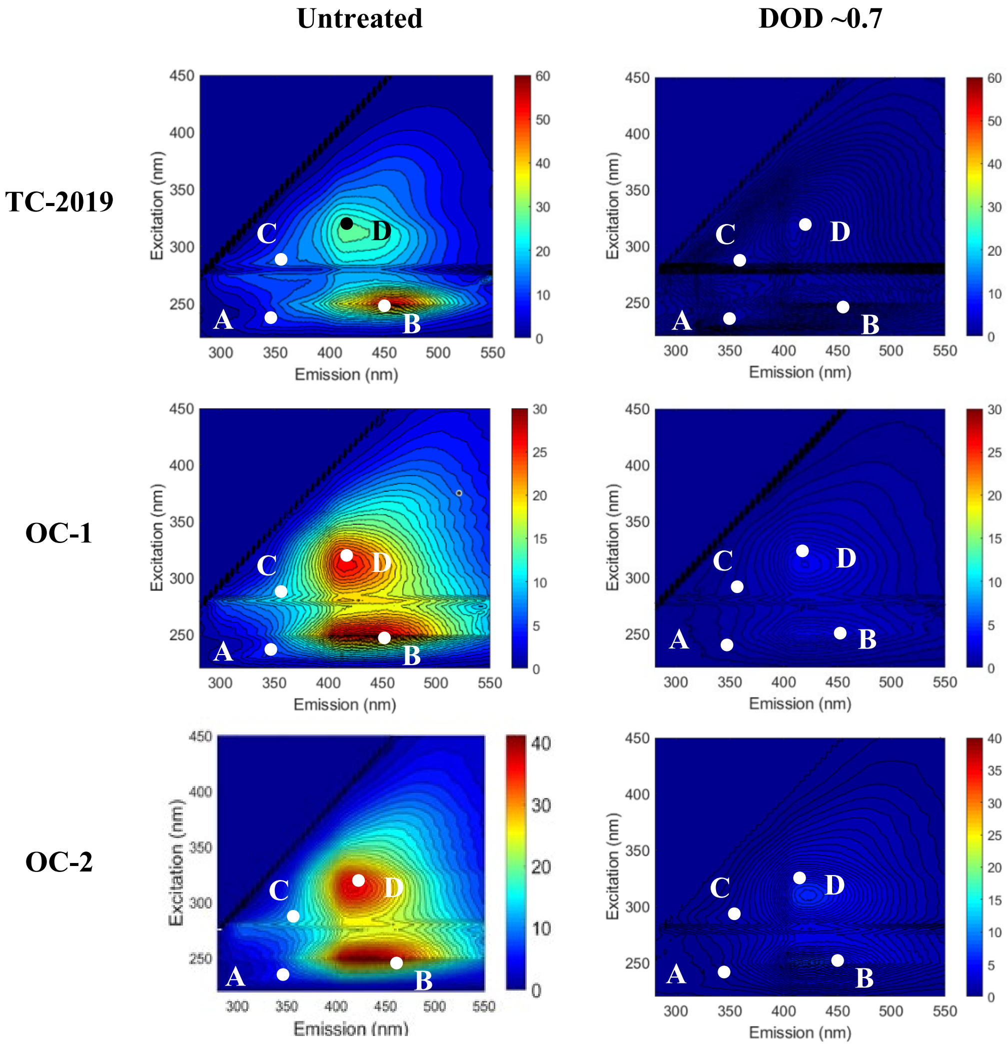


Figure 15: EEM of three different leachates treated by Fenton's oxidation at a DOD ~0.7.

From these results, one can see how poorly using DOD for Fenton's oxidation dosing is for treatment of leachate to remove UVQs. When looking at different leachates, the sCOD removal was similar for all, but a suitable UVA_{254} was not reached. As mentioned, research has found that DOC and UVA_{254} are correlated [13], [103]. Therefore, a better characteristic to understand the level of oxidant required for leachate treatment may be DOC or $SUVA_{254}$ instead. As shown, these characteristics are better related to the amount of UVQS present. For a treatment plant to be successful in treating landfill leachate, looking at COD alone will only give one side of the story, and will not be a proper representation of the UVQS present. Therefore, if one is trying to optimize treatment to reduce UVQS, the DOC or $SUVA_{254}$ will be more effective predictors.

5 CONCLUSIONS

From this study, the major conclusions are as follows:

- Adjusting the pH of the leachate samples can cause irreversible damage to the DOM, likely by breaking down the lignin that is present.
- sCOD removal had little dependence on pH and dosage, but pH 5.5 and pH 6.5 with 5 g/L $FeCl_3$ reached a maximum removal of 33.2% and 33.3%, respectively.
- For coagulation, maximum DOC removal occurred at pH 6.5 and 10 g/L $FeCl_3$ at 65.1% removal, but removal at pH 5.5 dominated at lower dosages.
- Maximum UVA_{254} reduction occurred with pH 6.5 at all concentrations, but 10 g/L $FeCl_3$ had the greatest reduction of 22.4 cm^{-1} to 2.6 cm^{-1}. This pattern followed with $SUVA_{254}$, with a maximum decrease from 1.86 L/mg-M to 0.62 L/mg-M.
- pH 5.5 and pH 6.5 plus 10 g/L $FeCl_3$ had the largest DOM EEM peak removals, but pH 6.5 only outperformed in removing the fulvic acid-like peak, indicting the fulvic acids are the dominant UVQS in TC-2019 since this sample had the lowest UV_{254}.
- When treating two leachates from Twin Chimney's with Fenton's reagent, removal of all characteristics increased with oxidant dosage. Maximum removal for sCOD was 42.3% (the only measurement that outperforming coagulation alone) and DOC at 48.8%. Fenton's oxidation decreased the UV_{254} and $SUVA_{254}$ from the same leachate as the coagulation experiment to 4.2 cm^{-1} and 0.63 L/mg-M, respectively.
- Similarly to the coagulation experiment, the fulvic acid-like peaks had the largest removals for Twin Chimney's Fenton's samples.

- Fenton’s increased the carboxylic acids and aliphatic bonds in the sample, likely from amino acid and aromatic compound degradation, respectively. But, as DOD increases the carboxylic acids begin to decrease, as well.
- As the DOD increased for Fenton’s, there is more mineralization, shown by the decreased aliphatic bonds on the sludge.
- When comparing the Orange County and Twin Chimney’s leachates to each other, the increased UV_{254} of the Organic County leachate did not correspond with larger EEM peaks, indicating a significant amount of Hpi present. This corresponds with the variation in treatment characteristics with sCOD being the only measurement with consistent removals for all leachate after a DOD ~0.7.

From these results, we can start making conclusions about our initial research questions and hypothesis. The first set of hypotheses were based on the removal of UVQS when using coagulation alone versus Fenton’s oxidation combined with coagulation/flocculation. A comparison of treatment of TC-2019 by coagulation/flocculation with an initial pH of 6.5 and a 10 g/L $FeCl_3$ dosage and Fenton’s oxidation with a 0.72 DOD can be seen in **Table 12**. Coagulation alone, Fenton’s oxidation, and Fenton’s coagulation were able to remove UVQS, but not to the degree preferred, only reaching a minimum UVA_{254} of 2.6 cm^{-1}, corresponding to a 0.25% UVT. Coagulation alone outperformed Fenton’s in all aspects, expect for sCOD removal, disproving the initial hypothesis. This is likely because Fenton’s is oxidizing the larger organics in smaller compounds that have less removal by Fenton’s coagulation. However, if this is occurring, the organics that are left over will also presumably be more biodegradable and readily available during biological treatment at POTW. Therefore, it is likely the sweep flocculation removal mechanism during Fenton’s coagulation has little effects on the treatment level. However, coagulation and Fenton’s can both successfully remove the DOM fractions shown in the EEM. Fenton's brought these peaks to a lower peak intensity, even with lower levels of treatment. This tells us that even though Fenton's has better DOM removal, coagulation alone is likely better at removing the Hpi fractions present that are not shown in the EEM. This can be concluded by the lower $SUVA_{254}$ for coagulation. However, the almost complete removal of EEM peaks but still reaching a 0.25% UVT indicates there is still room for further research in this topic to understand what UVQS is not being represented in the EEM. For example, is there residual iron that is attenuating the UV? Or, since Fenton's has little effect on ammonia, how much effect can this have on the UVA_{254}? The FTIR spectrum for coagulation and Fenton's were also similar showing aromatic bond decreases, but Fenton's was better at removing the carboxylic acids. However, with such a high iron dosage in coagulation, it is likely causing some interference with the FTIR spectrum. The little differences in the FTIR spectrum indicate, if used alone, it cannot give a in-depth analysis of treatment between samples. However, if used in conjunction with other analytical techniques it may be able to confirm hypothesizes.

Table 12: TC-2019 treatment comparison between coagulation with initial pH of 6.5 and a 10 g/L $FeCl_3$ dosage and Fenton's oxidation with a 0.72 DOD.

	Parameter	**Coagulation (pH 6.5 10 g/L dosage)**	**Fenton's (0.72 DOD)**
General Characteristics	sCOD (Removal %)	22	26
	DOC (Removal %)	65	49
	UVA_{254} (cm^{-1})	2.6	4.2
	UVT (%)	0.25	0.0063
	$SUVA_{254}$ (L/mg-M)	0.62	0.63
EEM Peak Fluorescence Intensity (RU)	A (tryptophan)	3	1
	B (fulvic acid)	5	2
	C (tyrosine)	4	1
	D (marine humic acid)	3	2
Functional Groups, Liquid	Compounds changes	Aromatic & aliphatic shift, increase carboxylic, decrease amide	Aromatic & aliphatic shift, decrease carboxylic, decrease amide
Functional Groups, Sludge	Absorbed compounds	Same as liquid	Amides, aliphatic (but may be decreasing with oxidant dose)

When looking at the second set of hypotheses, based on the treatment of UVQS in different leachates with the same Fenton's oxidation dosage, the removals trends were not consistent when using Fenton's. This can be seen in **Table 13** when comparing a 0.7 DOD treatment on TC-2019, OC-1, and OC-2. Therefore, when analyzing what treatment dosage for Fenton's is optimum for a leachate, one cannot consider COD alone, which DOD does. Instead, one must look at the DOC or $SUVA_{254}$, because it will shed light on the dominate DOC fraction within the leachate. This will allow one to have a deeper understanding of the UVQS than when using COD.

Table 13: Fenton's oxidation treatment comparison with a 0.7 DOD on TC-2019, OC-1, and OC-2.

Parameter	**TC-2019 (0.72 DOD)**		**OC-1 (0.70 DOD)**		**OC-2 (0.67 DOD)**	
sCOD (% Removal)	26		20		19	
DOC (% Removal)	49		64		41	
	Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**
UVA_{254} (cm^{-1})	22.4	4.2	43.6	13.3	53.0	18.7
UVT (%)	$3x10^{-21}$	0.0063	$3x10^{-42}$	$5x10^{-12}$	$1x10^{-51}$	$2x10^{-17}$
$SUVA_{254}$ (L/mg-M)	1.86	0.63	4.04	3.44	5.57	3.32
Peak A, tryptophan (RU)	10	1	6	1	8	1
Peak B, fulvic acid (RU)	48	2	26	2	34	5
Peak C, tyrosine (RU)	15	1	11	1	15	2
Peak D, marine humic acid (RU)	28	2	26	3	36	6

In conclusion, both treatments were able to remove UVQS, but due to the varying nature of leachate, oxidation methods may not always be the best option for treatment and one must conduct a deeper analysis to understand what the dominant DOM fraction is and what the most effective means are to remove it.

5.1 FUTURE WORK

Moving forward, further research on this topic should evaluate more leachates from varying landfill locations and ages. This will give a wider array of initial characteristics to confirm if analyzing UVQS treatment is best with sCOD (DOD) or another parameter, like DOC or $SUVA_{254}$. If DOC and $SUVA_{254}$ are shown to be better predictors, further research can include other treatment methods, not just coagulation/flocculation or Fenton's oxidation. It may include other complex methods, like advanced oxidation or electrochemical oxidation, or even simpler methods, like filtration.

A deeper analysis of the sCOD present in the leachate may also shed light on the lower removals. One could gain a deeper understanding of coagulation/flocculation and Fenton's oxidation ability to remove the various constituents of sCOD if these constituents that make up sCOD were known. Also, ammonia can also contribute to UVA_{254} and sCOD, so a deeper analysis of how that is affected during these treatments should be done. This may result in better optimization of the process and give a better correlation to the UVQS.

The analytical methods used should also be expanded to include size exclusion chromatography, an elemental/metal analysis, NMR, and gas chromatography-mass spectroscopy (GC-MS). These do not require pH changes but can still give a more in-depth analysis of what organics are being removed via physical means or oxidation. Size exclusion will also confirm or disprove the hypothesis that Fenton's oxidation is oxidizing the organics into small compounds that are less likely to be removed by coagulation. An elemental analysis will also strengthen this data with the ability to do a mass balance on the carbon present before and after treatment. The metal analysis will also show if there are any other compounds present that contribute to UVA_{254}, like iron and bromide. From the experimental photos in **Appendix B**, one can see there is still visible color within each sample, likely corresponding to either the organic matter still present or any soluble iron still present. A metal analysis will quantify how much iron is still present and contributing to the UVQS. NMR can show shifts in the chemical structure, which can indicate the changes in the compounds before and after treatment [36]. GC-MS can also what organic acids are being targeted during treatment, and, in the case of Fenton's oxidation, one can analyze the by-products formed.

Also, the effects of pH changes should be further analyzed, since changing the pH for coagulation and Fenton's oxidation experiments not only affects the iron speciation but may also cause some DOM to be removed in the process. Therefore, how much DOM is affected by each process should be studied. A metal analysis may also be useful, because, as mentioned above, when changing the pH to 4 for the untreated leachate, there were still some functional group changes seen in the FTIR. It was hypothesized that this was from any potential iron present in the leachate already. A metal analysis could also show how much residual iron is left in the samples which may be causing interference in other measurements.

Lastly, a tighter range of coagulant dosages could be studied. For sCOD there was not much difference between dosage and pH, but the other parameters did. Looking at a smaller increment of dosages would shed light on more trends between treatment. For example, do the changes begin to plateau? If so, when? Would increasing the pH 8.2 samples above a 10 g/L $FeCl_3$ dosage increase the removals back to the 5 g/L $FeCl_3$ dosage range?

Lastly, this study focused on landfill leachate pretreatment to optimize the removal of UVQS. As mentioned, the primary concern with leachate is the passage of these constituents through a POTW, resulting in negative effects on UV disinfection. Therefore, there should be additional experiments to gain a better understanding of how the UVQS present in leachate affect the POTW process after pretreatment by coagulation/flocculation or Fenton's oxidation. This can be done by measuring BOD_5, which will give an indication of the amount of biodegradable organic matter present in the leachate. Presumably if this value is high, the organic matter present will be easily removed during biological treatment at a POTW. One can also treat the leachate in a simulated SBR to show what the final UVA_{254} will be after biological treatment. A simulated SBR can also show if there are any constituents still present in the leachate that may inhibit biological treatment, like heavy metals.

With additional analytical methods used, and samples studied, it can help further understand how landfill leachate treatment can be optimized to alleviate the issues that occur when sending it to a POTW that uses UV disinfection. Even with a greater understanding of how coagulation/flocculation and Fenton’s oxidation treatment affects landfill leachate found during this research, there are still many unknowns that need to be studied.

6 APPENDICES

6.1 APPENDIX A: LANDFILL COMPOSITION

Table A-1. Total United States municipal solid waste materials landfilled in 2015 [1].

Material	Total MSW Landfilled	
	By Percent	By Ton
Food	22.0	30.1
Rubber, leather, and textiles	10.9	14.9
Wood	8.0	11.0
Plastics	18.9	25.9
Glass	5.1	7.0
Metals	9.5	13.0
Yard Trimmings	7.8	10.7
Paper and cardboard	13.3	18.2
Other	4.5	6.2
Total	100	137

6.2 APPENDIX B: EXPERIMENT PHOTOS

Figure B-1: Untreated Twin Chimney's leachate (February 2019)

Figure B-2: Jar experiment after rapid mixing for pH 8.2 (top), pH 5.5 (middle), and pH 6.5 (bottom) samples with 1 g/L (A, B), 5 g/L (C, D), and 10 g/L (E, F) $FeCl_3$ dosages.

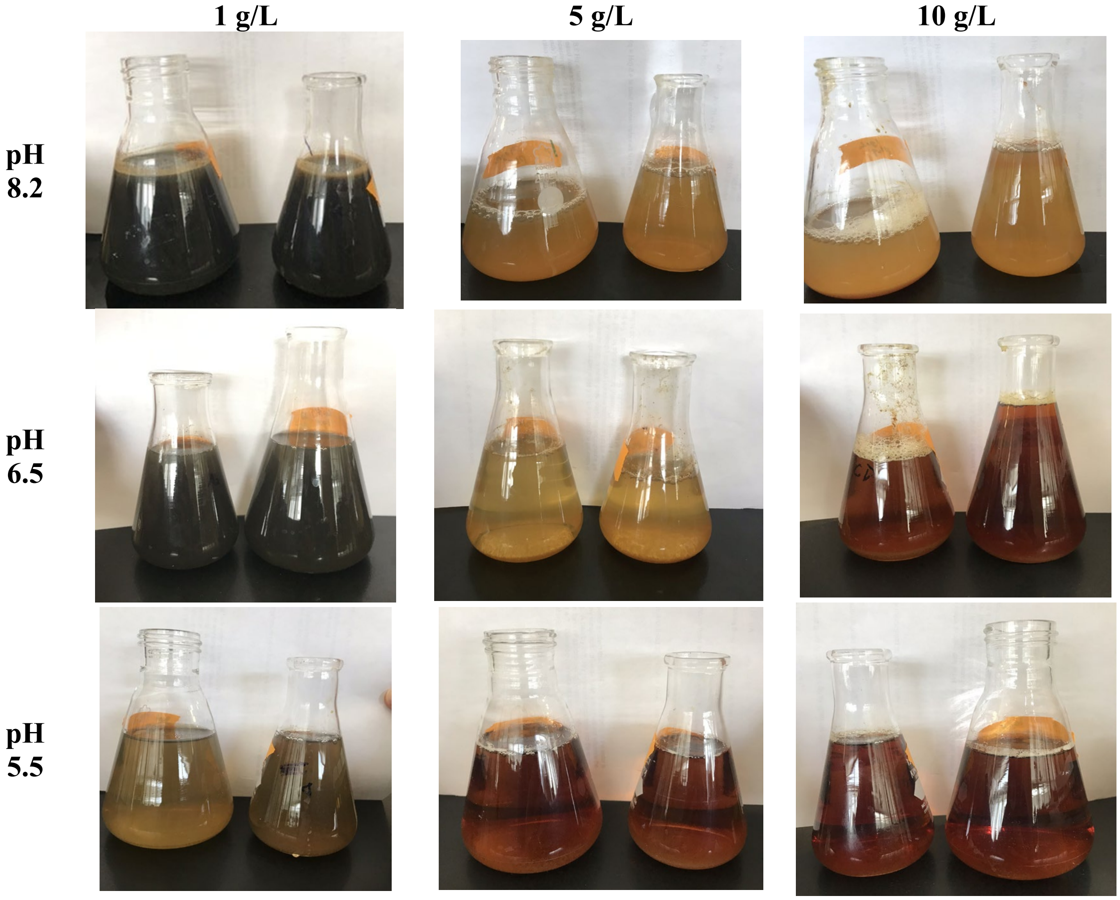


Figure B-3: Supernatant taken after sedimentation for coagulation treated samples and varying initial pH values and $FeCl_3$ dosages.

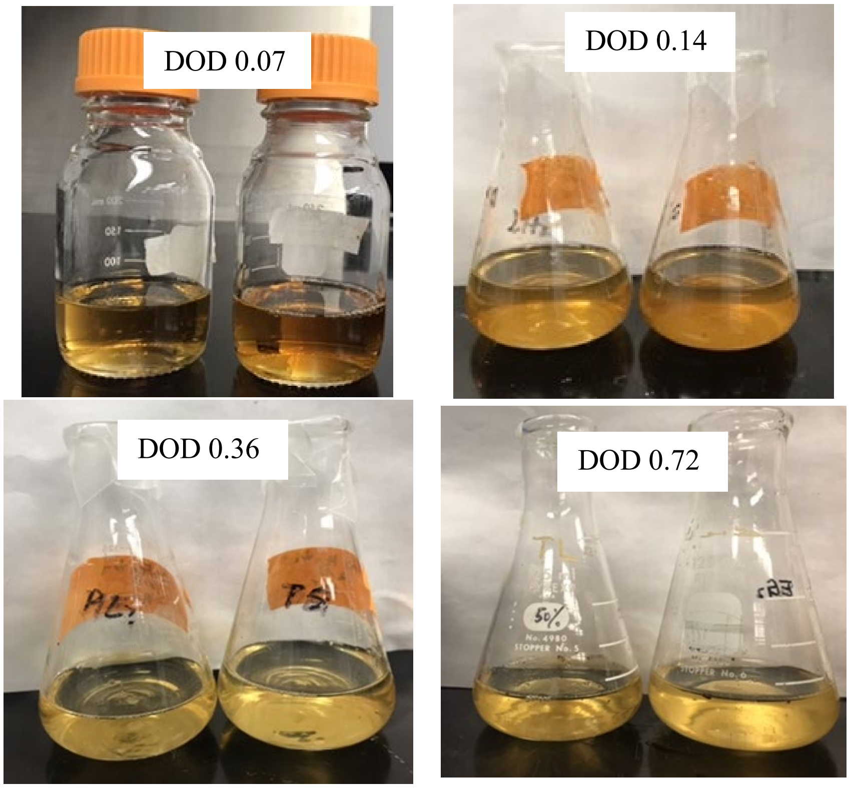


Figure B-4: Supernatant of Fenton's oxidation treated landfill leachate (February 2019) at varying DODs.

6.3 APPENDIX C: CONTROLS

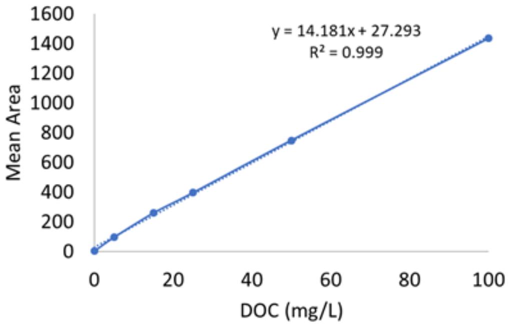


Figure C-1: Example DOC calibration curve used for experiments.

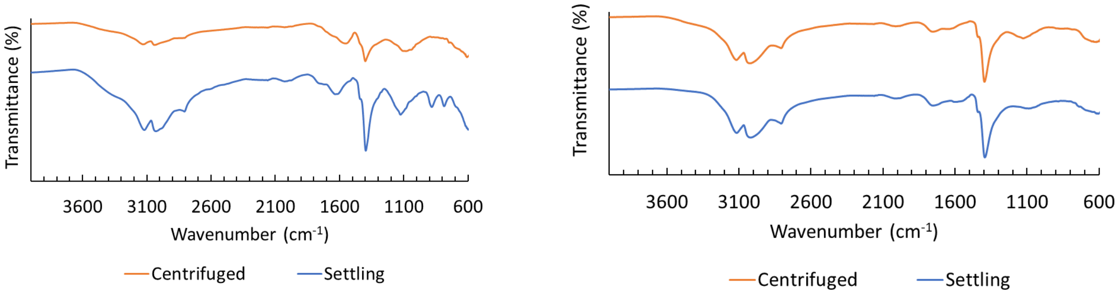


Figure C-2: FTIR of supernatant (left) and sludge (right) of pH 5.5 5 g/L $FeCl_3$ dose coagulation sample subject to centrifuging and settling.

Table C-1: H_2O_2 initial and final concentration after raising the pH to 12 and heating the sample at 80°C for 24 hours.

H_2O_2 Initial Concentration (mg/L)	H_2O_2 Final Concentration (mg/L)
4471	120
1756	118
945	120

Table C-2: Leachate characteristics after raising the pH to 12 then readjusting to pH 8.

pH	UV_{254} (cm^{-1})	DOC (mg/L)	sCOD (mg/L)
8	20.9	1340	6571
12	20.0	890	4407
8 (readjusted)	18.0	840	6525

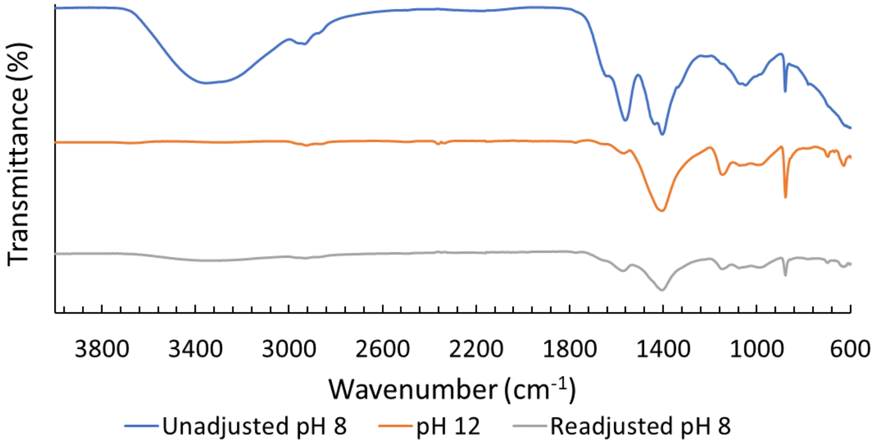


Figure C-3: Leachate FTIR after raising the pH to 12 then readjusting to pH 8

Table C-3: H_2O_2 initial and final concentration after the addition of catalase and mixed for 3 minutes at 125 rpm.

H_2O_2 Initial Concentration (mg/L)	H_2O_2 Final Concentration (mg/L)
4985	124
1994	139
997	126

Table C-4: Leachate characteristics after the addition of catalase and mixed for 3 minutes at 125 rpm.

Treatment	UV_{254} (cm^{-1})	DOC (mg/L)	sCOD (mg/L)
Untreated	24.3	723.17	6084
Catalase Addition	24.5	753.11	6920

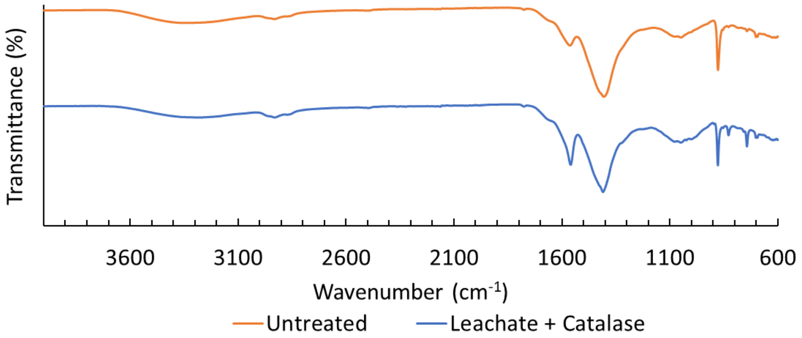


Figure C-4: Leachate FTIR after the addition of catalase and mixed for 3 minutes at 125 rpm.

Table C-5: Leachate characteristics untreated and after adjusting the solution pH to 4 then 8, adding catalase, and centrifuging.

Treatment	UV_{254} (cm^{-1})	DOC (mg/L)	sCOD (mg/L)
Untreated	24.5	753	6920
pH4 → pH8 with Catalase & Centrifuged	22.1	681	6822

Table C-6: Leachate characteristics untreated and after a 0.07, 0.13, and 0.33 DOD and a 0.33 DOD with a pH 4 adjustment.

Treatment	UV_{254} (cm^{-1})	DOC (mg/L)	sCOD (mg/L)
Untreated	35.7	1407	7208
0.07 DOD	34.3	1493	6023
0.14 DOD	34.8	1461	6390
0.33 DOD	32.4	1553	6940
0.33 DOD pH 4 → pH 8	31.4	1423	5948

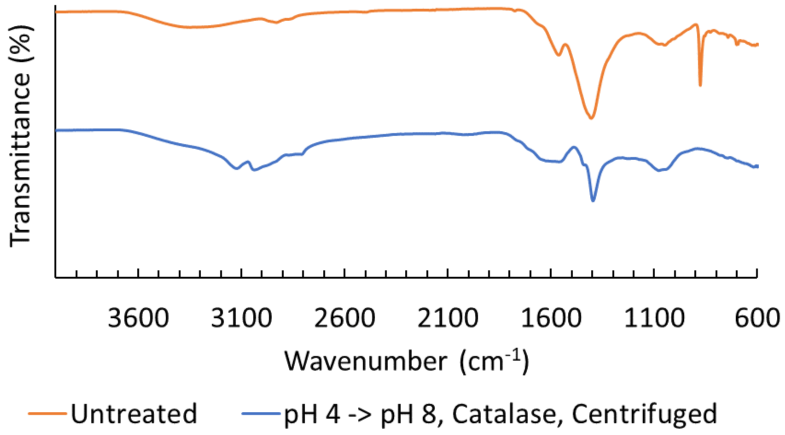


Figure C-5: FTIR of leachate that is untreated and after adjusting the solution pH to 4 then 8, adding catalase, and centrifuging.

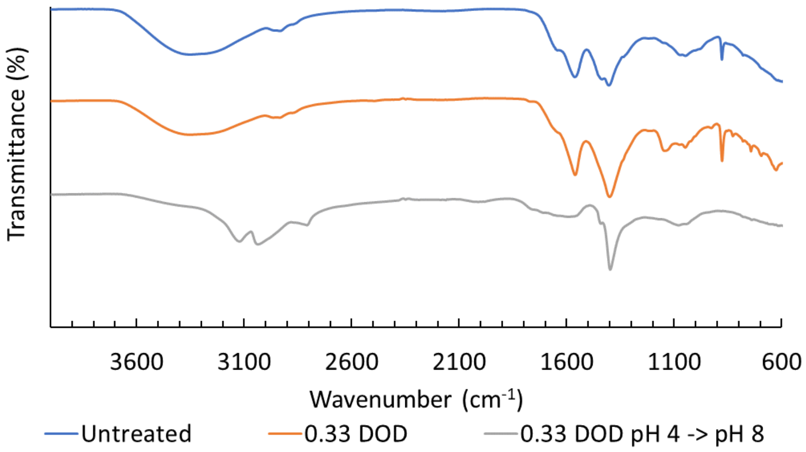


Figure C-6: FTIR of leachate that is untreated and after a 0.33 DOD without and without a pH 4 adjustment.

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