EFFECT OF NANO ZERO VALENT IRON ON DEGRADATION OF MUNICIPAL SOLID WASTE IN BIOREACTOR LANDFILLS

by

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ABSTRACT

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Nanotechnology has substantial potential for reducing contamination, toxicity and overall human health hazards and environmental risks. In recent times, nano zero valent iron has proved to be effective in contaminant reduction and pollution control. Iron is an important micronutrient for the microbes involved in the anaerobic decomposition of solid waste in bioreactor landfills. Landfill leachate sometimes contains toxic compounds which nano zero valent iron has proven to be very effective in removing, particularly chlorinated organics, heavy metals, and odorous sulfides. Iron can also potentially increase landfill methane generation by removing long chain fatty acids and sulfides that inhibit methanogenesis.

nZVI materials are highly reactive and have been previously used to remove contaminants from water and soil. However, no studies have been conducted regarding the effect of adding nZVI to Municipal Solid Waste (MSW) degradation. Therefore, the investigation of the nanoparticles in stabilizing

MSW was the primary goal of this study. The current study focuses on the change in gas production and leachate characteristics due to addition of nZVI particles to MSW in laboratory scale set ups of bioreactor landfills. The current study compared MSW decomposition in lab scale simulated bioreactors, with and without the presence of nano zero valent iron (nZVI). 6-gallon PVC lab scale bioreactors were filled with MSW collected from the Denton Landfill, with added sludge from a wastewater treatment plant as a source of microorganisms and moisture, along with leachate recirculation. nZVI (0.01% by weight of the total mass of solid waste present) was added to one of the reactors. The gas results show that the two reactors had a comparable percentage of methane. Both reactors produced similar quantities of gas during the first 20 days. However, the reactor with the added nZVI had a lag period of approximately 50 days after that, before its gas production peaked. The lag was probably due to microbes acclimating to the increased iron level. The hypothesis that iron would enhance methane production, however, turned out not to be true. The leachate results, for the most part are consistent with the results of the gas production. The lag in gas production for reactor 2 is also reflected in the leachate pH. The pH for both reactors dropped for the first couple of weeks and picked up with the start of methane production. In case of the second reactor there was a lag phase before the pH started to increase. Similarly, there was a lag in the COD decrease as well for reactor 2. However, the BOD results are not consistent as there is a marked difference in the leachate BOD for reactor 2 between the first and second months. This may be due to the presence of nZVI in the reactor 2 leachate. Also, the BOD and COD values for the second reactor leachate were considerably higher, possibly due to the presence of nZVI.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Figures Page

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Municipal Solid Waste (MSW), is generated within a community, from households and also various commercial, institutional, industrial, and municipal sources. MSW, commonly known as trash or garbage, includes various organic and inorganic things such as food scraps, paper, plastic, wood and yard wastes, metal, and glass. In 2005, 245 million tons of municipal solid waste were generated in the U.S., with approximately 54% of this waste buried in landfills (U.S. EPA, 2005). Waste minimization and accelerated waste decomposition are currently important aspects of Solid Waste Management world-wide. Due to rapid increases in population and spreading of city limits, space constraints have become a major stumbling block towards solid waste disposal. Hence, waste minimization or increasing the capacity of landfills within the same area is becoming a major consideration for the state agencies and federal regulatory bodies.

1.2 Evolution of Bioreactor Landfills for Municipal Solid Waste (MSW) Decomposition

Conventional landfills are designed and operated in accordance with RCRA Subtitle D, which minimizes amount of moisture entering and retained in the landfill waste. This is intended to reduce groundwater contamination and as a result waste degradation takes prolonged periods of time, even 50-100 years. This complicates the post-closure monitoring period, which is currently set as 30 years.

There have been substantial changes in the design and operation of landfills over the past twenty years. First suggested in the mid 1970s (Pohland, 1975), the concept of operating a landfill as a bioreactor has recently received increased attention (Pacey et al., 1999). A bioreactor landfill is operated to enhance refuse decomposition, gas production, and waste stabilization through leachate recirculation. There are several benefits associated with the operation of landfills as bioreactors including (1) more rapid settlement, which results in increased effective refuse density and air space, (2) in-situ leachate use, saving time and effort as also significant financial expenditure in terms of leachate treatment (3) increased gas production and subsequent conversion to energy and (4) ultimately the rapid stabilization of a landfill to a more environmentally benign state (Reinhart and Townsend, 1998). In addition to all these benefits, enhanced decomposition increases the rate of MSW settlement (Edil et al. 1990, El-Fadel et al. 1999, Hossain et al. 2003), which provides the landfill owner with additional airspace prior to closure, i.e. greater mass of waste can be buried per unit volume of landfills (Benson et. al, 2004). This also limits the potential for settlement induced damage of final cover (Benson, 2000). Increased air space results in a reduction of total land use for landfills. A schematic of a bioreactor landfill is represented in Figure 1.1.

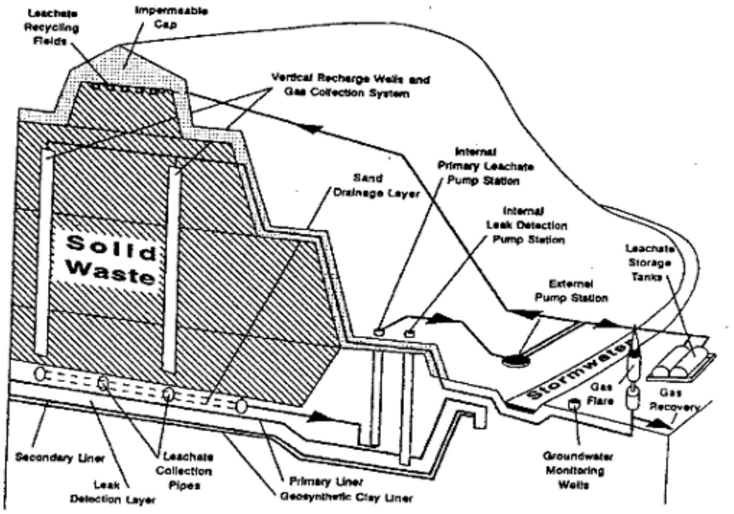


Figure 1.1 Schematic of a Bioreactor Landfill

In favorable conditions biological stabilization of the waste in a bioreactor landfill is expected to be much faster when compared to a conventional landfill. Moreover, it can be ensured that nutrients are all in sufficient supply to make the microbial population more effective in methane production. Iron is an important micronutrient which, if present in optimum quantity, may help in increasing methane production (Ahmed et al., 2001).

Although potential benefits can be obtained with bioreactors, the following issues need to be considered in design and operation of bioreactors: leachate recirculation using surface ponds, horizontal trenches, permeable beds and injection wells; maximum allowable leachate head on bottom liner to be less than 12 inch, as specified by US EPA; daily and intermediate covers to prevent perched water condition; and side seepage and stability of the side slopes due to the recirculated water.

1.3 Nanomaterials in MSW Degradation

Nanotechnology is an umbrella term that encompasses a wide variety of subjects and prospects; the field is extremely heterogeneous and there are various aspects of and goals in applying nanotechnology in modern civilization. Two opposing directions of development which can be distinguished in this context are: the top-down approach, in which increasing levels of refinement lead down to nano level technologies; and the bottom-up approach, which begins at the atomic or molecular level and generally involves the self-organized formation of complex molecules or nano systems. This is an approach that inherently generates less waste.

The application of nanomaterials is fairly a new concept in waste decomposition. Nano zero valent iron particles in particular may play a significant role in reducing contamination, toxicity and overall human health hazards and environmental risks. It is also important to study the life cycle of the nano materials themselves and the topic of potential effects of releasing more nano particles into the environment due to their increased usage (Lewinsky, 2008). Currently zero valent nano iron particles have been used quite successfully in the field of waste minimization and contaminant reduction.

Nano particles have greater surface area to volume ratio than larger particles, hence provide higher reactivity. nZVIs are highly effective against toxic chlorinated organics such as trichloroethylene (TCE) and polychlorinated biphenyls (PCBs). (Zhang, 2003). They are also effective sorbing metals and in precipitating malodorous sulfur compounds from the liquid phase (Li et al, 2007). The effects of the zero valent nano iron particles in solid waste decomposition and methane generation are not well documented. Further studies are required to investigate the effect of the zero valent nano iron particles on solid waste decomposition and gas generation.

1.4 Research Objectives

Iron is an important micronutrient for microbial species involved in the anaerobic degradation of MSW. For the current study, nano iron particles were selected due to the successful use of these particles in the fields of contaminant treatment and waste minimization. Two bioreactor landfills were simulated in the lab with MSW from the Denton Landfill. The control reactor was set up with the waste sample and a protocol of recirculating leachate, without any nutrients. The second reactor was setup in a similar fashion, with the only exception that nano zero valent iron particles (0.1% by weight of the solid waste sample) were added to the waste, sonicated in water as a slurry. The objective of this study was to evaluate the effect of iron nano particles on the decomposition of MSW and the rate of methane production. Bioreactor landfills are known for their usefulness in terms of energy recovery and hence any change made to their mode of operation should not reduce the production of landfill gas (LFG).

The specific objectives of the current study are as follows:

- To compare gas production from two lab scale bioreactors with and without zero valent iron nano particles.
- To compare the leachate characteristics of the two reactors.

1.5 Thesis Organization

The thesis is organized in the following manner:

The first chapter introduces the topic, background, research objective and thesis outline.

The second chapter presents a review of literature that includes a brief overview of MSW, bioreactor landfill operation, degradation of MSW in a bioreactor landfill, factors affecting methanogenesis under anaerobic conditions, the effect of the presence of iron in methane production under anaerobic conditions, and the scope of nano zerovalent iron in waste minimization and contaminant control.

The third chapter describes all the experimental variables and procedures including sample collection, characterization, reactor building and setup, monitoring, COD and BOD testing.

The fourth chapter presents and analyzes the experimental results. Comparison of the results with existing literature is also presented.

The fifth chapter summarizes the main conclusions from the current research and some key recommendations for future work.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Municipal Solid Waste and Landfills

2.1.1 Composition of Municipal Solid Waste

MSW, or more commonly called garbage or trash, is generated throughout the human civilization. It is comprised of innumerable items such as foodstuff, plastic packaging, Styrofoam, glass, concrete, yard waste, fabric, medical waste, electronic waste. The residential and commercial waste placed into the landfill can be divided by two groups: decomposable and non-decomposable/inert materials. Decomposable materials include food waste, clothes, papers, woods (slowly decomposable materials), whereas glass, metals, plastics, construction and demolition waste fall in the category of inert materials. The more easily the organic fraction of the waste decomposes, the faster will be the landfill gas generation rate. Food wastes typically fall into the easily-degradable category. Thus, a high percentage of food wastes in a landfill likely will lead to a faster landfill gas generation rate. Some decomposable wastes, such as large pieces of wood, are not inert, but decompose so slowly that for most practical purposes they do not contribute significantly to landfill gas generation. Landva and Clark (1990) classified waste based on biodegradability of the individual constituents. In Figure 2.1, the group OP is highly degradable under favorable conditions when compared to the other groups of materials. The other three groups possibly contain void-forming constituents, which may have a significant influence on hydraulic characteristics of MSW.

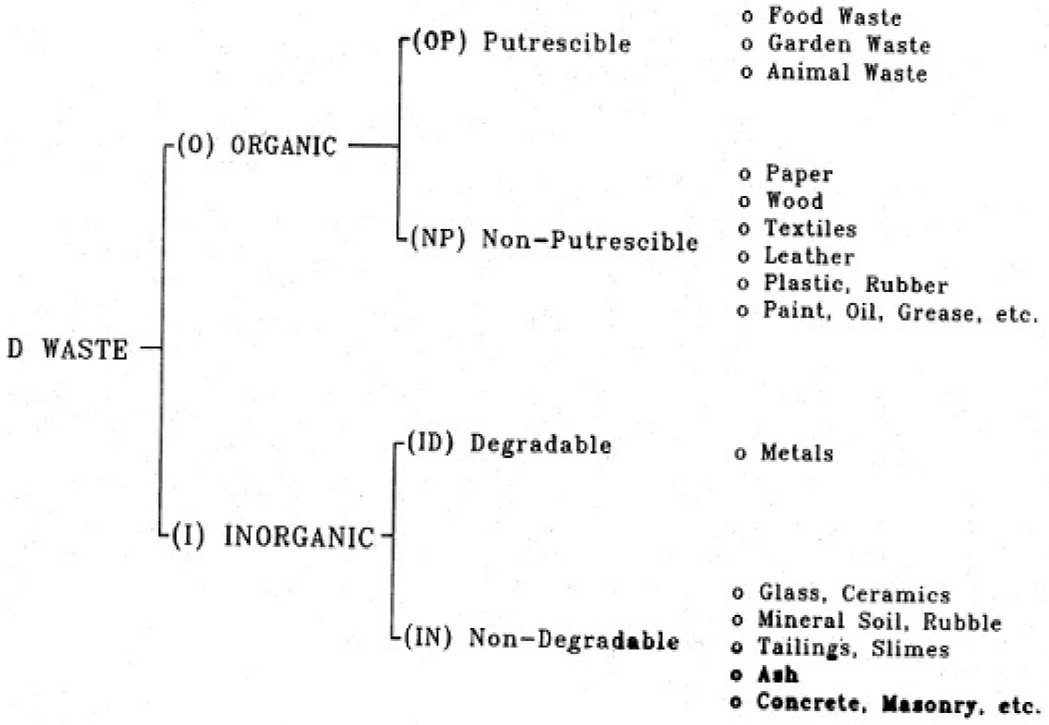
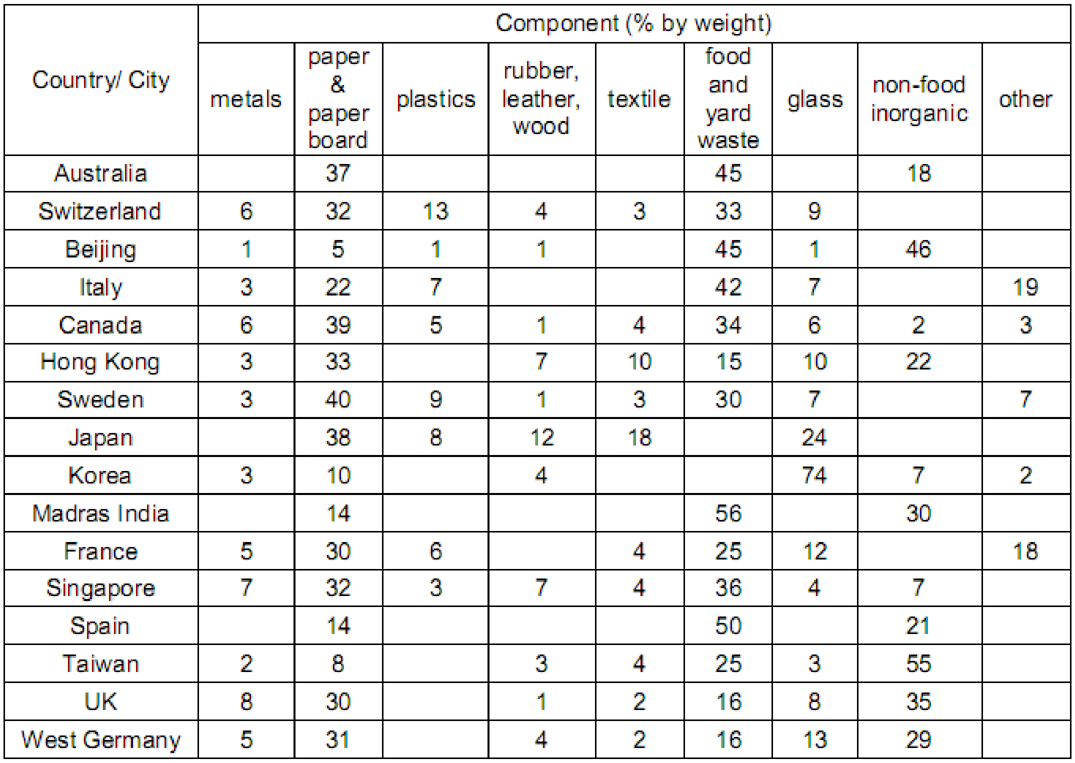


Figure 2.1 MSW Classifications by Landva and Clark (1990)

Oweis and Khera classified MSW samples from several countries according to several categories as shown in Table 2.1

Table 2.1 Composition of MSW in Different Countries by Oweis and Khera (1998)



Country/ City	Component (% by weight)								
	metals	paper & paper board	plastics	rubber, leather, wood	textile	food and yard waste	glass	non-food inorganic	other
Australia		37				45		18	
Switzerland	6	32	13	4	3	33	9		
Beijing	1	5	1	1		45	1	46	
Italy	3	22	7			42	7		19
Canada	6	39	5	1	4	34	6	2	3
Hong Kong	3	33		7	10	15	10	22	
Sweden	3	40	9	1	3	30	7		7
Japan		38	8	12	18		24		
Korea	3	10		4			74	7	2
Madras India		14				56		30	
France	5	30	6		4	25	12		18
Singapore	7	32	3	7	4	36	4	7	
Spain		14				50		21	
Taiwan	2	8		3	4	25	3	55	
UK	8	30		1	2	16	8	35	
West Germany	5	31		4	2	16	13	29	

In the United States, a total of 250 million tons of waste was generated in 2010 (U.S. E.P.A, 2008). The different components of this waste stream can be broken down as: Paper: 28.5%, Food Scraps: 13.9%, Yard Trimmings: 13.4%, Plastics: 12.4%, Metals: 9.0%, Rubber, Leather, and Textiles: 8.4%, Wood: 6.4%, Glass: 4.6% and Other: 3.4%. According to the Texas Commission on Environmental Quality (TCEQ), in 2000, 44.8 million tons of waste was generated in Texas. Approximately 64% of this generated MSW was disposed of in landfills and 35% of the waste was recycled and composted. In Texas, as in most other places in the United States, landfills will remain a significant aspect of MSW management for the foreseeable future.

2.1.2 Conventional and Bioreactor Landfills

Engineered landfilling is considered to be the most common, economical and environmentally acceptable method among all other solid waste disposal systems. The total amount of solid waste generated in United States on 2010 was 249.9 million tons, with 136 million tons (54.3% of the total generated waste) discarded in landfills (USEPA, 2011). Due to the absence of propitious surroundings and lack of nutrients in ‘conventional or dry tomb landfills’, refuse decomposition occurs at a suboptimal rate that can take as long as 50 to 100 years for the complete decomposition of refuse materials. This complicates the post-closure monitoring period, which is currently set as 30 years, and future development on top of the MSW landfills. Therefore, the idea of rapid biodegradation using supplemental water addition was brought to the forefront during 1970s.

‘Bioreactor or Enhanced Leachate recirculation (ELR) landfill’ operation offers an emerging technology where the presence of additional moisture leads to rapid waste decomposition. A major aspect of bioreactor landfill is the addition of liquid and recirculation of collected leachate back through the refuse mass with the goal of providing better contact between the waste and microorganisms via solvent medium. The injected moisture percolates through the waste mass and creates a friendly environment for the microbial activity.

Bioreactors stabilize the biodegradable portions of the waste within 5-10 years of the waste placement. This is much less than the 30 year post-closure time period of the RCRA Subtitle D landfills. In addition, the dry tomb landfills may have problems of environmental release due to failure of the contentment system even after 30 years due to waste still not degraded. Moreover, the bioreactor landfills are potentially more suitable due to the decomposition taking place faster, freeing up additional space available for MSW placement. A graphical comparison between a conventional landfill and a bioreactor landfill is shown in Figure 2.2.

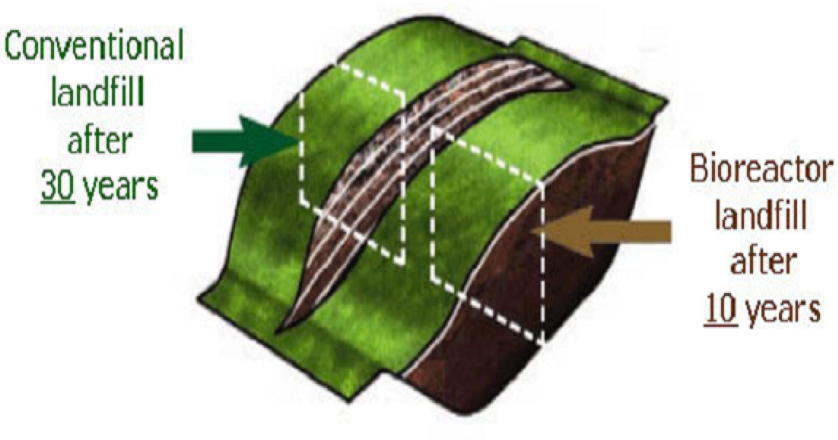


Figure 2.2 Comparison between Conventional and Bioreactor Landfills

In the past, several laboratory and field scale researches were performed on accelerated decomposition in bioreactors, such as Haque (2007), Penmethsa (2007), and Manzur (2010). The effect of the leachate recirculation was prominent in waste decomposition and gas generation as found by these researchers.

2.2 Biodegradation of Municipal Solid Waste

2.2.1 Steps of Fermentation of Organic Matter to form Methane

The steps involved in methane fermentation are: hydrolysis, acetogenesis and methanogenesis. Fermentative bacteria hydrolyze lipids, proteins and polysachharides producing acetate and other saturated fatty acids, carbon dioxide and hydrogen. The acetogens utilize the end products of hydrolysis to form hydrogen and acetate. The methanogens catabolize the end products of hydrolysis and acetogenesis to the formation of carbon dioxide and methane. The entire process is very important to the carbon cycle as it involves conversion of complex organic matter to a clean and easily purified gaseous end products, with very little bacterial yield. Methane retains more than 90% substrate energy. The following reactions describe the phenomena of acetogenesis and methanogenesis, by which microbes under anaerobic conditions convert organic wastes to methane.

Acetogenesis

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \qquad (1)$$

Methanogenesis

$$CH_3COOH \rightarrow CH_4 + CO \qquad (2)$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad (3)$$

(Reference: Perez et al., 2002)

A mixture of interacting microbial species takes part in the process of methane production, most of which do not produce methane as such. The main electron acceptors in the process such as carbon dioxide are produced from degraded organic substrates. In environments where electron acceptors such as oxygen, sulfate or nitrate are readily available, the process of anaerobic methanogenesis does not take place.

The stages in the fermentative process are shown in Figure 2.3.

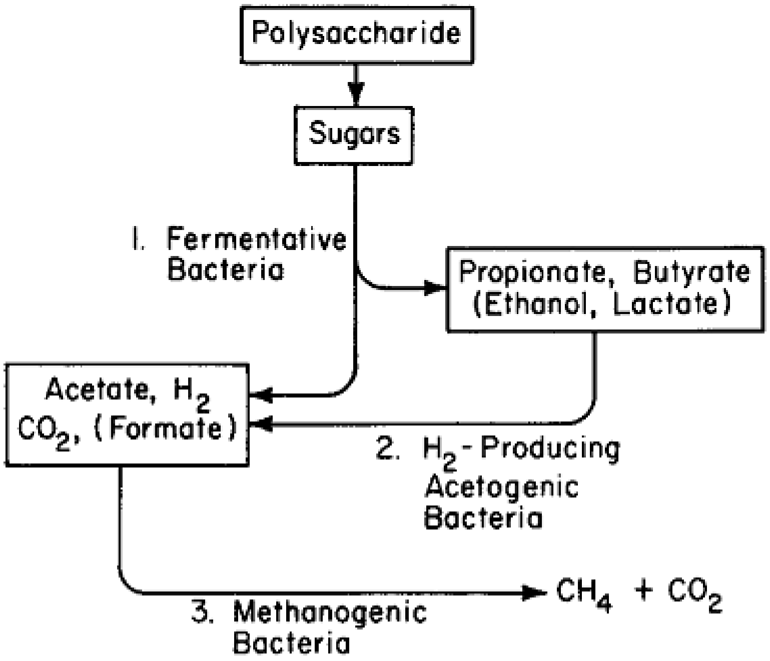


Figure 2.3 Stages of Fermentation in Methane Production

2.2.2 Phases of MSW Degradation in Landfills

MSW undergoes a number of different phases of degradation in a landfill. In a typical landfill, the waste goes through about five phases of decomposition, which are shown in Figure 2.4:

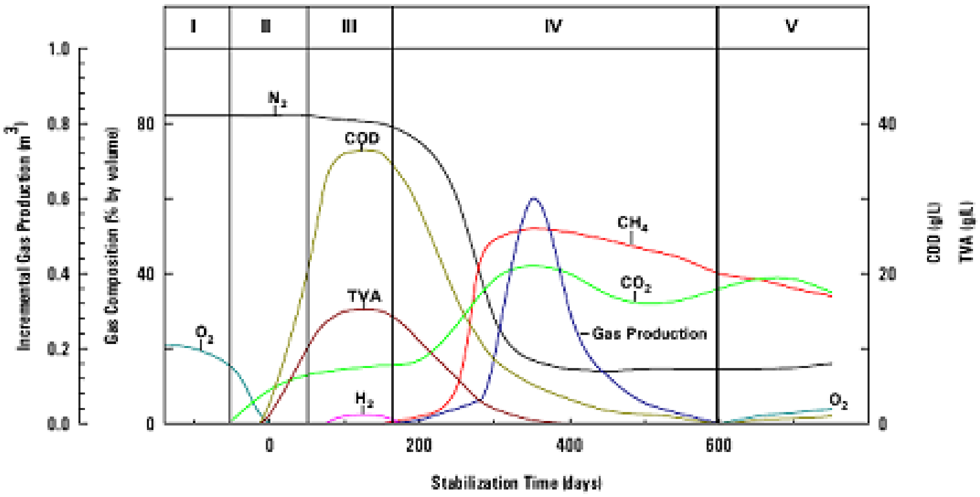


Figure 2.4 Phases of MSW Degradation in Landfills

Phase I: Initial adjustment phase – This is when the solid waste is placed in a landfill and a buildup of moisture is allowed in order to support an active microbial community. A lag period may be observed, during which the microbes acclimate and environmental components change in order to create conditions favorable to biochemical degradation.

Phase II: Transition phase - This particular phase is characterized by oxygen depletion and a shift from aerobic towards an anaerobic condition. Field capacity is sometimes exceeded and reducing conditions prevail. Electron acceptors are the nitrates and the sulfates and carbon dioxide displaces oxygen. A high concentration of COD and VOA can be found in the leachate

Phase III: Acid formation phase – Hydrolysis of solid waste takes place, with the formation of intermediate volatile organic acids (VOA). pH shows a downward trend and the mobilization of the metal species present occurs. There is considerable growth in the population of acetogenic bacteria, which consume substrate and nutrient alike.

Phase IV: Methane fermentation phase – During this phase, the methanogenic bacteria consume the intermediate VOA and produce methane and carbon dioxide. The sulfate and nitrate species are converted into sulfide and ammonia, respectively. The pH of the system goes up, being controlled by the bicarbonate buffering system. Heavy metals are precipitated out during this stage.

Phase V: Maturation phase – This is the final phase, when substrates and nutrients are limiting, and biological activity comparatively much slower. Gas production drops dramatically and a slow reappearance of oxygen and oxidized substances may sometimes be noted. The advent and status of this final phase depends on the physico-chemical and biological conditions, age of the waste, characteristics of the waste, mode of operation and waste management and site specific conditions.

2.2.3 Factors affecting Biodegradation in Landfills

Environmental conditions which have most significant impact upon biodegradation in landfills include pH, temperature, nutrients, absence of toxins, moisture content, particle size and oxidation-reduction potential. Details about some of these factors are provided below:

- Moisture content: Increasing the moisture content of the waste accelerates biodegradation. According to Pohland (1986) and Rees (1980), optimum moisture content for rapid waste decomposition and increased gas generation is about 60%. This is the fundamental principle behind a bioreactor landfill.
- pH: This is a measure of the hydrogen ion concentration and is one of the important factors governing the rate of biodegradation of waste. At pH 6 and up to a pH of 8, ideal conditions for methanogenesis are created. Below pH 6, acetogens out-compete the methanogens and therefore, production of methane is lower.
- Alkalinity: Alkalinity is the capacity of a solution to neutralize an acid, The optimum alkalinity for methanogenesis is 2000 mg/L (Farquhar and Rovers, 1973).
- Temperature: Hartz et al. (1982) reported the optimum temperature for methanogenesis to be 41ºC. At landfills, the phases of waste decomposition take place around 37-41ºC.

Therefore, the samples in this study were maintained in environmental growth chambers at a temperature of 100℉ throughout the period of study.

- Nutrients: Christensen and Kjelden (1989) reported that generally all nutrients are available in adequate quantities in the MSW from landfills. Iron, phosphorus, calcium, magnesium, trace minerals and vitamins fall under the category of nutrients.

Information on factors affecting MSW degradation is summarized in Table 2.2.

Table 2.2 Factors influencing MSW Degradation in Landfills

Sl.No.	**Influencing factors**	**Criteria/Comments**	**Reference**
1.	Moisture	Optimum: 60% and above	Pohland (1986); Rees (1980)
2.	Oxygen	Optimum redox potential for methanogens:	
		-200 mv	Farquhar & Rovers (1973)
		-300 mv	Christensen & Kjelden (1989)
		< -100 mv	Pohland (1980)
3.	pH	Optimum pH for methanogenesis:	
		6 to 8	Ehrig (1983)
		6.4 to 7.2	Farquhar & Rovers (1973)
4.	Alkalinity	Optimum alkalinity for methanogenesis: 2000 mg/L.	Farquhar & Rovers (1973)
		Maximum organic acid concentration for methanogenesis: 3000 mg/L	Farquhar & Rovers (1973)
		Maximum acetic acid/alkalinity ratio for methanogenesis: 0.8	Ehrig (1983)
5.	Temperature	Optimum temperature for methanogenesis;	
		40°C	Rees (1980)
		41°C	Hartz *et al* (1982)
		45 (34 – 38°C)	Mata-Alvarez *et al* (1986)
6.	Hydrogen	Partial hydrogen pressure for acetogenesis: $<10^{-6}$ atm	Barlaz *et al* (1987)
7.	Nutreints	Generally adequate	Christensen & Kjelden (1989)
8.	Sulphate	Increase in sulphate decrease in methanogenesis	Christensen & Kjelden (1989)
9.	Inhibitors	Cation concentration producing moderate inhibition (ppm)	McCarty & McKinney (1961)
		Ammonium (Total) : 1500 – 3000	
		Sodium : 3500 - 5500	
		Potassium : 2500 – 4500	
		Calcium : 2500 – 4500	
		Magnesium : 1000 – 1500	
		Heavy metals: No significance influence	Ehrig (1983)
		Organic compounds: Inhibitory effect only in significant amount.	Christensen & Kjelden (1989)

Source: (Yuen *et al*., 1994)(7)

2.2.4 Degradation of Lignocelluloses

Lignocellulose, which makes up about half of the matter produced by photosynthesis, is found in wood, grass, forestry and agricultural residues and MSW. It comprises the three polymers cellulose, hemi cellulose and lignin. They are connected by strong non covalent forces and covalent cross linkages. These bindings make degradation difficult in native substrate. However, there are many bacteria and fungi that help in the degradation by the use of hydrolytic or oxidative enzymes. Cellulose and hemicellulose are sugar derivatives, whereas lignin is made up of an aromatic polymer synthesized by phenylpropanoid precursors. Hemicellulose is made up of branches with short lateral chains containing different sugars. These sugars do not form aggregates and are easily hydrolysable. Cellulose and lignin are more abundant in nature than Hemicellulose. Lignin is not water soluble. Certain eubacteria and fungi, along with some anaerobic protozoa and slime molds, have been reported to be able to degrade cellulose. Under anaerobic conditions, the end products are carbon dioxide and methane. In nature 5-10% of cellulose degrades under anaerobic conditions. The complex structures of cellulose, hemicelluloses and lignin are represented in Figure 2.5.

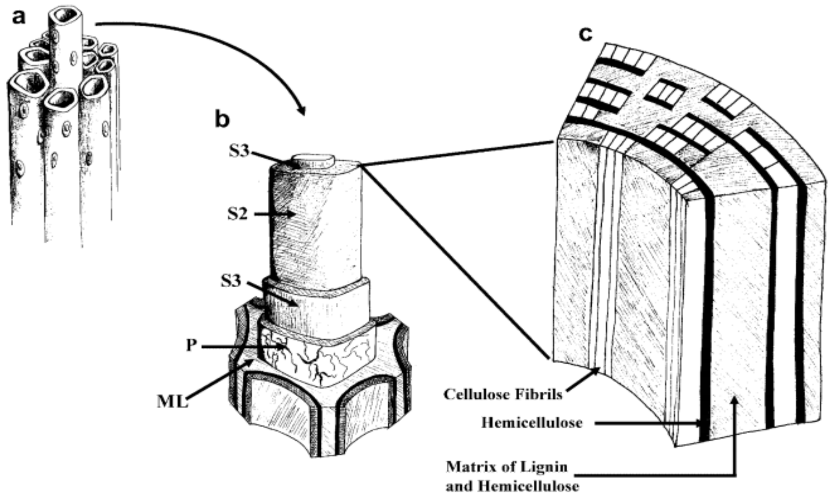


Figure 2.5 Structures of Cellulose, Hemicelluloses and Lignin in Wood Tissue

The microbial populations generally present in an anaerobic digester are: Clostridium aldrichii, Clostridium celerecrescens, Clostridium cellulovorans, Clostridium populeti (Cellulose degradation in anaerobic environments, Susan B. Leschine). The biochemical pathway for cellulose degradation as carried out by the microorganisms is shown in Figure 2.6:

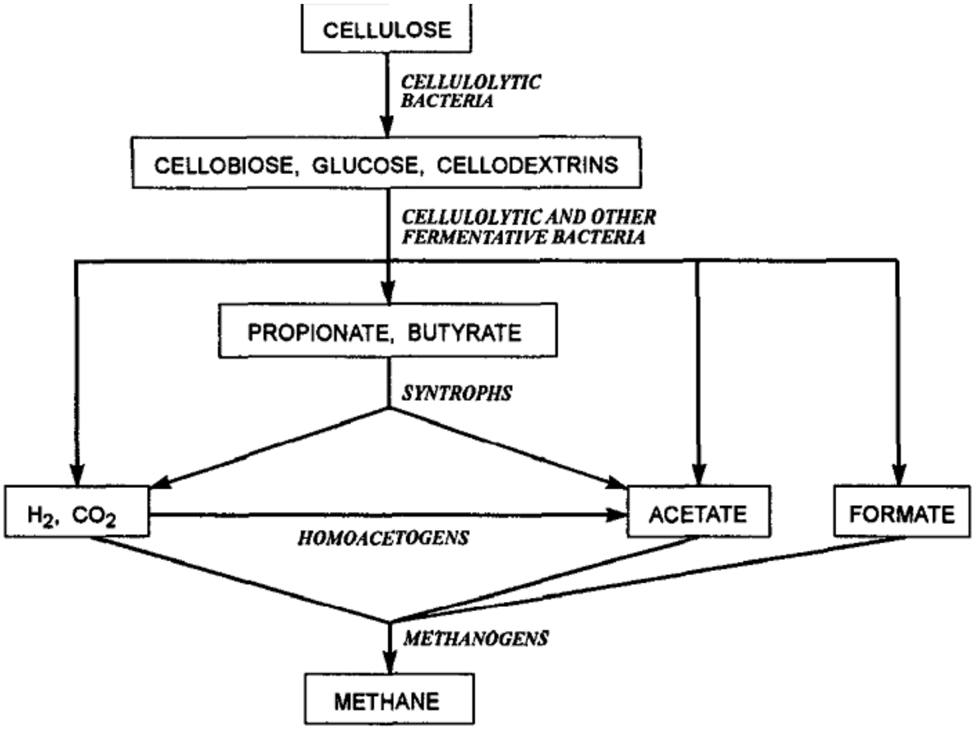


Figure 2.6 Biochemical Pathway of Cellulose Degradation

2.3. Landfill Leachate Characteristics

Leachate is any liquid that, in passing through matter, extracts solutes, suspended solids or any other component of the material through which it has passed. Leachate is a widely used term in the environmental sciences, where it has the specific meaning of a liquid that has dissolved or entrained environmentally harmful substances which may then enter the environment. It is most commonly used in the context of land-filling of putrescible or industrial waste.

The four groups of pollutants in MSW landfill leachate are:

1. Dissolved organic matter, measured as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), volatile fatty acids (accumulated during the acid phase of the waste stabilization, Christensen and Kjeldsen, 1989) and fulvic-like and humic-like compounds.
2. Inorganic macrocomponents: Ions like calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}),chloride (Cl^{-}), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^{-}).
3. Heavy metals: cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}),nickel (Ni^{2+}) and zinc (Zn^{2+}).
4. Xenobiotic organic compounds (XOCs) present in relatively low concentrations in chemicals used in households or industries (usually less than 1 mg/l of individual compounds). They include a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, and plastizers.

Compounds like borate, sulfide, arsenate, selenate, barium, lithium, mercury, and cobalt may also be present in landfill leachate, although generally present in low concentrations and of secondary importance. The variation in leachate composition depends on waste composition, waste age, and landfilling technology. Leachate sampling methods and sample handling routines may also influence the measured leachate quality.

Although the amount of hazardous waste that has been allowed into MSW landfills has decreased significantly over the last 20 years, many landfills may contain waste from a time period of fewer restrictions on hazardous waste disposal. A broad range of hazardous chemicals can be observed in landfill leachate, which is due to differences in waste composition, landfill technologies, and waste age. However, the most frequently found XOCs are: monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and halogenated hydrocarbons (tetrachloroethylene and trichloroethylene). Several of these compounds are designated as priority pollutants by the U.S. Environmental Protection Agency. Factors leading to extended lifetimes of XOCs in land-fills include the presence of special waste types having very high sorptive capacities, such as activated carbon (Kjeldsen and

Grundtvig, 1995) or insulation foams releasing CFCs (Kjeldsen and Jensen, 2001). In many older landfills and in some sanitary landfills, XOCs have been known to be disposed of in iron containers such as drums. Such containers had a high chance of maintaining the original integrity throughout the operational phase of the landfill. Any release from such container would depend upon the corrosion in iron and the physical load of waste in the landfill. Iron corrodes under anaerobic conditions, especially during the acid phase when low pH will lead to substantial corrosion (Scully, 1990). However, in many cases only slightly acidic pH is reached due to the presence of adequate buffer in the waste (Christensen et al., 1992). Anaerobic corrosion of iron follows the reaction (Reardon, 1995):

$$Fe\,(s)+2H_2O(l)= Fe^{2+}+2OH^{-}+ H_2(g)= Fe(OH)_2(s)+ H_2\,(g)$$

As shown, the reactions produces hydroxide-ions leading locally to increased pH, precipitating calcium, magnesium, and iron present in the leachate on the iron surfaces. As previously discussed, acidity may be produced in the landfill phases following the methanogenic phase due to oxidation of organic matter and sulfides. This may locally dissolve the passivating layer on the iron surface and expose it to aerobic corrosion. Aerobic corrosion is generally faster, especially if pitting corrosion takes place literally forming open holes in the iron surface (Scully, 1990).

A combination of effective microorganisms and methanogenic reactors using treated leachate recirculation maybe a good way to increase the degree of MSW stabilization, and enhance the rate and quality of gas production for energy recovery (He et al., 2005). Figure 2. 7 shows trends observed in landfill leachate properties.

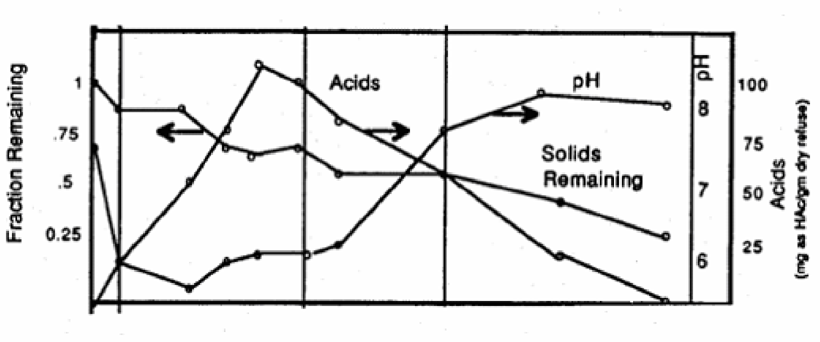


Figure 2. 7 Landfill Leachate Characteristics (Hossain, 2002)

2.4 Landfill Gas Characteristics

Landfill gas is primarily the by-product of anaerobic biodegradation of organic materials in landfills. Landfill gas generation is a biological process in which microorganisms decompose organic waste to produce carbon dioxide, methane, hydrogen sulfide and other gases, as discussed in previous sections. The landfill gases are categorized into two distinct groups as principal gases and trace gases. Principal gases are present in landfill gas in higher quantities (i.e. CH_4, CO_2), whereas the trace gases (i.e. H_2S) have lower amounts. Although the trace gases are present in small quantities, these may be toxic and pose a risk to public health. Table 2.3 gives the composition of landfill gas, as reported in a study by the Energy Information Administration, US Department of Energy, (1996).

Table 2.3: Composition of Landfill Gas (US DOE, 1996)

Compound	Compound average concentration (%)
Methane	50
Carbon dioxide	45
Nitrogen	5
Non-methanogenic organic compounds (NMOC)	2700 ppm_v
Hydrogen sulfide	<1

In bioreactor landfills, complete degradation of one ton of MSW would generate 208 standard cubic meters of methane biogas, or 0.149 tons of methane. This prediction is based on the waste characterization by US EPA (2003), which is shown in table 2.4 as follows.

Table 2.4: Characterization of MSW in U.S.A (US EPA, 2003)

Characterization of US MSW by USEPA

Biomass components	(%)	Petrochemical components	(%)
Paper/board	36.2	Plastics	11.3
Wood	5.8	Rubber, nylon, etc.[a]	3.7
Yard trimmings	12.1		
Food scraps	11.7		
Cotton, wool, leather[a]	3.7		
Total biomass	69.5%	Total man-made	15.0%

[a] Rubber, leather and textiles category of USEPA was assumed to be divided equally between natural and man-made products.

The rate of biodegradation of MSW in landfills was studied by Barlaz et al. (2006) in small pilot plant columns that provided ideal temperature and concentration conditions for bio-reaction. As shown in Figure 2.8, the reaction peaked at less than one hundred days and was nearly complete after about 320 days. Barlaz (2006) estimated that the total amount of gas generated during this period was 213 Mm^3 methane/dry ton of biomass reacted.

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2 \qquad (4)$$

$$C_6H_{10}O_4 + 1.5\ H_2O \rightarrow 3.25\ CH_4 + 2.75\ CO_2 \qquad (5)$$

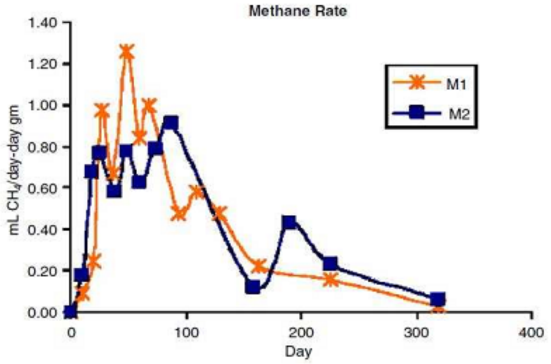


Figure 2.8 Generation of Methane in Simulated Bioreactor Landfills (Barlaz, 2006)

2.5 Nano Zero Valent Iron Particles and their Potential For Waste Treatment

Nanotechnology is the use and manipulation of matter of dimensions of 1- 100 nanometers. Nano particles have higher surface area to volume ratio than larger particles. This allows the particles to have more contact area, which increases their reactivity Figure 2.9 shows the relationship between surface area and diameter of nanoparticles (Lewinski,2008).

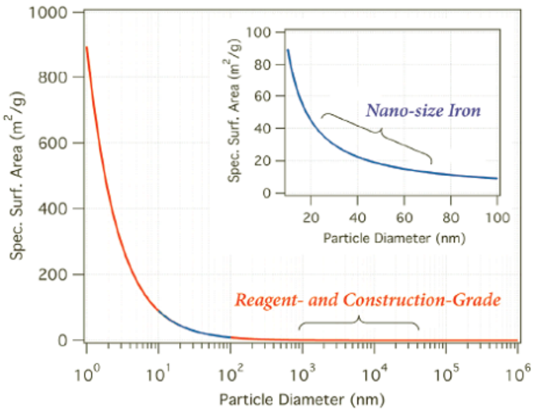


Figure 2.9 Relationship between Surface Area And Diameter of Nanoparticles (Lewinski, 2008)

In nature, iron is available in the form of Fe (II) or Fe(III). As a result, zero valent iron is artificially synthesized using a number of different methods in the laboratory. Synthesis of nanomaterials used in environmental remediation can be carried out using top down methods, which involve creation of nanoparticles from larger size materials by machining, milling, etching, etc.; or using bottom up methods, which involve growth of nanoparticles atom by atom via chemical synthesis, self-assembly, etc. Bottom up methods of nanoparticle synthesis include:

- Vacuum sputtering
- Synthesis from reduction of goethite and hematite particles with hydrogen gas at elevated temperatures, i.e. 200-600℃
- Decomposition of iron pentacarbonyl in organic solvents
- Electrodeposition of ferrous salts

- Reduction of ferric or ferrous salts with sodium borohydride
- Bimetallic nanoparticles can be prepared by soaking the freshly prepared nZVI in a solution of a less reactive metal salt such as Pd, Ni, etc.

Varying methods of synthesis cause a variation of surface properties in the iron nanoparticles. One of the advantages of the borohydride method is its relatively simplicity. There is no need for special instruments, and commonly available chemicals are used. The method involves slow addition of a 1:1 volume ratio of 0.25 M sodium borohydride into 0.045 M ferric chloride solution. A fume hood is used in the process due to the hydrogen gas that is a byproduct of the process. Also, explosion-resistant mixers are to be used. Nano particles produced can be collected by vacuum filtration. A Transmission Electron Microscope (TEM) image of nZVI particles is given below in Figure 2.10.

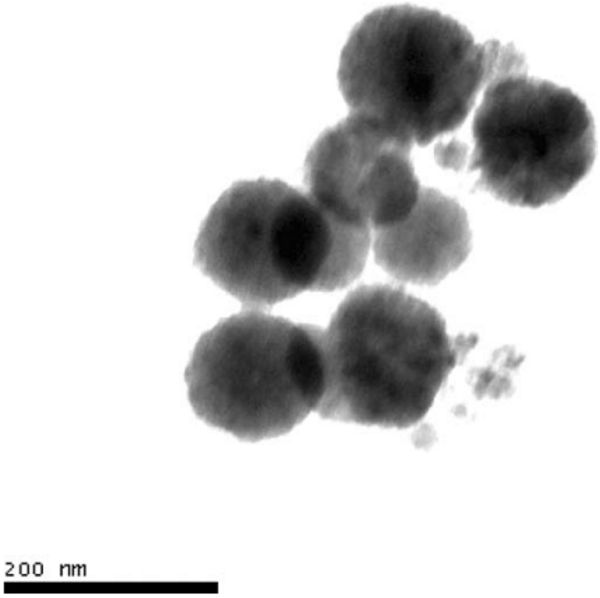


Figure 2.10 TEM Image of nZVI (Li et al, 2006)

Nano zero valent iron particles have a core-shell model, as shown in Figure 2.11. At the core of this model is the zero valent iron and on the shell are oxides and oxyhydroxides such as FeOOH. This structure enables the nZVI to exhibit reductive and sorbent properties.

Due to its relatively low oxidation-reduction potential, zero-valent iron has long been used as an inexpensive, efficient and environmental friendly reductant (Zhang et al., 1998; Zhang,2003). Iron forms ferrous ions when it donates two electrons. Ferrous iron (Fe(II)) can further donate an additional electron and be oxidized to ferric iron(Fe(III)). While oxygen and water are common electron acceptors in the environment, other substances including many environmental contaminants can serve as the ultimate electron acceptors.

In water, iron reacts to quickly form a layer of oxyhydroxide on the particle surface. The adsorption properties of ferrioxyhydroxide (FeOOH) in aquatic systems have been extensively studied and are well documented (Dzombak & Morel, 1990; Stumm,1992; Stumm & Morgan, 1996). In water, iron oxides can have coordination properties like metals or ligands depending on the solution chemistry. When the solution pH is below the isoelectric point (8.1–8.2), iron oxides are positively charged and attract ligands (e.g., phosphate,arsenate). When the solution pH is above the isoelectric point, the oxide surface becomes negatively charged and can form surface complexes with cations, such as Pb(II). With sufficient (e.g., >0.01 g/l) iron nanoparticles added to water, solution pH is typically in the range of 8–10 and favorable for metal ion adsorption.

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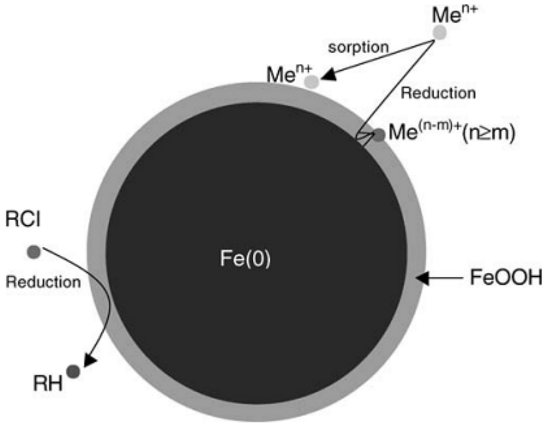


Figure 2.11 Core Shell Model of nZVI (Li et al., 2006)

Nano zero valent iron particles have been shown to degrade chlorinated organic contaminants like PCBs and pesticides, sequestrate metal ions like lead and mercury, and form stable and non volatile surface complexes with odor-causing sulfur compounds (Xiao-Quin Li et al., 2007). The end products themselves are harmless like iron oxides and iron minerals. The heavy metals form surface complexes with the oxide surface in the nZVI shell, which renders them immobile and therefore, toxicity of the water or soil is reduced. A relatively low dosage which < 0.1% of the total solids weight of nZVI can be used (Li et al., 2007). The ability of nZVI to treat each of these three categories of contaminants (chlorinated organics, metals, and odor-causing sulfur compounds) will now be discussed in turn.

2.5.1 Nano Zero Valent Iron*'s Potential to Reduce Chlorinated Organics*

Chlorinated organics are typically difficult for microbes to degrade; few specific anaerobes may be capable of doing so (Lovley,2001). However, even for the anaerobes which might be capable of degrading chlorinated hydrocarbons, consistent successes have not been reported. Removing chlorine atoms from organics can render them amenable to microbial degradation. This would be important in facilitating the anaerobic microbial degradation of chlorinated organic present in landfill waste.

As a reducing agent, iron is efficient due to its low oxidation-reduction potential and is itself oxidized to produce the ubiquitous iron oxides that are themselves quite harmless. Contaminant transformation has been documented by Zhang (2003), Li et al. (2007), Li et al. (2006) for halogenated organics such as Hexachlorocyclohexanes (HCH), Trichloroethylene (TCE) and Polychlorinated biphenols (PCB). The conversion of TCE to ethene involves the reactions as shown in Figure 2.12. The detailed biochemical pathway is presented in Figure 2.13.

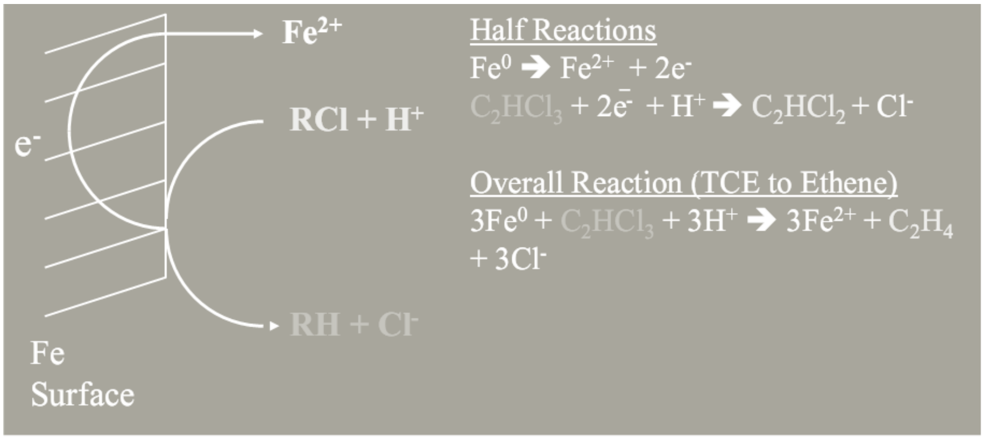


Figure 2.12 Conversion of TCE to Ethene (Golder Associates, 2012)

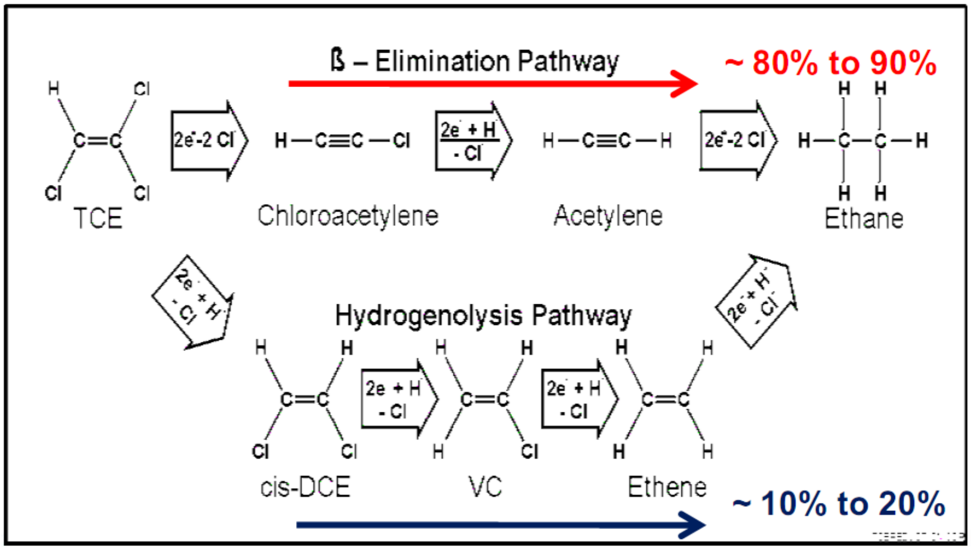


Figure 2.13 Reductive Elimination of Chlorinated Ethylene by ZVI Metals (Roberts et al., 1996)

Table 2.5 lists all common organic contaminants that can be converted by the use of nano scale zero valent iron particles.

Table 2.5 Organic Contaminants Converted by nZVI (Li et al., 2007)

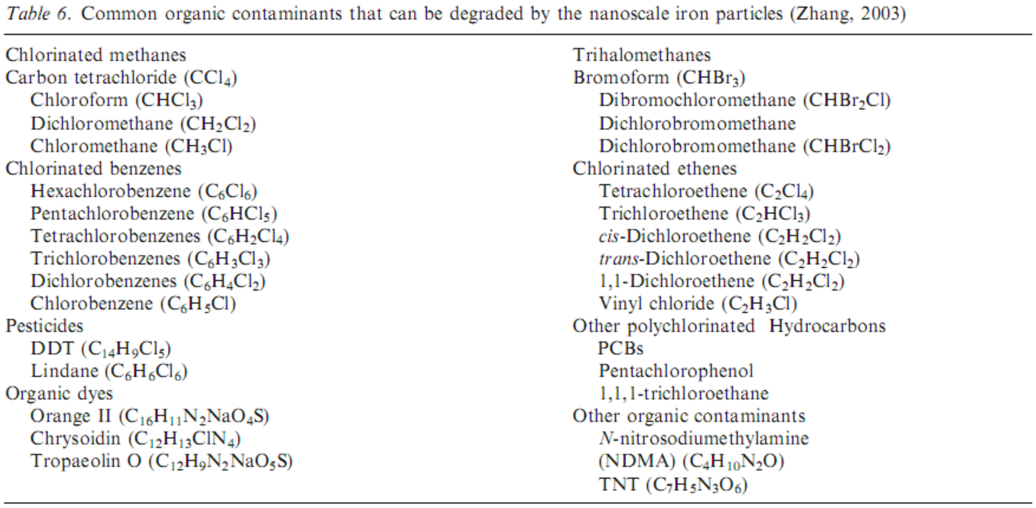


Table 6. Common organic contaminants that can be degraded by the nanoscale iron particles (Zhang, 2003)

- Chlorinated methanes
- Carbon tetrachloride (CCl_4)
  - Chloroform ($CHCl_3$)
  - Dichloromethane (CH_2Cl_2)
  - Chloromethane (CH_3Cl)
- Chlorinated benzenes
  - Hexachlorobenzene (C_6Cl_6)
  - Pentachlorobenzene (C_6HCl_5)
  - Tetrachlorobenzenes ($C_6H_2Cl_4$)
  - Trichlorobenzenes ($C_6H_3Cl_3$)
  - Dichlorobenzenes ($C_6H_4Cl_2$)
  - Chlorobenzene (C_6H_5Cl)
- Pesticides
  - DDT ($C_{14}H_9Cl_5$)
  - Lindane ($C_6H_6Cl_6$)
- Organic dyes
  - Orange II ($C_{16}H_{11}N_2NaO_4S$)
  - Chrysoidin ($C_{12}H_{13}ClN_4$)
  - Tropaeolin O ($C_{12}H_9N_2NaO_5S$)
- Trihalomethanes
- Bromoform ($CHBr_3$)
  - Dibromochloromethane ($CHBr_2Cl$)
  - Dichlorobromomethane
  - Dichlorobromomethane ($CHBrCl_2$)
- Chlorinated ethenes
  - Tetrachloroethene (C_2Cl_4)
  - Trichloroethene (C_2HCl_3)
  - *cis*-Dichloroethene ($C_2H_2Cl_2$)
  - *trans*-Dichloroethene ($C_2H_2Cl_2$)
  - 1,1-Dichloroethene ($C_2H_2Cl_2$)
  - Vinyl chloride (C_2H_3Cl)
- Other polychlorinated Hydrocarbons
  - PCBs
  - Pentachlorophenol
  - 1,1,1-trichloroethane
- Other organic contaminants
  - *N*-nitrosodiumethylamine (NDMA) ($C_4H_{10}N_2O$)
  - TNT ($C_7H_5N_3O_6$)

Wei-xian Zhang et al. (2003) described the successful implementation of nZVI to treat contaminated soil and groundwater at a U.S. Naval site. At first laboratory batch tests were carried out on samples obtained from the site. The groundwater sample contained 6070 µg/l of TCA, 4680 µg/l and few other chlorinated hydrocarbons < 100 µg/l. Batch tests were carried out with 80 ml water, 0-20 g soil and nanoparticles at varied concentrations. At regulated time intervals, 5-10µl aliquot was withdrawn from the headspace from each bottle and analyzed using gas chromotography. Greater than 99% removal efficiency was achieved. The researchers studied the effect of nanoparticles in the following areas, as-

- Installation of injection well and monitoring wells
- Analysis of groundwater samples from injection and monitoring wells to define baseline conditions

- Pilot test field injection and nanoparticle injection monitoring using continuous electronic measurements of flow rate, water level, ORP, DO, pH, specific conductance and temperature and also post injection monitoring

The iron nanoparticles were injected as a slurry suspension prepared onsite with potable water. In total 1600 gallons were injected with nanoprticle concentration of 1.9 g/l. Total 11.2 kg of nanoparticles were used during the study. The liquid injection was carried out for two days with 0.6 gpm of injection rate. Continuous mixing was utilized during the process. PCE, TCE and DCE concentrations were all considerably reduced, which is evident from Figure 2.14.

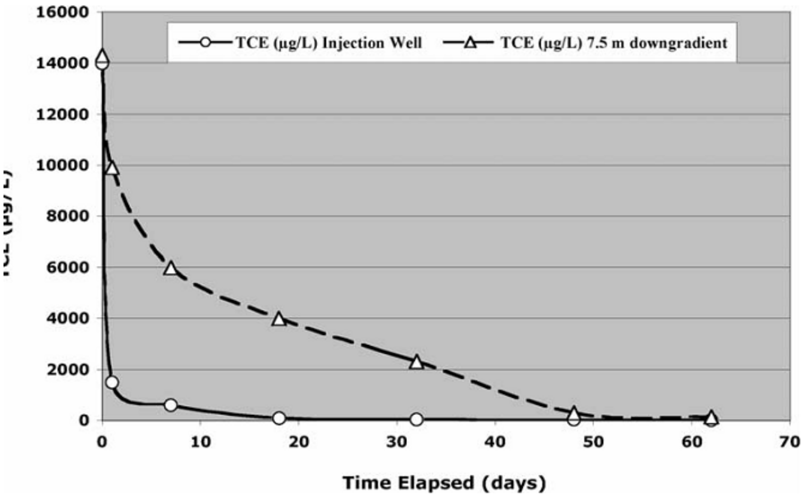


Figure 2.14 Reduction of TCE through Application of nZVI (Zhang et al., 2003)

A trend of pH increase and Oxidation-Reduction Potential (ORP) decrease was observed. Similar trends were observed by Shi et al in 2011. In Figures 2.15 and 2.16, the change in ORP with change in nZVI concentration and time are shown, respectively. This condition may favor the growth of methanogens by virtue of the increase in pH and this can accelerate biodegradation (Zhang,2003).

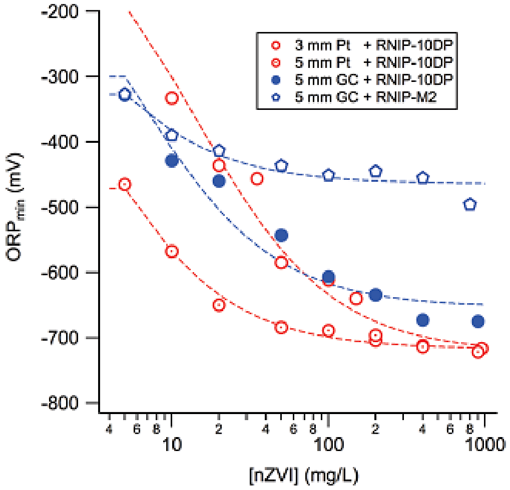


Figure 2.15 Change in ORP with nZVI Concentration (Shi et al. 2011)

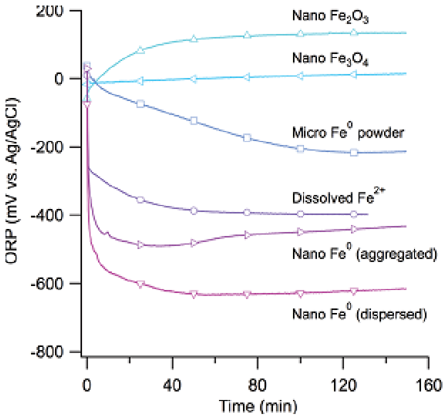


Figure 2.16 Change in ORP with Time (Shi et al. 2011)

2.5.2 Nano Zero Valent Iron*'s Potential to Remove Metals*

As a sorbent, feroxyhydroxide has been found to be quite effective. At lower pH, positively charged iron oxides attract ligands like phosphate and arsenate. In solution with pH above the isoelectric point, negatively charged iron oxide forms surface complexes with Pb. Also, as per classical corrosion chemistry, iron may serve as an electron donor for reduction and immobilization of heavy metal ions in water, e.g., Ni, Pb, Cu.

2.5.3 Nano Zero Valent Iron*’s Potential to Remove Odor- Causing Sulfides*

Reacting with water and oxygen, iron transforms into ferrous ions, which precipitate with sulfide as FeS. This is key to removing odor-causing sulfides, such as hydrogen sulfide. The reduction of hydrogen sulfide in the presence of nZVI has been documented, as shown in Figure 2.17.

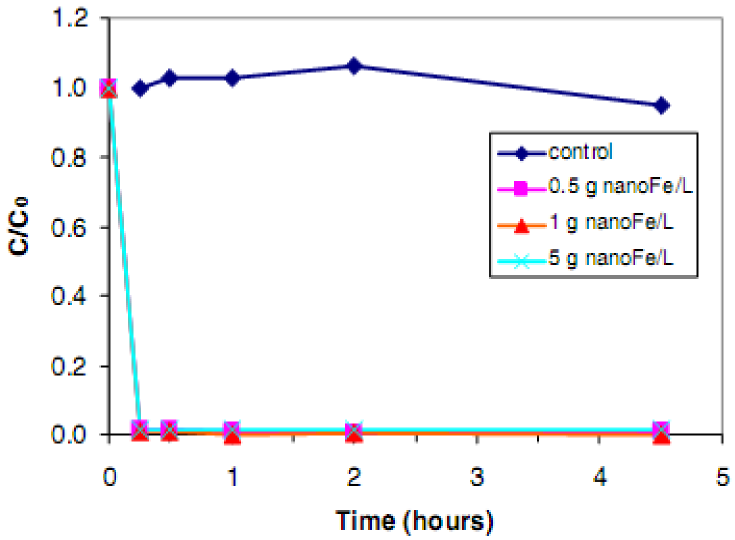


Figure 2.17 Reduction of Hydrogen Sulfide in Presence of nZVI (Li et al, 2007)

2.5.4 Challenges in the Use of Nano Iron Particles for Waste Treatment

Nano iron particles tend to aggregate and adhere to surfaces of natural materials. Hence the dispersion of nano particles is an area of concern. The mobility of iron nano particles depends on a number of factors:

- Particle size
- Solution pH
- Ionic strength
- Soil composition
- Groundwater flow velocity

Water soluble starch (He and Zhao, 2005), carbon pellets and Polyacrylic acid (PAA) (Mallouk et al,2004) have been used as good dispersants. Surface modification has also been used by Saleh et al., (2005).

The following are additional concerns/challenges involving the wide-scale use of nZVI:

- Materials chemistry: cost effective mode of production is necessary for widespread use of nZVI.
- Environmental chemistry: Detailed study of reaction rates, mechanisms and effect of environmental factors like pH, ionic strength, and competing contaminants on the transformation of targeted contaminant need to be carried out.
- Geochemistry: study of nZVI reaction with surface and ground water, interaction with soil and sediment, settling, aggregation, and transport phenomenon is needed.
- Environmental impact needs to be studied in greater detail.

2.5.5 Study of the Effect of Divalent Iron On Anaerobic Methane Production

Ahmed et al. (2001) studied the effect of divalent iron on methanogenic fermentation of fat-containing wastewater. The impact was reported as positive on long chain fatty acids (LCFA) like stearic acid, where the methane production rate increased in the presence of iron. Lipids such as grease, oil and fats undergo hydrolysis to produce long chain fatty acids, which are then degraded by the beta-oxidation in the anaerobic process (Ahmed et al., 2001). LCFA are known inhibitors of anaerobic microorganisms, possibly both acetogens and methanogens. Also they may be surface active and adsorb onto cell walls, thus inhibiting transport phenomena. Sometimes the presence of hydrogen sulfide due to the activity of sulfate reducing bacteria may also cause problems. However, iron precipitates with both LCFA and H_2S. Salt formation with H_2S by iron may diminish its concentration and subsequently its inhibitory effect on methanogenesis. Under the presence of ferric iron, sulfate reducing bacteria are outcompeted by the iron reducing bacteria for hydrogen.

Ahmed et al. observed that acetic acid propionic acid accumulated in the reactor when iron was not present or the COD/Fe ratio was higher than 20. This inhibited the process of methanogenesis. It was concluded from the study that iron inhibited methanogenesis in case of SCFA and had a positive effect on the anaerobic degradation of LCFA. Figure 2.18 shows the increase in COD removal efficiency with the application of varying doses of iron.

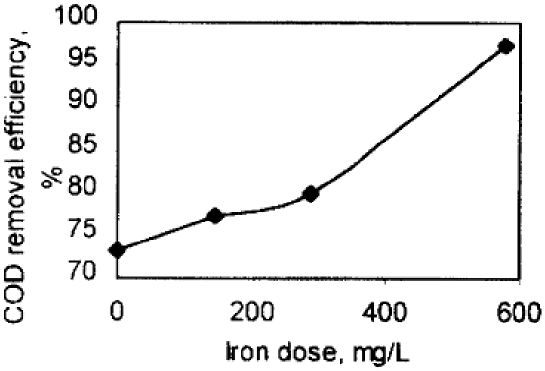
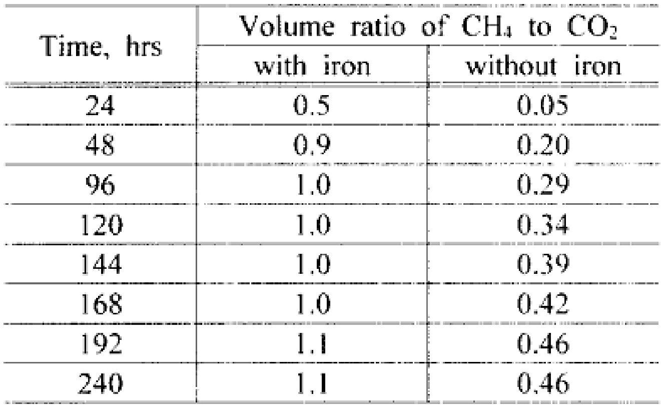


Figure 2.18 Improvement of COD Removal Efficiency with Varying Dosages of Iron (Ahmed et al., 2001)

Table 2.6 lists the volume ratio of methane to carbon dioxide during the fermentation of stearic acid with and without iron as a function of time.

Table 2.6 Ratio of Methane to Carbon Dioxide in Biogas during Fermentation of Stearic Acid. (Ahmed et al., 2001)



Time, hrs	Volume ratio of CH_4 to CO_2	
	with iron	without iron
24	0.5	0.05
48	0.9	0.20
96	1.0	0.29
120	1.0	0.34
144	1.0	0.39
168	1.0	0.42
192	1.1	0.46
240	1.1	0.46

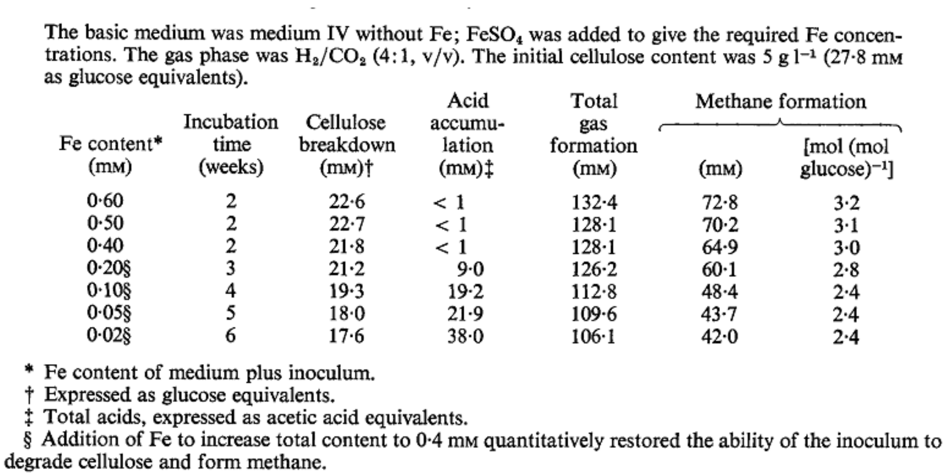
Among the various factors controlling the symbiotic-metabolic interaction between different species of micro-organisms present in an ecosystem, the composition of the medium is of prime importance in substrate utilization (Khan et al, 1979). Earlier work by Khan & Trottier on washed cells obtained from an ecosystem of anaerobes maintained on a synthetic medium had shown that the concentration as well as the nature of the sulfur source had a profound effect on the overall efficiency of the system. Therefore, that work was extended to study the effect of various nutrients in the basal medium on the process and to determine their concentration for optimum degradation of cellulose to methane.

In order to determine the effects of various nutrients on the degradation of cellulose under anaerobic conditions to form methane and carbon dioxide, a synthetic medium containing inorganic sources of nitrogen, phosphorous, iron, calcium, magnesium, trace minerals and essential vitamins was developed. A mixed population of anaerobic bacteria from sewage sludge and also from batch cultures was used to degrade 4g cellulose per liter per week. They produced about 710 ml gases per gram of cellulose degraded. The total gas comprised of 51-56% methane and the remaining was carbon dioxide.

Experimental results determined that the optimum Fe concentration for methane yield is around 0.4 to 0.6 mM. At lower Fe concentrations, the cellulose degrading capability of the cultures decreased and an accumulation of acid was observed, indicating inhibition of the acetogenic phase. Iron, which is the least toxic among the heavy metals, shows no toxic effect on methane production up to a concentration of 19.6 mM. Above this concentration, the toxic effects are also minimal, provided the pH of the medium is over 6.4 (Mosey and Hughes, 1975). In order to maintain Fe concentration of 0.3 mM Fe in solution, a strictly anaerobic condition needs to be maintained; otherwise Fe tends to precipitate as phosphate or carbonate. Even under anaerobic conditions, if high amounts of nitriloacetic acid are present, H_2S reacts with Fe to form an insoluble sulfide. The equilibrium between soluble and insoluble Fe depends on pH as well as presence of chelating compounds. Removal of sulfur and hydrogen sulfide due to precipitation benefits the process, by reducing their toxic effects on methanogenesis. Also, FeS acts as a reducing agent (Cappenberg, 1974; Brock and O'Dea 1977).

Table 2.7 shows the effect of iron content on cellulose degradation, acid accumulation and gas production.

Table 2.7 Effect of Iron Content of Medium on Cellulose Degradation, Acid Accumulation and Gas Production by Mixed Cultures of Microorganisms



The basic medium was medium IV without Fe; $FeSO_4$ was added to give the required Fe concentrations. The gas phase was H_2/CO_2 (4:1, v/v). The initial cellulose content was 5 g l^{-1} (27·8 mM as glucose equivalents).

Fe content* (mM)	Incubation time (weeks)	Cellulose breakdown (mM)†	Acid accumulation (mM)‡	Total gas formation (mM)	Methane formation (mM)	Methane formation [mol (mol glucose)$^{-1}$]
0·60	2	22·6	< 1	132·4	72·8	3·2
0·50	2	22·7	< 1	128·1	70·2	3·1
0·40	2	21·8	< 1	128·1	64·9	3·0
0·20§	3	21·2	9·0	126·2	60·1	2·8
0·10§	4	19·3	19·2	112·8	48·4	2·4
0·05§	5	18·0	21·9	109·6	43·7	2·4
0·02§	6	17·6	38·0	106·1	42·0	2·4

* Fe content of medium plus inoculum.

† Expressed as glucose equivalents.

‡ Total acids, expressed as acetic acid equivalents.

§ Addition of Fe to increase total content to 0·4 mM quantitatively restored the ability of the inoculum to degrade cellulose and form methane.

2.6 Goals for the Present Study

As discussed in Section 2.5 above, nano zero valent iron has the potential to treat chlorinated organics, metals, and odor-causing sulfides. Iron also has the potential to increase anaerobic methane production from organic matter, by precipitating long chain fatty acids and sulfides, which can inhibit methane production; and by providing an optimal level of nutrients for microbes.

In MSW, some amount of chlorinated organic can be expected. Some persistent contaminants like DDT, PCB and CFCs, although being phased out can still be found in small quantities in landfill waste. Bleach used in paper can be a source of chlorinated hydrocarbons. Sometimes persistent contaminants bioaccumulate in fat tissues and sometimes they biomagnify, higher up the food chain. Therefore we may find some chlorinated hydrocarbons in food waste such as meat products. If landfill waste streams contain PVC plastics, certain paint removers and insecticides, they might add to the quantity of chlorinated hydrocarbons. Dry cleaning chemicals contain chlorinated hydrocarbons. Therefore sometimes textile waste in a landfill contribute to chlorinated compounds as well. However, the cumulative quantity of chlorinated organic compounds in MSW is usually not high enough to be significant. MSW contains metal in a larger quantity. However, they are in large pieces so that degrading them only by means of microbial action without any pretreatment may not be possible. Hydrogen sulfide gas is generated in landfills and it has an odor like rotten eggs. The major source of hydrogen sulfide is C&D debris. However, MSW landfills generally do not receive much C&D debris in its waste stream. Other sources of sulfate however do give rise to sulfides and such malodorous compounds like the hydrogen sulfide gas.

It is difficult to estimate what quantity of nano zero valent iron, if present in the MSW waste stream might contribute towards an optimal level of nutrition for the microbes. It has been reported previously by Barlaz et al. that MSW generally contains adequate nutrition for the anaerobes and that it is usually not nutrient limited. However, it can be hypothesized by adding nZVI to MSW in lab scale bioreactors, methane production may be increased due to iron precipitating long chain fatty acids and sulfide compounds. nZVI has been previously used to remove contaminants from water and soil. However, no studies have been conducted regarding the effect of adding nZVI to facilitate municipal solid waste degradation and enhance methane production. Therefore, overall goal of this study was to evaluate the effect of iron nano particles on the decomposition of MSW and the rate of methane production

CHAPTER 3

METHODOLOGY

3.1 Introduction

The primary objective of this study is to determine the effect of nano zero valent iron on biodegradation of municipal solid waste (MSW) for bioreactor landfills. To evaluate the effect of nano zero valent iron, two reactors were built: one as a control reactor and another with addition of zero valent iron dispersed in the reactor by sonication. For the current study, municipal solid waste samples were collected from the City of Denton, TX, landfill. The sample collection procedure is described in Section 3.2.

This chapter includes the physical characteristics (i.e. physical composition, moisture content, unit weight, and organic content) of the MSW samples used in the lab scale bio reactors for the present study. During the operation of the reactors to evaluate the degradation phase of the MSW, pH, BOD and COD tests were performed on leachate on a monthly basis, as illustrated in Section 3.7. Generation and composition of gas was also monitored on a regular basis to evaluate the performance of zero valent iron addition in bioreactor in landfills.

3.2 Selected Study Area

The City of Denton Landfill is located on the south east side of Denton, Texas. An aerial view of the City of Denton Landfill is shown in Figure 3.1 below.

Figure 3.1 City of Denton Landfill (Aerial View)

The City of Denton Landfill was built in 1983. It is a standard landfill for the disposal of municipal solid waste (MSW) of type 1. The landfill follows operational rules cited in the 30 TAC 330 subchapter D . The landfill currently receives approximately 550 tons of MSW a day. 80% of this waste is commercial and 20% residential. In 2009 the landfill transitioned to an enhanced leachate recirculation landfill to increase the gas production and capacity of landfill space in the current working cell.

3.3 Sample Collection

Fresh MSW samples were collected from the working face of the City of Denton Landfill in December 2011. To collect representative samples, samples were taken from three random locations. First MSW was collected from a random location of the working face by a backhoe. Then it was thoroughly mixed and quartered on another surface as shown in Figure 3.2. One quarter was randomly selected for MSW characterization. Three bags were filled with MSW. Two other locations were chosen randomly and samples were collected as previously described. The weights of the samples varied from

40 lb. to 50 lbs. The samples were brought to the laboratory in plastic bags and preserved at about 4^{o}C in the environmental growth chamber as shown in Figure 3.3.

Figure 3.2 Sample Collection

Figure 3.3 Sample Storage

3.4 Determination of the Physical Characteristics of Fresh MSW

Physical composition, moisture content, volatile solids content and unit weight were determined for all the fresh MSW samples collected from the landfill. The test procedures are presented in this section.

3.4.1 Physical Composition

Physical composition refers to the individual components that make up a solid waste stream, such as food waste, paper, plastic, yard waste, glass, metal, Styrofoam, textile and others. Usually expressed as a percentage of the total weight, information on the physical composition of MSW is necessary in the selection and operation of equipment at a landfill, in assessing the feasibility of resource and energy recovery, and in the analysis and design of landfill disposal facilities (Tchobanoglous, 1993). MSW is heterogeneous in composition, from which facts about the lifestyle and economic conditions of a community can be assessed.

The sample sorting was done manually and divided into 10 different groups of Paper, Plastic, Food waste, Textile or fabric, Yard and wood waste, Metals, Glass, Styrofoam and sponge, Construction debris and Others (unclassified material, e.g. mud and fine particles). The groups were separately weighed and their percentage in comparison to the whole sample was computed. . The percentage of each component was calculated following the formula below:

$$\text{Percentage of each component} = \frac{\text{Weight of that component (lb)}}{\text{Weight of the whole sample (lb)}} \times 100 \qquad (1)$$

The percentage of degradable and non-degradable portion of the sample was also calculated, using the formula below.

$$\text{Degradable}(\%) = \frac{\text{total weight of food, textile, wood, yard trimming and paper wastes } \mathbf{(lb)}}{\text{weight of the whole sample } \mathbf{(lb)}} \times 100 \qquad (2)$$

$$\text{Non degradable} = \text{100-percentage of degradables} \qquad (3)$$

Figure 3.4 presents the sorted samples.

Figure 3.4 Sample Sorting

3.4.2 Moisture Content

Pohland (1975) determined that the control of MSW moisture content is the most important factor in obtaining accelerated waste degradation in landfills. An aqueous environment provides enhanced methanogenesis by establishing better contact between insoluble substrates, soluble nutrients, and microorganisms and hence stimulating microbial activity (Barlaz et al., 1990). Moisture content is a measure of the amount of liquid within the waste. The moisture content can be calculated on the basis of the dry waste mass, wet waste mass or the volume of the waste.

For the current study, moisture content of the samples were determined according to standard method ASTM D2974 – 00 and APHA 2540 – B (Kelly, 2002). For each test, a minimum 2 lbs of waste were taken, so that it would be more representative of the original MSW. The measured samples were then dried at 105℃ in the oven for 24 hours to determine the moisture loss. The percent loss was determined on both dry weight and wet weight basis. Equations 3.1 and 3.2 were used to determine moisture content on wet weight basis and dry weight basis, respectively. Figure 3.7 shows sample being dried in the oven for the determination of moisture content. The wet weight moisture content is expressed as follows (Tchobanoglous et al., 1977):

$$\text{moisture content (\%)} = \frac{\text{Initial weight of the sample-Final weight of the sample}}{\text{Initial weight of the sample}} \mathbf{X\,100} \qquad (4)$$

Similarly, the dry weight moisture content may be expressed as:

$$\text{moisture content(\%)} = \frac{\text{Initial weight of the sample-Final weight of the sample}}{\text{weight of dried sample}} \mathbf{X\,100} \qquad (5)$$

The moisture content test was performed twice for both reactors and the results were reported separately.

The procedure of drying the sample in oven is presented in Figure 3.5 below.

Figure 3.5 Sample Drying

3.4.3 Unit Weight

Unit weight is defined as the weight of waste per unit volume. Unit weight of MSW depends mainly on the composition of the waste, the degree of compaction, the type of cover soil, and stage of decomposition. For bioreactor landfills, unit weight is a critical parameter because it affects the permeability of the waste, and thus affects the amount of leachate that needs to be recirculated and the amount of leachate that will be produced. A wide range of unit weight values of MSW have been reported in literature.

The unit weights of the samples were determined at their natural moisture content. The municipal solid waste was compacted as per Standard Proctor Compaction ASTM D698. The compaction was performed using a 5.5 lb hammer under free fall from a 12 inch elevation. The sample was compacted in three layers and each layer was compacted with 75 drops. The volume of the mold was determined and consequently the unit weight was calculated by dividing the total weight by the volume. The compaction mold used in this test is shown in Figure 3.6.

Figure 3.6 Determination of Unit Weight

The unit weight of the sample was calculated according to the equation below:

$$\text{Unit weight(pcf)} = \frac{\text{wieght of the sample (lb)}}{\text{Volume of the mold}(\text{ft}^3)} \qquad (5)$$

3.4.4 Volatile Solids Content

Volatile solids are an indicator of the organic content of a sample . It is also an important indicator of the state of decomposition of an MSW sample. This is test was done before the reactors were built and also after dismantling the reactors. For the VS test, procedure 2540E in Standard Methods (AWWA-APHA, 2005) was used. First, the samples were oven dried at 105℃ temperature. These samples were then ground to smaller pieces. About 50 grams of sample were taken for each test. The samples were placed in the furnace at 550℃ for at least one hour to burn completely to ashes. Then, from the percentage of weight loss, the volatile organic content was determined. Volatile solids tests are relatively easy to perform and a good indication of the remaining gas generation potential of the waste. Figure 3.7 presents the Volatile Solids Test.

Figure 3.7 Volatile solids test (a) Dry Sample (b) Muffle Furnace and (c) Burnt Sample

3.5 Reactor Assembly and Operation

Lab scale simulated bioreactors were built in order to study the effect of the presence of nZVI along with the MSW in a bioreactor landfill. Two 6 gallon size PVC buckets were used to simulate ELR landfill in the laboratory; one was operated as a control reactor and another with addition of nano zero valent iron. The reactors were sealed to produce anaerobic conditions and tested for leaks before use. The reactor leak test using a u-tube manometer is shown in Figure 3.8. The reactors were filled with approximately 12 to 15 lb. of MSW samples collected from the working face of the Denton Landfill. Water (sonicated with nZVI in reactor 2) was added to increase the moisture content to 40% by wet weight basis. Also 15% wastewater sludge by weight was added to the MSW mix as a source of microorganisms. The reactors were then sealed using an O-ring and silicone sealant. A five-layer gas bag and a leachate bag were connected to each reactor. Cali-5-bond gas sampling bags were used. They contained five different layers of materials such as polyester on the outside, polyvinyledene chloride, aluminium foil, polyamide and high density polyethylene on the inside. Each gas bag had a capacity of 22L. The reactors were operated at a constant temperature of 37℃ in an environmental growth chamber for 4 months. The reactor schematic is presented in Figure 3.9.

Figure 3.8 Reactor Leak Test

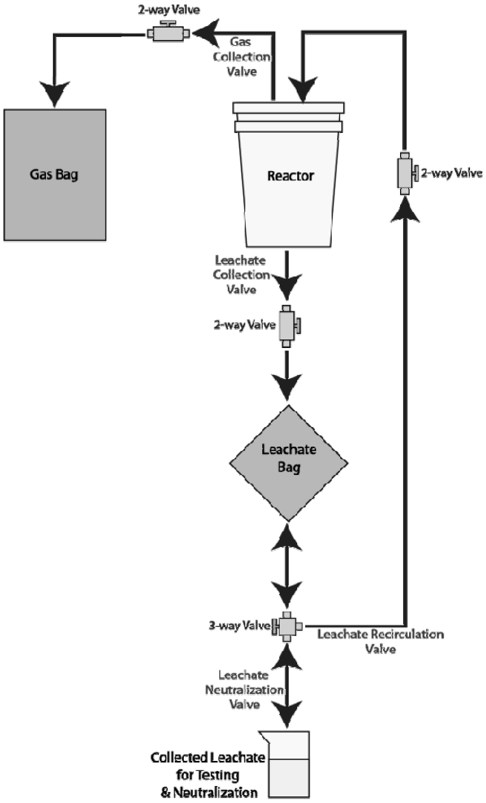


Figure 3.9 Schematic of Lab-scale Bioreactor

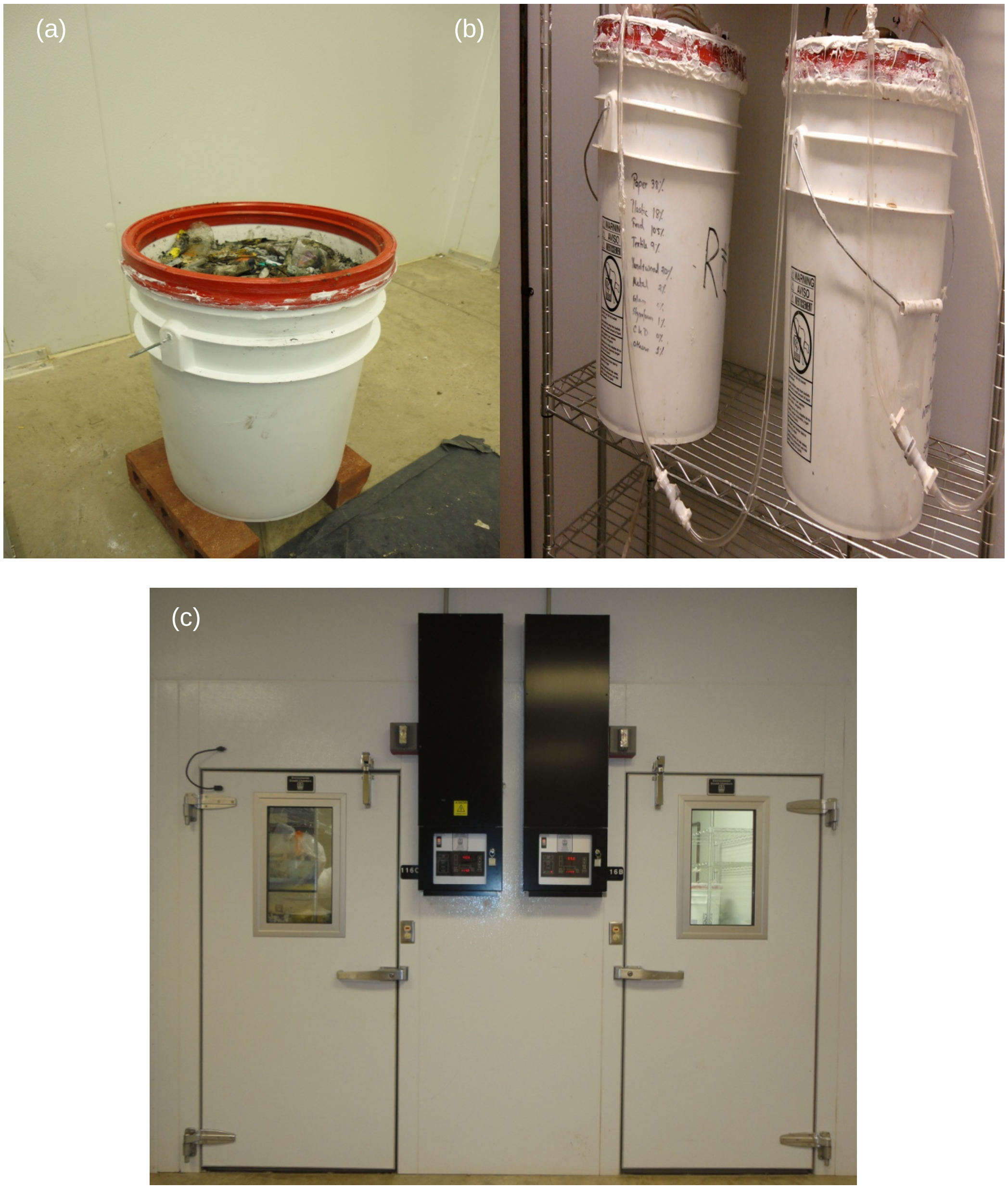


Figure 3.10 Reactor set up (a) Reactor Filling (b) Reactors in Operation and
(c) Environmental Growth Chambers

The leachate generated in the simulated ELR landfills was re-circulated back into the reactors. The leachate was neutralized (pH≈7) with KOH buffer as necessary and recycled three days a week. This was done to optimize methane production, according to literature. At pH 6 and up to a pH of 8, ideal conditions for methanogenesis are created. Below pH 6, acetogens out compete the methanogens and therefore, production of methane is lower. Figure 3.10 shows the reactor under operation. Different steps involved in leachate recirculation and reactor operation are presented in Figure 3.11.

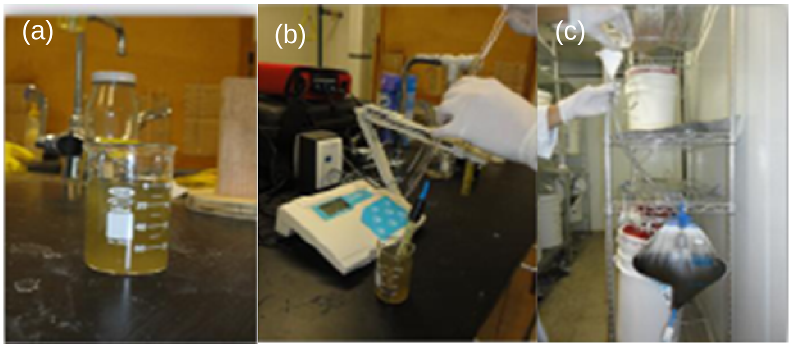


Figure 3.11 Leachate Recirculation (a) Collected Leachate (b) pH Measurement (c) Recirculation

During the reactor operation, generated gas was collected in five-layer gas bags, as shown in Figure 3.12.

Figure 3.12 Gas Collection

3.5.1 Monitoring Program

The gas and leachate samples were collected from both the reactors on a regular basis and tested for different parameters. The experimental program for these tasks is presented in Table 3.1.

Table3.1 Experimental Program

Test	Material	Testing Frequency
Gas Composition, and Gas Volume	Gas	Daily for first 2 weeks and then on weekly basis
pH	Leachate	Daily for first 2 weeks and then twice every week
COD	Leachate	Weekly for the first month, then monthly
BOD	Leachate	Monthly

3.5.2 Procedure for Adding nZVI to Reactor 2

Ultrasonic vibration was effectively utilized to thoroughly mix the nZVI particles in water. A MISONIX 4000 Sonicator was used for this purpose. In manual stirring the energy required to break nZVI particle agglomeration cannot be generated and therefore an unstable mix can be produced at best. However, by using the sonication procedure, a stable mix was procured which remained so even a few hours after mixing. The mechanism of mixing, using a MISONIX 4000, utilizes the alternate expansion and compression produced by transmission of ultrasonic waves. This causes pressure fluctuations and gives rise to microscopic bubbles. When the pressure falls, these bubbles implode, generating shock waves, acoustic streaming, high pressure and temperature. This produces a lot of energy which is sufficient to break the particle agglomeration of the nZVI and produce a stable suspension. Nano zero valent iron particles were added to water in batches and sonicated for 5 minutes for each addition. Forty minutes of total sonication time was used and the amplitude of mixing was varied between 50%and 75%. Total amount of nZVI added to the second reactor was 0.1% by weight of the total MSW in it. Accordingly 9.5 grams of nZVI was added.Li et al (2006) recommends the use of <0.1% by weight of nZVI for effective stabilization of biosolids. However, due to the very small diameter of the nanoparticles, it was assumed that some quantity of it may be lost if portion of the nZVI added came out through the geotextile in the leachate. Also it was noted that nZVI tends to form agglomerates and this may get stuck in the tubing connected to the leachate collection bag. This was confirmed when the tubings were seen to accumulate some nanoparticles during the course of reactor operation. However, this quantity was extremely small and the loss through the leachate was also not high as the leachate was recirculated. The following figure (3.13) shows the dispersion of nZVI in water using the method of sonication.

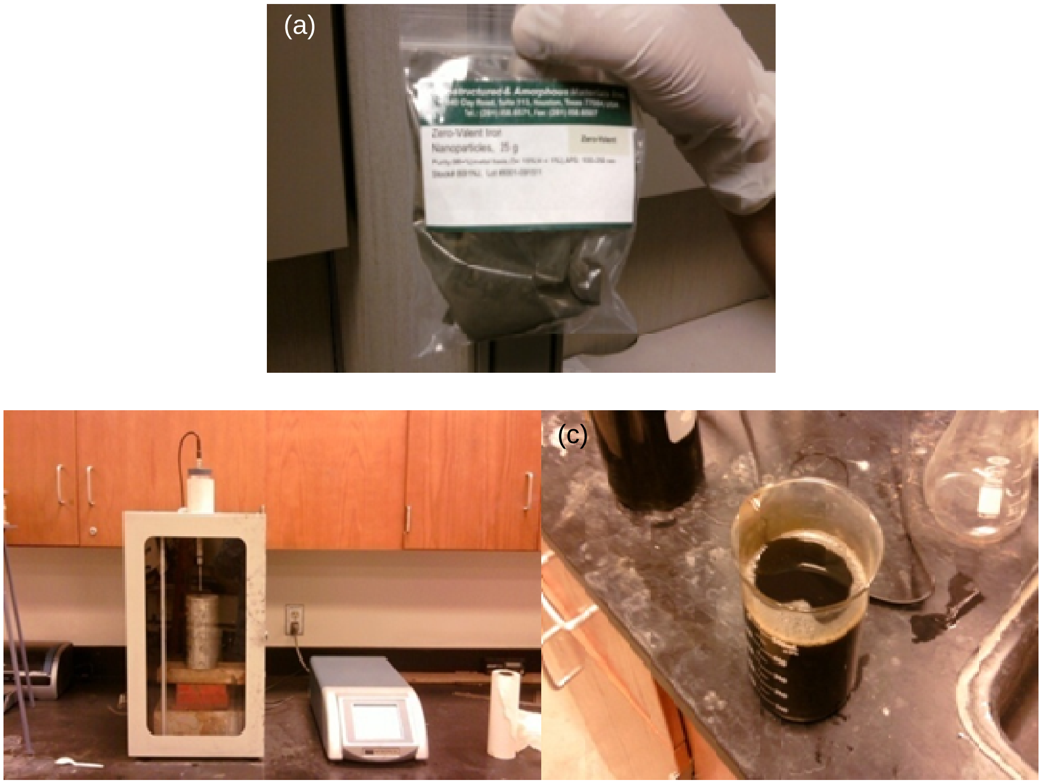


Figure 3.13 Sonication (a) Powdered nZVI (b) Sonicator and (c) Sonicated nZVI in water

3.6 Characteristics of Gas Generated from the Reactors

The gas generated was characterized by means of volume and composition as described in the following sub-sections.

3.6.1 Volume of Generated Gas

The volume of the gas was measured by emptying the gas bags with air sampling pump (Universal XR pump Model 44XR by SKC) with a flow rate of 1130 mL/min. The time taken to empty the gas bags were recorded. The process is presented in Figure 3.14.

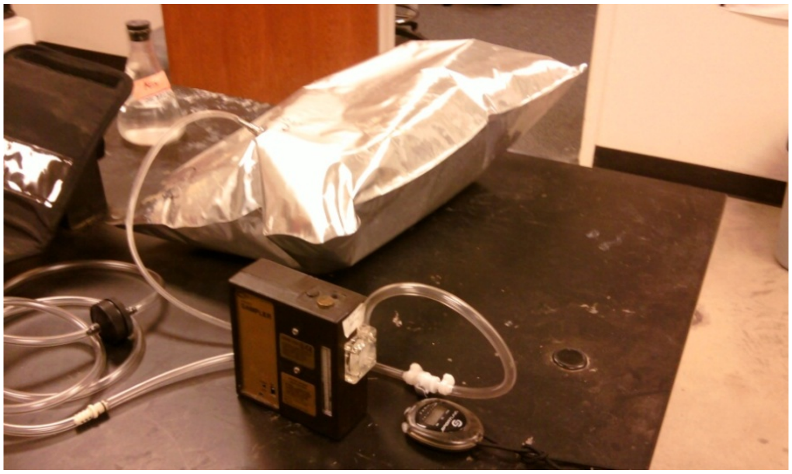


Figure 3.14 Air Sampling Pump

3.6.2 Composition of Generated Gas

The composition of the gas was measured by GEM2000 analyzer by LandTEC. The GEM measures methane and carbon dioxide using a dual wavelength infrared cell. The process is presented in Figure 3.15.

Figure 3.15 Landtec

3.7 Characteristics of Leachate Generated from the Reactors

3.7.1 pH and Conductivity of Generated Leachate

Leachate generated was recirculated. A small portion of the generated leachate was stored at 4℃ for analysis. The procedure of leachate accumulation and sample collection is shown in Figure 3.16.

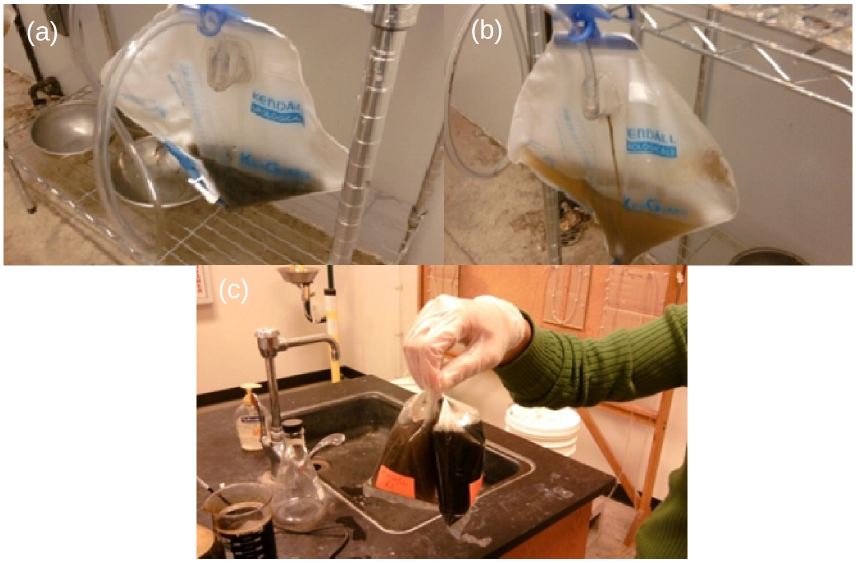


Figure 3.16 Leachate (a) Leachate accumulation in Reactor 1 (b) Leachate accumulation in Reactor 2 (c) Collected Leachate Samples

The pH and conductivity of the collected leachate was measured using a bench-top meter by OAKTON (Figure 3.17).

Figure 3.17 Bench top pH/Conductivity Meter

3.7.2 COD of MSW Leachate

The dichromate Chemical Oxygen Demand (COD) test measures the oxygen equivalent of the amount of organic matter oxidizable by potassium dichromate in a 50% sulfuric acid solution. Generally, a silver compound is added as a catalyst to promote the oxidation of certain classes of organics, and a mercuric compound may be added to reduce interference from the oxidation of chloride ions by the dichromate. End products are carbon dioxide, water, and various states of the chromium ion. After the oxidation step is completed, the amount of dichromate consumed is determined titrimetrically or colorimetrically. Other elements also may be oxidized. Chemical oxygen demand results are usually expressed by the amount of oxygen consumed during the oxidation of organic matter. In this study, the COD tests were done using premixed digestion vials from (Hach Product #**:** 2415925) and a spectrophotometer (Thermo Spectronic's Spectronic 200+) that determines the absorbance of the leachate sample. To determine the COD of MSW leachate, a calibration curve of absorbance vs. concentration was developed with solutions of known concentrations. From the calibration curve, for the corresponding absorbance recorded from the spectrophotometer, the COD value was determined.

The equipment and test setups are shown in Figures 3.18 - 3.20.

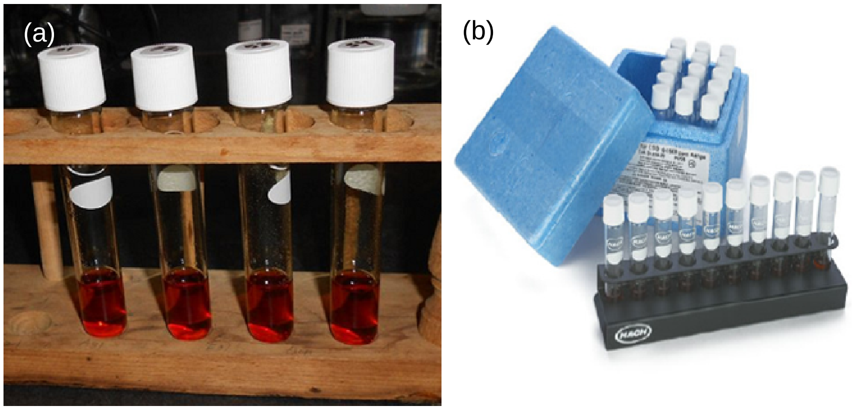


Figure 3.18 COD test (a) Digestion vials and (b) Digestion vials with added samples

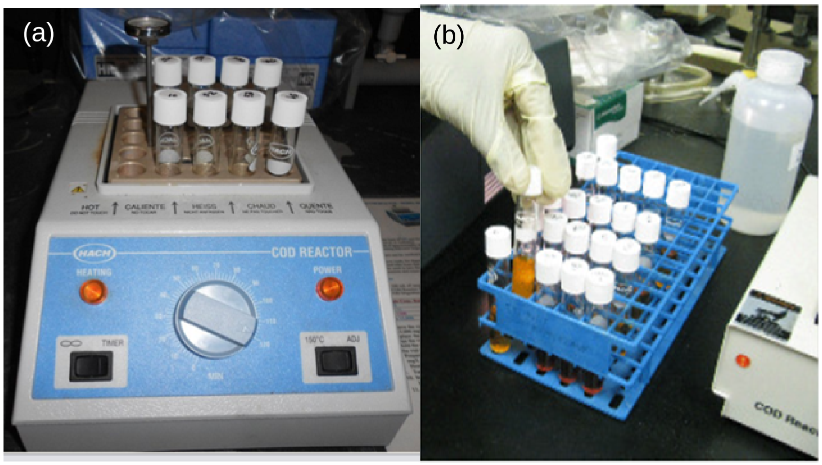


Figure 3.19 COD test (a) Digester and (b) Digested samples

Figure 3.20 Spectrophotometer for Absorbance Measurement

3.7.3 BOD of MSW Leachate

Biochemical oxygen demand, or BOD, is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The term also refers to a chemical procedure for determining this amount. This is not a precise quantitative test, although it is widely used as an indication of the organic quality of water. The laboratory test for BOD was carried out following the procedure outlined in Standard Methods for Wastewater Treatment.

The method consists of filling with sample, to overflowing, an airtight bottle of specified size and incubating it at the specified temperature for five days. Dissolved oxygen is measured initially and after incubation. BOD is computed from the difference between the intial and final dissolved oxygen. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occuring after this measurement is included in the BOD measurement. Based on the COD test results, the BOD was estimated and accordingly different dilutions of the leachate samples were prepared. The dilution water was prepared using the APHA (American Public Health Association) chemicals Phosphate buffer solution, Magnesium sulfate solution, Calcium chloride solution and Ferric chloride solution. The BOD test was conducted with seed control and the samples were triplicated. The test equipment and setup are shown in Figures 3.21-3.23.

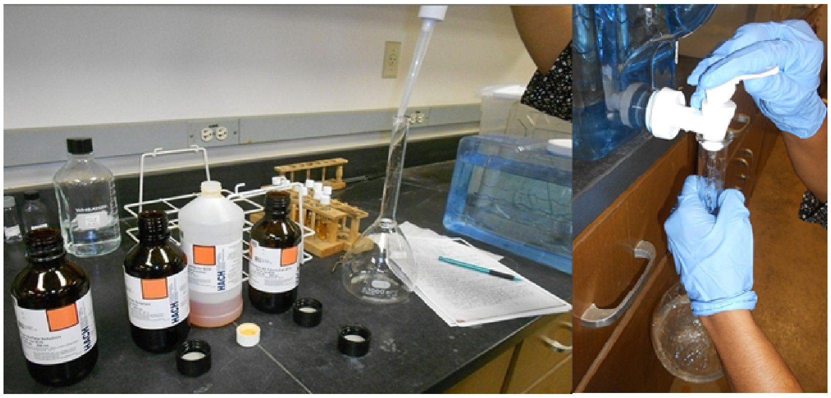


Figure 3.21 Preparation of Dilution Water with APHA chemicals for BOD test

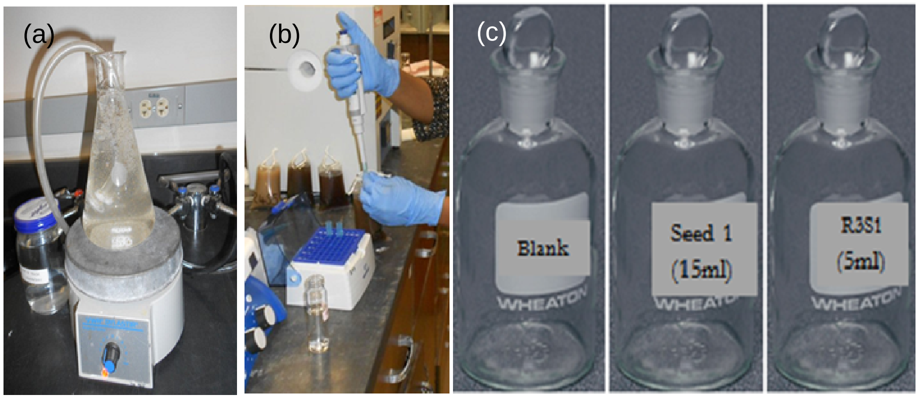


Figure 3.22 BOD test (a) Magnetic stirrer for aeration of seed (b) Preparation of seed and (c) Setting up samples

(a) (b)

Figure 3.23 BOD test (a) DO measurement(initial) and (b) Incubator (21℃)

3.8 Physical Characteristics of Reactor Samples Post Dismantling of Reactor

3.8.1 Volatile Solids (VS) Content

At the end of operation period, the reactors were dismantled and a volatile solids test carried out. This test indicated the amount of degradation undergone by the waste sample and reasonably predicted the current organic content

For VS test, first the samples were oven dried at 105℃ temperature. These samples were then shredded to smaller pieces and the volatile solids test carried out following the same method described in *3.3.4 Volatile Solids content*. Post dismantling the reactor can be seen in Figure 3.24.

Figure 3.24 Reactor after Dismantling

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, the experimental results are presented, discussed, and compared with the existing literature. The results of the characteristics of MSW samples (physical composition, moisture content, organic content, and unit weight) are first presented. The results of the gas and leachate tests, including the volume and composition of the gas generated and the results of the periodic COD and BOD tests on the leachate samples, are then presented and discussed.

4.2 Results of Sample Composition Tests

The physical composition of the landfill samples was determined and the results are presented in this section. Paper was the most dominant component found, followed by wood, yard waste and plastic. It was evident that in spite of recycling efforts, a lot of paper and plastic ends up at the landfills. Food waste was about 10-11% by weight in both reactors and it was the most biodegradable component present in the whole sample.

The results represent the weight of each component measured separately.

Table 4.1 shows the composition of each reactor along with the national average according to EPA. Figures 4.1 and 4.2 show the weight percent of each component present in the two reactors used for the study.

Figure 4.3 shows a column chart for comparison of the average waste composition used in the study with that published by the U.S. E.P.A.

Table 4.1 Physical Composition of the Waste

Components	Weight (%) R1	Weight (%) R2	Average weight (%)	National Average (U.S. E.P.A)
Paper	37.97	36.01	36.99	28.5
Plastic	17.75	24.35	21.05	13.9
Food	10.51	10.82	10.67	8.4
Textiles	9.45	0.95	5.20	17.8
Wood, Yard	20.08	14.07	17.07	12.4
Metal	1.99	2.43	2.21	9
Glass	0	4.30	2.15	---
Styrofoam, Sponge	1.26	3.67	2.47	4.6
C&D	0	1.35	0.67	---
Others	0.94	2.00	1.47	3.4

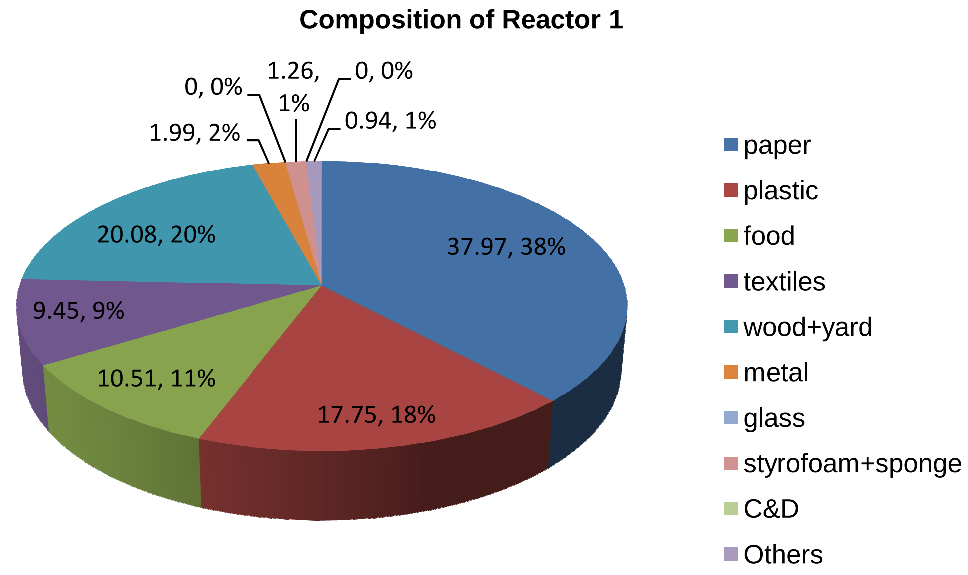


Figure 4.1 Physical Composition of Reactor 1 (Control)

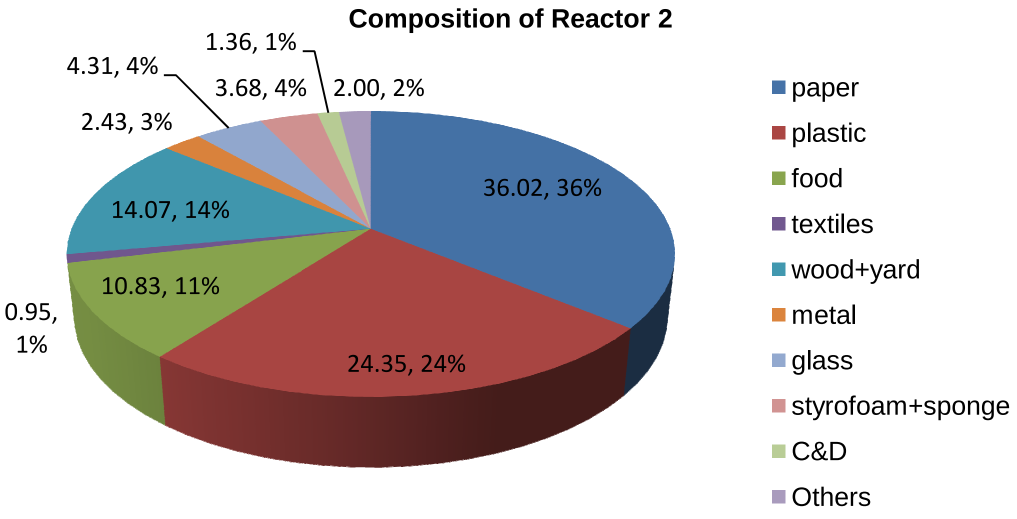


Figure 4.2 Physical Composition of Reactor 2 (with added nZVI)

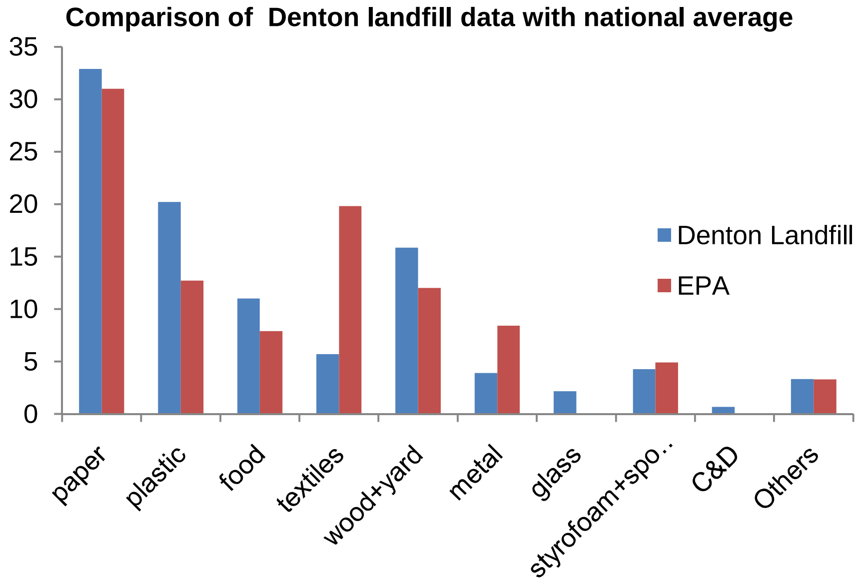


Figure 4.3 Comparison of Denton Landfill Data with the national average by EPA

From Table 4.1, it can be seen that the composition of the two reactors was very similar. The composition results were also similar to the national average data from EPA, with some slight differences. It is expected that waste percentages in any landfill will vary from the national average.

Waste sample from the Denton Landfill shows total degradable components(paper,food waste, textile and yard waste) to be 65% and the non degradable components to be 34%. This is a good composition in terms of potential landfill settlement, degradability and gas generation. The biodegradable portions of the waste such as food waste, wood and yard waste, paper and textiles will decompose much faster than non degradable components like metal, glass and C&D waste. This will directly affect the landfill settlement and gas generation, because the onset of each phase of decomposition will be faster for the more degradable components; hence enhanced waste settlement and gas production will be observed for these components faster than their non degradable counterparts.

4.3 Results of Moisture Content Tests

The moisture content of MSW samples was determined by drying the samples in an oven at 105 ºC for 24 hours as discussed in the methodology section. For fresh MSW, the moisture content depends on the composition of the waste, the season of the year, and weather conditions. The moisture content results are presented in Table 4.2.

Table 4.2 Results of Moisture Content Tests

Moisture content (%)	Reactor 1	Reactor 2	Average
Wet basis	41.42	44.18	42.8
Dry basis	70.72	79.16	74.94

For moisture content, the average amount was observed to be 39% (based on wet basis) and 65% (based on dry basis). These results show slightly higher values than the amount expected from a MSW sample, which varies between 21% and 35% (Sowers 1968). Also, Zornberg et al. (1999) reported that the average amount for moisture content based on a dry basis to be 28%. This may be due to rains taking place prior to sample collection and also the presence of a high amount of paper and food waste. The moisture content depends on the waste composition, in that paper tends to absorb a lot of moisture and food waste contains a high amount of moisture within itself.

The moisture content of the waste is an indicator of the decomposition level of the waste. Decomposed waste should ideally have less paper and food content, which are the main components that hold the moisture. Therefore if the degradation of the waste is higher, the moisture content should be lower than fresh waste.

According to Landva & Clark (1990), the moisture content increases with increasing organic content, which can be up to 120% (wet weight) and 65% (dry weight).

4.4 Results of Unit Weight Tests

The results of the unit weight test are presented in Table 4.3 .

Table 4.3 Results of Unit Weight Tests

Unit weight (pcf)	Reactor 1	Reactor 2	Average
	40.09	39.09	39.5

Unit weight of waste depends directly on the size of particles present in the landfill. For finer particles, there are fewer voids, so the unit weight becomes higher. For degraded samples, the particle sizes are smaller, so the unit weight increases.

The Denton landfill sample shows an average unit weight of 39.5 pcf. This sample was brought from fresh waste in the working phase of the landfill. Hence, the unit weight is on the lower side, as the waste is comparatively less degraded and contains large particles and hence more void spaces. In literature, the unit weight is usually within the range of 30-45 pcf (Oweis and Khera, 1998) with moderate to good compaction efforts. Taufiq (2010) determined the average unit weight for most MSW with standard proctor compaction method to be 35 pcf. Our unit weight results are found to be consistent with published literature.

4.5 Results of Volatile Solids Content Tests

The results of the volatile solids (VS) test are presented in Table 4.4 below.

:

Table 4.4 Results of Volatile Solids Tests

Volatile solids (%)	Test Condition	Reactor 1 (Control)	Reactor 2	Average
	Shredded	84	88.23	86
	Ground	86	84	85
	Average	85	86.12	85.5

For volatile solid percentage, the results showed that on an average 86% of shredded sample and 85% of ground sample is composed of organic material, which will ultimately degrade and leave the landfill. Volatile solids post dismantling of reactors were also calculated and the results are presented in Table 4.5.

Table 4.5 Results of Volatile Solids Content Tests Post Dismantling

Reactor	Volatile Solids (%)
1 (Control)	64
2	71

This data reasonably shows the amount of degradation undergone by the waste sample in each reactor and therefore the organic content post dismantling is less than that of the fresh sample. In literature, Barlaz et al. (1990) reported 79% organic content in fresh waste. Reddy et al. (2009) reported 76-84% organic content in fresh samples from Orchard Hills Landfill, Illinois. For aged waste, 33% organic content was reported at 19 m depth by Gabr and Valero (1995). Surface organic content within 43-63% and organic content at 11m depth at 56% was reported by Gomes et al (2005). In a study carried out for degraded MSW samples in lab scale reactors, Hossain and Haque (2009) recorded an organic content of 94% during phase 1 and 41% during phase 4 of decomposition. These results compare well with the current study. The organic content of the fresh waste was about 84-88 % and the organic content of the degraded waste was 64- 71%. It should be kept in mind that the reactors were dismantled after four months of operation, hence it is safe to assume that had the period of operation been longer, organic content post reactor dismantling would have been lower.

4.6 Gas Data

According to the experimental program, the gas bags were regularly emptied in order to record the volume and composition of the gas produced. The data gathered can be represented with the help of the following graphs:

Figures 4.4 and 4.5 present the change in gas composition of the two reactors over time.

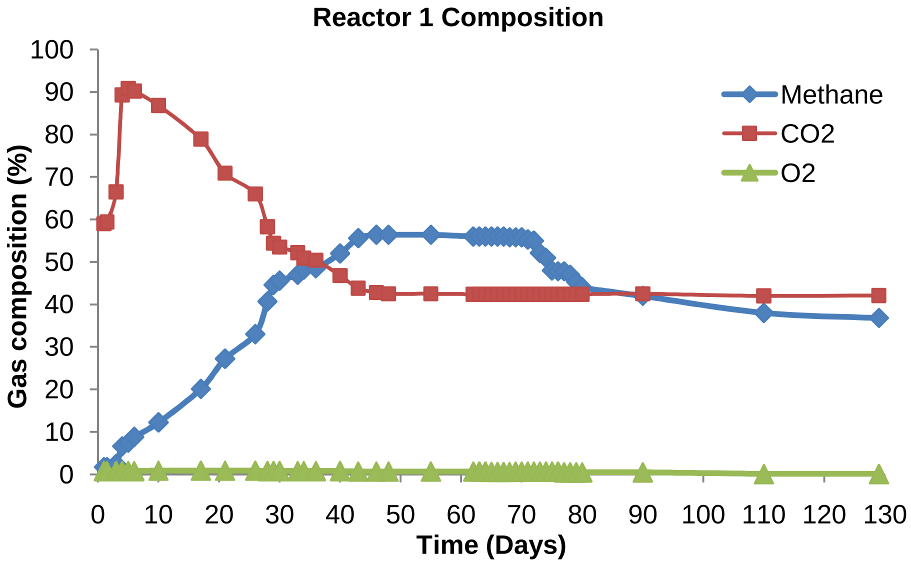


Figure 4.4 Gas Composition of Reactor 1 (Control Reactor)

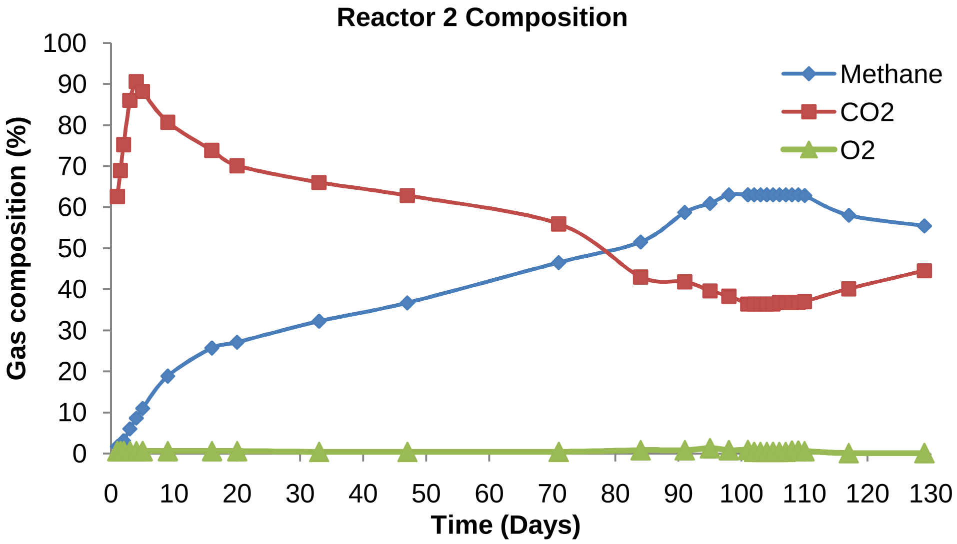


Figure 4.5 Gas Composition of Reactor 2 (With Nanomaterials)

Reactor gas compositions for both reactors show similar trends. As an anaerobic condition was maintained for both reactors, oxygen quantity is not appreciable. The methane percentage started increasing over time, reached a peak and then showed a gradual decrease. Carbon dioxide showed an initial increase and then started decreasing as methane production picked up. For reactor 1, carbon dioxide content was around 58% in day 1 and then increased to about 90% around the 10th day and then started decreasing after that, finally coming down to about 35% between the 100-110th day. Methane content increased slowly from the first day, finally reaching about 56% around the 46th day. Then it started decreasing and reached around 36% on the 129th day. For reactor 2, a similar trend was noted. Carbon dioxide content was around 60% in the first day and then increased to about 90% on the 10th day and then showed a gradual decrease, reducing to about 35% on the 110th day. Methane content increased slowly from the first day, finally reaching about 63% between the 100th and 110th day. Then it started decreasing very slowly, reaching 55% on the 129th day.

Figure 4.6 next presents the change in methane percentage over time.

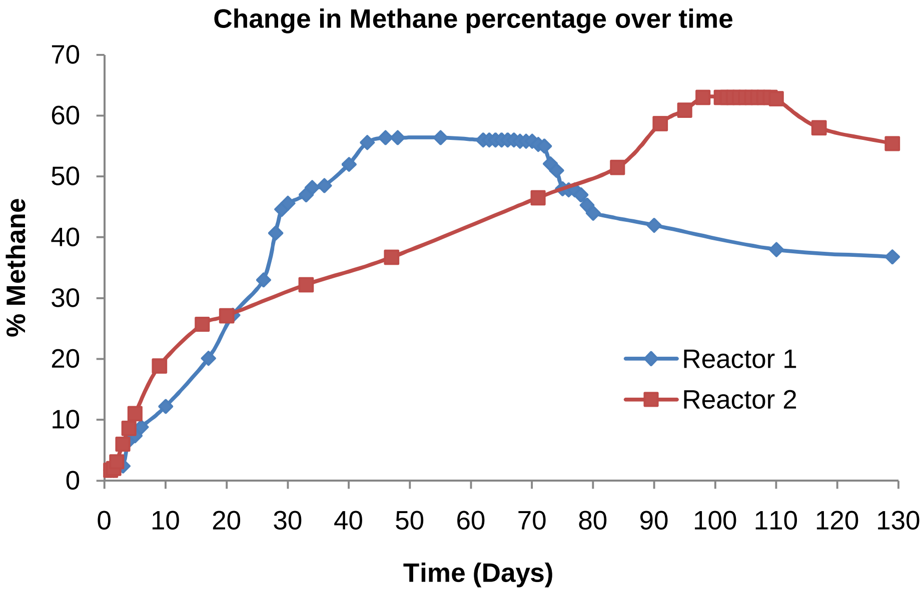


Figure 4.6 Change in Methane Percentage over Time

The change in methane percentage over time for the two reactors can be divided into three stages, depending upon the change in the pattern of methane content of the gas produced by each by the number of days.

0-20 Days: Reactor 1 (control) shows an increasing percentage of methane in the content of the total gas produced by its decomposing solid waste. On the 20th day, reactor 1 had a methane content of 25%.

Reactor 2 (with nZVI particles) shows a similar trend. On the 20th day, its methane content was 28%.

20-50 Days: Reactor 1 (control) continued to have increase in methane content over time and reaches a peak value of 56% around day 46. After that, very slowly a gradual decrease in the methane content for the first reactor could be noted until the 50th day.

Reactor 2 (with nZVI particles) during this time has steadily increasing methane content and on the 50th day reaches a value of approximately 35%.

50-129 Days: Reactor 1 (control) demonstrates a sharp decrease in its methane content and levels off around the 110th day at 34%.

Reactor 2 (with the nZVI particles) maintains an increasing trend till it reaches a peak value of 63% methane on day 101. After the 110th day, its methane content shows a decreasing trend, and reaches about 55% on the 129th day.

There is a lag phase between the peaks of the two reactors in terms of methane content. While the first reactor without added iron reaches its peak by the 46th day, the second one with added nZVI reaches the peak on the 101th day.

In the past, Manzur et al. (2010) reported 60% methane generation in the recirculating pipes at the City of Denton Landfill. Bayard et al. (2005) reported the following results in lieu of gas production during a comparative study of in-situ and lab scale conditions as presented in Figure 4.7. The results are comparable to both the control reactor and the reactor containing the nanoparticles.

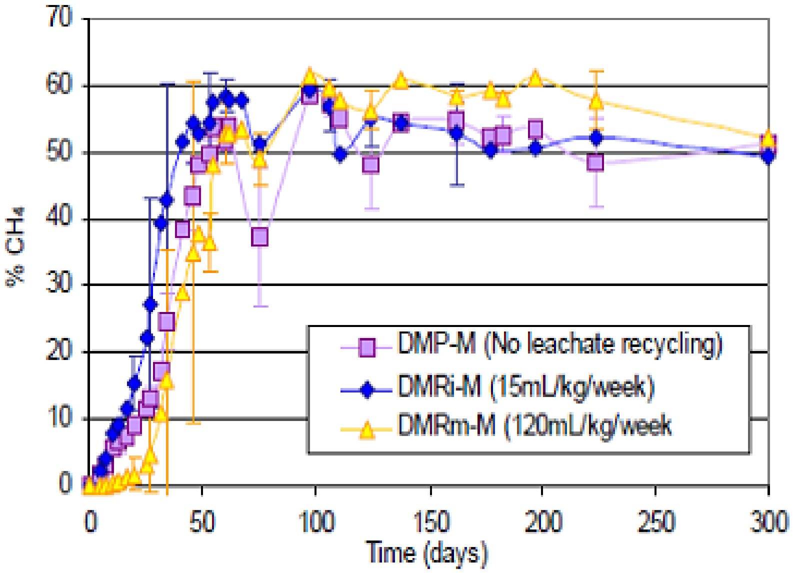


Figure 4.7 Methane Percentage (Bayard et al., 2005)

In Figure 4.8 Change in methane to carbon dioxide ratio with time is presented.

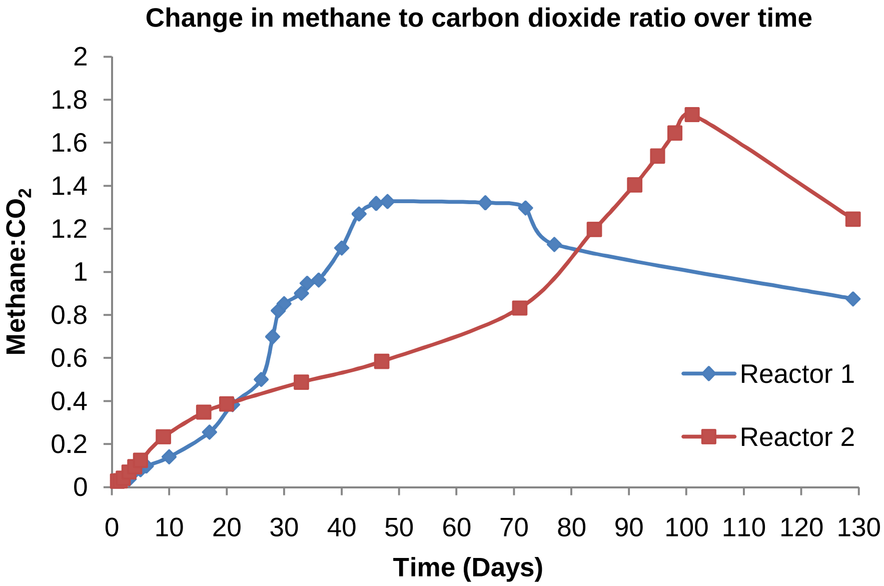


Figure 4.8 Change in Methane to Carbon Dioxide Ratio with Time

The change in methane to carbon dioxide ratio over time for the two reactors can be explained depending upon the temporal change in the content of the gas produced by each.

<u>0-20 Days</u>: Reactor 1 (control) shows an increase in the ratio of methane to carbon dioxide with respect to time between days 1 and 20. Reactor 2 (with added nZVI particles) follows a similar pattern.

<u>20-50 Days</u>: Reactor 1 (control) follows a rising trend and reaches a highest value of 1.3 around the 48th day and then shows a very gradually decreasing trend.

Reactor 2 (with the added nZVI) shows a steadily rising trend through the 50th day.

<u>50-130 Days</u>: Reactor 1 (control) shows a sharply falling trend, reaching about 0.8 on the 130th day.

Reactor 2 (with the added nZVI particles) keeps up an increasing trend and reaches a high value of almost equal to 1.8 around the 100th day and rapidly decreases afterwards to about 1.2 on the 130th day.

As such, there is a lag between the peaks, as observed in all the other curves.

Figure 4.9 shows the cumulative gas production per pound of waste for both the reactors.

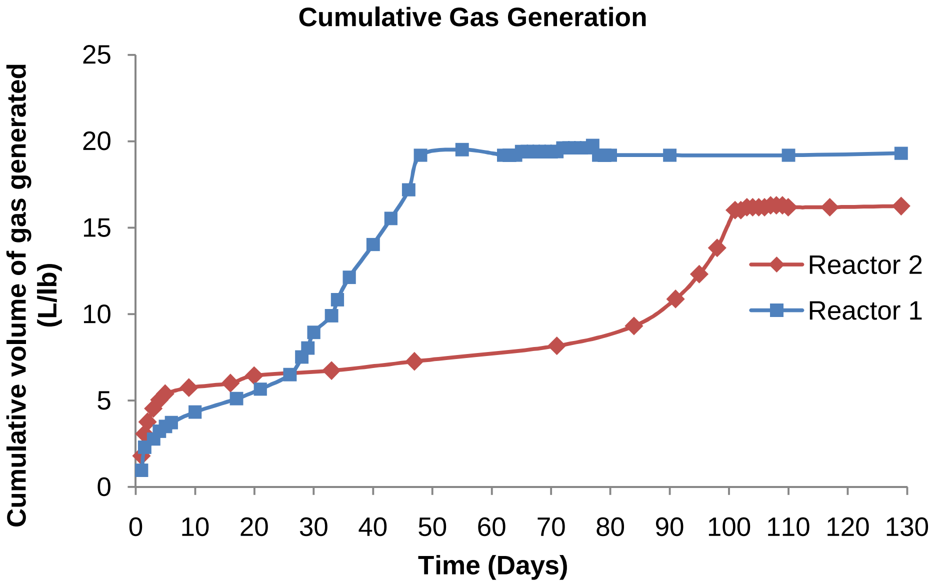


Figure 4.9 Cumulative Gas Production

Reactor 1 (control) exhibits an increasing trend as expected in the cumulative volume of gas generated in time. From day 1-20 it shows a gradual increase and after day 20, a sharp increase in the cumulative gas volume can be seen. A peak value of 18l/lb is reached around day 50, after which it levels off.

Reactor 2 (with added nZVI particles) exhibits a similar trend. In this case however, the cumulative gas production is slightly higher between days 0-28. After that the increase is very slow and gradual. A sharp increase can be noted around day 95 and a peak value is reached around the 100th day (16 l/lb) before leveling off.

As such there is a lag phase between the peaks of reactor 1 and reactor 2 of about 50 days. Morris et al. (2003) conducted field scale studies where cumulative gas production of a cell with moisture addition exceeded that of a conventional cell. Figure 4.10 shows these results.

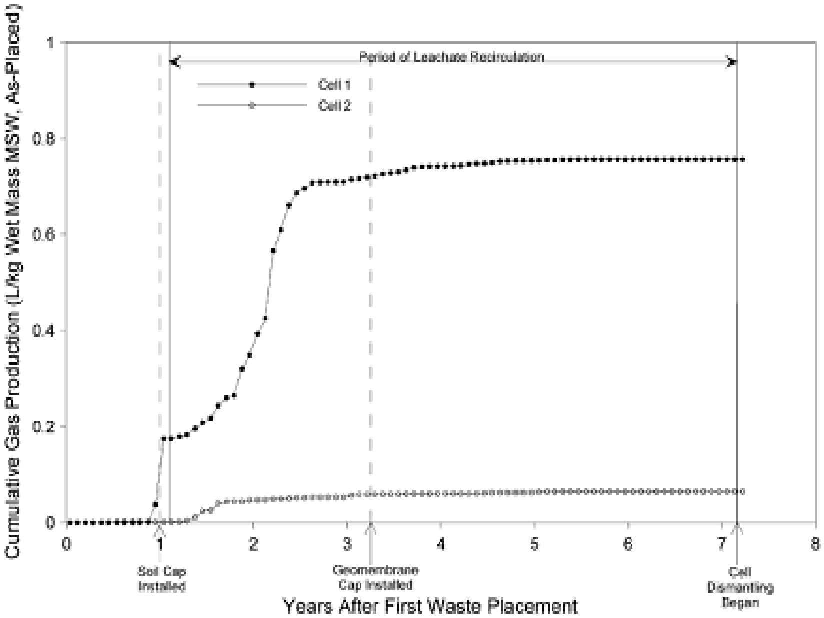


Figure 4.10 Cumulative Gas Production (Morris et al., 2003)

From this figure, we see that the overall trend of gas generation followed by a bioreactor cell is similar to the trend exhibited by both our control reactor and the reactor containing nano particles, but the unit of time is different. In case of the lab scale set up, the process is much accelerated due to various conditions and therefore, days are used as the unit of time, instead of years, as observed in field scale studies.

Figure 4.11 shows the cumulative methane yield by both reactors.

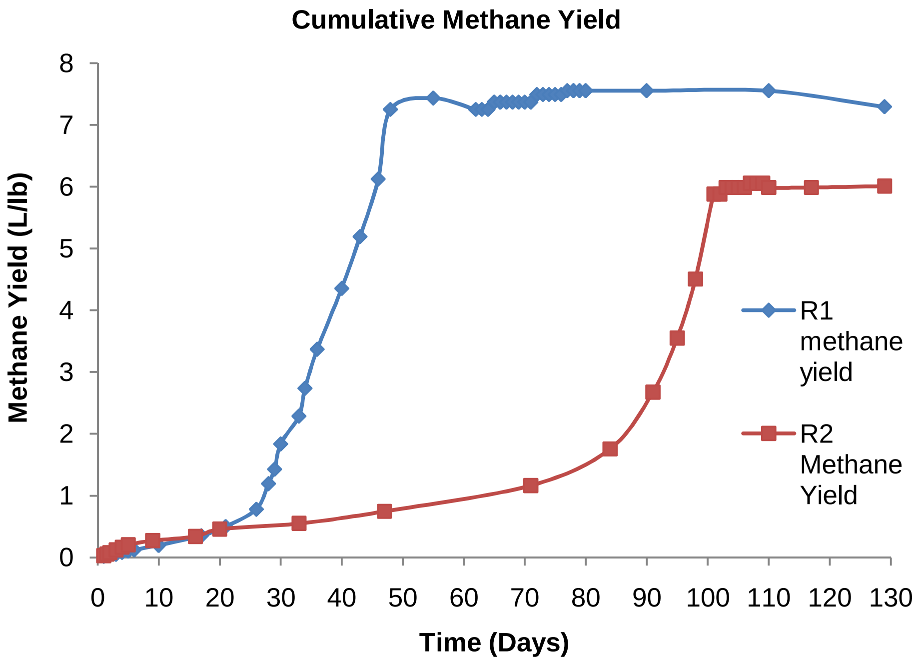


Figure 4.11 Cumulative Methane Yield

Reactor 1 (control) exhibits an increasing trend as expected in the cumulative volume of methane generated in time. From day 1-20 it shows a gradual increase and after day 20, a sharp increase in the cumulative gas volume can be seen. A peak value of 7.24l/lb is reached around day 48 after which it levels off.

Reactor 2 (with added nZVI particles) exhibits a similar trend. In this case, the cumulative gas production is similar to that of the control reactor between days 0-20. After that the increase is very slow and gradual. A sharp increase can be noted around day 95 and a peak value is reached around the 129th day (6.01 l/lb) before leveling off.

As such there is a lag phase between the peaks of reactor 1 and reactor 2 of about 81 days. Overall, it can be seen that the bioreactor with added nZVI was slower than the control reactor, in that it took longer to reach its methane production peak. This may be due to an adaptation period for the microorganisms to acclimate to the iron rich environment of the second reactor. Figure 4.12 depicts the rate of methane generation from the two reactors.

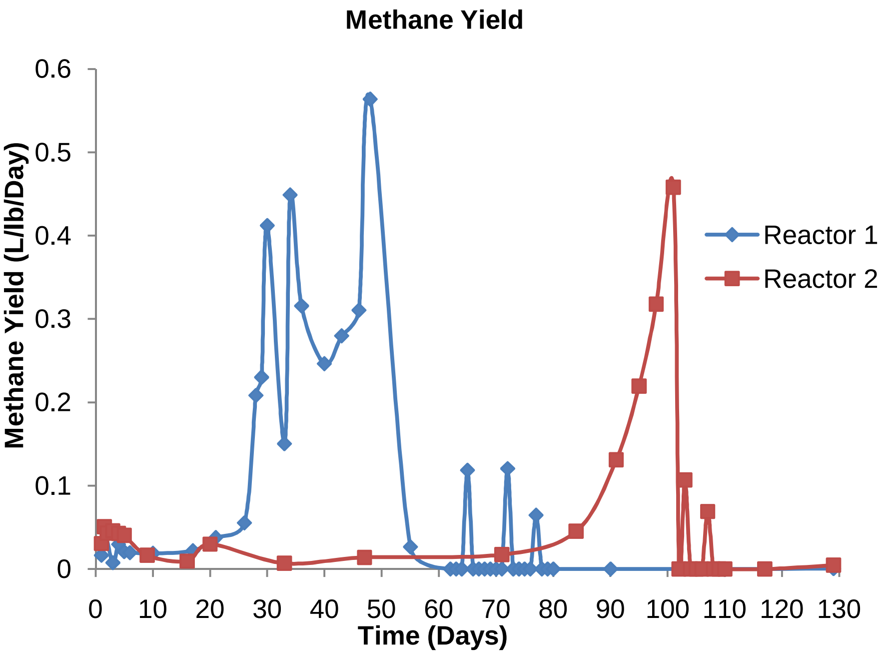


Figure 4.12 Methane Yield per pound of waste per day

The methane yield curves for the two reactors can be explained depending upon the change in the pattern of methane yield in liters per pound of waste per day.

0-20 Days: Reactor 1 (control) shows an increasing trend in methane yield. After day 2, the yield of methane picks up and very slowly demonstrates an upwardly rising curve.

Reactor 2 (with the nZVI particles), during this same phase, shows slightly higher methane yield in comparison to reactor 1 initially (day 2-8). However, after that, the methane yield decreases and again shows a slight increase around day 20.

20-50 Days: For Reactor 1 (control), the methane yield increases sharply till day 30 and then decreases to some extent in the next few days. It follows a subsequent pattern of intermittent increase and decrease till day 48, when it reaches the peak.

Reactor 2 (with the nZVI particles), during this same phase, does not increase much. It continues to yield methane at a much lower rate and when Reactor 1 reaches its peak, the yield curve of Reactor 2 does not show any dramatic change in its trend.

50-129 Days: Reactor 1 (control) methane yield falls off sharply around day 54. After that, although it shows slight spikes in the yield curve denoting upward trends around the 65th, 72nd and 78th days, it does not compare much to its peak methane yield. Towards the 129th day, the reactor 1 methane yield is almost zero. The methane percentage in the gas at that time was about 35%. However, the gas production was not noticeable. This may be a temporary phase, as the VOC tests indicate there are more volatile solids left for gas production. However, the period of operation was about four months, so it could not be observed whether there were multiple peaks for methane yield, which can sometimes occur.

Reactor 2 (with the nZVI particles), during this same phase, shows a gradually rising curve for methane yield and around the 101st day, the methane yield value for the second reactor peaks. After that, the yield falls off sharply and the yield pattern is similar to that of reactor 1, when it dies off after a couple of spikes around the 129th day. Similarly, it can be anticpated from the VOC test results that, had the period of operation been longer, additional gas production phases could have been seen.

The peak methane yield for the reactor containing MSW without additional nano zero valent iron particle is about 0.55 L/lb/day and for that of the reactor containing the added nano zero valent iron particles along with the MSW, the methane yield is about 0.45 l/lb/day.

There is also a lag of approximately 53 days between the respective peaks of the methane yield of reactor 1 and reactor 2.

A previous study by Haque (2007) reported the methane production rates with sludge addition, neutralization and leachate recirculation. Figure 4.13 presents the findings of this study. In this study the phases of decomposition were determined through leachate pH and accordingly, methane yield in each phase of decomposition was obtained. The peak methane yield in L/lb/day was 0.63, which is in the vicinity of the methane yield by the control reactor in the current study.

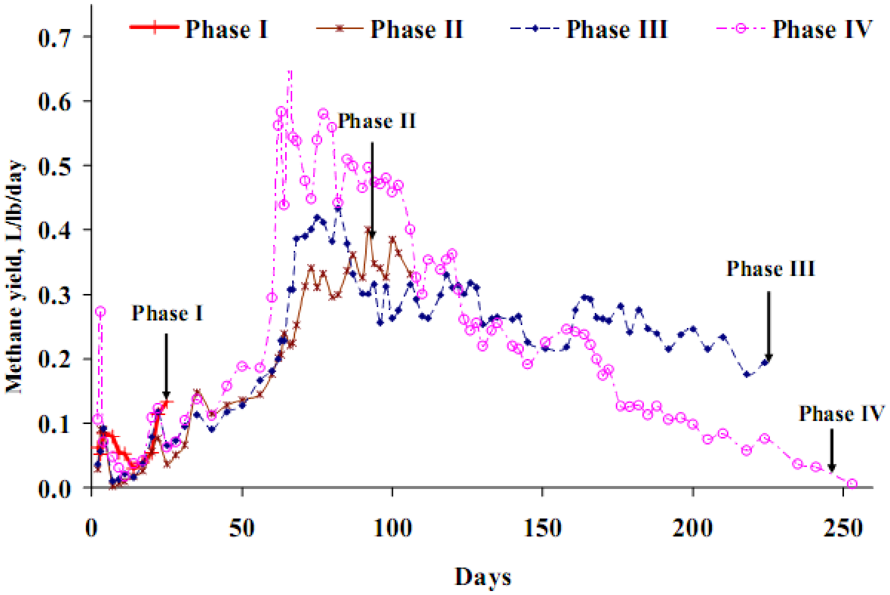


Figure 4.13 Methane Yield (Haque, 2007)

Figures 4.14 and 4.15 indicate the total gas generation rate and the total methane generation rate for the two reactors for the entire waste mass used. The trends are similar to the cumulative gas and methane generation rates per pound of waste.

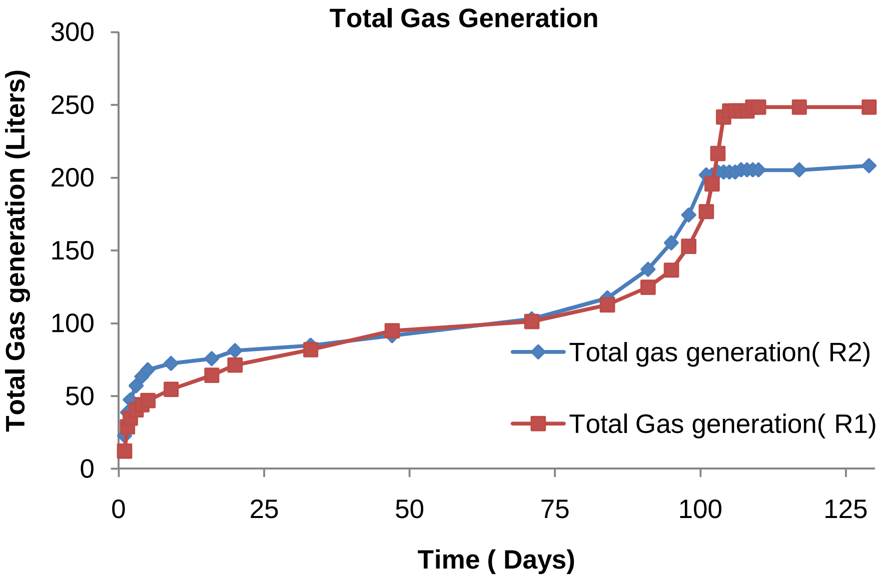


Figure 4.14 Total Gas Generation of Reactors 1 and 2

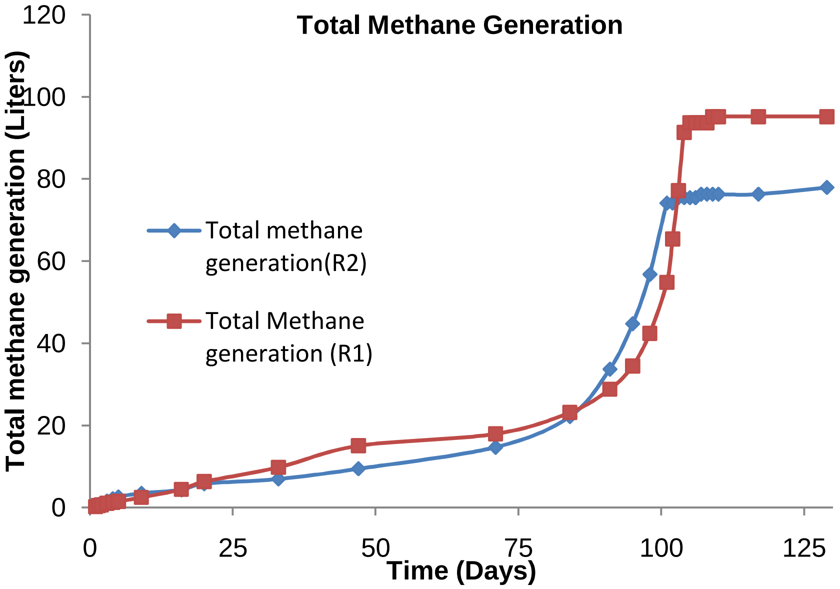


Figure 4.15 Total Methane Generation of Reactors 1 and 2

In case of gas generation, the initial hypothesis turned out not to be true. It is possible that the slow response of reactor 2 in terms of methane production may be due to microbial adaptation to the presence of nZVI. As a result, the phases of decomposition may have been occurring at a slower rate.

Also it can be seen from the pH data that the onset of phase 3, which is the methanogenic phase, was delayed in case of the reactor containing the nanoparticles.

4.7 Leachate Data

Leachate parameters like pH, conductivity, BOD and COD were measured and recorded over the period of time the bioreactors were operated. The results can be graphically represented as follows.

The change in leachate pH with time was recorded and the results are presented in Figure 4.16 as follows:

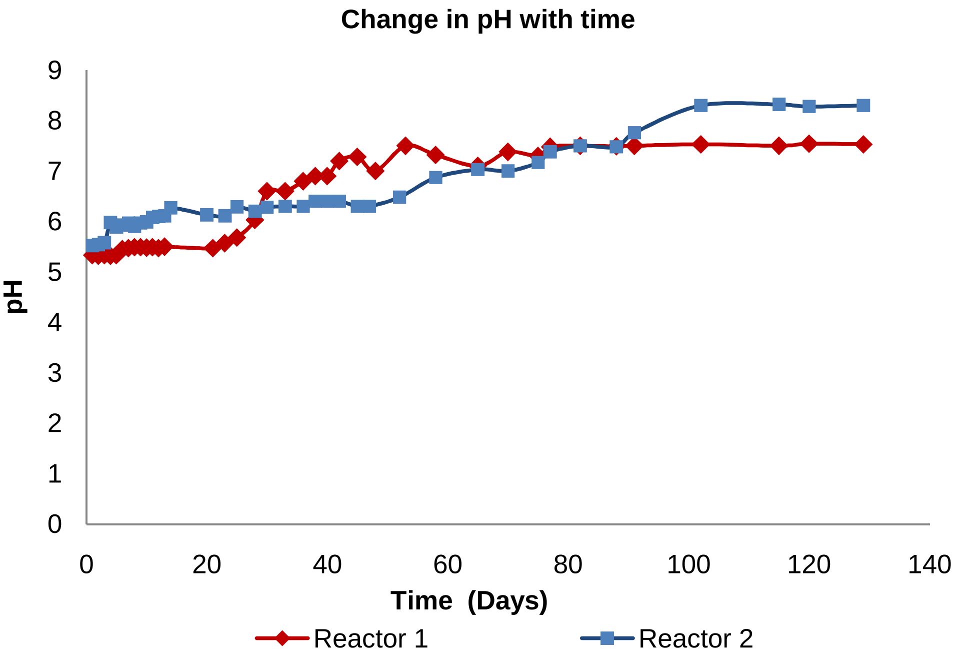


Figure 4.16 Change in Leachate pH over Time

The leachate pH initially kept on decreasing. As a part of operating procedure, the pH was adjusted to 7 with the help of KOH and recirculated. After around 15 days, the leachate started rising and over a period of time, reached over 7.

Decomposition of MSW comprises of an aerobic phase, an anaerobic acid phase, an accelerated methane production phase and a decelerated methane production phase (Barlaz et al., 1989). During the first phase, which is the aerobic phase, the oxygen contained in the waste is gradually depleted and there is no protocol to replenish it in current practice of landfill engineering. The major product is carbon dioxide and very little or no degradation of cellulose and hemicellulose can be observed. In the second phase, which is anaerobic, acid accumulation of such acids as carboxylic acids like acetic acid, propionic acid and butyric acids take place and the pH goes down further. The third phase of accelerated methane production is characterized by the conversion of accumulated carboxylic acids to methane and carbon dioxide due to favorable conditions for the associated microbes. The pH increases and the decomposition of cellulose and hemicellulose accelerates. The final phase sees a drop in the methane production rate and depletion in the carboxylic acids. The following table (Table 4.6) lists the different phases of decomposition as per the pH level from the results of the current study as follows:

Table 4.6 Phases of Waste Decomposition According to Changes in Leachate pH

Reactor 1 (Control) pH	Reactor 2 (with nZVI) pH	Phase of decomposition
0-10 days: pH 5.5	0-10 days: pH 6	1
10-22 days: pH 5	10-45 days: pH 5.5	2
22-80 days: pH > 7	45-100: pH>7	3
80-130 days: pH 7.2	100-130 days: pH 8	4

A study by Warith et al. (2002) records the change in landfill pH over time, which is shown in Figure 4.17 as follows and exhibits a trend that is similar to the results of the current study.

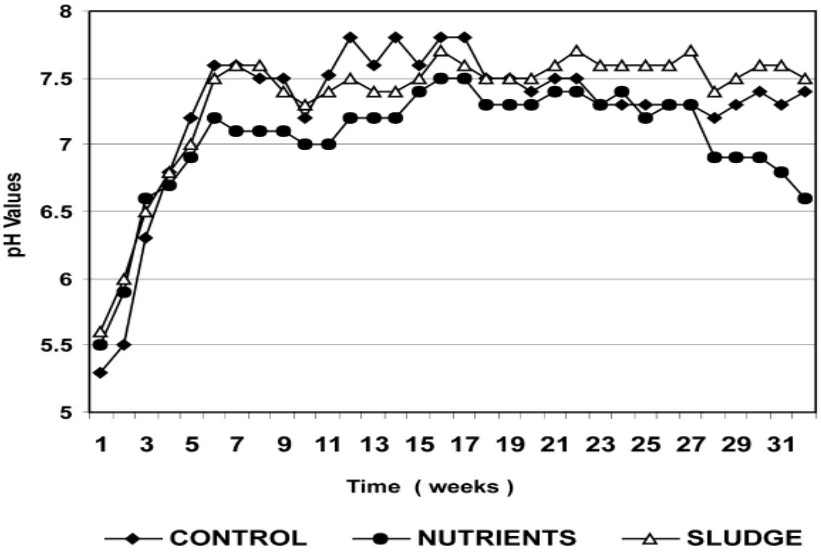


Fig. 2. Changes of leachate pH values over time.

Figure 4.17 Change in Leachate pH over Time (Warith et al, 2002)

Change in leachate conductivity with time is presented in Figure 4.18.

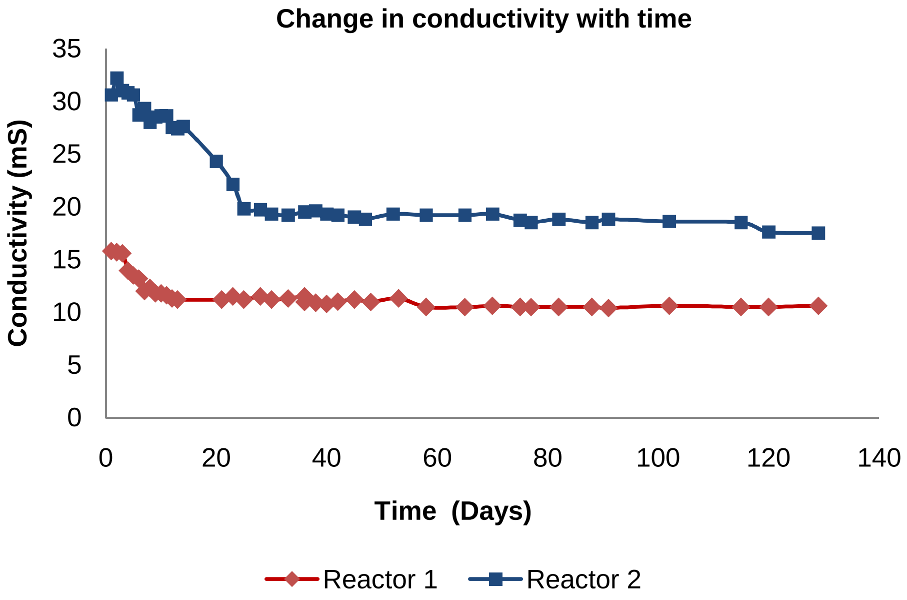


Figure 4.18 Change in Leachate Conductivity over Time

The conductivity of a solution is simply a measurement of the ions (charged particles from dissolving salt, acid or base, etc.) in the liquid. The more ions there are, the more conductive the solution is. This is basically because more ions means there are more molecules to carry electrons. Electrons are fundamental components of electricity, making the solution more conductive to current when a voltage is applied. Leachate conductivity gradually decreases with time. This is because the number of dissolved particles in the leachate gradually decreases with time and increasing MSW decomposition. The leachate from reactor 1 has conductivity in the range of 15 mS around day 1 and gradually goes down to around 10 mS after the 120th day. For reactor 2, the leachate conductivity is in a slightly higher range. At day 1 it is around 32 mS and gradually decreases to 16 mS around day 120. This can be explained by the fact that reactor 2 had added nano zero valent iron particles. We used a liner material made of geotextile for the lab scale bioreactor. However, the nZVI had much lower particle diameter (in nanoscale). Also it was observed that the leachate for reactor 2 was almost black in color and it could be assumed that nZVI particles were present in the leachate. Therefore the leachate was initially resonicated before recirculation. This would also explain the higher conductivity results for leachate samples from reactor 2.

The leachate BOD and COD test results are presented in Table 4.7 as follows:

Table 4.7 Results of BOD and COD Tests

Month	BOD (R1) mg/L	COD (R1) mg/L	BOD/COD (R1)	BOD (R2) mg/L	COD (R2) mg/L	BOD/COD (R2)
1	10096.5	19050	0.53	25000	40000	0.63
2	703.92	2000	0.35	14430	37000	0.39
3	680	1800	0.34	14060	15000	0.38
4	256	1660	0.16	2450	8750	0.28

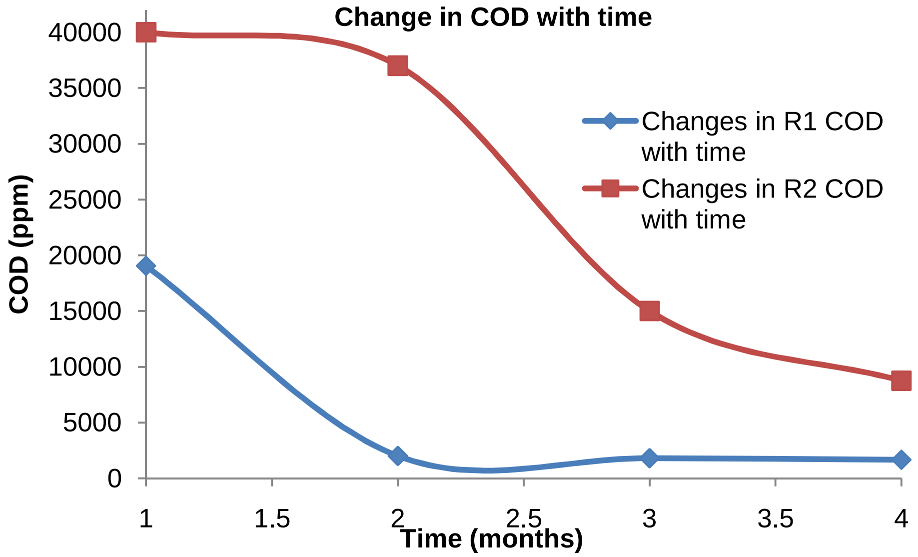


Figure 4.19 Change in Leachate COD over Time

The chemical oxygen demand for the leachate samples of both reactors showed an increasing trend within the first month and then started to deplete gradually. According to Barlaz et al. (1993), the highest BOD and COD values are recorded during the acetogenic phase and our data conforms to this according to Figure 4.19.

From the results of the leachate COD tests, we see from Figure 4.17 that for reactor 1, the initial COD values are in the range of 19,050 mg/l in the first month. Then with time, the COD values went down drastically to 2000, 1800 and 1660 mg/l respectively in the second, third and fourth months.

For reactor 2, containing nZVI particles, the COD values were 40,000, 37,000, 15,000 and 8750 mg/l respectively during the first, second, third and fourth months. The trend is similar over time as compared to the first reactor.

COD values were substantially higher for reactor 2 leachate. This can be explained by the fact that the leachate sample had higher iron content (as seen by the black color of the leachate sample). Since this iron was zero valent it had higher potential to undergo oxidation and as the COD process utilizes a strong oxidant to determine the oxygen demand, it is evident that the iron present had an additional effect on the oxygen demand due to the organics present in the leachate sample. As a result we see substantially higher COD values for reactor 2 leachate samples. However, this can be addressed by determining the iron content of the leachate sample and then subtracting the effect on COD results such iron content might be exerting. In the present study the primary focus was on the gas production, so these steps were not carried out during COD testing. However, it can be recommended that for future studies, this step be carried out as a precautionary measure. Instead of the COD test the Total Organic Carbon test may also be used. Also it is seen that between the first and second months, there is not a huge difference between the leachate COD for reactor 2. This is consistent with the gas production results that showed a similar lag period between the respective gas production peaks of the two reactors. From the third month on reactor 2 COD started decreasing at a higher rate.

In the initial phase of MSW degradation, the COD values are quite high. However, as the degradation of waste progressed and the waste stabilizes, the aged leachate matures and becomes more stable with a dramatically decreased COD. During the methanogenic phase, cellulose and hemicellulose decomposition begins. COD and BOD concentrations begin to decrease and the pH increases as acids are consumed. Similarly decreasing trends were observed in leachate COD by Warith et al. (2002) according to Figure 4.20.

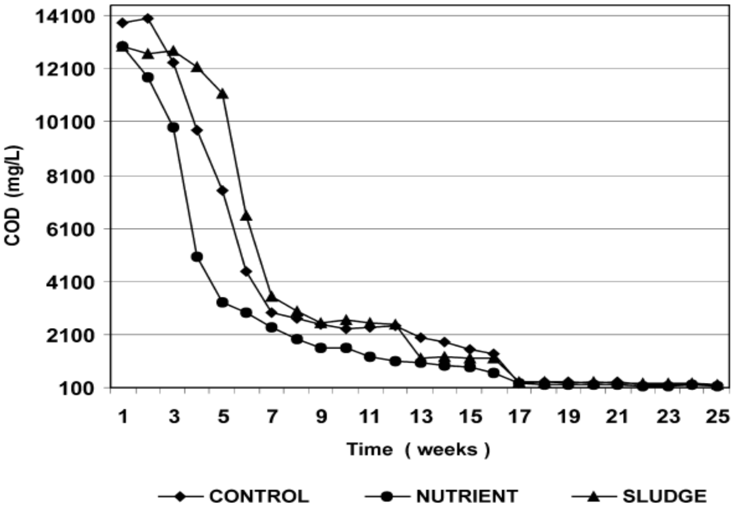


Fig. 4. Changes of leachate chemical oxygen demand concentrations over time.

Figure 4.20 Change in Leachate COD over Time (Warith et al. 2002)

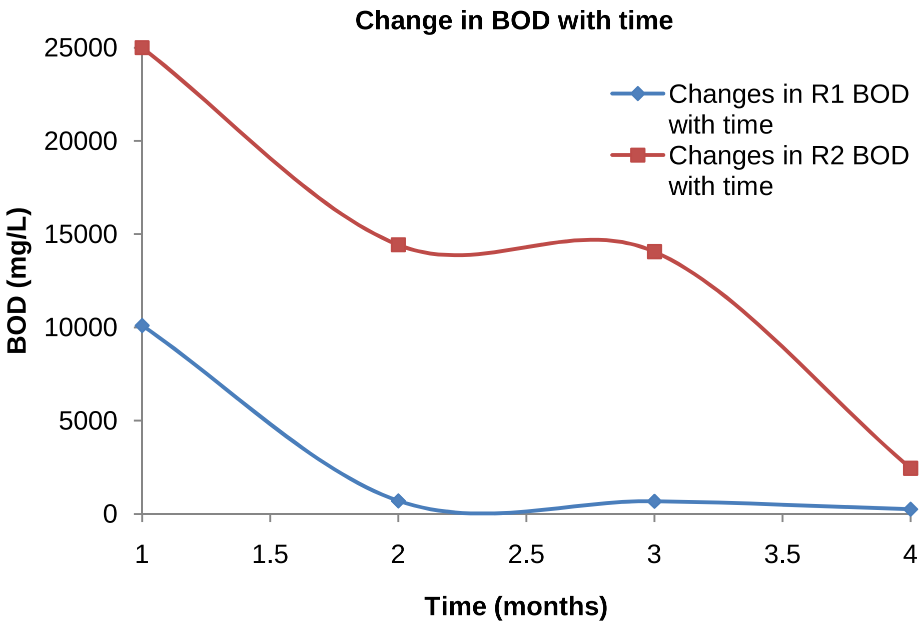


Figure 4.21 Change in Leachate BOD over Time

The BOD of the leachate samples shows a steadily decreasing profile. This happened as leachate recirculation maintained high moisture content in the reactors, thus aiding in accelerated waste degradation.

From Figure 4.21, Reactor 1 leachate BOD is 10,096.5 mg/l in the first month and then gradually decreases to 703.9,680 and 256 mg/l, respectively, in the subsequent months. Leachate from reactor 2 shows BOD values of 25,000, 14,430, 14,060 and 2450 mg/l respectively in the first, second, third and fourth months of reactor operation.

As with the COD, the BOD values for reactor 2 leachate were also much higher than that of reactor 1. It is due to the presence of nZVI in the leachate sample and typically zero valent iron being in a highly reduced state tends to get oxidized. This adds to the observed BOD and COD values for that leachate sample.

However, as with the gas production and COD results, the BOD results between the first and second months do not show a lag period. But the BOD results for the second and third month do not show marked change. This is not consistent with the COD results. This can be due to experimental error or some error due to the high iron content of the leachate from reactor 2.

Warith et al. (2002) reported BOD trends of leachate samples from bioreactors in experimental set up as well as in-situ as presented in Figure 4.22. Their results show trends similar to the present study.

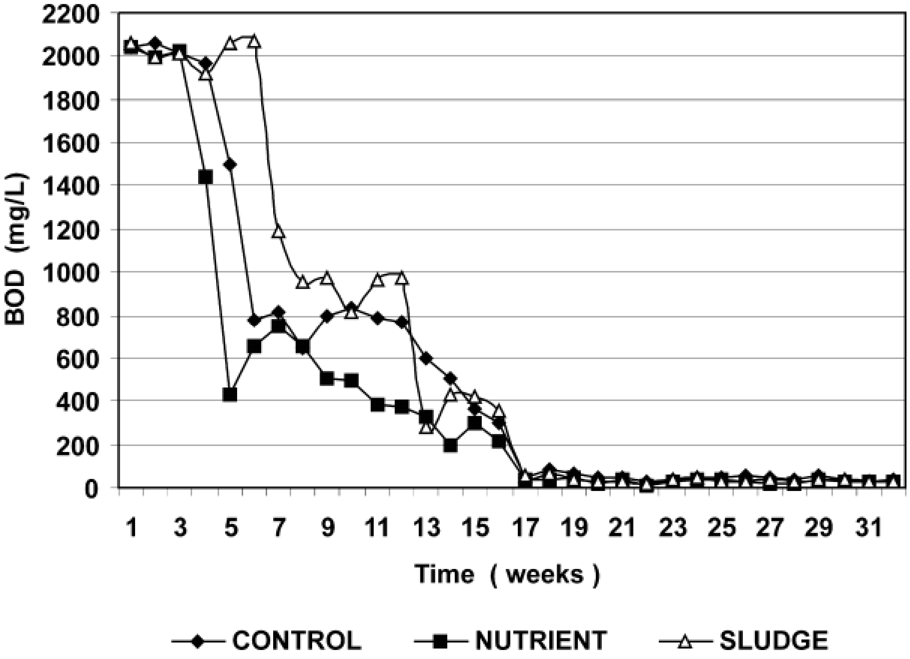


Figure 4.22 Change in Leachate BOD over Time (Warith et al, 2002)

For both reactors, the ratio of BOD to COD shows a decreasing trend over time, presented below in Figure 4.23. Leachate from reactor 1 shows a BOD: COD ratio of 0.53, 0.35, 0.34 and 0.16 during months 1, 2, 3 and 4. Reactor 2 leachate exhibits a similar trend of BOD: COD ratio of 0.63, 0.39, 0.38 and 0.28 for the first, second, third and fourth months. The BOD/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate. As the organic content biodegradation of MSW occurs, the BOD/COD ratio would decrease. The BOD:COD ratio in the acid phase has been reported to be above 0.4 (Ehrig, 1988) or 0.7 (Robinson, 1995). Warith et al. (2002) observed BOD:COD values in the range of 0.15-0.4 and stated that if this ratio is in the range of 0.4-0.8, the waste sample is highly biodegradable. Sponza et al. (2005) reported that this ratio went down from 0.97 to 0.5 from day 5 to day 47. In the stable methanogenic phase, with the consumption of carboxylic acids, a decreasing trend in the BOD: COD ratio has been reported and may fall below 0.1.

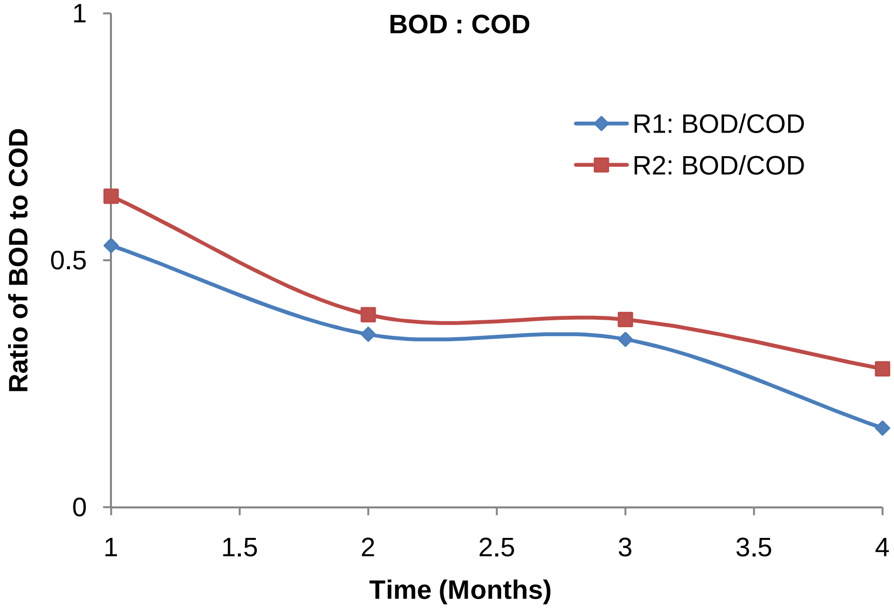


Figure 4.23 Change in BOD:COD Ratio over Time

Biochemical oxygen demand and chemical oxygen demand are, respectively, the oxygen taken up by microorganisms in order to fully decompose the organic and inorganic matter present in a landfill. Thus initially the values of BOD and COD are high. However, with progress of time and the phases of decomposition, these values decrease, as the oxygen required for the decomposition becomes lower than the initial requirement, since already a large part of the waste has been decomposed. This is evident from our data as the BOD and COD values follow a decreasing trend. In Figure 4.23, their ratio also gradually decreases with time. The phases of waste degradation can be predicted from the change in leachate BOD and COD over time.

Overall, the leachate parameters obtained in this study compare well with results of previously published results in the literature. The higher range of COD and BOD values observed in the leachate from the second reactor may have resulted from the higher iron content.. The general trends observed with the leachate pH, conductivity, BOD and COD from both reactors are similar to those reported previously.

4.8 Effect of nZVI particles on MSW Degradation

The experimental results are summarized below in Table 4.8.

Table 4.8 Summary of Experimental Results

Reactor	Time of operation (days)	Cumulative Methane Production (L/Lb.)	CH4 %		BOD:COD	VOC %	
			Final	Max		Initial	Final
1	129	7.29	34	56	0.16	86	64
2	129	6.01	55	60	0.28	84	71

From the lab results it was observed that both reactors initially started producing methane together, but the reactor 1 (without added nutrients) reached its methane producing peak faster, on the 48th day, but reactor 2 reached the peak value of methane yield only on the 101st day. On the 129th day, reactor 1 had produced 254.5 L of methane and reactor 2 had produced 208.2 L of methane. However, from the volatile solids test results it can be seen that the first and second reactors lost about 22% and 13% of their organic content, respectively; their organic contents are still on the higher side and therefore, more methane could have been produced if the time of operation been longer. It is possible that the slow response of reactor 2 in terms of methane production may be due to microbial adaptation to the presence of nZVI. As a result, the phases of decomposition may have been occurring at a slower rate. Also it can be seen from the pH data that the onset of phase 3, which is the methanogenic phase, was delayed in case of the reactor containing the nanoparticles. The final BOD: COD ratio for the control reactor 1 is

0.16, which is close to stabilization. The ratio of BOD: COD for the reactor with the nanoparticles is higher at 0.28. This is evident due to the delayed onset of methanogenesis in case of reactor 2.

Addition of nano zero valent iron particles did not show much improvement in gas production. Moreover, there was a lag period observed in the gas production from the reactor that had added nZVI in it. This may be due to a number of reasons. First, the lag period observed could be due to the microbes acclimating to the iron rich environment. In the end the gas production from reactor 2 picked up and it can be assumed that had the reactor been operated for a longer time, it would have produced more gas. Secondly, the amount of added nZVI (0.1% by weight of the total MSW) might not have been optimum for the microbes. For future experiments, this amount could be changed and the difference on gas production rate would tell us if we need to add less or more nZVI to get better results in terms of gas productions. However, based on the observed lag period, it is probable that a lower amount of iron added might have a more positive effect on the gas production rate. Also, in the MSW samples used for the current study, there was not much of chlorinated organics, small pieces of metals or C&D debris. This can also be a reason why the addition of nZVI did not show marked improvement in gas production. Further studies can be made using these particular types of waste to see if addition of nZVI leads to any improvement in gas production.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was undertaken in order to review the effect of adding nano zero valent iron particles to Municipal Solid Waste in lab scale anaerobic bioreactors. For this purpose fresh MSW sample was collected from the working phase of the City of Denton Landfill and set up in two different bioreactors, one of which had added nZVI. The results of the entire operation can be summarized as follows:

- The MSW sample had physical characteristics comparable to the national average. The sample contained 65% degradable in the form of food, paper, yard waste, and textiles, and 35% non degradable material in the form of plastic, metals, Styrofoam, C&D debris and others. The sample moisture content was 39% (wet basis) and 65% (dry basis). The sample unit weight was 39.5 pcf, and the sample contained about 85.5% volatile solids.
- The reactor without added nanoparticles reached its methane production peak faster than its counterpart (lag period of 53 days).
- Reactors 1 and 2 produced cumulative gas in the order of 254.5 L and 208.2 L, respectively. Reactor 2’s lower production was likely due to the lag period.
- The leachate trends were similar for both reactors. The leachate pH decreased at first and then started increasing after 15 days. The conductivity of the leachate decreased in time. The COD results showed a gradual decrease with time, and the BOD decreased steadily with time. The ratio of BOD to COD decreased with time as well.

- BOD and COD results for the second reactor were considerably higher than the first. This was due to the presence of nZVI in reactor 2 leachate samples. A lag in COD decline for the second reactor was noted, consistent to the gas production results, but for the same lag was not noted in case of BOD. This may be due to experimental error or due to the nZVI content in the leachate sample

The initial hypothesis about nZVI improving methane yield was not satisfied. There was a lag period in gas generation and methane yield. Both reactors had comparable yields of gas and the reactor without nano particles reached its methane producing peak 53 days ahead of its counterpart containing nZVI particles.

5.2 Future Recommendations

On the basis of the results obtained as explained in the above section, some recommendations can be made for future study.

- Effects of adding different concentrations of nZVI on MSW degradation in anaerobic bioreactors could be studied.
- Other sources of nutrition, such as animal waste or divalent iron, could be considered instead of zero valent nano iron, in order to reduce cost.
- The effect of nZVI on the microorganisms could be studied separately, by culturing the microorganisms usually present during the different phases of anaerobic degradation of MSW, on artificial substrates.
- Leachate treatment using nZVI could be carried out in the laboratory using field samples from an operating bioreactor and toxic screenings done, in order to see the effect of nZVI on the standard pollutants present in such samples.
- Effect of adding nZVI to different categories of waste such as C&D could be studied.

To conclude, it can be stated that nZVI did not inhibit gas production or MSW degradation. However, it apparently slowed down the process a little bit. Further extensive study of MSW degradation in the presence of various concentrations of nZVI should be made in order to really find out if there is an optimum concentration at which nZVI helps in MSW degradation. Also, the leachate should be analyzed for the presence of pollutants before and after addition of nZVI to establish its usefulness in terms of contaminant reduction.

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