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CHEMICAL AND BIOLOGICAL TREATMENT OF MATURE LANDFILL
LEACHATE

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Civil and Environmental Engineering
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at the University of Central Florida
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2006

Major Professor: Debra Reinhart

ABSTRACT

This dissertation is about treatment of the nonbiodegradable organic content of landfill leachate by chemical oxidation combined with biological treatment. It is divided into three parts. In the first part, ferrate was compared to Fenton's reagent for the purpose of removing non-biodegradable organic compounds from mature leachate. Oxidation conditions (time, pH, and dose) were optimized to yield maximum organic removal using two leachate samples from 20 and 12-year old solid waste cells. Results from this research demonstrated that ferrate and Fenton's reagent had similar optimum pH ranges (3-5), but different organic removal capacities, ranging from 54 to 79 % of initial leachate organic contents. An advantage of ferrate was that it was relatively effective over a wide pH range (Fenton's reagent lost its reactivity outside optimum pH range). Advantages associated with Fenton's reagent include a higher organic removal capacity, production of more oxidized organic compounds (measured as chemical oxygen demand/dissolved organic carbon), and production of more biodegradable byproducts (measured as 5-day biochemical oxygen demand/chemical oxygen demand). Finally, both treatments were found to oxidize larger molecules (>1000 dalton) and produce smaller molecules, as indicated by an increase in smaller molecule contribution to organic carbon.

In part two, effects of Fenton's reagent treatment on biodegradability of three landfill leachates collected from a Florida landfill were evaluated using biochemical oxygen demand (BOD), biochemical methane potential (BMP), and tertamethylammonium hydroxide (TMAH) thermochemolysis gas chromatography/mass

spectrometry (GC/MS). The hypothesis was that Fenton's reagent will remove refractory compounds that inhibit biodegradation and will produce smaller, more biodegradable organic molecules which will result in an increase in BOD and BMP values. Both BOD and BMP results demonstrated that Fenton's reagent treatment did not convert mature leachate to biodegradable leachate, as indicated by a low BOD₅ expressed as C /dissolved organic carbon (DOC) ratio of almost 0.15 in treated samples and a low net methane production / theoretical methane potential (less than 0.15). Ultimate BOD only slightly increased. However the first-order BOD reaction rate increased by more than five fold, suggesting that Fenton's reagent removed refractory and inhibitory compounds. BMP results demonstrated that the ratio of CO₂/CH₄ produced during anaerobic biodegradation did not increase in treated leachate (compared to untreated), indicating that small biodegradable organic acids produced by oxidation were removed by coagulation promoted by Fenton's reagent. Finally, the TMAH thermochemolysis results showed that several of the refractory and inhibitory compounds were detected fewer times in treated samples and that carboxylic acids did not appear in treated samples.

In the third part of this dissertation the application of flushing/Fenton's reagent oxidation to produce sustainable solid waste cells was evaluated. A treatment similar to pump and treat process utilizing Fenton's reagent on-site treated leachate combined with in-situ aeration was proposed. Treated leachate would be recycled to the landfill cell flushes releasable nonbiodegradable carbon from the cell and oxidizes it externally. This technique was demonstrated to have treatment cost and time benefits over other alternatives for producing completely stable solid waste cells such as anaerobic flushing and biological and/or mechanical pretreatment of solid waste (used in the EU).

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CHAPTER 1

INTRODUCTION

Significance

Leachate from mature landfill cells usually contains refractory organic compounds that cannot be removed by biological treatment methods (Ehrig, 1984). Hazardous household wastes such as paints, solvents, motor oils, cleaning compounds, degreasing compounds, pesticides and illegally disposed wastes contribute to the nonbiodegradable organic compounds in landfills (Reinhart, 1989). These nonbiodegradable substances are referred to as xenobiotic (foreign to the biosphere) organic compounds and are important to study because their natural attenuation in the environment is slow, allowing some of these compounds to persist in the environment for decades. Another source of nonbiodegradable organic compounds in landfills is humic substances. Humic substances are divided into three parts. Humic acid, the base soluble acid insoluble part, fulvic acid the acid and base soluble part, and humin, the insoluble part (MacCarthy, 2001). Humic substances are produced inside landfills as a result of biodegradation and remain in the leachate because microorganisms are unable to further degrade them. There is no universal formula for humic substance, however elemental analysis of humic substances extracted from landfill leachate showed mass ratios of C = 56%, N=9%, O=27%, and H=8% (Kang et al., 2002). Humic substances are considered to be the principal precursors of disinfection byproducts such as trihalomethanes (Reckhow et al., 1990) and can increase the mobility of hazardous compounds such as heavy metals (Christensen et al., 1996).

Objectives

The main objective of this research is to evaluate the removal of the refractory organic compounds in landfill leachates by means of combined chemical treatment and in situ biological treatment in landfills. The biodegradability of the refractory organics in leachate will be increased by means of chemical oxidation. It is hypothesized that adding an oxidant to mature leachate containing a high concentration of non-biodegradable organics will increase the biodegradability of the leachate such that subsequent biological in situ treatment will remove these organics.

This proposed approach has two main advantages, it will destroy the refractory organics, not merely transform them from one phase to another. Additionally, it is an in situ treatment technique; therefore there is no need to transport the leachate to an external treatment plant, which reduces cost and potential environmental impacts.

Dissertation Organization

There are six chapters in this dissertation. The second chapter is a literature review regarding landfill leachate generation and composition with emphasis on dissolved organic matter. Chapter 2 also contains discussion about leachate treatment with emphasis on chemical treatment methods.

In Chapter 3 (submitted to the *Journal of Environmental Engineering*), Fenton's reagent (H_2O_2 plus Fe^{+2}), from the advanced oxidation family, and ferrate ($\text{Fe}^{+6}\text{O}_4^{2-}$) an emerging oxidant, were tested on mature leachate samples from two Florida landfills that had 12 and 20-year old solid waste cells to determine best oxidation conditions (time, pH, and dose). Experiments focused on measuring organic removal efficiencies in addition to investigating the nature of the remaining dissolved organic matter after oxidation using

gross organic parameters such as chemical oxygen demand (COD), dissolved organic carbon (DOC), 5-day biochemical oxygen demand (BOD₅), and organic compound molecular weight (MW).

In Chapter 4 (to be submitted to *Environmental Science and Technology*), Fenton reagent was selected for further investigation. Experiments in this chapter focused on the biodegradability of oxidation byproducts. Biodegradability indicators were evaluated after treatment by Fenton's reagent, including ultimate BOD measurements, which evaluate aerobic degradation, as well as biochemical methane potential (BMP) measurements for anaerobic biodegradation. An attempt was also made to identify specific oxidation byproducts in leachate by performing tertamethylammonium hydroxide (TMAH) thermochemolysis gas chromatography/mass spectrometry (GC/MS) on treated and untreated leachate samples.

In Chapter 5 (to be submitted to *Waste Management*), the idea of Fenton's reagent on-site treated leachate flushing combined with in-situ aeration was evaluated. Microcosms were performed to determine aerobic degradation rates of solid waste and carbon mass balances calculations were used to evaluate treatment time and L/S requirements. These mass balance calculations have been conducted for three scenarios; flushing with clean water, flushing with on-site treated leachate, and flushing with on-site treated leachate combined with in-situ aeration.

Chapter 6 contains a discussion of the main conclusion and recommendations for this research. Two appendices describe in more details the analytical techniques and the raw data from all experiments performed.

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CHAPTER 2

BACKGROUND INFORMATION

Leachate Generation

Municipal solid waste landfills are designed to minimize leachate generation, however it is not economically feasible to eliminate all leachate generation. Lu et al. (1985) summarized the main conditions affecting leachate generation in landfills. These conditions are related to availability of water, landfill surface, refuse characteristics and underlying soil conditions. The major factors that affect these conditions are summarized in Figure 2.1.

Leachate Characteristics

Water infiltrating through waste collects contaminants from the waste by means of a combination of physical, chemical and microbial processes (Kjeldsen et al., 2002). In this section leachate characteristics and factors affecting these characteristics are discussed with emphasis on the non-biodegradable organic fraction.

Landfill Stabilization Phases

The composition of leachate is not constant over the life of a municipal solid waste landfill, it varies depending on the degradation phase of the buried waste. Further, it is well accepted that landfilled solid waste goes through five distinct phases of stabilization, These phases are described below (Reinhart and Townsend, 1998).

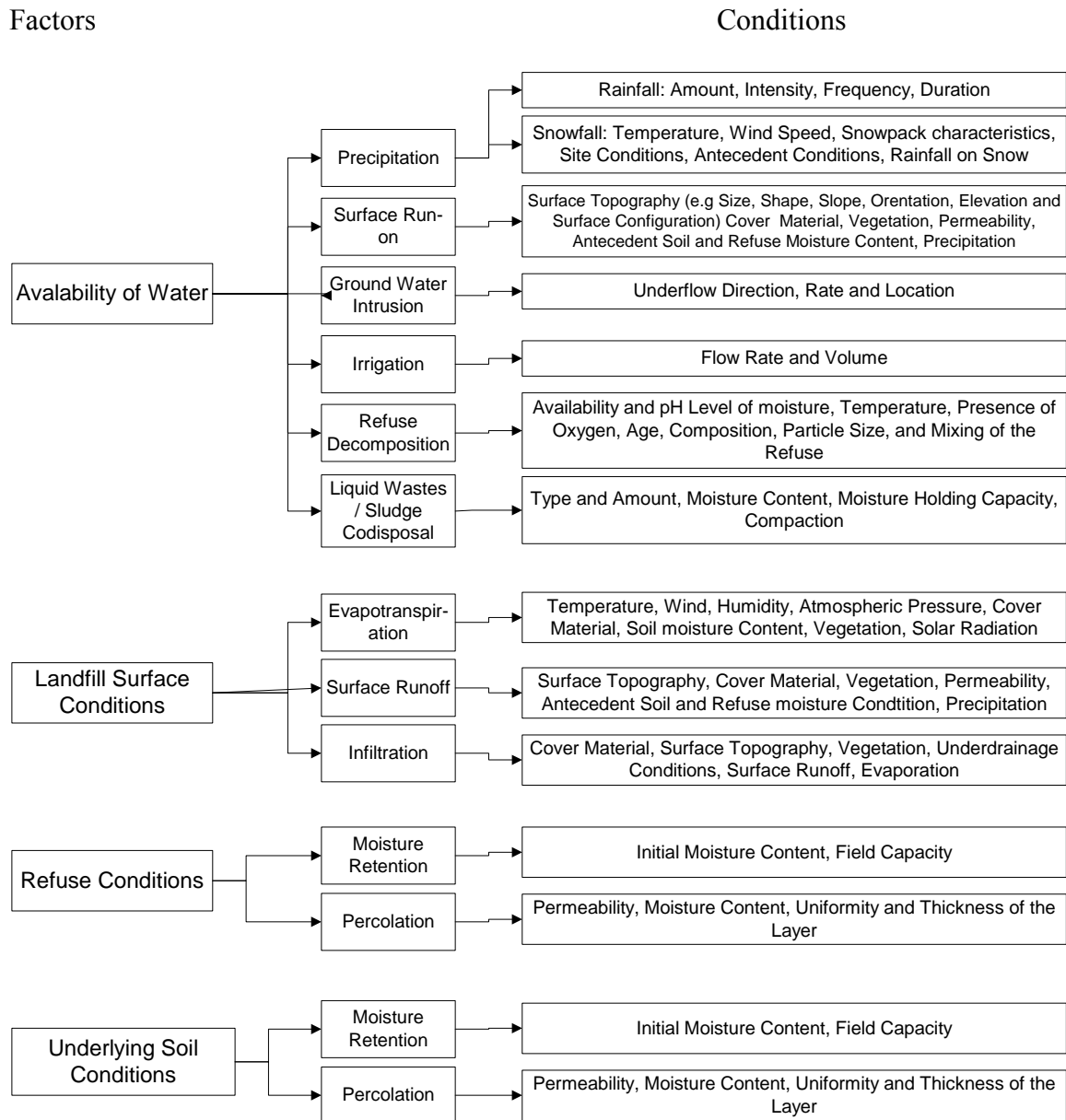


Figure 2.1 Factors Affecting Leachate Volume Generation (Lu et al., 1985)

Phase 1

Phase 1 is the initial adjustment phase and is associated with the time starting with the initial placement of the waste until sufficient moisture has accumulated to support microbial growth. Other preliminary environmental changes occur towards a more favorable environment for biochemical decomposition. During this phase the oxygen trapped in the waste voids is not yet depleted, so the environment is still predominantly aerobic.

Phase 2

Phase 2 is the transition phase, during which the environment changes to anaerobic marking the depletion of the trapped oxygen and the accumulation of carbon dioxide. Also reducing conditions prevail, and a shift in the electron acceptors from oxygen to nitrates and sulfates occurs. In addition during this phase the field capacity is usually exceeded and chemical oxygen demand and volatile organic acids start to accumulate in the leachate.

Phase 3

Phase 3 is the acid formation phase and is characterized by the production of intermediate organic volatile acids. The processes responsible for the organic volatile production are hydrolysis (solubilization) of solid waste and the degradation of organics in the solid waste matrix. Reduction in the pH, mobilization of the metal species, and development of an active microbial population consisting primarily of acidogenic bacteria can also be observed during this phase.

Phase 4

Phase 4 is the methane fermentation phase and is associated with the production of methane and carbon dioxide during consumption of acetate and hydrogen molecules. Sulfate is reduced to sulfide, and the pH value is elevated. Also during this phase, heavy metals are immobilized by complexation and precipitation.

Phase 5

Phase 5 is the maturation phase and is the final phase of the landfill stabilization. In this phase the microbial activity is reduced and is limited by the available substrate. A reduction in gas production occurs and the leachate organic strength is reduced and characterized by low biodegradability. In the long-term, air may infiltrate into the landfill and oxidized species may reappear.

Leachate Composition

Kjeldsen et al. (2002) provided an excellent review of the composition of municipal solid waste landfill leachate. This section is mainly adopted from that review. Leachate is a water-based solution of four main groups of pollutants, dissolved organic matter, inorganic macro matter, heavy metals, and xenobiotic organic compounds. Table 2.1 provides values of main leachate parameters for samples collected during acidic and methanogenic phases.

Dissolved Organic Matter

Dissolved organic matter (DOM) in leachate is composed of a variety of organics, including biodegradable organics (such as volatile acids), and recalcitrant organics (such as humic and fulvic acids). To describe DOM several parameters may be used including

total organic matter (TOC), chemical oxygen demand (COD) and the 5-day biochemical oxygen demand (BOD₅). Additionally the BOD/COD ratio is a measure of the degree of biodegradability of the DOM (the lower the ratio, the less biodegradable the DOM). This ratio tends to decrease as the landfill ages and usually drops below 0.1 in methanogenic leachate. This conclusion is supported by the data presented in Table 2.2 for leachate samples from a methanogenic phase.

Table 2.1. Leachate composition differences between acid and methanogenic phase (Kjeldsen et al., 2002). *

Parameter	Acidic phase		Methanogenic phase		Average
	Average	Range	Average	Range	
pH	6.1	4.5-7.5	8	7.5-9	
BOD ₅	13000	4000-40000	180	20-550	
COD	22000	6000-60000	3000	500-4500	
BOD ₅ /COD	0.58		0.06		
Sulfate	500	70-1750	80	10-420	
Calcium	1200	10-2500	60	20-600	
Magnesium	470	50-1150	180	40-350	
Iron	780	20-2100	15	3-280	
Manganese	25	0.3-65	0.7	0.03-45	
Zinc	5	0.1-120	0.6	0.03-4	
Chloride					2120
Potassium					1085
Sodium					1340
Total phosphorus					6.0
Cadmium					0.005
Chromium					0.28
Cobalt					0.05
Copper					0.065
Lead					0.09
Nickel					0.17
Ammonia-N					740

* mg/l except pH and BOD₅/COD ratio.

Table 2.2. BOD, COD and BOD/COD Ratio for Leachates from Landfills in the Methanogenic Phase (Kjeldsen et al., 2002)

BOD (mg/l)	COD(mg/l)	BOD/COD
290	1225	0.24
44	320	0.11
39	398	0.1
11	190	0.06
38	517	0.07
1.0	53	0.02
2.5	64	0.04
180	3000	0.06

Inorganic Macrocomponents

The concentration of many of the inorganic macrocomponents depends on the landfill stabilization phase. Concentrations of calcium, magnesium, iron, and manganese are lower during the methanogenic phase than the acidic phase due to an increase in the pH, which enhances sorption and precipitation. Typical concentrations of these compounds are found in Table 2.1. The concentration of sulfate is also reduced just prior to methanogenic phase due to microbial reduction of sulfate to sulfide. On the other hand, the concentration of ammonia increases with time. Ammonia-nitrogen concentration in leachate is typically in the range of 500 to 2000 mg/l. The main source of ammonia in the leachate is the decomposition of proteins. Since the only way the ammonia concentration can decrease in an anaerobic landfill is by wash out, it is considered by several researchers to be the most significant long-term leachate component (Kjeldsen et al., 2002).

Heavy Metals

Heavy metals that are found in leachate include cadmium, nickel, zinc, copper, lead and chromium. These metals usually have low concentrations in the leachate and are not considered to be a major concern. Low concentrations of heavy metals are found in the leachate because of attenuation processes such as sorption and precipitation that are favored in the landfill.

Xenobiotic Organic Compounds (XOCS)

This group of compounds is derived from the hazardous materials that have been allowed into the landfill and includes aromatic hydrocarbons, halogenated hydrocarbon, phenols, alkylphenols, pesticides, phthalates, aromatic sulfonates, phosphonates and other miscellaneous compounds. Over 200 compounds or classes of compounds were identified in a screening for XOCs in three Swedish landfills (Paxeus, 2000). Although there a large number of these compounds, they usually have low concentrations.

Characterization of Dissolved Organic Matter in Leachate

The identification of the main classes of organic compounds contributing to the organic matter dissolved in leachate both before and after oxidation is important in this research because it gives an idea of the effectiveness of the suggested treatment methods in removing certain classes of organic compounds. In addition to specific compounds analysis and gross organic parameters (BOD, COD and TOC), dissolved organic matter (DOM) can be characterized by its molecular weight (MW). The MW distribution can be measured using three techniques discussed below.

Membrane Ultrafiltration

Membrane ultrafiltration is used for fractionation of the organic compounds in leachate based on their molecular weight or size. In this technique, the migration of the molecules through the membrane is usually a combination of molecular diffusion and advective flow. The rate of ultrafiltration depends on the area of the membrane, the concentration gradient, molecular diffusion, and temperature (Amy et al., 1987). A series of membranes is usually used with different specific molecular weight cut-offs. Each of these membranes retains all compounds with molecular weight higher than its specific molecular weight cut-off. Ultrafiltration is usually followed by a detection step in order to measure the concentration of organics in every molecular weight range. Detection of the organics could be done using ultraviolet light sorption (UV), total organic carbon (TOC), or other tests that give an indication of organic compound concentrations. This technique has been applied to leachate by several researchers including Chain and DeWalle (1977), Harmsen (1983), Gourdon et al. (1989), Frimmel and Weis (1991), Calace et al. (2001), and Guardia et al. (2002).

Gel Permeation

Gel permeation also allows for fractionation of the organic compounds in leachate based on the MW. In this method each gel is effective for molecules within a specific MW range. Transport of the molecules inside the gel is affected mainly by electrostatic forces and adsorption due to Van Der Waals forces (Amy et al., 1987). The gel is usually packed inside a column and the leachate sample is allowed to flow through the gel. Molecules larger than the upper limit of the specific MW range will be totally excluded from the gel and will elute first at a volume equal to the bulk void volume (molecules

will flow through voids only). Molecules smaller than the lower limit of the MW range will elute last after introducing a volume approximately equal to the total bed volume. The other molecules will elute in between. The gel can fractionate the organic compounds depending on the molecular weight. However to know the molecular weight of each fraction a calibration step is needed. Calibration is usually done using standard calibration substances (usually biochemicals and synthetic chemicals of known MW) (Amy et al., 1987). Also for this method a detection step is needed in order to measure the concentration of organics in every molecular weight range, such as UV, TOC and other parameters that give an indication of the organic compound concentrations. This technique has been applied for leachate by several researchers including Chain and DeWalle (1977), Harmsen (1983), Gourdon (1989), and Frimmel and Weis (1991).

High Performance Liquid Chromatography

High Performance Liquid Chromatography (HPLC) can also be used to determine molecular distribution. The principle applied in this method is very similar to the gel permeation tests except here the fractionation gel column and the detector are both inside one instrument. The HPLC is a more accurate device and can achieve better fractionation of the organic matter. It has been used for leachate analysis by Gourdon (1989).

Biodegradability of Dissolved Organic Matter in Leachate

Many studies support the idea that biodegradability of DOM in landfill leachate decreases with time, including a study done by Harmsen (1983), where two samples of leachate taken from two waste landfills were analyzed. The first sample was taken during the acidification phase, the second sample was taken during the methanogen

phase. The analysis showed that for the acidic sample high values of TOC, COD and BOD were observed (20,000 mg-C/l, 60,000 mg/l and 30,000 mg-O/l) respectively. It was also observed that more than 95% of the TOC was volatile acids, which are considered to be biodegradable, and only 1.3% of the TOC had a high molecular weight (more than 1000). On the other hand in the second sample, lower values of TOC, COD and BOD were observed (2,100 mg-C/l, 7,000 mg-O/l and 50 mg-O/l respectively). Also 32% of the TOC had a high molecular weight (more than a 1000) and volatile acids could not be detected. Note the decrease in the BOD/COD ratio and the increase of the concentration of higher molecular size organics, indications of biodegradability reduction.

In addition to the BOD/COD ratio other parameters can be used to measure the biodegradability of the organic matter in leachate such as; the biochemical methane potential (BMP), toxicity, ultraviolet absorbance at 254 nm (UV_{254})/TOC, BOD/TOC, and the carbon average oxidation state (AOS). The toxicity is usually measured by the amount of organisms that are inactivated after exposure to a certain material. Several types of organisms can be used for toxicity assays. Gonze et al. (1999) used *Vibrio Fischeri* and *Dalphnia Magna*. The prior organism was detected by a luminometer due to its capacity to emit light. The luminous intensity is proportional to the concentration of living bacteria. *Dalphnia magna* toxicity was measured by the number of organisms immobilized after exposure to the tested material. The AOS of carbon can be calculated using Equation 2.1. The increase in the AOS of dissolved organic carbon for a constant TOC means that the organic matter is more oxidized so it needs less oxygen to be totally degraded, which usually means that it is more biodegradable. The TOC change pre- and

post oxidation only gives an indication of the amount of ultimate conversion of organics to either CO₂ or CH₄, whereas the COD change can give an indication of the degree of oxidation of the organics as well as the expected amount of ultimate conversion. The AOS then can be used as a measure of biodegradability if the TOC stays the same and the COD decreases (Scott and Ollis, 1995).

$$\text{Average Oxidation State} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \quad (2.1)$$

The UV₂₅₄ measures the concentration of some organics such as, humic substances and various aromatic compounds, which are mostly recalcitrant compounds. UV₂₅₄/TOC ratio decrease could be an indication of biodegradability increase.

Leachate Treatment

Initially leachate contains high concentrations of BOD and COD and toxic chemicals. However the characteristics of the leachate differ from landfill to landfill and over the life span of the same landfill (it becomes less biodegradable with time). As a result, a combination of biological and physico-chemical treatment processes is required to achieve complete and efficient leachate treatment over the life span of a landfill (Qasim and Chiang, 1994).

Biological Treatment

Both aerobic and anaerobic biological treatment schemes have been used for the treatment of landfill leachate, either exclusively or in combination with municipal wastewater. After experimenting with biological treatment of sanitary landfill leachate using lab, pilot and full-scale experiments employing aerated lagoons, an activated sludge process, and a rotating biological contactor, Ehrig (1984) concluded that generally

efficient treatment is possible and is very similar to domestic wastewater treatment except for some unique issues. These issues include high ammonium concentrations, low BOD/N-ratio, precipitation of inorganics and foaming which could cause clogging of aerators and other operational problems. It was also concluded from this study that the organic biodegradation could be predicted by BOD₅/COD ratio. The lower this ratio, the lower the COD reduction achieved. For further reduction, a physico-chemical treatment technique must be used.

The anaerobic digestibility of two types of landfill leachates representing mature and fresh leachate respectively were studied by Mendez et al. (1989). This study showed that an anaerobic digester can be used to greatly reduce the COD levels in fresh leachate. However it is ineffective for mature leachate due to the high concentrations of refractory organics. The organic compounds responsible for the resistance to both aerobic and anaerobic leachate biodegradation were shown to be the same compounds in a study conducted by Gourdon et al. (1989) on landfill leachate obtained from a mixed industrial and urban waste landfills. Most of these compounds were xenobiotic organic compounds and were non-biodegradable in anaerobic conditions but were up to 50% biodegradable under aerobic conditions. Characterization of the organic compounds of this leachate based on molecular size was done using membrane ultra-filtration, gel permeation and high performance liquid chromatography. These studies showed consistent results that most of the recalcitrant compounds in the leachate do not have a high MW (less than 500). These compounds were mostly industrial chemicals.

Physico-Chemical Treatment

The physico-chemical techniques used for leachate treatment include chemical precipitation, chemical oxidation, activated carbon, reverse osmosis and ammonia stripping (Lema et al., 1988). Using physico-chemical methods for leachate treatment has the potential of producing a well-treated leachate. However, the costs associated with construction and operation of a physico-chemical treatment plant can be excessive (Lema et al., 1988)

In Situ Treatment in Bioreactor Landfills

The transformations that occur in bioreactor landfills are basically the same as in conventional anaerobic landfills. However, these transformations are faster and more effective in bioreactor landfills due to optimized moisture conditions which lead to larger reaction zones and longer contact times in the landfill. Consequently, more effective overall treatment and more gas production is expected (Pohland and Kim, 1999). Moisture control not only helps biological landfill stabilization, but also is considered to be an in situ treatment technique because the concentrations of many of the pollutants in the leachate will decrease. However concentrations of ammonia, chloride and COD may remain relatively high. Moisture control is a cost efficient and environmentally safe method to reduce the strength of leachate, but not to completely purify the leachate (Robinson and Maris, 1985).

Aerobic versus Anaerobic Degradation in Solid Waste Test Columns

Several researchers studied aerobic versus anaerobic solid waste degradation via columns filled with solid waste in different conditions. Cossu et al. (2003) observed the

changes in pH, COD, BOD₅, TOC, and biogas in leachate recirculated through aerobic and anaerobic solid waste columns. The results of this experiment showed lower pH values in the anaerobic column of around 5.5 compared to 7 in the aerated column. This is a sign of a strong acidic phase in the anaerobic column. For the BOD₅ and COD, the aerobic reactor showed a much more rapid decrease over time. The BOD₅ and COD in the aerobic column decreased from 3,000 and 30,000 to 80 and 3,500 mg/L respectively compared to 20,000 and 45,000 to 10,000 and 20,000 mg/L respectively in the anaerobic column in 120 days. The aerobic column had higher biodegradation rates which lead to lower organic release demonstrated by a TOC of 1000 mg/L in the aerobic column compared to 5000 mg/L in the anaerobic column. The CH₄ gas did not appear until day 65 in the anaerobic column and a O₂ concentration of 20 % was noted through out the experiment in the aerobic column.

Oxidation Techniques

In the field of water and wastewater treatment, there are many oxidants that have been used for reducing the concentrations of organic contaminants. In this section well-known oxidation techniques used for wastewater treatment are briefly discussed. Advanced Oxidation Processes (AOPs) are usually used to oxidize complex refractory organics. The main active component in advanced oxidation is the hydroxyl free radical (HO[•]), which is typically produced by AOPs. (HO[•]) reacts with the dissolved compounds in a series of oxidation reactions, without being selective and under normal temperature and pressure conditions. Additionally the (HO[•]) is a very powerful oxidizing agent. The electrochemical oxidation potential of (HO[•]), along with some

other oxidants is shown in Table 2.3. AOPs usually include a combination of more than one reagent; examples of the reagents used to produce (HO•) are, ozone, UV, H₂O₂, ultrasonics, and Fenton's reagent.

Table 2.3 Comparison of Electrochemical oxidation potential (EOP) of various oxidizing agents (Tchobanoglous et al., 2003).

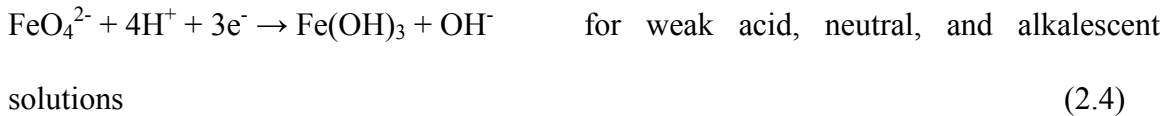
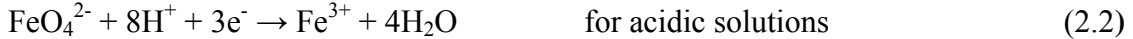
Oxidizing agent	Electrochemical oxidation potential (EOP), V	EOP relative to chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ferrate(acidic environment)	2.20	1.62
Ozone	2.08	1.52
Hypochlorite	1.49	1.1
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

Chemical oxidation may increase the biodegradability of recalcitrant organics in landfill leachate by several mechanisms as reported in the literature. Sarria et al. (2002) reported that HO• attacks organic molecules by abstracting a hydrogen atom or by adding to a double bond. Geenens et al. (2000) reported that oxidation of landfill leachate causes addition of hydroxyl and in cleavage of aromatic rings and double bonds.

Ferrate

Iron commonly exists in the +2 (ferrous) and +3 (ferric) oxidation states. Under strong oxidizing environments, iron moves to higher oxidation states such as +6 (ferrate). Ferrate (Fe⁺⁶O₄²⁻) is a powerful oxidant; its electrochemical oxidation potential has been estimated at 2.2 V under acidic conditions (see Table 2.3). Ferrate oxidation is known to be active over a wide pH range, however its decomposition is faster under acidic conditions (Sharma, 2002). Equations 2.2 to 2.4 show the decomposition of ferrate under

acidic, basic, and neutral conditions (Qu et al., 2003). When used to treat wastewater,



ferrate oxidizes organic compounds and reduces to ferric which, in turn, leads to precipitation as ferric oxide/hydroxide promoting physical removal of organic compounds (Graham et al., 2004). Reaction pH affects organic removal from leachate by ferrate in two ways. First, since ferrate is less stable under acidic environments it decomposes faster than under alkaline conditions (in acidic environments ferrate has a 2.2 electrochemical oxidation potential and in alkaline environments it is 0.7). Secondly, physical removal may increase under acidic environments, especially if pollutants treated have more affinity for the solid phase under acidic environment. For example humic substances would be less soluble and will have an affinity for more sorption to the solid phase under acidic conditions (Gu et al., 1994). Therefore will be attracted more to precipitating particles.

Fenton's Reagent

Fenton's reagent is one of the oldest advanced oxidation processes (AOP), discovered by Fenton in 1894 (Walling, 1974). Generally, in AOP, the main active component is the hydroxyl free radical (HO^\bullet). This radical reacts with dissolved compounds in a series of oxidation reactions with low selectivity. The HO^\bullet has an electrochemical oxidation potential of 2.8 V. Fenton's reagent is known to be a powerful

oxidant under acidic pH and will lose most of its oxidation powers under alkaline pH environments (Pignatello et al., 2006).

Using Fenton's reagent, ferrous iron (Fe^{2+}) reacts with hydrogen peroxide to produce HO^\bullet in a series of reactions shown in Equations 2.5 to 2.11 (Pignatello et al., 2006), which in turn reacts with organic compounds.



Similar to ferrate, Fenton's reagent also produces ferric iron that leads to precipitation although the particles produced may not be identical. Therefore, organic substances are again removed by a combination of oxidation and precipitation. Zhang et al. (2006) used Fenton's reagent for treatment of landfill leachate, finding COD and TOC reduction of 69% and 81%, respectively. Fenton's reagent was used for the treatment of landfill leachate as both pre and post-biological treatment (Bae et al., 1997 and Yoon et al., 1998) and was effective in both roles in reducing organic matter.

In the UV-activated Fenton's reagent process, the production of OH^\bullet is increased by the photo-reactions of Fenton reagents (H_2O_2 and/or Fe^{3+}). These reactions produce HO^\bullet as given in Equation 2.12 (Pignatello et al., 1999).



Photo-Fenton oxidation is considered an improvement over the Fenton's reagent method. It was tested on several chlorophenolic derivatives and showed superiority over both regular Fenton reagent and H₂O₂/UV (Benitez, 2001). Kim (1997) used a photo-Fenton reaction for treatment of refractory landfill leachate (COD of 1150 mg/l and BOD of 4 mg/l), and a COD reduction of over 70% was obtained under optimum conditions (Fe(II) of 1×10^{-3} mol l⁻¹, pH of 3 COD:H₂O₂ molar ratio of 1:1).

Ultrasound

It has been reported that ultrasound application leads to sonochemical transformations, where acoustic cavitation is thought to be the primary responsible phenomenon. Several modes of reactivity have been proposed including pyrolytic decomposition and hydroxyl radical oxidation. Pyrolytic decomposition occurs inside the cavities created during exposure to ultrasound where there is enough energy to break strong chemical bonds of organic compounds that penetrate the bubble (Gonze et al., 1999). On the other hand, hydroxyl reactive radicals may be generated by water dissociation inside the cavities. A portion of these radicals may migrate into the bulk solution where oxidation of the dissolved organics occurs (Okouchi et al., 1992; Gonze et al., 1999 and Drijvers et al., 1999). These mechanisms work simultaneously but the efficiency of each depends on the organic being oxidized. For example, hydrophobic and volatile compounds such as trichloroethylene (TCE) will primarily degrade inside the cavities by direct pyrolysis, hydrophilic compounds with a low vapor pressure such as phenol and chlorophenol will degrade mainly by hydroxyl free radical oxidation. For these types of compounds the addition of H₂O₂/CuO or H₂O₂ alone will increase the efficiency of the oxidation process (Drijvers et al., 1999 and Teo et al., 2001).

Gonze et al. (1999) studied the potential for using ultrasound to increase the biodegradability and decrease the toxicity of wastewater. Sodium pentachlorophenate was chosen as a model compound for this study. The results showed that ultrasound application decreased the toxicity of the solution and increased the biodegradability after up to five hours of ultrasound application. A frequency of 500 kHz (higher frequency results in more reactive ultrasound) and a power density of 220 kWm⁻³ were used. Ultrasound has been successfully used to degrade many refractory toxic organics dissolved in aqueous solutions, such as phenol (Okouchi et al., 1992)

Photochemical and sonochemical oxidation of organics rely on two very different phenomena. Using these two processes together was not theoretically expected to have great benefits. However, the combination of these two agents actually increased the oxidation efficiency to a great extent (Naffrechoux et al., 2000; Toma et al., 2001). Table 2.4 shows a comparison of degradation rates by various UV and ultrasound techniques of phenol in dilute aqueous solutions, showing the superiority of using these two methods together.

Table 2.4 Comparison of the pseudo-first order degradation rate of phenol in dilute aqueous solutions.(Naffrechoux et al., 2000)

Method of oxidation	Initial pH	Rate constant (10 ⁻⁴ S ⁻¹)
UV irradiation(high pressure mercury vapor lamp)	5.1	3.4
Ultrasound(20khz, 70W)	5.5	0.3
Ozone (100ml min ⁻¹)	5.5	26.5
Ultrasound (200khz, 100W)and ozone(100ml min ⁻¹)	5.5	31.7
UV and magnetic stirring (low pressure mercury vapor lamp, 15micro W cm ⁻²)	5.6	8.7
Ultrasound (485 khz, 100W)	5.5	20.3
Ultrasound(485 khz, 100W) and UV irradiation (low pressure mercury vapor lamp, 15micro W cm ⁻²)	5.5	38

Naffrechoux et al. (2000) considered that the high efficiency of this technique is due to three oxidation processes; photodecomposition, sonodecomposition, and ozone oxidation (produced by UV in the headspace). Another theory proposed by Toma et al. (2001) is that the effect of UV alone in any solution is high at the surface and decreases in the bulk solution, producing a non-uniform effect that reduces the efficiency of UV. However ultrasound will increase mixing to the extent that the effect of UV will be uniform over the volume of the reactor, which will greatly increase the efficiency of the reaction.

Potassium Permanganate

Manganese is the active element in the +7 oxidation state in potassium permanganate oxidation. In most of the applications involving KMnO_4 oxidation, a three electron transfer occurs (Equation 2.13) converting permanganate (MnO_4^-) to manganese dioxide ($\text{MnO}_2(\text{s})$), which is a black precipitate (Singer and Reckow, 1999).



Wang (1992) studied the effect of chemical pretreatment on the anaerobic biodegradation of phenolic compounds. The oxidants used included potassium permanganate, ozone and Fenton's reagent. It was concluded from this experiment that in order to significantly enhance biodegradation of one mole of o-cresol, a dose of four moles of hydrogen peroxide, seven moles of permanganate, or 25 moles of ozone was required. These were considered high doses and recommendations to improve the oxidation processes were made.

Hydrogen Peroxide

There are many advantages of using hydrogen peroxide for leachate treatment. It is a powerful oxidant (as shown in Table 2.3), it is a clean oxidant since it does not leave hazardous chemical residues and it is a widely used oxidant. Hydrogen peroxide can be converted to hydroxyl radicals (HO^\bullet), which is a much more powerful oxidation agent as shown in Table 2.3. HO^\bullet is produced by means of adding other reagents to the H_2O_2 solution. Oxidation by HO^\bullet was discussed earlier.

Chlorine

Chlorine is the most commonly used oxidant and disinfectant. When added to water, chlorine gas is rapidly converted to hypochlorous acid (HOCl) (Equation 2.14).



Subsequently the hypochlorous acid will dissociate partially to hypochlorite and hydrogen ions. The sum of the species Cl_2 , HOCl and OCl^- is called the free available chlorine (FAC). Chlorine is available in liquid (NaOCl) and solid ($\text{Ca}(\text{OCl})_2$) forms. One of the disadvantages of using chlorine as an oxidant for natural organics, especially humic and fulvic acids, is the production of chlorinated byproducts, such as trihalomethanes (Reckhow et al., 1990).

Ozone

Ozone is an unstable gas that must be generated on-site. The formation of ozone can be represented by Equations 2.15 and 2.16.



The decomposition of ozone depends on the water matrix. Parameters that are important are pH, natural organic matter, and alkalinity (Gunten, 2003). The pH is important because the hydroxide ion usually initiates the decomposition reaction of ozone (Equation 2.17) after which auto-decomposition of ozone occurs (Equations 2.18 to 2.22). Natural organic matter and alkalinity consume ozone in direct and indirect ways as O_3 and as HO^\bullet (Singer and Reckhow, 1999).



During ozone oxidation, ozone reacts in the aqueous solution following two pathways, a direct pathway, where it reacts as molecular ozone O_3 , and an indirect pathway where ozone is converted to hydroxyl free radicals. The two pathways take place simultaneously. However there are ways to increase the production of the hydroxyl free radicals, which may increase the efficiency of ozone. Traditional ozone treatment can be converted to an advanced oxidation process, such as by increasing the reaction time after ozone addition, increasing the pH, or adding hydrogen peroxide or applying UV light (Gunten, 2003). The difference between oxidation by O_3 and oxidation by HO^\bullet is that the former is more selective so the reaction rate can vary depending on the individual species available in the solution; whereas the HO^\bullet oxidation is more rapid and nonselective and therefore more efficient (Singer and Reckhow, 1999).

UV in the presence of ozone produces H₂O₂ (Equation 2.23), which, in turn, produces HO[•] through two different pathways shown in Equations 2.24 and 2.25 (Topudurti et al., 1998).



Ozone can also be used with hydrogen peroxide. The overall reaction that occurs after adding H₂O₂ to the ozone oxidation process is given in Equation 2.26.



Studies such as reported by Echegaray and Olivieri (1994) used ozone for wastewater treatment and achieved 99.96% removal of benzene and 100% reduction of toluene from industrial wastewaters. In a study by Trapido et al. (1998) a comparison between O₃, O₃/UV and O₃/ultrasound was conducted for the oxidation of phenols (2,4-dichloro- and 2,4-dimethylphenol). The degradation rates for both of the phenols followed the order O₃/ultrasound > O₃ > O₃/UV.

Oxidants Scavengers

High concentrations of carbonates/bicarbonates (CO₃/HCO₃) or alkyl compounds are expected to slow the reaction of HO[•] with organic substances (Steensen, 1997 and Kim et al., 1997) as shown in Reactions 2.27 and 2.28. Therefore the removal of the carbonates from the leachate prior to the oxidation step is expected to increase the available HO[•] for the destruction of organic pollutants. The removal of the inorganic carbon can be done by controlling the pH, which is one of the reasons pH is an important factor.



If hydrogen peroxide and ferrous iron are added in large amounts they too can contribute to the HO^\bullet scavengers as shown in Equations 2.29 and 2.30. So it is so desired to use an optimum H_2O_2 dose and Fe^{2+} for best degradation results (Kim et al., 1997).



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CHAPTER 3

LIQUID SODIUM FERRATE AND FENTON'S REAGENT FOR TREATMENT OF MATURE LANDFILL LEACHATE

Note: this paper has been submitted for publication in the *Journal of Environmental Engineering*

Introduction

Typically, leachate of mature landfill cells contains high concentrations of refractory organic compounds which cannot be removed using biological treatment methods (Ehrig, 1984). Non-biodegradable organic compounds in mature leachate can be categorized into two primary fractions. Humic substances, which are natural organic compounds produced in a landfill as a result of biodegradation of waste, and xenobiotic organic compounds, which are found at low concentrations in certain wastes placed in landfills. Humic substances are considered to be the principal precursors of disinfection byproducts such as trihalomethanes (Reckhow et al., 1990) and can increase the mobility of hazardous compounds such as heavy metals (Christensen et al., 1996). Many of the xenobiotic compounds are potential carcinogens. Therefore, an accidental release of such leachate to surface or ground water bodies can be problematic.

To remove this non-biodegradable organic matter, chemical and/or physical treatment methods must be used (Ehrig, 1984). Consequently, the environmentally

friendly oxidants that are able to effectively treat mature leachate are important and are the focus of this paper. A review of oxidants commonly used in wastewater treatment, identified two primary oxidation pathways, oxidant-organic reactions, and hydroxyl free radical-organic reactions (advanced oxidation). In this study, an oxidant representing each type was selected, including Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe}^{+2}$), from the advanced oxidation family, and ferrate ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$), from the non-advanced oxidation family. The selected oxidants were tested on mature leachate samples from two Florida landfills that had 12 and 20 year old solid waste cells. Experiments focused on measuring organic removal efficiencies in addition to investigating the nature of the remaining dissolved organic matter after oxidation using gross organic parameters such as chemical oxygen demand (COD), dissolved organic carbon (DOC), 5-day biochemical oxygen demand (BOD_5), and organic compound molecular weight (MW). Although, ferrate and Fenton's reagent come from different families of oxidants, they both lead to physical organic removal by precipitation and coprecipitation in addition to oxidation.

This paper presents results from experiments conducted to determine the optimum oxidation conditions and organic removal capacities of mature leachate by ferrate and Fenton's reagent. This study also contributes to the understanding of the role of oxidation and precipitation in each of the techniques studied. The nature of the remaining oxidized organic content is also explored, providing a comparison between the two oxidation pathways.

Ferrate Chemistry

Iron commonly exists in the +2 (ferrous) and +3 (ferric) oxidation states. Under strong oxidizing environments, iron moves to higher oxidation states such as +6 (ferrate).

Ferrate ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$) is a powerful oxidant; its electrochemical oxidation potential has been estimated at 2.2 V under acidic conditions (see Table 3.1). Ferrate oxidation is known to be active over a wide pH range, however its decomposition is faster under acidic conditions (Sharma, 2002). Equations 3.1 to 3.3 show the decomposition of ferrate under acidic, basic, and neutral conditions (Qu et al., 2003). When used to treat wastewater, ferrate oxidizes organic compounds and reduces to ferric which, in turn, leads to precipitation as ferric oxide/hydroxide promoting physical removal of organic compounds (Graham et al., 2004).

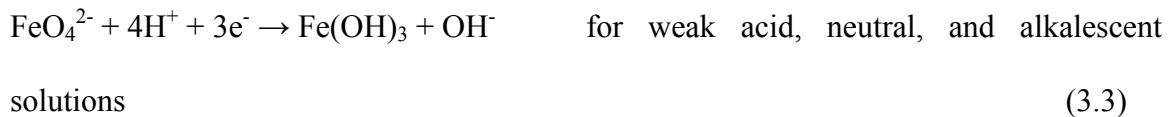


Table 3.1. Comparison of Electrochemical oxidation potential (EOP) of various oxidizing agents.

Oxidizing agent	Electrochemical oxidation potential (EOP),V
Hydroxyl radical	2.80
Ferrate (acidic environment)	2.20
Ozone	2.08
Hydrogen peroxide	1.78
Chlorine	1.36
Chlorine dioxide	1.27
Ferrate (basic environment)	0.7

Source: Tchobanoglous et al., 2003, and Sharma, 2002

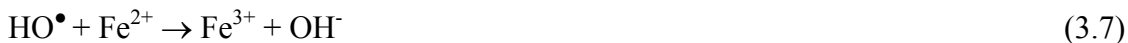
Reaction pH affects organic removal from leachate by ferrate in two ways. First, since ferrate is less stable under acidic environments it decomposes faster than under alkaline conditions (in acidic environments ferrate has a 2.2 electrochemical oxidation potential and in alkaline environments it is 0.7) . Secondly, physical removal may

increase under acidic environments, especially if pollutants treated have more affinity for the solid phase under acidic environment. For example humic substances would be less soluble and will have an affinity for more sorption to the solid phase under acidic conditions (Gu et al.,1994). Therefore will be attracted more to precipitating particles. This argument applies for both ferrate and Fenton's reagent because both promote precipitation.

Fenton's Reagent Chemistry

Fenton's reagent is one of the oldest advanced oxidation processes (AOP), discovered by Fenton in 1894 (Walling, 1974). Generally, in AOP, the main active component is the hydroxyl free radical (HO•). This radical reacts with dissolved compounds in a series of oxidation reactions with low selectivity. The HO• has an electrochemical oxidation potential of 2.8 V (see Table 1). Fenton's reagent is known to be a powerful oxidant under acidic pH and will lose most of its oxidation powers under alkaline pH environments (Pignatello et al., 2006).

Using Fenton's reagent, ferrous iron (Fe²⁺) reacts with hydrogen peroxide to produce HO• in a series of reactions shown in Equations 3.4 - 3.10 (Pignatello et al., 2006), which in turn reacts with organic compounds.





Similar to ferrate, Fenton's reagent also produces ferric iron that leads to precipitation although the particles produced may not be identical. Therefore, organic substances are removed by a combination of oxidation and precipitation. Zhang et al. (2006) used Fenton's reagent for treatment of landfill leachate, finding COD and TOC reduction of 69% and 81%, respectively. Fenton's reagent was used for the treatment of landfill leachate as both pre and post-biological treatment (Bae et al., 1997 and Yoon et al., 1998) and was effective in both roles in reducing organic matter.

Materials and methods

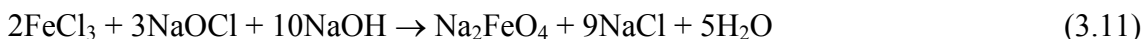
Leachate Collection and Characterization

Leachate was collected from two Florida landfills that had older, lined cells (waste was 12 and 20-year old). Samples were collected from leachate collection system manholes and were kept in one-L amber glass bottles with no headspace at 4°C until used. Samples collected were tested for COD, DOC, BOD₅, pH, alkalinity, ammonia, and chloride according to Standard Methods (1998). Organic compound molecular weight was determined using ultrafiltration by applying a permeation coefficient model according to Logan and Jiang (1990). A description of this method can be found in Appendix A.

Reagents

The preparation of the sodium ferrate followed the wet oxidation method described by Thompson et al. (1951). Ferrate is produced from the oxidation of ferric by hypochlorite in a strong basic solution as shown in Equation 3.11 (Perfiliev and Sharma,

2004). The ferric to ferrate conversion yield is approximately 70%. The resulting solution contains approximately 20 g/l ferrate as Fe. Because hypochlorite is added in excess, some unreacted hypochlorite remains. The concentration of residual chlorine was determined to be 14g/l as Cl₂ (0.7 g Cl₂: 1g Fe⁺⁶) using the 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid-diammonium (ABTS) method (Pinkernell et al., 2000). To minimize ferrate interference with the hypochlorite measurement, ferrate solution pH was adjusted to 2 to accelerate ferrate reduction to ferric (confirmed by color change). The measured value may overestimate the amount of residual chlorine because any residual ferrate could have reacted with ABTS. Research continues to minimize the amount of residual chlorine in the liquid ferrate product. The presence of chlorine in the solution could lead to the production of chlorinated organic compounds when added to leachate, although the extent of this production has not been evaluated. Industrial grade reagents were used; sodium hypochlorite (13.9% OCl⁻ by weight) was obtained from Odyssey manufacturing (Tampa, FL) and was stored at 4°C in the dark until use, Sodium hydroxide (50% by weight) and ferric chloride (40% by weight) were obtained from Brentag Mid-South, Inc. (Tampa, FL) and were stored at room temperature.



Ferrate concentration was measured in every batch produced and was used within an hour of production to minimize ferrate decomposition. Ferrate was measured using a spectroscopic technique. The absorbance of ferrate was measured using an Ocean Optics ISS-UV-VIS at a wavelength of 510 nm. Equation 3.12 was used to calculate the concentration of ferrate.

$$C = \frac{A}{\epsilon \times l} \quad (3.12)$$

Where,

A = Absorbance (at 510 nm)

ϵ = Extinction coefficient, $1150 \text{ M}^{-1}\text{cm}^{-1}$ (Lee, 2004)

l = Cell path length, 1 cm

C = Concentration (M)

All other reagents were obtained from Fisher Scientific. For Fenton's reagent, analytical grade 40% H_2O_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used.

Oxidation / Precipitation Experiments

The oxidation experiments were conducted following a five-step process using 600-ml glass beakers. The contents were mixed at room temperature (22°C) and atmospheric pressure. Prior to treatment, leachate was filtered using a $0.45\text{-}\mu\text{m}$ cellulose filter. The pH of the leachate was adjusted to the target value using 5N sodium hydroxide or 6N sulfuric acid. The oxidant was then added and the reaction was allowed to proceed. The pH was brought back to seven and the treated leachate was filtered to distinguish oxidation from precipitation. A sample was taken from the initial filtered leachate, from the oxidized-unfiltered samples, and from the oxidized filtered samples for COD analysis to determine organic removal percentages by oxidation and by precipitation. DOC was determined for filtered samples only (after the initial and the final filtration). Using this procedure best oxidation time, pH, and dose were determined for both oxidants and for both leachate samples. In addition, an investigation of the nature of oxidation byproducts was conducted by measuring BOD_5 and organic compounds MW distribution for treated and untreated leachate samples. In pH and dose optimization studies, the reaction was allowed to continue until no oxidant was detected

in the leachate to prevent residual oxidant from interfering with the COD and BOD₅ tests. Residual H₂O₂ from Fenton's reagent was monitored using hydrogen peroxide strips (Fisher Scientific). Ferrate reduction was determined to be complete when the color fully changed from purple to brown. The time of reaction used in these experiments was 60 minutes for ferrate optimization experiments. For Fenton's reagent a time of 60 minutes was used in optimum conditions and a time of 120 minutes for Fenton's reagent conditions that did not favor the HO• production process (such as an Fe: H₂O₂ ratio less than 0.2 or an alkaline pH).

Results and discussion

Maturity of leachate samples used was confirmed by several indicators suggested by Kjeldsen et al. (2002) to be properties of mature leachate. These indicators include low COD, low BOD₅, low BOD₅/COD ratio, a high percentage of large MW organic compounds (>1000 dalton), and an above neutral pH. Typical values of these parameters suggested for mature and for young leachate (adapted from Reinhart and Al-Yousfi, 1996 and Kjeldsen et al., 2002) in addition to values measured for each of the two leachate samples (12 and 20 yrs) are summarized in Table 3.2. It can be seen that the leachate samples have low COD, low BOD₅, low BOD₅/COD ratios, high percentage of large MW organic compounds (>1000 dalton), and an above neutral pH, which indicates maturity of leachate.

To make a fair comparison between ferrate and Fenton's reagent pH, time, and reagent dose that would yield best organic removal from leachate samples were determined. The oxidation removal capacity (measured as COD and DOC removal), MW distribution,

COD/DOC, and BOD₅/COD ratios of the oxidized leachate were also determined to compare the two oxidation methods.

For Fenton's reagent treatment, the pH was adjusted prior to the oxidation, for ferrate it was adjusted immediately after adding the oxidant because the ferrate solution used in this experiment included a large amount of NaOH which made it very hard to control the pH only by pre adjustment. After the completion of the reaction, pH was adjusted back to seven. The pH adjustment regime should be taken into consideration when comparing results of this study with other studies since organic removal efficiencies are very sensitive to pH values.

Table 3.2. Values of leachate parameters for samples used in the oxidation experiments

Parameter	Leachate (12 yrs)	Leachate (20 yrs)	Young leachate*	Mature leachate*
COD (mg/l)	1313	1842	1500-71000	3-900
DOC (mg/l)	553	729	-	-
BOD ₅ (mg/l)	9.4	36	1000-57000	4-120
BOD ₅ /COD	0.007	0.02	-	-
% DOC (>1000 Dalton)	-	49	1.3	32
pH	7.2	7.6	4.7-7.7	7.1-8.8
Alkalinity (mg/l as CaCO ₃)	3200	4500	-	-
Ammonia (mg/l as N)	443	902	-	-
Chloride (mg/l)	1061	2234	-	-

* Typical values for acid phase leachate (young) and mature leachate. Adapted from Reinhart and Al-Yousfi (1996) and Kjeldsen et al (2002)

Reaction time

The objective of the first test for each of the oxidants (ferrate and Fenton's reagent) was to determine the time requirements for each treatment. Oxidation reaction end points were determined by monitoring oxidized leachate DOC over time. For Fenton's reagent, a pH of 4, a dose of 1g H₂O₂: g COD, and a molar ratio of 0.6 Fe²⁺:

H₂O₂ were used initially because they were found to be optimal from preliminary exploratory studies. Similarly for ferrate, a pH of 4 and a dose of 0.7 g Fe⁶⁺: g COD were used. Results for both oxidants showed that the effective time of reaction was less than 15 minutes, after which no further reduction in DOC was observed. It was also observed for Fenton's reagent that although the effective reaction time was approximately 15 minutes, residual H₂O₂ in the leachate remained in low concentrations (less than 1 % of original H₂O₂ concentration used) for up to two hours. Zhang et al. (2005) made similar observations, reporting that the majority of COD and TOC removal from leachate using Fenton's reagent treatment occurred during the first 20 minutes of treatment.

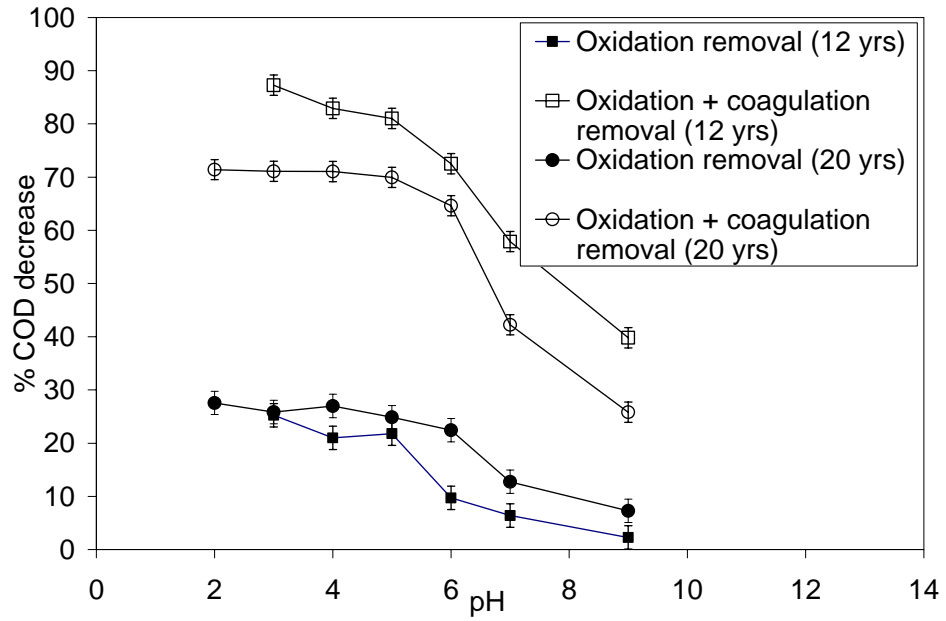
In Fenton's reagent oxidation, the HO[•] production step (shown in Reaction 3) is expected to be rate limiting compared to the step of organic compounds oxidation by the HO[•] (Walling, 1974), meaning that any condition that limits or delays the HO[•] production will significantly influence the organic oxidation efficiency. Ferrate on the other hand was observed to reduce rapidly under all conditions since it immediately reacts with organic compounds when added to leachate, contrary to the HO[•] which is produced in solution. Ferrate is an unstable product, especially in non alkaline solutions, undergoing simultaneous redox reactions with organic compounds and with water, producing O₂ and OH⁻, in addition to Fe⁺³ (DeLuca et al., 1983 and Graham et al., 2004).

Effect of pH

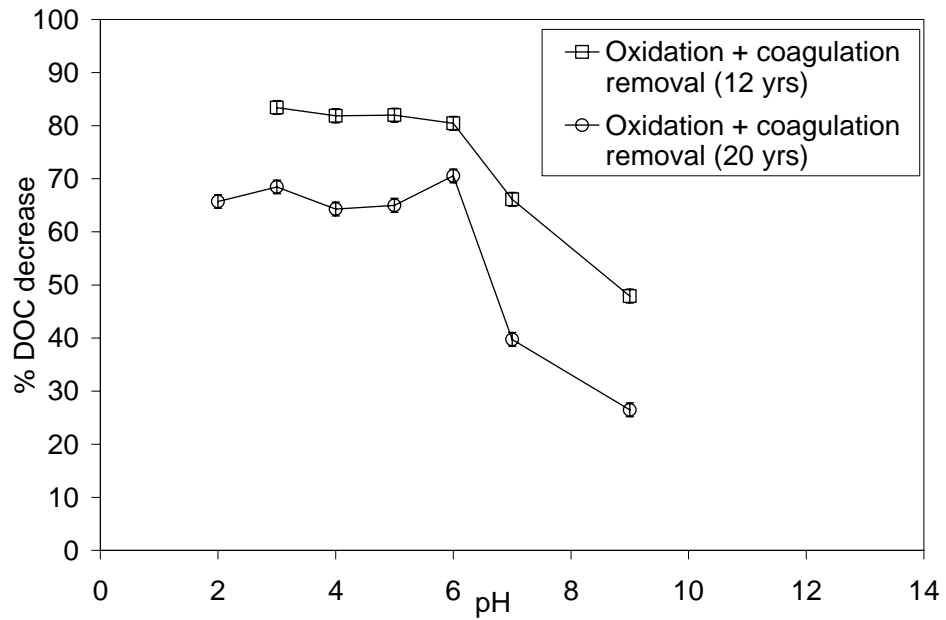
The tested pH range for Fenton's reagent was 2 to 9 using a dose of 1g H₂O₂: g COD, and a molar ratio of 0.4 Fe²⁺: H₂O₂. The tested pH range for ferrate was 3 to 10 using a dose of 0.7g Fe⁶⁺: gCOD. Results from the pH study showed that maximum total

organic removal (precipitation and oxidation) efficiencies using both Fenton's reagent and ferrate were at pH levels below 5 for both leachate samples (20 and 12-year old waste), and that increasing the pH decreased the removal efficiencies, as can be seen in Figures 3.1 and 3.2.

The efficiency of Fenton's reagent oxidation alone was very sensitive to pH, it reached negligible levels at pH above 8 (see Figure 3.1). This behavior was also observed during other studies on leachate oxidation by Fenton's reagent (Bae et al., 1997; Lopez et al., 2004). Reduced organic removal efficiencies in alkaline leachates using Fenton's reagent could be explained by the competition of carbonate and bicarbonate for OH^\bullet (Kim et al., 1997) and also by the deactivation of Fe^{+2} (the oxidation catalyst) by forming ferric hydroxide complexes at pH above 7 (Kang and Hwang, 2000 and Snoeyink and Jenkins, 1980). The increase in organic removal by Fenton's reagent in acidic leachates could also be attributed to an increase in sorption of natural organic matter by Fe^{+3} precipitates under acidic environments (Qu et al., 2003).



(a)



(b)

Figure 3.1. Effect of pH on organic removal from leachate using Fenton's reagent (a) measured as COD and (b) measured as DOC. Using a dose of 1g H₂O₂: g COD, and a molar ratio of 0.4 Fe²⁺: H₂O₂. Error bars represent standard deviation (n = 4)

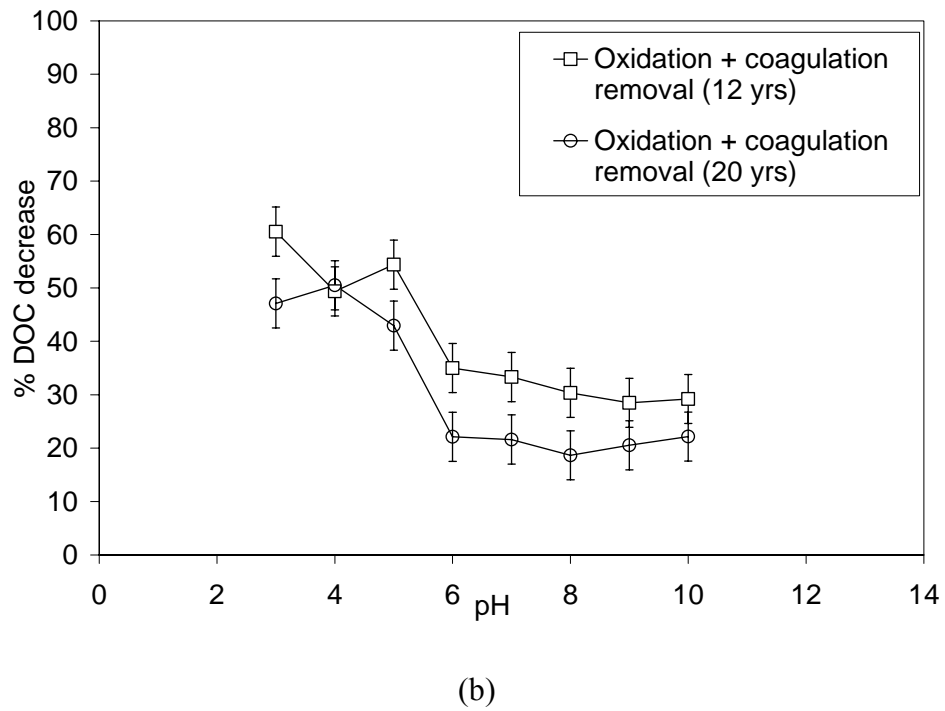
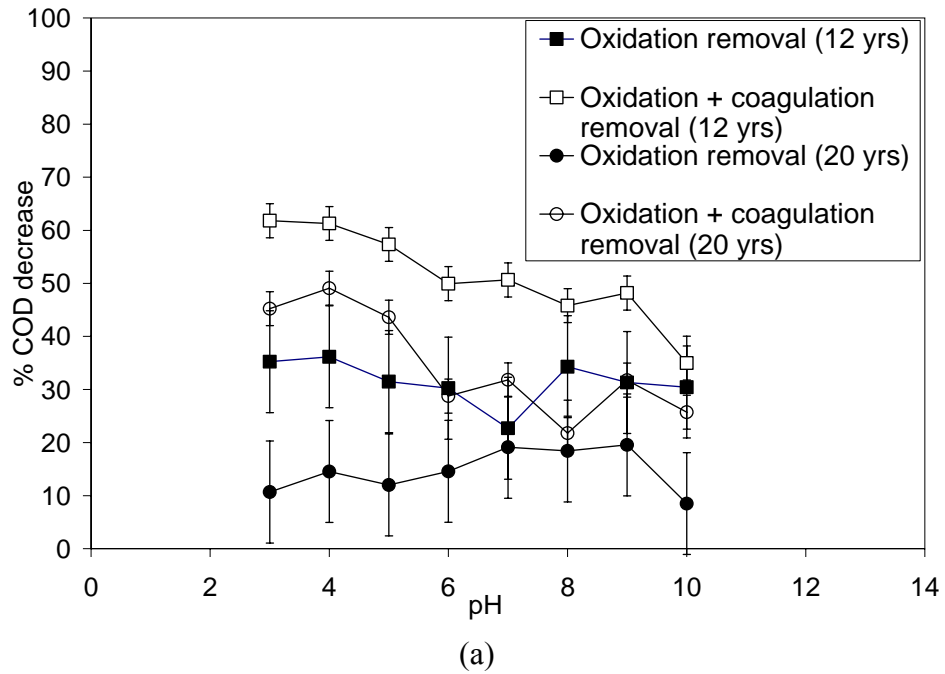


Figure 3.2. Effect of pH on organic compounds removal from leachate using ferrate treatment (a) measured as COD and (b) measured as DOC. Using a dose of 0.7 g Fe 6+: g COD. Error bars represent standard deviation (n = 4)

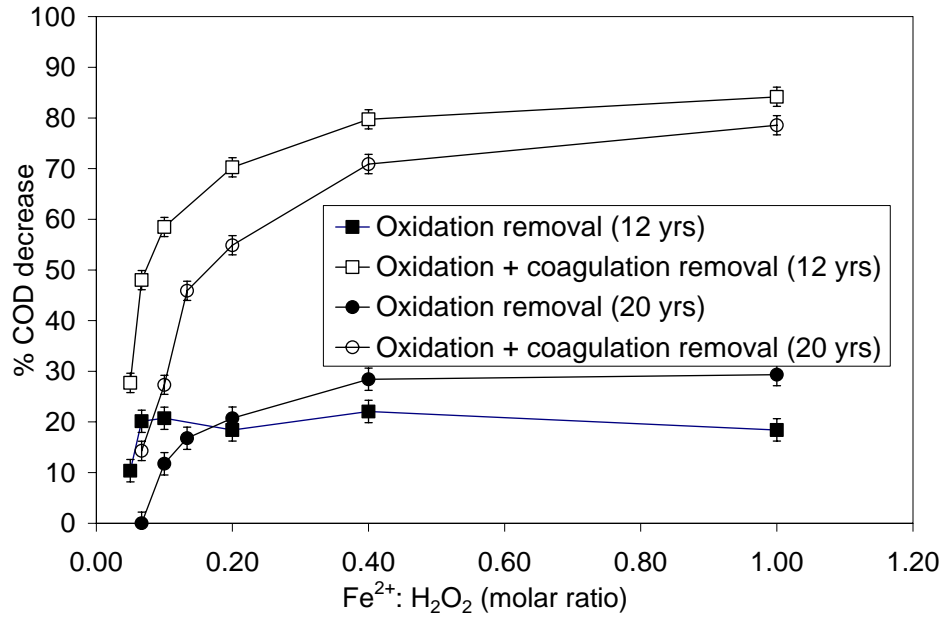
Oxidation by ferrate (with no physical removal) however, remained fairly consistent over the entire pH range tested (Figure 3.2 a), possibly due to the pH adjustment regime used. As mentioned earlier liquid ferrate produced using the method discussed here has a high content of NaOH which made it impossible to control the pH by pre adjustment only. Therefore pH was adjusted after ferrate dose addition to leachate, possibly allowing ferrate to start reacting for a minute or so before the pH was completely adjusted to desired value. At alkaline pH values (7-9), it can be seen that ferrate had higher removal efficiencies than Fenton's reagent by oxidation alone for both of the tested leachates. This observation correlates well with results reported by Xing et al. (2002), who concluded that increasing the pH from 3 to 7 increased the efficiency of microcystin oxidation by ferrate. Also, Graham et al. (2004) observed that in the pH range 5.8 to 11, the optimum pH for trichloroethylene oxidation by ferrate was 8.5, and Qu et al. (2003) reported similar results with reduction of fulvic acid in drinking water by ferrate, where 8 to 9 was the optimum pH range. It has been reported that ferrate is more stable in alkaline environments (electrochemical oxidation potential of 0.7 V) compared to acidic environments (electrochemical oxidation potential of 2.2 V) (Sharma, 2002 and Graham et al., 2004), allowing ferrate to persist longer and more effectively react with pollutants. The total organic removal efficiency for ferrate however increased when the pH fell below 5 for both of the leachate samples tested (see Figure 3.2), presumably related to an increased sorption affinity of organic matter for precipitating iron particles. Sorption of natural organic matter, which is the majority of the nonbiodegradable organic

in leachate, onto precipitating iron solids was also found to be higher under acidic environments by Qu et al. (2003).

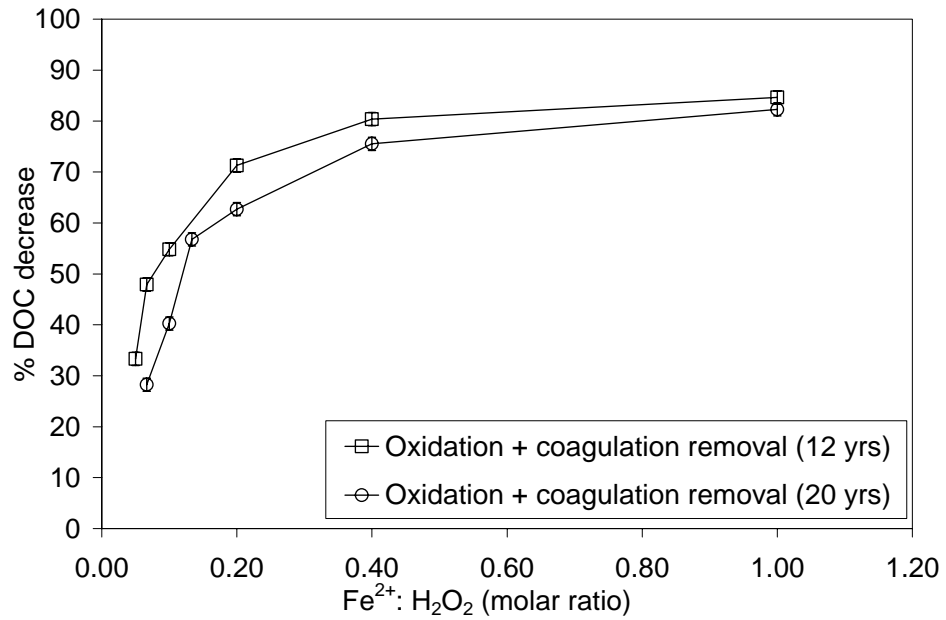
The overall organic removal (oxidation plus precipitation) was affected in a similar way for both of the oxidants by changes in pH values (optimum pH was less than 5). This similarity was probably due to the fact that physical removal was the dominant removal mechanism for both oxidation methods, which was more significant under acidic environments.

Dose

In Fenton's reagent, hydrogen peroxide is catalyzed by ferrous iron to produce the active OH^\bullet radical, consequently, it is important to optimize the dosage of both H_2O_2 and Fe^{2+} . The molar ratio of $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ is important since too little iron will result in unutilized H_2O_2 and excessive Fe^{2+} will destroy produced OH^\bullet radical (Pignatello et al., 2006). Figure 3.3 shows the COD and DOC removal for the $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ molar ratios tested. When the $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ ratio was varied over a range of 0.067 to 1.0 at a pH of 4 and a dose of 1g H_2O_2 : g COD, an increase in the efficiency of oxidation and precipitation was observed up to a $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ ratio of 0.4, after which no significant improvement was realized. A wide range of recommended molar ratios has been reported in the literature, as low as 0.05 by Lopez et al., 2004 and as high as 0.9 by Lau et al., 2001. This wide range for the iron dose reflects the complexity of Fenton's reagent process. When the peroxide dose was varied over a range of 0.2 to 2.0 (g H_2O_2 : g COD) at a pH of 4 and a molar ratio of 0.4 $\text{Fe}^{2+} : \text{H}_2\text{O}_2$, an increase in oxidation efficiency up to 1g H_2O_2 : g COD (Figure 3.4 a and b) was observed, after which no significant improvement was observed.



(a)



(b)

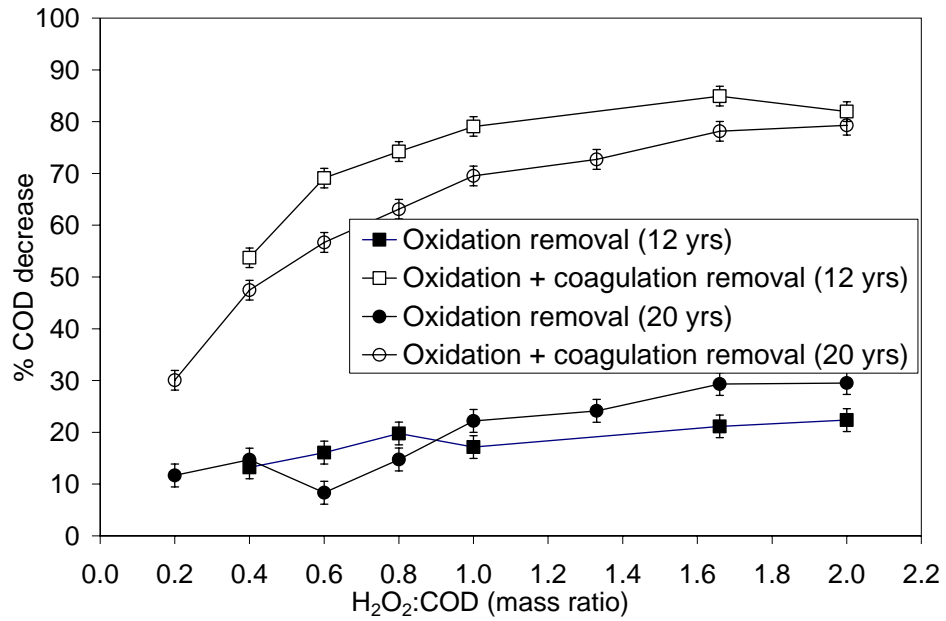
Figure 3.3. Effect of iron dose on organic compounds removal from leachate using Fenton's reagent (a) measured as COD and (b) measured as DOC. Using a pH of 4 and a dose of 1g H₂O₂: g COD. Error bars represent standard deviation (n = 4)

The recommended ratio of H_2O_2 : COD reported in the literature varied from 0.18 (Lau et al., 2001) to 2.0 (Steensen, 1997).

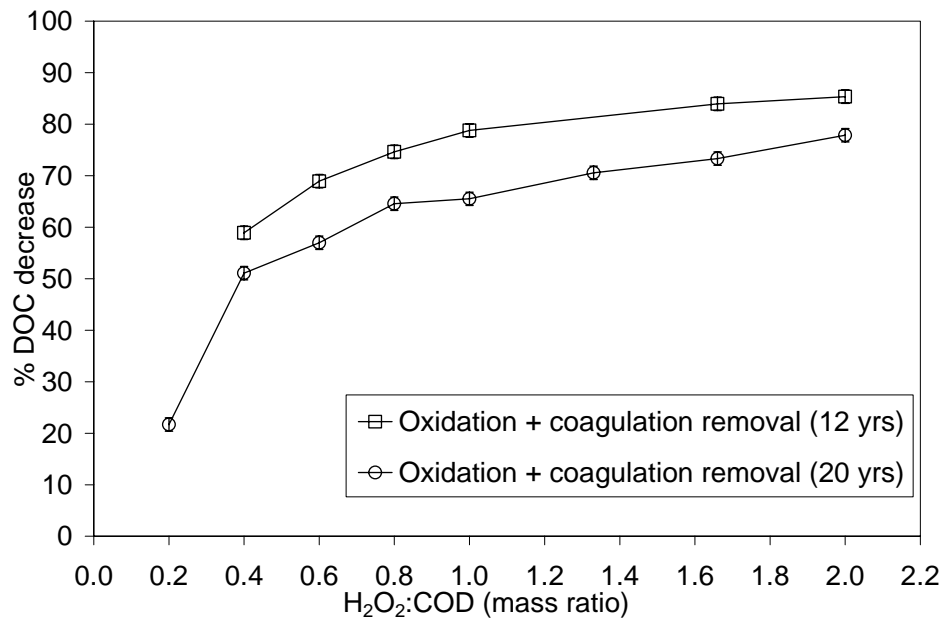
When ferrate dose was varied over a range of 0.15 to 1.5 g ferrate (as Fe) : g COD, the recommended dose for ferrate was found to be 0.7 g Fe^{6+} : g COD (Figure 3.5 a and b). Ferrate has never been used for leachate treatment before but has been used to treat specific organic compounds. Jiang and Wang (2003) used 0.67 g Fe^{6+} : g TOC to remove 80% of a 9.54 mg C /l humic acid solution and Graham et al. (2004) used 3.7 g Ferrate (as Fe) : g TCE to remove 85% of a 0.014 mM TCE solution.

A dose of 1 g oxidant : g COD removed 54 % of the COD and 59 % of the DOC from the 12-year old leachate, and 56 % COD and 59 % DOC from the 20-year old sample using ferrate. However, Fenton's reagent (1g oxidant: g COD) efficiency was higher for both leachate samples. It removed 79.1 % of the COD and 78.8 % of the DOC from the 12-year old leachate and 69.5 % COD and 65.5 % DOC from the 20-year old sample.

The role of physical removal was more significant in both of the treatment methods than of oxidation for organic removal over the range of pH and dosages tested. Oxidant dose experiments showed that from the total COD removal, ferrate removed 60 to 75 % and Fenton's reagent removed 68 to 78 % by precipitation. One gram of added iron removed more organics by coagulation in Fenton's reagent than in ferrate. At recommended conditions (pH equal to 4 and doses of 0.7 g Fe^{+6} : g COD for ferrate and 1.0 g H_2O_2 : g COD with a molar ratio of 0.4 Fe^{+2} to H_2O_2 for Fenton's reagent) it was found that 1 g of added iron physically removed 0.63 and 0.45 g COD from the 12 and 20 year leachates respectively using ferrate compared to 1 g and 0.73 g COD removed by

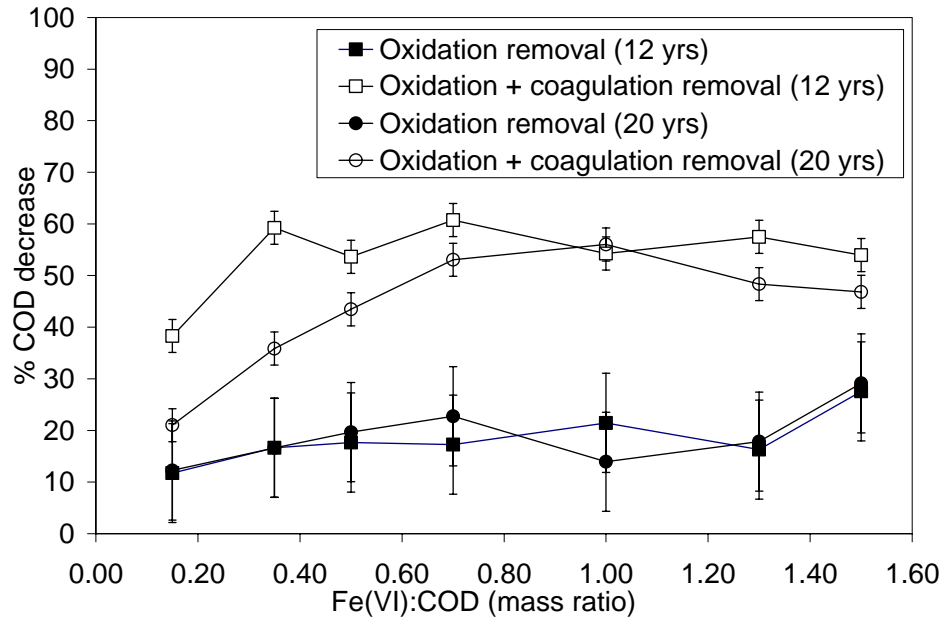


(a)

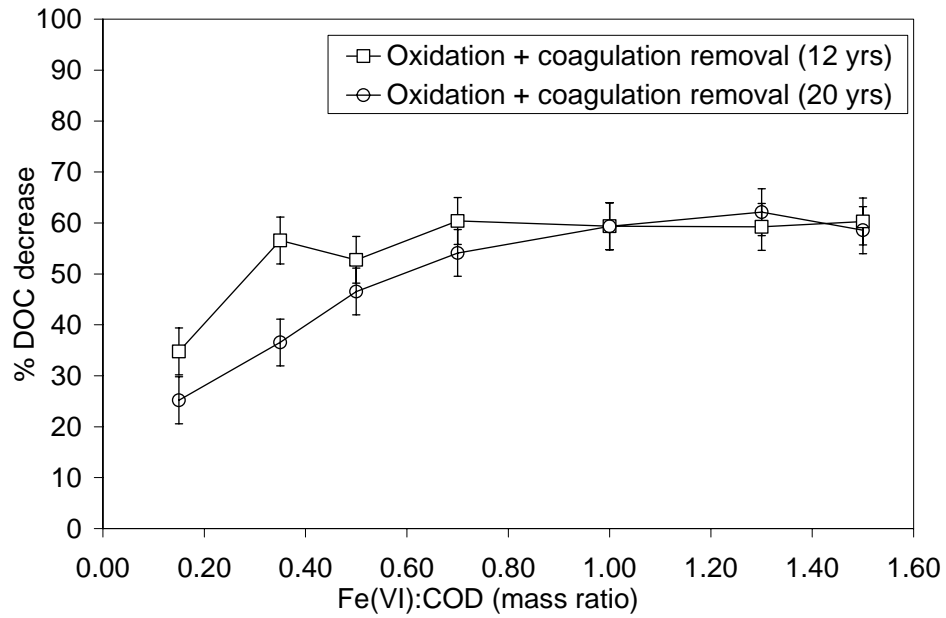


(b)

Figure 3.4. Effect of oxidant dose on organic compounds removal from leachate using Fenton's reagent (a) measured as COD and (b) measured as DOC. Using a pH of 4 and a molar ratio of 0.4 Fe²⁺: H₂O₂. Error bars represent standard deviation (n = 4)



(a)



(b)

Figure 3.5. Effect of oxidant dose on organic compounds removal from leachate using ferrate treatment (a) measured as COD and (b) measured as DOC using a pH of 4. Error bars represent standard deviation (n = 4)

Fenton. Producing charged organic oxidation byproducts could increase adsorption of these byproducts to precipitating iron particles leading to increased physical removal (DeLuca et al., 1983). Later in this paper it is suggested that Fenton's reagent produces more partially oxidized byproducts than ferrate, possibly explaining why iron added in Fenton's reagent removed more organic compounds by coagulation than ferrate. It has been reported that in wastewaters with high organic content and high organic molecular size such as mature leachate, Fenton's reagent will typically remove more organics by coagulation than oxidation (Yoon, et al., 2002).

Humic substances, which make up the majority of the dissolved organic matter in mature leachate tend to be more hydrophobic under acidic environments which promotes the removal of organic compounds by sorption to the iron-precipitating particles. Removal efficiencies were not the same for the two leachate samples, which could be due to the large variability in organic compounds contributing to leachate organic matter.

Nature of oxidized dissolved organic matter in leachate

An emerging approach to the treatment of wastewaters containing recalcitrant organic compounds is to combine chemical and biological methods. This integration has provided an economical and effective option for many non-biodegradable wastewater streams (Scott and Ollis, 1995; Tabrizi and Mehrvar, 2004). If the biodegradability of dissolved organic matter in mature leachate after oxidation is enhanced, then applying combined chemical and biological treatment could be an attractive option for mature leachate.

Humic substances make up the majority of the dissolved organic matter in mature leachate. There is no one universal structural formula describing humic substances

(MacCarthy, 2001). Repeating structures in humic substances include (as reported in MacCarthy, 2001) structural moieties (such as benzene rings, aliphatic segments, hexose and pentose units, and amino acids), functional groups (such as carboxyl, hydroxyl, and amine), and linkages (such as ester, amide, and ether). Oxidation of humic substances produces a variety of compounds including aromatic acids such as benzenedi- to benzenehexa-carboxylic acids as well as from mono- to trihydroxy and hydrocarbon substituents on the aromatic rings and aliphatic acids (Abbt-Braun, 2004).

In this study, gross organic parameters were used to assess changes in the nature of leachate organic matter. Organic compound MW distribution, COD/DOC, and BOD₅/COD were used to characterize the oxidized dissolved organic matter. The distribution of organic compound MW examines the combined effect of chemical and physical organic removal since both processes can target larger molecules either by reducing their molecular size or by completely removing them. Changes in COD/DOC and BOD₅/COD ratios reflect changes mediated mainly by chemical oxidation, because organic removal by precipitation is not expected to significantly alter the nature (biodegradability or oxidation state) of the remaining dissolved organic matter in leachate.

Organic compound MW distribution was selected because it has been correlated to the biodegradability of leachate organic matter. Leachate with high molecular weight organic compounds tends to have high concentrations of humic substances, which have low biodegradability (Kjeldsen et al., 2002). Also, smaller organic molecules may have greater bioavailability compared to larger organic molecules because their smaller radii makes them more hydrophilic and therefore easier for microbes to access (Kerc et al.,

2004). In this study the MW distribution of leachate organic compounds was measured using ultrafiltration. Four oxidation experiments were conducted on the 20-year old leachate, two using ferrate and two using Fenton's reagent. The oxidation pH was 4 and the doses were 0.35 and 0.7 g Fe^{+6} : g COD for ferrate and 0.5 and 1.0 g H_2O_2 : g COD for Fenton's reagent with a molar ratio of 0.4 Fe^{+2} to H_2O_2 . Leachate tested contained almost 50% of the DOC in high MW organics (>1000 dalton) indicating a high content of humic substances. Results presented in Figure 3.6 shows that as oxidant dose increased the proportion of the smaller molecules (<1000 dalton) increased for both Fenton's reagent and ferrate treatments. This shift in molecule size of the dissolved organic matter suggests that the large molecules initially present in leachate were preferentially removed by precipitation and/or partially converted to smaller organic compounds by partial oxidation. Both complete removal of larger molecules and converting large to smaller molecules potentially produces more biodegradable dissolved organic matter in leachate. However in this study the organic compound MW distribution changes did not correlate well with biodegradability increases. Ferrate the oxidant that had less BOD_5/COD ratio increase, produced a larger percentage of smaller (<1000 dalton) organic compounds (see Figure 3.6). This observation could be explained by the selectivity of ferrate (discussed below).

The COD/DOC ratio was also used to compare oxidation products to initial organic molecules in leachate. A dose of 1 g oxidant: g COD was used for both oxidants at pH of 4 and a molar ratio of 0.4 Fe^{+2} : H_2O_2 for Fenton's reagent. Although there was no statistical difference between treated and untreated samples, the dissolved COD/DOC

ratio slightly increased when using ferrate and slightly decreased in one of the Fenton's

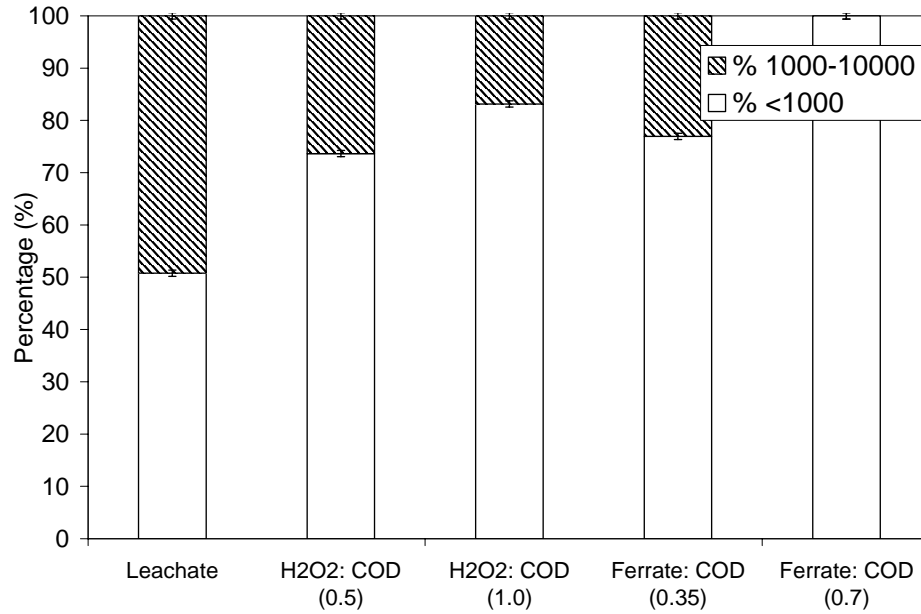


Figure 3.6. Molecular weight distribution before and after two treatments doses of each Fenton's reagent and ferrate using the 20-yr old leachate. Error bars represent standard deviation (n = 3)

reagent experiments. This ratio increased from 2.4 and 2.5 to 2.6 and 2.7 for the 12 and 20 years old respectively using ferrate and decreased when using Fenton's reagent for the 20 years old sample from 2.5 to 2.3 and stayed constant for the 12 year old sample. This behavior suggests that Fenton's reagent oxidation produced more partially oxidized molecules than ferrate since a decrease in DOC can only occur when organic compounds are completely removed from the system, while a COD decrease may result from both partial and complete oxidation. Ferrate appears to lead to a more complete mineralization of organic molecules compared to Fenton's reagent, which causes more partial oxidation. The nonselectivity of OH^\bullet radical may lead to this because OH^\bullet radicals react rapidly with many kinds of compounds (Singer and Reckhow, 1998) and attack all sites of an

organic molecule (Kerc et al., 2004). Ferrate, on the other hand, is usually more selective (DeLuca, 1983; Sharma, 2002) and it reacts with a narrower range of molecules than Fenton, possibly leading to more complete mineralization than Fenton's reagent.

From the BOD₅/COD data presented in Figure 3.7 and Table 3.3, it can be seen that both of the oxidants increased the aerobic biodegradability of leachate organic compounds. Fenton's reagent, however, appeared to improve the biodegradability of leachate more than ferrate again possibly due to the greater tendency to alter compounds rather than mineralizing them. The maximum increase in the BOD₅/COD ratio was achieved when Fenton's reagent was applied on the 12 year old leachate, increasing this ratio from 0.05 to 0.17. The effect of Fenton's reagent on leachate BOD₅/COD ratio has been investigated before. Lopez et al. (2004) found that this ratio increased from 0.2 to >0.5 after Fenton's reagent. Also Morais and Zamora (2005) measured an increase in the BOD₅/COD ratio after Fenton's reagent application from 0.13 to 0.37.

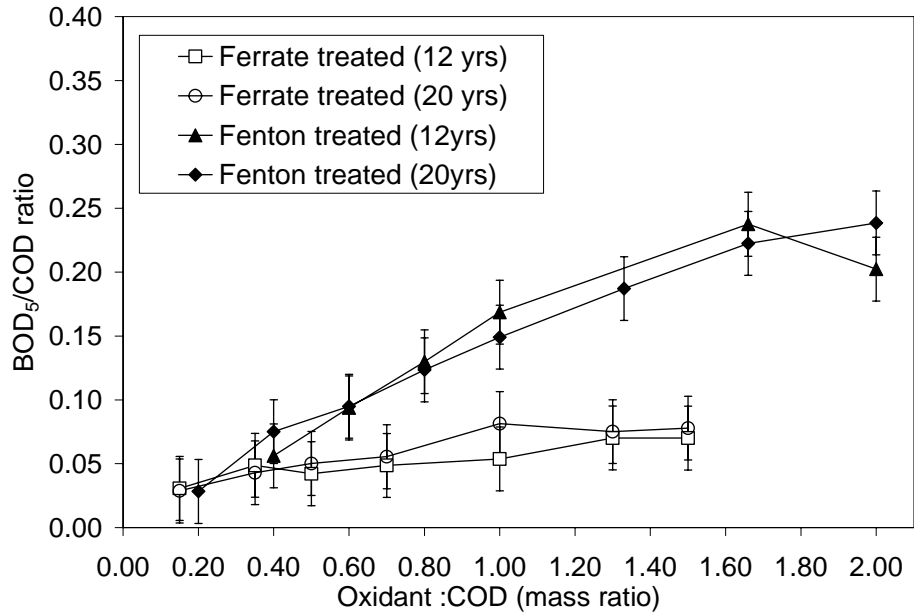


Figure 3.7. BOD₅/COD for Fenton and ferrate treated leachate samples using a pH of 4, and an Fe to H₂O₂ ratio of 0.4 for Fenton's reagent. Error bars represent standard deviation (n = 2).

Table 3.3. Organic removal for treated leachate samples using a dose of 1 g oxidant to 1 g COD for both Fenton's reagent and ferrate and Fe to H₂O₂ ratio of 0.4 for Fenton's reagent.

Sample	% COD removal	% COD removed by oxidation only	% DOC removal	BOD ₅ /COD
Ferrate treated (12yrs)	54.3 ± 3.2	21.5 ± 9.6	59.4 ± 4.6	0.05 ± 0.025
Ferrate treated (20yrs)	56 ± 3.2	13.9 ± 9.6	59.3 ± 4.6	0.08 ± 0.025
Fenton's reagent treated (12yrs)	79.1 ± 1.9	17.2 ± 1.1	78.8 ± 1.3	0.17 ± 0.025
Fenton's reagent treated (20yrs)	69.5 ± 1.9	22.2 ± 1.1	65.5 ± 1.3	0.15 ± 0.025

± Standard deviation (n=2 for BOD₅/COD and 4 the rest)

Summary and Conclusions

Ferrate and Fenton's reagent were both effective in the removal of dissolved organic content from mature leachates. Using optimum conditions, Fenton's reagent resulted in more COD and DOC removal than ferrate, and it produced more oxidized and more biodegradable organic byproducts. Ferrate, however, was active over a wider pH range, making it more beneficial for situations in which pH adjustment is not an option.

Organic content removal by either of the tested methods was a combination of physical and chemical removal. The amount removed by each process, physical or chemical, depended on the pH of the reaction. Physical removal of organic compounds in both of the tested techniques was more significant under acidic environments. Thus, management of the produced solids is important to consider. At recommended oxidation conditions (pH equal to 4 and doses of 0.7 g Fe⁺⁶: g COD for ferrate and 1.0 g H₂O₂: g COD with a molar ratio of 0.4 Fe⁺² to H₂O₂ for Fenton's reagent), it was observed that 1 g of iron added in Fenton's reagent caused coagulation removal 1.6 times the removal caused by 1 g of iron added in ferrate.

Fenton's reagent caused greater changes in the nature of organic compounds remaining in solution after treatment. Organic byproducts produced by Fenton's reagent were more biodegradable (as can be seen from BOD₅/COD data) and contained more partially oxidized organic molecules (as can be seen from COD/DOC) data. Fenton's reagent is therefore recommended for combined chemical and biological treatment, where as ferrate is best used in cases where biodegradability increase is not advantageous.

The percentage of smaller organic molecules (<1000 dalton) increased after chemical oxidation for both tested methods. This decrease in molecule size did not correlate well with biodegradability increase since ferrate, the method that increased biodegradability less, produced a higher percentage of smaller organic compounds (<1000 dalton). Thus using the MW distribution as the sole parameter for investigating biodegradability increase for a treatment could be misleading.

Applying ferrate or Fenton to mature leachate will reduce the organic content, possibly allowing for safer disposal or reuse of the leachate. Alternatively, since Fenton's reagent increased the biodegradability of leachate, it can be used to partially oxidize leachate as a pre-treatment step before further biological treatment, which could be achieved by injecting the oxidized leachate into the landfill. Treatment of leachate in-situ will result in reduced long-term environmental threat, possibly reducing postclosure care requirements

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CHAPTER 4

EFFECTS OF FENTON'S REAGENT ON AEROBIC AND ANAEROBIC BIODEGRADABILITY OF LANDFILL LEACHATE

Introduction

Advancements in landfill technology produced modern leachate and gas management systems that allow more control of biological processes. This control contributes to faster waste stabilization while minimizing environmental impacts. However, over the long-term an important issue remains, which is the fate of the nonbiodegradable organic compounds in mature leachate. After the majority of biodegradable organic compounds in solid waste are depleted, mainly cellulose and hemicellulose (Barlaz et al., 1998), organic content in leachate is primarily humic substances and xenobiotic organic compounds (Kjeldsen et al., 2002). Another group of compounds that may exist in leachate are terpenoids, which can occur either in open chain or cyclic structures in several possible structural arrangements (Leenheer, et al., 2003). For the most part, these compounds are nonbiodegradable and their percentage of organic content tends to increase in leachate as landfills mature, leading to a decline in BOD/ chemical oxygen demand (COD) ratios.

Fenton's reagent has been proven to remove organic matter from mature leachate by chemical and physical means, in addition to increasing the BOD₅/COD ratio of leachate (Batarseh, 2006). The physico-chemical capabilities of Fenton's reagent for leachate treatment have been extensively investigated (Zhang et al., 2006 and Lopez et

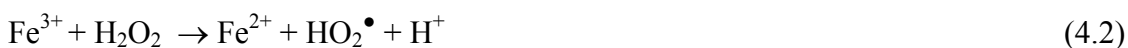
al., 2004). However, the effects of oxidation on biodegradability of leachate have not been thoroughly studied. Previous studies have been limited to measurement of changes in BOD/COD and organic molecular size promoted by Fenton's reagent. Lopez et al. (2004) found that the BOD₅/COD ratio increased for leachate from 0.2 to >0.5 after Fenton's reagent treatment. Also Morais and Zamora (2005) measured an increase in the BOD₅/COD ratio for leachate after Fenton's reagent application from 0.13 to 0.37. Batersch (2006) reported an increase in the proportion of the smaller organic molecules (<1000 dalton) after Fenton's reagent treatment for similar leachate samples.

Mature leachate has a BOD₅/COD ratio of below 0.1 (Kjeldsen et al., 2002). In this investigation, leachate used had a BOD₅/COD well below 0.1, biodegradability indicators were determined after treatment by Fenton's reagent, including ultimate BOD measurements, which evaluate aerobic degradation, as well as biochemical methane potential (BMP) measurements for anaerobic biodegradation. An attempt was also made to identify oxidation byproducts in leachate by performing TMAH thermochemolysis on treated and untreated leachate samples.

Fenton's Reagent Chemistry

Fenton's reagent is one of the oldest advanced oxidation processes (AOP), discovered by Fenton in 1894 (Walling, 1974). Generally, as in other AOP, the main active component in Fenton's reagent is the hydroxyl free radical (HO[•]). This radical reacts with dissolved compounds in a series of reactions with high oxidation potential and low selectivity. The HO[•] is one of the strongest oxidizing agents, having an electrochemical oxidation potential of 2.73 V (Pignatello et al., 2006). In Fenton's

reagent, iron ions react with hydrogen peroxide in a series of reactions shown in Equations 4.1 - 4.7 (Pignatello et al., 2006).



Typical reactions of HO^\bullet with organic compounds include abstraction of H from C-H, N-H, or O-H bonds; addition to C=C bonds; and addition to aromatic rings. These reactions of HO^\bullet with organics are known to be second order with rate constants ranging between 10^7 and 10^{10} $\text{l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ (Pignatello et al., 2006).

Materials and Methods

Leachate Collection and Characterization

Leachate was collected from a Florida landfill that had three separate lined cells (waste was 6, 10, and 17 yrs old), with separate leachate collection systems. Samples were collected from leachate collection system manholes serving each of the three cells and were kept in one-L amber glass bottles with no headspace at 4°C until used. Samples collected were tested for COD, DOC, BOD₅, ammonia, and chloride (see Table 4.1) according to Standard Methods (1998). Low BOD₅/COD (0.02) was observed for the

Table 4.1. Characteristics of leachate samples

Sample Age	Cl- (mg/l)	NH ₃ (mgN/l)	DOC (mg/l)	BOD ₅ (mg/l)	COD (mg/l)	BOD/COD
1988	2630	1240	1009	51	2019	0.020
1995	1520	904	681	32	1641	0.020
1999	1298	667	669	34	1646	0.020

three leachate samples, indicating maturity of leachate. The chloride and ammonia concentrations measured were observed to increase with age of leachate. Ammonia ranged from 667 to 1240 mg/l and chloride from 1298 to 2630 mg/l, confirming differences in leachate because of age and also confirming leachate maturity.

Reagents

BOD bottles were seeded using capsules obtained from Hach (Loveland, Colorado). For BMP tests, anaerobically digested sludge was used for seed and was obtained from a local wastewater treatment plant anaerobic digester with a solid retention time of 20 days. All other reagents were obtained from Fisher Scientific (Atlanta, Georgia). For Fenton's reagent, analytical grade 40% H₂O₂ and FeCl₂·4H₂O was used.

Fenton's Reagent Experiments

Laboratory work in this study consisted of first determining an optimum iron dose using previously identified pH and H₂O₂ dose (Batarseh, 2006). Samples from the three leachate sources were oxidized using selected doses and pH. Samples of treated and untreated leachates were then evaluated for aerobic and anaerobic biodegradability and prepared for TMAH thermochemolysis analysis.

Fenton's reagent experiments were conducted in 600-ml glass beakers. The contents were continuously mixed at room temperature (22°C) and atmospheric pressure. Prior to treatment, leachate was filtered using a 0.45- μm cellulose filter. The pH of the leachate was adjusted to four using 6N hydrochloric acid. Ferrous chloride (0.4 Fe: H_2O_2 molar ratio) and then hydrogen peroxide solutions (1g H_2O_2 : g COD) were added and the reaction was allowed to proceed. The pH was brought back to seven using 5N sodium hydroxide. Residual H_2O_2 from Fenton's reagent was monitored using hydrogen peroxide strips (Fisher Scientific) and mixing was continued until all residual disappeared, at which point the treated leachate was filtered. Untreated and oxidized filtered leachate samples were prepared for DOC, BOD, BMP, and TMAH thermochemolysis.

Biodegradability of treated leachate was measured by two types of tests. BMP assays were used to explore improvements in the anaerobic biodegradability of leachate and BOD assays were used to evaluate aerobic biodegradability improvements. BMP was determined using the ASTM E 1196-92. In this test, samples were incubated at 35 ± 2 °C after the addition of seed (anaerobically digested sludge) and a variety of nutrients and other chemicals to optimize microbial growth in 250-ml gas-tight bottles. Test bottles were placed in an incubator for eight weeks or until biodegradation of the sample was completed as indicated by cessation of methane production. The volume of the gas produced from each bottle was measured using a frictionless glass syringe. The needle of the glass syringe was inserted into BMP bottles to allow for the extra produced gas to escape to the syringe, leaving the remaining gas under atmospheric pressure. Methane concentrations were measured using a Shimadzu – 14 gas chromatograph with an FID

detector and a DB-1 capillary column. The column temperature was held constant at 100° C. The concentration of CO₂ gas was measured using a Shimadzu – 14 GC equipped with TCD detector and a Carboxyn column. The temperature was held at 20°C for 5 minutes then raised to 225°C.

To identify organic compounds removed and oxidation byproducts, TMAH thermochemolysis was used. This analysis was performed on filtered untreated samples and treated, filtered leachate samples. All samples were freeze dried and the test was performed according to the procedure developed by Nanny and Ratasuk (2002). Glass ampoules (Wheaton) were filled with accurately weighed amounts of sample ranging from 2.5-3.0 mg. Then 100 µL of methanol and 100 µL of TMAH (25% in methanol; Aldrich) were added to the samples which were allowed to remain at room temperature for 30 to 45 minutes in order for the solid sample to become saturated with TMAH. The methanol was then evaporated under vacuum for 30 min.; after which the ampoule was sealed under vacuum and baked in an oven at 250 °C for 30 minutes. Upon cooling, the ampoule was opened and thoroughly washed with CH₂Cl₂. This solution was then dried under a gentle stream of N₂ and reconstituted in 100-µL of CH₂Cl₂ containing 40 ng of n-eicosane/µL as a standard. Thermochemolysis products were analyzed using a HP 5890 gas chromatograph interfaced with a HP 5970 mass spectrometer. A DB-5 fused silica capillary column 30m X 0.25mm i.d., was used. Initial temperature of the column was 60°C and programmed to reach 150°C at a rate of 15°C/min and then to 240°C at a rate of 4°C/min. after the temperature reached 240°C, the temperature was held constant for 10 min. All samples were analyzed in duplicates.

Results and Discussion

Oxidant dose

Optimization of Fenton's reagent dose normally includes finding the iron dose and the H₂O₂ dose that provide the best removal of targeted organic contaminants. Optimum iron and H₂O₂ doses have been previously determined for similar leachate samples using FeSO₄. However FeSO₄ was found to have inhibitory impacts on the BMP test used to evaluate the anaerobic biodegradability of treated leachate due to the high sulfate concentrations remaining in the treated leachate samples which stimulates sulfidogens. These bacteria reduce sulfate to sulfide which is inhibitory to methanogenic bacteria (Parkin and Owen, 1986). Also these bacteria out compete methanogens for organic carbon, reducing the total amount of methane produced in BMP tests. Therefore FeCl₂ was substituted for FeSO₄. FeCl₂ dose was varied between 0.1 and 0.9 Fe²⁺: H₂O₂ molar ratio; a dose of 0.4 Fe²⁺: H₂O₂ molar ratio was selected because after this point only marginal increases in DOC removal were observed as can be seen in Figure 4.1. This iron dose was used at pH 4 with two H₂O₂ doses (1 and 0.5 g H₂O₂ : g COD) to oxidize the three leachate samples. DOC removal from leachate was 50 - 70 % as can be seen in Figure 4.2. These removal efficiencies were similar to the FeSO₄ Fenton's reagent oxidation experiment performed on similar leachate samples previously (Batarseh, 2006)

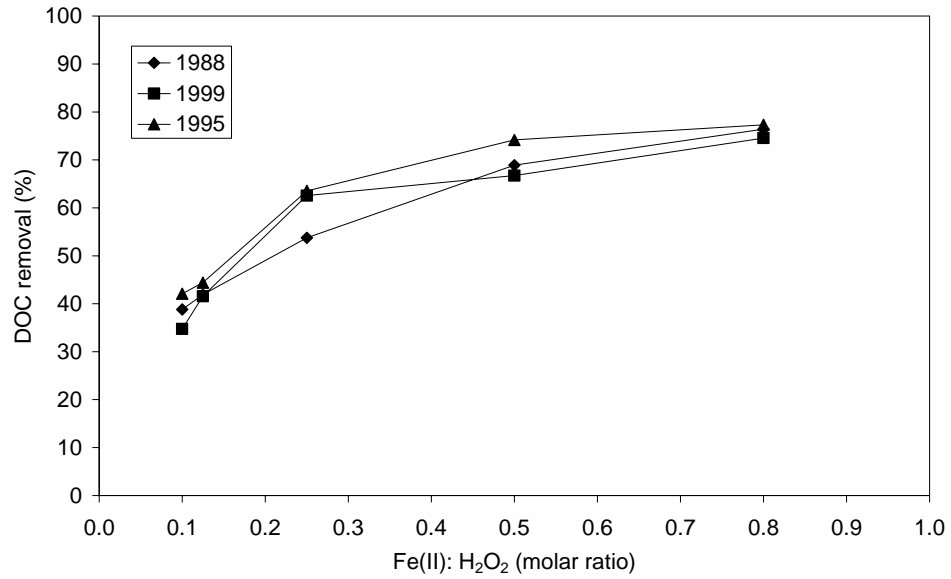


Figure 4.1. Effect of iron dose on DOC removal from 1988, 1995, and 1999 leachate samples after Fenton's reagent treatment using a dose of 1 g H₂O₂ to g COD and a pH of 4.

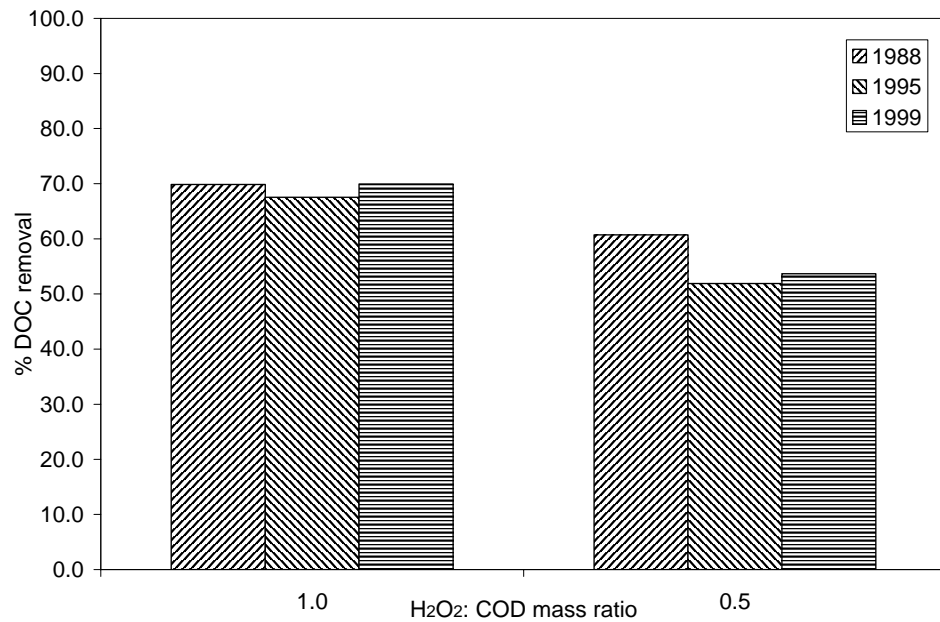


Figure 4.2. DOC removal from 1988, 1995, and 1999 leachate samples after Fenton's reagent treatment using doses of 0.5 and 1 g H₂O₂ to g COD with an Fe to H₂O₂ ratio of 0.4 and a pH of 4.

Effect of Fenton's Reagent on Leachate Biodegradability

Fenton's reagent is known to alter the nature of many organic substances and is expected to improve the biodegradability of leachate by removing refractory inhibitory compounds or by producing organic molecules that are more biodegradable. As mentioned earlier, humic substances and xenobiotic organic compounds are the two major types of recalcitrant organic compounds that are found in leachate (Kjeldsen et al., 2002). Unlike humic substances, some xenobiotic compounds are toxic, consequently their removal could improve biodegradability rates of other organic compounds in leachate. The lack of a universal structural formula for humic substances and the existence of a huge variety of terpenoids occurring in almost every possible structural arrangement (open chain and cyclic structures) (Leenheer et al, 2003) and the big variety of xenobiotic compounds made identifying and measuring oxidation products difficult. Also the non-selective nature of HO[•] radicals results in a variety of organic byproducts (Pignatello and Sun, 1995). The organic compounds remaining after oxidation are expected to include low molecular weight acids such as acetic, maleic, and oxalic acids. These acids accumulate after Fenton's reagent treatment because of the inability of hydroxyl free radical to oxidize these compounds (Bigda, 1995). Oxidation byproducts are also expected to include compounds with aromatic rings still intact (Pignatello and Sun, 1995).

Aerobic biodegradability

The portion of organic matter remaining in leachate after Fenton's reagent treatment that could be aerobically biodegraded was measured as the ratio of BOD (expressed as carbon) to the DOC for the three leachate samples tested (6, 10, and 17 yrs

old). This ratio represents the amount of biodegradable organic carbon present relative to the total organic carbon and is roughly equivalent to BOD/COD, which represents organic compounds in terms of oxygen demand. BOD was measured at day 5 and day 28 for all treated and untreated leachate samples. Results from BOD₅C/DOC experiments (Table 4.2) indicate that the remaining organic content after Fenton's reagent oxidation was not completely biodegradable. BOD₅C /DOC increased from 0.02 to 0.15, which is still less than the BOD₅/COD of 0.4 that is usually associated with biodegradable waste streams (Chamarro et al., 2001). BOD₂₈C / DOC increased to 0.24. The third biodegradability indicator, BOD₅/BOD₂₈ is related to the rate of aerobic biodegradation. The BOD₅/BOD₂₈ (Table 4.2) increased from 0.3 to approximately 0.6 or more after Fenton's reagent treatment suggesting a greater rate of aerobic biodegradation after Fenton's reagent treatment.

Table 4.2. BOD based measurements for treated and untreated leachate samples. Using doses of 0.5 (0.5 D) and 1 (D) g H₂O₂ to g COD with an Fe to H₂O₂ ratio of 0.4 and a pH of 4.

Sample	BOD ₅ as C /DOC	BOD ₂₈ as C /DOC	BOD ₅ /BOD ₂₈
Leachate 1988	0.02	0.06	0.28
Treated 1988 (0.5D)	0.10	0.16	0.64
Treated 1988 (D)	0.15	0.22	0.70
Leachate 1995	0.02	0.06	0.29
Treated 1995 (0.5D)	0.07	0.14	0.51
Treated 1995 (D)	0.14	0.22	0.62
Leachate 1999	0.02	0.07	0.30
Treated 1999 (0.5D)	0.08	0.15	0.55
Treated 1999 (D)	0.13	0.24	0.56

Values of first-order reaction rate constant for BOD were calculated from BOD₅/BOD₂₈ data (Tchobanoglous et al., 2003). These values increased from around 0.05 to more than 0.25 day⁻¹ for all the treated leachate samples (Table 4.3). To further demonstrate the

improved biodegradation rate after Fenton's reagent, an ultimate BOD test was performed on treated and untreated leachate samples (1995), measuring BOD at 5-day intervals up to 30 days. Projection of ultimate BOD measurements (Figure 4.3) demonstrated that the ultimate BOD was not affected by the treatment. BOD_u was 119

Table 4.3. First order BOD reaction rate, k (1/d) using a dose of 1 g H_2O_2 to g COD with an Fe to H_2O_2 ratio of 0.4 and a pH of 4.

Sample	1988	1995	1999
Untreated	0.045	0.049	0.053
Treated	0.245	0.290	0.301

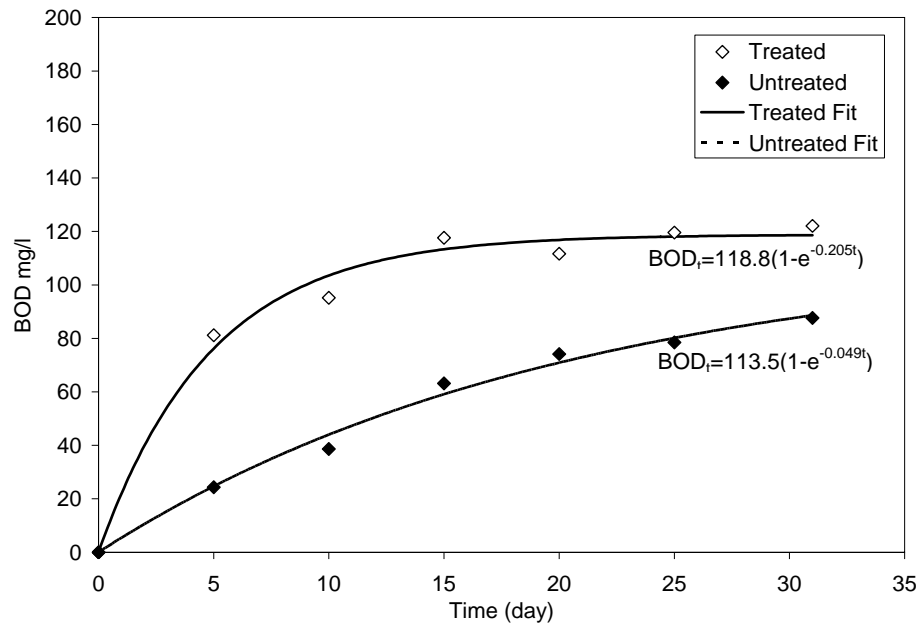


Figure 4.3. Ultimate BOD for treated and untreated leachate sample using a dose of 1 g H_2O_2 to g COD and an iron dose of 0.4 Fe to H_2O_2 and a pH of 4.

mg/l for the treated sample and 114 mg/l for the untreated. However the first-order reaction rate constant changed significantly; k was 0.049 for the untreated and 0.205 day⁻¹ for the treated leachate.

The improved rates and amounts of aerobic biodegradation suggest that Fenton's reagent completely or partially removed some of the inhibitory compounds that inhibited aerobic biodegradation.

Anaerobic biodegradation

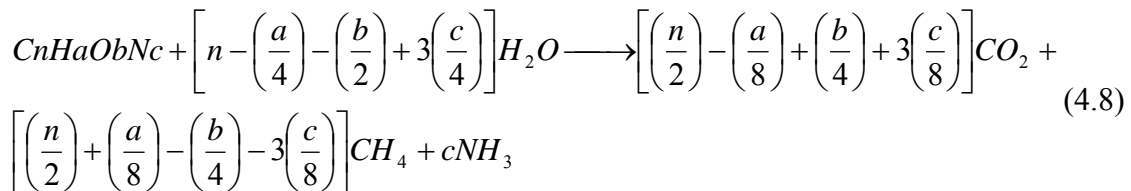
The biodegradable organic fraction of leachate in anaerobic treatment systems was measured by determining the ratio of methane that is produced in BMP bottles to the amount of methane that would be produced if the organic content of leachate was completely transformed to methane (theoretical BMP). BMP tests were performed on treated and untreated leachate samples (6, 10, and 17 yrs old). Leachate samples were treated with 1 and 0.5 g H₂O₂ to g COD and 0.4 molar ratio of Fe²⁺ : H₂O₂ at a pH of 4. Net methane generation from each sample was calculated by subtracting total methane produced by blank bottles (seed and media only) from total methane produced in sample bottles (Table 4.4). The net methane volume was converted to a mass value and divided by the theoretical methane potential. The theoretical methane potential was calculated by assuming that the organic content in mature leachate could be represented by humic substances extracted from leachate samples. This assumption is more relevant in mature leachate samples such as the ones studied here, as confirmed by the very low BOD₅/COD ratio (Table 4.1). To determine a molecular formula that represents humic substances in leachate, elemental analysis data reported by Nanny and Ratasuk (2002) were used. In that study three leachate samples were analyzed (2 to 75 yrs old waste) for acid precipitated (AP) (similar to humic acid) and acid soluble (AS) (similar to fulvic acid) fractions of dissolved organic contents.

Table 4.4. Methane production in BMP bottles for treated and untreated leachate samples along with maximum theoretical methane potential. Using doses of 0.5 (0.5D) and 1 (D) g H₂O₂ to g COD with an Fe to H₂O₂ ratio of 0.4 and a Ph of 4.

Sample	Methane (ml)	Net Methane (ml)	Net Methane (mg)	Maximum Methane Potential (mg)*	Produced/Potential, %
Leachate 1988	5.6	1.2	0.76	4.85	15.7
Treated 1988 (0.5D)	4.9	0.5	0.32	5.44	5.82
Treated 1988 (D)	4.7	0.3	0.19	5.84	3.25
Leachate 1995	4.5	0.1	0.06	5.01	1.26
Treated 1995 (0.5D)	5.1	0.7	0.44	5.66	7.83
Treated 1995 (D)	5.7	1.3	0.82	6.47	12.7
Leachate 1999	5.5	1.1	0.70	4.99	14.0
Treated 1999 (0.5D)	5.8	1.4	0.89	5.66	15.7
Treated 1999 (D)	5.2	0.8	0.51	6.59	7.69
Benzoic	10.88	6.48	4.10	4.03	101.9

* Maximum theoretical methane potential calculated from DOC values.

A weighted average mass percentage was calculated for every element based on elemental analysis results for both AS and AP using a ratio of 4 AS: 1 AP. Weighted average values calculated were 56.4 % C, 6.6 % H, 29.8 % O, and 2.2 % N. These percentages were converted to molar ratios and normalized to carbon. The resulting molecular formula was CH_{1.4}O_{0.4}N_{0.03}. To determine the amount of methane that could be produced from complete biodegradation of the organic content, these molar ratios were plugged into an empirical formula (Equation 4.8) adopted from Parkin and Owen (1986). This equation resulted in a conversion factor of 0.57 mole of methane produced per mole of organic carbon, which was measured as DOC.



Biodegradability of the samples treated and untreated as indicated by BMP was low. Net methane production/theoretical methane potential was less than 15% for all the samples (before and after treatment) suggesting that the treated and untreated leachates are nonbiodegradable anaerobically. In most cases the ratio actually declined with treatment (Table 4.4). Shelton and Tiedje (1984) reported that when more than 75% of the theoretical methane production was measured, the substance can be considered biodegradable and when 30 to 75 % was produced, the substance was considered partially biodegradable.

Along with leachate samples, the BMP of benzoic acid was evaluated as a control. Benzoic acid was also added to untreated and treated leachate samples as spikes to evaluate possible inhibitory effects of oxidation on anaerobic biodegradability. Net methane production/theoretical methane potential for benzoic acid sample was consistently around 1.0. Also, benzoic acid spiked untreated and treated leachate samples produced net methane production amounts similar to benzoic acid samples, confirming the low biodegradability of leachate and noninhibitory nature of the leachate DOC for anaerobic microorganisms.

During anaerobic degradation, the ratio of CH_4 to CO_2 produced will vary depending on the mean oxidation state of carbon in degraded organic molecules. As mean oxidation state increases, more CO_2 and less CH_4 is expected to be produced during anaerobic digestion (Gujer and Zehnder, 1983). Organic substances that have a high oxidation state of carbon such as formic and oxalic acids are expected to increase after Fenton's reagent oxidation, possibly causing an increase in amount of carbon converted to CO_2 . Oxalic acid, for example, will produce approximately 90 % CO_2 and

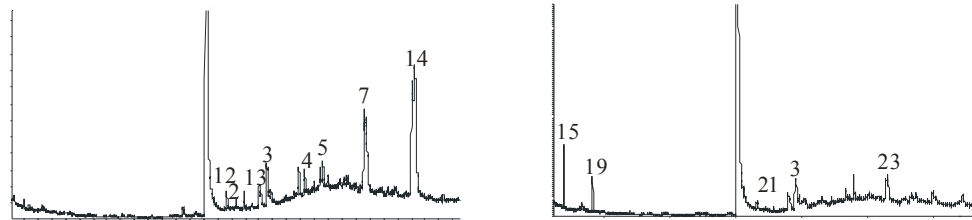
10 % CH₄ (Gujer and Zehnder, 1983). A set of BMP bottles were run specifically to determine whether biodegradability of treated samples increased but carbon was converted to CO₂ rather than CH₄. These BMP tests were performed on treated and untreated leachate samples. CO₂ production and DOC were measured in addition to CH₄ production. Five BMP replicates for treated and five for untreated were conducted on the 1988 sample. CH₄%, CO₂%, and DOC samples were taken almost every 14 days for a duration of 70 days. Results from this test show that there was no significant difference in the CO₂ % to CH₄ % ratio in the gas produced from samples before and after oxidation. The average value of CO₂ % to CH₄ % actually decreased after treatment (0.67 for the untreated and 0.61 for the treated samples). Also the DOC of solutions in BMP bottles did not decrease significantly during the tests. In the untreated samples DOC was 60.5 mg/l at day 1 and 60.9 mg/l at day 70. For the treated samples DOC was 46.9 mg/l at day 1 and 35.8 mg/l at day 70. The DOC in benzoic acid BMP bottles, however, decreased from 62 to 11 mg/l. Both of these observations suggest that the organic byproducts in treated leachate are not anaerobically biodegradable.

TMAH Thermochemolysis Analysis

Figure 4.4 show the total ion current (TIC) profile of TMAH thermochemolysis products from untreated leachate samples and Fenton treated samples. Table 4.5 lists the products identified by TMAH thermochemolysis. Despite the rather large amounts used, all identified products were present in trace amounts although this analysis did not permit quantification of products. Many alkylated siloxane compounds are seen in several profiles that are produced from column degradation as a result from the harsh analysis reagents used (peaks 6, 12, 15, 19, 21, 22).

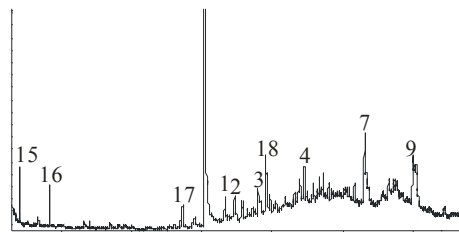
Although replicate samples were run, GC profiles were not identical, which is an indication of the high level of heterogeneity in the sample matrix. Even though differences exist among the three untreated leachate samples, the variability makes it difficult to come to any conclusions regarding organic matter composition as a function of leachate age. However, treatment of the whole leachate does seem to result in a decrease in observed compounds originating in the leachate (more column degradation alkylated siloxane peaks are observed in the treated samples than the untreated).

The compounds that may originate from the dissolved organic matter in the leachate can be classified into four groups: fatty acids (FA), resin acids (RA), alkanes and alkenes (ALK), and organic contaminants (OC). Fatty acids (compounds 1, 2, 3, 10, 11 and 17) are indicative of microbial activity and it is no surprise that they are present to some degree in the untreated leachate samples. Hexadecanoic acid, 2-hydroxy methyl ester (3) is present in almost all samples, octadecadienoic acid (1,2) was found in some untreated samples and ocatnoic acid (11) was found in one of the Fenton treated sample. Contrary to expectations an increase in the low molecular weight organic acids was not observed here. Charged organic oxidation byproducts (such as short organic acids discussed here) usually have a high adsorption affinity to precipitating iron particles (DeLuca at al., 1983).

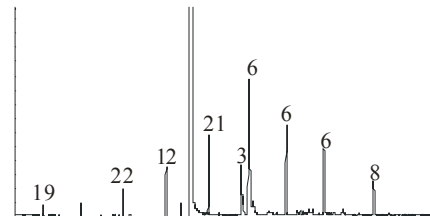


(a)

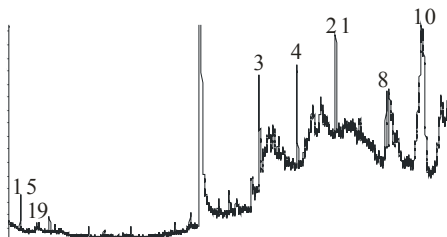
(d)



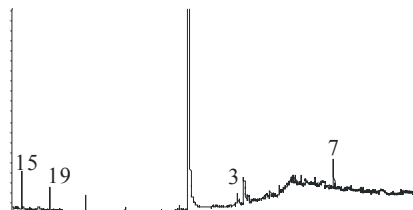
(b)



(e)



(c)



(f)

Figure 4.4. Thermochemolysis GCMS total ion current profile of untreated 1988, 1995, and 1999 leachate samples (a, b, and c respectively) and Fenton's reagent treated 1988, 1995, and 1999 leachate samples (d, e, and f respectively).

Table 4.5: TMAH Thermochemolysis products

Peak	Compounds identified
1	8,11-octadecadienoic acid, methyl ester
2	7-octadecadienoic acid, methyl ester
3	Hexadecanoic acid, 2- hydroxy methyl ester
4	Phenanthrene-1-carboxylic acid 1,2,3,4,4a,9,10,10a-octahydro-1, 4a- dimethyl-7-(1- methylethyl)-, methyl ester,[1R-[1.alpha,4a beta, 10a.alpha]]-(dehydroabiatic acid)
5	1-Nonadecene
6	Cyclononasiloxane, octadecamethyl-
7	Bis(2- ethylhexyl) phthalate-
8	Benzoic acid, 2,5 -bis(trimethylsiloxy)- trimethylsilyl ester
9	Methylene-bis(N,N-diethyldithiocarbamate)
10	Hexadecanoic acid, 2-pentadecyl-1,3-dioxan-5yl ester, cis
11	Octanoic acid, 2-methyl, methyl ester
12	Cyclodecasiloxane, eicosamethyl
13	9-octadecanone
14	Benzenamine, N-[1-(dimethoxymethyl)-2-methylpropylidene]-
15	Cyclohexasiloxane dodecamethyl
16	carbamodithoic acid, diethyl-, methyl ester
17	Hexadecanoic acid, methyl ester
18	1-Octadecene
19	Cycloheptasiloxane, tetradecamethyl
20	Benzeneacetic acid, alpha., 3,4-tris((trimethylsilyloxy)- trimethylsilyl ester
21	Cyclopentasiloxane, decamethyl
22	Cyclohexasiloxane, dodecamethyl
23	1-Phenanthrene carboxylic acid 1,2,3,4,4a,4b,5,9,10-decahydro-1, 4a- dimethyl-7-
24	(1- methylethyl)-, methyl ester,[1R-[1.alpha,4a beta, 10a.alpha]]-
25	2,6,10,14,18,22-tetracosahexane, 2,6,10,15,19,23-hexamethyl

In Batarseh (2006) it was reported that of the total organic content removed by Fenton's reagent, 70 % was removed by precipitation in similar leachate samples. These two facts suggest that although low molecular weight organic acids may have been produced by oxidation, these acids were most likely removed by coagulation and do not contribute to biodegradability increase of leachate.

Resin acids (4, 23) result from paper products either as inherently present in the wood used to produce the paper or added as an oil sizing agent to provide paper with specific properties that make it amenable for printing. Dehydroabietic acid is found in fresh wood and is also a degradation product of abietic acid, another prominent resin acid found in woods. The origin of dehydroabietic acid is probably from leaching of newsprint and the microbial degradation of abietic acid. Dehydroabietic acid was detected four times in untreated replicates and only once in treated samples, demonstrating a reduction but not a complete removal of this compound after Fenton's reagent treatment. It has been reported in previous studies that resin acids are recalcitrant and are even toxic to anaerobic bacteria, specifically methanogens (Chen et al., 2004). Aerobic biodegradation however, was reported to have high capabilities for resin acids reduction to non-detectable levels (Liver and Hall, 1996). The resin acids (identified in this study) contain three rings and a carboxyl group (Chen et al., 2004). Therefore it can be concluded that the presence of resin acids in treated leachate is one of the reasons that treated leachate is more aerobically biodegradable than anaerobically.

A few alkanes and alkenes (5, 13, 18, 24) were detected in the untreated leachate samples and were absent in the treated samples. These alkanes and alkenes are possibly related to degradation of lignin (Amirta et al., 2003) and also may be related to decomposition of lipids (Moucawi et al., 1981). Lipids in landfills come from both soil organic matter and solid waste. However, compound #24(1-methylethyl)-, methyl ester, [1R-[1.alpha.,4a.beta.,10a.alpha.]] has antifungal properties and may result from disposal of antifungal materials (need ref). This observed removal of these

nonbiodegradable, and in the case of compound #24, toxic compounds may have contributed to the slight biodegradability increase.

Of the organic compounds (7, 9, 14, 16, 25), bis (2-ethylhexyl) phthalate (7) is seen in many of the samples, both untreated and treated. This compound is widely used in plastics and is always detected in trace amounts in any GC/MS profile, regardless of the origin of the sample. For example, it leaches from plastic pipette tips and it is nearly impossible to conduct GC/MS analysis without finding it in trace amounts. Methylene-bis(N,N-diethyldithiocarbamate) (9) is used in industry as lubricating oil additives (Szoboszlay, 1995). They are also used as collection reagents for gold from mines and Pd from industrial waste (Jain, 2003; Fan et al., 2001; Mendoza et al., 1997). Six-methoxy-8-nitro-5-[4-trifluoromethoxy] quinoline (25) is related to antimalarial drugs (Nodiff et al., 1982). Carbamodithioic acid, diethyl, methyl ester (16) has been used as a nematocide (Hodogaya Chemical Co., 1982) and herbicide (Konecny et al., 1971). Again these compounds were observed less frequently in treated samples (once in treated samples and six in the untreated samples), indicating reduction but not complete removal. These xenobiotic compounds are made to be resistant to biodegradation to be able to perform their intended purpose. The slight increase in biodegradability may be attributed partially to the removal of these compounds.

Summary and Conclusions

Using Fenton's reagent with the objective of improving biodegradability of mature leachate may not always be successful. For mature leachate with BOD₅/COD below 0.1, using Fenton's reagent before an anaerobic biological process will remove organic carbon from leachate more than improving its biodegradability. If Fenton's

reagent was used on the same mature leachate but prior to an aerobic biological process, then in addition to the removal of organic carbon, an increase in the rate of aerobic biodegradation for the treated leachate will occur, reducing size and air requirements of the aerobic treatment process.

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CHAPTER 5

REDUCING LONG-TERM ORGANIC CONTENT OF LANDFILL LEACHATE BY FENTON'S REAGENT TREATMENT

Introduction

The majority of leachable organic carbon in landfilled solid waste is biodegradable and can be removed by biological processes, which can be accelerated by operating a landfill as a bioreactor. However, as landfills mature, organic content of solid waste is enriched with compounds that are nonbiodegradable by nature (Kjeldsen et al., 2002). Hazardous household wastes such as paints, solvents, motor oils, cleaning compounds, degreasing compounds, pesticides and illegally disposed wastes contribute to this nonbiodegradable source of carbon in landfills (Reinhart, 1989). These substances are referred to as xenobiotic (foreign to the biosphere) organic compounds. Another source of nonbiodegradable carbon in landfills is humic substances. Humic substances are divided into three categories; base soluble and acid insoluble humic acid, acid and base soluble fulvic acid, and insoluble humin (MacCarthy, 2001). These organic substances are products of microbial degradation of waste and remain in landfills because microorganisms are unable to further degrade them.

Flushing bioreactor landfills have been introduced as a method for the rapid removal of these organic compounds from landfill cells because they could have long-term environmental impacts potentially lasting for centuries (IWM, 1999; Cossu et al., 2003). In the flushing bioreactor, large amounts of water are needed to completely

remove the releasable carbon from the solid waste. A modification of the flushing bioreactor landfill is suggested here, which could be called a pump and treat flushing bioreactor landfill. This suggested method is recommended to be applied as a post bioreactor landfill treatment step with the objective of producing stable solid waste cells. This method uses leachate indigenous to the landfill cell as the flushing media as apposed to using clean water. As leachate is flushed, it is chemically treated outside the cell, and subsequently pumped back into the cell to transport more of the releasable carbon, as can be seen in Figure 5.1. Additional carbon could be removed from the landfill cell by aerobic biodegradation if air is injected into landfill. Aeration of old landfill cells has been used in Europe with the objective of producing stable landfill cells significantly faster than anaerobic methods (Ritzkowski et al., 2006).

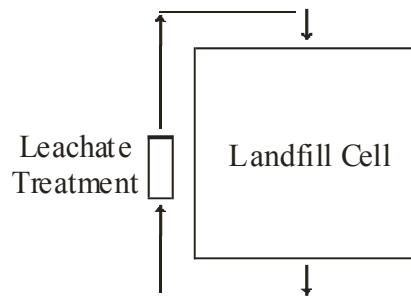


Figure 5.1 Pump and treat flushing bioreactor landfill

Fenton's reagent is proposed as the leachate treatment method outside the landfill cell. Fenton's reagent has been shown to remove organic matter from mature leachate by chemical and physical means in addition to increasing the biochemical oxygen demand/chemical oxygen demand (BOD₅/COD) ratio of leachate (Batarseh, 2006; Zhang et al., 2006; Lopez et al., 2004).

In this work, aerobic solid waste microcosms were utilized to estimate the rate of carbon removal (as CO₂) from mature solid waste mixed with Fenton's reagent treated leachate. These microcosms were also used to evaluate any effect that Fenton's reagent might have on microbial processes in landfills. Aerobic systems were evaluated because Fenton's reagent had improved the aerobic biodegradability of treated leachate and not the anaerobic biodegradability (Batarseh, 2006). To evaluate the feasibility of this approach a comparison of treatment time and cost among flushing with clean water, flushing with on-site treated leachate, and flushing with on-site treated leachate combined with aeration was performed using simplified mass balance calculations. These calculations were based on three carbon removal mechanisms which are aerobic biological carbon removal rate from the solid waste (obtained from this experiment), carbon removal percentage by Fenton's reagent (Batarseh, 2006), and biological removal of oxidized carbon (Batarseh, 2006).

Fenton's Reagent Chemistry

The main active component in Fenton's reagent (discovered by Fenton in 1894) is the hydroxyl free radical (HO•) (Walling, 1975). HO• is one of the strongest oxidizing agents known, having an electrochemical oxidation potential of 2.73 V under acidic environments (Pignatello et al., 2006). In Fenton's reagent, iron ions react with hydrogen peroxide in a series of reactions shown in Equations 5.1-5.7 (Pignatello et al., 2006). These reactions produce HO•, which then reacts with organic compounds.





Reactions of HO^\bullet with organic compounds are known to be second order with rate constants ranging between 10^7 and $10^{10} \text{ l mol}^{-1} \cdot \text{sec}^{-1}$ (Pignatello et al., 2006). Fenton's reagent also produces ferric ions which promotes precipitation by ferric hydroxides. Therefore, organic substances are removed by a combination of oxidation and precipitation in Fenton's reagent treatment.

Materials and Methods

Five-liter gas sampling bags (SKC, Inc., Pennsylvania) were used to evaluate impacts of chemical oxidation on biological degradation of leachate and solid waste after using Fenton's reagent and to estimate aerobic biodegradation rate (CO_2 production rate) of mature solid waste. These bags had gas sampling ports and were modified to allow for solid and liquid phase sampling. Each reactor was loaded with 200 g of wet digested solid waste (described below) and 200 ml of leachate (described below) leaving 4.5 L of head space. Head space air was replaced with every sampling event to ensure an aerobic environment in the bags. Incubation temperature was 35°C and bags were continuously shaken. A shaker table was modified to ensure that bags were not touching to avoid pressurizing head space. Reactors were seeded with 5 ml of BOD seed (Hach, Colorado) at the time of loading except for the abiotic control reactor (solid waste and leachate autoclaved for two hours). Produced CO_2 as well as CH_4 and O_2 were measured in the gas phase using a Shimadzu – 14 GC equipped with thermal conductivity detector (TCD)

and a Carboxyn column. The temperature was held at 20°C for 5 minutes then raised to 225°C at a rate of 20°C per minute. The dissolved organic carbon (DOC) of the leachate in the reactors was measured using a UV persulfate Phoenix total organic carbon (TOC) analyzer. Fenton reagent was added to leachate before it was introduced to the reactors using a dose of 1 g H₂O₂ per 1 g COD, a Fe to H₂O₂ ratio of 0.4, and a pH of 4 (pH of treated leachate was brought back to 7 using NaOH before addition to the microcosms). Selected oxidation dose and conditions were determined from previous experiments on similar leachate (Batarseh, 2006).

Leachate Characterization

Leachate was collected from a Florida landfill that had an older, lined cell (waste was approximately 18 years old). Samples were obtained from a leachate collection system manhole and kept in one-L amber glass bottles with no headspace at 4°C until used. Samples collected were tested for COD, DOC, BOD₅, ammonia, and chloride (Table 5.1) according to Standard Methods (1998).

Table 5.1. Characteristics of leachate sample

<i>Waste Age(yrs)</i>	<i>Cl- (mg/l)</i>	<i>NH3 (mgN/l)</i>	<i>DOC (mg/l)</i>	<i>BOD₅ (mg/l)</i>	<i>COD (mg/l)</i>	<i>BOD/COD</i>
18	2630	1240	1009	51	2019	0.020

Mature Solid Waste

Digested solid waste samples were collected from the Sumter County (Florida) solid waste composting facility. Sumter County operates a materials recovery process to remove plastic containers, paper, metal, glass before composting the remaining solid waste in an aerobic vessel (typical waste composition given in Table 5.2). Stabilized

wastewater treatment plant biosolids are added at one part biosolids to four parts solid waste.

Table 5.2 Typical waste composition

<i>Waste Constituent</i>	<i>% Composition by weight</i>
Paper	22
Plastics	8
Textile	2
Food Waste	5
Yard Waste	9
Glass	3
Metal	15
Construction and Demolition Debris	25
Other	11

The mixture remains in the vessel for 72 hours and is then stored outside for approximately one year. A sample collected from the holding area was placed in a 50-L drum, which was designed to permit leachate drainage and air addition. Water was flushed through this reactor to remove the releasable carbon (Figure 5.2). Wood chips were added to solid waste (1g wood chips per g digested solid waste) to improve leachate flow through the reactor. The produced solid waste was assumed to be similar to solid waste after treatment in a bioreactor landfill.

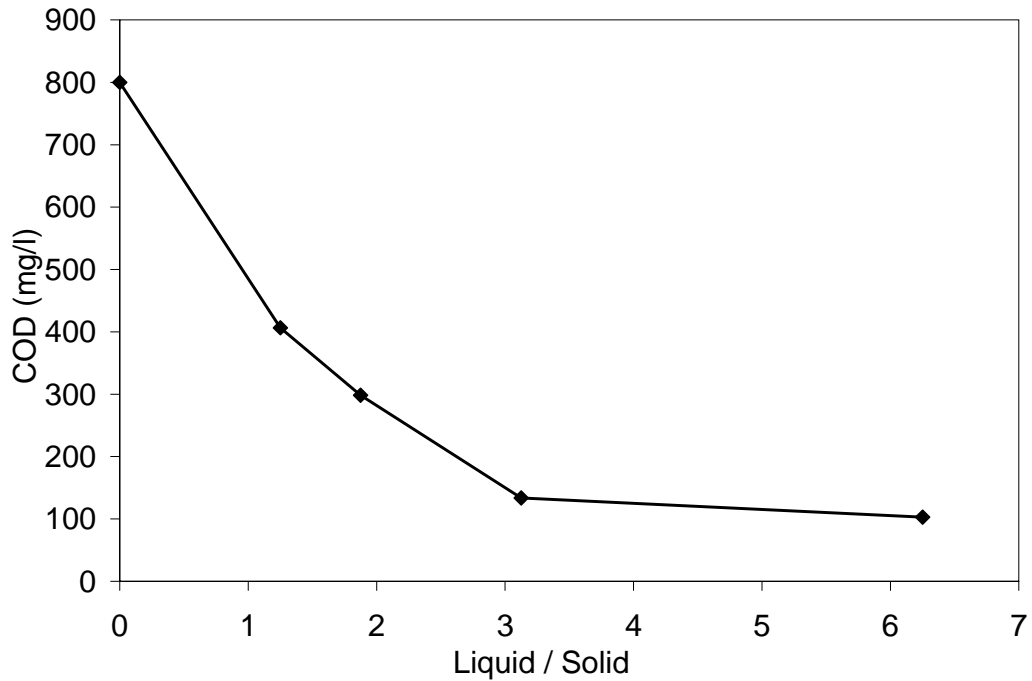


Figure 5.2 Impact of flushing on leachate COD

Microcosm Results

Cumulative CO₂ (as C) generated by the treated and untreated solid waste reactors is plotted in Figure 5.3 along with the carbon mass in the leachate in each reactor. The stable production of CO₂ gas compared to a constant dissolved organic carbon suggested that the dissolved carbon is in dynamic equilibrium with solid carbon. In an abiotic control reactor containing autoclaved solid waste and leachate, microbial activity was not totally stopped but was significantly reduced. Produced CO₂ in the abiotic reactor was almost half the biotic reactor (22.1 mg C/d compared to 40.7 mg C/d).

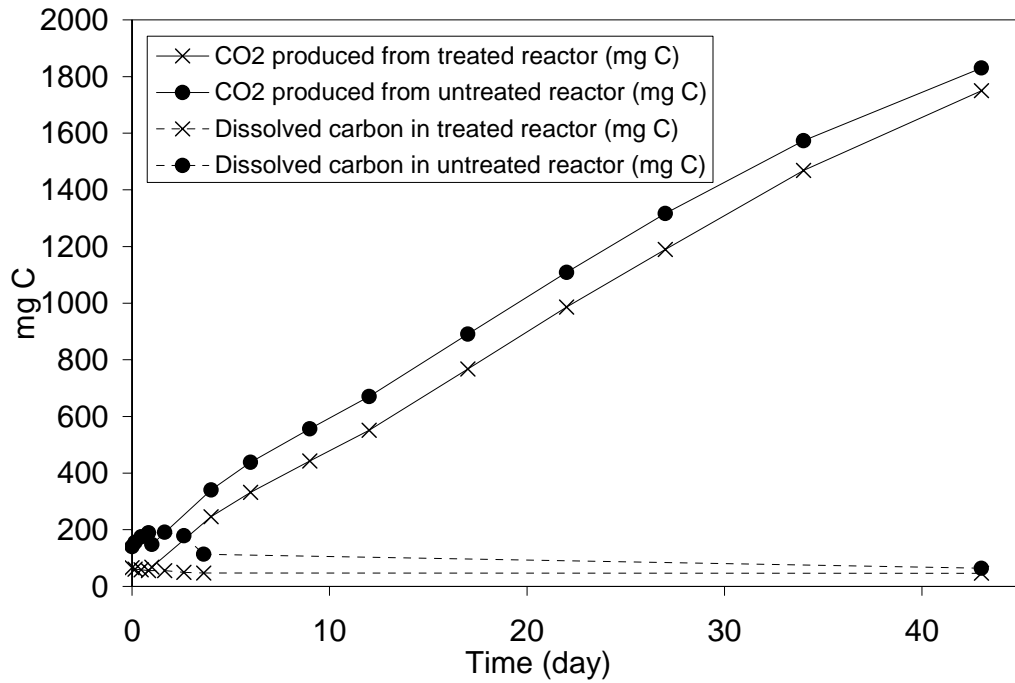


Figure 5.3. DOC and net CO₂ mass production from digested solid waste reactors containing treated and untreated leachate samples. (1 g H₂O₂ to g COD, Fe to H₂O₂ ratio of 0.4, and a pH of 4 was used for treatment)

The aerobic biodegradation rate, appeared to be first order with respect to time as presented in Figure 5.4 ($r^2=0.7$). C_o in Figure 5.4 was assumed to be 0.0165 of the total dry solid waste weight. This assumption is described in more details below. The rate constant (0.03 day^{-1}) is used in the mass balance calculations presented below to determine the effect of aeration on treatment.

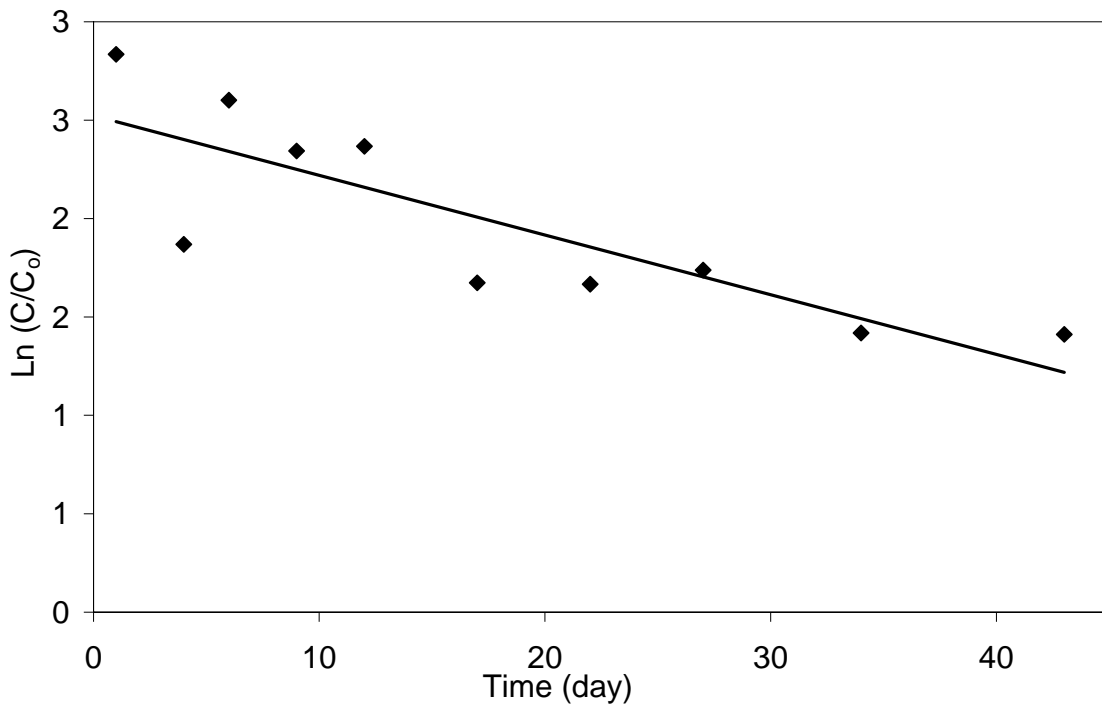


Figure 5.4. Carbon removal from treated leachate reactor fitted to first order removal rate

Mathematical Model for Three Treatment Scenarios

To investigate the potential advantages of pump and treat treatment combined with landfill aeration, carbon mass balances have been conducted for three scenarios; flushing with clean water, flushing with on-site treated leachate, and flushing with on-site treated leachate combined with in-situ aeration. The mass balance calculations were used to determine the mass of the remaining releasable carbon as a function of treatment time. This information was used to estimate the liquid/solid (L/S) mass ratio required to reduce the mass of releasable organic content from landfill cells three orders of magnitude. Additionally, treatment time and cost were estimated.

Assumptions

In order to evaluate the concept of the pump and treat flushing aerobic bioreactor landfill, a simplified model was developed which required numerous assumptions. The organic carbon in the solid waste is assumed to be completely dissolved in the leachate that is in the post bioreactor landfill which overstates the available carbon because (1) not all of the carbon will actually dissolve and (2) dissolution will be controlled by mass transfer kinetics and will not be constant over time. Further, this assumption may underestimate the time required for all the releasable carbon to leach out due to nonhomogenous wetting of the cell. The aerobic degradation of the solid waste is assumed to be constant over time; however, degradation rates may decline as material becomes less available to microorganisms. In addition, the landfill cell was assumed to be completely mixed. This assumption has also been used before in landfill flushing studies and has been reported to correlate reasonably well with the actual behavior of landfills (IWM, 1999). In the pump and treat flushing bioreactor landfill no leachate is removed or added from outside the system. Also, it was assumed that liquid moves at a rate equal to the waste hydraulic conductivity, and that this rate remains constant over time, and that it will not be impacted by particulates produced from Fenton's reagent treatment.

Case 1 Flushing with Clean Water

In flushing bioreactors clean water is pumped into the landfill cell and is subsequently collected for treatment as described in Figure 5.5. The change in releasable carbon leachate concentration (C) with time can be described by Equations 5.8 to 5.12

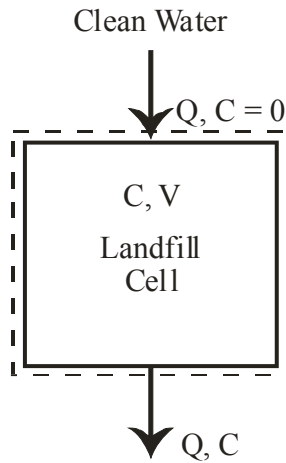


Figure 5.5 Schematic for flushing bioreactor landfill with clean water

$$V \frac{dC}{dt} = -CQ \quad (5.8)$$

$$\int_{C_o}^C \frac{dC}{C} = -\frac{Q}{V} \int_0^t dt \quad (5.9)$$

$$\ln \frac{C}{C_o} = -\frac{Qt}{V} \quad (5.10)$$

$$\Rightarrow C = C_o e^{-\frac{Qt}{V}} \quad (5.11)$$

$$\text{where } \frac{Qt}{V} = BV \quad (5.12)$$

Q is the recirculation rate of liquid, V is the total volume of water recirculated, t is time of treatment, BV is the number of bed volumes, and C_o is the initial carbon concentration in leachate at time zero.

Case 2 Pump and Treat Anaerobic Flushing Bioreactor Landfill

The pump and treat anaerobic flushing bioreactor landfill provides onsite treatment of recirculated leachate using Fenton's reagent then uses this treated leachate to

flush the landfill cell (Figure 5.6). Therefore, the need for clean water from an external source will be eliminated.

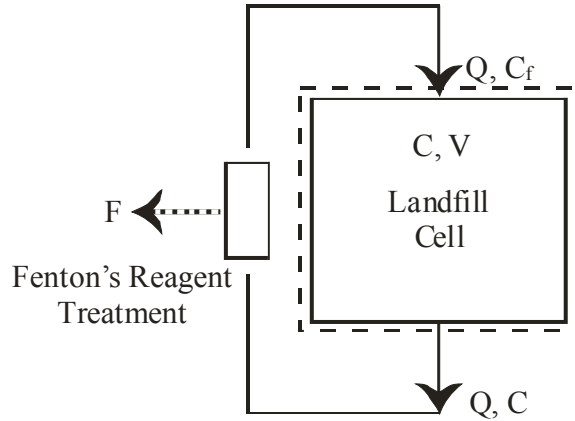


Figure 5.6 Schematic for flushing with on-site treated leachate

The change in releasable carbon leachate concentration (C) with time can be described by Equations 5.13 to 5.19.

$$V \frac{dc}{dt} = C_f Q - C Q \quad (5.13)$$

where: C_f is the concentration of carbon in leachate after Fenton's reagent treatment and is equal to $0.7 C$ and F is the carbon mass removal rate during Fenton's reagent treatment.

This removal efficiency is obtained from batch reactor studies performed on similar leachate samples (Batarseh, 2006). Therefore:

$$V \frac{dC}{dt} = 0.3 C Q - C Q \quad (5.14)$$

$$\frac{dC}{dt} = -0.7 \frac{C Q}{V} \quad (5.15)$$

$$\int_{C_o}^C \frac{dC}{C} = -0.7 \frac{Q}{V} \int_0^t dt \quad (5.16)$$

$$\ln \frac{C}{C_o} = -0.7 \frac{Qt}{V} \quad (5.17)$$

$$\Rightarrow C = C_o e^{-0.7BV} \quad (5.18)$$

$$\text{where } \frac{Qt}{V} = BV \quad (5.19)$$

Case 3 Pump and Treat Aerobic Flushing Bioreactor Landfill

Experimental tests showed that both leachate and solid waste continue to degrade aerobically in mature solid waste. In-situ aeration of the landfill cell therefore, may reduce the time and cost of treatment significantly compared to flushing without treatment or aeration as shown in Figure 5.7.

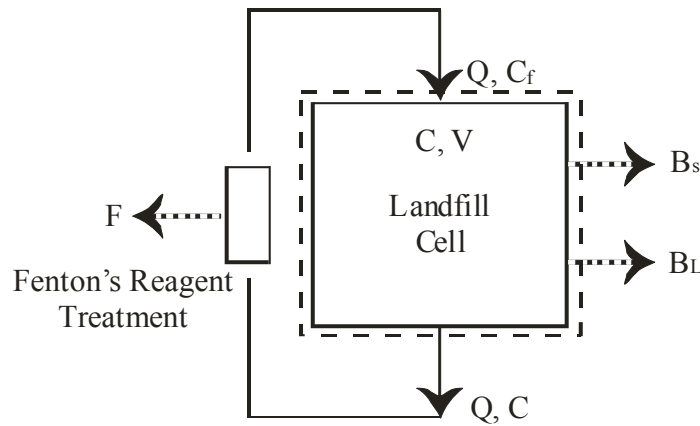


Figure 5.7 Schematic for flushing with on-site treated leachate combined with aeration

The change in releasable carbon leachate concentration (C) with time can be described by Equations 5.20 to 5.29.

$$V \frac{dC}{dt} = QC_f - B_s - B_L - CQ \quad (5.20)$$

B_s is the rate of mass removal from the solid waste by aerobic biological degradation and is estimated based on the degradation rate obtained from microcosms. B_L is the rate of

mass removal by aerobic degradation of the oxidized leachate dissolved organic carbon that was converted to biodegradable carbon. B_L was determined to be 0.15 of C_fQ from BOD experiments on similar treated leachate samples (Batsrseh, 2006). Therefore:

$$C_f = 0.3C \quad (5.21)$$

$$B_s = kCV \quad (5.22)$$

$$B_L = 0.045CQ \quad (5.23)$$

$$V \frac{dC}{dt} = 0.3CQ - kCV - 0.045CQ - CQ \quad (5.24)$$

$$\frac{dC}{dt} = -0.745C \frac{Q}{V} - kC \quad (5.25)$$

$$\int_{C_o}^C \frac{dC}{(-0.745 \frac{Q}{V} - k)C} = \int_0^t dt \quad (5.26)$$

$$\frac{1}{(-0.745 \frac{Q}{V} - k)} \ln \frac{C}{C_o} = t \quad (5.27)$$

$$\ln \frac{C}{C_o} = -0.745 \frac{Qt}{V} - kt \quad (5.28)$$

$$\Rightarrow C = C_o e^{-0.745BV - kt} \quad (5.29)$$

where $\frac{Qt}{V} = BV$

Input Parameters

Typical properties of bioreactor landfills were obtained from a practice review of bioreactor/recirculation landfills (Benson et al., 2006), where properties of five landfills

operating as bioreactors across the US were described. Some input parameters were obtained from other sources as discussed below. All input parameters and their sources are summarized in Table 5.3.

Table 5.3 Input parameters used in calculations

Parameter	Picked Value
Depth of Solid Waste (m) ^a	26.4
Hydraulic Conductivity (cm/sec) ^b	1×10^{-4}
Releasable Carbon in degraded waste (% mg C/mg dry waste) ^c	1.65
Solid waste dry weight (ton) ^a	1110000
Volume of water (m ³) ^a	740000
Oxidation removal from leachate (%) ^d	70
Leachate aerobic biological removal(%) ^d	15
Solid waste aerobic biodegradation rate constant (day ⁻¹) ^e	0.03

Adopted from Benson et al. (2006)^a, Jain et al. (2006)^b Barlaz et al. (1989)^c Batarseh (2006)^d, and Figure 5.4^e

Releasable Carbon

This value represents the amount of carbon that can be released by flushing from a bioreactor landfill after biodegradable material is largely removed anaerobically. The majority of this releasable carbon after bioreactor operation should be humic substances, xenobiotic organic compounds, and lignin, which do not degrade under anaerobic environments (Kolilis and Ham, 2003). The releasable carbon per dry weight of refuse was assumed to be equal to the organic carbon content of dry waste mass measured after anaerobic biodegradation. This value was measured after 90 to 111 days by Barlaz et al. (1989) to be 0.015 to 0.018 mg C/mg dry waste(0.0165 was picked). This value represent the total organic carbon content of treated solid waste which is assumed to be completely releasable, a conservative estimate.

Solid Waste Dry Weight

The dry weight of solid waste was calculated from an average volume of waste and a dry specific weight value of 0.43 metric ton/m³ (Tchobanoglous et al., 1993). The volume of total solid waste in the landfill cell was calculated from an average area of solid waste cells and average thickness described in Benson et al. (2006). The average area was 97600 m² (9.76 ha) and the average depth was 26.4 m, resulting in a total solid waste dry weight of approximately 1,110,000 metric tons of waste.

Volume of Water

The volume of water (740000 m³) was calculated assuming a moisture content of 40% and using the solid waste dry weight calculated above. This water volume is the amount that will be introduced per flush, or the bed volume.

Oxidation and Biological Removal Efficiencies

An oxidation removal efficiency of 70% was used. This oxidation removal efficiency was determined from Fenton's reagent optimization experiments performed on mature leachate samples (Batarseh, 2006). The recommended oxidation conditions were a pH range of 3-5 and a 1.0 g H₂O₂ per g COD dose with a molar ratio of 0.4 Fe⁺² to H₂O₂ and a time of reaction of at least 15 minutes. The biological removal efficiency is related to the aerobic biological degradation of treated leachate. The biochemical oxygen demand as Carbon / dissolved organic carbon (BOD_{asC}/DOC) was increased from almost zero to 0.15 after oxidation of similar leachate samples (Batarseh, 2006), indicating that 15% of the organic carbon remaining after Fenton's reagent is aerobically biodegradable.

Results of Mathematical Model

Equations 5.11, 5.18, and 5.29 were used to determine the remaining carbon mass as a function of L/S (Figure 5.8). Flushing with on-site treated leachate combined with aeration was the most effective scenario. Carbon removal when flushing with clean water was observed to require lower L/S than when flushing with treated leachate because clean water is able to remove more carbon per flush than treated leachate. It is important to note however, that although flushing with clean water requires a lower L/S, the total liquid volume required by clean water flushing is significantly more than the on-site treated leachate option because the same leachate can be used over and over in the latter case.

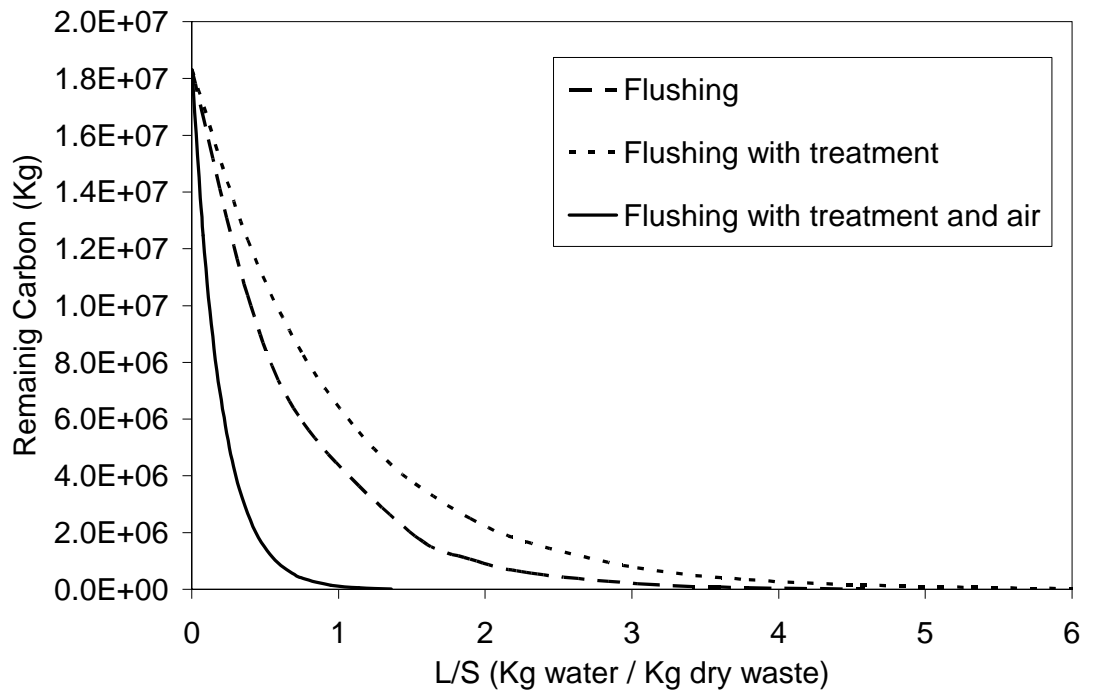


Figure 5.8 Remaining carbon mass in treated cell versus L/S

Treatment time to reduce the remaining carbon mass by three orders of magnitude (from approximately 18000 to 18 metric tons) using the three treatment scenarios is presented in Figure 5.9. The intersection point with the x axis of the lines in Figure 5.9 provides the treatment time for that treatment scenario. Aeration of landfill cell was found to significantly decrease the time requirements to achieve landfill stabilization. Out of the total organic carbon removed in the flushing with on-site treated leachate combined with aeration system, 76 % was removed by Fenton's reagent, 22 % was removed by aerobic solid waste decomposition, and 2 % was removed by aerobic decomposition of oxidized leachate. Aeration was not the major removal mechanism; however it significantly reduced treatment time by reducing the tailing effects of flushing. Tailing is one of the limitations of any pump and treat system and is expected to be exacerbated by heterogeneity (Nyer et al., 2001) typical of landfills.

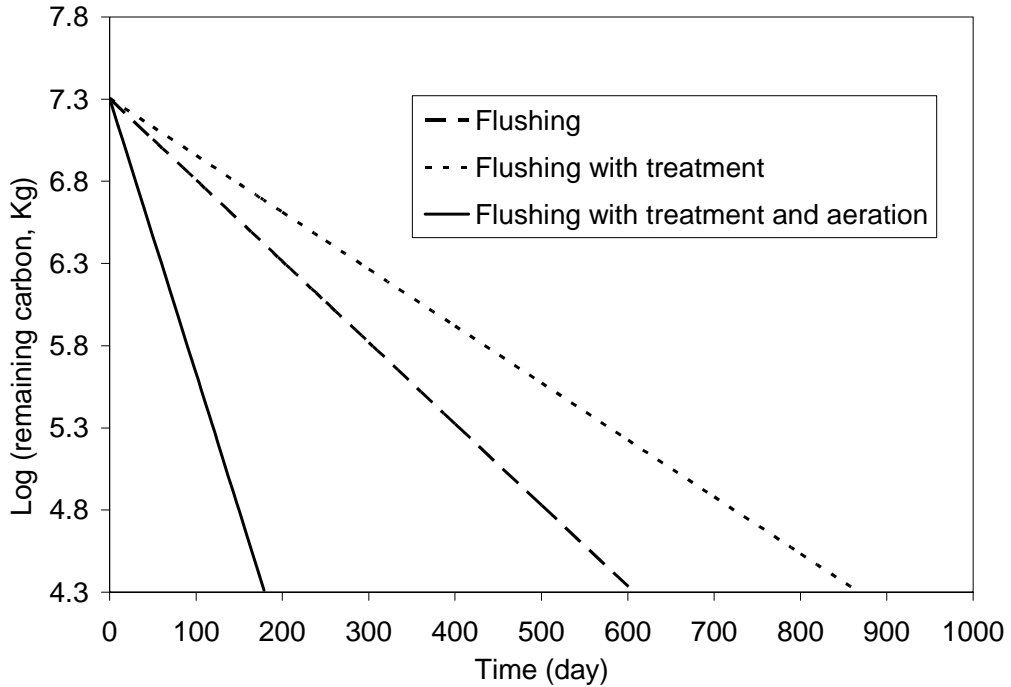


Figure 5.9 Treatment time to reduce the mass of remaining carbon by three orders of magnitude.

Costs Analysis

Because the demand for Fenton's reagents is a function of TOC concentration, an equation was developed to determine the cost of Fenton's reagent treatment (Equation 5.11) based on the molar ratios of H_2O_2 and Fe^{2+} to organic carbon required for treatment. These costs provide for all facilities and to add reagents and remove any solids generated.

$$C\left(\frac{\$}{l}\right) = \left\{ ([TOC] \times \left(\frac{[H_2O_2]}{[TOC]} \times \frac{\$}{mole H_2O_2} + \frac{[Fe^{2+}]}{[TOC]} \times \frac{\$}{mole Fe^{2+}} \right) \right\} + Z \quad (5.11)$$

Where: Z accounts for construction, electricity, and miscellaneous chemical costs from Choi (1998). After adjustment to present day value using an inflation rate of 3%, Z is \$0.0045/L. $[H_2O_2]/[TOC]$ equals to 0.93 (for every mole of carbon to be treated 0.93 moles of H_2O_2 is required) and $[Fe^{2+}]/[TOC]$ equal to 0.37 (for every mole of carbon to

be treated 0.37 moles of Fe^{2+} is required) to achieve the recommended 1g H_2O_2 per g COD dose and 0.4 moles of Fe^{2+} per mole H_2O_2 . Current market prices of H_2O_2 and FeCl_2 were obtained from PVS Technologies (New Berlin, New York). The cost of ferrous chloride (25%) was \$0.38/gal and the cost of H_2O_2 (35%) was \$2.25/gal (\$0.051/mole H_2O_2 and \$0.042/mole Fe^{2+}). The cost of Fenton's reagent treatment depends on the concentration of organic carbon in leachate to be treated, which is a time dependent value (Figure 5.8). To illustrate, the cost of leachate treatment using Fenton's reagent for Case 3 was calculated and plotted versus time in Figure 5.10. Cost used for leachate treatment in clean water flushing was 5.8 cents per liter (\$0.22/gal) and was obtained from (Berge, 2006) as an average value for ex-situ leachate treatment.

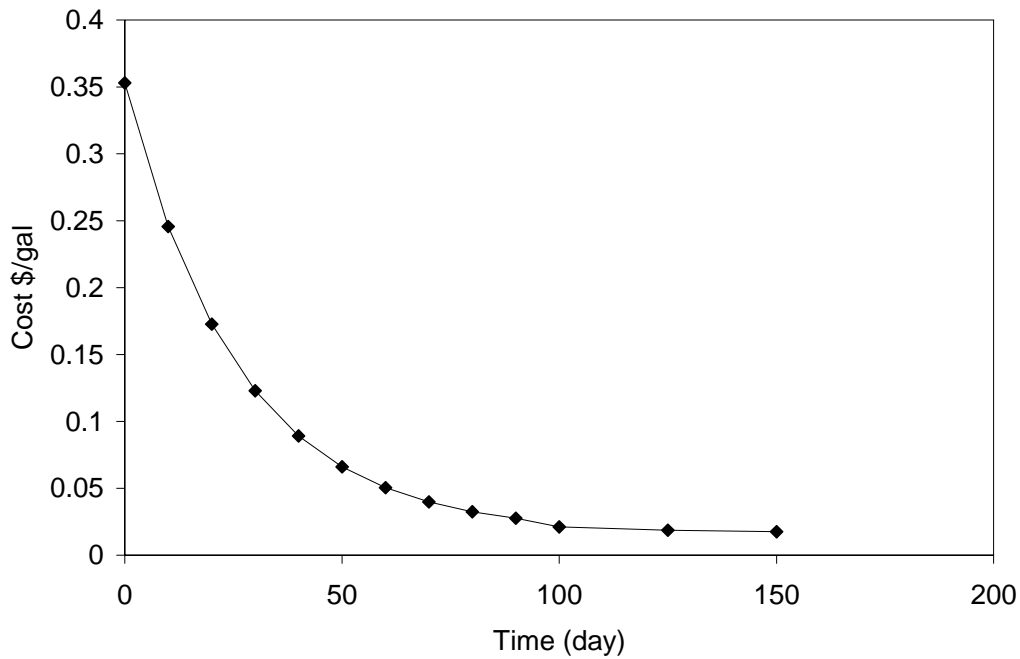


Figure 5.10 Cost of leachate treatment versus time for the aerobic flushing bioreactor using onsite treated leachate.

The total cost of treatment for each of the three cases is presented in Table 5.4, including air injection costs for Case 3 (Reinhart et al. 2006). The lowest treatment cost was the pump and treat with aeration (Case 3). In this case, the treatment cost per metric ton of landfilled waste is \$23, which represents 50 – 75 % of typical US landfill tipping fees. This cost may appear high however when compared to other alternatives for producing completely stable cells such as the ones presented here (cases 1 and 2), mechanical, biological and/or thermal pretreatment methods that are mandatory in the EU, or environmental impairment due to leachate or gas emissions, the cost compares favorably. Another potential benefit of Case 3 is ammonia removal. Ammonia accumulates in traditional and bioreactor landfills because there is no degradation pathway for ammonia in anaerobic systems and also poses significant long-term environmental risk (Berge, 2006). Berge has demonstrated efficient ammonia removal during in situ aeration of mature solid waste.

Table 5.4 Cost results

Cost Item	Case 1: Flushing with clean water (\$million)	Case 2: Pump and treat with no air addition (\$million)	Case 3: Pump and treat with air addition(\$million)
Leachate treatment cost	292	165	30
Air addition cost	0	0	0.68
Total cost	292	165	30.7

Summary and Conclusions

Final disposal of MSW requires assurance that contaminant release will be minimized or prevented. This is accomplished through waste acceptance criteria such as

those established by the European Union (EU) that prohibit land disposal of untreated organic matter. In the EU, mechanical, biological and/or thermal pretreatment of MSW is therefore necessary prior to landfilling which is complicated and costly. In other parts of the world, treatment within highly engineered landfills is under development, known as bioreactor landfills. However, the completed bioreactor landfill still contains material, largely carbon and nitrogen that may be released to the environment over the long-term. This paper provides a conceptual analysis of an approach to ensure landfill sustainability by the rapid removal of these remaining materials, the pump and treat flushing aerobic bioreactor landfill.

The advantages of this concept are that it provides nearly complete removal of carbon (and potentially nitrogen) at costs that may be less than that of site remediation should release of emissions to the environment occur. Further there is reduced demand on natural resources than that of the flushing bioreactor landfill. The complete removal of releasable carbon may not always be necessary in all cases from a risk point of view depending on proximity of landfill to natural resources.

Results from the conceptual model developed in this paper are favorable in terms of reducing cost and time for producing a completely stable landfill cell. However the model used here is limited by its simplifying assumptions. In reality the hydraulic conductivity may reduce with time, carbon may require longer periods to leach out, there likely will be sites of unreleased carbon at the end of the treatment, and biodegradation will not occur through out the landfill equally. Large scale experiments and modeling are necessary to develop data that will permit rigorous analysis to account for such factors.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Highly engineered bioreactor landfills are now being developed and used to stabilize the biodegradable organic content of solid waste. However, the completed bioreactor landfill still contains material, largely carbon and nitrogen that may be released to the environment over the long-term. The goal of this dissertation was to investigate the use of combined chemical and biological treatment for stabilizing mature landfills. To achieve this goal experiments were designed to (1) select an effective oxidant and oxidation conditions (time, pH, and dose) to be used for mature leachate treatment, (2) estimate organic carbon removal by oxidation, (3) determine effects of the selected oxidant on biodegradability of leachate, and (4) estimate the aerobic biodegradation rate of mature solid waste. Results from the aforementioned laboratory experiments were used as input parameters in a conceptual model developed to investigate the feasibility of a new landfill management method which could be called a pump and treat flushing aerobic bioreactor landfill. The simple modeling approach adopted in this work utilized mass balance equations to estimate a liquid to solid ratio and time required for stabilizing a solid waste cell using one of three options (1) flushing with clean water, (2) flushing with on-site Fenton's reagent treated leachate, or (3) flushing with on-site Fenton's reagent treated leachate combined with in-situ aeration.

A literature search revealed two promising oxidants to be tested for mature leachate treatment (Fenton's reagent and ferrate). Fenton's reagent and ferrate were both effective in the removal of dissolved organic content from mature leachates. However,

using optimum conditions (pH equal to 4 and doses of 1.0 g H₂O₂ per g COD with a molar ratio of 0.4 Fe⁺² to H₂O₂) Fenton's reagent resulted in more COD and DOC removal than ferrate, and it produced more oxidized and more biodegradable organic byproducts. Therefore it was selected for use in subsequent tests.

Results also demonstrated that Fenton's reagent did not have inhibitory impacts on microbial processes in landfills, as evidenced by BMP and BOD tests. Further, if Fenton's reagent was used prior to an aerobic biological process, then in addition to the removal of organic carbon, an increase in the rate of aerobic biodegradation for the treated leachate will occur, although there was no impact on anaerobic biodegradation (probably due to the physical removal of the short organic acids, which are the oxidation byproducts that are anaerobically biodegradable). Dissolved organic carbon of mature leachate samples was converted by Fenton's reagent from almost 0 % biodegradable to 15 % biodegradable as measured by the BOD_{asC}/DOC ratio.

Results from the conceptual model developed in this dissertation for investigating the feasibility of the pump and treat flushing aerobic bioreactor landfill were favorable in terms of reducing treatment cost and time to produce a completely stable landfill cell (compared to anaerobic flushing). However, the model used in this study is limited by its simplifying assumptions. In reality, the hydraulic conductivity may reduce with time, carbon may require longer periods to leach out, there likely will be sites of unreleased carbon at the end of the treatment, and biodegradation will not occur uniformly throughout the landfill. Pilot and field scale experiments, therefore are necessary to develop data that will permit rigorous analysis to account for such factors.

An extra cost of \$23 per metric ton of waste was estimated for achieving a truly stable landfill cell using the flushing aerobic bioreactor landfill method. This cost may appear high but if compared to alternatives, such as biological, mechanical, and/or thermal pretreatment of municipal solid waste (which is mandatory in the European Union) or environmental impairment due to leachate or gas emissions the cost compare favorably.

Although the complete removal of releasable carbon from solid waste cells may not always appear necessary (depending on proximity of landfill to natural resources), there are tremendous benefits associated with waste management practices that minimize the risks of future environmental impacts. The need for landfill post-closure care should not be passed on to the next generation.

APPENDIX A

METHODS FOR ORGANIC COMPOUNDS MOLECULAR WEIGHT

DISTRIBUTION AND BIOCHEMICAL METHANE POTENTIAL

Organic Compounds Molecular Weight

Ultrafiltration was used to determine the MW distribution of dissolved organic matter. An Amicon model 8050 stirred cell, shown in Figure A.1 (D = 44.5 mm, V = 50 ml) was used with YM membranes of 1000, 10,000, 30,000, and 100,000 Dalton



Figure A.1 Amicon model 8050 stirred cell

membrane cut offs. These MW measurements were conducted in the parallel mode with a sample size of 50 ml for every membrane cut off. Membranes used in ultrafiltration are designed to keep all molecules larger than a certain size (membrane cut off) from permeating through. However this does not necessarily mean that all other smaller molecules will directly permeate through the membrane. What usually happens is that flow of the smaller molecules will be retarded due to accumulation of solute molecules at the membrane surface. To account for this phenomenon, Logan and Jiang (1990) suggested a permeation coefficient model (PCM) which is given in Equation A.1. This model is obtained from a mass balance over the pressurized ultrafiltration cell.

$$C_p = PC_{r_0} F^{p-1} \quad (\text{A.1})$$

Where,

C_p = Instantaneous solute concentration in permeate at time t

P = Permeation coefficient

C_{r_0} = the initial concentration of the solute molecules with an apparent molecular weight smaller than the membrane cutoff.

$F = 1 - (V_r/V_0)$ = the fractional reduction in retentate volume at time t

V_r = Volume of retentate at time t

V_0 = Initial volume used

The goal here is to estimate C_{r_0} for every molecular weight membrane cut off and that was done by converting Equation A.1 to the linear form shown in Equation A.2 below.

$$\ln C_p = \ln(PC_{r_0}) + (p-1) \ln F \quad (\text{A.2})$$

For a single point in a MW size distribution measurement, an array of F versus C_p was determined experimentally by running the ultrafiltration unit and measuring the permeate DOC at three V_r values (40, 30, and 20 ml). Finally, $\ln F$ and $\ln C_p$ are calculated and plotted to get a linear line with a slope equals to $(p-1)$ and an intercept equal to PC_{r_0} .

Biochemical Methane Potential

BMP was determined using the ASTM E 1196-92. In this test, samples were incubated at 35 ± 2 °C after the addition of seed (anaerobically digested sludge) and a variety of nutrients and other chemicals to optimize microbial growth in 250-ml gas-tight bottles. Seed source used was anaerobically digested sludge obtained from an anerobic digester and stored for no longer that 10 days in a reactor incubated at 35 °C as shown in figure A.2.



Figure A.2 Anaerobic seed reactor inside incubator

Anaerobic media was prepared under nitrogen gas flushing to maintain a reduced environment and was transferred to test bottles using a bench scale pump under nitrogen gas flushing as shown in Figure A.3.

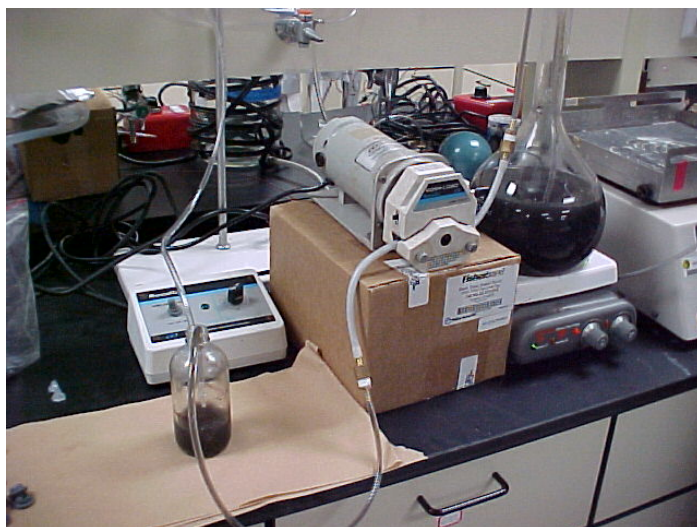


Figure A.3 Transfer of media to test bottles under nitrogen gas flushing

Test bottles were placed in an incubator for eight weeks or until biodegradation of the sample was completed as indicated by cessation of methane production. The volume of the gas produced from each bottle was measured using a frictionless glass syringe (Figure A.4).

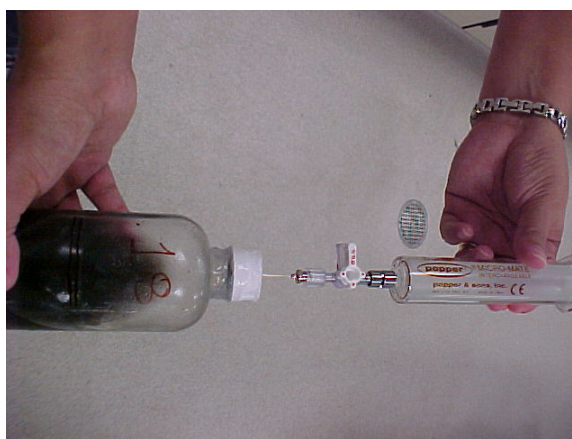


Figure A.4 Measuring volume of gas produced in BMP bottles

The needle of the glass syringe was inserted into BMP bottles to allow for the extra produced gas to escape to the syringe, leaving the remaining gas under atmospheric

pressure. Methane concentrations were measured using a Shimadzu – 14 gas chromatograph with an FID detector and a DB-1 capillary column. The column temperature was held constant at 100° C. The concentration of CO₂ gas was measured using a Shimadzu – 14 GC equipped with TCD detector and a Carboxyn column. The temperature was held at 20°C for 5 minutes then raised to 225°C.

APPENDIX B

RAW DATA FOR OPTIMIZATION OF OXIDATION CONDITIONS

AND MW MEASUREMENTS

Fenton's Reagent on 20-year old Samples

H₂O₂ Dose

Table B.1 Doses used in H₂O₂ dose experiment for Fenton's reagent on 20-yr old leachate

pH	4	4	4	4	4	4	4	4
Leachate volume (ml) =	200	200	200	200	200	200	200	200
H ₂ O ₂ : COD (g:g) required =	0.2	0.4	0.6	0.8	1	1.33	1.66	2
H ₂ O ₂ (mg/l) required =	360	720	1080	1440	1800	2394	2988	3600
H ₂ O ₂ : Fe(II) (molar ratio) required =	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Fe (II) conc [M] =	0.0042	0.008	0.0126	0.017	0.021	0.028	0.0343	0.041
Fe(II) conc (mg/l) required =	236.04	470.7	703.88	935.7	1166	1543	1917	2298

Table B.2 DOC results from H₂O₂ dose experiment for Fenton's reagent on 20-yr old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.2	0.60	2.37	5.6	8.57	524.70	547.2	698.7	21.7
0.4	1.21	4.79	4.15	10.15	325.27	341.8	698.7	51.1
0.6	1.81	7.25	4.4	13.46	281.58	300.5	698.7	57.0
0.8	2.42	9.75	4.15	16.32	228.93	247.6	698.7	64.6
1.0	3.02	12.30	5.1	20.42	218.56	240.9	698.7	65.5
1.33	4.02	16.61	5.6	26.23	181.84	205.7	698.7	70.6
1.66	5.01	21.06	6.1	32.17	160.51	186.3	698.7	73.3
2	6.04	25.79	6.65	38.48	129.7	154.7	698.7	77.9

Table B.3 Filtered COD results from H₂O₂ dose experiment for Fenton's reagent on 20-yr old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.2	0.60	2.37	5.6	8.57	1207.95	1259.7	1801.3	30.1
0.4	1.21	4.79	4.15	10.15	900.66	946.4	1801.3	47.5
0.6	1.81	7.25	4.4	13.46	731.13	780.3	1801.3	56.7
0.8	2.42	9.75	4.15	16.32	614.57	664.7	1801.3	63.1
1.0	3.02	12.30	5.1	20.42	498.01	548.9	1801.3	69.5
1.33	4.02	16.61	5.6	26.23	434.44	491.4	1801.3	72.7
1.66	5.01	21.06	6.1	32.17	339.07	393.6	1801.3	78.1
2	6.04	25.79	6.65	38.48	312.58	372.7	1801.3	79.3

Table B.4 Unfiltered COD results from H₂O₂ dose experiment for Fenton's reagent on 20-yrs old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.2	0.60	2.37	5.6	8.57	1525.83	1591.2	1801.3	11.7
0.4	1.21	4.79	4.15	10.15	1462.25	1536.5	1801.3	14.7
0.6	1.81	7.25	4.4	13.46	1547.02	1651.1	1801.3	8.3
0.8	2.42	9.75	4.15	16.32	1419.87	1535.7	1801.3	14.7
1.0	3.02	12.30	5.1	20.42	1271.52	1401.3	1801.3	22.2
1.33	4.02	16.61	5.6	26.23	1207.95	1366.4	1801.3	24.1
1.66	5.01	21.06	6.1	32.17	1096.69	1273.1	1801.3	29.3
2	6.04	25.79	6.65	38.48	1064.90	1269.8	1801.3	29.5

Table B.5 BOD₅ results from H₂O₂ dose experiment for Fenton's reagent on 20-yrs old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	BOD final	BOD adjusted
0.2	0.60	2.37	5.6	8.57	34.20	35.7
0.4	1.21	4.79	4.15	10.15	67.65	71.1
0.6	1.81	7.25	4.4	13.46	69.45	74.1
0.8	2.42	9.75	4.15	16.32	75.90	82.1
1.0	3.02	12.30	5.1	20.42	74.25	81.8
1.33	4.02	16.61	5.6	26.23	81.30	92.0
1.66	5.01	21.06	6.1	32.17	75.45	87.6
2	6.04	25.79	6.65	38.48	74.55	88.9

Fe⁺² Dose

Table B.6 Doses used in Fe⁺² dose experiment for Fenton's reagent on 20-yrs old leachate

H2O2: COD	1	1	1	1	1	1
Leachate volume (ml) =	200	200	200	200	200	200
H2O2 : COD (g:g) required =	1	1	1	1	1	1
H2O2 (mg/l) required =	1800	1800	1800	1800	1800	1800
H2O2: Fe(II) (molar ratio) required =	15	10	7.5	5	2.5	1
Fe(II): H2O2 (molar ratio) required =	0.06667	0.1	0.1333	0.2	0.4	1
Fe (II) conc [M] =	0.00348	0.0052	0.007	0.01	0.02086	0.0522
Fe(II) conc (mg/l) required =	194.359	291.54	388.72	583.1	1166.15	2915.4

Table B.7 DOC results from Fe⁺² dose experiment for Fenton's reagent on 20-yr old leachate

fe(II) mg/l	Volume added	DOC final	DOC adjusted	DOC initial	%DOC decrease
194.4	5	507.46	520.1	724.8	28.2
291.5	4.2	424.08	433.0	724.8	40.3
388.7	6	304.22	313.3	724.8	56.8
583.1	4.8	264.02	270.4	724.8	62.7
1166.2	6	172.18	177.3	724.8	75.5
2915.4	5	125.16	128.3	724.8	82.3

Table B.8 Filtered COD results from Fe⁺² dose experiment for Fenton's reagent on 20-yr old leachate

fe(II) mg/l	Volume added	COD final	COD adjusted	COD initial	% COD decrease
194.4	5	1594.61	1634.5	1907.0	14.3
291.5	4.2	1357.58	1386.1	1907.0	27.3
388.7	6	1002.02	1032.1	1907.0	45.9
583.1	4.8	840.40	860.6	1907.0	54.9
1166.2	6	538.72	554.9	1907.0	70.9
2915.4	5	398.65	408.6	1907.0	78.6

Table B.9 Unfiltered COD results from Fe⁺² dose experiment for Fenton's reagent on 20-yr old leachate

fe(II) mg/l	Volume added	COD final	COD adjusted	COD initial	% COD decrease
194.4	5	1860.01	1906.5	1907.0	0.0
291.5	4.2	1648.48	1683.1	1907.0	11.7
388.7	6	1540.74	1587.0	1907.0	16.8
583.1	4.8	1476.09	1511.5	1907.0	20.7
1166.2	6	1325.25	1365.0	1907.0	28.4
2915.4	5	1314.48	1347.3	1907.0	29.3

pH

Table B.10 Doses used in pH experiment for Fenton's reagent on 20-yr old leachate

pH	2	3	4	5	6	7	9
Leachate volume (ml) =	200	200	200	200	200	200	200
H ₂ O ₂ : COD (g:g) required =	1	1	1	1	1	1	1
H ₂ O ₂ (mg/l) required =	1900	1900	1900	1900	1900	1900	1900
H ₂ O ₂ : Fe(II) (molar ratio) required =	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Fe (II) conc [M] =	0.022	0.022	0.022	0.02	0.022	0.02	0.022
Fe(II) conc (mg/l) required =	1229.9	1230	1229.9	1230	1229.9	1230	1230
FeSO ₄ .7H ₂ O conc (mg/l) required =	6112.2	6112	6112.2	6112	6112.2	6112	6112
volume of 100 g/l FeSO ₄ to be added (ml)	13.02	13.02	13.02	13.02	13.02	13.02	13.02

Table B.11 DOC results from pH experiment for Fenton's reagent on 20-yr old leachate

pH	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
2.0	3.19	13.02	8.5	24.71	222.60	250.1	729.7	65.7
3.0	3.19	13.02	6	22.21	207.09	230.1	729.7	68.5
3.0	3.19	13.02	6	22.21	216.95	241.0	729.7	67.0
4.0	3.19	13.02	6.4	22.61	233.96	260.4	729.7	64.3
5.0	3.19	13.02	4.5	20.71	231.37	255.3	729.7	65.0
5	3.19	13.02	5.2	21.41	217.83	241.1	729.7	67.0
6	3.19	13.02	3.25	19.46	195.94	215.0	729.7	70.5
7	3.19	13.02	1.1	17.31	404.6	439.7	729.7	39.7
9	3.19	13.02	2.5	18.71	490.6	536.5	729.7	26.5

Table B.12 Filtered COD results from pH experiment for Fenton's reagent on 20-yr old leachate

pH	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
2.0	3.19	13.02	8.5	24.71	473.68	532.2	1861.4	71.4
3.0	3.19	13.02	6	22.21	484.21	538.0	1861.4	71.1
3.0	3.19	13.02	6	22.21	505.26	561.4	1861.4	69.8
4.0	3.19	13.02	6.4	22.61	484.21	539.0	1861.4	71.0
5.0	3.19	13.02	4.5	20.71	568.42	627.3	1861.4	66.3
5	3.19	13.02	5.2	21.41	505.26	559.4	1861.4	69.9
6	3.19	13.02	3.25	19.46	600.00	658.4	1861.4	64.6
7	3.19	13.02	1.1	17.31	989.47	1075.1	1861.4	42.2
9	3.19	13.02	2.5	18.71	1263.16	1381.3	1862.4	25.8

Table B.13 Unfiltered COD results from pH experiment for Fenton's reagent 20-yr old leachate

pH	H₂O₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
2.0	3.19	13.02	8.5	24.71	1200.00	1348.3	1861.4	27.6
3.0	3.19	13.02	6	22.21	1242.11	1380.0	1861.4	25.9
3.0	3.19	13.02	6	22.21	1178.95	1309.9	1861.4	29.6
4.0	3.19	13.02	6.4	22.61	1221.05	1359.1	1861.4	27.0
5.0	3.19	13.02	4.5	20.71	1284.21	1417.2	1861.4	23.9
5	3.19	13.02	5.2	21.41	1263.16	1398.4	1861.4	24.9
6	3.19	13.02	3.25	19.46	1315.79	1443.8	1861.4	22.4
7	3.19	13.02	1.1	17.31	1494.74	1624.1	1861.4	12.7
9	3.19	13.02	2.5	18.71	1578.95	1726.7	1862.4	7.3

Fenton's reagent on 12-yrs old samples

H₂O₂ Dose

Table B.14 Doses used in H₂O₂ dose experiment for Fenton's reagent on 12-yrs old leachate

pH	4	4	4	4	4	4
Leachate volume (ml) =	200	200	200	200	200	200
H ₂ O ₂ : COD (g:g) required =	0.4	0.6	0.8	1	1.66	2
H ₂ O ₂ (mg/l) required =	500	750	1000	1250	2075	2500
H ₂ O ₂ : Fe(II) (molar ratio) required =	2.5	2.5	2.5	2.5	2.5	2.5
Fe (II) conc [M] =	0.0059	0.009	0.012	0.015	0.024	0.029
Fe(II) conc (mg/l) required =	327.45	490.2	652.2	813.5	1341	1610

Table B.15 DOC results from H₂O₂ dose experiment for Fenton's reagent on 12-yrs old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.4	0.84	3.31	2.5	6.65	213.24	220.3	536.0	58.9
0.6	1.26	4.99	2.5	8.75	159.58	166.6	536.0	68.9
0.8	1.68	6.70	2.75	11.13	128.82	136.0	536.0	74.6
1.0	2.10	8.43	3	13.52	106.35	113.5	536.0	78.8
1.66	3.48	14.28	3.75	21.51	77.70	86.1	536.0	83.9
2	4.19	17.40	4.1	25.69	69.6	78.5	536.0	85.4

Table B.16 Filtered COD results from H₂O₂ dose experiment for Fenton's reagent on 12-yrs old leachate

Dose H ₂ O ₂ : COD	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.4	0.84	3.31	2.5	6.65	589.47	609.1	1315.8	53.7
0.6	1.26	4.99	2.5	8.75	389.47	406.5	1315.8	69.1
0.8	1.68	6.70	2.75	11.13	321.05	338.9	1315.8	74.2
1.0	2.10	8.43	3	13.52	257.89	275.3	1315.8	79.1
1.66	3.48	14.28	3.75	21.51	178.95	198.2	1315.8	84.9
2	4.19	17.40	4.1	25.69	210.53	237.6	1315.8	81.9

Table B.17 Unfiltered COD results from H₂O₂ dose experiment for Fenton's reagent on 12-yr old leachate

Dose H2O2: COD	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.4	0.84	3.31	2.5	6.65	1105.26	1142.0	1315.8	13.2
0.6	1.26	4.99	2.5	8.75	1057.89	1104.2	1315.8	16.1
0.8	1.68	6.70	2.75	11.13	1000.00	1055.6	1315.8	19.8
1.0	2.10	8.43	3	13.52	1021.05	1090.1	1315.8	17.2
1.66	3.48	14.28	3.75	21.51	936.84	1037.6	1315.8	21.1
2	4.19	17.40	4.1	25.69	905.26	1021.6	1315.8	22.4

Table B.18 BOD₅ results from H₂O₂ dose experiment for Fenton's reagent on 12-yr old leachate

Dose H2O2: COD	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	BOD final	BOD adjusted
0.4	0.84	3.31	2.5	6.65	33.10	34.2
0.6	1.26	4.99	2.5	8.75	36.50	38.1
0.8	1.68	6.70	2.75	11.13	41.70	44.0
1.0	2.10	8.43	3	13.52	43.50	46.4
1.66	3.48	14.28	3.75	21.51	42.50	47.1
2	4.19	17.40	4.1	25.69	42.60	48.1

Fe⁺² Dose

Table B.19 Doses used in Fe⁺² dose experiment for Fenton's reagent on 12-yr old leachate

H2O2: COD	1	1	1	1	1	1
Leachate volume (ml) =	200	200	200	200	200	200
H2O2 : COD (g:g) required =	1	1	1	1	1	1
H2O2 (mg/l) required =	1150	1150	1150	1150	1150	1150
Fe(II): H2O2 (molar ratio)	0.05	0.0667	0.1	0.2	0.4	1
Fe (II) conc [M] =	0.00168	0.0022	0.0034	0.007	0.0134	0.0335
Fe(II) conc (mg/l) required =	93.6334	124.84	187.27	374.5	749.067	1872.7

Table B.20 DOC results from Fe⁺² dose experiment for Fenton's reagent on 12-yr old leachate

fe(II) mg/l	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	%DOC decrease
93.6	1.93	0.93	3.5	6.36	394.93	407.5	611.0	33.3
124.8	1.93	1.25	3.3	6.48	308.34	318.3	611.0	47.9
187.3	1.93	1.88	3.05	6.86	266.85	276.0	611.0	54.8
374.5	1.93	3.79	3.2	8.92	167.99	175.5	611.0	71.3
749.1	1.93	7.73	3.9	13.56	112.25	119.9	611.0	80.4
1872.7	1.93	20.52	5.65	28.10	82.3	93.8	611.0	84.6

Table B.21 Filtered COD results from Fe⁺² dose experiment for Fenton's reagent on 12-yr old leachate

fe(II) mg/l	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
93.6	1.93	0.93	3.5	6.36	978.34	1009.5	1396.2	27.7
124.8	1.93	1.25	3.3	6.5	703.18	726.0	1396.2	48.0
187.3	1.93	1.88	3.1	6.9	560.51	579.7	1396.2	58.5
374.5	1.93	3.79	3.2	8.9	397.45	415.2	1396.2	70.3
749.1	1.93	7.73	3.9	13.6	264.97	282.9	1396.2	79.7
1872.7	1.93	20.52	5.65	28.1	193.63	220.8	1396.2	84.2

Table B.22 Unfiltered COD results from Fe⁺² dose experiment for Fenton's reagent on 12-yr old leachate

fe(II) mg/l	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
93.6	1.93	0.93	3.5	6.36	1212.74	1251.3	1396.2	10.4
124.8	1.93	1.25	3.3	6.5	1080.25	1115.3	1396.2	20.1

187.3	1.93	1.88	3.1	6.9	1070.06	1106.8	1396.2	20.7
374.5	1.93	3.79	3.2	8.9	1090.45	1139.1	1396.2	18.4
749.1	1.93	7.73	3.9	13.6	1019.11	1088.2	1396.2	22.1
1872.7	1.93	20.52	5.65	28.1	998.73	1139.0	1396.2	18.4

pH

Table B.23 Doses used in pH experiment for Fenton's reagent on 12-yr old leachate

pH	3	4	5	6	7	9
Reactor Size (ml) =	250	250	250	250	250	250
Leachate volume (ml) =	200	200	200	200	200	200
COD mg/l =	1400	1400	1400	1400	1400	1400
H ₂ O ₂ : COD (g:g) required =	1	1	1	1	1	1
H ₂ O ₂ (mg/l) required =	1400	1400	1400	1400	1400	1400
H ₂ O ₂ : Fe(II) (molar ratio) required =	2.5	2.5	2.5	2.5	2.5	2.5
Fe (II) conc [M] =	0.0163	0.01628	0.0163	0.01628	0.0163	0.0163
Fe(II) conc (mg/l) required =	910.02	910.018	910.02	910.018	910.02	910.02

Table B.24 DOC results from pH experiment for Fenton's reagent on 12-yr old leachate

pH	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
3	2.35	9.47	4.45	16.27	82.88	89.6	540.6	83.4
4	2.35	9.47	4.1	15.92	90.87	98.1	540.6	81.9
5	2.35	9.47	3.05	14.87	90.68	97.4	540.6	82.0
6	2.35	9.47	1.65	13.47	99.02	105.7	540.6	80.4
7	2.35	9.47	0.3	12.12	172.63	183.1	540.6	66.1
9	2.35	9.47	0.75	12.57	264.9	281.6	540.6	47.9

Table B.25 Filtered COD results from pH experiment for Fenton's reagent on 12-yr old leachate

pH	H ₂ O ₂ (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
3	2.35	9.47	4.45	16.27	175.34	189.6	1490.0	87.3
4	2.35	9.47	4.1	15.92	235.62	254.4	1490.0	82.9
5	2.35	9.47	3.05	14.87	263.01	282.6	1490.0	81.0
6	2.35	9.47	1.65	13.47	383.56	409.4	1490.0	72.5
7	2.35	9.47	0.3	12.12	591.78	627.6	1490.0	57.9
9	2.35	9.47	0.75	12.57	843.84	896.9	1490.0	39.8

Table B.26 Unfiltered COD results from pH experiment for Fenton's reagent on 12-yrs old leachate

pH	H2O2 (ml)	iron (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
3	2.35	9.47	4.45	16.27	1030.14	1113.9	1490.0	25.2
4	2.35	9.47	4.1	15.92	1090.41	1177.2	1490.0	21.0
5	2.35	9.47	3.05	14.87	1084.93	1165.6	1490.0	21.8
6	2.35	9.47	1.65	13.47	1260.27	1345.2	1490.0	9.7
7	2.35	9.47	0.3	12.12	1315.07	1394.8	1490.0	6.4
9	2.35	9.47	0.75	12.57	1369.86	1456.0	1490.0	2.3

Ferrate on 20-year old Samples

Ferrate Dose

Table B.27 Doses used in ferrate dose experiment on 20-yrs old leachate

pH	4	4	4	4	4	4	4
Leachate volume (ml) =	200	200	200	200	200	200	200
Ferrate : COD (g:g) required =	0.15	0.35	1.3	1.5	0.5	0.7	1
Ferrate as Fe (mg/l) required =	270	630	2340	2700	900	1260	1800

Table B.28 DOC results from ferrate dose experiment on 20-yrs old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.15	4	6.3	16.5	22.78	511.07	569.3	760.9	25.2
0.35	4	15.3	38	53.30	381.27	482.9	760.9	36.5
0.50	4	20.1	44.25	64.35	307.78	406.8	760.9	46.5
0.70	4	30.0	65.25	95.25	236.54	349.2	760.9	54.1
1	4	44.9	91.25	136.15	184.04	309.3	760.9	59.3
1.30	4	71.7	145.5	217.21	138.16	288.2	760.9	62.1
1.50	4	85.4	164.5	249.88	140.11	315.2	760.9	58.6

Table B.29 Filtered COD results from ferrate dose experiment on 20-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.15	4	6.3	16.5	22.78	1483.44	1652.4	1883.0	12.2
0.35	4	15.3	38	53.30	1239.74	1570.1	1883.0	16.6
0.50	4	20.1	44.25	64.35	1144.37	1512.6	1883.0	19.7
0.70	4	30.0	65.25	95.25	985.43	1454.7	1883.0	22.7
1	4	44.9	91.25	136.15	964.24	1620.6	1883.0	13.9
1.30	4	71.7	145.5	217.21	741.72	1547.3	1883.0	17.8
1.50	4	85.4	164.5	249.88	593.38	1334.7	1883.0	29.1

Table B.30 Unfiltered COD results from ferrate dose experiment on 20-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.15	4	6.3	16.5	22.78	1335.10	1487.2	1883.0	21.0
0.35	4	15.3	38	53.30	953.64	1207.8	1883.0	35.9
0.50	4	20.1	44.25	64.35	805.30	1064.4	1883.0	43.5
0.70	4	30.0	65.25	95.25	598.68	883.8	1883.0	53.1
1	4	44.9	91.25	136.15	492.72	828.1	1883.0	56.0
1.30	4	71.7	145.5	217.21	466.23	972.6	1883.0	48.4
1.50	4	85.4	164.5	249.88	445.03	1001.1	1883.0	46.8

Table B.31 BOD₅ results from ferrate dose experiment on 20-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	BOD final	BOD adjusted
0.15	4	6.3	16.5	22.78	38.33	42.7
0.35	4	15.3	38	53.30	40.95	51.9
0.50	4	20.1	44.25	64.35	40.43	53.4
0.70	4	30.0	65.25	95.25	33.23	49.0
1	4	44.9	91.25	136.15	40.13	67.4
1.30	4	71.7	145.5	217.21	35.03	73.1
1.50	4	85.4	164.5	249.88	34.65	77.9

pH

Table B.32 Doses used in ferrate pH experiment on 20-yrs old leachate

pH	3	4	5	6	7	8	9	10
Leachate volume (ml)	200	200	200	200	200	200	200	200
Ferrate : COD (g:g) required	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Ferrate as Fe (mg/l) required	1260	1260	1260	1260	1260	1260	1260	1260

Table B.33 DOC results from ferrate pH experiment on 20-yrs old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.7	3	30.0	53.1	83.10	260.55	368.8	697.0	47.1
0.7	4	30.0	60	90.00	237.96	345.0	697.0	50.5
0.7	5	30.0	57	87.00	277.11	397.7	697.0	42.9
0.7	6	30.0	50	80.00	387.64	542.7	697.0	22.1
0.7	7	30.0	54.6	84.60	383.96	546.4	697.0	21.6
0.7	8	30.0	52.6	82.60	401.26	567.0	697.0	18.7
0.7	9	30.0	53	83.00	391.42	553.9	697.0	20.5
0.7	10	30.0	52	82.00	384.7	542.4	697.0	22.2

Table B.34 Filtered COD results from ferrate pH experiment on 20-yrs old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.7	3	30.0	53.1	83.10	729.82	1033.1	1886.3	45.2
0.7	4	30.0	60	90.00	662.46	960.6	1886.3	49.1
0.7	5	30.0	57	87.00	741.05	1063.4	1886.3	43.6
0.7	6	30.0	50	80.00	960.00	1344.0	1886.3	28.7
0.7	7	30.0	54.6	84.60	903.86	1286.2	1886.3	31.8
0.7	8	30.0	52.6	82.60	1044.21	1475.5	1886.3	21.8
0.7	9	30.0	53	83.00	909.47	1286.9	1886.3	31.8
0.7	10	30.0	52	82.00	993.68	1401.1	1886.3	25.7

Table B.35 Unfiltered COD results from ferrate pH experiment on 20-yr old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.7	3	30.0	53.1	83.10	1190.18	1684.7	1886.3	10.7
0.7	4	30.0	60	90.00	1111.58	1611.8	1886.3	14.6
0.7	5	30.0	57	87.00	1156.49	1659.6	1886.3	12.0
0.7	6	30.0	50	80.00	1150.88	1611.2	1886.3	14.6
0.7	7	30.0	54.6	84.60	1072.28	1525.9	1886.3	19.1
0.7	8	30.0	52.6	82.60	1089.12	1538.9	1886.3	18.4
0.7	9	30.0	53	83.00	1072.28	1517.3	1886.3	19.6
0.7	10	30.0	52	82.00	1223.86	1725.6	1886.3	8.5

Ferrate on 12-year old Samples

Ferrate Dose

Table B.36 Doses used in ferrate dose experiment on 12-yr old leachate

pH	4	4	4	4		4	4
Leachate volume (ml)	200	200	200	200	200	200	200
Ferrate : COD (g:g) required	0.15	0.35	0.5	0.7	1	1.3	1.5
Ferrate as Fe (mg/l) required	195	455	650	910	1300	1690	1950

Table B.37 DOC results from ferrate dose experiment on 12-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.15	4	3.9	10.35	14.25	347.30	372.0	570.5	34.8
0.35	4	9.3	22.2	31.53	214.07	247.8	570.5	56.6
0.50	4	14.2	32.35	46.53	218.63	269.5	570.5	52.8
0.70	4	20.1	45.2	65.25	170.40	226.0	570.5	60.4
1	4	29.36	63.7	93.06	158.18	231.8	570.5	59.4
1.30	4	39.7	82.3	122.00	144.48	232.6	570.5	59.2
1.50	4	46.2	92.3	138.53	133.83	226.5	570.5	60.3

Table B.38 Filtered COD results from ferrate dose experiment on 12-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.15	4	3.9	10.35	14.25	755.41	809.2	1311.5	38.3
0.35	4	9.3	22.2	31.53	461.64	534.4	1311.5	59.3
0.50	4	14.2	32.35	46.53	493.11	607.8	1311.5	53.7
0.70	4	20.1	45.2	65.25	388.20	514.8	1311.5	60.7
1	4	29.36	63.7	93.06	409.18	599.6	1311.5	54.3
1.30	4	39.7	82.3	122.00	346.23	557.4	1311.5	57.5
1.50	4	46.2	92.3	138.53	356.72	603.8	1311.5	54.0

Table B.39 Unfiltered COD results from ferrate dose experiment on 12-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.15	4	3.9	10.35	14.25	1080.66	1157.7	1311.5	11.7
0.35	4	9.3	22.2	31.53	944.26	1093.1	1311.5	16.7
0.50	4	14.2	32.35	46.53	876.07	1079.9	1311.5	17.7
0.70	4	20.1	45.2	65.25	818.36	1085.4	1311.5	17.2
1	4	29.36	63.7	93.06	702.95	1030.0	1311.5	21.5
1.30	4	39.7	82.3	122.00	681.97	1098.0	1311.5	16.3
1.50	4	46.2	92.3	138.53	561.31	950.1	1311.5	27.6

Table B.40 BOD₅ results from ferrate dose experiment on 12-yr old leachate

Dose ferrate: COD	pH	Dose (ml)	pH adj (ml)	Volume added	BOD final	BOD adjusted
0.15	4	3.9	10.35	14.25	23.20	24.9
0.35	4	9.3	22.2	31.53	22.50	26.0
0.50	4	14.2	32.35	46.53	20.80	25.6
0.70	4	20.1	45.2	65.25	18.90	25.1
1	4	29.36	63.7	93.06	22.00	32.2
1.30	4	39.7	82.3	122.00	24.30	39.1
1.50	4	46.2	92.3	138.53	25.00	42.3

pH

Table B.41 Doses used in ferrate pH experiment on 12-yr old leachate

pH	3	4	5	6	7	8	9	10
Leachate volume (ml) =	200	200	200	200	200	200	200	200
Ferrate : COD (g:g) required	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Ferrate as Fe (mg/l) required	980	980	980	980	980	980	980	980

Table B.42 DOC results from ferrate pH experiment on 12-yr old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	DOC final	DOC adjusted	DOC initial	% DOC decrease
0.7	3	22.5	43.1	65.60	165.43	219.7	556.6	60.5
0.7	4	22.5	41	63.50	213.90	281.8	556.6	49.4
0.7	5	22.5	40	62.50	193.57	254.1	556.6	54.4
0.7	6	22.5	40	62.50	275.69	361.8	556.6	35.0
0.7	7	22.5	40.6	63.10	282.14	371.2	556.6	33.3
0.7	8	22.5	40.2	62.70	295.13	387.6	556.6	30.4
0.7	9	22.5	40.6	63.10	302.58	398.0	556.6	28.5
0.7	10	22.5	42.4	64.90	297.5	394.0	556.6	29.2

Table B.43 Filtered COD results from ferrate pH experiment on 12-yr old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.7	3	22.5	43.1	65.60	500.68	664.9	1741.0	61.8
0.7	4	22.5	41	63.50	511.56	674.0	1741.0	61.3
0.7	5	22.5	40	62.50	565.99	742.9	1741.0	57.3
0.7	6	22.5	40	62.50	663.95	871.4	1741.0	49.9
0.7	7	22.5	40.6	63.10	653.06	859.1	1741.0	50.7
0.7	8	22.5	40.2	62.70	718.37	943.6	1741.0	45.8
0.7	9	22.5	40.6	63.10	685.71	902.1	1741.0	48.2
0.7	10	22.5	42.4	64.90	854.42	1131.7	1741.0	35.0

Table B.44 Unfiltered COD results from ferrate pH experiment on 12-yrs old leachate

Dose ferrate: COD	pH	Ferrate (ml)	pH adj (ml)	Volume added	COD final	COD adjusted	COD initial	% COD decrease
0.7	3	22.5	43.1	65.60	848.98	1127.4	1741.0	35.2
0.7	4	22.5	41	63.50	843.54	1111.4	1741.0	36.2
0.7	5	22.5	40	62.50	908.84	1192.9	1741.0	31.5
0.7	6	22.5	40	62.50	925.17	1214.3	1741.0	30.3
0.7	7	22.5	40.6	63.10	1023.13	1345.9	1741.0	22.7
0.7	8	22.5	40.2	62.70	870.75	1143.7	1741.0	34.3
0.7	9	22.5	40.6	63.10	908.84	1195.6	1741.0	31.3
0.7	10	22.5	42.4	64.90	914.29	1211.0	1741.0	30.4

Organic Molecular Weight

Ultrafiltration data was modeled according to PCM using the method discussed in more details in Appendix A.

Leachate

Table B45. Estimation of DOC with size <1000 dalton for 20-yrs old leachate

MWCO: 1000					
Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	ln Cp
5	50	0.9	-0.11	182	5.20
15	50	0.7	-0.36	210	5.35
25	50	0.5	-0.69	237	5.47

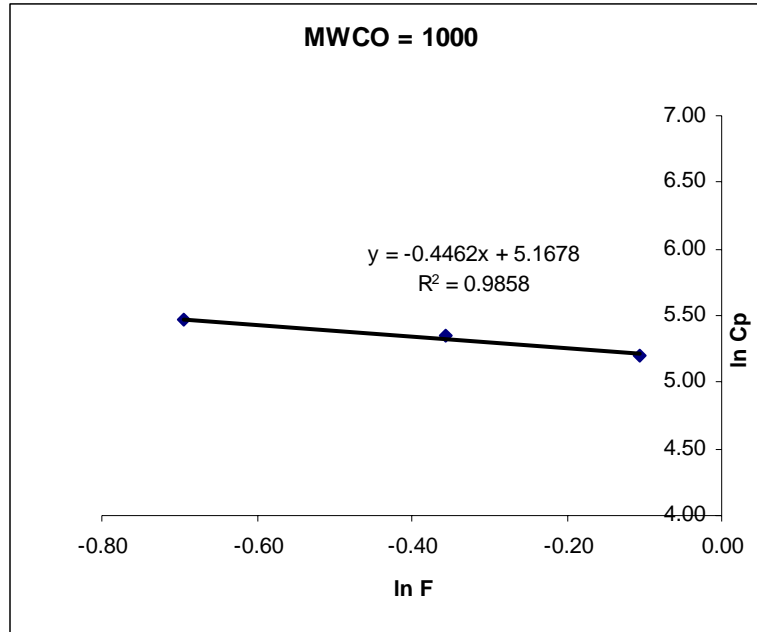


Figure B1. Estimation of DOC with size <1000 dalton for 20-yr old leachate

Table B46. Estimation of DOC with size <10000 dalton for 20-yr old leachate

MWCO: 10000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	446	6.10
15	50	0.7	0.36	497	6.21
25	50	0.5	0.69	531	6.28

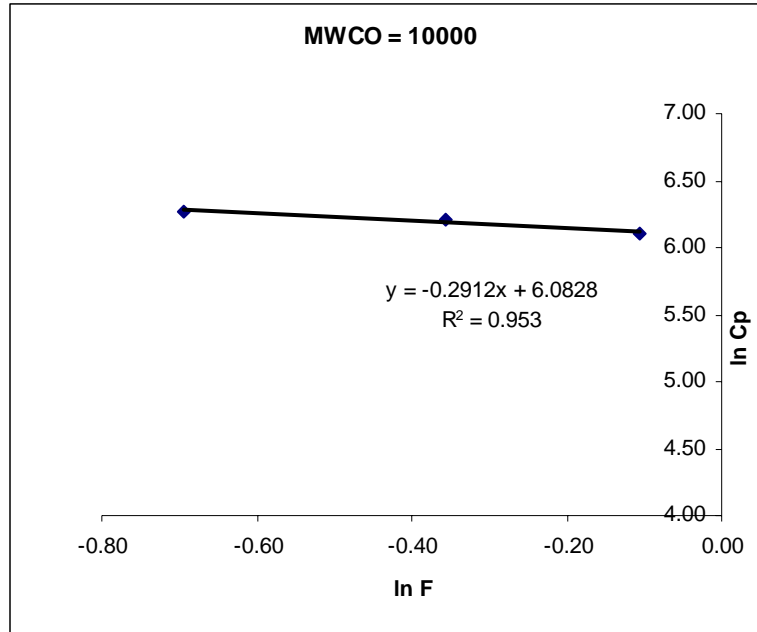


Figure B2. Estimation of DOC with size <10000 dalton for 20-yr old leachate

Fenton's Reagent Treated Leachate

Table B47. Estimation of DOC with size <1000 dalton for 20-yr old leachate treated with half of Fenton's reagent optimum dose

MWCO: 1000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	129	4.86
15	50	0.7	0.36	146	4.98
25	50	0.5	0.69	159	5.07

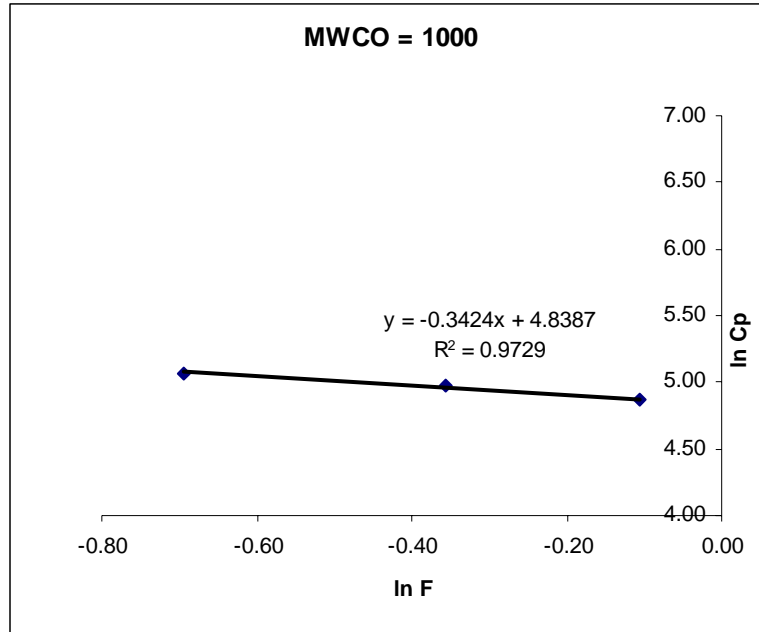


Figure B3. Estimation of DOC with size <1000 dalton for 20-yrs old leachate treated with half of Fenton's reagent optimum dose

MWCO: 10000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	263	5.57
15	50	0.7	0.36	270	5.60
25	50	0.5	0.69	260	5.56

Table B48. Estimation of DOC with size <10000 dalton for 20-yrs old leachate treated with half of Fenton's reagent optimum dose

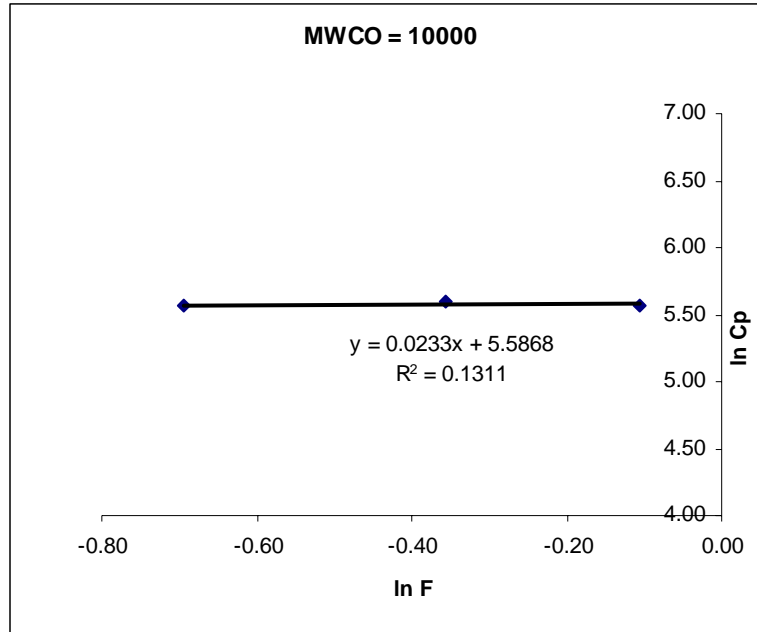


Figure B4. Estimation of DOC with size <10000 dalton for 20-yr old leachate treated with half of Fenton's reagent optimum dose

Table B49. Estimation of DOC with size <1000 dalton for 20-yr old leachate treated with Fenton's reagent optimum dose

MWCO: 1000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	-	119	4.78
15	50	0.7	-	124	4.82
25	50	0.5	-	134	4.90

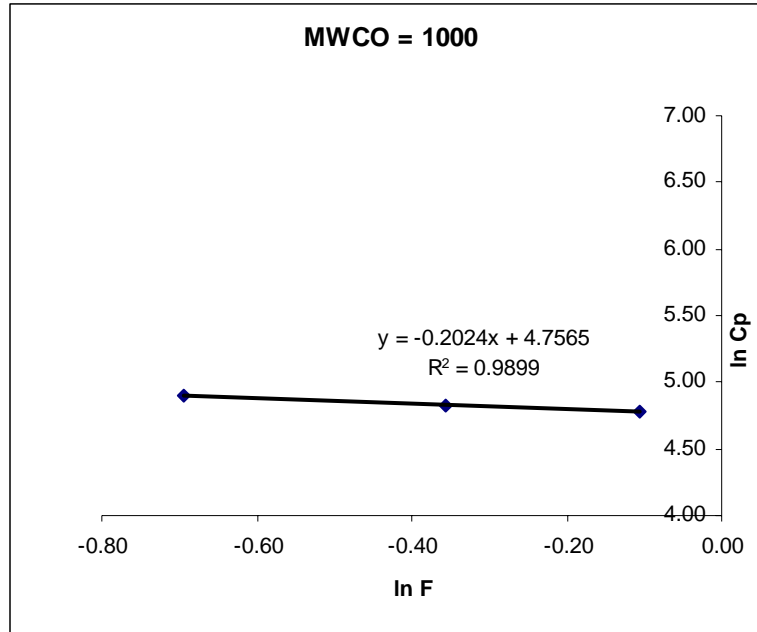


Figure B5. Estimation of DOC with size <1000 dalton for 20-yr old leachate treated with Fenton's reagent optimum dose

Table B50. Estimation of DOC with size <10000 dalton for 20-yr old leachate treated with Fenton's reagent optimum dose

MWCO: 10000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	ln Cp
5	50	0.9	0.11	178	5.18
15	50	0.7	0.36	175	5.17
25	50	0.5	0.69	177	5.17

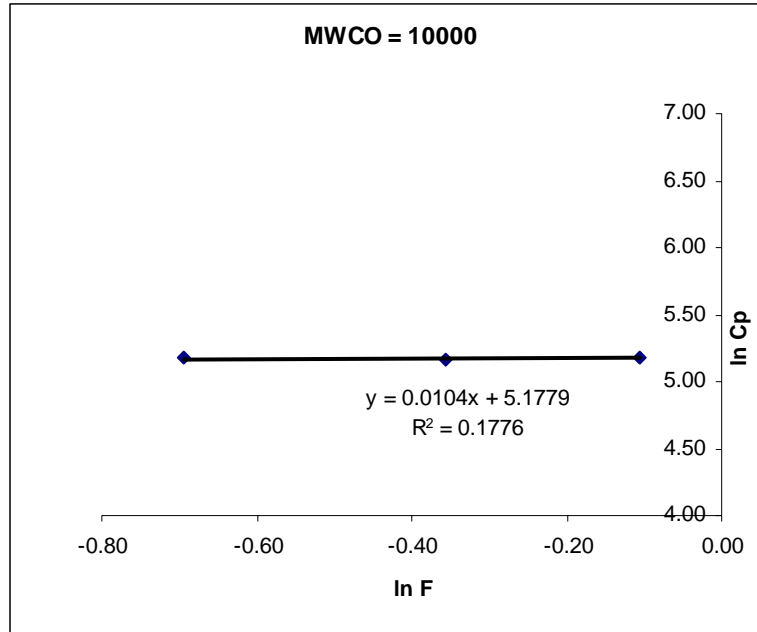


Figure B6. Estimation of DOC with size <10000 dalton for 20-yr old leachate treated with Fenton's reagent optimum dose

Ferrate Treated Leachate

Table B51. Estimation of DOC with size <1000 dalton for 20-yr old leachate treated with half of ferrate's optimum dose

MWCO: 1000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	200	5.30
15	50	0.7	0.36	228	5.43
25	50	0.5	0.69	254	5.54

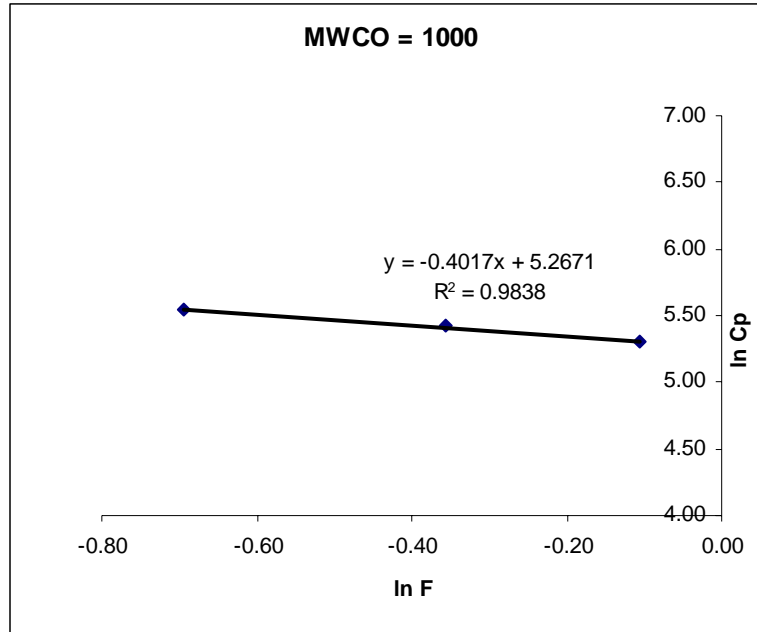


Figure B7. Estimation of DOC with size <1000 dalton for 20-yrs old leachate treated with half of ferrate's optimum dose

Table B52. Estimation of DOC with size <10000 dalton for 20-yrs old leachate treated with half of ferrate's optimum dose

MWCO: 10000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	337	5.82
15	50	0.7	0.36	342	5.83
25	50	0.5	0.69	384	5.95

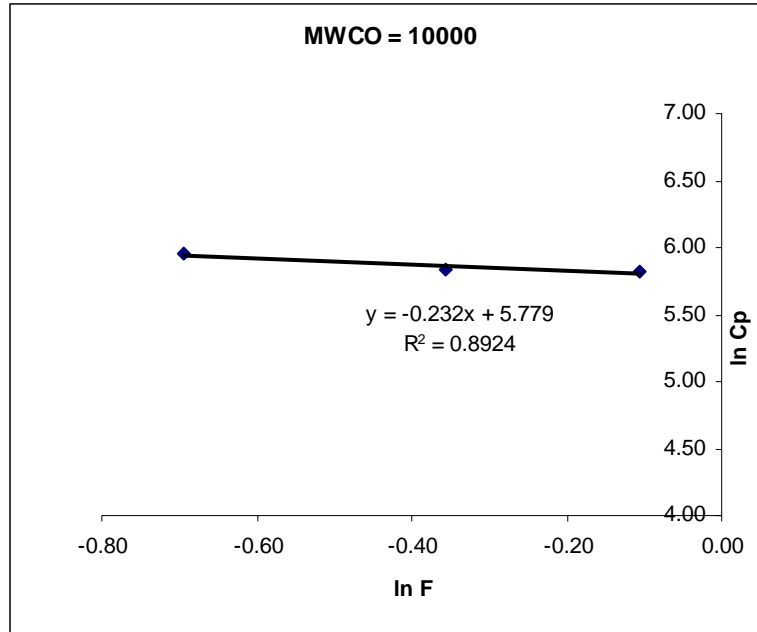


Figure B8. Estimation of DOC with size <10000 dalton for 20-yr old leachate treated with half of ferrate's optimum dose

MWCO: 1000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	ln Cp
5	50	0.9	0.11	178	5.18
15	50	0.7	0.36	177	5.18
25	50	0.5	0.69	196	5.28

Table B53. Estimation of DOC with size <1000 dalton for 20-yr old leachate treated with ferrate's optimum dose

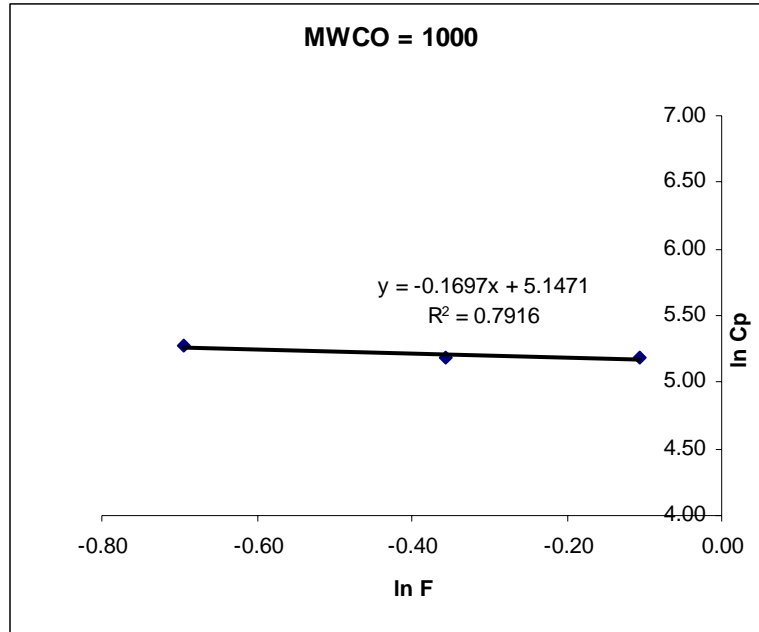


Figure B9. Estimation of DOC with size <1000 dalton for 20-yrs old leachate treated with ferrate's optimum dose

Table B54. Estimation of DOC with size <10000 dalton for 20-yrs old leachate treated with ferrate's optimum dose

MWCO: 10000

Vf	Vi	F= 1-(Vf/Vi)	ln F	Cp	<u>ln Cp</u>
5	50	0.9	0.11	227	5.42
15	50	0.7	0.36	242	5.49
25	50	0.5	0.69	245	5.50

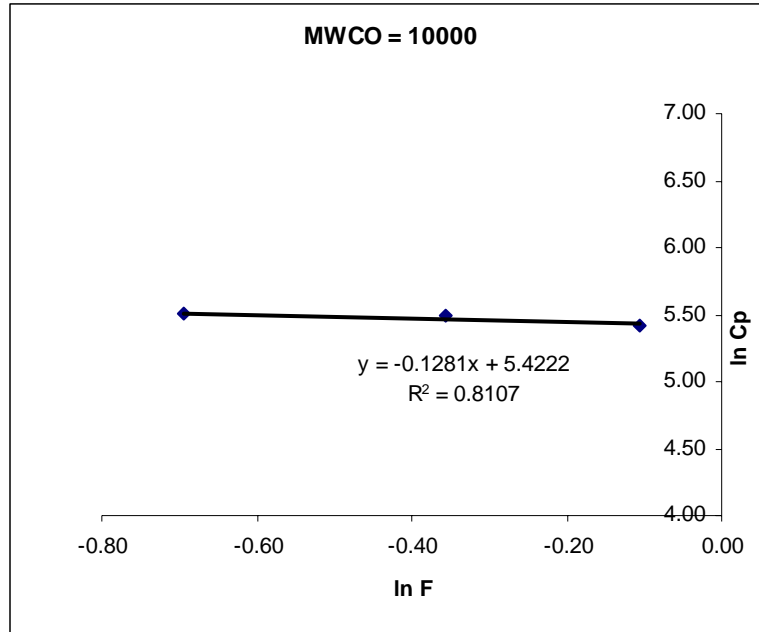


Figure B10. Estimation of DOC with size <10000 dalton for 20-yrs old leachate treated with ferrate's optimum dose

APPENDIX C
IN-SITU FENTON'S REAGENT

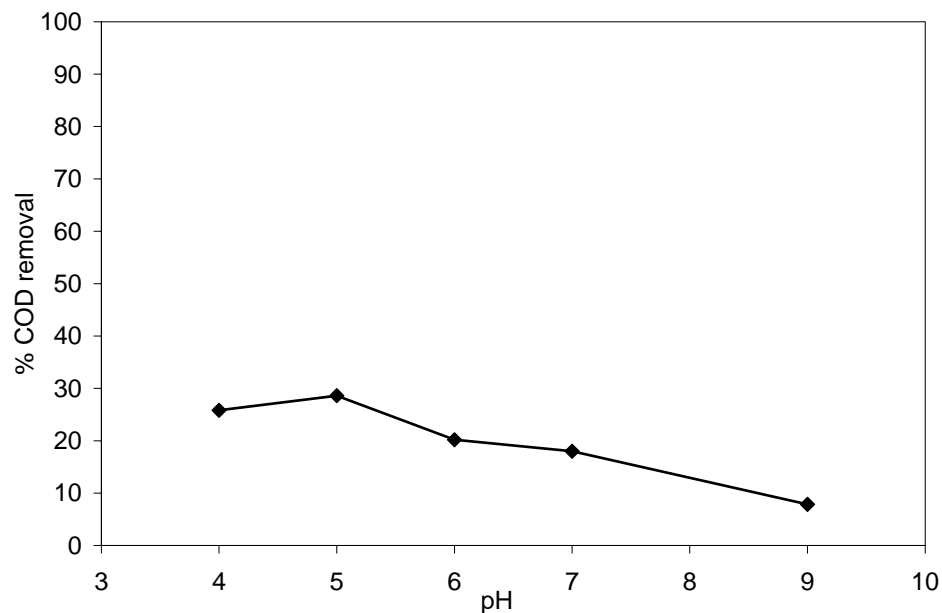
Method

In-situ oxidation experiments were performed using 1000-ml glass flasks. Two hundred ml of wet digested solid waste were mixed with 200 ml of leachate at room temperature (22°C) and atmospheric pressure. The pH of the mixture was adjusted to the target value (4 -9) using 5N sodium hydroxide or 6N sulfuric acid. The oxidant was then added and the reaction was allowed to proceed with continuous fast shaking using a shaker table. The pH was brought back to 7 and the treated mixture was filtered and sampled for COD to determine organic removal. Experiments performed were designed to determine optimum iron and H₂O₂ dose and best oxidation pH.

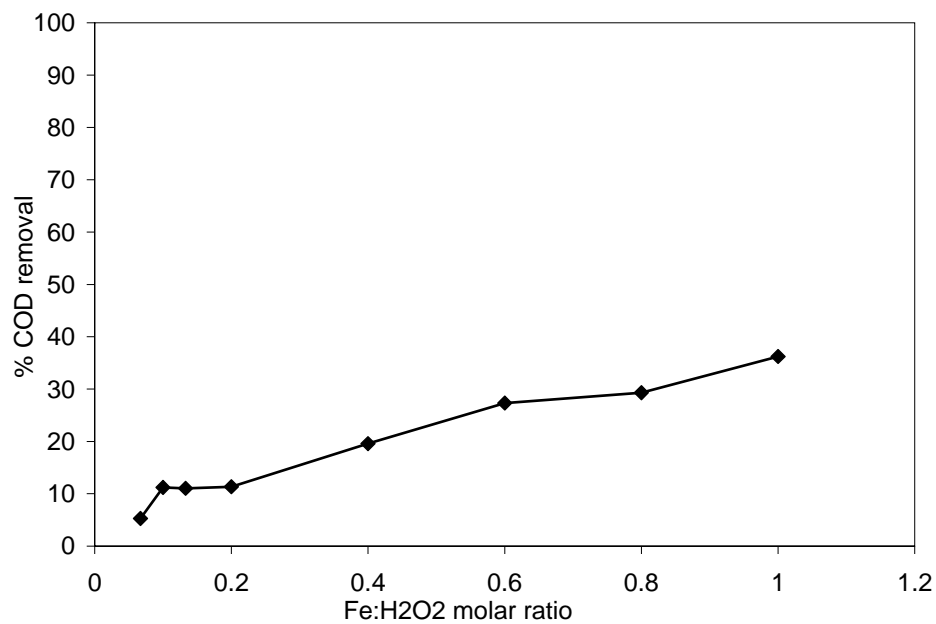
Results and Discussion

Three conditions were evaluated to get the best Fenton's reagent in-situ condition. These parameters were pH, Fe:H₂O₂ molar ratio, and H₂O₂: COD values (Figure C1). When pH was varied from 4 to 9, it was observed that the best COD removal occurred at pH values in the range 4-5. This observation correlates well with external Fenton's reagent oxidation. Optimum pH for Fenton's reagent has been repeatedly reported to be below 5 (Batarseh, 2006, Zhang et al., 2006). Reduced organic removal efficiencies under alkaline conditions using Fenton's reagent could be explained by the competition of carbonate and bicarbonate for OH[•] (Kim et al., 1997) and also by the deactivation of Fe⁺² (the oxidation catalyst) by forming ferric hydroxide complexes at pH above 7 (Kang and Hwang, 2000; Snoeyink and Jenkins, 1980).

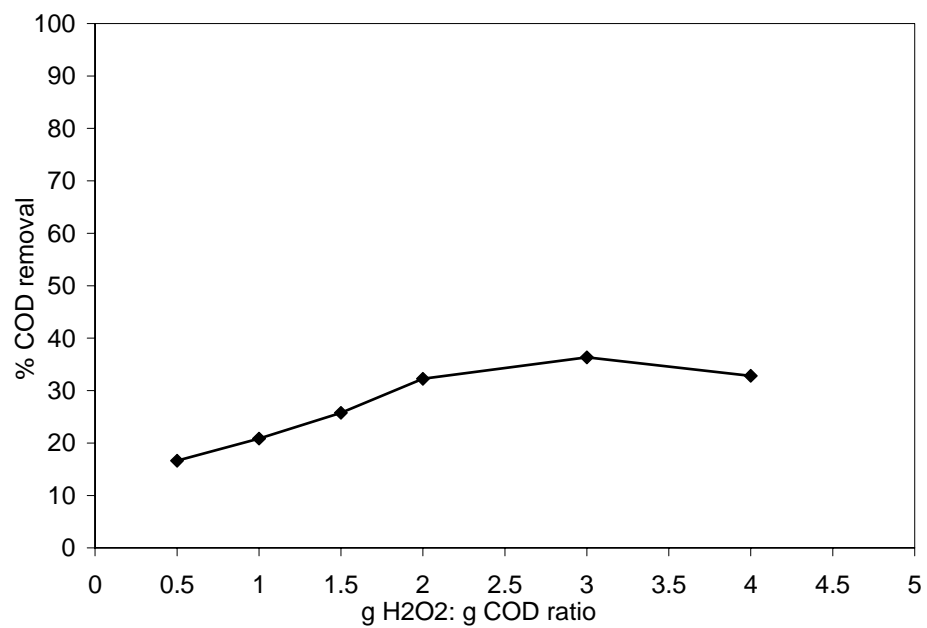
When the Fe:H₂O₂ molar ratio was varied between 0.1 and 1, the best COD removal efficiencies were at ratios above 0.6. Traditional liquid Fenton's reagent usually requires less iron. This ratio was reported to be 0.4 for similar leachate in previous work (Batarseh, et al., 2006). The molar ratio of Fe²⁺ : H₂O₂ is important since too little iron will result in unutilized H₂O₂ and excessive Fe²⁺ will destroy produced OH• radical (Pignatello et al., 2006). When H₂O₂: COD dose was varied from 0.5 to 4.0, the best COD removal was observed to be above 2.0. A dose of 2 g H₂O₂:1 g COD removed 30 to 40 % of the dissolved COD, whereas in a leachate only system a dose of 1 g H₂O₂:1 g COD removed around 70 to 80 % of dissolved COD from similar leachate samples (Batarseh, 2006)



(a)



(b)



(c)

Figure C1. COD removal with varying Fenton's reagent conditions. A) different pH values. B) different Fe:H₂O₂ molar values and C) different H₂O₂: COD values.