Geochemical Analysis of the Leachate Generated After Zero Valent Metals

Addition to Municipal Solid Waste

by

Gandhar Abhay Pandit

A Thesis Presented in Partial Fulfilment
of the Requirements for the Degree
Master of Science

Approved June 2019 by the
Graduate Supervisory Committee:

Hinsby Cadillo – Quiroz, Co – Chair
Larry Olson, Co - Chair
Treavor Boyer

ARIZONA STATE UNIEVRSITY

August 2019

ABSTRACT

Zero-Valent Metals (ZVM) are highly reactive materials and have been proved to be effective in contaminant reduction in soils and groundwater remediation. In fact, zero-Valent Iron (ZVI) has proven to be very effective in removing, particularly chlorinated organics, heavy metals, and odorous sulfides. Addition of ZVI has also been proved in enhancing the methane gas generation in anaerobic digestion of activated sludge. However, no studies have been conducted regarding the effect of ZVM stimulation to Municipal Solid Waste (MSW) degradation. Therefore, a collaborative study was developed to manipulate microbial activity in the landfill bioreactors to favor methane production by adding ZVMs. This study focuses on evaluating the effects of added ZVM on the leachate generated from replicated lab scale landfill bioreactors. The specific objective was to investigate the effects of ZVMs addition on the organic and inorganic pollutants in leachate. The hypothesis here evaluated was that adding ZVM including ZVI and Zero Valent Manganese (ZVMn) will enhance the removal rates of the organic pollutants present in the leachate, likely by a putative higher rate of microbial metabolism. Test with six (4.23 gallons) bioreactors assembled with MSW collected from the Salt River Landfill and Southwest Regional Landfill showed that under 5 grams /liter of ZVI and 0.625 grams/liter of ZVMn additions, no significant difference was observed in the pH and temperature data of the leachate generated from these reactors. The conductivity data suggested the steady rise across all reactors over the period of time. The removal efficiency of sCOD was highest (27.112 mg/lit/day) for the reactors added with ZVMn at the end of 150 days for bottom layer, however the removal rate was highest (16.955 mg/lit/day) for ZVI after the end of 150 days of the middle layer. Similar trends in the results was observed in TC analysis. HPLC study

indicated the dominance of the concentration of heptanoate and isovalerate were leachate generated from the bottom layer across all reactors. Heptanoate continued to dominate in the ZVMn added leachate even after middle layer injection. IC analysis concluded the chloride was dominant in the leachate generated from all the reactors and there was a steady increase in the chloride content over the period of time. Along with chloride, fluoride, bromide, nitrate, nitrite, phosphate and sulfate were also detected in considerable concentrations. In the summary, the addition of the zero valent metals has proved to be efficient in removal of the organics present in the leachate.

ACKNOWLEDGMENTS

I would like to express my heartfelt gratitude to Dr. Hinsby Cadillo – Quiroz as my advisor, who trusted me and gave me a wonderful opportunity to work on this project. As my advisor and mentor, he has supported me constantly and guided me throughout my master's not only professionally but also personally to a great extent. Thanks for inspiring me, and making sure that I felt comfortable working in the lab. I consider myself immensely fortunate to have worked in your lab and benefitted from your insight, experience, and organized working style. This would not have been possible without your patience, support, constant motivation right from the day I started working in lab. I would also like to sincere thank my department chair Dr. Larry Olson for allowing me to work on this project. Thank you for your support and constant motivation right from the first day in the department. Also sincerely thanks to Dr. Trevor Boyer for providing timely valuable guidance and support. I would also like to thank Mr. Albert Brown for his constant support and help during my thesis.

I would like thank Mark Reynolds, my mentor and friend, for training me in the lab from the first day and for being available whenever I needed help. His support helped me learn and grow technically. I would also like to thank Jacqueline Winston, our undergrad in the Cadillo lab for helping out in some of the chemical analysis and data contribution. I would also like to thank Christopher Ashe (Chris) from the SoLS for helping out in LC-MS analysis, Michael Edgar from CBBG for the TC analysis and Mugdha Thakur from the Applied Mathematics department for helping out with statistical analysis.

iii

I would also like to thank Analissa, Mike, Jullian and Steffen from the Cadillo Lab and my friends from the Swette Center of Environmental Biotechnology, thank you for helping me professionally as well as personally and making my work place a memorable and happy one.

I would not have been here without the incredible love and support from my parents and family. Thank you for all the motivation and encouragement to pursue this master's degree. Lastly, thank you to all my friends from India and USA. I would like to dedicate this thesis to my parents, grandmother and my family.

TABLE OF CONTENTS

CHAPTER   Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Municipal Solid Waste

The Resource Conservation and Recovery Act of 1976 defines municipal solid waste (MSW) as any garbage or refuse, sludge from a water supply and/or waste water treatment plant, air pollution control facility and other discarded materials generated within the community resulting from any kind of industrial, commercial and agricultural operations. Solid waste not only defines waste that is physically solid but also includes waste that is liquid, semi – solid or contained gaseous. Solid waste is generally that material which is either discarded by being abandoned or refused. MSW is also termed as trash commonly consists of product packaging, furniture, clothes, food waste, appliances, paint, batteries, milk cartons, yard wastes, plastic plates. MSW is usually managed by the concept of integrated solid waste management. This concept include practices like source reduction of waste, reuse or recycling of the waste products, composting of the biodegradable organic waste, combustion of the waste for energy recovery and lastly disposal of waste by landfilling (US EPA, 2019). According to 2015 statistics, 262.4 million tons of MSW was generated out of which 67.8 million tones was recycled and 23.4 million tons was composted. 33.57 million tons of MSW was combusted for energy recovery and about 137.7 million tons was sent to landfill for disposal (US EPA, 2019). Thus around 52.48% of the total generated MSW was disposed of by landfilling.
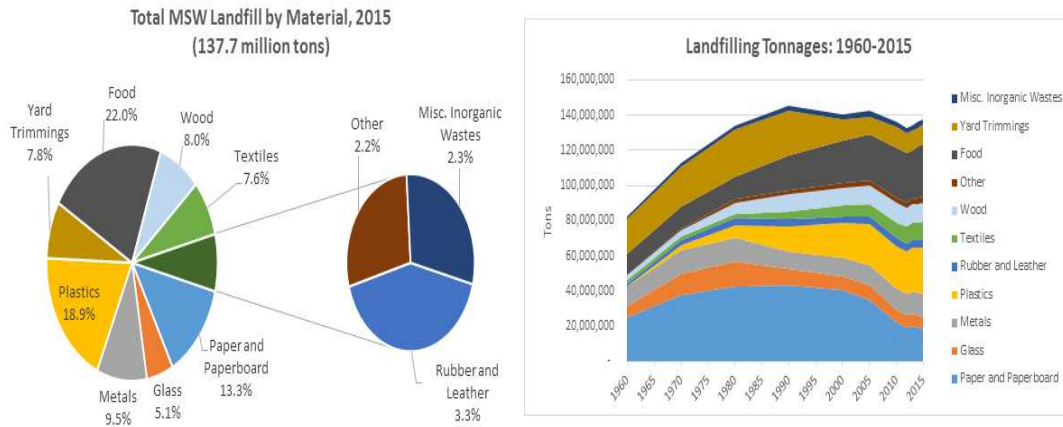
Figure 1. Total MSW Landfilling data for 2015 (Source EPA, 2015)

1.2 Bio reactor landfills – Introduction

A MSW landfill is usually a discrete area of land which is well engineered and well managed facility for disposal of solid waste. Landfills are designed, operated and monitored in accordance with Resource Conservation and Recovery Act, 1976 subtitle D. Landfills are designed in such a way to protect the environment and surrounding ecology from the transport of the contaminants through air or water. Landfills are usually monitored for ground water contamination and for landfill gas. In In 2009, approximately 1908 landfills were operated and managed across the US by federal and state government (US EPA, 2019). In recent years, the concept of a bioreactor landfill has received increased attention (Pacey, 1999). A bioreactor landfill is typically a solid waste landfill in which waste degradation and stabilization is enhanced by adding liquid and air to enhance the microbial degradation process (US EPA, 2019). Depending on the external application of air, the bioreactor landfills are usually differentiated as aerobic bioreactor landfills and anaerobic bioreactor landfills. In aerobic bioreactor landfills, waste liquid that is generated in landfills is recirculated along with air injection to promote and accelerate waste

2

degradation activity. In an anaerobic bioreactor landfill, moisture in the form of recirculated leachate is added to the waste in the absence of air injection (US EPA, 2019).
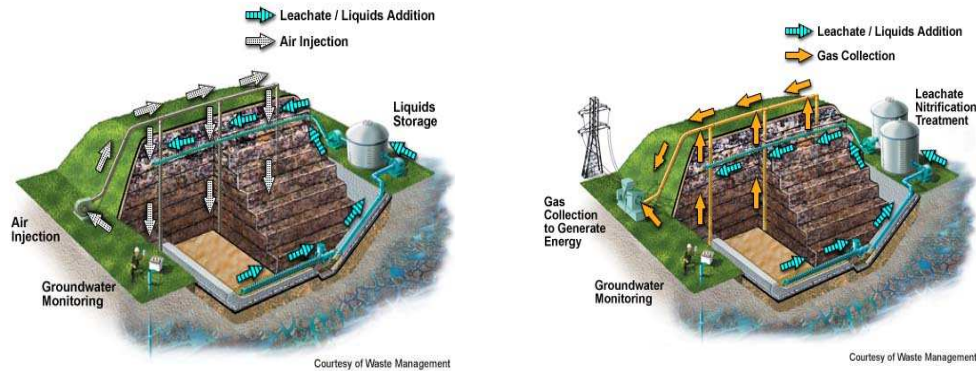
Figure 2. Difference between Aerobic bioreactor and Anaerobic Biorector (US EPA, 2019)

Bioreactor landfills are usually operated to achieve enhanced decomposition rates resulting in rapid waste stabilization and increased gas production. Advantages of operating a landfill as a bioreactor landfill includes rapid stabilization and degradation of waste resulting in effective increase in space due to increased density of waste mass, recirculation of the leachate resulting in reduced leachate disposal cost, increase in the landfill gas production resulting in the increase in the waste to energy practice and finally reduction in the post closure cost due to rapid stabilization of landfill (Reinhart and Townsend, 1998).

1.3 Landfill as an anaerobic digester

When refuse is buried in a landfill, a complex series of biological and chemical reactions occurs as the refuse decomposes. Generally, it is accepted that landfills undergo at least four phases of decomposition,

(1) An initial aerobic phase,

(2) An anaerobic acid phase,

(3) An initial methanogenic phase, and

(4) A stable methanogenic phase.

During the initial aerobic phase, oxygen present in the void spaces of the freshly buried refuse is rapidly consumed, resulting in the production of CO_2 and maybe an increase in waste temperature. The aerobic phase in a landfill lasts only a few days because oxygen is not replenished once the waste is covered. Most leachate produced during this phase results from the release of moisture during compaction as well as short-circuiting of precipitation through the buried refuse. (Christensen and Kjeldsen, 1995). As oxygen sources are depleted, the waste becomes anaerobic, which supports fermentation reactions. Cellulose and hemicellulose comprise 45 to 60% of the dry weight of MSW and are its major biodegradable constituents. Cellulose and hemicellulose biodegradation are carried out by three groups of bacteria:

(1) The hydrolytic and fermentative bacteria that hydrolyze polymers and ferment the resulting monosaccharides to carboxylic acids and alcohols;

(2) The acetogenic bacteria that convert these acids and alcohols to acetate, hydrogen, and carbon dioxide;

(3) The methanogens that convert the end products of the acetogenic reactions to methane and carbon dioxide.

In the second phase the hydrolytic, fermentative, and acetogenic bacteria dominate, resulting in an accumulation of carboxylic acids, and pH decreasing. The highest BOD and COD concentrations in the leachate is measured during this phase. The BOD: COD ratio in the acid phase is usually 0.7 or above. As the pH is acidic, acid phase leachate is chemically aggressive and increases the solubility of many compounds. The onset of the

4

initial methanogenic phase (3) occurs when measurable quantities of methane are produced. The onset of this phase is likely associated with the pH of the refuse becoming sufficiently neutralized for at least limited growth of methanogenic bacteria. During this phase, the acids that accumulated in the acid phase are converted to methane and carbon dioxide by methanogenic bacteria, and the methane production rate increases. Cellulose and hemicellulose decomposition also begins. COD and BOD concentrations begins to decrease and the pH is increased as acids are consumed. The BOD to COD ratios also decreases as carboxylic acids are consumed.

In the stable methanogenic phase, the methane production rate reaches its maximum. In this phase, the rate of CH_4 production is dependent on the rate of cellulose and hemicellulose hydrolysis. Some COD is present in the leachate, but it is mostly recalcitrant compounds such as humic and fluvic acids. The BOD: COD ratio generally fall below 0.1 in this phase because carboxylic acids are consumed as rapidly as they are produced. (Christensen and Kjeldsen, 1995).

1.4 Addition of micro nutrients and trace elements for enhancing methane production

During anaerobic digestion process, carbon is usually used as a substrate in most of the reactions. Nitrogen is required for protein biosynthesis while sulfur is an important constituent of important amino acid for methanogenic bacterial growth. Phosphate is important for providing the energy carriers ATP and NADP during metabolism (Mao et al, 2015). Thus, micronutrients like nitrogen, potassium and magnesium are required by many microbes for the activation or proper functioning in the anaerobic biological processes. The requirements of the micronutrients are usually assessed on bacterial composition, growth yields and biomass composition (Mao et al, 2015). Generally, a ratio of C:N:P:S is

maintained as 600:15:5:1 (Weiland P, 2010). Studies have reported the optimum C:N:P ratio to be 200:5:1 (K Rajeshwari et al, 2000). Studies have proved that both micronutrients and trace elements are both economic and environmentally friendly for stimulating the anaerobic digestion of the organic material. Microorganisms need trace elements as the building block for the growth as well as to carry out the enzymatic activities and chemical reactions (Mao et al, 2015). Reda et al, 2008 reported that Nickel can be utilized as a stimulator in the biogas production. The studies showed that addition if Nickel not only stimulated the biogas production but also increased the methane content of biogas. Addition of calcium and magnesium salts can also enhance methane production. The effects of mixtures with addition of Cobalt, Nickel and Iron, Cobalt and Nickel have been observed. A mixture of Cobalt, Molybdenum, Nickel, Selenium and Tungsten was found to increase the production of methane gas in range of 45 – 65% (Facchin et al, 2013). Supplementation of micronutrients and trace elements can help to achieve the anaerobic digestion process stabilization and can also result in enhanced efficient biogas generation.

Table 1 Stimulatory micro nutrients and trace elements for enhancing methane production (Mao et al, 2015)

	Element	Feedstock	Function	Stimulatory concentration	Stimulatory effect
Micronutrients	Iron	Municipal solid waste, Energy crops	CODH, Precips sulfides Constituent of enzymes	1000–5000 ppm (DB)	Promote organic degradation; Aid hydrogenotrophic metabolism
	Nickel	Animal excrete	CODH, other hydrogenases	0.029–27 mg/L	Reduce ammonia and sulfide toxicity; Stabilize VFA levels
	Selenium	Crops residues, Food waste	F430, Benzoyl-COA	0–10 mg/kg TS	Improve process stability; Enhance the growth of microorganisms
	Tungsten	Stillage-fed	FDH	0.658–100 mg/L	Promote process start-up; Eliminate foam
	Zinc	Waste water	FDH, CODH, other Hydrogenases	0.0327–2 mg/L	Enhance methane content; Improve biogas production rate
	Chromium			4–15 mg/L	
	Molybdenum		FDH	0.044–100 mg/L	
	Cobalt		Corrinoids CODH	0.029–5 mg/L	
Macronutrients	Carbon		Energy and cell material		
	Nitrogen		Protein synthesis		
	Potassium		Cell wall permeability	< 400 mg/L	
	Phosphorus		Nucleic acid synthesis	465 mg/L	
	Sulfur		Numerous enzymes	3.05–6.18 g/kg TS	
	Magnesium				

1.5 Application of zero valent iron in enhancing the methane production

Zero valent iron (ZVI) is a common application in environmental bioremediation due to its nontoxic, abundant, cheap and easy to manufacture properties (Sun et al, 2016). ZVI is readily oxidized while the other reactants are reduced by the electron transfer between ZVI and other reactants (Hwang Y et al, 2018). ZVI is also used for treating the refractory and toxic pollutants in the groundwater and industrial waste water through the process of reductive transformation due its strong reducing capacity of $- 0.447$ V (O'Carroll et al, 2018).

Studies by Daniels et al, 1987 showed that methanogenic bacteria use molecular hydrogen and carbon dioxide to produce methane and during the process of reducing carbon dioxide to methane uses either pure elemental iron (Fe°) or iron in mild steel as a source of electrons. These methanogenic bacteria uses Fe° oxidation for its energy generation and growth. The mechanism adopted for oxidation of Fe° was cathodic depolarization in which the electrons from Fe° and H^+ produce molecular hydrogen (H_2) which is then used by methanogens.

Reactions:

$Fe + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH$……………………………………………………… (1)

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$………………………………………………………. (2)
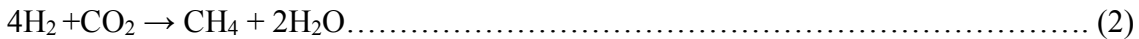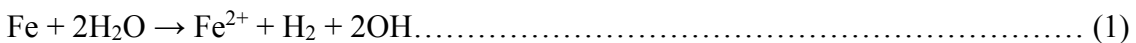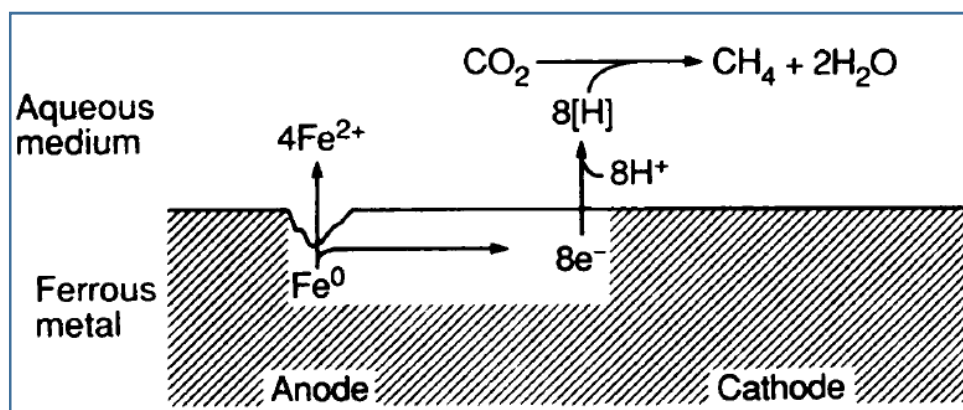
Figure 3. Schematic showing cathodic depolarization by methane producing bacteria.

(Daniels et al, 1987)

This study motivated for the application of the ZVI to the anaerobic processes. Zhang et al, 2015 found out that addition of ZVI positively affects the anaerobic digestion process by enhancing organic matter degradation and methane production yield. Adding ZVI to the anaerobic process shortens the lag time of methanogenesis process and thus increases the methane yield by 91.5%. In addition to that, ZVI also helps in hydrogen sulfide removal, acts as a stimulant for key enzyme for acidogenesis and decrease the oxidation reduction potential (Feng et al, 2014 and Puyol et al., 2018). Addition of ZVI to anaerobic processes helps to enhance the overall methane production by two different pathways. First pathway is hydrogen (H_2) generated from ZVI corrosion which can be directly utilized by hydrogenotrophic methanogens which convert carbon dioxide (CO_2) to methane (CH_4) as described in the following equation:

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ with $\Delta G° = -131$ kJ/mol…………………………..………. (3)
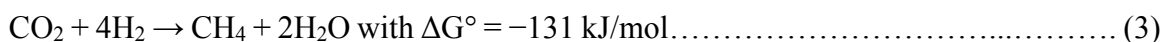
The second pathway is the homoacetogenesis coupled with acetoclastic methanogenesis that convert the carbon dioxide (CO_2) to acetic acid (CH_3COOH) in the presence of ZVI.

The acetic acid is then fermented to produce carbon dioxide (CO_2) to methane (CH_4) (Kato et al., 2015, Zahedi et al., 2016).

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \text{ with } \Delta G° = −95 \text{ kJ/mol} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ with } \Delta G° = −75.5 \text{ kJ/mol} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5)$$
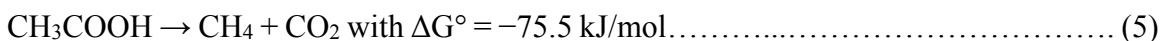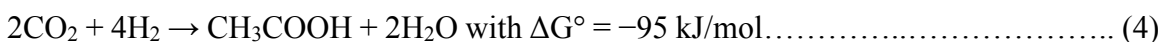
1.6 Landfill Leachate Studies

Landfill leachate is defined as an aqueous effluent produced when water percolates through the waste in a landfill. Thus, it is a liquid draining from a landfill site in the form of suspended materials, dissolved components of waste materials, by products from degradation etc., through percolation within the site. Because leachate contains harmful and complex compounds, i.e. organic matter leading to high Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD), and heavy metals, e.g., iron, copper etc, leachate can adversely affect plant growth, contaminate the drinking water and impair the ecosystem as it penetrates the soils or groundwater. It is a highly complex mixture of soluble, insoluble, organic, inorganic, ionic, non-ionic and bacteriological constituents in an aqueous medium. (Zhao et al, 2012)

The landfill leachate generation depends on the type of MSW being dumped, landfill age, moisture content, seasonal weather variations, site hydrology, the stage of decomposition in the landfill and pH. Produced leachate could contain large amounts of contaminants measured as COD, BOD_5, NH_3–N, heavy metals, phenols, phosphorus etc. Obviously, as the landfill age increases, the biodegradable fraction of organic pollutants in leachate decreases as an outcome of the anaerobic decomposition occurring in landfill site. Thus, mature or stabilized leachate contains much more refractory organics than young leachate. (Aziz and Mojiri, 2015).

Pollutants in MSW landfill leachate can be divided into four groups: (Kjeldsen et al, 2002)

- Dissolved organic matter analyzed as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), volatile fatty acids and more refractory compounds such as fulvic-like and humic-like compounds.

- Inorganic macro components 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^-).

- Heavy metals like cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}).

- Xenobiotic organic compounds (XOCs) originating from household or industrial chemicals and present in very relatively low concentrations (usually less than 1 mg/l of individual compounds).

1.7 Characteristics of leachate

The composition of leachate is highly dependent on the degradation stage of the waste. In the acid phase, concentrations are generally higher due to enhanced formation of dissolved organic matter and release of ammonia. In the methanogenic phase, the content of dissolved organic matter significantly decreases and the composition of the organic matter changes indicated by BOD: COD ratios below 0.10. The ammonia concentration seems not to follow the same decreasing trend and may constitute one of the major long-term pollutants in landfill leachate. The content of heavy metals in the leachates generally very low because of attenuating processes (sorption and precipitation) that take place within the disposed waste. At landfills in arid regions, where the waste is dry and there is little infiltration, the

landfill may remain in the acid phase or early methane production phase for decades or longer. (Kjeldsen et al, 2002)

Physio-chemical characteristics of leachates change over the course of a landfill's life. On so-called young landfills, the concentrations of pollutants in the leachates are high but as they age the value of BOD_5/ COD ratio decreases. This phenomenon results from the fact that young landfills contain many organic compounds that readily succumb to biodegradation, giving rise to refractory compounds that accumulate with the exploitation of landfill and are resistant to biochemical degradation.

Table 2 Characteristics of leachate generated from decomposition of MSW (Kjeldsen et al, 2002)

Parameters	Typical Range of Values (mg/L)
pH	4.5 to 9.0
Alkalinity ($CaCO_3$)	300 to 11,000
BOD5	20 to 40,000
COD	500 to 60,000
Calcium	10 to 250
Chloride	100 to 5,000
Potassium	10 to 2,500
Sodium	50 to 4,000
Magnesium	40 to 1,150
TDS	0 to 42,300
Total SS	6 to 2,700
Hardness	0 to 22,800

Organic Nitrogen	10 to 4,250
Ammonia NH_3	30 to 3,000
Nitrite Nitrogen NO_2^-	0 to 25
Nitrate Nitrogen NO_3^-	0.1 to 50
Total Nitrogen	50 to 5,000
Total Phosphate	0.1 to 30
Sulphate SO_4^{2-}	20 to 1,750
Manganese	0.03 to 65
Total Iron	3 to 2,100
Copper	4 to 1,400
Lead	8 to1,020
Zinc	0.03 to 120

1.8 Scope of the present study

Based on the researches mentioned in the previous section, zero valent metals have potential to increase anaerobic methane production from the organic materials. But most of the studies have been performed on enhancing the methane production from anaerobic digestion of waste water sludge. Since the landfills also contain organic matter and tends to produce methane though anaerobic digestion, there was a need to study the effects of adding the zero valent metals to MSW. Also very few studies (Gangopadhyay, 2012) have been conducted regarding the effects of the zero valent metals in the MSW. Thus, the main objective of these study was to manipulate the microbial community in the bioreactor landfill to favor the total methane (CH_4) production by adding the zero valent metals. Since

most of the studies have been conducted on ZVI, it was also desired to compare the efficiency of ZVI with other ZVM. With the same purpose, ZVMn was also included in the scope of study to compare the results of adding these ZVM to MSW. Although several studies have been developed to evaluate the effects of ZVM metals addition to the performance of the anaerobic digestion and methane gas production, to the best of our knowledge no paper has evaluated this aspect of addition of these metals on the leachate derived during these processes. Thus, the goal of this study was to analyze the change in the leachate generated by landfill simulating bioreactors after the addition of the ZVM. This work had particular goals of detecting the physical and chemical changes the formation of any new byproducts due to the addition of treatments. The specific objective of the study was to investigate the effects of the adding the ZVM on the organic byproducts and inorganic pollutants in the leachate. The hypothesis for the objective was that adding of the ZVM including ZVI and Zero Valent Manganese (ZVMn) will enhance the removal rates of the organic pollutants present in the leachate by a putative higher rate of microbial metabolism. Along with it the other objective of the study was to evaluate whether significant differences on the effects of the two different ZVM developed in terms of organic and inorganic removal rates.

CHAPTER 2

MATERIALS AND METHODS

The primary objective of this study was to determine the effects of adding zero valent metals on the changes in the geochemical properties of the leachate generated from the experimental bioreactor landfill. Hence to evaluate these effects, bioreactor landfill simulating reactors were constructed in the Cadillo Lab to emulate the conditions in a local MSW landfill. A set of two reactors were operated as injection controls (with just water addition, but without addition of treatments), and two reactors were added with zero valent iron (5 grams/liter dosage) and two were added with zero valent manganese (0.625 grams/liter dosage).

2.1 Municipal Solid Waste Sample Collection

Solid waste samples were collected from 2 different landfills – South West Regional Landfill (Buckeye, Arizona) and Salt River Landfill (Scottsdale, Arizona) with the aim to have samples representing differing landfilling ages. The Municipal Solid Waste (MSW) samples collected from South West Regional Landfill (SWRL) represented 8-11 years old age while the MSW samples collected from two distinct locations within Salt River Landfill (SRL) represented 20 years old and 5 years old age respectively. Sampling locations across the landfills were selected according to the routine maintenance at SWRL and a personal request at SRL regarding sample collection was made to collect the samples. MSW samples were collected and stored in PVC buckets (38 lbs (17.23 kg) capacity). The samples were immediately brought to lab and were stored at 4°C for preservation.

2.2 Experiment Setup

As a part of experimental work of PhD Candidate, Mark Reynolds, (Cadillo Lab, and personal communication) six laboratory scale reactors were constructed to simulate an anaerobic landfill bioreactor. Six laboratory scale reactors were constructed to stimulate an anaerobic landfill bioreactor. The bioreactors were constructed using 8 inches (20.32 cms) diameter PVC plastic pipes with a total height 18 inches (45.72 cm). The bottom and top part of the PVC pipes was sealed using 8 inches diameter PVC caps using PVC cement and primer. Epoxy putty was additionally applied externally to areas where leaks were identified during pressure test with nitrogen gas. A gravel layer was placed at the bottom of each reactor as a filtration layer. Each reactor was partitioned in to three layer each layer representing different MSW solid was samples. The bottom most layer was packed with 10 years old SWRL MSW sample. A layer of soil was placed on the top of MSW sample layer to facilitate the even distribution of sample in the reactor and to replicate the onsite landfilling conditions. A leachate distribution injector made out of perforated tube was placed on the top of the MSW sample for evenly distribution of the recirculated leachate. The middle layer in the reactor was packed with 20 years SRL and the top most layer in the reactor was packed with 5 years SRL. Each layer represented a total height of 4.75 inches (12.06 cms). A headspace gas collection port was installed on the top of each reactor along with three leachate injection ports. Each leachate injection port was connected via 1/8 inches OD PTFE tubing to the corresponding MSW layer's leachate distribution injector to allow the delivery of leachate to a specific MSW layer. The outlet of the gas collection port was connected to a 10 liters Tedlar Gas Bag (CEL Scientific) in order to collect the gas formed in the headspace. All the reactors were fitted with pressure gauge.

A port in the form of tap was also provided at the bottom of each layer to collect the leachate generated in the reactor. All the reactors were incubated at about 35°C in a temperature controlled room. The reactor schematic is presented in the following figure.
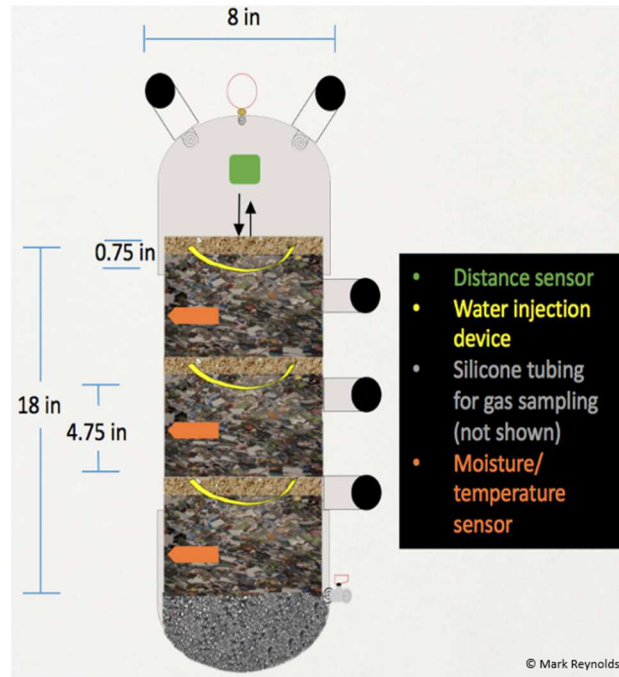
Figure 4. Schematic of Lab Scale Landfill Bioreactor Set Up

After initial dry incubation of 126 days, anaerobic deionized water flushed with nitrogen was injected to the bottom layer through leachate injector to maintain a total moisture content of 60% by weight using the moisture content formula which is applied on site. The moisture level in the reactors were checked continuously using moisture capacitance sensors. The controls received anaerobic deionized water while two reactors received anaerobic deionized water added with dosage of 5 grams/liter of zero valent iron (ACROS Organics, particle size no greater than 149 um, purity >97% w/v (Fe)) while the rest two reactors received anaerobic deionized water with dosage of 0.625 grams/liter of zero valent manganese. (Fisher Scientific, particle size no greater than 420 um, purity >99% (Mn)). The injection occurred on per layer basis starting with the bottom most layer followed by

the middle layer and then finally the top layer. During the reactor operation, leachate generated in the bottom of the reactors was collected after 7, 21, 51, 75, 100, 125 and 150 days through the leachate collection port and recirculated back on the same day through layer specific leachate injection port. After a period of 283 days, anaerobic deionized water flushed with nitrogen was added to the middle layer through leachate injector to maintain a total moisture content of 60% by weight. As the previous injection, two reactors received non-treatment added anaerobic deionized water while other two reactors received 5 grams/liter of zero valent iron (Fisher scientific, particle size no greater than 149 um, purity >97% w/v (Fe)) anaerobic deionized water and 0.625 grams/liter of zero valent manganese (Fisher Scientific, particle size no greater than 420 um, purity >99% (Mn)) added anaerobic deionized water respectively. During the reactor operation, leachate generated in the bottom of the reactors was collected after 7, 25, 51, 75, 100, 125 and 150 days through leachate collection port and recirculated back on the same day through layer specific leachate injection port. After sampling, the remaining leachate was purged with the nitrogen gas to establish anaerobic conditions prior to it being recirculated in the reactors through the corresponding leachate injectors.

2.3 Leachate sample collection and storage

The leachate samples were collected for the measurement of Conductivity, High Performance Liquid Chromatography (HPLC), Soluble Chemical Oxygen Demand (sCOD), Total Carbon Analysis, Ion Chromatography and Fe^{2+}/Mn^{2+} quantifications. All the sample aliquots were filtered via 0.2um filtration. For preserving HPLC and sCOD samples, 1.8 ml of leachate was mixed with 0.2 ml of 50mM sulfuric acid. For preserving

total carbon samples, 0.9 ml of sampled leachate was mixed with 0.6 ml of 1M HCl. All the samples were preserved in -4°C freezer using 2 ml flip cap Eppendorf tubes.

2.4 Leachate Analysis

2.4.1 Conductivity measurement

The pH and the temperature of the leachate was measured using a portable pH probe calibrated regularly with 4, 7, and 10 standard solutions from the Vernier. The conductivity of the leachate was measure using a Vernier conductivity probe. The conductivity probe was calibrated to 10, 100 and 1000 µS/cm using 1000 µS/cm NaCl conductivity standard solution straight from Vernier and was operated within the range of 0 – 2000 µS/cm.

2.4.2 High Performance Liquid Chromatography (HPLC) measurement

The HPLC analysis was carried out using Shimadzu, USA. The HPLC was equipped with an Aminex HPX-87H column (Bio-Rad, Hercules, CA). Detection of chromatographic peaks was achieved using a photodiode array detector at 210 nm and a refractive index detector. The eluent was 5 mM Sulphuric Acid with a total detection time of 150 min. The oven temperature was kept constant at 65□. The eluent flow rate was 0.6 mL/ min.The HPLC was analyzed for volatile fatty acids C - 1 to C – 7 which included Succinate, Formate, Acetate, Propionate, Isobutyrate, Butyrate, Isovalerate, Valerate, Isocaproinate, Caproianate and Heptonoate. Calibration curves were generated for each run using standard mix serially diluted from 2X to 0.005X. The detection limit for the VFAs of interest was 1 mg/ml.

2.4.3 Soluble Carbon Oxygen Demand (sCOD) Measurement

The sCOD was quantified using Hach COD kit with a range of 500 – 1500 mg/lit. The standards were prepared using Potassium Hydrogen Phthalate and for each run, a 3 point

standard curve (50, 500, 800 mg/lit) was generated. The samples were digested using Hach DRB 200 heater for time of 120 minutes at 150°C. After digesting, the samples were analyzed using Hach DR 2800 Spectrometer at 540 nm wavelength to get the correspondence absorbance value.

2.4.4 Total Carbon Measurement

The Total Carbon measurement was carried out using Shimadzu (TOC − L, 680 □, and Combustion Oxidation Detection method). Detection range of the instrument was from 0.004 mg/liter to 30000 mg/liter. The eluent was HCl acidified water with a total sample run time of 20 minutes per sample. The oven temperature was kept constant at 680□. A 4 point calibration curve was generated for each run using Potassium Hydrogen Phthalate standard

2.4.5 Ion Chromatography

The ion chromatography analysis was carried out using Metrohm (930 Compact IC) using Metrosep A supp 5 − 150/4.0 column. The eluent flow rate was 0.7 ml/minute. All the samples were run on 18 minutes run time. The lowest detection limit of the instrument was 0.1 ppm. The oven temperature was kept constant at 30°C. All the samples were analyzed for fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate. A 5 point calibration curve was generated for each run using Metrohm customized standard mix.

2.4.6. Data Analysis

The statistical analysis was performed using R software (V 1.1.463). Wilcoxon signed rank test was choose to identify the significant differences in between the data as the data was non parametric. A paired difference test was performed to analyze data across layer and

with layer across treatments. Further simple linear regression analysis was performed over

the data to calculate the rates of removal or increase over the span of time.

CHAPTER 3

RESULTS AND DISCUSSION

In this chapter, results related to the physical and chemical analysis of the leachate are presented and discussed. The leachate that was sampled was used for the analysis of physical parameters like pH, temperature, and conductivity along with chemical parameters like soluble Chemical Oxygen Demand, Total Organic Carbon, High Performance Liquid Chromatography and Ion Chromatography.

3.1. pH Measurements
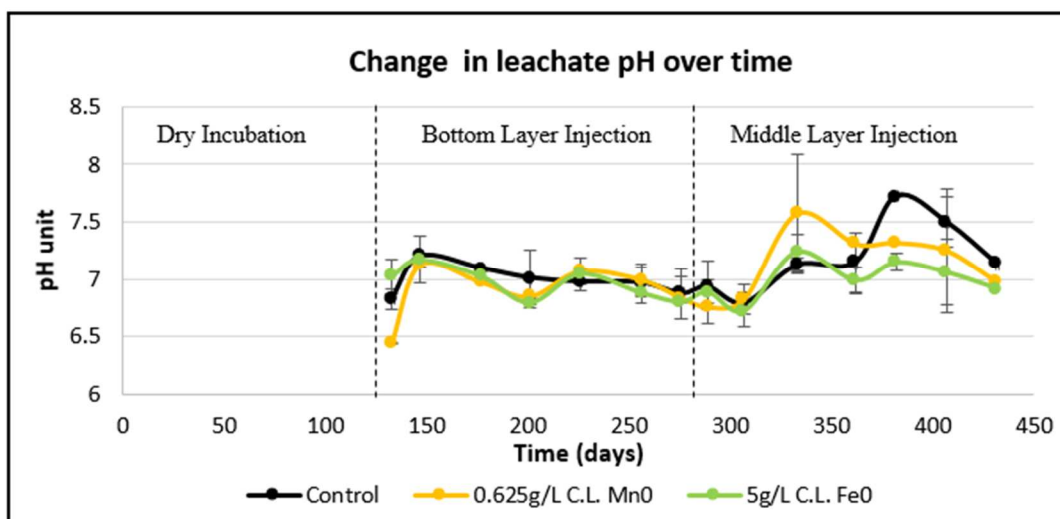
Figure 5. Change in pH over time

The pH, Temperature and Conductivity was measured as a part of quick leachate matrix during the time of sampling. The pH was measured immediately after the leachate was sampled from the reactors. Figure 5 shows the change in the pH over time. No data was available during the dry incubation as no water was introduced to the reactors at that point of time. After initial dry incubation of 125 days, anaerobic anoxic MiliQ water (18M Ω) of pH ~ 6.04 was injected to the bottom layer.

As seen from the figure 5, for reactors acting as controls the pH was 6.99 ± 0.11, whereas in case of reactors added with ZVMn, the pH was around 6.89 ± 0.06. The reactors added with ZVI observed pH around 6.96 ± 0.08. The early drop in the pH of the reactors added with ZVMn can be because of the high reactivity of the ZVMn as comparison to to ZVI. Because of the high reactivity of the ZVMn as compared to ZVI, the ZVMn tends to release more hydrogen ions which stabilizes the pH of the leachate to acidic phase. A Wilcoxon Signed Test was performed and it indicated that there is no significant difference in between the pH data for the controls and the treatments.

Again after 150 days, anaerobic anoxic MiliQ water (18M Ω) of pH ~ 6.04 was injected to the middle layer. After second injection, the pH of the reactors acting as control was about 7.14 ± 0.09. The pH of reactors added with Zero Valent Manganese and Zero Valent Iron observed pH of 7.15 ± 0.13 and 6.99 ± 0.15 respectively. Even after the second injection, the pH of the reactors added with ZVMn continues to be lower as compared to controls and ZVI added reactors. Further, Wilcoxon Signed test was performed and it indicated that there is no significant difference in between the controls and the treatments. Christensen and Kjeldsen (1989) reported that the initial transition of MSW degradation from aerobic to anerobic phase is represented by the pH levels in the range from 6.0 to 6.5 followed by anaerobic degradation phase where methanogenic bacteria start to appear slowly. As the methane gas production rate increases, the hydrogen, carbon dioxide and volatile fatty acids concentration decreases resulting in the increase in the pH. Up to 300 days, the pH of the leachate generated from the controls as well as the treatment is below 7.00 but after that there is a rise in the pH. The rise in the pH can be well supported by the fact that there may be increase in the production of the methane gas which resulted in decreasing in the

concentration of hydrogen, carbon dioxide and volatile fatty acids. This can be further validated from the methane gas measurement data and volatile fatty acids data. Christensen and Kjeldsen (1989) also reported that methane fermentation phase occurs when the pH levels are in the neutral range of 6.0 – 8.0. As the pH data displays the pH of the controls as well as the treatments are in the range of 6.0 – 8.0, the addition of the treatments has not caused any significant change in the pH due to release of hydrogen from the oxidation of ZVM as reported by Daniels et al (1987).

3.2. Temperature Measurement

Like pH, the temperature was also measured immediately after the leachate was sampled from the reactors.
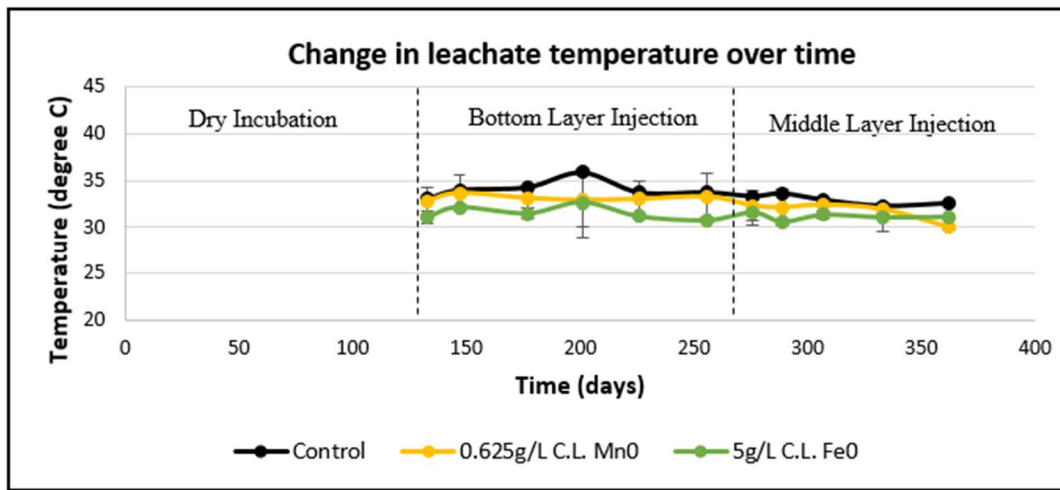
Figure 6. Temperature Data

From figure 6, it can been that the temperature of the leachate maintained in between 30 – 35°C in case of all reactors. The temperature of the leachate generated from reactors acting as controlled was observed to be $33 \pm 3°C$. The temperature of the leachate generated from reactors added with ZVMn was around $32 \pm 1°C$ whereas temperature of the leachate generated from reactors added with ZVI was around $31 \pm 0.8°C$. A Wilcoxon Signed Test

was performed and it indicated that there is no significant difference in between the temperature data for the controls and the treatments.

3.3. Conductivity Measurements

The electrical conductivity is the measure of the ability of a solution to conduct an electrical current. As the electrical current is transported by the ions, the more ions, the more is the conductivity of the solution (Metcalf and Eddy, 2003). The change in the conductivity was recorded over time and the data is presented in the figure below:
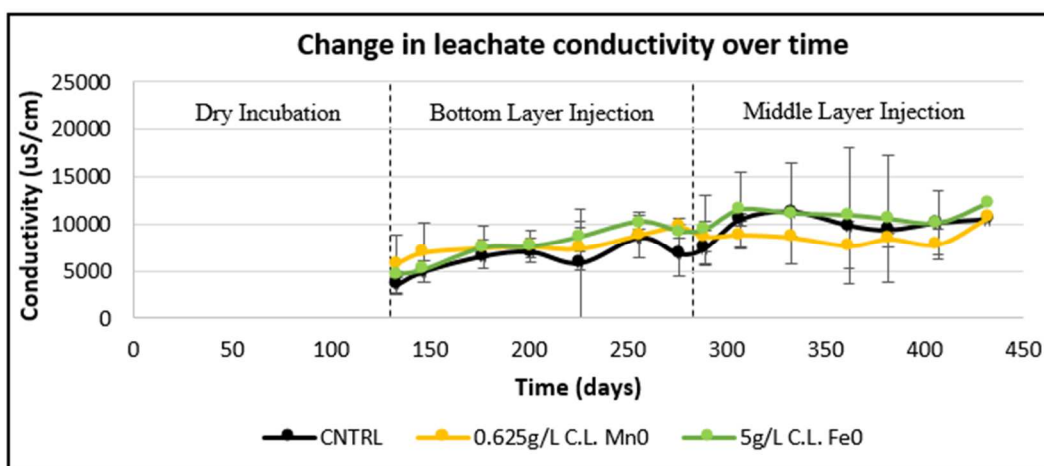

Figure 7. Change in Leachate Conductivity over time

The data suggests that initially the conductivity of the leachate from the reactors that acted as controls was 3540 µS/cm whereas the conductivity of the leachate added with ZVMn was around 5824 µS/cm and leachate added with ZVI was around 4620 µS/cm. There is a steady rise in the conductivity for controls as well as treatments as eventually the conductivity for controls and treatment reaches above 10,000 µS/cm and continues to rise further. Studies by Ziyang et al, (2009), Salem et al, (2008) and Bagchi (1990) also reported conductivity of landfill leachate in range of 480 – 72500 µS/cm. The gradual change in the conductivity values suggest the gradual increase in the soluble inorganics in the leachate. (Tatsi and Zouboulis, 2002). Conductivity is the measurement of the ability of the solution

to carry electric currents which depends on the presence of the ions. Also, total dissolved salts is a function of electric conductivity (Aziz, 2006). The rise in the conductivity over time in our study can be due to the presence of high amount of salts in the solid waste. Further, the ion chromatography analysis was performed to confirm the findings.

Wilcoxon Signed Test was performed and it showed a significant difference in between the injection of bottom layer and middle layer. Further, it indicated that there was a significance difference in between the conductivity data of the leachate generated from controls and ZVMn added reactors (μ value 3 and p value 0.01563) and controls and ZVI added reactors (μ value 0 and p value 0. 03125) for bottom layer. Similar results were also obtained for the middle layer data analysis which suggested that there is a significance difference in between the conductivity data of the leachate generated from controls and ZVMn added reactors and controls and ZVI added reactors. However linear regression analysis suggested that the rate of increase of conductivity after bottom layer injection was higher as compared to the rate of increase of conductivity after middle layer injection.

3.4. Soluble Chemical Oxygen Demand Measurements

The COD test is used to measure the oxygen equivalent of the organic material in the leachate that can be oxidized chemically using dichromate in an acid solution. (Metcalf and Eddy, 2003). sCOD analysis of the collected samples was carried out and the results are presented in the figure below:
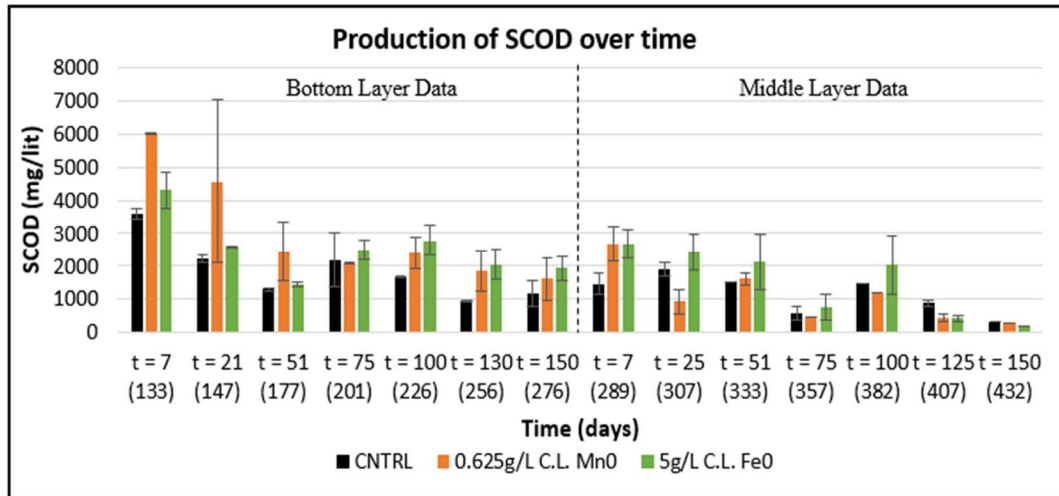
Figure 8. Production of sCOD over time

After the injection of the moisture to the bottom layer, for the controls, initial sCOD value was about 3589 mg/l just after 7 days of injection while at the end of 150 days, the sCOD value of 927 mg/lit was observed. Now, for the reactors that were aided with ZVMn, the initial sCOD values were in the range of 6012 mg/l just after 7 days of injection while at the end of the 150 days, value in range of 1608 mg/lit was observed. Similarly for the reactors that were aided with ZVI, the initial sCOD values were in the range of 4300 mg/l just after 7 days of injection while after 150 days it dropped to 1926 mg/lit.

After the moisture injection in the middle layer, reactors that acted as controls had the initial sCOD value around 1453 mg/l just after 7 days of injection, however after 150 days, it dropped to 300 mg/lit. Similar trends of drop in the sCOD values were observed in case of leachate generated from reactors added with ZVMn and ZVI after the middle layer water injection. However the rates of the removal were different across controls and treatments. Further, Wilcoxon Signed Test was performed to find out if is there any significant difference in between the data generated by two layers and the test indicated that there is significant difference in between the treatments. However there was no significant

26

difference in between control for bottom layer and middle layer. Linear regression analysis was performed on the data to determine the removal rates. It was observed that the removal efficiency was highest for the reactors added with ZVMn with removal rate of 27.112 mg/lit/day followed by controls with removal rate of 13.676 mg/lit/day. ZVI added reactors has lowest removal rate 9.747 mg/lit/day at the end of 150 days for bottom layer. However the removal rate was highest for ZVI after the injection to the middle layer. The linear regression indicated the rate of 16.955 mg/lit/day for ZVI treatment followed by rate of 12.394 mg/lit/day for ZVMn. The controls had the lowest removal rate of 8.279 mg/lit/day at the end of 150 days after injection of water to middle layer.

It was observed that after the addition of water to the bottom layer, the sCOD value was highest for ZVMn added leachate across all reactors but the removal rate was also highest in the ZVMn added leachate. After addition of water to the middle layer, slight increase was observed across all the reactors although it never reached the values as high as the values observed after the injection of the water to the bottom layer. As reported by Jiang et al (2013) as the first step of anaerobic digestion in landfills, insoluble organic polymers like carbohydrates, proteins, and fats are broken down into simple sugars, fatty acids and amino acids. The solubilization of these solid organic fraction can cause increase in sCOD values and hence we might have observed the rise in the sCOD values after the injection of moisture to the bottom and middle layer. The addition of moisture must have triggered the first step of anaerobic digestion and thus have resulted in the increase in the sCOD values. According to the studies by Kim et al (2003) and Lim et al (2008) maximum sCOD values are usually observed when the pH is in the range of 6.5 - 7.0 and even in our study the pH was observed to be around 6.5 – 7.0.

3.5. Total Carbon Measurements

The Total Carbon test was done instrumentally to determine the total carbon (organic and inorganic) present in the leachate. The test methods for TC utilizes heat and oxygen, UV radiation, chemical oxidants or some combination of these methods to convert organic carbon to carbon dioxide which is measured with an infrared analyzer (Metcalf and Eddy, 2003). The total carbon analysis of the collected samples was carried out and the results are presented in the figure below:
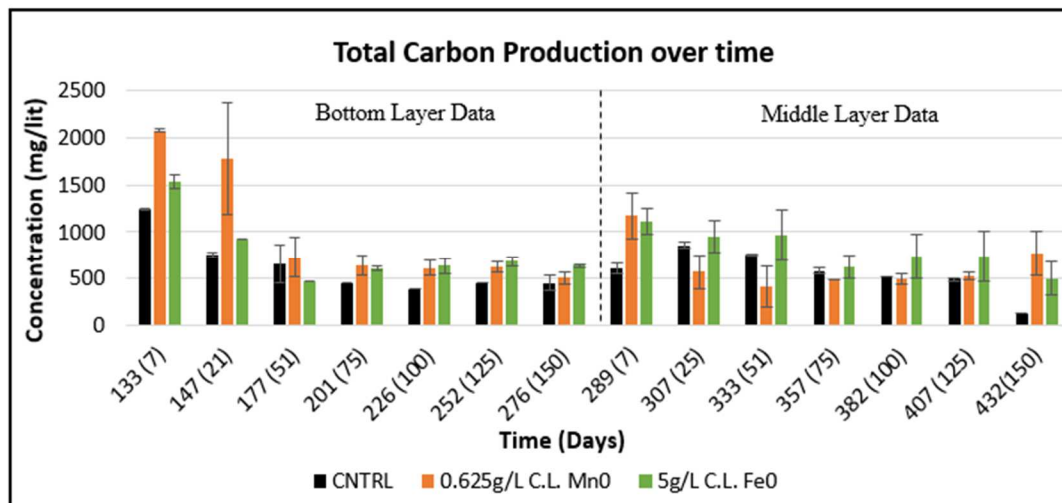

Figure 9. Change in the Total Carbon content (TC) over time

From the results of the total organic carbon analysis of the leachate tests, it was observed that the TC followed the similar trend like sCOD. After the injection of the water in the bottom layer, the maximum concentration of TC were observed across all reactors. As the time progressed, the decline in the concentration was observed at varying rate. After the injection of the water to the bottom layer, for reactors that acted as controls, the initial TC value was about 1242 mg/l just after 7 days of injection but by the end of 150 days, the TC value dropped down to 455 mg/l. Linear regression analysis was performed and it depicted a rate of 4.670 mg/lit/day. Similarly, for the reactors that were aided with ZVMn, the initial

TC value was about 2073 mg/l just after 7 days of injection and by the end of 150 days, the TOC value drops down to 505 mg/l whereas for reactors added with ZVI, the initial TC value was 1538 mg/l just after 7 days of injection but by the end of 150 days, the TC value also drops down to 635 mg/l. Similar to sCOD results, the removal rate was observed to be highest (10.389 mg/lit/day) in case of leachate generated from ZVMn added treatment followed by controls and then ZVI added treatment (4.287 mg/lit/day).

After the injection of the water to the middle layer, a slight increase in the TC concentrations across all reactors was observed. However it never reached the values as high as values obtained after bottom layer injection. ZVMn added leachate had the lowest removal rate of 1.578 mg/lit/day while the ZVI added leachate reported the highest removal rate of 3.77 mg/lit/day.

The higher removal rate of TC in controls as compared to ZVI for the bottom layer can be due to the recirculation of leachate. As reported by Warith (2002), the recirculation of the leachate has positive effect on the rate of biological degradation of MSW. The leachate circulation also enhance the rapid removal organics from the leachate. Studies by Martins et al (2012) and Taha and Ibrahim (2014) also reported that adding zero valent iron enhances the organics removal efficiency.

The difference in the removal rates clearly suggests that the treatments are effective in removal of sCOD and TC as compared to control. The high removal rate of sCOD and TC in leachate generated from ZVMn added reactors and late higher removal rate of sCOD and TC in leachate generated from ZVI can be explained by the fact of early reactivity of ZVMn as compared to ZVI. The lower values of sCOD across all reactors after the injection of water in the middle layer might be due to the attached growth of the bacteria to the MSW

in the bottom layer. As the leachate generated from the middle layer passes through the bottom layer before getting collected in the leachate collection chamber in the reactors, the microbial community attached to the MSW in the bottom layer must have converted the organic fraction present in the leachate to byproducts. Analysis of the microbial community should be conducted in order to validate this conclusion.

3.6. High Performance Liquid Chromatography Measurements

Volatile Fatty Acids (VFAs) are produced by anaerobic digestion of organic waste (Kim et al, 2006). The results obtained by the HPLC analysis showed the detection of Acetate, Butyarate, Propionate, Isovalerate and Heptanoate. .
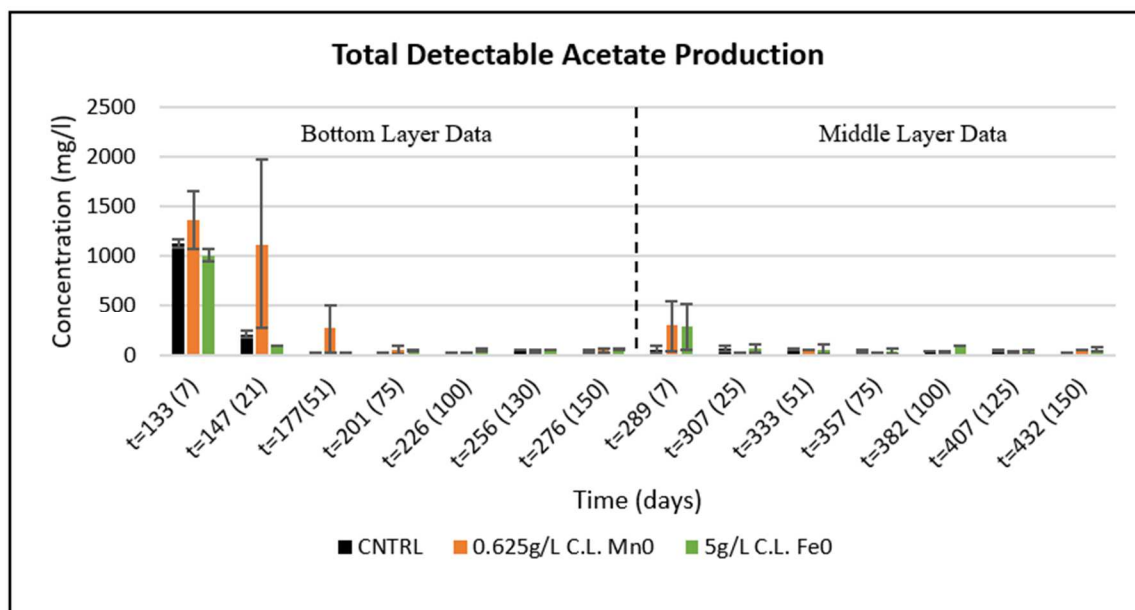

Figure 10. Change in the acetate production over time.

After the injection of water in the bottom layer, the acetate production was high across all reactors. The reactors that acted as controls had the initial concentration of 1133 mg/lit. Then by the end of 150 days, the value dropped down to 53.64 mg/l. The consumption rate of 6.780 mg/lit/day was observed for controls. The reactors that were aided with ZVMn, the initial acetate value was 1360 mg/l just after 7 days of injection but by the end of 150

days, the value dropped down to 37.50 mg/l with a consumption rate of 11.957 mg/lit/day.
A consumption rate of 5.516 mg/lit/day was observed in the reactors added with ZVI.
Again after the injection of water in the middle layer, there was again rise in the production
of acetate but not as high as the production after the injection in the bottom layer. However
a lower consumption rates than the bottom layer were observed across all reactors. Mah et
al (1978) reported that the acetate is rapidly consumed by the methanogens for the
production of the methane as acetate is the direct precursor of the methane. However the
low production of the acetate in our study can be due to the higher generation of the
methane during the same period. Coupling this acetate results with the methane generation
data can help us to validate the conclusion.

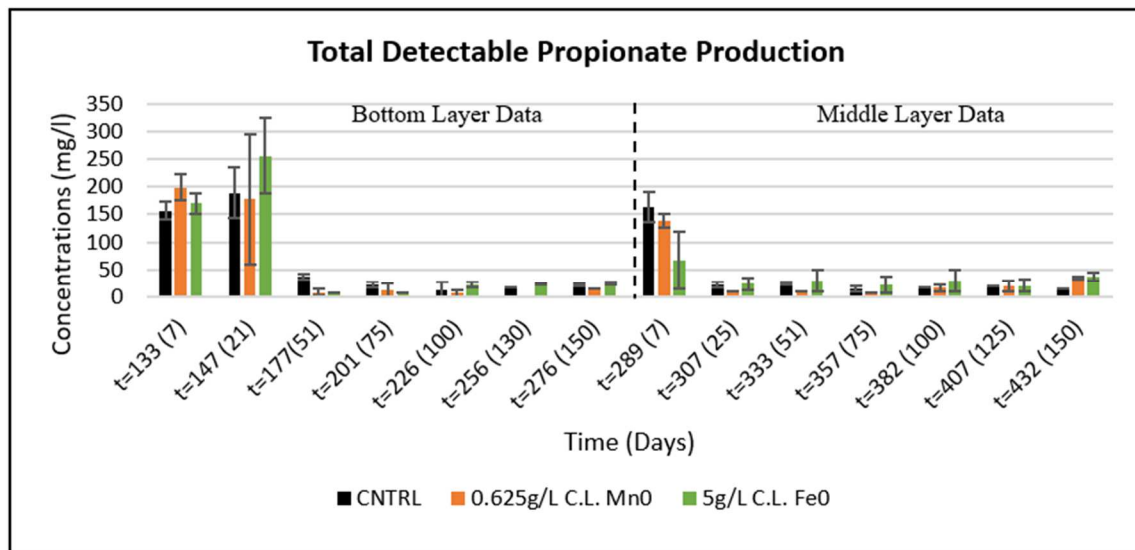Figure 11. Change in the propionate production over time.

Figure 11 shows the changes in the concentration of propionate over time. After the
injection to the water in the bottom layer and the middle layer, the consumption pattern of
propionate followed a similar pattern in consumption just like the acetate. However the
consumption rates across the layers and the treatments varied. After the injection of the

water in the bottom rate, highest production of propionate was observed across all the reactors. Reactors added with ZVMn and ZVI observed the highest consumption rate of propionate of around 1.7828 mg/lit/day followed by control with a rate of 1.4789 mg/lit/day. However, after the injection of the water in the middle layer, there was again rise in the production of propionate but not as high as the production after the injection in the bottom layer. However a lower consumption rates than the bottom layer were observed across all reactors.
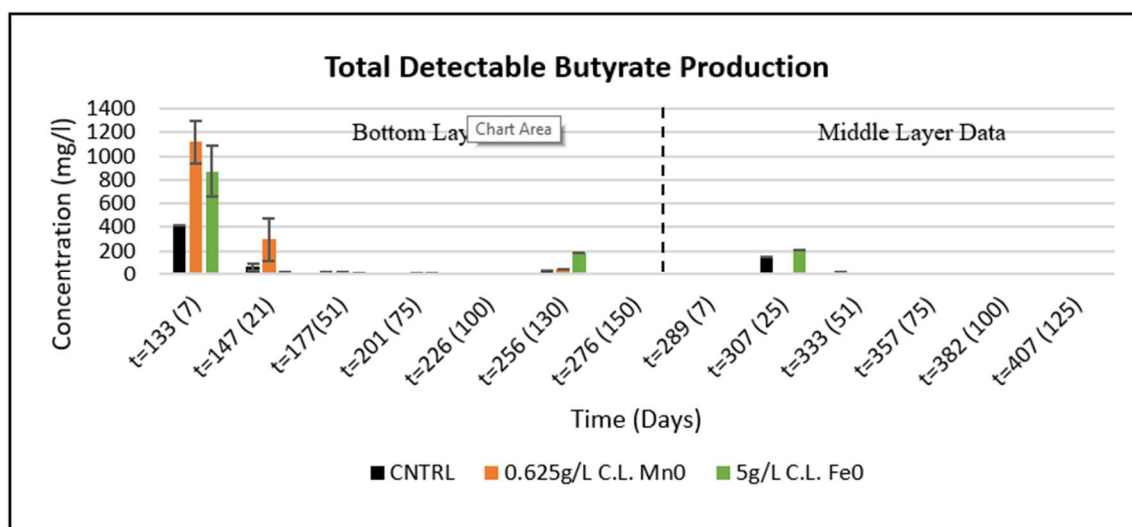

Figure 12. Change in the butyrate production over time

Figure 12 shows the changes in the concentration of butyrate over time. Butyrate was also found in the initial stage after the injection of water to the bottom layer but was rapidly consumed. In the later stage of injection, very little formation of butyrate was observed. Figure 13 shows the changes in the concentration of heptanoate over time. After the injection of the water in the middle layer, concentrations of heptanoate was detected across all reactors however after the injection of water in the middle layer, the concentrations of heptanoate was detected only in the leachate that was generated from the reactors added with ZVMn.

As from the figure 14, it can been seen that concentration of isovalerate were detected during the transition phase from bottom layer injection to middle layer injection. It's the same phase where the concentrations of heptanoate were not detected.

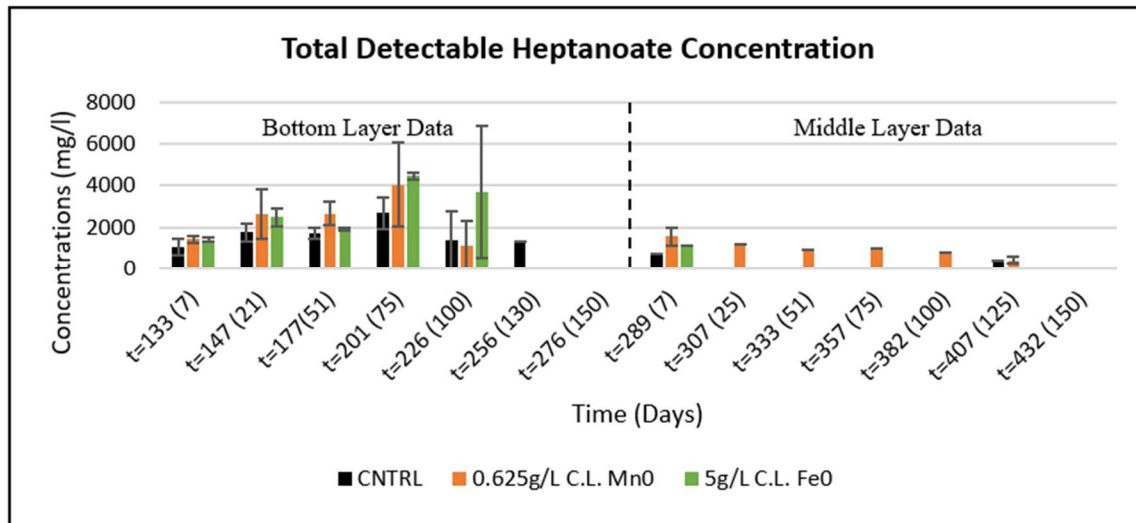Figure 13. Change in the heptonoate production over time.
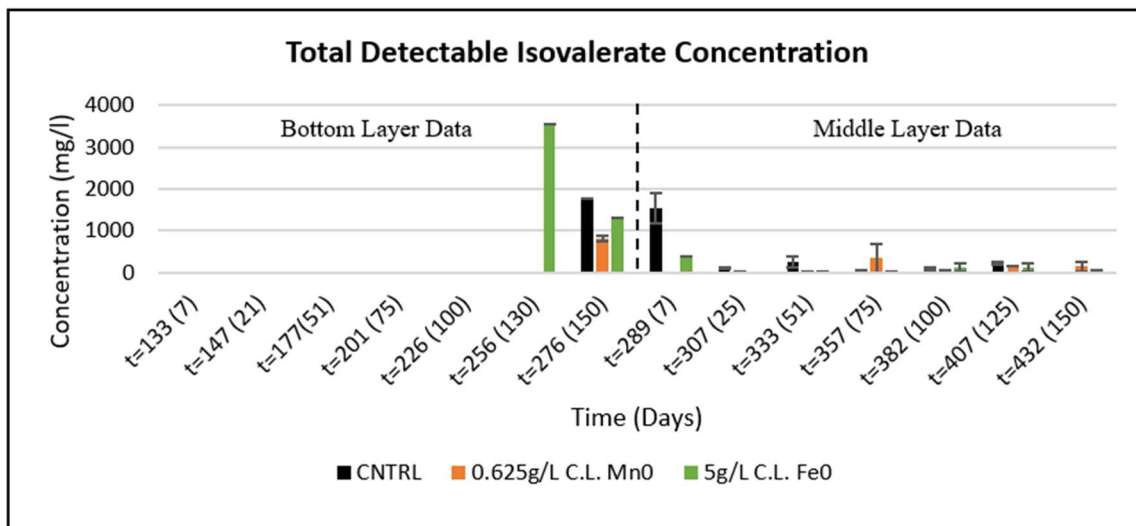

Figure 14. Change in the isovalerate production over time.

Studies by Rees et al (1980) reported that the leachate generated from the waste mainly consists of acetate. However, due to favorable environment, the other acids like propionate, butyrate, valerate which are the products of digestion of carbohydrates also start to appear.

33

Butyrate is mainly formed due to hydrolysis of lipids. Iso butyrate and iso valerate are formed due to digestion of proteins. Similarly in our study, acetate, propionate, butyrate along with isovalerate and heptanoate were detected. The degradation of organic matter in the landfill is a sequential process initiated by hydrolysis of complex organic matter in to simple carbohydrates, amino acids and fatty acids. These simple compounds provide energy for growth of fermenting bacteria producing volatile organic acids and hydrogen. These volatile acids are patially oxidized to produce additional hydrogen and acetic acid which are main substrate used by methanogens to produce methane (Tchobanoglous et al, 1993 and Cardoso et al, 2006). Column studies by Iglesias et al (1998) reported that butyrate was the most abundant while the studies by Nakakubo et al (2008) reported that acetate and propionate was abundant in their study. Studies by Bilgil et al (2012) reported that hexanoate and acetate were major components in their study. Thus, it can be concluded that the dominance of these VFAs particularly depend on the biochemical composition of the solid waste. If more carbohydrates are present in the MSW sample, more will be the production of acids like propionate, butyrate due to the digestion of carbohydrates. Similarly in our study the concentration of heptanoate and isovalerate were found to be higher in the leachate generated from the bottom layer. Although the heptanoate was not detected across controls and ZVI added leachate after the middle layer injection, but it was dominant in the leachate generated from the ZVMn added reactors. The high production of heptanoate and isovalerate might be due to presence of high amounts of protein rich compounds in the given MSW samples. Further biochemical analysis of the MSW samples should be conducted to confirm this conclusion.

However limited studies like Bilgili et al, 2011 have been confirmed and reported the occurrence of heptanoate concentration in VFA analysis. From the studies reported by (Bilgili et al (2011), it has not been observed of heptanoate exceeding the acetate concentration. Thus, it makes our study unique and perhaps difficult to set in literature due to not identification of heptanoate and isovalerate in leachate chemistry. One factor that might have hindered the detection of these particular compounds might be due to the long retention time (50 minutes for isovalerate and 140 mins for heptanoate) and thus this might have been the reason for the detection of these compounds in other studies. Further in our study, LC-MS Analysis was conducted to confirm the presence of these particular compounds, however the presence of high amount of salts in the sample hindered the detection of these compounds and thus none of these compounds were detected over the analysis.

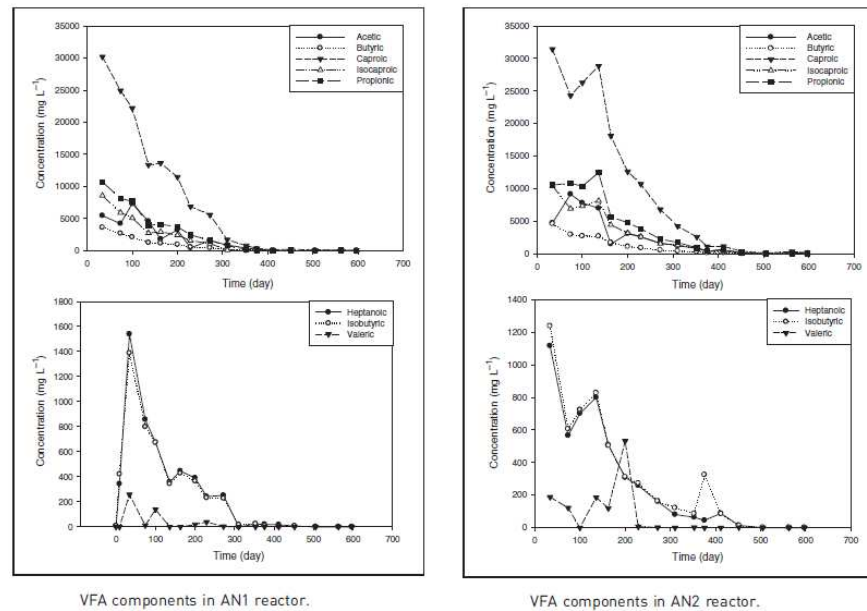VFA components in AN1 reactor.   VFA components in AN2 reactor.

Figure 15. Shows the detection of isovalerate and heptanoate in the anaerobic bioreactor with leachate circulation (AN1) and traditional landfill bioreactor (AN2)

3.7. Inorganic Analysis

The inorganics that are present in the leachate depends on the leaching of inorganics constituents present in the MSW during the stabilization process (Naveen et al, 2017). In our study samples, we found considerably high concentrations of chloride. Considerable amount of Bromide, Nitrite and Sulfate were also detected. Comparatively low concentrations of Nitrate, Fluoride and Phosphate were also detected.
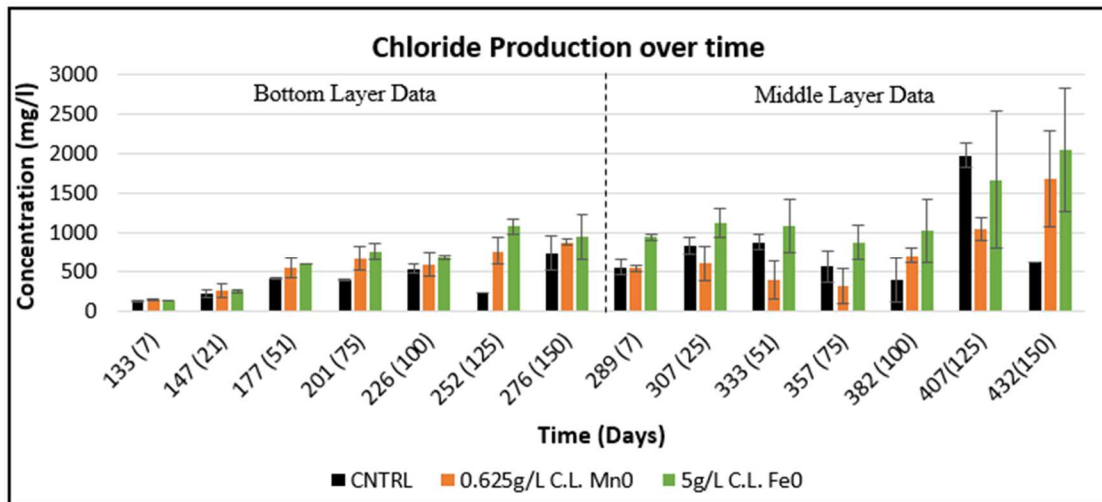

Figure 16. Change in the chloride concentration over time

After the injection in the bottom layer, reactors that acted as controls showed the initial concentration of chlorides was low across all reactors. However, the concentration of chloride continued to increase over the time of 150 days are varying rate. The rate of production of chloride was observed to be highest (6.156 mg/lit/day) in the leachate generate from ZVI added reactors followed by a rate of 4.77 mg/lit/day in the leachate generated from reactors added with ZVMn. The lowest rate of 2.93 mg/lit was observed in leachate generated from controls. After the injection in the middle layer, the controls and the ZVI added reactors showed almost similar rate in the production of chloride, however increase of approx. 2 mg/lit/day was observed in the leachate generated from the ZVMn added reactors. A Wilcoxon Signed Test further confirmed that there was significant

difference in between the chloride data for the controls and the treatments. High amount of chloride content in the leachate samples reflects the presence of significant amount of soluble salts in the MSW (Naveen et al, 2017). Studies by Andreottola and Cannas (1992), Chu et al (1994), Kjeldsen et al (2002), (Naveen et al, 2017) reported the chloride concentration in the range of 150 – 4500 mg/lit and has also reported a similar steady increase in the production which can be observed even in our study.
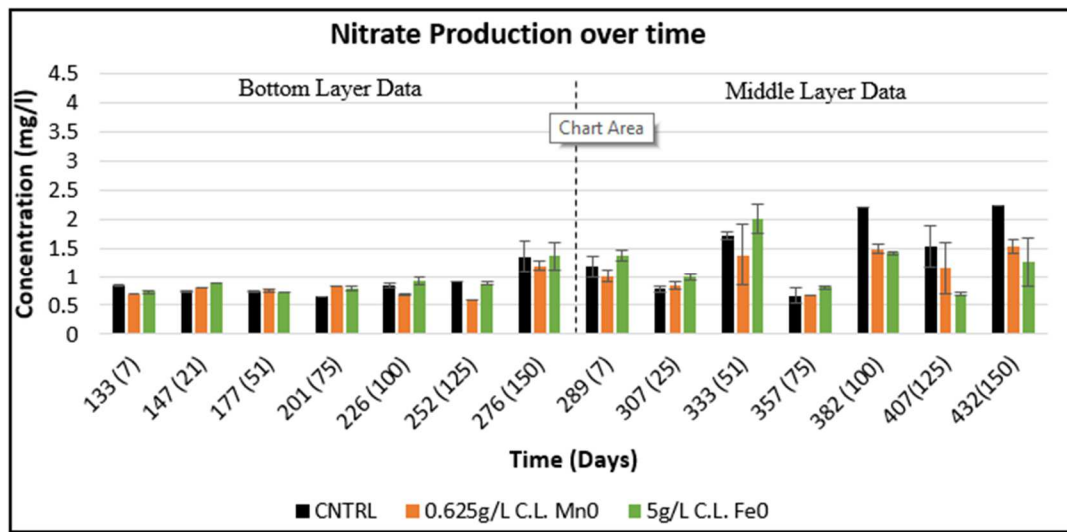

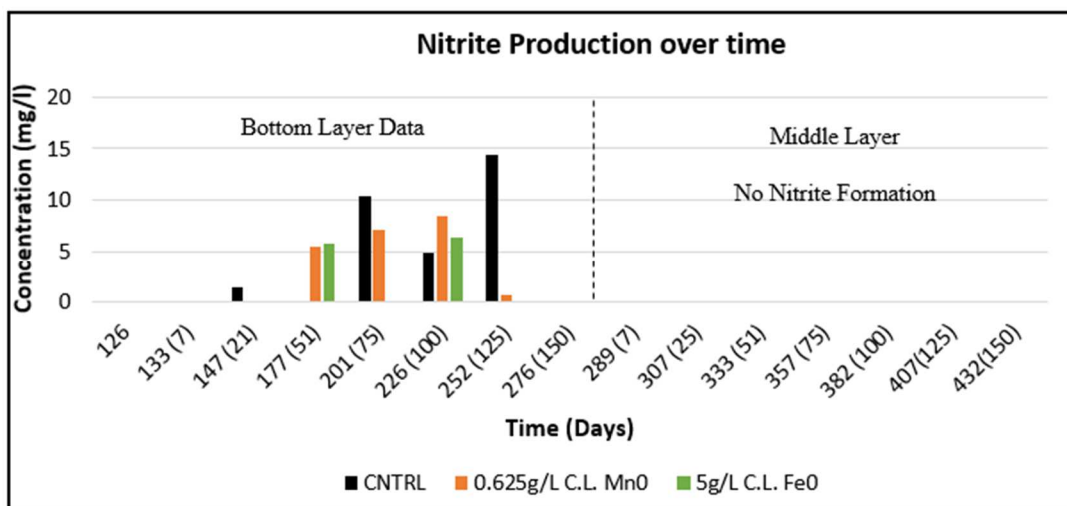Figure 17. Change in the nitrate concentration over time

Figure 18. Change in the nitrite concentration over time

Figure 17 and 18 shows the changes in the concentration of nitrate and nitrite over time respectively. Nitrates represent the most oxidized form of nitrogen. In leachate samples it is formed mostly as a result of oxidation of ammonia to nitrite and subsequently to nitrates by nitrification process (Naveen et al, 2017). After the injection in the bottom layer, both nitrates were detected in the leachate across all reactors. Nitrite was dominant in the bottom layer leachate only at particular time points. The nitrates have a steady concentration during the bottom layer phase however it starts to increase in the later middle layer phase. After the middle layer injection, the nitrates are found mostly in high concentration in controls as compared to treatments. The presence of the nitrates and absence of the nitrites might be due to the presence of the nitrifying bacteria in the system. Nitrifying bacteria convert the ammonia to nitrite and then to nitrate. Microbial community analysis of the leachate generated from the middle layer can further confirm our observations.

Figures 19 to 21 shows the changes in the concentration of bromide, phosphate and fluoride over time respectively.
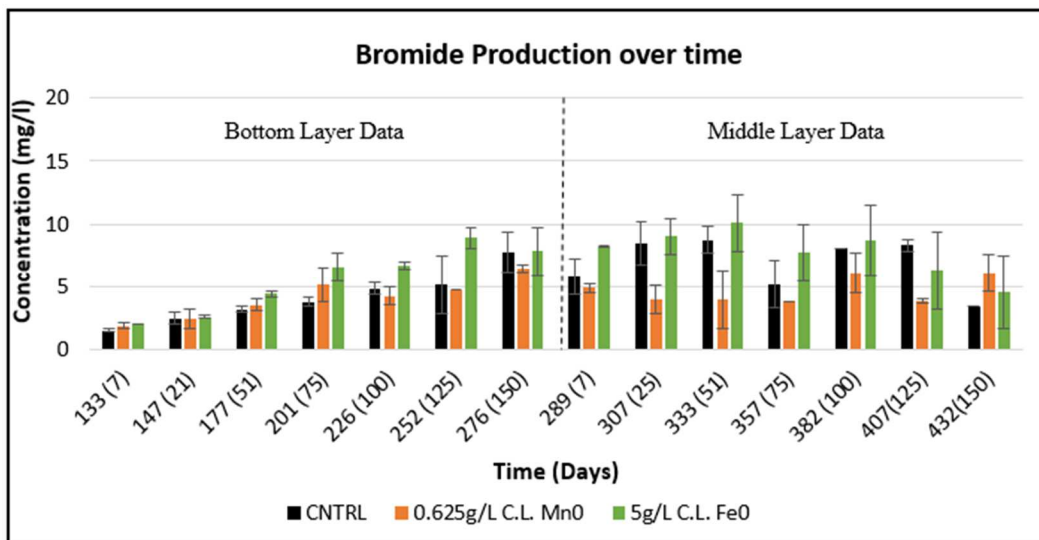

Figure 19. Change in the bromide concentration over time

The initial concentration of bromide in the leachate generated from controls was 1.15 mg/lit. Over the span of 432 days, the concentration increased to 8.08 mg/lit. In case of leachate generated from reactors aided with ZVMn, the initial concentration of bromide in the leachate generated from controls was 1.86 mg/lit. Over the span of 432 days, the concentration increased to 6.11 mg/lit. For the leachate generated from reactors aided with ZVI, the initial concentration of bromide in the leachate generated from controls was 2.06 mg/lit. Over the span of 432 days, the concentration increased to 8.67 mg/lit. The steady rise in the concentration of bromide was observed in case ZVMn added reactors. However after the middle layer injection, the concentration of the bromide in the leachate generated from the ZVMn added reactors was reported to be lowest of all.

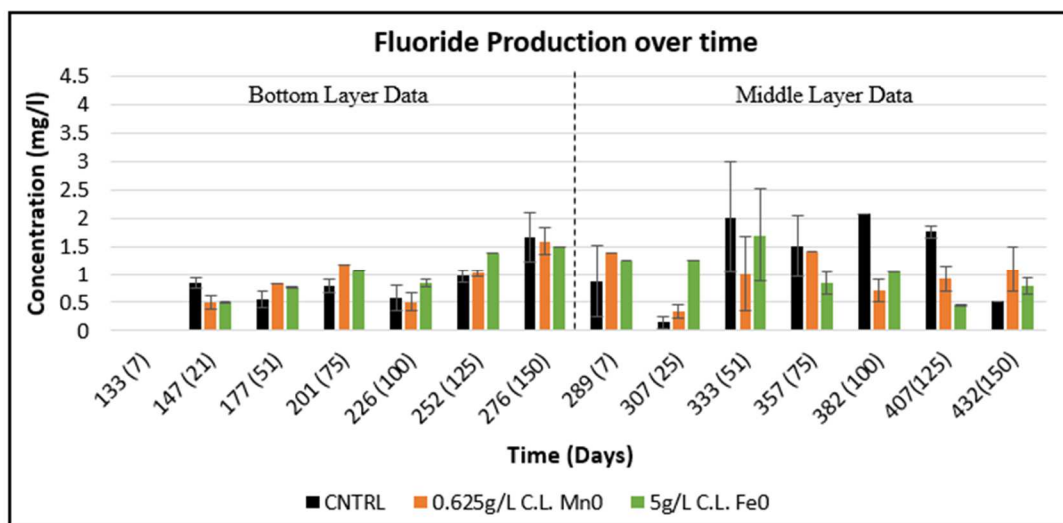Figure 20. Change in the fluoride concentration over time

After the injection of the water in the bottom layer, the concentration of the fluoride was below detection level for the first time point. Later on it started to increase steadily. Eventually it followed the same trend as of bromide except the fluoride concentration was not the least in the leachate generated from the ZVMn added reactor.
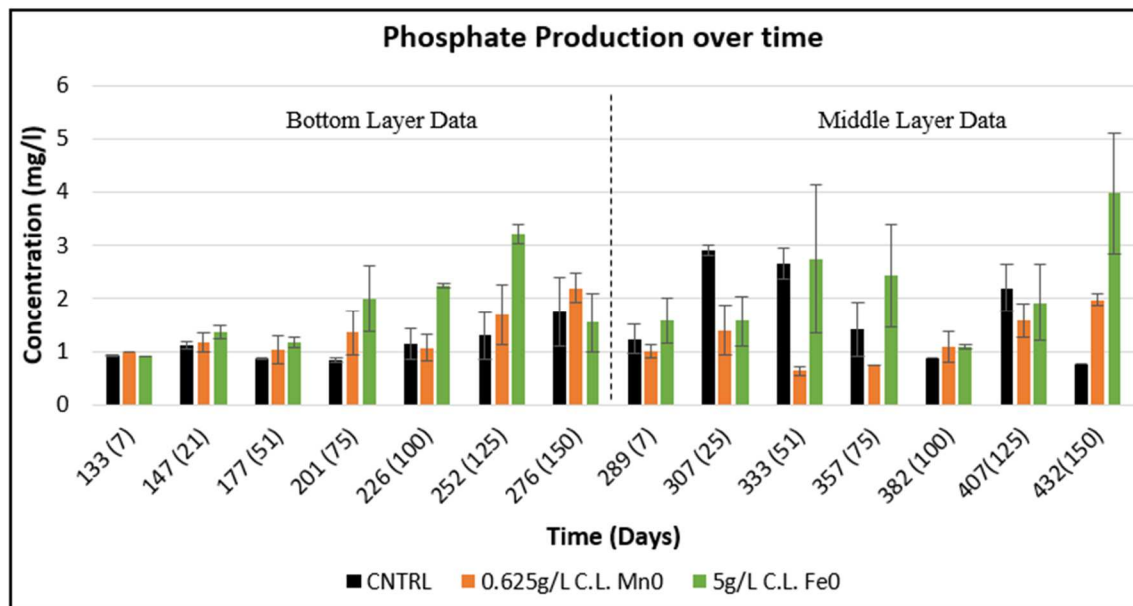
Figure 21. Change in the phosphate concentration over time

The knowledge of phosphate is important in predicting the nutrient status as these ions are important in predicting the nutrient which usually appears as a result of decomposition and mineralization of organic matter (Naveen et al, 2017). The initial concentration of phosphate in the leachate generated from controls was 0.93 mg/lit. Over the span of 432 days, the concentration fluctuated a lot and was stabilized back to 0.86 mg/lit. In case of leachate generated from reactors aided with ZVMn, the initial concentration of phosphate in the leachate generated from controls was 0.98 mg/lit. Over the span of 432 days, the fluctuated and concentration increased to 1.08 mg/lit. For the leachate generated from reactors aided with ZVI, the initial concentration of phosphate in the leachate generated from controls was 0.90 mg/lit. Over the span of 432 days, the concentration increased to 4 mg/lit.
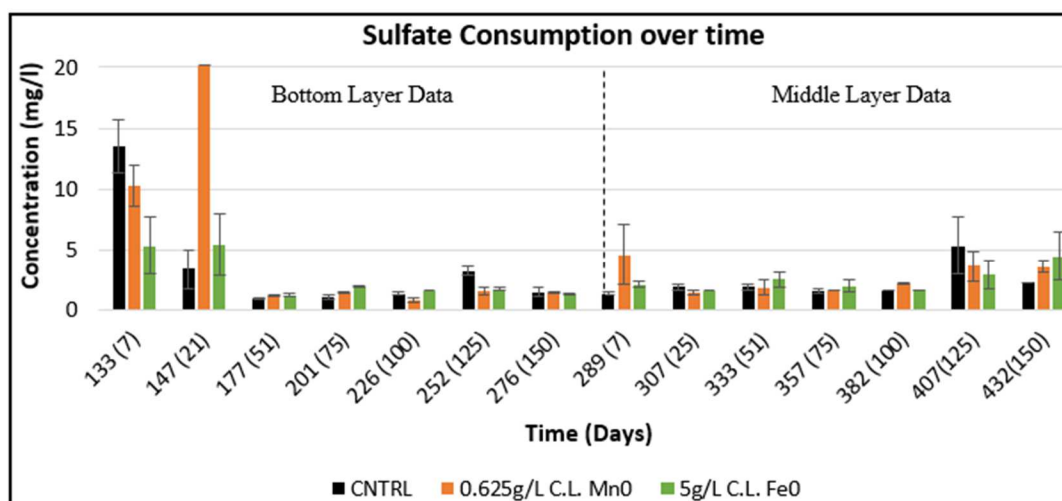
Figure 22. Change in the sulfate consumption over time

After the injection of water in the bottom layer, the sulfate production was high across all reactors. The initial concentration of sulfate in the leachate generated from controls was as high as 13.5 mg/lit whereas for leachate generated from ZVMn and ZVI added reactor was about 10 mg/lit and 5 mg/lit respectively. However over the span of 51 days it go reduced to values less than 4 mg/lit across all reactors and continued the same for next 100 days. Again after the injection of water in the middle layer, there was again rise in the production of sulfate but not as high as the production after the injection in the bottom layer. An observed decline in the sulfate concentration after the first two time points in our study does not necessarily mean that the rate of sulfate reduction has decreased. Sulfate may have been solubilized by acidic leachate and then immediately reduced to hydrogen sulfide as the Sulfate reducing bacteria have capacity to outcompete methanogenic bacteria for hydrogen generation (Robinson and Tiedje, 1984).

CHAPTER 4

CONCLUSION AND FUTURE RECOMMENDATION

4.1. Conclusion

This study was undertaken in order to review the effect of adding ZVM particles to MSW in lab scale anaerobic bioreactors. For this purpose MSW sample was collected from the working phase of the two different landfills (Salt River Landfill and SouthWest Regional Landfill) and set up in eight different bioreactors, two of which had added ZVI, two of which had added ZVMn and two acted as controls (without addition of treatments). After the dry incubation (no addition of water) of 130 days, the reactors were added with 5 g/lit concentration of ZVI and 0.625 g/lit concentration of ZVMn. The leachate generated from the respective reactors was sampled after every 7, 25, 51, 75, 100, 125 and 150 days. Similarly after 150 days all the leachate that was generated from the bottom layer was taken out and the same procedure was repeated for the middle layer. The leachate generated from the middle layer was allowed to pass through the bottom layer and was then sampled for after 7, 25, 51, 75, 100, 125 and 150 days. The leachate samples that were collected were analyzed for physical parameters like pH, temperature and conductivity. Later the samples were stored and further analyzed for biochemical parameters like sCOD, TC, HPLC and IC Analysis for anions measurement. As a part of post lab analysis, statistical data analysis was conducted over the data using the R – Statistical Analysis tool. Wilcoxon Signed Test to identify if is there any significant data across the treatments and controls and later Linear Regression Analysis was performed to determine the rate of change over time.

It was concluded based on the statistical analysis that the addition of the treatments don't have any significant difference in the pH and temperature of the leachate generated from

these reactors. However the conductivity data suggested the steady rise in the conductivity across all reactors over the period of time. Further, the statistical analysis confirmed that there is significant difference in between the treatments and the controls across the layer. It was observed that the removal efficiency of sCOD was highest for the reactors added with ZVMn with removal rate of 27.112 mg/lit/day followed by controls with removal rate of 13.676 mg/lit/day. ZVI added reactors has lowest removal rate 9.747 mg/lit/day at the end of 150 days for bottom layer. However the removal rate was highest for ZVI after the injection to the middle layer. The linear regression indicated the rate of 16.955 mg/lit/day for ZVI treatment followed by rate of 12.394 mg/lit/day for ZVMn. The controls had the lowest removal rate of 8.279 mg/lit/day at the end of 150 days after injection of water to middle layer. Similar trends in the results was observed in TC analysis. In both the analysis, a slight increase in the sCOD and TC concentrations across all reactors was observed after the water injection in the middle layer. However it never reached the values as high as values obtained after bottom layer injection.

HPLC study indicated the dominance of the concentration of heptanoate and isovalerate were leachate generated from the bottom layer across all reactors. Although the heptanoate was not detected across controls and ZVI added leachate after the middle layer injection, but it was dominant in the leachate generated from the ZVMn added reactors. The high production of heptanoate and isovalerate might be due to presence of ZVMn in the given MSW samples. From the studies reported by (Bilgili et al (2011), it has not been observed of heptanoate exceeding the acetate concentration. Thus, this made our study unique and perhaps difficult to set in literature due to not identification of heptanoate and isovalerate in leachate chemistry. IC analysis concluded the chloride ion was dominant in the leachate

generated from all the reactors and there is a steady increase in the chloride content over the period of time. Nitrates and Nitrites data indicated that after the injection in the bottom layer, both nitrates were detected in the leachate across all reactors. Nitrite was dominant in the bottom layer leachate only at particular time points. The nitrates have a steady concentration during the bottom layer phase however it starts to increase in the later middle layer phase. After the middle layer injection, the nitrates are found mostly in high concentration in controls as compared to treatments. The presence of the nitrates and absence of the nitrites might be due to the presence of the nitrifying bacteria in the system. Bromide, Fluoride and Phosphate data showed a similar trend of increase in the content over the period of time. A rapid decline in the sulfate data after the first 2 time points suggested the sulfate reduction had occurred after the injection of water in the bottom layer. In conclusion, the results in this work show that the addition of ZVM has positive effects in removal of organics from the leachate based on the differences in the removal rates as compared to controls. At the same time, treatments don't have any negative impacts on the other physical parameters like pH and temperature of the leachate. Introduction of ZVMn results in the formation of the highest concentrations of the heptanoate and isovalerate in the leachate. However further analysis should be conducted to confirm the presence of the same compounds by other analysis apart from HPLC. Also studies regarding the biochemical properties of the MSW samples should be conducted to determine the presence of protein rich matter in the samples. Finally linking this study with the gas generation data can help us to dive deep in to the insight of the other processes that are occurring in the reactors after the addition of treatments.

4.2 Future Recommendation

On the basis of the results obtained, some recommendations for future studies are as follows:

- Test the effects of adding different concentrations and varying mesh sizes of ZVM on MSW degradation in anaerobic bioreactors could be studied.

- Test the effect of ZVM on the microbial community present in the landfill could be studied separately, by culturing the microbial communities usually present during the different phases of anaerobic degradation of MSW, on artificial substrates.

- Develop a cost analysis of treating the leachate aided with ZVM could be carried out to economically justify the use of ZVM in enhancing the methane production as well as treating the leachate generated from it.

- Test and effect addition ZVI to different categories of waste with varying moisture content and varying degradation stage can be studied.

REFERENCES

1. U.S. Environmental Protection Agency (EPA) (2019) Advancing Sustainable Materials Management: 2015 Fact Sheet.

2. Reda T, Plugge C M, Abram N J, Hirst J, "Reversible Inter conversion of Carbon dioxide and formate by an electroactive enzyme", Proc Natl Acad Sci, 2008.

3. Facchin V, Cavinato C, Pavan P, Bolzonella D, "Batch and contimuous mesophilic anaerobic digestion of food waste: effect of trace elements supplementation", Chem Engg, 2013, page 32.

4. Rajeshwari K, Balakrishnan M, Kansal A, Lata K, Kishore V, "State of the art of anaerobic digestion technology for industrial wastewater treatment", Renewable Sustainable Enenrgy, Reviews, 2000, page 135 – 56.

5. Chunlan Mao, Youngzhong Feng, Xiaojiao Wang, Guangxin Ren, "Review on research achievements of biogas from anaerobic digestion", Renewable Sustainable Energy Reviews, 2015, page 540 – 555.

6. Sun Y, Li J, Huang T, Guan X, "The influence of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero valent iron: A review, Water Resource, 2016, page 277 – 295

7. Yuhoon Hwang, Periyasamy Sivagurunathan, Mo-Kwon Lee, Yeo – Myeong Yun, Young – Chae Song, Dong Hoon Kim, "Enhanced hydrogen fermentation by zero valent iron addition", International Journal of Hydrogen Energy, 2018

8. O'Carroll, D Sleep, B Krol, M Boparai, H Kocur, "Nano Scale zero valent iron and bimetallic particles for contaminated site remediation, Water Resource, 2018, Pg 104 – 122

9. Zhen G, Xuegin Lu, Yu You Li, Yuan Liu, Youcia Zhao, "Influence of zero valent scrap iron supply on methane production from waste activated sludge" Chemical Engineering Journal, 2015, Pages – 461 – 470

10. Feng, Y., Zhang, Y., Quan, X., Chen, S., "Enhanced anaerobic digestion of waste activated sludge digestion by addition of zero valent iron", Water Resource, 2014 Page 242 – 250

11. Puyol, D., Flores-Alsina, X., Segura, Y., Molina, R., Padrino, B., Fierro, J.L.G., Martinez, F., "Exploring the effects of ZVI addition on resource recovery in the anaerobic digestion process", Chemical Engineering, 2018 Page 703 – 711

12. Souichiro Kato, Isao Yumoto, Yoichi Kamagata, "Isolation of Acetogenic Bacteria that induce Biocorrosion by utilizing metallic iron as a sole electron donor", Appl. Environ. Microbiol. Dec 2014, 81 (1) 67-73

13. S. Zahedi, R. Solera, F. Micolucci, C. Cavinato, D. Bolzonella, "Changes in microbial community during hydrogen and methane production in two-stage thermophilic anaerobic co-digestion process from KIM

14. ", Waste Management, 2016 Pg 40- 46

15. Rui Zhao, Tao Huang and Michael McGuire, "From a Literature Review to an Alternative Treatment System for Landfill Gas and Leachate", 2012, Challenges, Page 278-289.

16. Shuokr Qarani Aziz, Amin Mojiri, "Control and treatment of landfill leachate for sanitary waste disposal", (2015), Reseach Gate Net Publication, DOI: 10.4018/978-1-4666-9619.

17. Peter Kjeldsen,I, Morton A. Barlaz, Alix P. Rooker, Anders Baun, Anna Ledin, and Thomas H. Christensen (2002), "Present and Long-Term Composition of MSW Landfill Leachate: A Review", Critical Reviews in Environmental Science and Technology, 32(4) Page 297-336.

18. Christensen, T. H., & Kjeldsen, P. "Landfill Emissions and Environmental Impact: An Introduction." In Proceedings of Sardinia 95 - Fifth International Landfill Symposium, 1995 (Vol. 3, pp. 3-12)

19. Hector Alvarez – Vazquez, Bruce Jefferson and Simon J Judd, "Membrane Bioreactor vs Conventional biological treatment of landfill leachate: a brief review", Journal of Chemical Technology and Biotechnology, 2004, Pg 1043 – 1049

20. O'Carroll, D Sleep, B Krol, M Boparai, H Kocur, "Nano Scale zero valent iron and bimetallic particles for contaminated site remediation, Water Resource, 2018, Pg 104 – 122

21. Zhen G, Xuegin Lu, Yu You Li, Yuan Liu, Youcia Zhao, "Influence of zero valent scrap iron supply on methane production from waste activated sludge" Chemical Engineering Journal, 2015, Pages – 461 – 470

22. Feng, Y., Zhang, Y., Quan, X., Chen, S., "Enhanced anaerobic digestion of waste activated sludge digestion by addition of zero valent iron", Water Resource, 2014 Page 242 – 250

23. Christensen TH, Kjeldsen, P., "Basic biochemical processes in landfills, sanitary landfilling: process, technology and environmental impact, editors Toronto Academic Press, 1989

24. Murphy RJ, Jones DE, Stessel RI., "Relationship of microbial mass and activity in biodegradation of solid waste, Waste Management and Research, 1995, 13, page 485 – 497.

25. Robinson JA and Tiedje JM, "Competition in between sulfate reducing and methanogenic bacteria for hydrogen under resting and growing conditions", Arch. Microbial, 1984, 127, page 26 – 32

26. Pacey John, "The bioreactor landfill – an innovation in solid waste management", Seminar report, 1999.

27. Reinhart DR and Townsend TG, "Landfill Bioreactor Design and Operations, Lewis Publishers, Boca Raton, Florida, 1998.

28. Metcalf and Eddy, Inc, "Wastewater Engineering", McGraw Hill Companies, New York, 2003.

29. Mao Chunlan, Feng Yongzhong, Wang Xiaojiao, Ren Guangxin, "Review on research achievements of biogas from anaerobic digestion", Renewable and Sustainable Energy Reviews, 2015, Vol 45, Page 450 – 555.

30. Weiland P., "Biogas production: Current state and perspectives", Applied Microbiology and Biotechnology, 2010, Vol 85(4), Page 849 – 860.

31. Daniels L, Belay N, Rajagopal BS and Weimer PJ, "Bacterial methanogenesis and growth from CO_2 with elemental iron as the sole source of electrons", Science, 1987, Vol 237, Page 509 – 511.

32. Ziyang L, Zhao Y, Yuan T, Song Y, Chen H, Zhu N, Huan R, "Natural attenuation and characterization of contaminants composition in the landfill leachate under disposing ages", Science of the Total Environment, 2009, Vol 407 (10), Page 3385 – 3391.

33. Salem Z, Hanouri K, Djemaa R, Allia K, "Evaluation of Landfill Leachate pollution and treatment, Desalination, 2008, Vol 220 (1 - 3), Page 108 – 114.

34. Bagchi A, "Design, Construction and Monitoring of Sanitary Landfill, John Wiley and Sons Inc, New Jearsey, 1 edition, 1990.

35. Tatsi A A and Zouboulis A I, "A field investigation of the quantity and quality of leachate from the municipal solid waste landfill in a Mediterranean climate

(Thessaloniki, Greece)", Advances in Environmental Research, 2002, Vol 6 (3), Page 207 – 219.

36. Jiang J, Zhang Y, Li K, Wang Q, Gong C, Li M, "Volatile fatty acids production from food waste: effects of pH, temperature and organic loading rate", Biosource Technology, 2013, Vol 143, Page 525 – 530.

37. Martin M, Fajardo C, Ortiz LT, Rodriguez-Membibre ML, Nande M, Lobo MC, "Assessing the impact of zero valent iron (ZVI) nanotechnology on soil microbial structure and functionality: A molecular approach", Chemosphere, 2012, Vol 86 (8), Page 802 – 808.

38. Taha MR, Ibrahim AH, "Characterization of nano zero valent iron (nZVI) and its application in sono-Fenton process to remove COD in palm oil mill eluent", Journal of Environmental Chemical Engineering, 2014, Vol 2 (1), Page 1 – 8.

39. Mah Robert A and Michael R Smith, "Growth and Methanogenesis by *Methanosarcina* Strain 227 on Acetate and Methanol", Applied and Environmental Microbiology, 1978, Vol 36 (6), Page 870 – 879.

40. Andreottola, G., and Cannas, P., "Chemical and biological characteristics of landfill leachate in Landfilling of waste" Christensen, T.H., Cossu, R., and Stegmann, R., Eds., Elsevier Applied Science, London, UK, 1992, 65.

41. Chu, L.M., Cheung, K.C., and Wong, M.H., "Variations in the chemical-properties of landfill leachate", Environ. Management, 1994, Vol 18, Page 105.

42. Bilgili MS, Demir A, Varank G, "Effect of leachate recirculation and aeration on volatile fatty acid concentrations in aerobic and anaerobic landfill leachate", Waste Management and Research, 2012, Vol 30 (2), Page 161 – 170.

43. Kim M, Gomec, Ahn CY, Speece RE, "Hydrolysis and acidogenesis of particulate organic material in thermophilic anaerobic digestion", Environ Technol, 2003, Vol 24 (9), Page 1183 – 1190.

44. Kim HJ, Kim SH, Choi Y J, Kim GD, "Effect of enzymatic pretreatment on acid fermentation of food waste", Journal of Chemical and Biotechnology, 2011, Vol 81, Page 974 – 980.

45. Lim SJ, Kim BJ, Jeong CM, Choi JDR, "Anaerobic organic production of food waste in once a day feeding and drawing off bioreactor", Bioresource Technology, 2008, Vol 99 (16), Page 7866 – 7874.

46. Cardoso AJ, Levine AD, Nayak BS, Harwood VJ and Rhea LR, "Lysimeter comparison of the role of waste characteristics in the formation of mineral deposits

in leachate drainage systems", Waste Management & Research, Vol 24, Page 560–572.

47. Iglesias JR, Castrillon L, Maranon E and Sastre H, "Solid-state anaerobic digestion of unsorted municipal solid waste in a pilot-plant scale digester." Bioresource Technology, 1998, Vol 63, Page 29–35.

48. Nakakubo R, Moller HB, Nielsen AM and Matsuda J, "Ammonia inhibition of methanogenesis and identification of process indicators during anaerobic digestion", Environmental Engineering Science, 2008, Vol 25, Page 1487–1496.

49. Rees JF, "The fate of carbon compounds in the landfill disposal of organic matter", Journal of Chemical Technology, 1980, Vol 30, Page 161–175.