Suspended Fiber Biofiltration for the Treatment of Landfill Leachate. Year II. Incorporation of Advanced Oxidation and Phosphorous Removal in a Single Unit

August 31, 2016

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Report #

FINAL REPORT

September 1, 2015 to August 31, 2016

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TAG MEMBERS: Peter Grasel, Owete Owete, John Hallas, Lin Chen, Hafiz Ahmad and Matthew Hendrix

KEY WORDS: Landfill Leachate, Suspended Fiber, Biofiltration, Advanced Oxidation, and Phosphorous Removal.

ABSTRACT (1 page only)

During the first year of the project, we investigated organic, iron and chloride removal using aerated leachate recirculation and suspended fiber biofiltration, together with the ultra-high lime with aluminum process. As a cost- and space-saving technology, suspended fiber biofiltration can effectively remove organics and iron from landfill leachate. Especially, suspended fiber biofiltration promotes biological contact oxidation, during which organics and iron can be removed more efficiently. For the second year, advanced oxidization was introduced to a specially designed fiber biofilter for xenobiotic degradation and phosphorous removal of landfill leachate in a single unit. The introduced advanced oxidation also led to improved aerobic biodegradation of organics and precipitation of heavy metals. After xenobiotic destruction by advanced oxidation, iron, phosphorous and organics were removed step by step by a series of suspended fiber biofilters. The combination of advanced oxidizing processes, i.e., the usage of oxidizing chemicals and the subsequent suspended fiber biofiltration in a single treatment unit provides a novel and cost- and space-saving treatment alternative for handling landfill leachate at landfill sites.

Metrics:

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

Last name, first name	Rank	Department	Professor	Institution
Houzhen Wei	Postdoctoral Researcher	Civil and Environmental Engineering	Gang Chen	Florida State University
Boya Wang	Ph.D.	Civil and Environmental Engineering	Gang Chen	Florida State University

2. List undergraduate researchers working on this Hinkley Center project

Last name, first name	Department	Professor	Institution
Quinn Zacharias	Civil and Environmental Engineering	Gang Chen	Florida State University

3. List research publications resulting from this Hinkley Center project
Wang, B., Grasel, P., Owete, O., Hallas, J., Ahmad, H. and Chen, G. “Advanced Oxidation and Suspended Fiber Biofiltration for the Treatment of Landfill Leachate”, International Journal of Water and Wastewater Treatment, 2016, under review.

Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. “Landfill Leachate Treatment by Aerated Recirculation and Pressurized Suspended Fiber Biofiltration”, Frontier in Environmental Engineering, 2015, 4 (1) 7-18.

4. List research presentations resulting from this Hinkley Center project
Li, R., Wang, B. and Chen, G. “Arsenic and Phosphorous Removal from Landfill Leachate by Biofiltration”. 2016 Florida Branch Meeting, American Society for Microbiology, Miami, FL. Oct. 14-16, 2016.

Wang, B. and Chen, G. “Xenobiotic Removal from Landfill Leachate by Combined Advanced Oxidation and Microbial Degradation”. 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA, Nov. 13-15, 2015.

5. List who has referenced or cited your publications from this project?
Current research has been submitted to Environmental Technology and currently is under review. Following is the information of citation of recently finished projects:

Power generation and nitrogen removal of landfill leachate using microbial fuel cell technology
Lee, Y., L. Martin, P. Grasel, K. Tawfiq and G. Chen*, 2013, Power generation and nitrogen removal of landfill leachate using microbial fuel cell technology, Environmental Technology, 34, 2727-2736.

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6. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?
"Electromagnetic Waves-Induced Heavy Metal Removal for Biosolids" by Gang Chen and Youneng Tang will be submitted to Environmental Research and Education Foundation in response to High Need Topics in Solid Waste Research.

7. What new collaborations were initiated based on this Hinkley Center project?
We have initiated collaboration with John Hallas from Talquin Electric Cooperative, Inc. and Hafiz Ahmad from Florida State University at Panama City Campus from this research. In addition, we have been contacted by Jeffrey Cunningham from University of South Florida and requested for collaboration through an EPA-funded research center (http://usf-reclaim.org/). They are interested in investigating the removal and recovery of nutrients (nitrogen and phosphorus) at centralized wastewater treatment plants. They are currently conducting research on recovery and removal of N and P through a combination of engineered struvite precipitation and microbial fuel cells, which we have investigated through the projects sponsored by the Hinkley Center. They learned about our research through our web sites and requested for collaboration. Other people involved in the collaboration include Daniel Yeh (USF), Treavor Boyer (UF), and Jim Mihelcic (USF).

8. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum).
We presented our research at Leon County Landfill and Springhill Regional Landfill. Leon County Solid Waste Management Director, Leon County Solid Waste Superintendent, District Manager of Waste Management at Springhill, Market Area Engineer of Waste Management, Inc. and Environmental Protection Manager of Waste Management, Inc., etc. attended the presentation. The technical achievement of this project was discussed and suggestions were provided for further research. We also shared the results with FDEP through TAG members of Owete Owete and Peter Grasel, who are in charge of old landfill and groundwater monitoring. In addition, we discussed the results with Talquin Electric Cooperative, Inc., which operates seven wastewater treatment plants.

EXECUTIVE SUMMARY

September 1, 2015 to August 31, 2016

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PROJECT TAG MEMBERS: Peter Grasel, Owete Owete, John Hallas, Lin Chen, Hafiz Ahmad and Matthew Hendrix

COMPLETION DATE: August 31, 2016

Objective:

In our prior research, we investigated organic, iron and chloride removal using aerated leachate recirculation and pressurized suspended fiber biofiltration, together with the ultra-high lime with aluminum process. As a cost- and space-saving technology, leachate recirculation and pressurized suspended fiber biofiltration provided a new alternative means for the treatment of landfill leachate with high organic and iron contents. In order to degrade xenobiotic compounds and remove phosphorous from landfill leachate, advanced oxidizing processes, i.e., the usage of UV or oxidizing chemicals were introduced to the leachate treatment and suspended fiber biofiltration was re-configured to enhance iron and phosphorous removal in addition to organic degradation. The specific objectives of this research project included:

1. Reactor Design, Setup and Parameter Characterization. A reactor was designed to include advanced oxidation and suspended fiber biofiltration in a single unit. The hydraulic parameters were characterized and the design of the reactor was optimized to achieve the desired xenobiotic, iron and phosphorus removal goals.
2. Reactor Operation. Advanced oxidation processes including UV, ozone and hydrogen peroxide were tested for the decomposition of xenobiotics and suspended fiber biofiltration was tested for iron and phosphorous removal in addition to organic degradation.
3. System Optimization and Cost Analysis. The best design and operation parameters were identified and optimized for advanced oxidation, iron and phosphorous removal and organic decomposition. Cost- and space- saving was analyzed and compared with that of conventional treatment processes.

Methodology:

Many of the landfills may contain xenobiotic compounds including monoaromatic hydrocarbons and halogenated hydrocarbons. Xenobiotics are well documented to have negative effects in the aquatic environment and are resistant to biodegradation. Besides xenobiotic compounds, high phosphorous content is also an important issue for landfill leachate management. As alternatives to biodegradation, advanced oxidation processes, i.e., the usage of UV radiation or oxidizing chemicals such as ozone (O_3) and hydrogen peroxide (H_2O_2) can effectively break the stable xenobiotic structures. In addition, iron oxides formed during advanced oxidation have high binding strength for phosphorus, which has the potential implementations of phosphorus removal. For this research, in order to degrade xenobiotic compounds and remove phosphorous from landfill leachate, advanced oxidizing processes, i.e., the usage of UV or oxidizing chemicals were introduced to the leachate treatment and suspended fiber biofiltration was re-configured to enhance iron and phosphorous removal in addition to organic degradation. This novel design provides a new alternative means for the treatment of landfill leachate with high organic, xenobiotic, iron and phosphorous contents. Besides the effluent quality, this research also takes into consideration of the treatment costs. Cost benefits of the landfill leachate treatment were analyzed and compared with those of conventional treatment processes and reported in this research.

Results:

Landfill leachate was treated by combined advanced oxidation and suspended fiber biofiltration in this research. Advanced oxidation destructed xenobiotics in the landfill leachate and the following biofiltration decomposed the organic compounds. With advanced oxidation, ferrous iron in the landfill leachate was oxidized to iron oxide and coated the suspended fiber, which removed the phosphorous from the landfill leachate through adsorption. Through advanced oxidation, 76% of the organics was removed. In the following up series of biofilters, organics were further removed with the effluent from the third stage biofilter meeting the discharge requirements. For iron removal, advanced oxidation only contributed to iron transformation. The following three stages of biofiltration removed iron by 99% to meet the discharge requirements. Phosphorous was also effectively removed in this system through adsorption to the iron oxide-coated suspended fiber. With an input close to 12 mg/L, an effluent of 1 mg/L was achieved, which complied with the discharge requirements.

This technology has potential markets for small landfills that serve low population areas and landfills that are at a distance from sewage treatment systems. It provides a sustainable and profitable solution for landfill managers to handle landfill leachate with high xenobiotics, organic, iron and phosphorous contents at the landfill sites. Besides being practical, this treatment process also has the benefits of lowering the treatment costs.

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1. Introduction

1.1 Advanced Oxidation for Xenobiotic Degradation

Many of the landfills might have received xenobiotic organic compounds (XOCs) from the time period when there were fewer restrictions on the disposal of hazardous waste in municipal solid waste (MSW) landfills (Kjeldsen et al., 2002). The most frequently found XOCs in these landfills are the monoaromatic hydrocarbons (i.e., benzene, toluene, ethylbenzene and xylenes, etc.) and halogenated hydrocarbons (i.e., tetrachloroethylene and trichloroethylene, etc.). Selected XOCs that are commonly present in the landfill leachate are summarized in Table 1 (Kjeldsen et al., 2002). XOCs in the landfill leachate also include synthetic organochlorides such as plastics and pesticides, naturally occurring organic chemicals such as polyaromatic hydrocarbons (PAHs), and some fractions of crude oil and coal, etc. (Ragle et al., 1995; Renou et al., 2008). The structure of xenobiotic molecules is usually characterized by “unphysiological” substituents and stable chemical bonds, making xenobiotics resistant to degradation. These pollutants are well documented to have negative effects in the aquatic environment (Lonborg et al., 2006). Several of these compounds have been designated as priority pollutants by the U.S. Environmental Protection Agency. Besides being resistant to biodegradation, there are some other factors that may also lead to significantly extended lifetime of these xenobiotics in the landfills. For instance, the presence of special waste types that have very high sorptive capacities such as activated carbon or insulation foams that release chlorofluorocarbons (CFCs) may extend the lifetime of XOCs considerably (Kjeldsen et al., 1995; Kjeldsen et al., 1998). In addition, slow desorption from the organic waste may also govern the release of XOCs, a fact that has been observed in several studies with soils (Baun et al., 2004). Besides the fact that the “unphysiological” substituents and stable chemical bonds impede or even prevent biodegradation of xenobiotics by microorganisms, unfavorable concentrations of xenobiotics also affect the biodegradation (Wittich, 1996). At high concentrations, many xenobiotics are toxic to microorganisms, including the degradative bacteria (Perez-Leblic et al., 2012). The rates of xenobiotic biodegradation in the environment may range from days and weeks to years and decades. Therefore, the feasibility of the usage of advanced oxidation to enhance the biodegradability of xenobiotics and shorten the treatment duration is therefore of great interest to landfill managers (Baun et al., 2004).

Table 1. Selected Xenobiotic Organic Compounds in Landfill Leachate

Aromatic Hydrocarbons	Range (μg/L)	**Halogenated Hydrocarbons**	Range (μg/L)
Benzene	0.2-1630	Chlorobenzene	0.1-110
Toluene	1-12300	1,2-Dichlorobenzene	0.1-32
Xylenes	0.8-3500	1,3-Dichlorobenzene	5.4-19
Ethylbenzene	0.22329	1,1,1-Trichloroethane	0.01-3810
Trimethylbenzene	0.3-250	Trans-1,2-Dichloeoethylene	1.6-6582
n-propylbenzene	0.3-16	Trichloroethylene	0.05-750
t-Butylbenzene	2.1-21	Tetrachloroethylene	0.01-250
o-Ethyltoluene	0.5-45	**Phenols**	
m-Ethyltoluene	0.3-21	Phenol	0.6-1200
p-Ethyltoluene	0.2-10	Cresols	1-2100
Naphthalene	0.1-260	Bisphenol A	200-240

Advanced oxidation processes have demonstrated the capacity of degrading the recalcitrant XOCs. Therefore, advanced oxidation processes, i.e., the usage of oxidizing chemicals such as ozone (O_3), hydrogen peroxide (H_2O_2) and UV radiation, etc. can be used as alternatives to biodegradation to effectively break the stable xenobiotic structures in the landfill leachate treatment (von Sonntag, 2008). In practice, the use of O_3, H_2O_2, UV radiation and other oxidizing compounds to degrade recalcitrant organic compounds has evoked interest during the last couple of years (Gulyas, 1997; Wang and Xu, 2012). Oxidation potential and the relative strength of these oxidizing compounds to that of oxygen are summarized in Table 2 (Siegrist et al., 2001). By destructing the xenobiotic organic matters, advanced oxidation increases the biodegradation of landfill leachate for the subsequent bio-associated treatment processes (Petruzzelli et al., 2005; Petruzzelli et al., 2007; Qiao et al., 2014). Since the common organic compounds present in the leachate such as amines, amides, alcohols, aliphatic compounds, and carboxylic acids can be easily decomposed in the landfill during leachate recirculation (if available), the advanced oxidizing processes mainly change the characteristics of xenobiotic compounds present in the leachate, making them degradable in the following biological treatment processes (Arslan-Alaton and Alaton, 2007). During advanced oxidation, hydroxyl radicals of $^{\bullet}OH$ are produced, which have very high electronic potential and can oxidize a variety of organic compounds. Most of the oxidizing agents mentioned above produce free $^{\bullet}OH$ radicals, which can indiscriminately destroy organic matter. These radicals can be initiated into the water by means of a certain type of substance (activator). Table 3 compares the reaction rate constant of $^{\bullet}OH$ and ozone (O_3) for some common organic compounds (Yu et al., 2012). The versatility of advanced oxidation is enhanced by the fact that they offer different possible ways for the production of $^{\bullet}OH$ radicals, thus allowing a better compliance with the specific treatment requirements (Schrank et al., 2004). Table 4 illustrates the reactions that can lead to the generation of free hydroxyl radicals of $^{\bullet}OH$, which are extremely reactive with a low selectivity of attack. It should be noted that although both H_2O_2 and O_3 have the potential to release $^{\bullet}OH$ radicals, the $^{\bullet}OH$ radicals produced per incident photon are different (Table 4). Especially, for advanced oxidation, it is quite clear that the efficiency is strongly compound specific. The theoretical quantities of oxidants required to obtain a certain quantity of $^{\bullet}OH$ radicals in the O_3/H_2O_2/UV Systems are summarized in Table 5 (Palenik et al., 1991; von Sonntag, 2008).

Table 2. Oxidation Potential and Relative Strength of Commonly Used Oxidants

Oxidant	Standard Oxidation Potential (Volts)	Relative Strength (Oxygen = 1)
Hydroxyl Radical	2.3	1.92
Ozone	2.1	1.75
Sodium Persulfate	2.0	1.67
Hydrogen Peroxide	1.8	1.50
Potassium Permanganate	1.7	1.42
Oxygen	1.2	1.0

Table 3. Reaction Rate Constant of $^{\bullet}OH$ Radicals vs. O_3

Compounds	$^{\bullet}OH$ (s^{-1})	O_3 (s^{-1})
Chlorinated alkenes	10^9-10^{11}	10^3-10^4
Phenols	10^9-10^{10}	10^3
N-containing organics	10^8-10^{10}	10-10^2
Aromatics	10^8-10^{10}	1-10^2
Ketones	10^9-10^{10}	1
Alcohols	10^8-10^9	10^{-2}-1

Table 4. Formation of •OH Radicals from H_2O_2 and O_3

Oxidant	$\varepsilon_{254\ nm}$ (M^{-1} cm^{-1})	Stoichiometry	$^{\bullet}OH$ Formed per Incident Photon
H_2O_2	20	$H_2O_2 \rightarrow 2^{\bullet}OH$	0.09
O_3	3300	$3O_3 \rightarrow 2^{\bullet}OH$	2.00

Table 5. Theoretical Amount of Oxidants and UV Required for the Formation of $^{\bullet}OH$ Radicals in O_3/H_2O_2/UV Systems

System	Molecules of O_3/Mole $^{\bullet}OH$	Moles of UV Photons, Einsteins/Mole $^{\bullet}OH$	Moles of H_2O_2/Mole $^{\bullet}OH$
O_3/H_2O_2	1.5	0	1.0
O_3/UV	0.5	0.5	0
H_2O_2/UV	0	0.67	0.67
O_3/H_2O_2/UV	1.0	0.58	0.83

The most difficult problem in the practical application of advanced oxidation is the choice or design of the most efficient oxidation system for the given pollutants. Advantages and disadvantages of the usage of specific oxidizing agents are ascertained. Prior study has also demonstrated the existence of severe limitations of the application of a single oxidizing compound for the treatment of certain pollutants (Tong et al., 2005; Diya'uddeen et al., 2012). It is therefore recommended oxidizing compounds be combined to treat certain chemicals. For instance, it was discovered that photolytic oxidation of naphthalene and pentachlorophenol by the combined UV radiation and H_2O_2 treatment led to higher oxidation rates and shorter half-lives of organic substances than mere photolysis (Trapido et al., 1995). The UV/H_2O_2 oxidation process seemed to involve the action of different radical species including not only $^{\bullet}OH$ radicals but possibly also carbonate ion radicals. The feasibility of O_3/H_2O_2 and UV/H_2O_2 treatments for the purification of groundwater contaminated with TCE and PCE was also studied and both methods showed rapid and extensive removal of the chlorinated ethylenes (Hirvonen et al., 1996). It should be noted that compared to UV/H_2O_2 treatment, partial stripping of TCE and PCE might occur during ozonation. Different UV-assisted advanced oxidation methods were also compared for the photochemical mineralization of 4-chlorophenol (Bin and Sobera-Madej, 2012). It was found that under illumination with a 150 W high pressure mercury lamp, the degradation efficiency for 4-chlorophenol had the following order: UV/H_2O_2/Fe^{2+} > UV/O_3 > UV/H_2O_2. For advanced oxidation of polyaromatic hydrocarbons (PAHs), it was concluded that the order of the efficiency of advanced oxidation for anthracene oxidation followed: O_3/H_2O_2 = O_3 > O_3/UV > O_3/H_2O_2/UV > UV (Trapido et al., 1994). Similar results were obtained for other PAHs, indicating that the $^{\bullet}OH$ radicals obviously played a minor role in anthracene destruction (Beltran et al., 1996a, b). Similarly, although oxidation with O_3, O_3/H_2O_2 and O_3/H_2O_2/UV radiation can degrade nitrophenols, the combination of O_3 with UV or H_2O_2 accelerated the degradation of nitrophenols and decreased the O_3 specific consumption, especially at low pH values (Trapido and Kallas, 2000). The order of the efficiency of the combination of O_3 with UV radiation and H_2O_2 for the degradation of nitrophenols follows: O_3/H_2O_2/UV > O_3 (pH 9.5) > O_3/H_2O_2 > O_3/UV > O_3 (pH 2.5). Therefore, to achieve an increase in the reaction rate and a reduction in O_3 consumption, the O_3/H_2O_2/UV combination is recommended to be used at low pH values. Since UV- and O_3-based advanced oxidation can be simply applied and H_2O_2 addition is very economic, these three oxidation methods are very commonly practiced. For xenobiotic degradation, O_3 combined with H_2O_2, or O_3 with UV radiation, or H_2O_2 with UV radiation, or O_3 with H_2O_2 and UV radiation can be utilized.

1.2 Advanced Oxidation Mechanisms

The mechanisms of O_3/H_2O_2, O_3/UV, H_2O_2/UV and $O_3/H_2O_2/UV$ in advanced oxidation are summarized below (Han et al., 2002; Rosenfeldt et al., 2006, 2008):

- Ozone + hydrogen peroxide (O_3/H_2O_2) – (peroxone)

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of $^{\bullet}OH$ radicals:

$H_2O_2 \rightarrow HO_2^- + H^+$ **Equation (1)**

$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$ **Equation (2)**

The reaction continues along the indirect pathway described above and $^{\bullet}OH$ radicals are produced. The combination of different reaction steps shows that two ozone molecules produce two $^{\bullet}OH$ radicals:

$2O_3 + H_2O_2 \rightarrow 2^{\bullet}OH + 3O_2$ **Equation (3)**

- Ozone-UV radiation (O_3/UV)

Ozone readily absorbs UV radiation at the 254 nm wavelength (the extinction coefficient $\varepsilon_{254\ nm}$=3300 $M^{-1}cm^{-1}$), producing H_2O_2 as an intermediate, which then decomposes to $^{\bullet}OH$ radicals:

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ **Equation (4)**

$O(^1D) + H_2O \rightarrow H_2O_2 \rightarrow 2^{\bullet}OH$ **Equation (5)**

- Hydrogen peroxide-UV radiation (H_2O_2/UV)

The direct photolysis of hydrogen peroxide leads to the formation of $^{\bullet}OH$ radicals:

$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH$ **Equation (6)**

Also HO_2^-, which is in an acid-base equilibrium with H_2O_2, absorbs the UV radiation at the wavelength of 254 nm:

$H_2O_2 \Leftrightarrow HO_2^- + H^+$ **Equation (7)**

$HO_2^- \xrightarrow{h\nu} {}^{\bullet}OH + O^{\bullet -}$ **Equation (8)**

H_2O_2/UV process has been successfully used for the destruction of chlorophenols and other chlorinated compounds. It has also been demonstrated that atrazine, desethylatrazine and simazine can be mineralized finally to carbon dioxide within reasonable radiation time in the presence of hydrogen peroxide.

- Ozone-hydrogen peroxide-UV radiation ($O_3/H_2O_2/UV$)

The addition of H_2O_2 to the O_3/UV process accelerates the decomposition of ozone, which results in an increased rate of $^{\bullet}OH$ generation. In processes involving pollutants that are weak absorbers of UV radiation, it is more cost effective to add H_2O_2, externally at a reduced UV flux. If direct photolysis of pollutants is not a major factor, O_3/H_2O_2 should be considered as an alternative to photo-oxidation process.

A great deal of research focusing on chemical oxidation as pre-treatment has been undertaken over the past 20 to 25 years. It is now well accepted that chemical oxidation may systematically be combined with biological processes (Figure 1) (Luyten et al., 2013). It should be pointed out that there are a lot of factors that may impact the integrated processes on the effectiveness of the overall system compared with that of direct biological treatment.

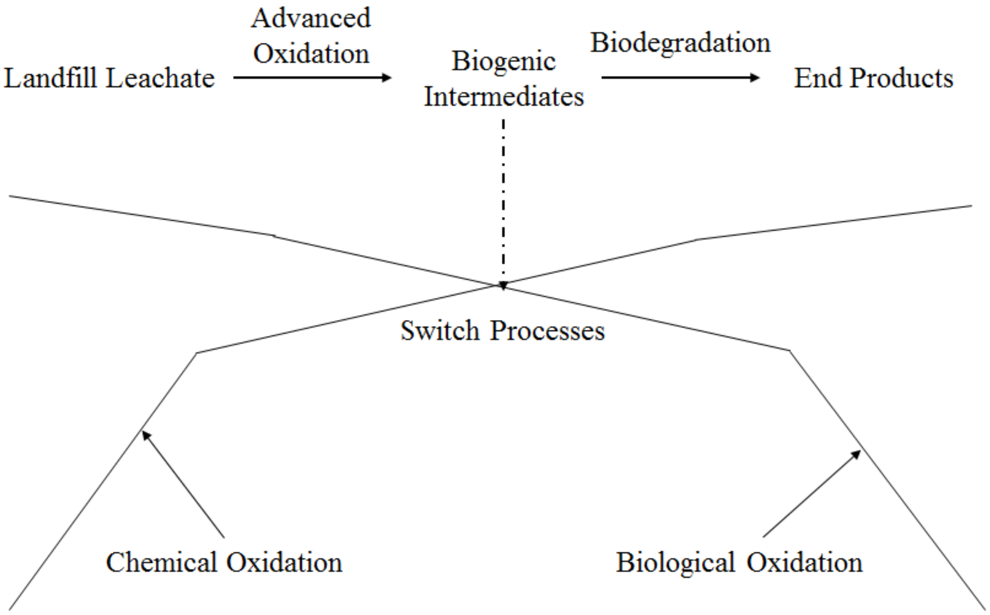


Figure 1. Integration of Chemical Oxidation with Biodegradation

Chemical pre-treatment by means of advanced oxidation should ideally be highly selective towards the least biodegradable fractions of the landfill leachate, thus leaving the most biodegradable species intact for the subsequent biological step. Unfortunately, the dominant mechanism through which the majority of advanced oxidation degrades organic pollutants is the formation of hydroxyl radicals that are highly reactive but poorly selective (Ananpattarachai et al., 2016). Ozone has many of the oxidizing properties desirable for the usage in landfill leachate treatment. Unlike other oxidants, ozone degrade organic pollutants by direct electrophilic attack and indirect attack through the formation of hydroxyl radicals (Cortez et al., 2011). Direct attack by molecular ozone (commonly known as ozonolysis) occurs at acidic or neutral conditions and is a selective reaction resulting in the formation of carboxylic acids as the end-products that cannot be oxidized further by molecular ozone (Wu et al., 2004). Compounds susceptible to ozonolysis are those containing C=C double bonds, specific functional groups (i.e., -OH, $-CH_3$ and $-OCH_3$) and atoms carrying negative charges (i.e., N, P, O, S). This unique feature renders ozonation an attractive pre-treatment for certain pollutants such as polyphenols. At high pH values, ozone decomposes to non-selective hydroxyl radicals which, in turn, attack the organic pollutants (Wu et al., 2004). Therefore, the pH is a major factor determining the efficiency of ozonation as pre-treatment since it can alter degradation pathways (and consequently the distribution of intermediates) as well as kinetics.

1.3 Advanced Oxidation Kinetics

For ozonation, second order oxidation kinetics are commonly assumed, i.e., first order in ozone and first order in the compound (Alnaizy and Akgerman, 2000):

$$S + O_3 \rightarrow \text{Product}$$ **Equation (9)**

$$-\frac{d[S]}{dt} = k[S][O_3]$$ **Equation (10)**

For a batch-type or plug-flow reactor, Equation (10) can be integrated to:

$$\ln\left(\frac{[S]}{[S_0]}\right) = -k\int [O_3]dt$$ **Equation (11)**

where S is the organic compound concentration, S_0 is the initial organic compound concentration, and k is the second-order rate constant. With the formation of $^{\bullet}OH$ radicals, ozonation kinetics can be formulated as follows:

$$-\frac{d[S]}{dt} = k_{O_3}[S][O_3] + k_{^\bullet OH}[S][^\bullet OH]$$ **Equation (12)**

For a batch-type or plug-flow reactor,

$$\ln(\frac{[S]}{[S_0]}) = -k\int[O_3]dt - k_{^\bullet OH}\frac{[^\bullet OH]}{[O_3]}\int[O_3]dt$$ **Equation (13)**

where k_{O3} and k_{OH} are the second-order rate constant.

Oxidation by hydrogen peroxide and UV radiation can be represented by (Alnaizy and Akgerman, 2000):

$$r = \Phi_{H_2O_2} f_{H_2O_2} I_0(1-e^{-A_t})$$ **Equation (14)**

where Φ_{H2O2} is the hydrogen peroxide quantum yield, f_{H2O2} is the fraction of radiation that is absorbed by H_2O_2, I_o is the UV radiation intensity, and A_t is the solution total absorbance.

For pCBA oxidation, the oxidation kinetics can be formulated as (von Gunten, 2003):

$$\ln(\frac{[pCBA]}{[pCBA]_0}) = -R_{ct}k_{^\bullet OH,pCBA}\int[O_3]dt$$ **Equation (15)**

where $k_{OH,pCBA}$ is the second order rate constant and R_{ct} is the ratio of $[^\cdot OH]$ to $[O_3]$.

4-nitrophenol (4-NP) oxidation by OH radicals can be expressed by (Zhang et al., 2003):

$$-\frac{dC}{dt} = k_{4-NP,^\bullet OH}[^\bullet OH]C$$ **Equation (16)**

where C is the concentration of 4-NP at radiation time t and $k_{4\text{-}NP,OH}$ is the second order rate constant of 4-NP reacting with $^\bullet OH$. The equation can further be simplified if $^\bullet OH$ is a constant when the combination of hydrogen peroxide and UV radiation is used:

$$-\frac{dC}{dt} = k_1C$$ **Equation (17)**

where k_1 represents the product of $k_{4\text{-}NP,OH}$ and $[^\bullet OH]$ and the reaction can thus be defined as pseudo-first order:

$$\mathrm{Ln}(\frac{C_t}{C_0}) = -k_1 t$$ **Equation (18)**

where C_t and C_0 are the 4-NP concentrations at time t and initial concentration, respectively.

UV radiation also follows first order oxidation kinetics (Alaton et al., 2002):

$$\mathrm{Ln}(\frac{A}{A_0}) = -k_d t$$ **Equation (19)**

where k_d stands for the first order rate constant. The abatement of UV_{280} (UV absorbance at λ=280 nm) could also be evaluated in terms of the first order kinetic equation:

$$\mathrm{Ln}(\frac{UV_{280}}{UV_{280,0}}) = -k_{UV280} t$$ **Equation (20)**

where k_{UV280} is the first order UV_{280} abatement rate constant.

1.4 Phosphorus Removal

As an innovative technology for wastewater treatment, the suspended fiber biofiltration makes biological contact oxidation possible, which can significantly improve BOD and COD removal and decrease the sludge yield. For iron removal, contact oxidation is achieved by microbial mediated iron oxidation and fixation during which ferrous iron is oxidized to ferric iron and fixed onto the filter media (Lin et al., 2009). Consequently, there is minimal ferric iron suspending in the solution that can escape the filtration. When suspended fiber biofiltration is used for the landfill leachate treatment, iron and phosphorous will be removed in series. Specifically, iron will first be oxidized by contact oxidation if advanced oxidation is included and removed as iron oxides by coating the suspended fiber (Figure 2). Since iron oxides have high binding strength for phosphorus, the iron oxide coating makes the suspended fiber has the potential implementations of phosphorus removal for landfill leachate (Arias et al., 2006; Boujelben et al., 2008). The prominent correlation between phosphorus and iron oxides has led to numerous examinations of phosphorous adsorption capacities and mechanisms by iron oxides. The mechanism of phosphorous adsorption onto iron oxides is generally dominated by ligand exchange in which two singly coordinated hydroxyl groups or water molecules are replaced by a single phosphate anion, resulting in the formation of a bidentate, binuclear complex (Kang et al., 2003) (Kang et al., 2003; Ma et al., 2009). The phosphate surface complexes are very stable, resulting in slow exchange rates and an apparent irreversibility (hysterisis) of phosphorus adsorption (Chen et al., 2006; Banu et al., 2008). Phosphorous adsorption on hematite has been investigated by IR spectroscopy, which suggests that monodentate inner-sphere complexation is the primary adsorption mechanism (Elzinga and Sparks, 2007). It has also been demonstrated that phosphorous adsorption by synthetic and naturally occurring iron oxides can be described by Langmuir and Freundlich isotherms, although limitations exist for both of them (Kang et al., 2003).

Figure 2. Suspended Fiber Used for Biofiltration

In our prior research, we have demonstrated that phosphorus is able to adsorb to iron species, during which phosphate replaces singly coordinated OH^- groups and then reorganizes into a very stable binuclear bridge between the cations. This chemisorption process is coupled with the release of OH^- ions, thus this process is favored by low pH values. Since the suspended fiber biofilter has dramatically increased surface areas, phosphorous removal can thus achieve a significantly high efficiency. In this proposed research, phosphorous removal will be included in this novel reactor where advanced oxidation and suspended fiber biofiltration are integrated in a single unit.

For suspended fiber biofiltration, polypropylene fiber can be arranged to be suspended layer by layer, to which microorganisms attach to fulfill the contact oxidation function for organic decomposition and iron fixation. In our prior research, we have observed both iron oxide coating and microbial consortia accumulation on the polypropylene fiber surfaces (Figure 3).

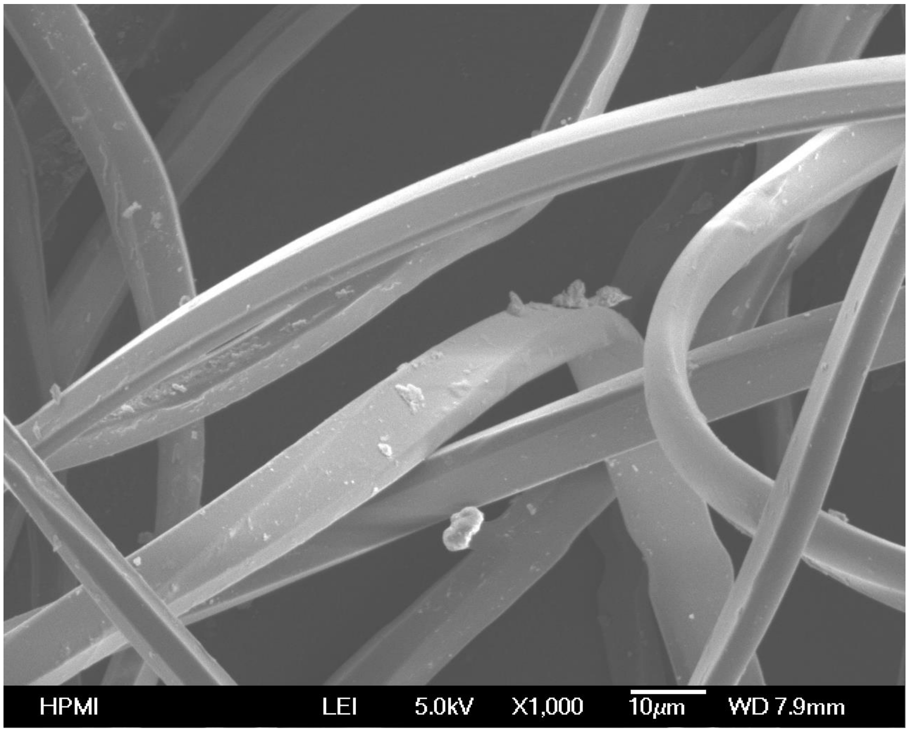


Figure 3. Ferric Iron Oxide Accumulation on Polypropylene Fiber Surfaces

Degradation of complex molecules is known to be carried out better by bacterial cultures in consortia than in monocultures. In addition, the performance of consortia for degradation of complex molecules requires a stability of association, which can be best achieved by growing compatible cultures in a mixture. These consortia strategically position themselves on the suspended fiber to form a biofilm. Bacteria in the biofilm produce a matrix of materials to further affix them to the fiber. Using cultures in consortia for efficient degradation of proteins, carbohydrates and lipids has been demonstrated. This is an importance discovery since proteins, carbohydrates and lipids are major organic components in landfill leachate (Turker and Celen, 2007).

1.5 Objectives

In the first year of this research, we have investigated organic, iron and chloride removal using aerated leachate recirculation and pressurized suspended fiber biofiltration, together with the ultra-high lime with aluminum process. As a cost- and space-saving technology, leachate recirculation and pressurized suspended fiber biofiltration provided a new alternative means for the treatment of landfill leachate with high organic and iron contents. In order to degrade xenobiotic compounds and remove phosphorous from landfill leachate, advanced oxidizing processes, i.e., the usage of UV or oxidizing chemicals were introduced to the leachate treatment and suspended fiber biofiltration was configured to enhance iron and phosphorous removal in addition to organic degradation. The specific objectives of this research project included:

1. Reactor Design, Setup and Parameter Characterization. The reactor was designed to include advanced oxidation and suspended fiber biofiltration in a single unit. The hydraulic parameters were characterized and the design of the reactor was optimized to achieve the desired xenobiotic, iron and phosphorus removal goals.

2. Reactor Operation. Advanced oxidation processes including UV, ozone and hydrogen peroxide were tested for the decomposition of xenobiotics and suspended fiber biofiltration was tested for iron and phosphorous removal in addition to organic degradation.

3. System Optimization and Cost Analysis. The best design and operation parameters were identified and optimized for advanced oxidation, iron and phosphorous

removal and organic decomposition. Cost- and space- saving was analyzed and compared with that of conventional treatment processes.

2. Background

2.1 XOCs in Landfill Leachate

The composition of landfill leachate is complicated, which may vary dramatically with the aging of the landfill. Typically, the pollutants in municipal solid waste landfill leachate can be divided into dissolved organic matter, dissolved salts, heavy metals and xenobiotic organic compounds (Kulikowska and Klimiuk, 2008). Dissolved organic matter is often quantified as chemical oxygen demand (COD) or Total Organic Carbon (TOC), which includes volatile fatty acids and more refractory compounds such as fulvic-like and humic-like compounds. Inorganic salts include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^{-}), etc. Heavy metals include cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}). Xenobiotic organic compounds (XOCs) originate from household or industrial chemicals and are commonly present in relatively low concentrations (usually less than 1 mg/L). These compounds include among others a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, and plastizers (Baun et al., 2003). Adsorbable organic halogen (AOX) has in some cases been used as an aggregated parameter for the content of XOCs containing halogens. The total range of XOCs of typical landfill leachate was 30 to 27,000 μg/L and AOX was in the range of 200 to 5000 μg/L (Goi et al., 2004). Total organic halogens (TOX) has also been used in the characterization of XOC in the landfill leachate (Goi et al., 2004; Kristiana et al., 2015).

Usually, household and non-hazardous industrial waste disposed in municipal solid waste landfills contains a mixture of many chemical compounds originating from the various discarded products. A number of these chemicals are released during the lifetime of the landfill and result in emission of XOCs with an anthropogenic source to the environment (Slack et al., 2005). Consequently, unknown XOCs at variable concentrations may be present in the landfill leachate, which constitutes a potential risk to the quality of receiving water bodies (i.e., surface water or groundwater) when the leachate is released into the environment (Slack et al., 2005). Fate of XOCs in the landfill leachate has been the focus of quite a few studies, but the database is still limited. There is therefore an urgent need for more information about the compounds present in the leachate with respect to both the identity and the concentrations. This information is extremely important for the selection of treatment methods as well as for the risk assessment of landfill operations. In most landfill leachate studies, the information on organic compounds in terms of collective parameters like TOC, dissolved organic carbon (DOC), non-volatile organic carbon (NVOC), COD and biological oxygen demand (BOD) is provided (Kjeldsen et al., 2002). These parameters are relatively easy to measure and can be used to quantify the oxygen consuming potential during the treatment. However, information about the identity of XOCs and thereby the assessment of their toxicity, bioaccumulation, and persistence is usually not provided.

Most of the XOCs have been designated as priority pollutants by the U.S. Environmental Protection Agency and the amount of XOCs that has been allowed into municipal solid waste landfills has decreased significantly over the last 20 years (Boethling et al., 1989). However, many of the landfills may contain XOCs from a time period when there were fewer restrictions on the disposal of hazardous waste in municipal solid waste landfills. Broad ranges of XOCs have been observed, reflecting differences in solid waste composition, landfill operations and waste age. It has been demonstrated that the most frequently found XOCs are the monoaromatic hydrocarbons (i.e., benzene, toluene, ethylbenzene and xylenes) and halogenated hydrocarbons (i.e., tetrachloroethylene and trichloroethylene) (Ejlertsson et al., 1996). These pollutants are also the ones found at the highest concentrations as XOCs. The general public has concerns about these two groups of XOCs because of their well-documented negative effects in the aquatic environment. Information about hydrophobic, volatile, aromatic and aliphatic organic substances, including benzene, toluene, ethylbenzene and xylenes, polyaromatic hydrocarbons, and chlorinated aliphatic and aromatic compounds can be found in a variety of studies (Kjeldsen et al., 2002). Especially, concentrations of monoaromatic hydrocarbons with halogenated aliphatics and aromatics are analyzed and compared in the study of 13 municipal sanitary landfills in Wisconsin, USA (Krug and Ham, 1991) and the study of 104 old Danish municipal solid waste landfills (Kjeldsen and Christophersen, 2001). In both studies, BTEX were the most frequently found compounds with concentrations generally lower at the Danish landfills. The reported frequent presence of halogenated hydrocarbons at relatively high concentrations reflected the co-disposal of hazardous waste at some of the sites (Krug and Ham, 1991). At the old Danish sites, the concentrations of the halogenated hydrocarbons were very low as compared to US landfills. It has also been discovered that the concentrations of XOCs at the old municipal solid waste landfills were generally higher than those of the newer ones (Brandstatter et al., 2014).

Compounds containing polar/ionic groups including phthalates, phenols and pesticides as well as aliphatic, alicyclic and aromatic carboxylic acids are also important pollutants in the municipal solid waste landfill leachate (Abdel daiem et al., 2015). In addition, degradation products of XOCs is drawing more and more attention since they are important indicators of on-going degradation, which may be more polar than the parent compounds (Xiaoli et al., 2010). Examples of degradation products that may be found in municipal solid waste landfill leachate include benzylsuccinic acid (BSA) related to toluene degradation, nonylphenol-ethoxycarboxylates (NPECs) generated when the non-ionic detergents such as nonylphenol-ethoxylates (NPEs) are degraded, and monoesters of *o*-phthalic acid originating from the degradation of diesters of *o*-phathalic acid. Data on polar and ionic organic pollutants are scarcer, although the number of investigations including these more water-soluble pollutants is increasing (Mersiowsky et al., 2001; Huang et al., 2015; Rout et al., 2015). For instance, phenol and cresols are commonly analyzed in the old studies, while some newer investigations also include chloro- and nonyl-phenols.

Phenoxyalkanoic acid herbicides have been identified in municipal solid waste landfill leachate, which could be of importance when evaluating the impact of landfill leachate on the environment. For instance, twenty-one different pesticides were identified from a screening for a total of 101 pesticides in 10 Danish landfills, including MCPP or mecoprop (9 landfills), bentazon (6 landfills), and MCPA (3 landfills) (Baun et al., 2004). MCPP has also been reported in other landfill leachate studies (Omura et al., 1992; Oman and Hynning, 1993; Khattabi et al., 2002; Eggen et al., 2010). Other types of pesticides including ametryn, atrazine, chlorpropham, dichlobenil and hexazinon have also been identified (Haarstad and Borch, 2004). Detergent and surfactant compounds such as benzene and naphthalene sulfonates have also been found in the landfill leachate. Benzenesulfonates (*p*-toluenesulfonate) and naphthalenesulfonates (naphtalene-1-sulfonate, naphtalene-2-sulfonate, naphtalene-1,5-disulfonate, naphtalene-1,6-disulfonate, naphtalene-2,7-disulfonate, and 2-aminonaphtalene-2,7-disulfonate) at concentrations ranging from a few µg/L up to 11 mg/L have been detected (Benskin et al., 2012). The sulfonates include some of the surfactants used in laundry detergents and shower soaps. Other types of surfactants that could be expected to be present in landfill leachate are the alkylphenol polyethoxylates including nonylphenol mono- and di-ethoxylate as well as degradation products, nonylphenol mono- and di-carboxylate (Li et al., 2015).

The phthalates are also pollutants of concern. The most frequently observed phthalates are di-(2-hexylethyl) phthalate, di-ethyl-phthalate, di-*n*-butyl-phthalate, and butyl-benzyl-phthalate. The highest concentrations are, however, observed as the degradation product of phthalic acid (up to 14 mg/L) (Wang et al., 2013). It should also be noted that methyl-tert-butyl-ether (MTBE), which is used as a gasoline additive, has been found at concentrations up to 35 µg/L in the leachate from eight Swedish landfills (Ghosh et al., 2015). Dioxanes and dioxolans, synthetic cyclic ethers from waste disposal of alkyd resin production as well as painting and coating have also been identified (Oman and Hynning, 1993).

2.2 Chemical Oxidation

Chemical oxidation is one commonly used means for the treatment of effluents containing refractory compounds such as landfill leachate. To enhance the oxidation, advanced oxidation processes, including the usage of ozone (O_3), hydrogen peroxide (H_2O_2) and ultraviolet (UV) as well as the combination of two or three of above oxidants have drawn more and more attention (Azbar et al., 2004). Advanced oxidation processes are able to oxidize organic substances to their highest stable oxidation states (i.e., complete mineralization) and improve the biodegradability of recalcitrant organic pollutants up to a value compatible with the subsequent economical biological treatment (Sarathy and Mohseni, 2010). The advanced oxidation processes are commonly evaluated in terms of COD, BOD, and BOD/COD. Initially, ozonation was the first to demonstrate to have the effectiveness in eliminating COD (about 50 to 70% reduction in most cases) of the wastewater effluent (Yang and Yuan, 2016). However, the efficiency of ozonation on the oxidation of stabilized leachate has not been consistent. For some cases, only 30% COD depletion was observed after 1 hour of ozonation with an ozone consumption of 1.3 to 1.5 g O_3/g COD (Renou et al., 2008). On the other hand, COD removal was dramatically increased when ozonation was combined with other advanced oxidation means such as hydrogen peroxide. The removal efficiency as high as 90% was achieved for the O_3/H_2O_2 process (Slomczynska et al., 2004; Liu et al., 2014). Concerning the H_2O_2/UV process, the BOD_5/COD ratio also increased significantly, from 0.1 to 0.45 (Ghazi et al., 2014). Fenton and photo-Fenton processes can decrease COD by 45 to 75% and 70 to 78%, respectively. In term of biodegradability improvement, BOD_5/COD ratios close to 0.5 after oxidation have been reported by the Fenton process (Ismail and Tawfik, 2016). Table 6 summaries the changes of COD and BOD/COD ratio after typical advanced oxidation processes (Renou et al., 2008).

Table 6. Changes of COD and BOD/COD Ratio after Advanced Oxidation

COD (mg/L)	BOD (mg/L)	pH	COD Removal	BOD /COD	O3/COD (g/g)	H_2O_2/O_3 (g/g)	UV (W)	Reference
Zonation								
1610	-	-	44	-	1.3			132
2300	210	8	62	-	1.5			133
2300	210	3	50	-	0.5			
2300	210	8	50	-	1			
740	240	-	-	-	-			134
4000	230	8.5	25	-	0.53			135
640	205	-	-	0.4	1.28-1.92			127
460	-	-	71	-	1.8			136
1050	-	8.5	67	-	1.7			
500	30	7	-	140 mg/L BOD_5	0.11			1.37

300-1200	<10	7.0-8.0	80	-	3			1.38
151	5	8.1	33	0.35	-			87
330	<8	7.5	35	0.15	3.5			94
1585	111	8.2	23-32	-	1.7			11
518	-	8.3	66	-	1.7			139
895	43	8.2	30	0.11	1.11			140
3500	25	8.2	67	0.21	0.7			141
480	25	7.7	>50	0.25	0.5			89
14600	2920	7.8	56	0.32	3.1			142
2300-4970	290-850	7.90-9.02	30	0.25	1.3-1.5			117
6500	500	8.1	15	0.5	1.2 g/L O_3			34
3460	150	8.3	2.5-48	-	0.1-3 g/L O_3			7
O_3/H_2O_2								
2000	-	-	95	-	3.5	0.4		143
600	-	-	92	-	3.3	0.4		
2000	160	8.4	92	0.13	1.5	0.3		133
-	-	8	97	-	2.5g/L O_3	1		144
-	-	8	70	-	-	0.5		
895	43	8.2	28	0.14	0.76	-		145
1360	<5	8.4	93	0.32	1.5	0.3		
480	25	7.7	40	0.13	0.05-0.5	0.25-1		89
O_3/UV								
1280	100	2	54	-	-		100	146
1280	100	2	47	-	-		500	
2300	210	8	50	-	1		15	133
430TOC	-	-	51TOC	-	0.1 g/L O_3		300	147
26000	2920	7.8	63	0.32	3.5		1500	142
26000	2920	7.8	61	0.35	4.7		1500	

2.3 Comparison of Performance of Various Advanced Oxidation Processes

Advanced oxidation processes can improve landfill leachate treatment in two ways: (i) oxidize organic substances to their highest stable oxidation states (i.e., carbon dioxide and water) and (ii) enhance the biodegradability of recalcitrant organic pollutants. The outstanding treatment performance and optimum conditions of various advanced oxidation processes for COD removal in these two aspects can also be found in Table 6. The ozone-based process can achieve 40 to 95% of COD removal with COD concentrations ranging from 2000 to 26,000 mg/L, while electrochemical oxidation process and Fenton process can achieve 70 to 90% of COD removal with COD concentrations ranging from 1855 to 8894 mg/L. It should be noted that the treatment efficiency of Fenton process is better than ozone-based process and electrochemical oxidation. In term of biodegradability improvement, BOD/COD ratios of 0.29 to 0.88 and 0.1 to 0.5 were reported after oxidation by Fenton process and ozone-based oxidation, respectively (Table 7) (Li et al., 2010).

Table 7. Comparison of the Performance of Advanced Oxidation Processes

AOPs	Condition	Initial COD (mg/L)	COD Removal	References
O_3	3 g/L	3460	48	24
O_3/H_2O_2	O_3: 3.5 g/gCOD H_2O_2 g/g O_3	2000	95	28
O_3/UV	O_3: 3.5 g/gCOD UV: 1500W	26,000	63	36
Fenton	pH: 2.5, [H_2O_2]: 0.15 M, H_2O_2/Fe^{2+} (molar ration): 3	8894	89	48
Photo-Fenton	Fe^{2+}: 2000 mg/L, H_2O_2: 10000 mg/L	3823.8	86	51
Electro-Fenton	pH: 3, H_2O_2: 0.34 M, Fe^{2+}: 0.038 M, I: 2A, d=2.1 cm	5000	83	54
Electrochemical Oxidation	Current Density: 116.0 mA/cm^2	1855	73	61

Electrochemical oxidation, wet air oxidation and ultrasound oxidation are more expensive due to the high demand of electrical energy. However, this is not the case for the Fenton's process. Under acidic conditions, the Fe^{2+}/H_2O_2 mixture produces •OH radicals in a very effective way. It was estimated that the cost of O_3/H_2O_2 system was about $2.3 per kg COD (Chen et al., 2014; He et al., 2015) and the ozone-granular activated carbon adsorption was $2 to $4 per m^3 (Kurniawan et al., 2006). On the other hand, the estimated operational cost for the Fenton treatment of landfill leachate was $5.19 per m^3 (Amaral-Silva et al., 2016). Fenton process has been recognized to be the best compromise because of the simple technology, no mass transfer limitation (homogeneous mature) and cheap and nontoxic characteristics of iron and hydrogen peroxide (Del Moro et al., 2012; Singh et al., 2013). It should be noted that the Fenton's process requires low pH, which limits its wide applications.

2.4 Biological Processes Combined with Advanced Oxidation

Landfill leachates may contain large amounts of recalcitrant organic compounds. The composition and concentration of the contaminants are influenced by the type of deposited waste, the quality of the refuse, the hydrogeological factors and mainly by the age of the landfill (Renou et al., 2008). In general, the leachates originated from recent domestic waste landfill have high BOD_5 values while leachate from mature landfills is very complex, consisting of high concentrations of humic and fulvic acids (Renou et al., 2008). Although biological treatment is cost-effective when compared to other treatment options, it is not efficient when treating leachate from mature landfills that contain recalcitrant and/or non-biodegradable organic substances. Advanced oxidation involves the generation of the hydroxyl radical, which has very high oxidation potential and is able to oxidize almost all organic pollutants. Advanced oxidation is generally expensive since energy is consumed for UV radiation and ozone and hydrogen peroxide generation. One attractive potential alternative is to combine advanced oxidation processes, which can convert the initially persistent organic compounds into more biodegradable intermediates, with conventional biological processes, which can degrade these intermediates to lower the treatment costs. Studies have shown the promising future of the combined treatment option (Li et al., 2010). It should be noted that the percentage of advanced oxidation should be minimal in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. The key issue is to design the process for the best overall economic and ecological performance.

It has been demonstrated advanced oxidation can efficiently enhance the biodegradability of non-biodegradable and/or toxic compounds in the leachate. In combined advanced oxidation and biological treatment processes, it is very important to characterize the destruction of a persistent contaminant by each individual advanced oxidation treatment. It should also be sure to have the biological treatment processes compatible with advanced oxidation by adjusting environmental parameters such as temperature, salinity, pH, oxygen concentration, redox potential, the concentration and nature of various substrates and nutrients, and the presence of toxic substances (Moravia et al., 2011). When considering combined advanced oxidation and biological processes for treating recalcitrant contaminants, biodegradability assessment is required.

2.5 Adsorption of Phosphate onto Metal (Hydr)oxides

The interaction of anions during simultaneous adsorption may be caused by direct competition for adsorption sites. With the anion adsorption on the surface, accumulated negative charges may lead to either synergistic effects in terms of adsorption (e.g., Ca^{2+} and PO_4^{3-}) or competitive effects (e.g., SO_4^{2-} and PO_4^{3-}). During the landfill leachate treatment, sulfate, bicarbonate and organic acids as anions and calcium as cation were considered to affect phosphate adsorption due to their high concentrations (Yue et al., 2011). It was discovered that phosphate was much stronger than sulfate in competition despite sulfate can form inner-sphere complexes (Rahnemaie et al., 2006). For bicarbonate adsorption, the formation of inner-sphere complexes was also proposed. Calcium was found to significantly affect phosphate adsorption to iron oxides by co-adsorption (Antelo et al., 2015). Due to the structural diversity of natural organic matter, a larger number of binding sites can be involved in adsorption, as dominated by ligand exchange reactions between the hydrated hydroxyl groups of the metal oxide surface and the acidic carboxyl groups of the non-organic matter. Phosphorous adsorption increases with decreasing pH, which reaches a maximum near pH 5. The adsorbent characteristics of ferric and aluminum oxides are summarized in Table 8.

Table 8. Adsorbent Characteristics of Ferric and Aluminum Oxides

	Granulated Ferric Hydroxide	Activated Aluminum Oxide
Composition	β-FeOOH	Al_2O_3, Na_2O, CaO, Fe_2O_3
Specific Surface Area (m^2/g)	280	230-300
Particle Size (mm)	0.32-2	0.3-1
Point of Zero Charge	pH 7.5-8.2	pH 8.1-9.1
Water Content (%)	43	0.4
Bulk Density (kg/m^3)	1250	900

Thermodynamic modeling of phosphate adsorption onto metal oxides has been formulated and the formed complexes has been identified with IR spectroscopic investigations (Devau et al., 2009). It is generally agreed that phosphate forms inner-sphere complexes on iron oxide surfaces. However, there is still some discussion about the exact structure of the surface complexes. It has been argued about the formation of a bidentate complex on goethite, which protonates at low pH. It seems that monodentate complexes which only differ in the degree of protonation are formed (Belelli et al., 2014; Tiberg and Gustafsson, 2016). Concerning adsorption on aluminium oxides, a formation of inner-sphere complexes is also suggested. There is also evidence that outer-sphere complexes and surface precipitation of $AlPO_4$ exist at low pH.

2.6 Iron Removal

2.6.1 Oxidation

Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron, manganese, or other chemicals being treated to the oxidizing agent. Specifically, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $Fe(OH)_3$ (Moravia et al., 2011). Reduced manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble (MnO_2). The most commonly used chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, and ozone. Oxidation using chlorine or potassium permanganate is frequently applied in small groundwater systems. The dosing is relatively easy and requires simple equipment. Chlorination is widely used for oxidation of divalent iron and manganese. However, the formation of trihalomethanes (THMs) in highly colored water may be a problem. Chlorine feed rates and contact time can be determined by simple jar tests. As an oxidant, potassium permanganate is normally more expensive than chlorine and ozone. But for iron and manganese removal, it is efficient and requires considerably less equipment and capital investment. The dose of potassium permanganate, however, must be carefully controlled. Too little permanganate will not oxidize all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color.

Permanganate can also form precipitates that cause mud ball formations on filters, which are difficult to remove and compromise the filter performance. Ozone may be used for iron and manganese oxidation. However, ozone may not be effective for oxidation in the presence of humic or fulvic materials (Serikov et al., 2009). If not dosed carefully, ozone can oxidize reduced manganese to permanganate and result in pink color as well.

Manganese dioxide particles, formed during oxidation of reduced manganese, must also be removed. A low-cost method is to use oxygen in the air as the oxidizing agent in a tray aerator (Olsinska and Bragiel, 2015). Water simply passes down a series of porous trays to have enhanced contact with air. No chemical dosing is required, which allows for unattended operation. This method is not effective for water in which the iron is complexed with humic materials or other large organic molecules. Oxygen is not an oxidizing agent strong enough to break the strong complexes formed between iron or manganese and the large organic molecules. Furthermore, the rate of reaction is low below pH 9.5.

The presence of other oxidizable species in water hinders oxidation of the desired reduced compounds. Volatile organic chemicals as well as other organic compounds, or taste- and odor-causing compounds may also result in an oxidant demand. This additional oxidant demand must be accounted for when dosing the oxidant. The expense of operation derives from the chemical usage in most cases, and therefore is directly related to the source water quality.

2.6.2 Filtration

In general, manganese oxidation is more difficult than iron oxidation because of the low reaction rate. A longer detention time (10 to 30 minutes) following chemical addition is therefore needed prior to filtration to allow the reaction to take place. There are different filtration media for the removal of iron and manganese, including manganese greensand, anthra/sand or iron-man sand, electromedia, and ceramic. Manganese greensand is by far the most common medium in use for removal of iron and manganese through pressure filtration (Skoczko et al., 2016). Greensand is a processed material consisting of nodular grains of the zeolite mineral glauconite coated with manganese oxide. The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation-reduction reactions necessary for iron and manganese removal (Barlokova et al., 2015). The coating is maintained through either continuous or intermittent feed of potassium permanganate.

Anthra/sand (also iron-man sand) is another type of medium available for the removal of iron and manganese. It consists of anthracite and sand with a chemically bonded manganese oxide coating. Unlike manganese greensand, this medium is conditioned in the filter after installation. Electromedia, a proprietary multi-media formulation which uses a naturally occurring zeolite, provides a slightly different option as compared to the manganese oxide coated media. It does not require potassium permanganate regeneration. Macrolite is also used for iron and manganese removal. Unlike the other media, it is not a naturally occurring material. It is a manufactured ceramic material with a spherical shape and a rough, textured surface, which requires processing for iron and manganese removal purposes. The principal removal mechanism is physical straining rather than contact oxidation or adsorption. Since each medium has its advantages and disadvantages, selection of a medium and oxidant should be based on all necessary design criteria.

3. Materials and Methods

3.1 Landfill Leachate Collection

Landfill leachate and solid waste were collected from the Leon County Landfill, located in Tallahassee, Florida and Springhill Landfill, located in Campbellton, Florida. Leon County Landfill accepts Class III commercial and residential waste through Marpan Recycling, which includes yard trash, C&D debris, processed tires, asbestos, carpet, cardboard, paper, glass, plastic, furniture (other than appliances), and other materials approved by Florida Department of Environmental Protection. Yard debris (leaves and limbs) and waste tires are accepted through the Solid Waste Management Facility. Besides, Leon County Landfill also receives electronics, computers and peripherals, televisions, video game systems, handheld electronics, cell phones, household hazardous waste, and stryofoam TM (packaging foam only), etc. Owing to the contract with Marpan Recycling to process and recycle construction debris and packaging materials, over 50% of these materials are now being recycled rather than buried in the landfill. Currently, the Class III site of Leon County Landfill is closed to the public. But the facility still accepts tires, clean yard waste (no plastic bagged yard waste), wood debris, electronics, recycling and household hazardous waste. Domestic solid wastes from Leon County are processed at the Gum Road Transfer Station and delivered to the Springhill Landfill for disposal. Springhill Landfill currently accepts domestic wastes. In addition, Springhill Landfill offers the following non-hazardous waste disposal services: asbestos-friable, asbestos-non-friable, auto shredder fluff, biosolids, construction and demolition debris, drum management-liquids, drum management-solids, industrial and special waste, liquifix (solidification services), municipal solid waste, tires, yard waste and CERCLA waste.

In this research, the leachate was collected in temperature-controlled containers at $4^{o}C$ and transported to the laboratory immediately. The leachate was stored under refrigeration at $4^{o}C$ until the treatment. BOD_5, COD, phosphorus and chloride were characterized in our laboratory following the standard methods. NH_4^+-N and NO_3^- concentrations were quantified colorimetrically by means of spectrophotometry

(Mccrady, 1966). Dissolved oxygen concentration was measured directly by a dissolved oxygen meter (WTW Oxi 315i, Cellox 325, Germany).

The landfill leachate collected from Leon County Landfill had a BOD_5 in the range of 189 to 295 mg/L, COD in the range of 854 to 1,352 mg/L, and NH_4^+-N in the range of 246 to 367 mg/L. The Springhill Landfill leachate had a BOD_5 in the range of 346 to 512 mg/L, COD in the range of 1,278 to 1,767 mg/L, and NH_4^+-N in the range of 416 to 674 mg/L. It should be noted that these measurements were based on the supernatant of the collected samples. Compared to Springhill Landfill leachate, the Leon County Landfill leachate had a darker color and obvious solid precipitation after settling over 24 hours. These solid precipitates also contained high organics. To analyze the components of the solid precipitates, EDX analysis was conducted and the results showed that the Leon County Landfill leachate solid precipitate had 78% C, 12% O, 7% Si, and 3% Fe. For comparison, Springhill Landfill Leachate was centrifuged to obtain solid precipitate, which had 74% C, 16% O, 9% Si and 1% Fe.

3.2 Leachate Treatment Process

3.2.1 Reactor Design, Setup and Parameter Characterization

Landfill leachate was treated by advanced oxidation in the oxidation reactor, after which the leachate was further treated in a series of suspended fiber (polypropylene) biofilters (Figure 4). During the advanced oxidation, xenobiotics were destructed and the following up suspended fiber biofiltration further degraded the residuals of the organics. For the first year of this project, suspended fiber biofiltration has been tested and proven to be effective for the treatment of landfill leachate in terms of organic, iron and chloride removal. In this research, a laboratory-scale reactor was designed to include advanced oxidation and phosphorous removal. The oxidation reactor can be configured for ozonation, hydrogen peroxide application, UV radiation or the combination of more than one oxidation means. In Figure 4, the illustrated oxidation reactor was for ozonation. For UV radiation to be used as the major means of advanced oxidation, the UV lamps were arranged in the reactor. The landfill leachate first passed through the UV lamps (with possible combination with O_3, H_2O_2 or both) for advanced oxidation, after which the leachate was further treated in a series of suspended fiber biofibers.

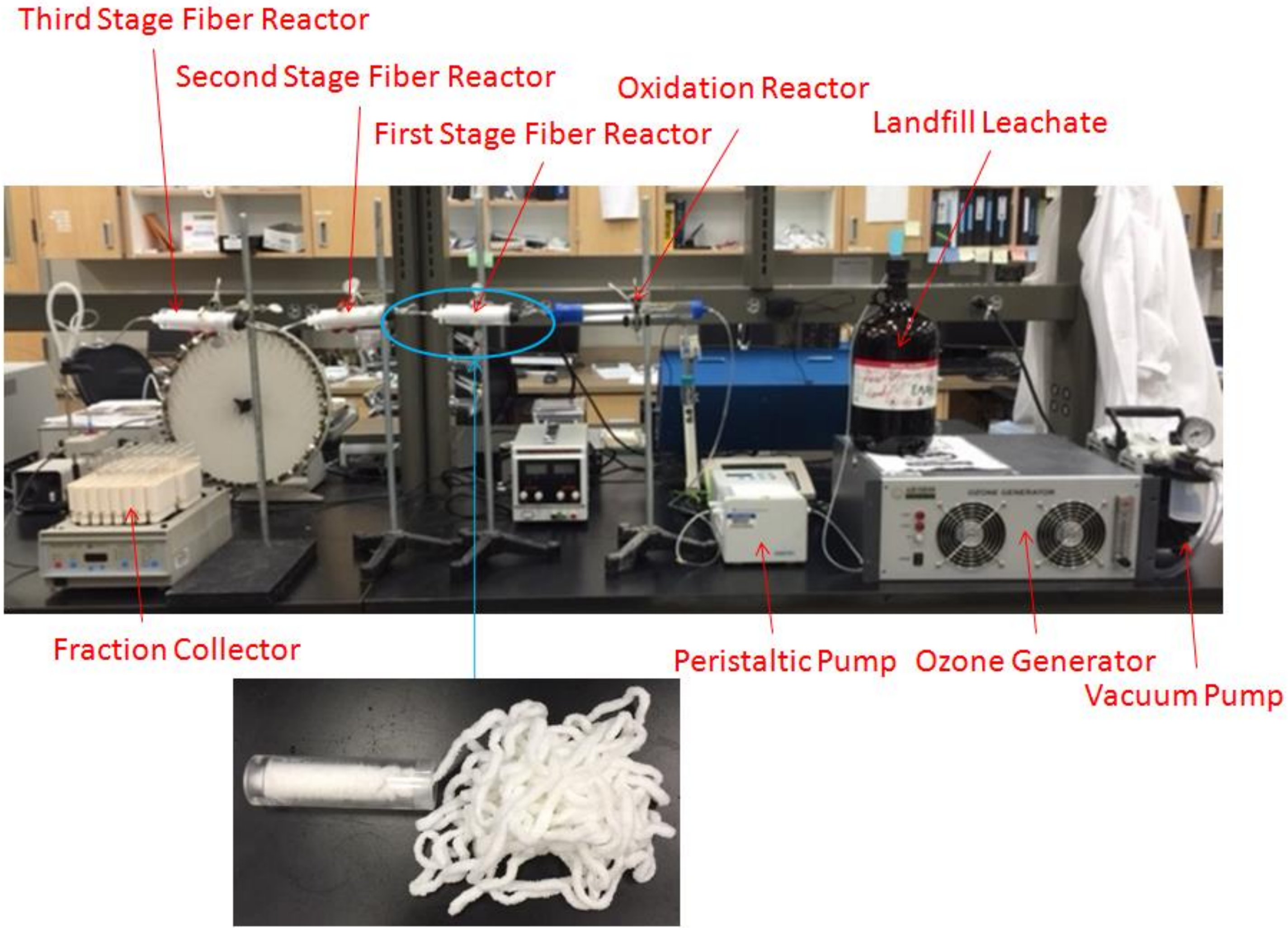


Figure 4. Experimental Setup of Combined Advanced Oxidation and Suspended Fiber Biofiltration

Inside the first stage suspended fiber biofilter, the fiber was coated with iron hydroxides through contact oxidation after advanced oxidation. The iron-coated fiber had a strong binding strength for phosphorus. The second and third stage fiber biofilters were inoculated with bacterial strains that were responsible for organic decomposition. During advanced oxidation, xenobiotics were destructed and the byproducts and residuals were further degraded within the suspended fiber biofilters by the inoculated microorganisms.

3.2.2 Reactor Operation

For this research, advanced oxidation of the leachate was evaluated using ozone, hydrogen peroxide and UV radiation as well as the combinations of these oxidants. Ozone was produced from oxygen using a 4 g/hr ozone generator (RMU 16-04, Azcozon Industries, Langley, B.C. Canada V1M 3E5, Canada) (Figure 5). This ozone generator was capable of producing up to 4 g/hr of ozone gas using compressed oxygen with glass/quartz electrodes. Fresh ozone stock solution was generated by bubbling O_3 gas (1.5% - 3%) into a 250 mL ozone gas washer with 10 mM phosphate buffered solution at pH 6. The concentration of ozone rich solution was 30 to 35 mg O_3/L. To minimize the decay of ozone in the stock solution, the ozone washer was surrounded by ice to maintain at < 6°C.

Figure 5. RMU 16-04 Ozone Generator

Ozone concentration was determined following the standard method (4500-O_3 B Indigo Colorimetric Method) (Jain et al., 2005). The thus measured concentration of the ozone stock solution was 33 mg/L O_3. Aliquots of ozone stock solution were transferred to the oxidation reactor by ozone-demand-free glassware to achieve the selected ozone doses. During ozonation, the UV absorbance was measured by a spectrophotometer. If the UV absorbance of the solution was more than 1 at $\lambda = 600$ nm, further dilution with DI water was required.

UV radiation was achieved by exposing under a UV collimated beam. The collimated beam was generated using 4 germicidal-UV lamps (15 W each), emitting primarily at $\lambda = 253.7$ nm (G15T8, General Electric Co., Cleveland, OH). The UV absorbance in the solution was determined using a Cary 60 UV-VIS spectrophotometer. The incident light intensity for each sample was measured by an IL 1700 radiometer equipped with SED240 sensor (International Light, Peabody, MA, U.S.A.). The corresponding UV dose was calculated by multiplying the radiation time by the intensity of the UV lamp as measured at the wavelength of 254 nm. H_2O_2 was obtained from Sigma-Aldrich.

The following dosage was tested in this research: ozone up to 10 mg/L, hydrogen peroxide up to 5 mg/L and UV up to 100 mJ/cm^2 (by varying the exposure time from 0 to 15 min). Since oxidation reactions were impacted by pH, reactions that were influenced by pH were also investigated at variable pH by adjusting the pH with hydrochloric acid or sodium hydroxide. Variable reaction time was also tested in this research. The xenobiotic compounds present in the leachate included aromatic hydrocarbons, halogenated hydrocarbons, polychlorinated biphenyls (PCBs), dioxins, naphthalene, and phenanthrene, etc. The xenobiotics investigated in this research are summarized in Table 9.

High-pressure liquid chromatography (HPLC) equipped with a UV-VIS detector, operating in reverse-phase was used to measure the concentration of BPA (Figure 6). The wavelength of the UV detector was 234 nm and the retention time was 17 min.

Table 9. Xenobiotics Investigated in this Research

Parameters	Method	Detection Limit	Reference
Bisphenol-A (BPA)	HPLC	0.1 µg/l	Method 8082A
Naphthalene	HPLC	21.5-100.0 µg/l	Method 8100
Phenanthrene	HPLC	8.4-133.7 µg/l	Method 8100
Benzene	HPLC	0.009 µg/l	Method 8021
Ethylbenzene	HPLC	0.005 µg/l	Method 8021
Toluene	HPLC	0.01 µg/l	Method 8021
o-Xylene	HPLC	0.02 µg/l	Method 8021
m-Xylene	HPLC	0.01 µg/l	Method 8021
p-Xylene	HPLC	0.01 µg/l	Method 8021
4-Chlorobenzoic Acid	HPLC	0.05 µg/l	Method 8021

Figure 6. HPLC Used for this Research

Chlorophenol was also quantified by means of HPLC equipped with the UV-VIS detector at a wavelength of 210 nm. Analytical details are detailed in Table 10.

Table 10. Analytical Method for Chlorophenol using HPLC

Analysis Conditions	Compounds	
	Phenols	Organic Acids and Real Water
Column	Platinum C-18 (Alltech), 250 × 4.6 mm	Prevail Organic Acid (Grace), 150 × 4.6 mm
Mobile Phase	60:40 (Water: Methanol)	KH_2PO_4, 25 mMol in Water (pH =2.5)
λ (nm)	210	
Flow Rate	1 mL/min	
Sample Volume	30 µL	

Naphthalene and phenanthrene were analyzed using the HPLC equipped with the UV-DIS detector. An ODS hypersil column (Hewlett Packard, Palo Alto, CA.) was used for the separation. The mobile phase was 80% methanol (high-pressure liquid chromatography grade) mixed with 20% nanopure DI water (V/V) (Barnstead Thermodyne, Debuque, IO). The flow rate was 1 ml/min and the injection was 25 µL. Naphthalene and phenanthrene concentrations were quantified against external standards. Benzene, toluene, and xylene (BTX) were also monitored by means of the HPLC equipped with the UV-VIS detector. The samples were extracted with methanol and chromatography was isocratic in a mobile phase consisting of water-methanol (30-70) with a flow rate of 1 mL/min.

Biodegradation experiments for naphthalene and phenanthrene were performed using naphthalene-acclimated (NMO) and phenanthrene-acclimated microorganisms (PMO). The biodegradation experiments were conducted in a closed 500 mL amber glass reactor with a Teflon-lining septum sampling port. Oxygen was supplied from a pressure cylinder at a flow rate of 0.1 mg/min. Excess oxygen passed through the oxygen pressure regulator to provide an atmospheric seal and to maintain a constant pressure inside the reactor. Produced carbon dioxide was removed from the atmosphere by potassium hydroxide held in a glass tube inside the reactor. Each reactor contained 250 mL mineral salt media with 30 mg/L naphthalene or 1.0 mg/L phenanthrene serving as the carbon source. The inoculum was 5 mg/L as COD of NMO or PMO. The contents of the flask were continuously stirred at 150 RPM throughout the course of the experiments. Samples were withdrawn periodically from the reactor and analyzed for naphthalene and phenanthrene concentrations and total protein for biomass determination.

3.3 Consortia Cultivation

In the series suspended fiber biofilters, it was expected organic compounds and iron can be removed through biodegradation and contact oxidation, which depended on the corresponding microorganisms to degrade the organics and fix iron. These consortia strategically positioned themselves on the suspended fiber to form a biofilm. Usually, in the biofilm, both gram negative bacteria (57%) and gram positive bacteria (43%) were present in almost equal frequencies in the consortia (Buswell et al., 1998). *Bacillus* dominated the generic composition by 25%, which was followed by *Vibrio* (17%). Dominance of *Bacillus* was in agreement with the prior findings (Chianese et al., 1999). The other genera resembled the *Enterobacteriaceae* group, *Arthrobacter*, *Brevibacterium*, *Aeromonas*, and *Pseudomnas*, etc. Recently, some iron fixation bacteria that can derive energy and multiply by oxidizing dissolved ferrous iron (or the less frequently available manganese) have also been identified (Weinberg, 1989). They were known to grow and proliferate in solutions containing as low as 0.1 mg/L of iron. However, at least 0.3 ppm of dissolved oxygen was needed to carry out the oxidation (Di Palma et al., 2002). For this research, we cultured organic degrading and iron fixation consortia using collected soil samples as the inocula (Barnes et al., 2007). Continuous cultivation and enrichment were carried out immediately after the samples were transported back to our laboratory.

For organic degrading consortia, 10 mg soil was transferred into a 250 mL Erlenmeyer flask containing 100 mL sterilized culture media. The media had a composition (mg/L) of KH_2PO_4, 160; K_2HPO_4, 420; Na_2HPO_4, 50; NH_4Cl, 40; $MgSO_4 \cdot 7H_2O$, 50; $CaCl_2$, 50; $FeCl_3 \cdot 6H_2O$, 0.5; $MnSO_4 \cdot 4H_2O$, 0.05; H_3BO_3, 0.1; $ZnSO_4 \cdot 7H_2O$, 0.05; $(NH4)_6Mo_7O_{24}$, 0.03; glucose, 200; and ammonia chloride, 60. The pH of the media was adjusted to 7.4

with 1 M HCl or 1 M NaOH, after which the media were sterilized by autoclaving (121^{o}C and 1 atm) for 20 min. Glucose was filter-sterilized and aseptically added to the autoclaved media. The Erlenmeyer flask was capped with a foam stopper and the inoculated Erlenmeyer flask was put into a rotary-shaker (150 rpm at 35°C) for at least 1 week until the consortia were observed to be formed. After centrifugation (6000 *g*, 15 min), the consortia were enriched in 100 mL fresh culture media with 200 mg/L glucose. The consortia were harvested by centrifugation (6000 *g*, 15 min) and the biofilters were inoculated with the consortia. For iron fixing bacteria culturing, 10 mg soil was transferred into a 250 mL Erlenmeyer flask containing 100 mL sterilized culture media. The media had a composition (mg/L) of KH_2PO_4, 160; K_2HPO_4, 420; Na_2HPO_4, 50; NH_4Cl, 40; $MgSO_4{\cdot}7H_2O$, 50; $CaCl_2$, 50; $FeCl_3{\cdot}6H_2O$, 0.5; $MnSO_4{\cdot}4H_2O$, 0.05; H_3BO_3, 0.1; $ZnSO_4{\cdot}7H_2O$, 0.05; $(NH4)_6Mo_7O_{24}$, 0.03; $FeSO_4{\cdot}7H_2O$, 250, and ammonia chloride, 60. The pH of the media was adjusted to 7.4 with 1 M HCl or 1 M NaOH, after which the media were sterilized by autoclaving (121^{o}C and 1 atm) for 20 min. The inoculated Erlenmeyer flask was capped with foam stopper and put into a rotary-shaker (150 rpm at 35°C) for at least 1 week until the iron fixation bacteria were observed. The iron fixation bacteria were harvested by centrifugation (6000 *g*, 15 min) and inoculated the biofilter.

3.4 Phosphorous Removal Consideration

After advanced oxidation, organics were removed in the suspended fiber biofilters through biodegradation and iron was oxidized and fixed on the fiber by contact oxidation. During this process, low biomass was produced. Therefore, the suspended fiber biofilters can last a long operation period. Once the biofilter capacity was reached, the polypropylene fiber was taken out for washing and repacked to the reactor. Phosphorous was removed mainly in the first stage suspended fiber biofiber. After advanced oxidation, the fiber was coated with iron hydroxides by contact oxidation, which removed phosphorous by adsorption. In our prior research, we discovered that a low pH was preferred for phosphorous adsorption on the iron oxide-coated fiber. This process was also affected by alkalinity. The phosphorous detection methods are summarized in Table 11.

Table 11. Analytical Method for Phosphorus

Total Iron	USEPA FerroVer Method	0.02 mg/l	Method 8008
Total Phosphorus	Ascorbic Acid Method	1.5 to 15.0 mg/L	Method 10210
Ortho-Phosphorus	Ascorbic Acid Method	0.5 to 5.0 mg/L	Method 10209

4. Results

4.1 Advanced Oxidation of Landfill Leachate

4.1.1 Ozonation

Ozonation can be used for the treatment of landfill leachate, especially for landfill leachate with high organic contents. Ozonation can also remove the organic coverage of clay minerals, promoting the solid precipitation. Ozonation has become a preferential oxidation method and the amount of ozone to be used is closely related to the properties of the leachate to be treated. In our prior research, we used ozonation as a pre-treatment means to promote solid precipitation from the landfill leachate through coagulation. At lower ozone dosage, ozonation produced some hydrophobic neutral and intermediate organic compounds, which can be removed efficiently in the following coagulation process. On the contrary, at higher ozone doses, the organics were oxidized further into more hydrophilic and low molecular-sized compounds, which were more difficult to coagulate. The beneficial effect of ozonation towards better coagulation of non-humic fraction had also been observed. Pre-oxidation prior to coagulation was observed to increase coagulation efficiency by 15%, most likely because the oxidation changed the characteristics of the organics and degraded organic molecules to lower molecular weight compounds. The organics coated clay mineral particles had been proven to interfere with clay mineral coagulation because most organics were non-charged. Oxidation seemed to be the best option for the removal of the organics that coated the mineral clays. Ozonation also encouraged ferrous iron oxidation and subsequent ferric iron hydrolysis and precipitation. Through ozonation, denser structure of iron precipitates was observed as compared to that of non-ozonation. COD removal also increased accordingly with the increase of ozone dosage/COD molar ratio (Figure 7).

In this research, landfill leachate collected from Springhill Landfill was ozonated at different ozone dosage/COD molar ratios. Both COD and BOD_5 values were found to decrease with the increase of the ozone dosage (Figure 8). However, the BOD_5/COD value increased with enhanced oxidation, which would be beneficial for the following biological degradation processes. It was suspected that through ozonation, some recalcitrant organic compounds were broken into simple organic compounds that can be degraded biologically.

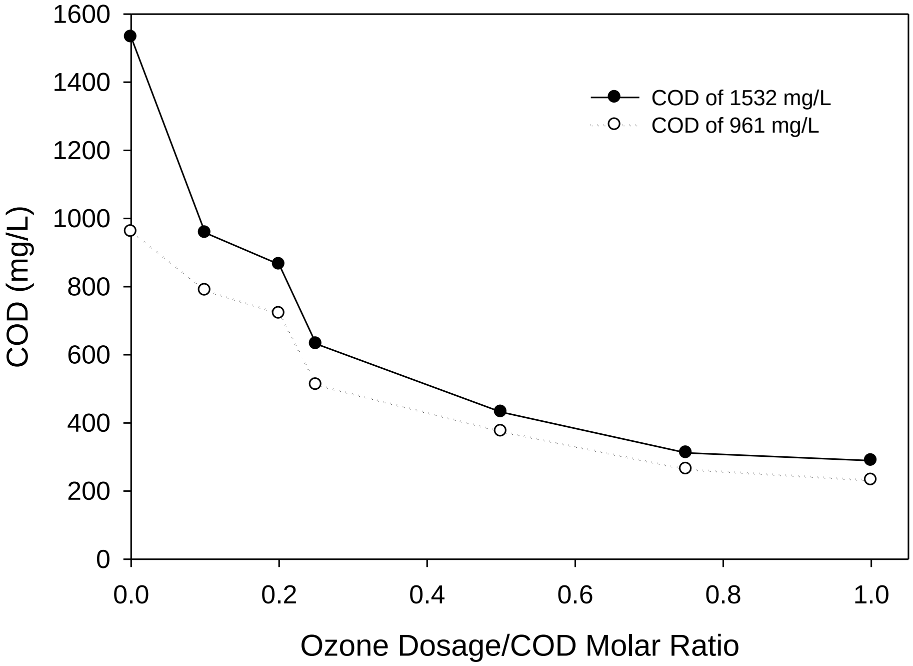


Figure 7. COD Removal as a Function of Ozone Dosage/COD Molar Ratio for Springhill Landfill Leachate

Before we further investigated the byproducts by ozonation, we first used UV spectra to observe the organic content variation by ozonation. In the case of landfill leachate ozonation, a significant decrease of organic compound concentration was observed in the UV spectra (Figure 9). In Figure 9, organic acid contents are reflected in the region of λ = 210 nm. After 5 minutes of ozonation at an ozone concentration of 8.9 mg/L, 65% of organic acids was depleted. With 10 minutes of ozonation, 75% of the organic acids were found to be depleted. After 20 minutes, increased ozonation time did not lead to further organic decomposition. Therefore, the susceptible organic matter to be ozonated can be completely within 20 minutes.

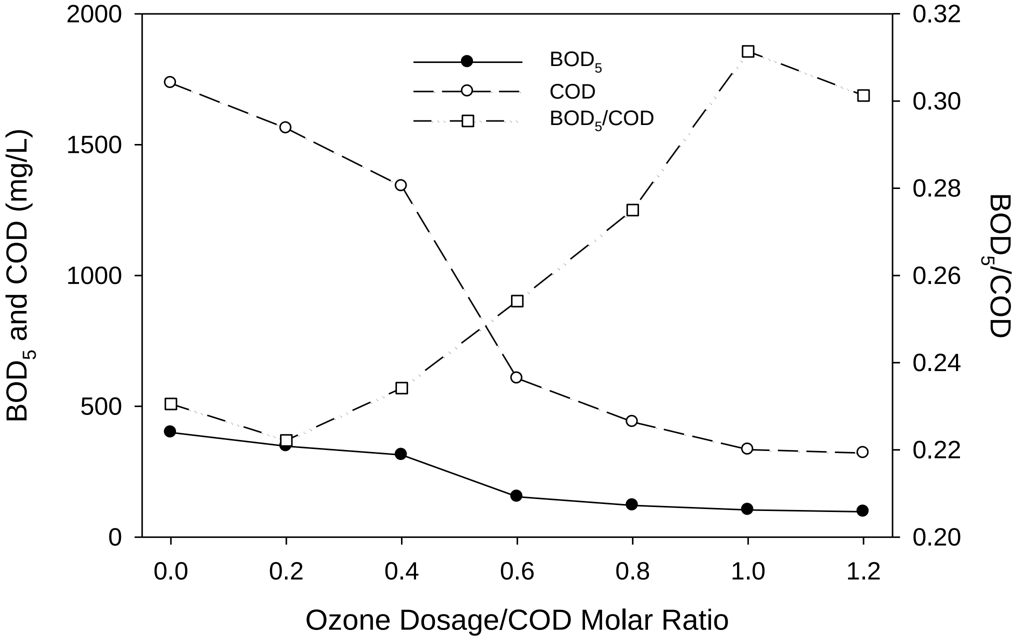


Figure 8. BOD5/COD Ratio as a Function of Ozonation

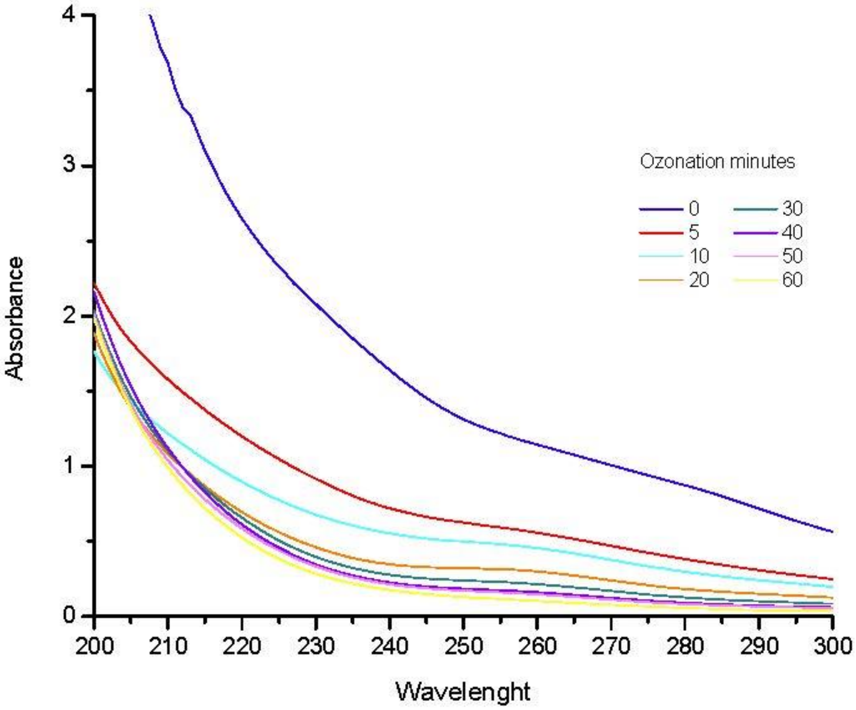


Figure 9. UV-VIS Spectrum Variation of the Landfill Leachate Collected from Springhill Landfill after Ozonation

The ozonation of landfill leachate was monitored by HPLC to observe the decomposition dynamics. The major byproducts were found to include hydroquinone, catechol and simple organic acids such as maleic acid and several unidentified compounds. Accumulation of recalcitrant oxalic acid ($C_2H_2O_4$) was also discovered during ozonation. Oxalic acid increased from 21 mg/L before ozonation to 45 mg/L after 50 minutes' ozonation (Figure 10).

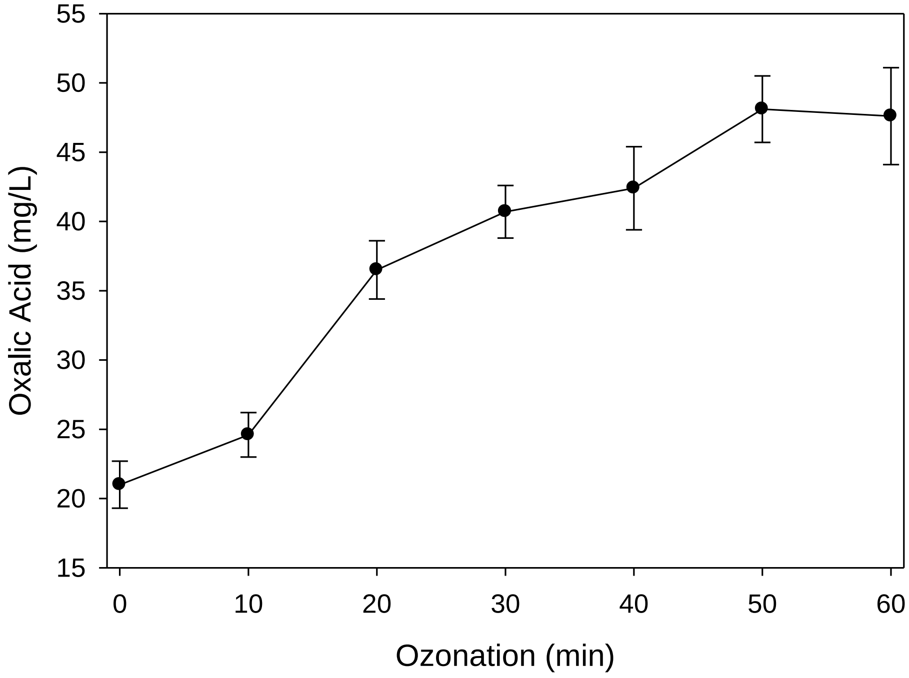


Figure 10. Oxalic Acid Accumulation after Ozonation

We further tested the biodegradation of the final products, a mixture of oxalic and formic acids with a concentration of 100 mg/L of each. Microorganisms were able to eliminate both compounds during two days. These results demonstrated the promising application potentials of ozonation for the treatment of landfill leachate, i.e., highly toxic substrates that cannot be eliminated by bioprocesses can be degraded by ozonation and transformed into compounds that can be biologically decomposed. The consortia that were responsible for oxalic and formic acid degradation were the ones we cultured and inoculated the suspended fiber. They showed the capability to eliminate the ozonation products. So, it was expected that ozonation followed by biological degradation can be applied for the treatment of landfill leachate, which might be resistant to traditional biological treatment processes. The combined processes should be more efficient than individual ones.

Impact of ozonation on the depletion of humic acids and aromatic acids was also investigated. Aromatic acid concentration decreased sharply within 5 minutes after ozonation at an ozone concentration of 8.9 mg/L, after which the decrease became moderate. On the contrary, humic acid decreased almost linearly with the ozonation (Figure 11).

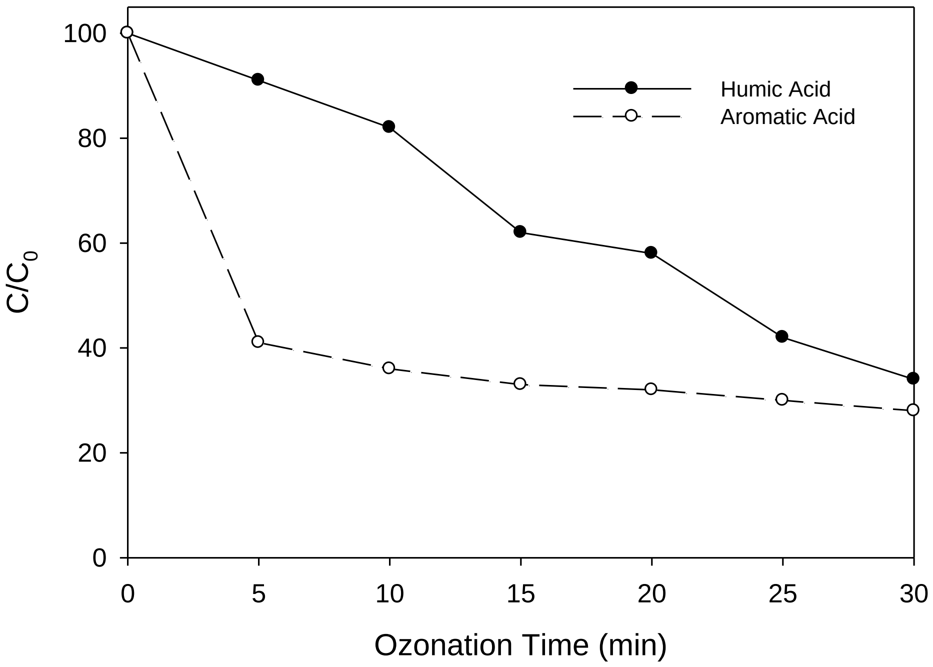


Figure 11. Humic Acid and Aromatic Acid Depletion with Ozonation

Aromatic hydrocarbons including toluene, ethylbenzene, and xylene are commonly found in the landfill leachate. With advanced oxidation, these aromatic hydrocarbons can be easily degraded. In this research, more than 90% of toluene was removed when ozone was applied at a concentration of 8.9 mg/L at pH 9.0 (Figure 12).

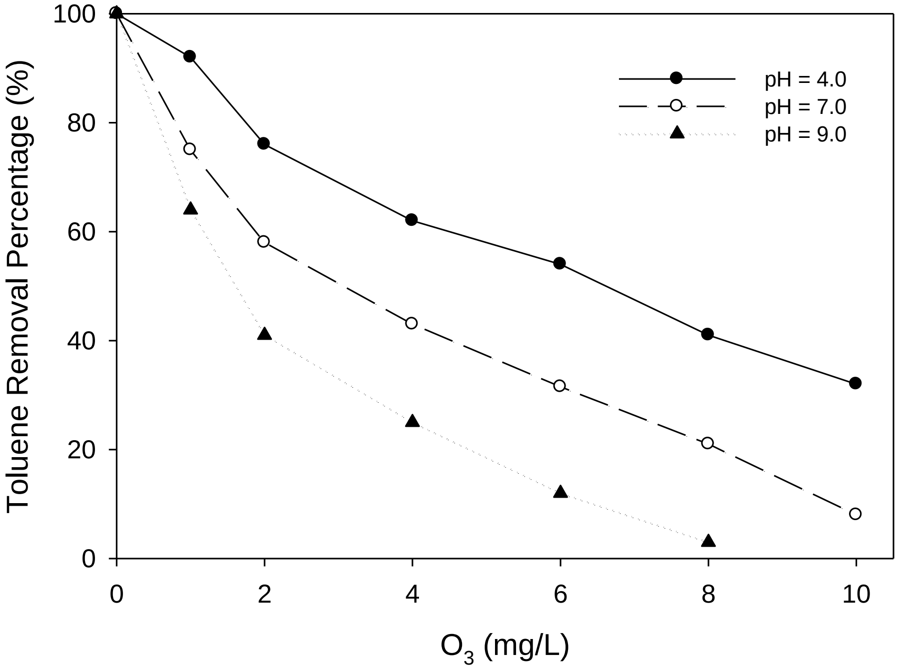


Figure 12. Toluene Removal by Ozonation

Bisphenol A (BPA), a plastic additive, is used in the production of polycarbonate plastics and epoxy resins. Studies have shown that significant amounts of BPA can leach from plastics and enter the environment including the landfill leachate, creating a public health concern. As a xenobiotic organic compound (XOC), the concentration of BPA in the leachate varies depending on the age and composition of the waste in the landfill. The typical BPA concentration in the landfill leachate is in the range of 0.07 to 269 μg/L. The conventional biological treatment of landfill leachate is not efficient in removing BPA. In this research, BPA removal was found to increase with the increase of ozone dosage, which was also a function of pH (Figure 13). At ozone dosage of 10 mg/L and pH 9.5 with a reaction time of 10 minutes, 60% of BPA can be removed.

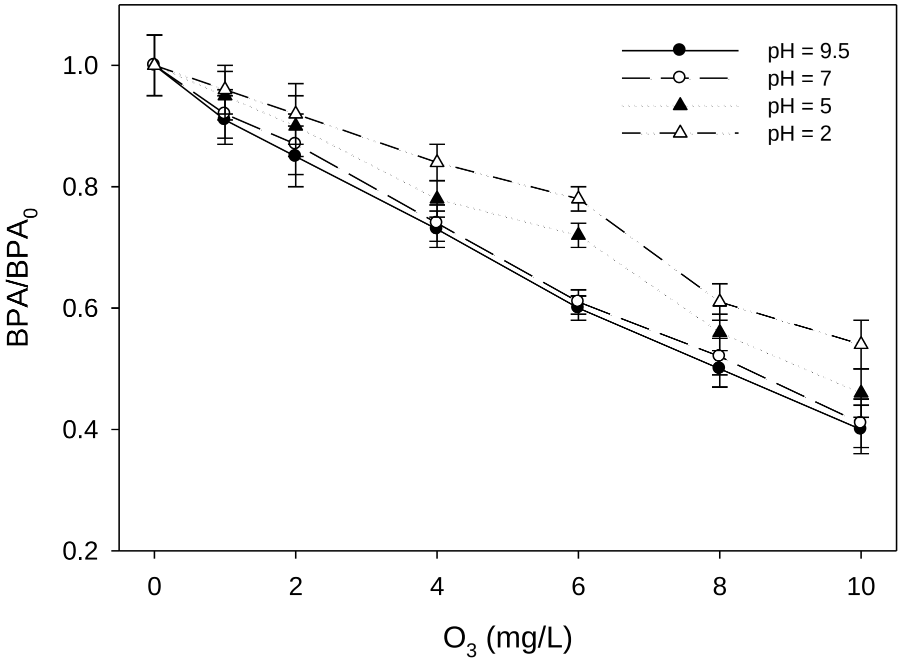


Figure 13. BPA Removal by Ozonation as a Function of pH

Oxidation kinetics of BPA in landfill leachate was also investigated in this research with an ozone dosage of 8.9 mg/L. BPA depletion increased with the reaction of ozonation for all the pH conditions investigated in this study. However, the BPA depletion with ozonation was more pronounced at pH 7 and 9 as compared to that of pH 5 (Figure 14). It seemed that BPA depletion was more effective by ozonation after five minutes. Similarly, after 10 minutes' ozonation, the depletion became moderate again. In a separate experiment, we also tested BPA depletion using combined ozone and hydrogen peroxide. The results showed that applying ozone alone was more efficient in BPA depletion than combined ozonation with hydrogen peroxide. It is therefore recommended ozonation at pH 10 with a reaction time of 10 minutes be used for BPA destruction. Under these conditions, 80% BPA can be depleted within 10 minutes.

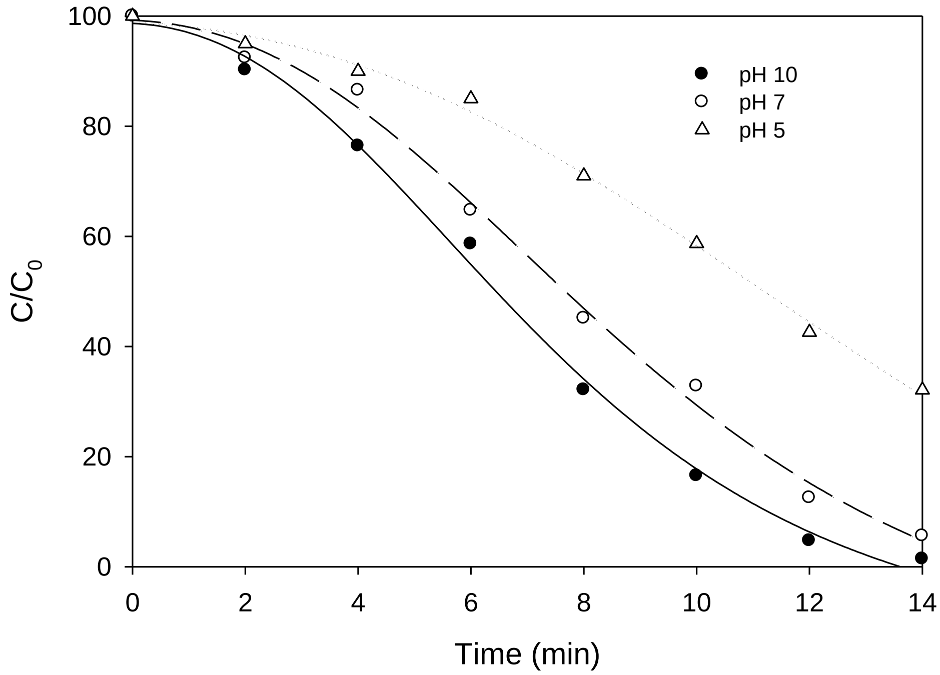


Figure 14. BPA Depletion Kinetics by Ozonation

Phenols are frequently present in the landfill leachate because of their widespread use in commercial products. In addition, as by-products of petrochemical, pulp and paper, plastic, and glue manufacturing processes, they are drawing more and more attention. The concentration of phenolic compounds in the landfill leachate can be as high as 20 mg/L. It should be noted that phenol-containing pesticides and wood preservatives may cause significant health hazards even at μg/L levels. Consequently, it is important to monitor phenols and substituted phenols in the environment. In this research, landfill leachate containing phenol at a concentration of 0.5 mM was ozonated with an ozone dosage of 8.9 mg/L. It was discovered that phenol depleted exponentially with the reaction time. After 25 minutes of ozonation, 95% of phenol can be depleted through ozonation (Figure 15).

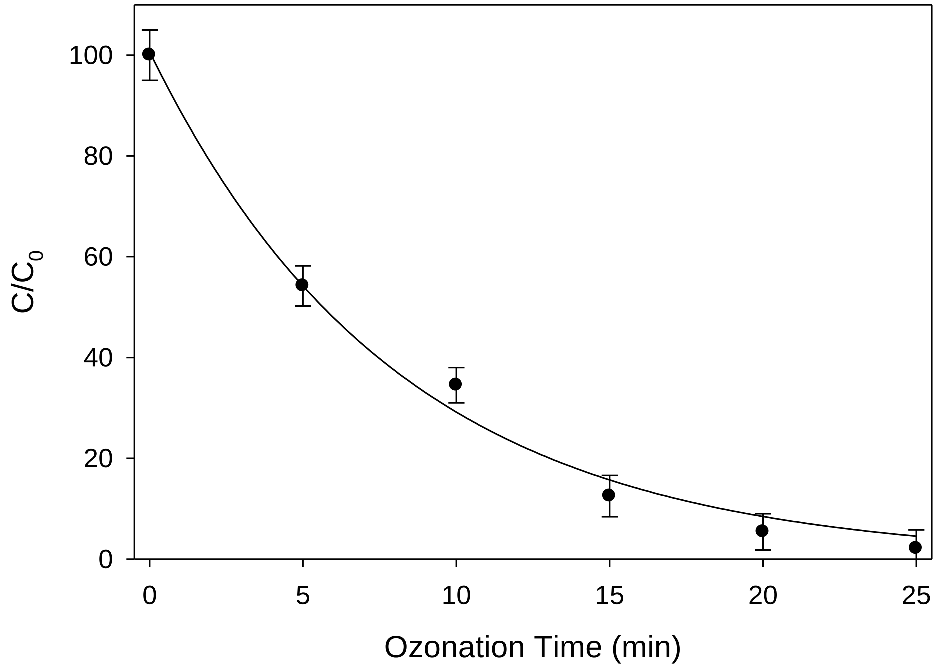


Figure 15. Depletion Kinetics by Ozonation

4.1.2 Hydrogen Peroxide

Following ozonation, hydrogen peroxide was tested for the treatment of landfill leachate. Landfill leachate collected from Springhill Landfill was reacted with hydrogen peroxide at different H_2O_2/COD molar ratios at pH 7.4 and 9.6. COD removal was found to increase with the increased H_2O_2 concentration for both pH levels (Figure 16). COD removal was better observed for pH 7.4 than that of 9.6. Compared to ozonation, hydrogen peroxide was more effective in removing COD from the landfill leachate. For instance, when hydrogen peroxide was applied at a molar ratio of 0.2, 0.5 and 1.0 to COD, 72 – 75%, 75 – 80% and 80-90 % COD removal were achieved. On the contrary, around 40%, 50% and 70% COD removal were observed with corresponding ozone application dosages, i.e., ozone to COD molar ratios of 0.2, 0.5 and 1.0. However, it was too early to conclude that hydrogen peroxide should be used in the treatment system without further investigation of following the biodegradation of the residual organics in the suspended fiber biofilters.

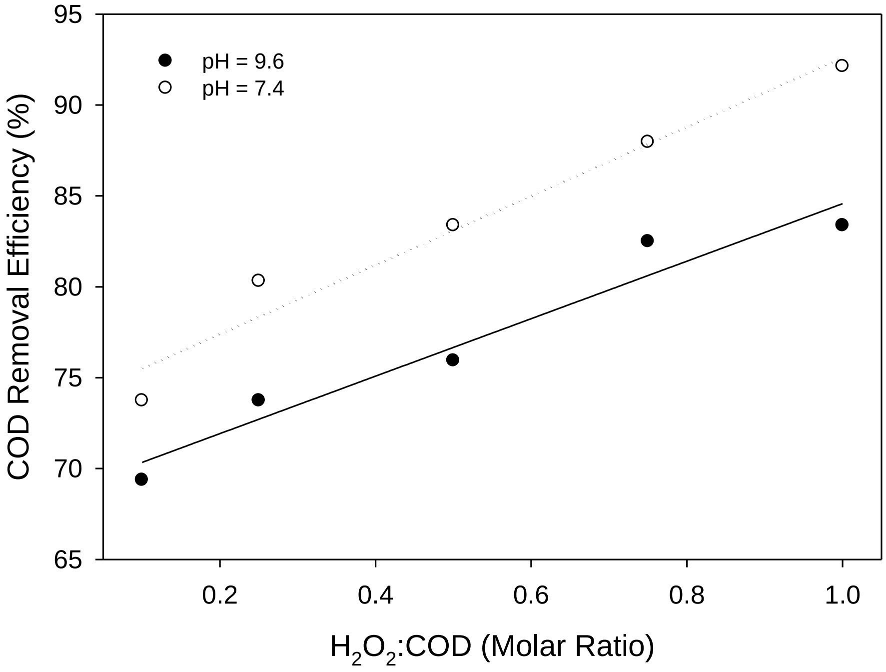


Figure 16. COD Removal with Variable H_2O_2 Dosages at pH 7.4 and 9.6

Landfill leachate collected from Springhill Landfill was further reacted with hydrogen peroxide at different H_2O_2/COD molar ratios to test the impact of hydrogen peroxide applications on BOD_5/COD ratios. Both COD and BOD_5 values were found to decrease with the increase of the hydrogen peroxide concentration (Figure 17). However, the BOD_5/COD value increased with increased hydrogen peroxide dosage, which again would be beneficial for the following biological degradation processes. Compared to ozonation, hydrogen peroxide depleted COD more rapidly at low hydrogen peroxide dosages. For instance, at H_2O_2/COD molar ratio of 0.4, 70% of COD was depleted. However, at ozone/COD molar ratio of 0.4, only 25% of COD was depleted. On the other hand, at high dosages, similar COD depletions were observed for both hydrogen peroxide and ozonation. At hydrogen peroxide/COD or ozone/COD molar ratio greater than 0.8, COD depletion became moderate for both hydrogen peroxide application and ozonation. At variable O_3/H_2O_2 molar ratios, COD depletion was illustrated in Figure 18.

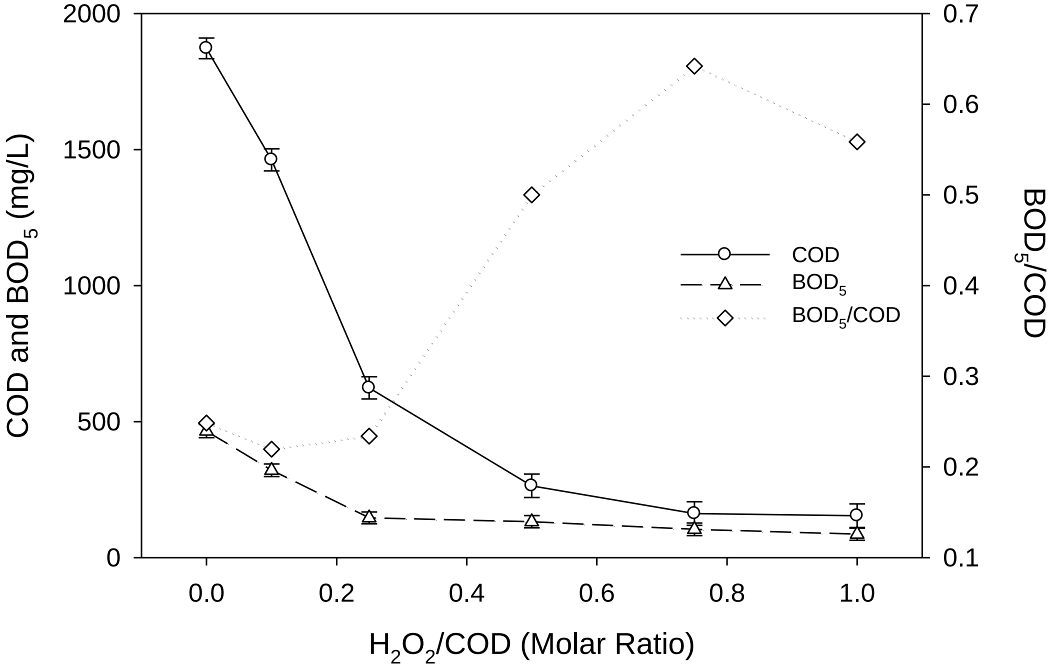


Figure 17. COD and BOD$_5$ Removal as a Function of H$_2$O$_2$ Dosage

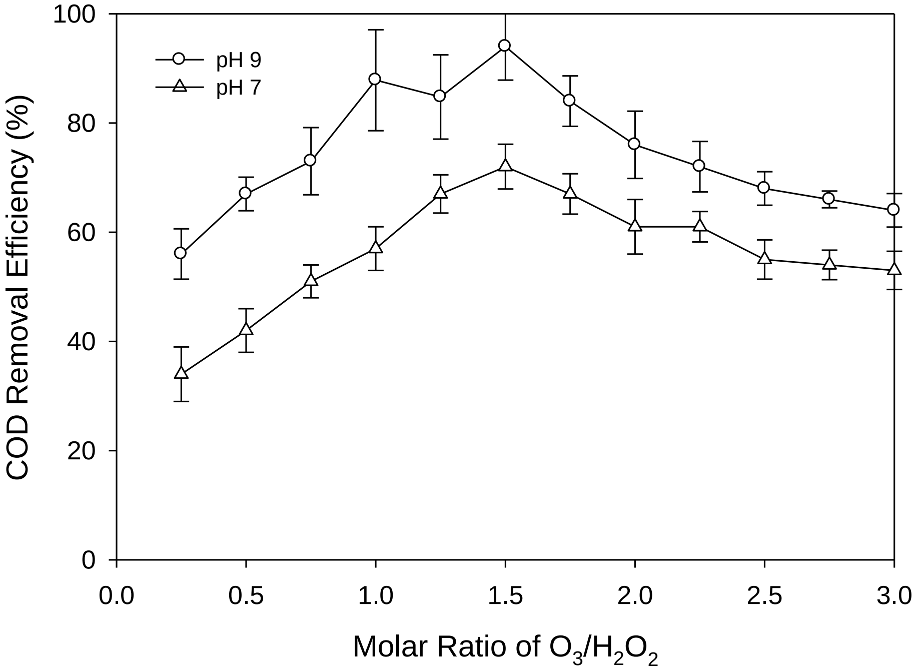


Figure 18. COD Depletion at Variable O$_3$/H$_2$O$_2$ Molar Ratios

When using ozonation for the treatment of landfill leachate, ammonium concentration was observed to first increase then decrease with the increased ozone dosage owing to increased ammonium release by the reaction of ozone with the organic nitrogen and the subsequent nitrification (Figure 19). However, ammonium concentration increase was not observed for hydrogen peroxide applications. One possible explanation was that the released ammonium was oxidized to nitrate immediately. This was evidenced by the increased nitrate concentration with increased ozone and hydrogen peroxide dosages.

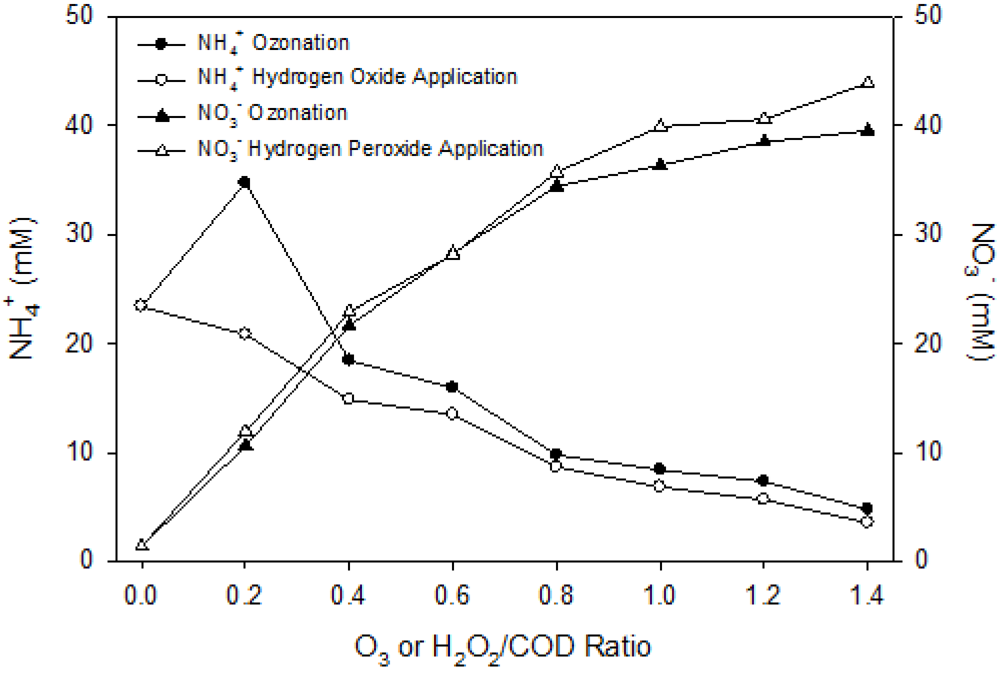


Figure 19. NH_4^+ Oxidation and NO_3^- Production during Advanced Oxidation

4.1.3 UV Radiation

Following ozonation and hydrogen peroxide applications, UV radiation was also tested for the treatment of landfill leachate. UV radiation in the range of 10 to 100 mJ/cm^2 (by varying the exposure time from 0 to 15 min) was applied to Springhill Landfill leachate at pH 4.0, 7.4 and 9.6 (Figure 20). The results demonstrated UV radiation had better COD removal efficiency at high and low pH values than that of neutral pH. However, the removal efficiency was low for all the tested pH levels. When H_2O_2 and UV radiation were combined, high COD removal efficiency was observed at low H_2O_2 dosage (H_2O_2: COD = 0.25:1), especially at low and high pH values (Figure 21). At low and high pH and H_2O_2 dosage of H_2O_2: COD = 0.25:1, COD removal increased with the increase of UV radiation, reaching 96% for pH 4.0 and 90% for pH 9.6. At pH of 7.4, around 75% of COD can be removed and variation of UV radiation showed minimal effect. It is therefore recommended that UV not be used alone for the treatment of landfill leachate. In other experiments, UV radiation combined with ozonation was also studied and the results were not satisfactory.

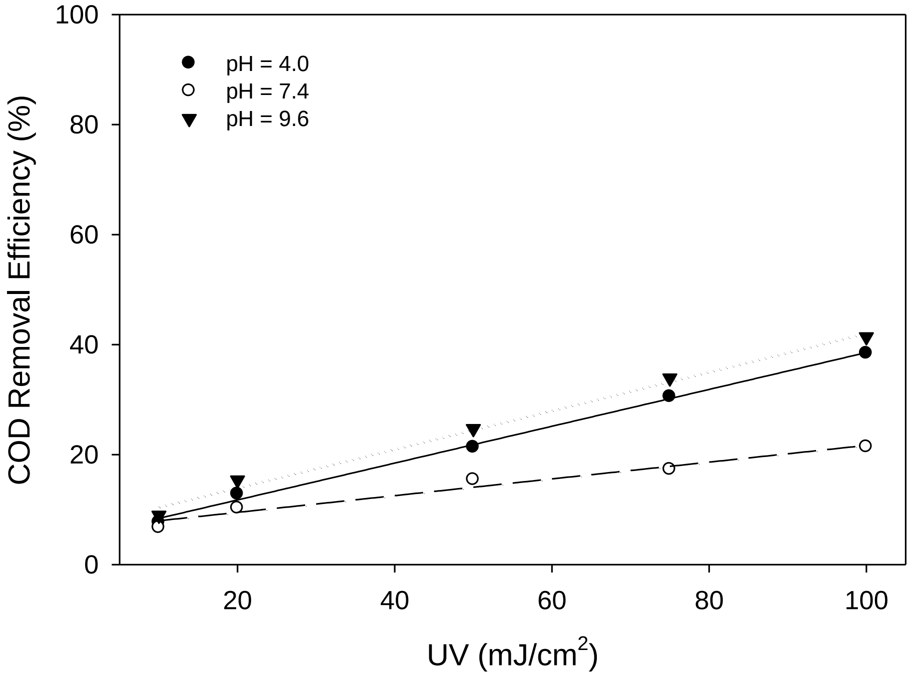


Figure 20. COD Removal with Variable UV Radiation at pH 4.0, 7.4 and 9.6

Similar as ozonation, NH_4^+ concentration was observed to increase and then decrease with the increased UV radiation owing to increased NH_4^+ release by the reaction of UV radiation with the organic nitrogen and further nitrification (Figure 22).

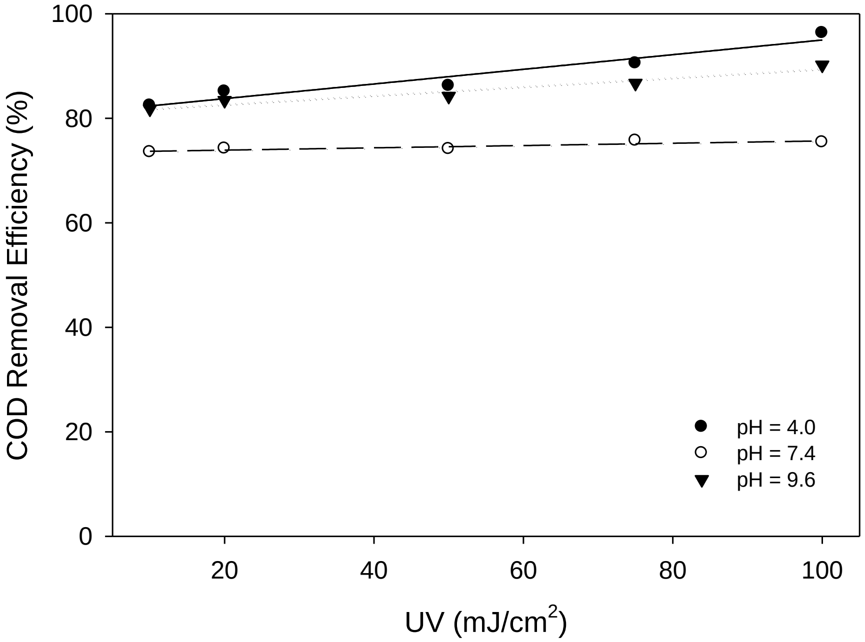


Figure 21. COD Removal with Variable UV Radiation at H_2O_2 Dosage of H_2O_2: COD = 0.25:1 and pH 4.0, 7.4 and 9.6

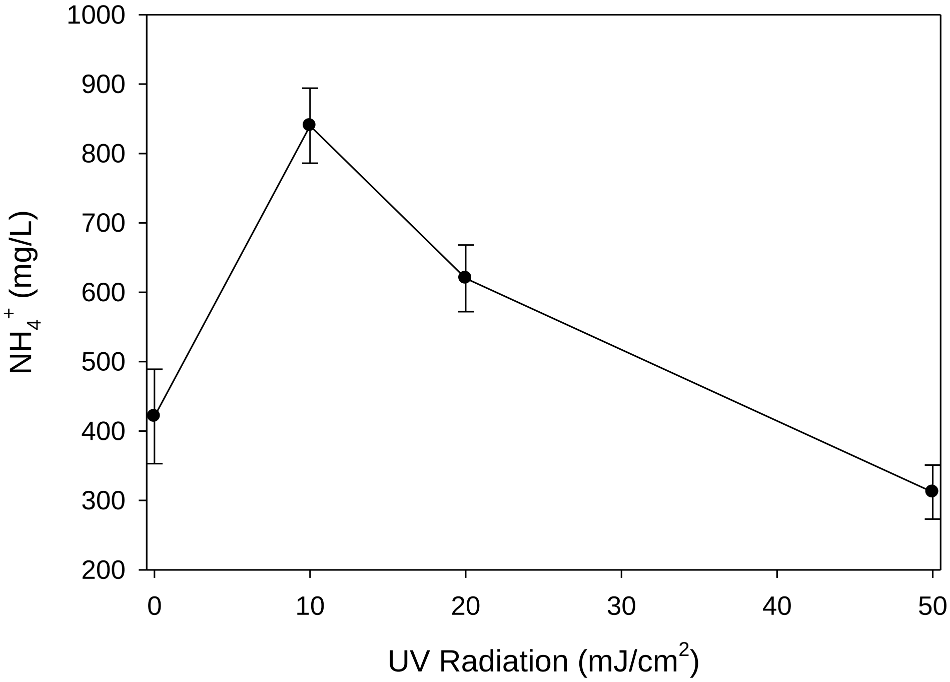


Figure 22. NH_4^+ Release as a Function of UV Radiation

4.2 Reactor Performance

After advanced oxidation, the treated leachate was introduced to the series of suspended fiber biofilters. Inside the biofilters, different microbial consortia cultured separately were inoculated, which strategically positioned themselves on the suspended fiber to form a biofilm. With the incorporation of microbial consortia, organics were further reduced to meet the discharge requirements.

For different advanced oxidation applications, we had different COD removal observations (Figures 23 – 26). For these four advanced oxidation treatments followed by corresponding suspended fiber biofiltration, ozonation combined with hydrogen peroxide application had the best treatment results, i.e., COD was reduced from 1,750 mg/L to 70 mg/L (Figure 27). UV radiation alone had the lowest COD removal observations, which could only reduce the COD to 200 mg/L after oxidation and three stages of biofiltration.

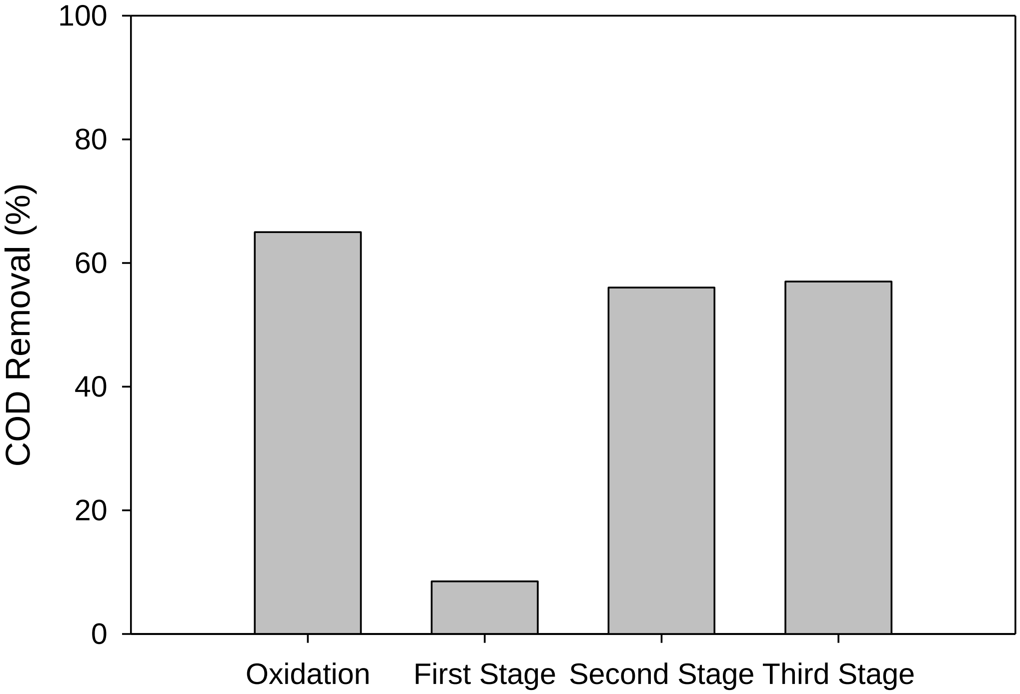


Figure 23. COD Removal in the Treatment System with Ozone as the Advanced Oxidation Means

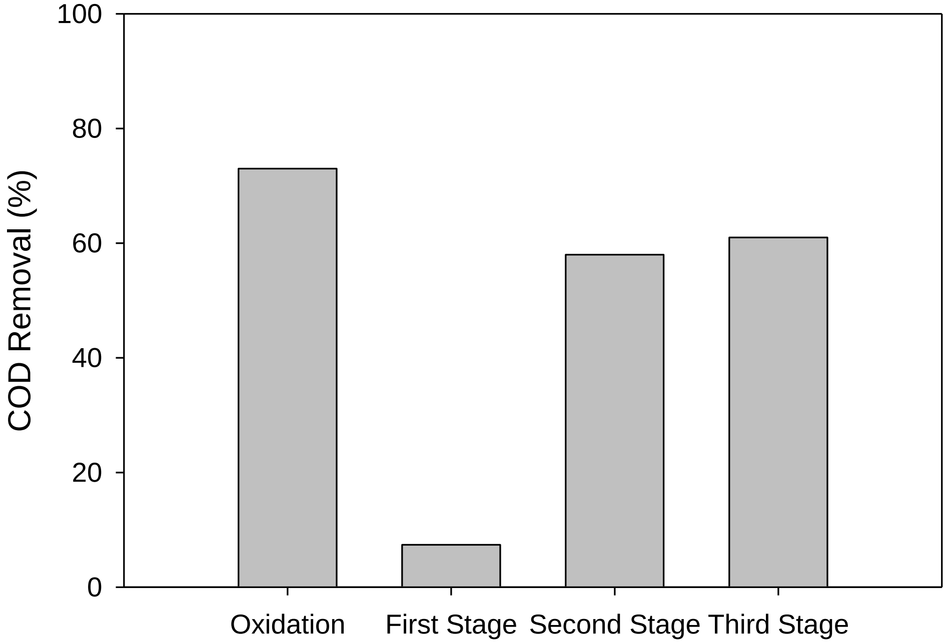


Figure 24. COD Removal in the Treatment System with Hydrogen Peroxide as the Advanced Oxidation Means

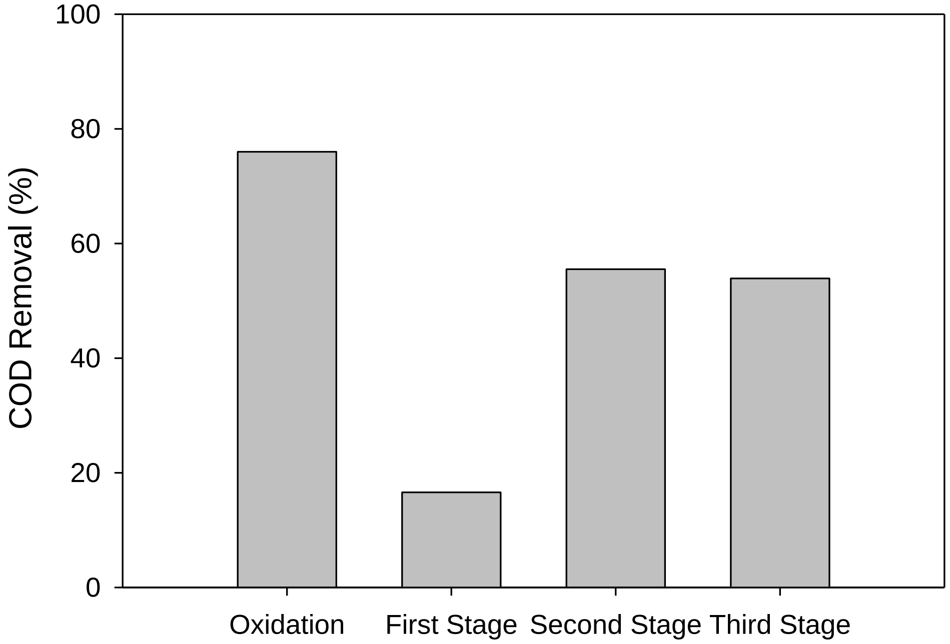


Figure 25. COD Removal in the Treatment System with Combined Ozone and Hydrogen Peroxide as the Advanced Oxidation Means

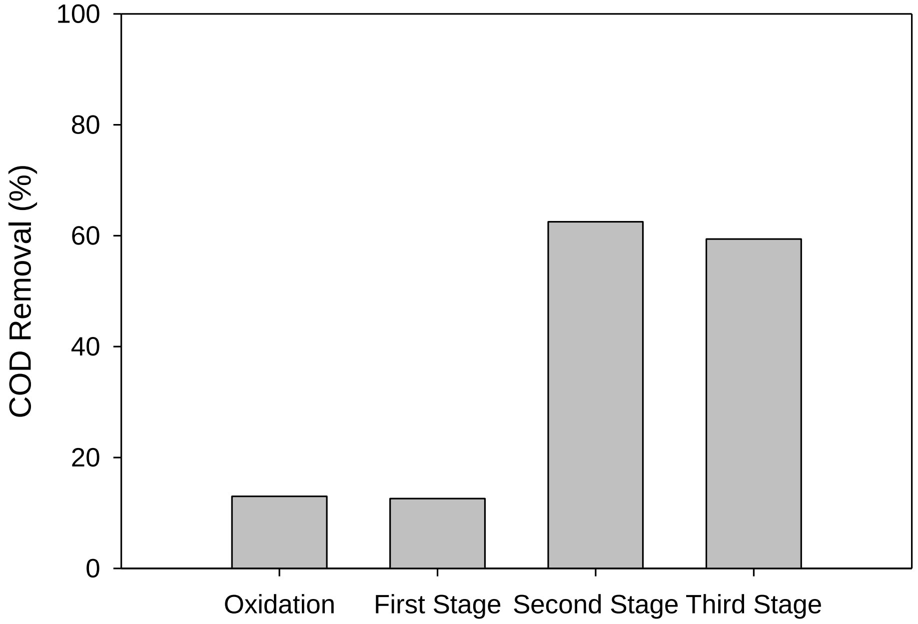


Figure 26. COD Removal in the Treatment System with UV Radiation as the Advanced Oxidation Means

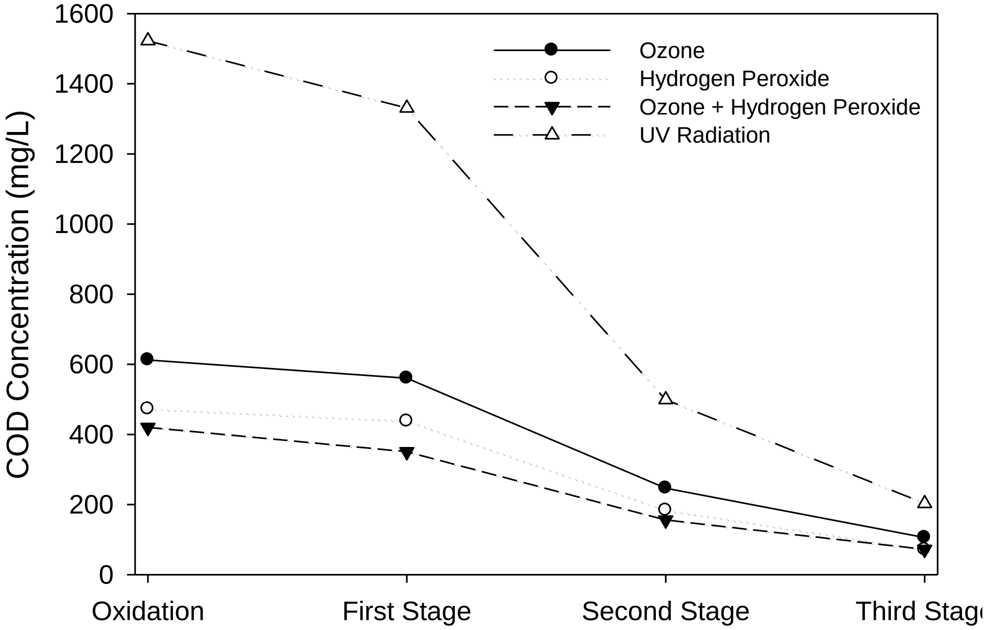


Figure 27. Comparison of COD Removal for Different Advanced Oxidation Means

4.3 Naphthalene and Phenanthrene Removal

4.3.1 Naphthalene and Phenanthrene Adsorption

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of anthropogenic pollutants. The concern of these compounds arises primarily from the fact that a small fraction of the PAHs generated and released to environment has been shown to be carcinogenic and mutagenic. PAHs have also been reported to disrupt the endocrine system in humans. PAHs may exist in landfill leachate through landfilling of municipal solid wastes. Among the PAHs, naphthalene (a double cyclic aromatic hydrocarbon) and phenanthrene (a tricyclic aromatic hydrocarbon) are the two simplest forms. Naphthalene is slightly soluble in water (31 mg/L at 1 atm and 25°C). Once in the solution, biodegradation may occur if conditions are aerobic. Phenanthrene is weakly soluble in water (1.2 mg/L at 1 atm and 25°C), therefore, the biodegradation is strictly limited by its bioavailability.

It was suspected naphthalene and phenanthrene would have strong sorption to the suspended fiber. Batch sorption isotherms were then used to determine naphthalene and phenanthrene affinity to the fiber. To determine the sorption of naphthalene on the fiber, a series of 25 mL vials containing naphthalene solutions (20 mL) at the concentrations of 0.25, 0.5, 1, 5, 10, 15, 20, and 30 mg/L and 4 g fiber media (including blank controls) (sealed with Teflon-lined screw caps) were agitated on a Wrist Action Shaker (Burrel Scientific, Model 75) for 24-hours (pre-determined to be sufficient) to reach equilibrium. For phenanthrene sorption on the fiber, phenanthrene solutions (20 mL) at the concentrations of 0.001, 0.025, 0.05, 0.075, 0.1, 0.5, 0.75, and 1 mg/L and 1 g fiber media (including blank controls) were used. The suspension was then centrifuged at 12,000 × g for 15 mins, after which naphthalene and phenanthrene concentrations in the supernatant were measured.

Based on five replicates, naphthalene displayed exponential sorption isotherms on the suspended fiber (Figure 28).

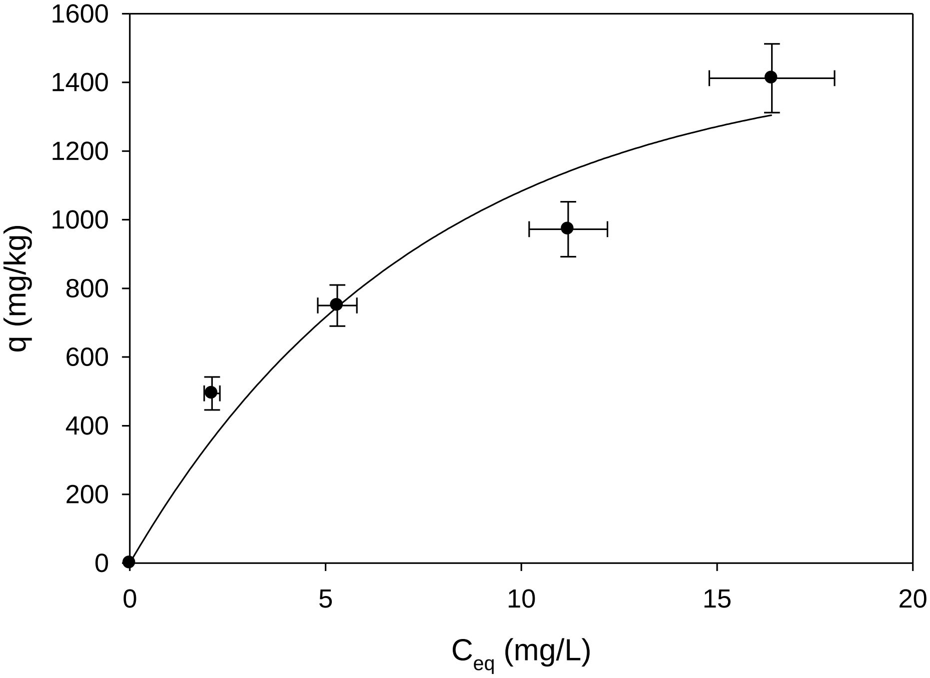


Figure 28. Batch Sorption Isotherm of Naphthalene on the Fiber

Phenanthrene displayed linear sorption isotherms on the fiber (Figure 29). Phenanthrene partitioning to the fiber was calculated based on the following equation:

$$q_s = \frac{(C_0 - C_{eq})V}{M_s} = K_s C_{eq}$$ **Equation (21)**

where q_s is the phenanthrene concentration on the fiber (mg/kg), C_0 is the initial phenanthrene aqueous concentration (mg/L); C_{eq} is the phenanthrene aqueous equilibrium concentration (mg/L); V is the aqueous volume (mL); M_s is the mass of the fiber (kg); and K_s is the phenanthrene partition coefficient between the aqueous phase and the fiber (L/kg). Phenanthrene had a partition coefficient of 860 L/kg on the fiber.

4.3.2 Naphthalene and Phenanthrene Biodegradation

94% of naphthalene and 78% of phenanthrene were degraded within 50 hours using the consortia cultured for this research (Figure 30). Naphthalene and phenanthrene biodegradation had a lag period of ∼10 hours.

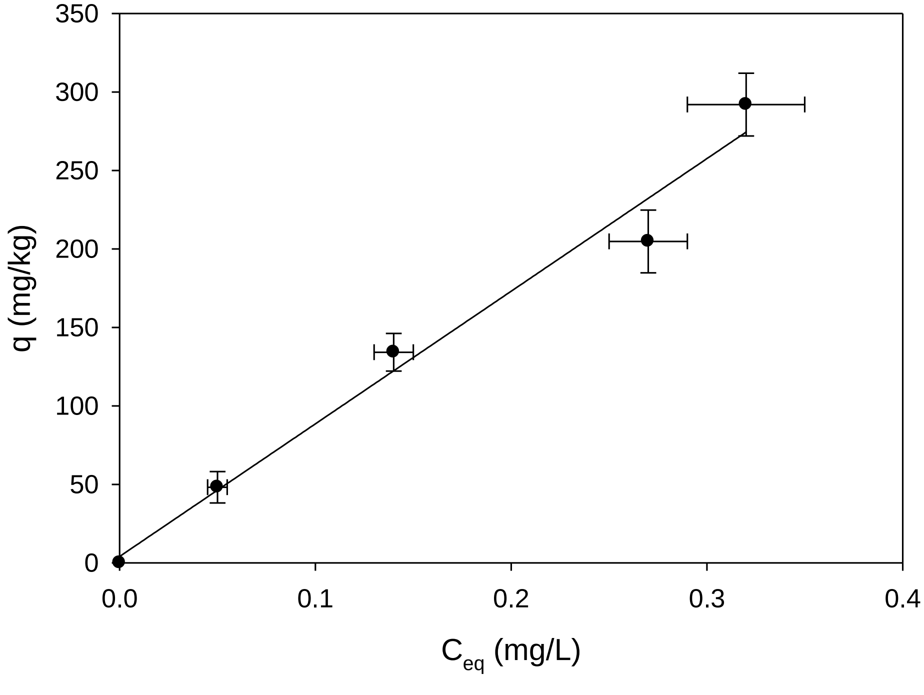


Figure 29. Batch Sorption Isotherm of Phenanthrene on the Fiber

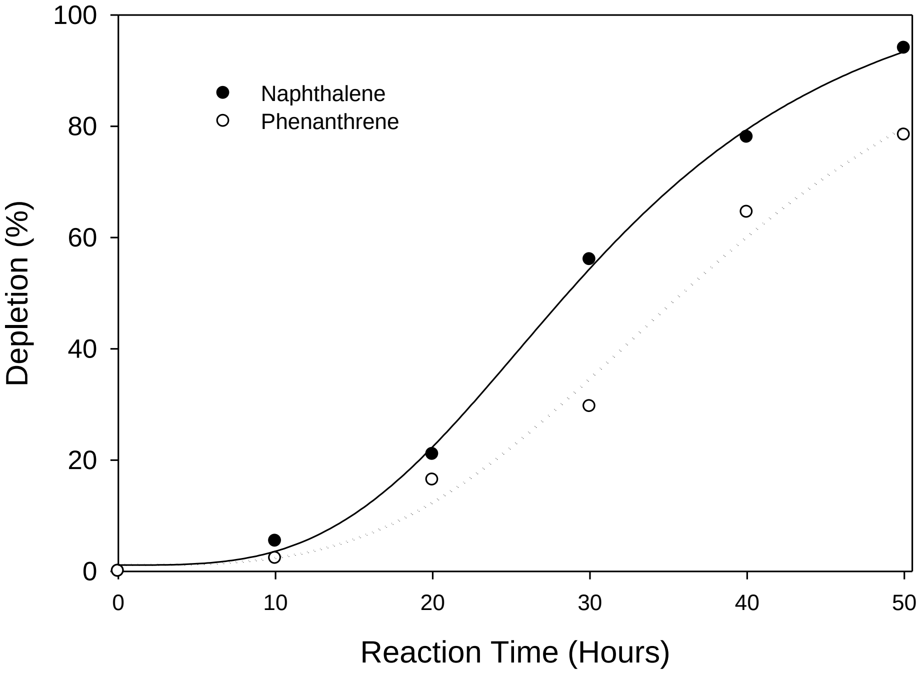


Figure 30. Naphthalene (a) and Phenanthrene Depletion Curves

During batch biodegradation experiments, if microbial growth is coupled with substrate depletion and Monod-type kinetics are assumed to describe microbial growth, substrate and biomass concentrations over time can be described by following equations (Monod, 1949):

$$\frac{dS}{dt} = -\frac{1}{Y}\frac{\mu_m SX}{K_s + S} \qquad \textbf{Equation (22)}$$

$$\frac{dX}{dt} = \frac{\mu_m SX}{K_s + S} - \frac{bX}{K_s + S} \qquad \textbf{Equation (23)}$$

where S is the organic substrate concentration, which is usually expressed in terms of COD (mg/L); μ_m is the maximum specific growth rate (hr^{-1}); X is the microbial concentration (g/L); t is the elapsed time (hr); Y is the growth yield coefficient (g biomass per g substrate); K_s is the half-saturation coefficient (g/L); and b is the microbial decay coefficient (hr^{-1}). By ignoring the decay rate coefficient, Y can be used to estimate the microbial production based on organic substrate depletion, such that:

$$Y = -\frac{\Delta X}{\Delta S}$$ **Equation (24)**

$$X = X_0 + Y(S_0 - S)$$ **Equation (25)**

By substituting equations (24) and (25) into equation (22), substrate depletion can be expressed as:

$$\frac{dS}{dt} = -\frac{1}{Y}\frac{\mu_m S[X_0 + Y(S_0 - S)]}{K_s + S}$$ **Equation (26)**

The simulated half-saturation coefficient K_s (mg/L), growth yield coefficient Y (g biomass per g substrate), and maximum specific growth rate μ_m (day^{-1}) are listed in Table 12. Naphthalene had lower K_s values than that of phenanthrene, indicating that the naphthalene culture had greater affinity to the components. The Y and μ_m values were similar for these two compounds.

Table 12. Naphthalene and Phenanthrene Degradation Parameters

	K_S (mg/L)	Y (g/g)	μ_{max} (d^{-1})
Naphthalene	876.4	0.0678	0.0164
Phenanthrene	1704.6	0.0437	0.0094

4.4 Iron Removal

Iron removal is very important for the landfill leachate treatment in Northwest Florida owing to the high iron content in the soil. During landfill operation, ferric iron (Fe^{+3}) is reduced to ferrous iron (Fe^{+2}) and released to the leachate. Ferrous iron can be removed by oxidation and precipitation. High pH was found to favor ferrous iron oxidation in batch experiments. However, this physicochemical oxidation process is not practical owing to the high operation costs. There are many known iron-oxidizing microorganisms available in the environment. These microbes can effectively compete with the abiotic process for iron oxidation. At the same time, microbes must compete with each other for the energy sources. Consequently, organisms that are able to utilize the iron faster in a particular environment make up the predominant part of a community.

Ferric hydroxide ($Fe(OH)_3$) is the direct result of ferrous iron oxidation and precipitation. With time, ferric hydroxide is mineralized. The principal forms of mineralized ferric iron are: amorphous hydrous ferric oxide ($Fe_2O_3 \cdot XH_2O$), maghemite (gamma-Fe_2O_3), lepidocrocite (gamma-FeOOH), hematite (alpha-Fe_2O_3), and goethite (alpha-FeOOH). The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing oxidation/reduction potential conditions has a solubility of 0.6 µg/L, which is three orders of magnitude greater than that of goethite. However, a high concentration of iron in groundwater is not rare.

Iron readily undergoes reduction or oxidation, depending upon surrounding conditions. As a consequence, there are many microbiological metabolic pathways that utilize redox couples between ferrous and ferric iron. Organic material can be biodegraded with ferric iron as the terminal electron acceptor, resulting in the production of reduced soluble ferrous iron. As the crystallinity of the ferric iron mineral increases (as discussed above) the microbiological availability decreases. Or contrarily, iron fixing bacteria can oxidize ferrous iron to ferric iron, even under oxygen poor conditions. This can be achieved by many methods including the extraction of carbon dioxide from ferrous bicarbonate or the utilization of iron bearing organic acid complexes as a carbon source, resulting in precipitated ferric hydroxide. These reactions are typically responsible for iron fouling of well screens, piping systems and air strippers that are used to remediate iron rich groundwater.

In this research, iron removal after ozonation and a series of suspended fiber biofiltration is illustrated in Figure 31. For an input iron concentration around 100 mg/L, an effluent iron concentration of 1 mg/L can be achieved after the third stage biofiltration. We further tested different input iron concentrations using the system (Figure 32). It was discovered that for almost all the input iron conditions, the treatment can meet the iron discharge requirements.

4.5 Phosphorous Removal

For phosphorous removal, iron oxide coated on the fiber surfaces played the key role, on which phosphorus was adsorbed (Figure 33). For phosphorus to adsorb to iron oxide surfaces, phosphorus replaced singly coordinated OH^- groups and then reorganized into a very stable binuclear bridge between the cations. This sorption process was coupled with the release of OH^- ions, thus this process was favored by low pH values (Luk, 1999). This was because phosphorous sorption process released OH^-, increasing the solution pH, which prevented the Fe^{3+} hydrolysis process that also preferred low pH.

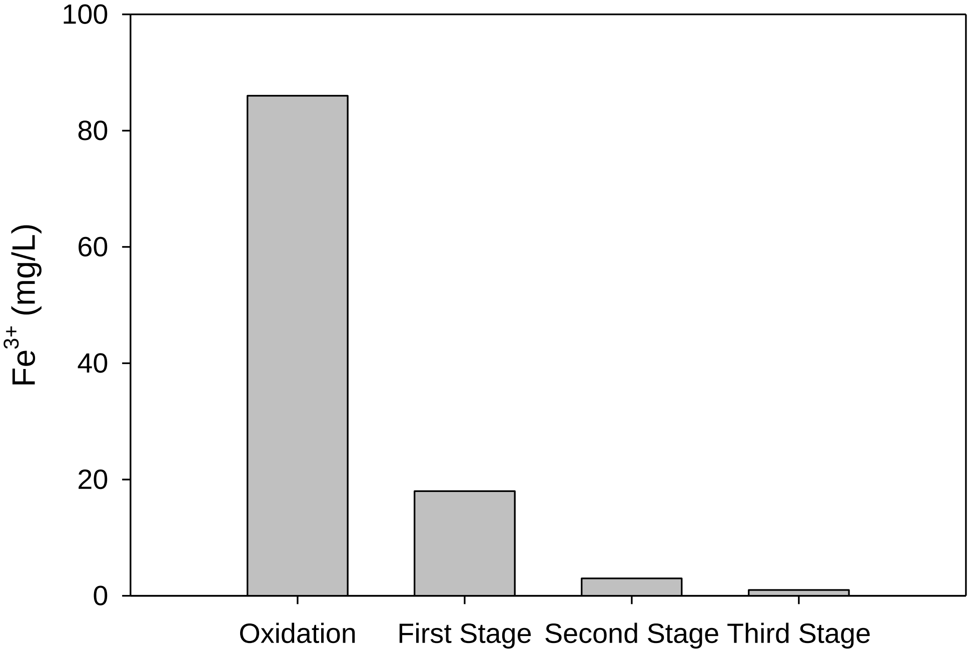


Figure 31. Iron Removal in the Treatment System with Ozone as the Advanced Oxidation Means

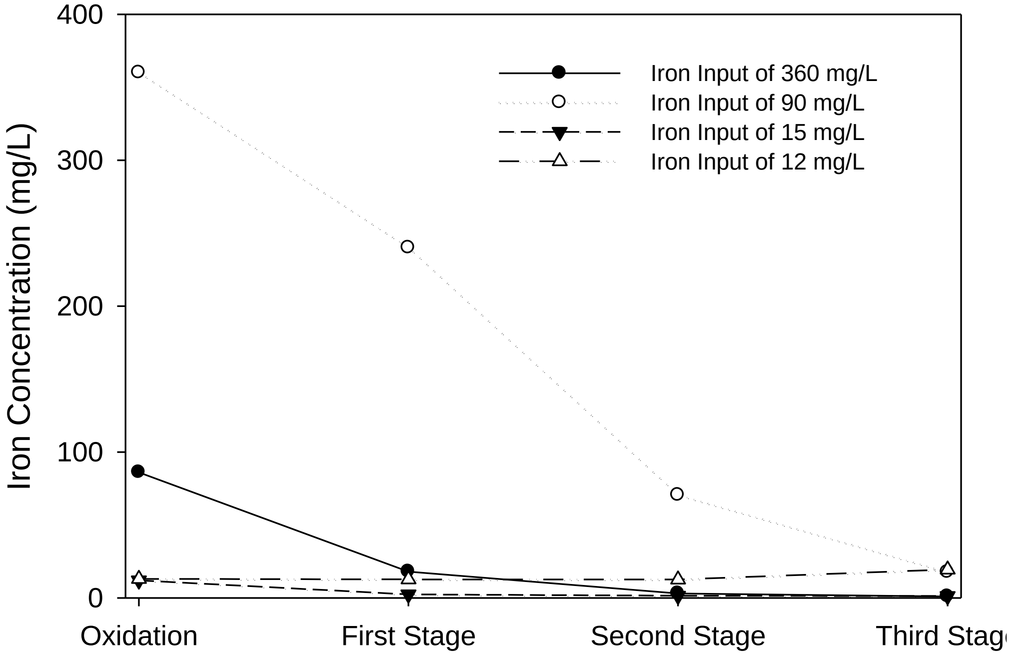


Figure 32. Iron Removal for different Input Iron Concentrations

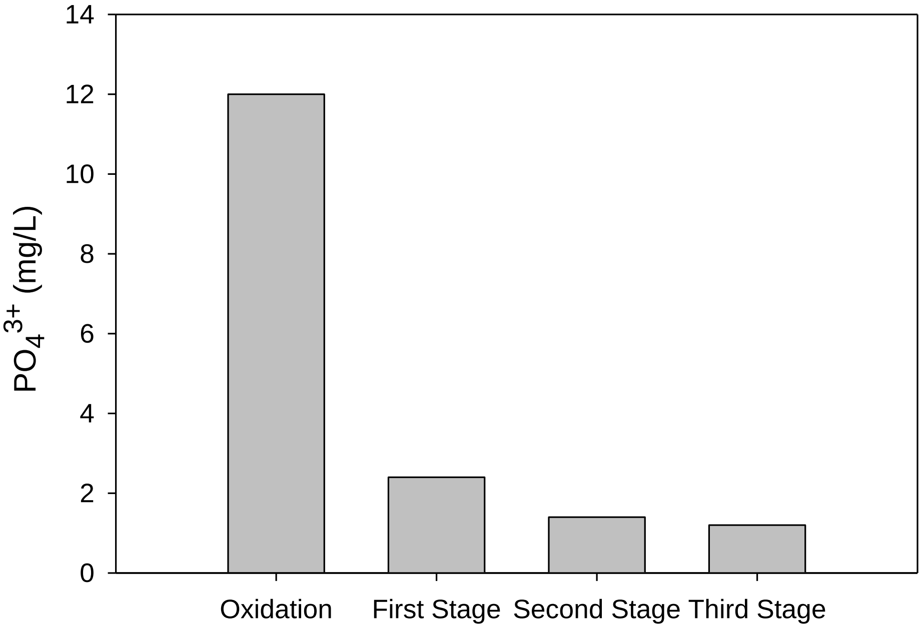


Figure 33. Phosphorous Removal with Ozone as the Advanced Oxidation Means

5. Discussion

5.1 Xenobiotic and Organic Removal by Advanced Oxidation

Over the last decades, more and more attention is being turned to xenobiotics, which persist in the environment and can bioaccumulate throughout the food chain, and are toxic to biotic communities, thus posing a risk to human health and the environment (Baun et al., 2004). The common organic xenobiotics includes polycyclic aromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethylbenzene and xylene), petroleum hydrocarbons, polychlorinated biphenyls (PCBs), chlorinated solvents, explosives, dyes, pharmaceuticals and personal care products, phenolic compounds and pesticides. Because of the many competing interactions, the fate of xenobiotics is not easy to predict and, in many cases, their ecotoxicological effects are difficult to assess. For the destruction of organic xenobiotics, advanced oxidative processes, activated carbon adsorption, membrane filtration and membrane bioreactors have been practiced (Baun et al., 2004). Most of these processes are not satisfactory either because of the low efficiency or the high costs.

Advanced oxidation combined with conventional biological processes have been studied for the destruction of recalcitrant xenobiotic organic compounds as well as natural organic compounds. These processes have several advantages over separated chemical oxidation process or biological process, including the high efficiency and low costs. The advanced oxidation initiates hydroxyl radical reactions, which can destruct xenobiotic compounds. The radical reactions are nonselective, and can lead organic compounds to the ultimate mineralization. Among advanced oxidation options, ozone is one of the chemical processes that have recently received considerable attention in landfill leachate treatment because of its oxidation potential and ability to reduce the amount of non-biodegradable organics in the landfill leachate.

The characteristics of landfill leachate are affected by many factors, such as age, precipitation, weather variation, and waste types and compositions. Owing to the complicated composition and processes, besides amino-acids, carbohydrates and carboxylic acids which are generally present in landfill leachate, recalcitrant xenobiotic organic compounds are commonly found in the landfill leachate. To address landfill leachate's heterogeneous and undefined character, advanced oxidation processes (AOPs) have demonstrated the effectiveness in eliminating organics and xenobiotics. Traditionally, chemical oxidation has been widely used for the treatment of effluents containing refractory compounds such as landfill leachate. Currently, AOPs are drawing more and more attention, especially the AOP processes that use a combination of strong oxidants, e.g. ozone, hydrogen peroxide and UV radiation, etc. These combined AOP processes have shown great enhancement in organic removal and xenobiotic destruction. For instance, organic removal efficiency as high as 90% has been reported for the combined ozone and hydrogen peroxide processes. Practically, AOPs have been adapted to old and well-stabilized landfills to oxidize organic substances to their highest stable oxidation states (complete mineralization) and/or improve the biodegradability of recalcitrant organic pollutants up to a value compatible with subsequent economical biological treatment. In the term of biodegradability improvement, BOD/COD ratios have been found to increase after oxidation. The high production of OH· radicals due to the combination of oxidant compounds are the mechanisms for advanced oxidation applications. On the other hand, the UV radiation may be an effective method for the decomposition of ammonia-nitrogen in the landfill leachate.

Common drawbacks of AOPs are the high demand of energy costs as compared to that of the biological treatment processes. In addition, complete degradation (mineralization) of the pollutants requires high oxidant doses. Furthermore, some intermediate oxidation products can actually raise the toxicity of the leachate. To further evaluate the advanced oxidation processes, the UV spectra of the treated leachate was further analyzed. As presented before, UV–VIS spectra of the treated samples were obtained with the spectrophotometer within the wavelength range of 200 to 800 nm. The E2/E3 and E4/E6 ratios (parameters that are inversely related to molecular weight and aromaticity, and proportional to the O, C, and carboxyl group content and total acidity) were determined by measuring the absorbance at 254 and 365 nm for E2/E3 ratio and at 465 and 665 nm for E4/E6 ratio. In general, the UV–VIS spectra exhibited an exponential decline with increasing wavelength. The absorbance at $\lambda < 250$ nm might result from the absorption of radiation by the double bonds, especially the aromatic $C=C$ and ketonic $C=O$ functional groups of aromatic chromophores and/or other organic compounds.

NMR analysis was further performed using a Varian Unity 600-MHz instrument at 298 K. About 50 mg of the samples was dissolved in 1 mL of deuterium oxide (D_2O, Sigma, 99.9 % atom D) (Figure 34). 1H-NMR spectra were recorded at 600 MHz under the following conditions: 1.7 s acquisition time, 1.0 s relaxation delay and pulse width of 45° (Figure 35).

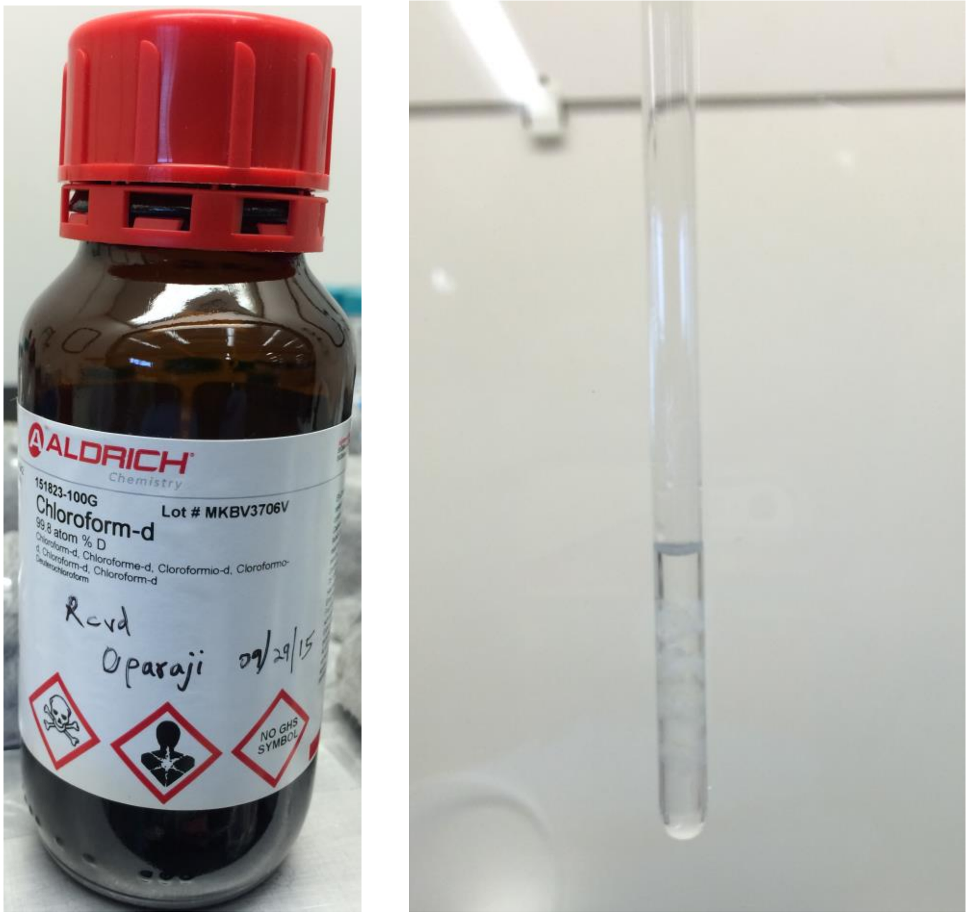


Figure 34. Sample Preparation for NMR

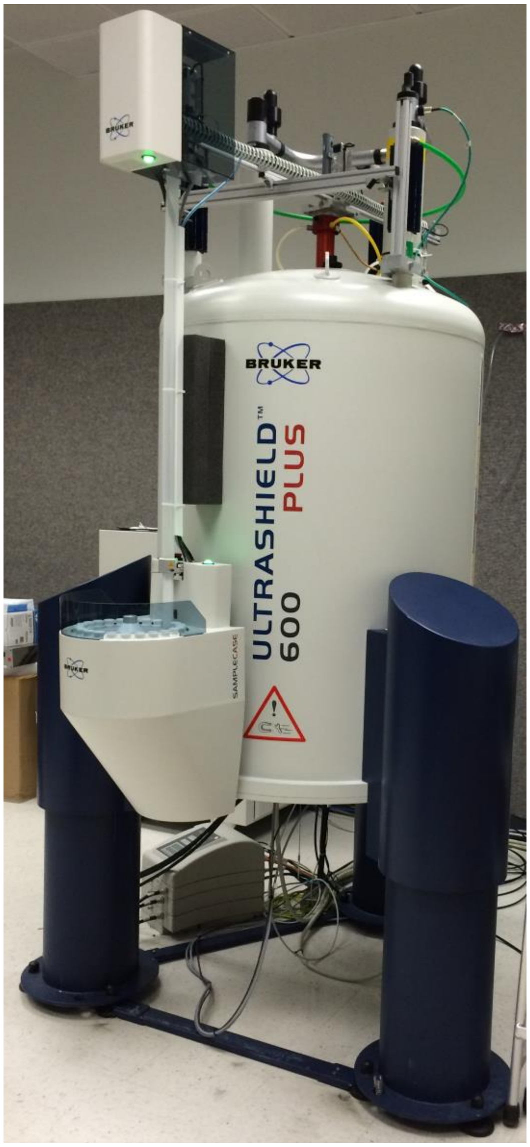


Figure 35. NMR Analysis

1H-NMR spectra included the aliphatic protons region, a broad resonance assigned to protons on carbons attached to O or N atoms (carbohydrate) and the aromatic, phenol, and carboxylic proton region. Different advanced oxidation resulted different chemical shift values, which differed in intensity and linewidth. In general, advanced oxidation led to decreased aromatic, phenol and carboxylic proton and increased carbohydrate contents (Figure 36).

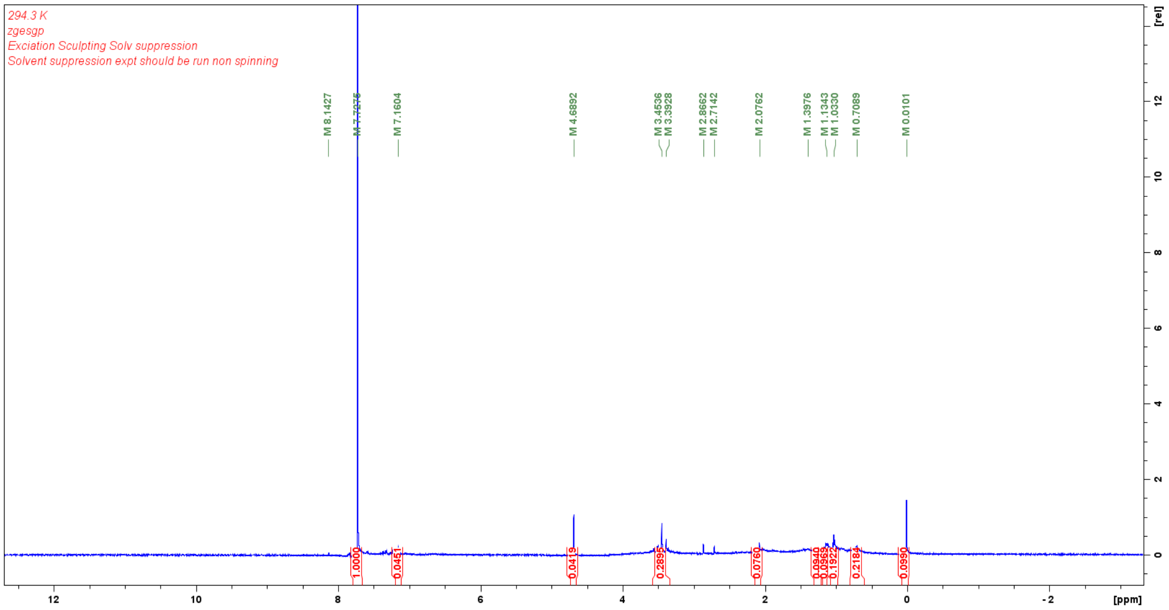


Figure 36. NMR Results of the Leachate

The NMR analysis of the fiber that was used in the biofilters was also conducted before and after the leachate treatment (Figure 37 and Figure 38). The aromatic carbohydrate proton region and the aliphatic region were minimal for the fiber before the leachate treatment. However, after the leachate treatment, the spectra showed a highly resolved signal arising from aliphatic acids. A relatively high amount of aromatic proton was also observed, indicating that aromatic structures accumulated in the fiber during the leachate treatment. In the regions of carbohydrates and proteins, there was obvious increase in the resonance intensity, indicating sugar-like component accumulation. The resonance signals that attributed to CHOH and CH_2OH functional groups (i.e., polysaccharides moieties) as well as aminomethine groups [−CH(NH−)] and methylene groups that were bonded to amide functional groups [$-CH_2(NHCO-)$] were also observed. These observations demonstrated that advanced oxidation contributed to the destruction of xenobiotics and the released low-molecular weight compounds had a chance to accumulate in the fiber media and be decomposed by the microorganisms in the system.

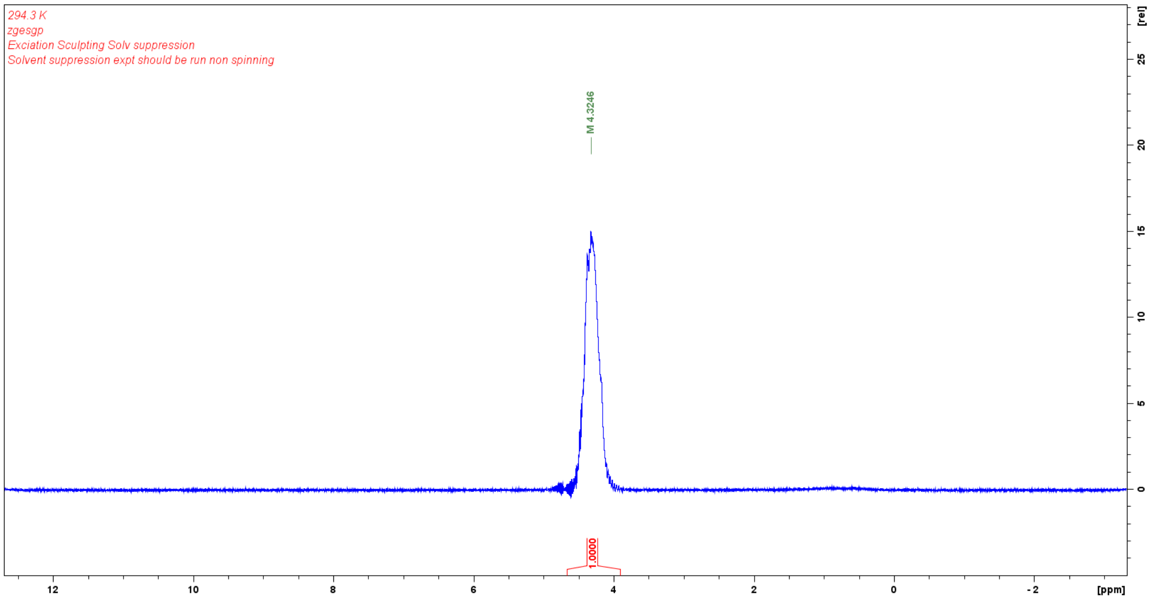


Figure 37. NMR Results of the Fiber before Leachate Treatment

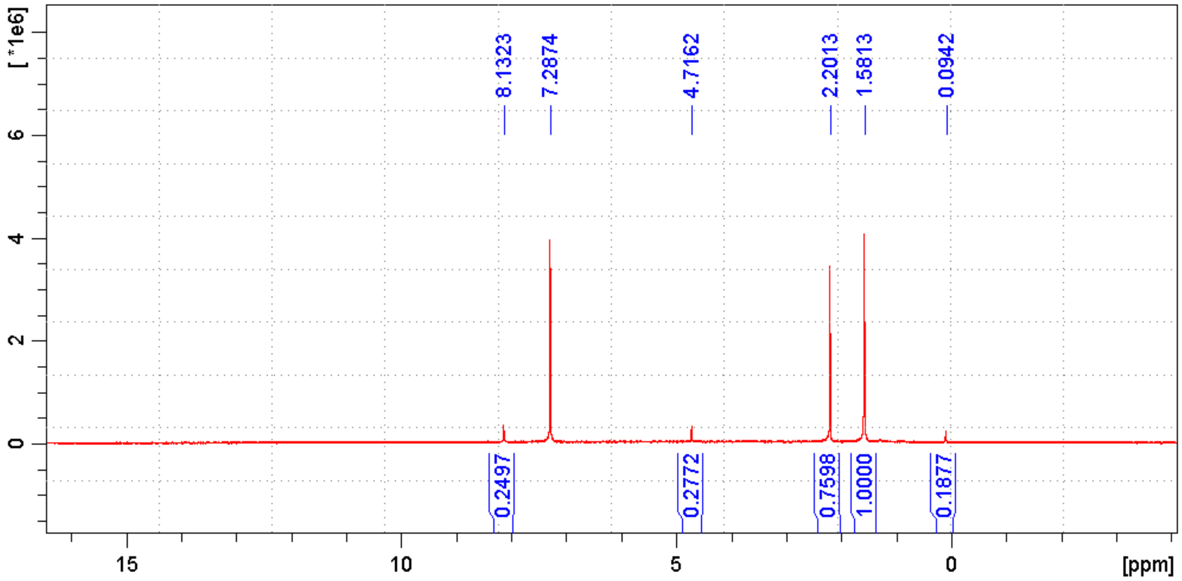


Figure 38. NMR Results of the Fiber after Leachate Treatment

In the aliphatic region, the peaks were believed to be attributed to aliphatic carbons (methyl or methylene groups), which were attached to functional groups such as carboxyl group or aromatic ring. The intensity of the signals for the aliphatic, aromatic, and carboxyl groups tended to vary, depending on the origin and type of humic matters. These results are consistent with those obtained previously from the UV–VIS spectra.

5.2 Iron and Phosphorous Removal

Iron is one of the most abundant metals of the Earth's crust. It occurs naturally in water in soluble form as ferrous iron (bivalent iron in dissolved form of Fe^{2+} or $Fe(OH)^{+}$) or complex form as ferric iron (trivalent iron of Fe^{3+} or precipitated as $Fe(OH)_3$). Nearby landfills in Northwest Florida, owing to the high iron contents in the soil, elevated iron concentrations are commonly observed. In general, iron does not present a danger to human health or the environment, but it brings unpleasantness of an aesthetic and organoleptic nature. Indeed, iron gives a rust color to the water, which can stain linen, sanitary facilities or even food industry products. Iron also gives a metallic taste to water, making it unpleasant for consumption. It can also be at the origin of corrosion in drain sewers, due to the development of the microorganisms of *ferrobacteries*. However, treated leachate must meet the drinking water standard of 0.3 mg/L total iron before being discharged to the receiving water bodies.

Ferrous iron is soluble as a cation, while ferric iron is not. For the natural removal of dissolved iron, the redox potential of the water promotes the oxidation of ferrous iron to ferric iron, which can precipitate in the form of ferric iron hydroxide, $Fe(OH)_3$:

$$Fe^{2+} \xrightarrow{\text{Oxidation}} Fe^{3+} \xrightarrow{\text{Precipitation}} Fe(OH)_3 \qquad \textbf{Equation (27)}$$

Once ferrous iron is oxidized, hydrolysis proceeds:

$$[Fe_m(OH)_x]_n^{(3m-x)n+} + yOH^- \rightarrow [Fe_m(OH)_{x+(y/n)}]_n^{[3m-x-(y/n)]n+} \qquad \textbf{Equation (28)}$$

The oxidation kinetics of ferrous iron is well known to be pH dependent, with the slow oxidation kinetics of ferrous iron at low pH. This is important for microbial-mediated iron oxidation and fixation. Many known iron-oxidizing microorganisms in the environment can also oxidize ferrous iron at neutral pH. Since the abiotic oxidation of iron is very fast, these microbes must compete effectively with the abiotic process. Additionally, microbes must compete with each other for the available ferrous iron. The organisms that are able to utilize the iron faster in the particular environment make up the predominant part of the iron oxidizing community. Ferric hydroxide ($Fe(OH)_3$) is the direct result of ferrous iron oxidation. The principal forms include amorphous hydrous ferric oxide ($Fe_2O_3 \cdot XH_2O$), maghemite (gamma-Fe_2O_3), lepidocrocite (gamma-FeOOH), hematite (alpha-Fe_2O_3), and goethite (alpha-FeOOH). The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing redox conditions has a solubility of 0.6 µg/L, which is three orders of magnitude greater than that of goethite. With the increasing pH, the concentration of metal ions such as iron is generally low due to the decreasing solubility of many different metal ions. However, lead is an exception since it forms a very stable complex with humic acids. Besides the effect of shifting pH on metal ions, there is a possibility of sulphate reduction to sulphide, which increases the precipitation of metals ions.

Adsorption of phosphorous onto iron hydroxides is attributed to the iron hydroxides coated on the polypropylene fiber. It is believed that phosphorous adsorption on iron hydroxides is generally dominated by ligand exchange in which two singly coordinated hydroxyl groups or water molecules are replaced by a single phosphate anion (Du et al., 2009). Since H_2O is a more mobile ligand than OH^-, adsorption is therefore favored at lower pH. It is believed that four key characteristics impact phosphorus adsorption on the iron hydroxide surfaces, i.e., the easiness of hydroxyl release, the specificity toward binding sites, hysteresis, and the surface charges (Du et al., 2009; Weng et al., 2012). Iron hydroxides formed under advanced oxidation conditions contribute positively for phosphorus removal in the treatment system.

5.3 Cost Analysis

The major costs of the combined advanced oxidation and biofiltration are the chemical costs. Since advanced oxidation is combined with traditional biofiltration in this research, only low dosage of oxidants is required during the treatment. Subsequently, chemical costs can be reduced as compared to the complete advanced oxidation treatment processes. In addition, compared to traditional biological system, this treatment produces less sludge, leading to reduced sludge handling costs. The combined system can also be configured depending on the treatment requirements by adding or deleting series of suspended fiber biofilters. The infrastructure costs can therefore be adjusted. The cost analysis is summarized in Table 13. Although high chemical costs are associated with the advanced oxidation processes for the treatment of landfill leachate, this treatment technology has obvious advantages. For instance, currently there is no other effective biological options for xenobiotic destruction. Advanced oxidation that is adopted in this treatment system is one of the available options.

Table 13. Treatment Cost Comparison with Traditional Biological Leachate Treatment

	Advanced Oxidation Combined with Biofiltration	Biological Treatment	Treatment Cost Saving
Sludge Production	Low	High	Around 50% for Sludge Treatment
Chemical Costs	High	Low	Increased Chemical Costs
Space Requirements	Low	High	Reduced Infrastructure Costs

The chemical costs associated with the combined advanced oxidation and biofiltration are analyzed based on the chemical unit cost, which is illustrated in Table 14.

Table 14. Unit Chemical Costs per 1,000 Gallon Leachate (Not Including Capital Costs)

	Value ($)
Ozone	0.15
Hydrogen Peroxide	0.40
UV	0.56

The chemical costs for the landfill leachate treatment range from $0.15 to $0.56 per 1,000 gallon of leachate depending on the treatment requirements. The more contaminants that need to be removed, the higher the associated costs will be. The major contaminants that will increase the treatment costs are xenobiotics. To reduce the chemical costs, combined oxidation may be the option. From this research, the combination of ozone and hydrogen peroxide can have a good xenobiotic destruction at reduced chemical costs as compared to ozone or hydrogen peroxide alone.

6. Conclusions

From this research, it is demonstrated that landfill leachate can be treated by combined advanced oxidation and suspended fiber biofiltration. Advanced oxidation can destruct xenobiotics in the landfill leachate and the following biofiltration can decompose the organic compounds. Most importantly, with advanced oxidation, ferrous iron in the landfill leachate is oxidized to iron oxide and coat the suspended fiber, which can remove phosphorous from the landfill leachate through adsorption. Through advanced oxidation, 76% of the organics can be removed. In the following up series of biofilters, organics are further removed with the effluent from the third stage biofilter meeting the discharge requirements. For iron removal, advanced oxidation only contributes to iron transformation. However, the following three stage biofiltration can remove iron by 99% and also meet the discharge requirements. It seems that the treatment system performs better for landfill leachate with high iron contents. Finally, phosphorous can be effectively removed in this system through adsorption to the iron oxide that coat the suspended fiber. With an input of 12 mg/L, an effluent of 1 mg/L can be achieved, which complies with the discharge requirements.

The chemical costs are the major disadvantages of this treatment process. To save operational costs, combined ozone and hydrogen peroxide is recommended. Combined ozone and hydrogen peroxide can provide an effective treatment result with reasonable treatment costs. Most importantly, owing to the low sludge production, the costs associated with sludge handling can be dramatically reduced.

7. Recommendation

From this research, it was discovered that the factors that influence the leachate treatment followed the following order (from most influence to least influence): leachate quality > advanced oxidation selection > number of series of biofiltration. The greatest influential factors were leachate quality, i.e., xenobiotic composition and concentration. Based on the experimental observations, the following recommendations are made:

- Advanced Oxidation:
  - Ozone/COD: 0.8
  - Hydrogen Peroxide/COD: 0.75
- Iron Removal:
  - Three Stages of Suspended Fiber Biofiltration
  - Hydraulic Loading < 1.0 $m^3/m^2/hr$
- Phosphorous Removal:
  - Three Stages of Suspended Fiber Biofiltration
  - Hydraulic Loading < 1.0 $m^3/m^2/hr$

8. Future Work

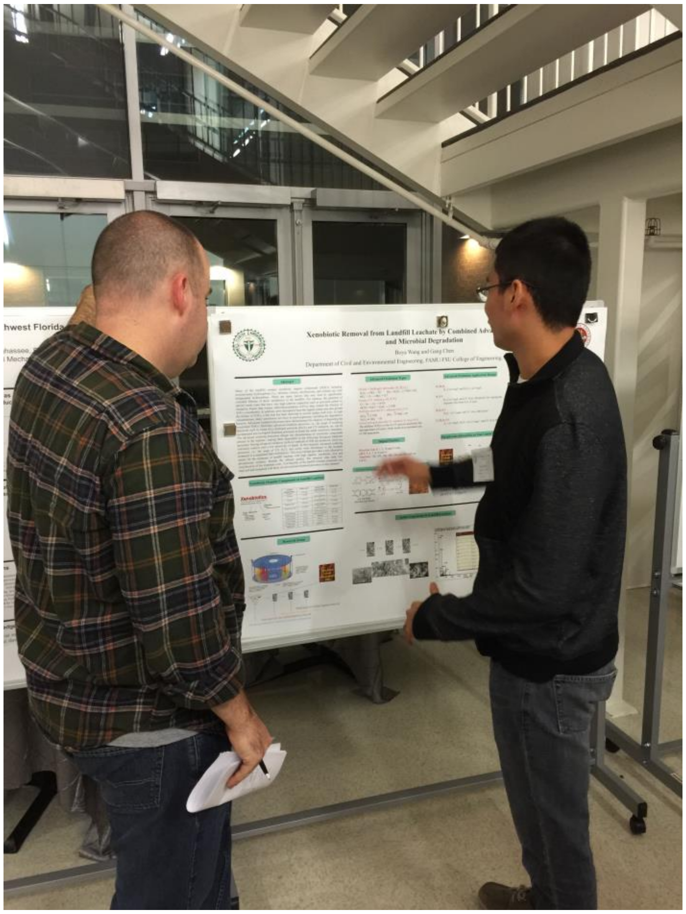
To further improve the performance of the biofiltration, limestone biofiltration will be tested. Limestone biofiltration can efficiently remove organics from landfill leachate without further pH adjustment. In addition, the low construction and operation costs and ease of operation and maintenance also make limestone biofiltration a promising treatment method for degrading organic contaminants. Depending on the specific requirements, limestone biofilteration can be operated either aerobically or anaerobically. Owing to the high calcite content, limestone promotes the microbial mediated organic degradation and metal precipitation by raising the water alkalinity and pH.

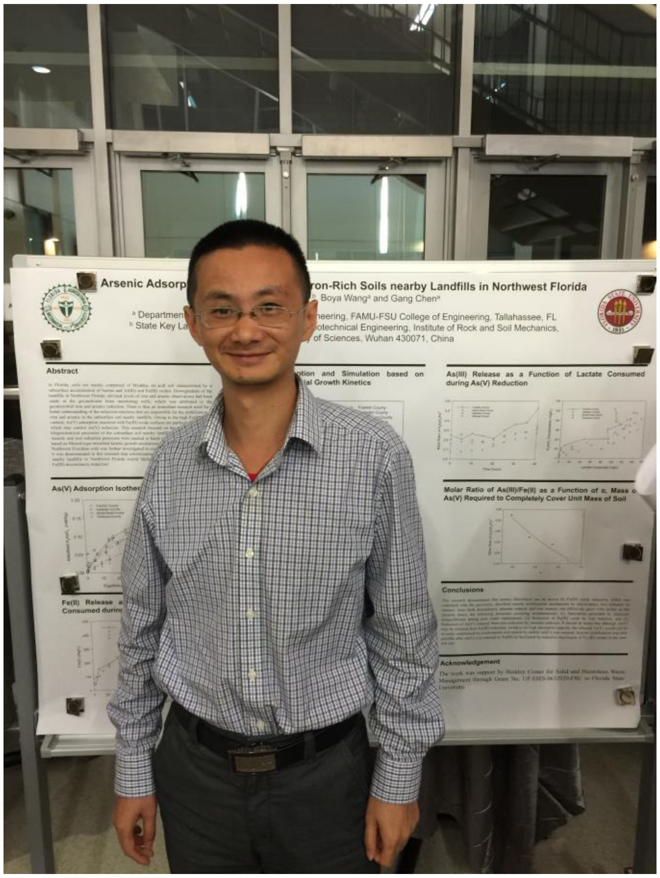
Future research will also be focused on the identification of the forms of mineralized ferric iron after ferrous iron oxidation, namely, amorphous hydrous ferric oxide ($Fe_2O_3 \cdot XH_2O$), maghemite (gamma-Fe_2O_3), lepidocrocite (gamma-FeOOH), hematite (alpha-Fe2O3), and goethite (alpha-FeOOH). We understand that some of these iron species may work as a catalyst for the continuation of ferrous iron oxidation. We will use Visual MINTEQ 2.51 to quantify the iron speciation in the water. The MINTEQ 2.51 computer code is an equilibrium chemical reaction model. In addition to support evaluations of speciation, MINTEQ 2.51 computer code can be used to calculate aqueous complexation to determine the ionic state and composition of the dominant species for the system. We will also use MINTEQ 2.51 to predict technically defensible maximum concentration limits for iron as a function of pH and index cations and realistic bounding values for the maximum concentration attainable in the system. In addition, we will use this code to analyze initial and final geochemical conditions to determine if the measurements have been affected by processes such as metal precipitation which might have compromised the derived values.

There has also been a major impetus to investigate the ability of microorganisms to biodegrade hydrocarbons in the absence of oxygen. This is motivated by the fact that landfill leachate usually has low oxygen content. Studies of microbial degradation of monoaromatic hydrocarbons have resulted in the identification and isolation of a number of different anaerobic bacterial strains capable of degrading one or more monoaromatic hydrocarbons. Of these compounds, the anaerobic biodegradation of toluene is probably the most comprehensively understood. Toluene is biodegradable with nitrate, Mn(IV), Fe(III), humic substances, sulfate, and CO_2 as terminal electron acceptors. More recently, it has been demonstrated that toluene can also be assimilated anaerobically as a carbon source by anoxygenic phototrophs.

9. Student Training

One graduate student, Boya Wang was trained in this project. Boya Wang is currently pursuing his Ph.D. in our laboratory. He joined our group in August 2014 as a master student. He finished his mater study in 2016 and continued with his Ph.D. study accordingly. He was very active and productive in his research. So far, he has published three technical journal papers in leading professional journals based on the work sponsored by the Hinkley Center for Solid and Hazardous Waste Management. In addition, he has presented multiple times at national conferences. A postdoctoral research associate, Houzhen Wei is also trained in this project. He joined our research group in August 2015 and was involved in this research ever since. The following images were taken when Boyang Wang and Houzhen Wei presented their work at 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA in November 2015.




Arsenic Adsorp
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Boya Wang[a] and Gang Chen[a]
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[b] State Key La
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Abstract
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10.1 Peer-Reviewed Journal Paper Publication:

1. Wang, B., Grasel, P., Owete, O., Hallas, J., Ahmad, H. and Chen, G. "Advanced Oxidation and Suspended Fiber Biofiltration for the Treatment of Landfill Leachate", International Journal of Water and Wastewater Treatment, 2016, under review.
2. Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. "Landfill Leachate Treatment by Aerated Recirculation and Pressurized Suspended Fiber Biofiltration", Frontier in Environmental Engineering, 2015, 4 (1) 7-18.

10.2 Conference Presentation:

1. Li, R., Wang, B. and Chen, G. "Arsenic and Phosphorous Removal from Landfill Leachate by Biofiltration". 2016 Florida Branch Meeting, American Society for Microbiology Florida Branch, Miami, FL. Oct. 14-16, 2016.
2. Wang, B. and Chen, G. "Xenobiotic Removal from Landfill Leachate by Combined Advanced Oxidation and Microbial Degradation". 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA, Nov. 13-15, 2015.

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