PERFORMANCE OF LANDFILLS WITH COAL COMBUSTION BYPRODUCTS AGGREGATES AS AN ALTERNATIVE REACTIVE DAILY COVER

By

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ABSTRACT

A landfill is an engineered facility for the disposal of wastes. It is designed and operated to minimize public health and environmental impacts. However, land availability is the limiting factor for the operation and development of landfills. Landfill daily cover is a standard practice where inorganic soil is placed over the waste to: keep waste from blowing away; minimize disease vectors; restrict access to rodents, birds, and insects, to control leachate and erosion, reduce fire hazard potential and noxious odors, and provide an aesthetic appearance.

The use of alternative materials for daily covers could conserve landfill space and soil resources while also meeting environmental and operational requirements. Energy wastes, such as coal combustion byproducts aggregates (CCAs), can meet dual purposes simultaneously. They can achieve resource recovery and reclamation as a reactive daily cover (ADC) by being reutilized in landfills as a key design and operating component for daily cover. The CCAs are an agglomerate of fly ash and bottom ash that are produced during the coal combustion process. The purpose of this research was to evaluate the potential of the CCAs as ADC materials to achieve resource recovery, enhance biological decomposition, and induce early settlement of landfills.

Biochemical decomposition and settlement were simulated using physical landfill models (PLMs) in an environmental chamber (one PLM used sandy soil as a daily cover, whereas another PLM used CCAs). The environmental chamber was equipped with a thermal circulator to support the rate of waste decomposition in lab-scale PLMs. The PLMs were equipped with gas extraction ports, water spraying systems on the top, and leachate drain ports on the bottom. Settlement was monitored through a side-wall window on the PLMs. Synthetic solid wastes were formulated in accordance to the average characteristics of Puerto Rican solid wastes. Rate of leachate production through the CCAs cover, as a measure of hydraulic performance, was quantified by comparing infiltration rates through the soil cover under identical hydrological conditions. Leachate volume and the concentrations

of organic and inorganic substances in leachate were monitored and compared between the CCAs PLM and control PLM.

Results showed that physical conditions in the control and CCAs PLMs produced similar hydraulic characteristics (leachate quantity) are attributed to similar void fractions controlling the flow through the sand and CCA. The concentrations of organic and inorganic components were found reduced more in the CCA PLM than in the control PLM. Higher microbial activity resulting from more optimal pH conditions for methanogens and higher contribution of nutrients for microbial growth. Higher active biodecomposition of solid waste is also supported by higher settlement and biogas production in the CCAs PLM, compared to the control PLM.

To understand potential influence of the CCAs packing density on leachate characteristics, three smaller physical landfill models (SPLMs) were constructed. One had the same packing density of the CCAs PLM, another had the same packing density of the control PLM, and the other had a higher packing density than the CCAs PLM (1.23). Results of this study indicated that packing density of the CCA did not significantly alter the production of leachate substances. The concentrations of organic and the inorganic compounds were reduced and the production of biogas increased regardless of the packing density validating the results of the CCA PLM.

An important aspect in the use of CCAs as an ADC is the possibility of using it as a reactive daily cover for heavy metals removal. Removal of heavy metals by CCAs was confirmed in SPLM tests. Quantification of the CCA's point of zero charge, which was found at 8.7 ± 0.2, suggests that removal is mainly caused by precipitation processes, not by adsorption.

Microbial activity enhancement due to CCAs was confirmed with a separate experiment where four order of magnitude greater colony forming unit (CFU) was observed from the system having CCAs than the control system without them (30~150 x 10^{10} CFU/100 mL vs. 140 x 10^6 CFU/100 mL). Therefore, the greater microbial populations, activity, and enhanced biological waste decomposition are expected to occur in landfills with CCAs as daily cover, as was observed in the CCAs PLM. This also provides extra space for more wastes to be disposed of in the landfill and leads to significant conservation of natural soils which otherwise would have been excavated for use as daily cover.

RESUMEN

Un vertedero es una estructura ingenieril construida para la eliminación de desperdicios sólidos, es diseñado y operado para minimizar el impacto a la salud pública así como al ambiente. Sin embargo, la disponibilidad de terrenos es el factor limitante para el funcionamiento y desarrollo de los vertederos. En un vertedero el uso de una cubierta diaria es una práctica estándar que utiliza típicamente suelo inorgánico para mantener los residuos lejos del viento, minimizar la proliferación de enfermedades, restringir el acceso a roedores, pájaros e insectos, controlar los lixiviados y la erosión, reducir el potencial de riesgo de incendio, reducir los olores nocivos, y proporcionar un aspecto estético.

El uso de materiales alternativos para cubierta diaria podría conservar el espacio en un vertedero y los recursos del suelo, y al mismo tiempo cumplir con los requisitos ambientales y operacionales. Desperdicios de la producción energía, tales como los subproductos agregados de la combustión de carbón (CCAs) pueden cumplir una doble función: lograr la recuperación de recursos y la reutilización de estos como una cubierta diaria alternativa (ADC), convirtiéndose en un elemento clave para el diseño y el funcionamiento para la cubierta diaria del vertedero. Los CCAs son un aglomerado de las cenizas livianas y pesadas que se producen durante el proceso de combustión de carbón. El propósito de esta investigación fue evaluar el potencial de los CCAs como materiales para ADC y lograr la recuperación de recursos, mejorar la descomposición biológica e inducir el asentamiento temprano en un vertedero.

La descomposición bioquímica y el asentamiento fueron simulados utilizando modelos físicos de vertederos (PLMs) en una cámara ambiental (un PLM es utilizado como control usando suelo inorgánico mientras que el otro PLM usaba CCAs). Una cámara ambiental fue equipada con un sistema de recirculación térmica como soporte para la velocidad de descomposición de los desperdicios sólidos. Los PLMs estaban equipados en la parte superior con puertos de extracción de gas y un sistema de aspersión de agua, mientras que en la parte inferior poseen un orificio de drenaje para lixiviados. El asentamiento fue

monitoreado a través de una ventana transparente en la pared lateral de los PLMs. Los desperdicios sólidos sintéticos que fueron utilizados corresponden a la composición de los desperdicios sólidos en Puerto Rico. La tasa de producción de lixiviado a través de la cubierta de CCAs, fue utilizada como una medida del desempeño hidráulico y fue cuantificada mediante la comparación de las tasas de infiltración a través de la cobertura diaria utilizando suelo inorgánico bajo condiciones hidrológicas idénticas. El volumen del lixiviado y las concentraciones de componentes orgánicos e inorgánicos en el agua infiltrada fueron medidos y comparados entre el PLM con CCAs y el PLM control.

Los resultados muestran que las condiciones físicas en los PLMs control y el de CCA producen características hidráulicas muy similares (cantidad de lixiviados), esto es atribuido a las fracciones de vacíos que controlan el flujo a través del suelo y de los agregados. Reducción en las concentraciones de componentes orgánicos e inorgánicos. Mayor actividad microbiana resultante de las condiciones de pH optimas para los metanógenos y una mayor aportación de nutrientes para en crecimiento de la actividad microbiana. Una mayor y activa biodescomposición de los residuos sólidos es sustentado por el aumento de los asentamientos y la producción de biogas en el PLM de CCA en comparación con el de control.

Para entender la potencial influencia de la densidad de empaque de los CCAs sobre las características de los lixiviados, tres pequeños modelos físicos de vertederos (SPLMs) fueron construidos. Uno tenía la misma densidad de empaque del PLM con CCAs, otro tenía la densidad de empaque que corresponde al PLM de control y el último poseía una mayor densidad de empaque del PLM con CCAs (1.23). Los resultados de este estudio indican que la densidad de empaque no altera significativamente la producción de sustancias en el lixiviado. Las concentraciones de los compuestos orgánicos e inorgánicos fueron reducidas y se incrementó la producción de biogas, independientemente de la densidad de empaque validando los resultados del PLM con CCA.

Un aspecto importante en el uso del CCAs como una ADC es la posibilidad de utilizarlo como una cubierta diaria reactiva para la eliminación de metales pesados. La remoción de metales pesados por los CCA fue confirmada en experimentos con los SPLMs. La cuantificación del punto cero de carga fue encontrada en 8.7 ± 0.2, sugiriendo que la remoción es principalmente causada por procesos de precipitación y no de adsorción.

El mejoramiento de la actividad microbiana, debido a la presencia de los CCAs fue confirmada con un experimento separado, donde se observó un cuarto orden de magnitud mayor en las unidades de colonias formadas (CFU), en el sistema con CCAs fueron mayor que el sistema de control sin CCAs (30~150 x 10^{10} CFU/100 mL vs. 140 x 10^{6} CFU/100 mL). Por lo tanto, las mayores poblaciones microbianas y la mayor actividad, corroboran el mejoramiento biológico en la descomposición de los residuos y se espera que ocurra en los vertederos, como se observó en el PLM con CCAs. Esto también podrá proporcionar espacio adicional para que más desperdicios sólidos puedan ser dispuestos en el vertedero y conduce a la conservación de suelos naturales que de otro modo habrían tenido que ser excavados.

To God, my eternal company

To Paula and Sara, the motor of my life

To Boris, for his love and unconditional support

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ADC	Alternative Daily Cover.
ARDC	Alternative Reactive Daily Cover.
BOD	Biochemical Oxygen Demand.
CCAs	Coal Combustion Byproducts Aggregate.
CFU	Colony Forming Unit.
COD	Chemical Oxygen Demand.
DP	Dry Period.
DP2	Dry Period 2.
DP3	Dry Period 3.
DP4	Dry Period 4.
FTIR	Fourier Transform Infrared Spectroscopy.
MP	Moderate Period.
MP2	Moderate Period 2.
MP3	Moderate Period 3.
PLMs	Physical Landfill Models.
PZC	Point of Zero Charge.
RP	Recirculation Period.
RP2	Recirculation Period 2.
RP3	Recirculation Period 3.
RP4	Recirculation Period 4.
SEM	Scanning Electron Microscope.
SPLMs	Smaller Physical Landfill Models.
TDS	Total Dissolved Solid.
THB	Total Heterotrophic Bacteria.
WP	Wet Period.
XRD	X-ray Diffraction.

1. INTRODUCTION

In the United States, 229.2 million tons (MT) of municipal solid wastes were generated in the year 2001, of which 55.7% were placed in landfills (US-EPA, 2003). This represents an average of 0.804 MT/per capita. In comparison, in Puerto Rico, 3.6 million tons of municipal solid wastes were generated for the year 2003, of which 75% were disposed of in landfills (Soto, 2004) and which represent an average of 0.789 MT/per capita. Recently, the US Environmental Protection Agency (US EPA) issued orders to close landfills in Toa Baja, Aguadilla, Santa Isabel, Florida, and Vega Baja within three years (US-EPA, 2006).

A landfill is an engineered facility for the disposal of solid waste materials to minimize the environmental and public health impacts that can be resulted from them, if not managed appropriately. Putting a soil daily cover on the top of a day's deposition of wastes is a standard practice in landfill operations. The cover is used to keep waste from blowing away, minimize disease vectors, restrict access to rodents, birds, and insects, minimize water infiltration, control leachate and erosion, reduce fire hazard, minimize wind-blown litter, reduce noxious odors, provide an aesthetic appearance, allow accessibility regardless of weather, and provide additional overburden pressure (Tchobanoglous and Kreith, 2002).

The use of alternative materials instead of soil for daily cover has drawn significant interest in the operation of a landfill (DeMello, 1990; Hurst et al., 2005; Myers, 2007; Safari and Bidhendi, 2007). Alternative materials for daily cover could conserve landfill space and soil resources while meeting environmental and operational requirements. Alternative materials may include: municipal waste compost (Hurst et al., 2005), composting yard waste (Haaren, 2010), lime (Safari and Bidhendi, 2007), and other materials. This research aims to evaluate performance of landfill with coal combustion byproducts aggregates (CCAs) as an alternative reactive daily cover (ARDC). The CCAs to be tested are manufactured aggregates which are solidified agglomerates of fly and bottom ashes produced during the coal combustion process for electricity production at the AES Puerto Rico in Guayama, PR.

1.1 BACKGROUND

Landfills are very complex systems where various biogeochemical interactive processes occur simultaneously. The most common issues related with landfills are the physical stability of the landfill (i.e., settlement) and the control of the gases and leachate from biochemical decomposition of the wastes (Durmusoglu et al., 2005). These physical and biochemical phenomena are highly intermingled together. For instance, gas generation, as results of biochemical waste decomposition changes the fill pressures in landfills and causes physical settlements. Biochemical waste decomposition accounts for a large part of the total landfill settlement (Durmusoglu et al., 2005). Since the organics deposited in landfills are decomposed as a result of various stages of microbial activities, the landfills undergo a time-dependent settlement (Durmusoglu et al., 2005).

The general practice is to add the six inches of inorganic soil as a daily cover on 2-ft of compacted waste cells; therefore daily covers take approximately 20% of total landfill volume initially. However, it is decreased to about 5% due to the compression under self-weight and the absorptive migration into the waste void fractions (Tchobanoglous and Kreith, 2002). Because of the cost to place six or more inches of soil each day as a daily cover and the values of air space that it consumes, many landfill sites are using alternative daily covers. The savings in soil hauling costs and, especially, the value of air space, are very significant. The short term costs savings involved in switching to a fiber-based daily cover were immediate, it was reported that the long term costs savings involved with extending the site were immense (Griffin, 2003).

Energy wastes (e.g., CCAs) can meet dual purposes simultaneously. They can achieve resource recovery and reclamation as an ARDC by being reutilized in landfills as a key design and operating component. CCAs have characteristics of sandy gravel (Kochyil and Little, 2004). They can be used effectively and economically as an ARDC, giving higher overburden pressure, and exerting greater overall settlement which would save the fill space (Ling et al., 1998). In addition, CCAs will produce smaller post-closure settlements which can lead to the development of sport fields, golf courses, parking lots, and wildlife and environmental conservation areas (O'Leary and Walsh, 2003).

Biochemically, CCAs have advantages over conventional soil covers. They may enhance sequestration of heavy metals by precipitation or adsorption (Erol et al., 2005), and reduce of nitrogen, phosphorus, organic dyes, and chemical oxygen demand (COD) by adsorption (Chaudhuri and Sur, 2000). It has alkaline characteristics so as to buffer the pH reduction by acidogenesis phase, therefore a higher growth rate of methanogens at neutral pH producing more methane (CH_4) gas (i.e., acceleration of biostabilization processes) (Park and Lee, 2005).

1.1 JUSTIFICATION

Currently, one of the major environmental problems is associated with the generation and subsequent disposal of solid wastes. The main way of disposal of the solid wastes is using a landfill. However, land availability for landfills has been the limiting factor for the operation and development of landfills. This is especially true for Puerto Rico of which most landfills are subject to closure in 3-5 years (Juan, 2006).

An important environmental contribution in this research is resource recovery in conjunction to waste management. Coal combustion byproducts are materials produced when coals are burn to produce electricity. These materials can be comprised of fly ash, flue gas desulfurization materials, bottom ash, boiler slag, and other power plant byproducts. This research presents for the first time, an innovative aspect of the utilization of CCAs as ARDC, the subsequent environmental benefits. These benefits include resource recovery and natural resources conservation because the need to extract and transport virgin soils is eliminated.

The CCAs can be used effectively as an alternative daily landfill cover, it gives higher overburden pressure, therefore exerting greater overall settlement which would save the landfill volume available and facilitate post-closure development (Ling et al., 1998). This would produce a smaller post-closure settlement and facilitated subsequent use of the landfill after post-closure (O'Leary and Walsh, 2003).

1.2 HYPOTHESIS DEVELOPMENT

Based on the literature review and the CCA characteristics, it was hypothesized that CCAs as an ARDC would:

- Reduce the concentrations of organic and inorganic compounds in leachate;
- Enhance the rate of waste decomposition;
- Expedite the settlement process increasing the useful life of landfills; and
- Provide temporal biochemical characteristics of leachate that serve as an indicator of biological waste decomposition in landfills leading to the physical settlement of them.

1.3 OBJECTIVES

The primary goal of this research was to develop and evaluate performance of landfills with CCAs as an ARDC material. Particularly, this research aimed to address the:

1. Applicability of CCAs as ARDC materials replacing soil excavation and transportation which often degrade environmental quality;
2. Extent and rate of biological decomposition and settlement of landfills with CCAs as ARDC materials; and
3. Performance of landfill with the CCAs cover in comparison with the inorganic soil daily cover.

To meet these objectives and to assess the established hypothesis, several major tasks were followed. These include:

- Design, construct, and develop lab-scale, physical landfill models (PLMs) equipped with leachate collection systems on the bottom, gas collection systems on the top, and a settlement monitoring window on the side wall;
- Produce artificial solid wastes which resemble the characteristics of the real solid wastes produced in Puerto Rico;
- Determine the effects of hydrologic cycles on the behavior of landfill biochemistry;
- Compare biochemical characteristics of leachate from PLMs to establish relationships between biological decompositions of solid wastes and subsequent physical settlement;
- Assess the feasibility to use the PLMs as landfills bioreactors which are expected to enhance overall performance of PLMs;
- Evaluate CCAs application and landfill compaction modes to achieve better performance of PLMs when used as ARDC materials;
- Determine if the presence of CCAs helps to increase microbial activity (biomass); and
- Calculate the point of zero charge to suggest the mechanisms the heavy metals removal and to improve its understanding.

1.4 SCOPE OF EXPERIMENTAL WORK

This research was conducted to develop a reliable and alternative reactive daily cover (ARDC) that would reduce associated landfill costs and conserve natural soil environments. Hydraulic and biochemical properties of aggregates as an ARDC were compared with those of a conventional inorganic soil daily cover. Biochemical decomposition and settlement were simulated using the PLMs in a temperature-controlled environmental chamber. The PLMs contained solid wastes representing Puerto Rico's typical waste characteristics. One PLM used inorganic sand as daily cover, whereas the other PLM used CCAs as an ARDC. Different stages of hydrologic events and leachate recirculation were simulated. Leachate quantity and quality, extent of settlement, and gas production trends were analyzed to correlate biological decompositions and settlement in the CCAs-amended PLM and control PLM. For the comparison of the results from the main PLMs, smaller-scale PLMs were run under different CCAs application and landfill compaction modes.

Results of this study indicated that the use of CCAs as an ARDC instead of soil could enhance landfill operations and environmental control. The CCAs would be easily applied, saving landfill capacity, decreasing soil requirements, augmenting leachate control. Batch experiments were conducted to assess the point of zero charge characteristics of the CCAs and its influence in heavy metal removal. Another experiment was carried out to check the microbial activity improvement in the presence of the CCAs.

1.5 RESEARCH SIGNIFICANCE

The purpose of this research was to evaluate the potential of the CCAs as ARDC materials enhancing biological decomposition and subsequently inducing early settlement of landfills. Hence, CCAs would physically conserve landfill space by providing greater overburden pressure landfill closure and facilitate post-closure management due to smaller post-closure settlement. In addition, the resource recovery CCAs can be used effectively and economically as an ARDC for landfills because they can conserve natural resources and, as a result, the need to extract virgin materials is eliminated.

The CCAs have neither been studied nor used in landfills despite their properties to be used as a daily covers. Therefore, the use of CCAs will be opening an area not explored so far in implementing this technology in landfill engineering. Due to the expected physical, chemical and biochemical benefits of CCAs, there would be a decrease in leachate components concentration and an increment on the waste decomposition rate; therefore increasing landfill space and soil resources, and facilitating post-closure management. Thus, success of this research would increase the life of landfills as a broad benefit to the societies which rely on landfills as the ultimate solid wastes disposal method.

1.6 THESIS ORGANIZATION

This dissertation consists of several integral parts, including: the importance of daily cover in landfill, the relevance and environmental application of CCAs, the design and development of experimental systems and methodology to evaluate PLMs, laboratory experiments for biological and chemical analyses of leachate and the performance results of landfills with CCAs as an ARDC.

These are addressed in the different chapters. Chapter 1 is the introductory part of the dissertation and is composed of the justification, hypothesis, and objectives established in the research and the scope of work. Chapter 2 describes the background information on the daily cover in the landfill, use of CCAs and its environmental applications, landfills bioreactor with leachate recirculation, physical and biological parameters, and inorganic and organic constituents in a landfill, microbial activities and heavy metals removal. Chapter 3 describes the materials and methods that were used for the experimental work, as well as the methodology applied to determine the performance of CCAs as an ARDC. Chapter 4 to 7, contain the description of the PLMs experiment, smaller physical landfill models (SPLMs), removal of the heavy metals, point of zero charge, and microbial activities. Chapter 8 discusses the conclusions and recommendations for the application of the CCA as an ARDC. Chapter 9 contains the references used in this dissertation and Appendixes provides details of the results obtained from this research.

2. LITERATURE REVIEW

This chapter presents the state of the art knowledge on landfills, daily covers, coal combustion byproducts and their applications in environmental engineering, bioreactor landfill with leachate recirculation, microbial activities, and heavy metals removal. The reviewed information and the characteristics of CCAs were the driving force of the current research on the performance of landfills with CCAs as an ARDC.

2.1 LANDFILLS

Landfilling is a controlled method of waste disposal. The landfill cover is the most important consideration in the design of a modern municipal solid waste landfill because it encapsulates the wastes, insolates them from the surrounding environment, prevents leachate escape, limits rainfall infiltration, and affects gas generation (Quian et al., 2002). The main components of landfills are: the liner system (separates solid waste and subsequent leachate from groundwater), leachate collection and removal system (collects water that has percolated through the landfill and contains contaminating substances), gas collection and control systems (collects methane gas), daily covers and final cover system (seals the top of the landfill) (Quian et al., 2002). Below are presented the functions of each of these components (Figure 1):

- *Liner system:* A liner consists of multiple barrier and drainage layers, but the barrier may consist of a compacted clay layer, geomembrane, geosysnthectic clay layer, and/or a combination of these. This system is placed on the bottom and lateral sides of a landfill. The liner system has the purpose to isolating the solid waste and preventing contamination of the surrounding soil and groundwater; it also acts as a barrier against the advective (hydraulic) and diffusive transport of leachate (Quian et al., 2002).
- *Leachate collection and removal system:* Leachate is generated from liquid squeezed out of the waste itself and by water that infiltrates into the landfill and that percolates through the waste. It consists of carrier liquid and dissolved substances. A leachate

collection and removal system is used to collect the leachate produced in a landfill, prevent the buildup of leachate head on the liner, and drain leachate (Quian et al., 2002).

- *Gas collection and control system:* The solid waste can generate large quantities of gas during the decomposition. The two primary gaseous constituents in a landfill are methane (CH_4) and carbon dioxide (CO_2). The gas collection and control system is used to collect the landfill gases during decomposition of the organic components of the solid waste (Quian et al., 2002).
- *Daily cover:* The placement of a daily cover of inorganic soil is a standard practice in landfill operation. This cover is placed over waste fill to keep waste from blowing away, restrict access to rodent, birds and insects, and provide additional overburden pressure (Quian et al., 2002).
- *Final cover system:* The main purpose of a landfill final cover is to minimize water infiltration into the landfill to reduce the amount of leachate generated after closure. The final cap or cover system consists of barrier and drainage layers (Quian et al., 2002).

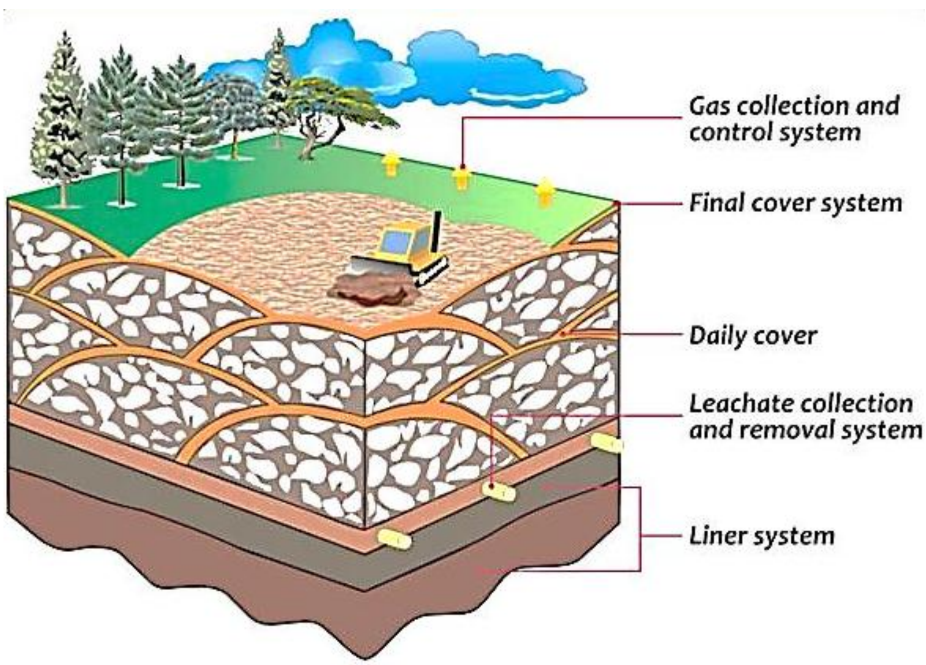

Figure 1 Hypothetical Cross Section of a Landfill (Bluewater, 2011).

2.1.1 *Processes in a Landfill*

Solid wastes placed in a landfill are subject to a number of simultaneous and interrelated biological, chemical, and physical changes. The most important biological reactions occurring in landfills are those related to the conversion of the organic material in solid waste, leading to the evolution of landfill gases and, eventually, leachate (Durmusoglu et al., 2005). Chemical reactions that occur within the landfill include dissolution, biological conversion products in the liquid percolating through the waste, evaporation, volatilization of chemical compounds and vaporization of water into the evolving landfill gas, sorption of volatile and semivolatile organic compounds into the landfilled material, dehalogenation and decomposition of organic compounds, and oxidation-reduction reactions affecting metals and the solubility of metal salts. Furthermore, the more important physical changes in landfills is the settlement caused by consolidation and decomposition of landfilled material (Tchobanoglous and Kreith, 2002).

2.1.2 *Landfill Gases*

The principal gases that can be produced in landfills include ammonia, carbon dioxide, methane, nitrogen and oxygen (Warith, 2003). These gases are produced from the decomposition of the organic fraction of municipal solid waste: methane and carbon dioxide are considered the main landfill gases (Warith, 2003). The generation of landfill gases is thought to occur in five phases, as illustrated in Figure 2. Each of these phases are described below (Tchobanoglous and Kreith, 2002):

- *Phase I (Initial Adjustment):* This phase is the initial adjustment phase; the organic biodegradable components of the solid waste begin to undergo bacterial decomposition. Biological decomposition occurs under aerobic conditions because a certain amount of air is trapped within the landfill.

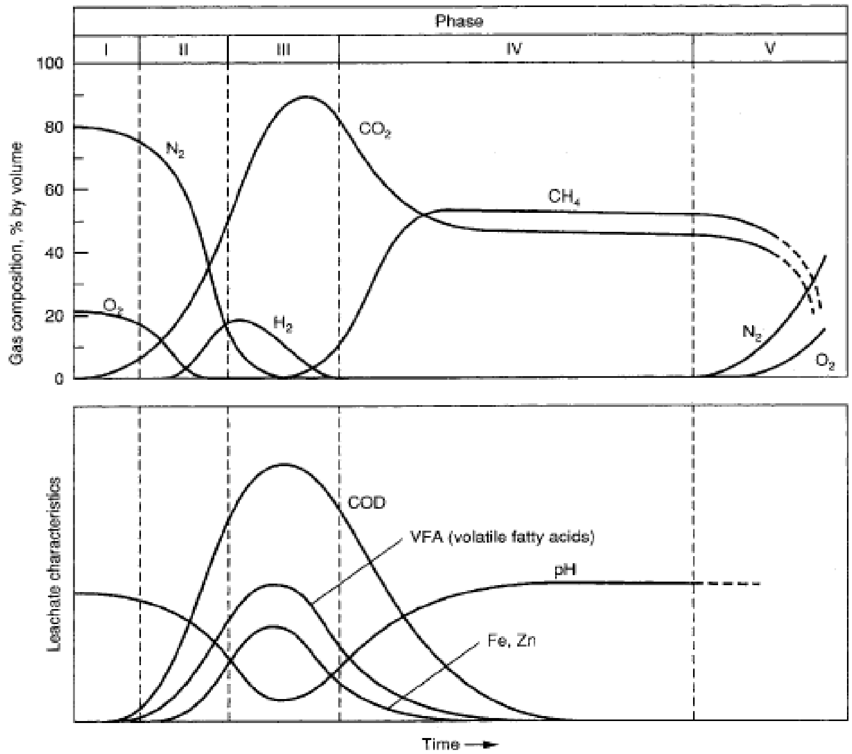

Figure 2 Generalized Phases in the Generation of Landfill Gases (I – Initial Adjustment Phase, II – Transition Phase, III – Acid Phase, IV – Methane Fermentation, and V – Maturation Phase) ((Tchobanoglous and Kreith, 2002))

- *Phase II (Transition Phase):* In the transition phase, oxygen is depleted and anaerobic conditions begin to develop. The conditions in the landfill becomes anaerobic, nitrate and sulfate, which can serve as electron acceptors in biological conversion reactions, and are often reduced to nitrogen gas and hydrogen sulfide. Measurements of oxidation/reduction potential indicate that under anaerobic conditions, the reduction of nitrate and sulfate occur at about −50 to −100 mV and the production of methane occurs in the range from −150 to −300 mV. As the oxidation/reduction potential decreases, microorganisms responsible for the conversion of the organic material in solid waste to methane and carbon dioxide begin a process in which the complex organic material is converted to organic acids and other intermediate products. In this phase, the pH of the leachate starts to drop due to the presence of organic acids and the effect of the elevated concentrations of carbon dioxide (Figure 2). The carbon dioxide forms carbonic acid when dissolved in water, because it dissociates into H^+ ions and bicarbonate ions therefore the pH is decrease.

- *Phase III (Acid Phase):* The bacterial activity initiated in phase II is accelerated with the production of significant amounts of organic acids and lesser amounts of hydrogen gas. The first step in the process involves the enzyme mediated transformation (hydrolysis) of higher molecular mass compounds (e.g., lipids, organic polymers, and proteins) into compounds suitable for use by microorganisms as a source of energy and cell carbon. Then begins a new step in the process (acidogenesis) that involves the bacterial conversion of the compounds resulting from the first step into lower molecular weight intermediate compounds as typified by acetic acid and small concentrations of fulvic and other more complex organic acids. Carbon dioxide is the principal gas generated during this phase and smaller amounts of hydrogen gas are also produced. The microorganisms (acidogens or acid formers) involved in this conversion, are described collectively as nonmethanogenic, consist of facultative and obligate anaerobic bacteria. Because of the acids produced during phase III, the pH of the liquids held within the landfill drops to a value of 5 or lower because of the presence of the organic acids and the effect of the elevated concentrations of carbon dioxide. The biochemical oxygen demand (BOD_5), the chemical oxygen demand (COD), and the conductivity of the leachate will increase significantly during this phase due to the dissolution of the organic acids in the leachate. Many essential nutrients are removed in the leachate in phase III and if the leachate is not recycled, the essential nutrients will be lost from the system. It is important to note that if leachate is not formed, the conversion products produced during phase III will remain within the landfill as absorbed constituents and in the water held by the waste as defined by the field capacity.
- *Phase IV (Methane Fermentation Phase):* In this phase, a second group of microorganisms, which converts the acetic acid and hydrogen gas formed in the acid phase to methane and carbon dioxide, becomes more predominant. In some cases, these organisms begin to develop toward the end of phase III. The bacteria responsible for this conversion are strictly anaerobes and are called methanogenic. In this phase, both methane and acid fermentation proceed simultaneously, although the

rate of acid fermentation is considerably reduced. The pH of the leachate, if formed, rise, and the concentration of BOD_5 and COD and the conductivity value of the leachate reduced.

- *Phase V (Maturation Phase):* As the moisture continues to migrate through the waste; portions of the biodegradable material that were previously unavailable will be converted. The rate of landfill gas generation diminishes significantly in phase V because most of the available nutrients have been removed with the leachate during the previous phases and the substrates that remain in the landfill are slowly biodegradable. The principal landfill gases evolved in phase V are methane and carbon dioxide while the leachate often contains higher concentrations of humic and fulvic acids, which are difficult to process further biologically.

The duration of the phases in the production of landfill gases vary depending on the distribution of the organic components in a landfill, the availability of nutrients, the moisture content of waste, moisture routing through the waste material, and the degree of initial compaction (Tchobanoglous and Kreith, 2002). There are several factors that influence the rate of landfill gas generation. These parameters include (Warith, 2003):

- *Moisture content:* This parameter provides the environment necessary for gas production and serves as a medium for transporting nutrients and bacteria throughout the landfill, therefore, is considered the most important parameter in solid waste decomposition and gas production. Landfill gas is produced at all landfills because the substance moisture level required by methanogenic bacteria is very low and occurs even in dry landfills. In a landfill, the field capacity is the amount of liquid that a given mass of material will absorb prior to downward percolation of that liquid due to gravitational forces. Gas production is increased as moisture content is increased up to field capacity because nutrients, alkalinity, pH, and bacteria are not transferred within the landfill. When the moisture content in the waste exceeds the field capacity, the moving liquid carry nutrients and bacteria to other areas within the landfill, creating an environment favorable to increase gas production.

- *Nutrient content:* Nutrients are necessary for the microorganisms that participate in anaerobic degradation of solid waste and for their growth. These nutrients include carbon, hydrogen, oxygen, nitrogen, phosphorus, sodium, potassium, calcium, magnesium and other trace materials. The presence of the toxic materials such as heavy metals can slow the bacterial growth and delay gas production.
- *pH level:* The pH of the refuse and leachate significantly influences the chemical and biological processes. An acidic pH increases the solubility of many constituents, decreases adsorption, and increase the ion exchange between the leachate and organic matter.
- *Bacterial content:* The bacteria involved in aerobic biodegradation and methanogenesis exist in the soil and refuse. But, the addition of bacteria from other sources to the refuse can result in a faster rate of development of the bacteria population, for example: digested effluent and wastewater sludge.
- *Oxygen content:* Aerobic bacteria in the top of the landfill will cause to consume the oxygen and limit the aerobic zone of the compacted waste.
- *Temperature:* The heat is a result of anaerobic decomposition process that can result in a temperature rise within the landfill environment. The heat flux from the landfill to the surroundings can also be resulted from the insulating effect of the solid waste. The rate of methane generation can be increased (up to 100 times), when the temperature rises from 20 to 40 ºC.

2.1.3 *Production of Leachate*

Leachate is a liquid that has percolated through solid waste and extracted dissolved or suspended materials and is composed of the liquid that has entered the landfill from external sources, such as rainfall and surface drainage and the liquid produced from the decomposition of the wastes. When water percolates through solid wastes that are undergoing decomposition, both biological materials and chemical constituents are leached into solution (Warith, 2003).

The type of solid wastes, physical, chemical, and biological activities that occur in the solid wastes determine the quality of leachate. Leachate can cause serious problems since it is able to transport contaminating materials that may cause a pollution of soil, groundwater, and surface water (Warith, 2003). The chemical composition of leachate varies greatly depending on the age of landfill. Biodegradability of the leachate will also vary with time. The ratio of the BOD_5/COD can be used to monitor changes in the biodegradability of the leachate: initially, the BOD_5/COD ratios will be around 0.5, in the range from 0.4 to 0.6 are taken as an indication that the organic matter in the leachate is readily biodegradable. In mature landfills, the BOD_5/COD ratio is often in the range of 0.05 to 0.2; the reason that the BOD_5/COD ratio drops is that the leachate from mature landfills typically contains humic and fulvic acids, which are not readily biodegradable (Tchobanoglous and Kreith, 2002).

The leachate characteristics also depend on time of production: *young leachate* contains a biodegradable organic matter for the first few years and tends to be acidic due to the presence of volatile fatty acids. The pH is generally in the range of 6 to 7 and may be lower in dry stressed landfills. The young leachate is derived from processes such as the complex biodegradation of organics (e.g., cellulose) and simple dissolved organics (e.g., organic acids), and gradually, leachate becomes less strong and simply dissolved organics (e.g., gases CH_4, CO_2, H_2, H_2O and biomass). In an *old leachate*, the pH of leachate will increase to a range of 7 to 8, due to the depletion of the biodegradable organics and the production of gases. The changes occur after 4 to 5 years of waste deposited in the landfill (Tchobanoglous and Kreith, 2002).

2.1.4 *Settlement of Landfill*

Settlement is an important parameter in the management of municipal solid waste landfills. The organic material is decomposed and weight is lost as landfill gas and leachate components, as consequence the landfill settles. Equally, the settlement also occurs as a result of increasing overburden mass as landfill lifts are added and as water percolates into and out of the landfill. In a landfill, the organic components of the waste will decompose, resulting in loss of as much as 30 to 40 percent of the original mass (Tchobanoglous and Kreith, 2002). The rate of decomposition is directly related to the moisture content of the waste, with wet waste decomposing the fastest and the loss of mass results in a loss of volume (Tchobanoglous and Kreith, 2002).

The settlement of landfills affects the design of protection systems such as covers, barriers, and drains. Settlement of landfill begins rapidly as load is placed and continues to occur for long periods thereafter. The main mechanisms in waste settlement are (Quian et al., 2002):

- *Mechanical compression:* Compression caused by the self weight of the landfill and imposed loads, occurs in the form of initial, and/or primary consolidation, and/or secondary compression.
- *Raveling:* The movement of finer particles into larger voids or cavities within the fill.
- *Physical-Chemical change:* Due to the deterioration and volume loss of waste products by corrosion, oxidation, and combustion.
- *Biochemical decomposition:* A reduction of waste mass by fermentation and decay, both in aerobic and anaerobic processes.

The magnitude of the settlement is affected by different factors and several of them are interrelated: initial density (including the types and amount of daily cover used); waste compaction effort and placement sequence; content of the decomposable materials in the waste; overburden pressure and stress history (such as conducting vertical expansion to overfill over an old landfill); leachate level and fluctuations in landfill; landfill operation methods; and environmental factors (Quian et al., 2002). Also, landfill settlement is characteristically irregular. Initially, there is a large settlement within one or two months after completing construction, followed by a substantial amount of secondary compression over an extended period of time. The magnitude of settlement decreases over time and with increasing depth below the surface of the landfill. Waste settlement under its own weight typically ranges from 5 to 30% of the original thickness, with most of the settlement occurring in the first one or two years (Quian et al., 2002).

Settlement of solid wastes is a function of different factors: the material and the thickness of the cover, solid waste composition, and density achieved after compaction of the landfill, self-weight, overburden, climate, method of filling, mode of operation, etc. Therefore, the principal causes for settlement are: reduction in void space and compression of loose material due to overburden weight, volume changes due to biological and chemical reactions and dissolution of waste matter by leachate, movement of smaller particles into larger voids, and settlement of underlying soils (Swati and Joseph, 2008).

The sequential settlements occurring in a landfill can be classified into initial (immediate and rapid due to overburden pressure), primary (due to dissipation of pore water and void gases) and secondary (due to decomposition of refuse skeleton and biological decay). This gradual settlement is further classified into: primary compression attributed to loss of liquids and escape of gas; and secondary compression, mainly a consequence of biochemical solid waste mass losses, apart from other reasons like long-term material behavior due to continuous stress (Swati and Joseph, 2008).

2.1.5 *Daily Cover*

Covering solid wastes after a day operation is a standard practice at most landfills. This is to: minimize disease vectors; restrict access to rodents, birds, and insects; control leachate and erosion; reduce fire hazard potential; minimize wind-blown litter; reduce noxious odors; provide an aesthetic appearance; or allow accessibility regardless of weather. Different ADCs have been studied. An example is geotextile sheets which were applied by spreading canvas-like geotextiles over the working surface of a landfill. Such sheets were, however, costly and lacked structural stability (DeMello, 1990). Another example was using soil and lime as daily cover for the removal of manganese and zinc (Safari and Bidhendi, 2007). This experiment indicated that the effect of lime on increasing the pH of the leachate in the pore spaces of the soil could be considered the predominant mechanism for removal of Mn and Zn. This was confirmed by the increase in the concentrations of these metals in the effluent when pH was decreased, as a result of lime having been used up in the precipitation reactions. But an extensive increase in the pH values of the effluents can be inappropriate in terms of any further biological treatment scheme, if required (Safari and Bidhendi, 2007).

As a result of the demand for utilizing recycled products, development of ADCs with resource recovery has been greatly increased recently (Haaren, 2010; Myers, 2007). A method to develop an ADC using wastewater sludge and certain portions of municipal solid waste was studied (Myers, 2007). Care should be given to the physiochemical characteristics of sludge, which may cause pathogenic disease and aesthetic problems. Another material with potential for use as ADC is the yard waste (Myers, 2007). A study compared the environmental impacts of composting yard wastes in windrows with using them in place of soil as ADC in landfills and showed that the ADC scenario was more beneficial for the environment than windrow composting (Haaren, 2010). The use of ADC is also a less costly means of disposal of yard wastes. But, this finding applies only in cases where there are sanitary landfills in the area that are equipped with gas collection systems. It is necessary to make the life cycle assessment and other studies to compare yard waste with other ADC materials (Haaren, 2010).

Hurst et al. (2005) investigated the ability of municipal waste compost as a daily cover material to reduce the odorous emissions associated with landfill surfaces. Odors are often associated with sulphur compounds including hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide (Hurst et al., 2005). The results showed that the use of a compost daily cover could potentially reduce the impact of odor emissions by reducing the release of individual compounds. Reduction of odor reduces the amount of complaints and thus facilitates better relations between the general public, operators and regulators. The most significant disadvantages associated with the use of daily cover materials are the volume space it occupies that could be available for primary waste.

2.2 BIOREACTOR LANDFILLS WITH LEACHATE RECIRCULATION

Different techniques are used to enhance biological degradation of the waste such as: shredding, leachate recirculation, and the addition of nutrients and sludge. The bioreactor landfill is a sanitary landfill that enhances microbiological processes to transform and stabilize the readily and moderately decomposable organic waste constituents (Warith, 2002). The concept of bioreactor landfill is to use specific design and operation practices to accelerate the decomposition of food waste, green waste, paper and other organic wastes in a landfill using optimum moisture content and sufficient nutrients for the microorganisms to degrade the waste. The extensive reduction in organic parameters and shorter half lives of organic degradation indicate that rapid anaerobic degradation of organic matter can be achieved through leachate recirculation (Swati and Kurian, 2007). Leachate recirculation system in a bioreactor landfill is the technique that can be used to enhance solid waste biodegradation and accelerates the rate at which the waste is broken down, thus decreasing the time required to stabilize the landfill (Warith, 2003).

During the early stages of landfill operations, the leachate will contain significant amounts of total dissolved solid (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), and heavy metals (Tchobanoglous and Kreith, 2002). When leachate is recirculated, biological, physical and chemical reactions will occur by the provided various nutrients in recirculated leachate, which are required for the growth of bacteria responsible for anaerobic degradation of the waste. Moisture is essential for the microbial because it serves as a medium for transporting nutrients and bacteria. During leachate recirculation, the leachate is returned to a lined landfill for its reinfiltration into the municipal solid waste. This is considered a method of leachate control because, as the leachate continues to flow through the landfill, it is treated through biological processes, precipitation, and/or adsorption. In this regard, it benefits the landfill by increasing the moisture content, which in turn increases the rate of biological degradation in the landfill, the biological stability of the landfill, and the rate of methane recovery

(Karthikeyan and Joseph, 2000; Warith, 2003).

The leachate recirculation allows more wastes to fit in the same air space (Tchobanoglous and Kreith, 2002). This reveals the advantages of the leachate recirculation and its effect on accelerating waste biodegradation, as well as increasing the rate of landfill gas generation. Also, the addition of a supplemental material to the leachate during recirculation was found to have positive effect on the rate of biological degradation of solid wastes. Adding primary sludge and supplemental nutrients enhanced conditions such that there were a rapid decrease in BOD and COD concentrations in the effluent samples (Warith, 2002). There are several methods of leachate recirculation (Tchobanoglous and Kreith, 2002). These include:

- *Direct application to the waste during disposal:* The leachate is added to the incoming solid waste while it is being unloaded, deposited, and compacted. This application requires a leachate storage facility for periods such as when high winds, rainfall, and landfill shutdown prevent leachate application.
- *Spray irrigation of landfill surface:* The leachate is applied to the landfill surface in the same method that irrigation water is applied to the crops. This method is beneficial because it allows the leachate to be applied to a larger portion of the landfill. Also, the leachate volume is reduced due to evaporation.
- *Surface application:* This is achieved through ponding or spreading the leachate. The ponds are generally formed in landfill areas that have been isolated with soil or within excavated sites in the solid wastes.
- *Subsurface application:* This method is achieved throughout placing either vertical recharge wells or horizontal drains fields within the solid waste. There is a large amount of excavation and construction required with this method, but the risk of atmosphere exposure is radically reduced.

Landfills settle due to the weight and biodegradation of wastes. Biodegradation induced settlement is a direct result of rearrangement of waste skeleton in response to the conversion of waste mass into landfill gases (Hettiarachchi et al., 2007). The rate of initial settlement occurring under aerobic conditions has been greater than that under anaerobic conditions. Elagroudy et al. (2008) proved a model feasible for different waste compositions, sludge presence and/or absence, addition of enzymes, and different operational conditions. But, the model needed to verify the validation on field-scale bioreactor landfills (Elagroudy et al., 2008).

To increase microbiological activity, a bioreactor landfill should be used to transform and stabilize the decomposable organic waste. Recirculation of leachate helps the landfill maintain a wet environment in addition to supply the nutrients needed for the biodegradation (Hettiarachchi et al., 2007). Enhancement of waste stabilization by leachate recirculation to reduce the time required for waste degradation, improves leachate quality and enhances the rate of gas production (Erses et al., 2008). Leachate recirculation is projected to be an effective measure in increasing the potential filling capacity of a landfill site (Chan et al., 2002).

Leachate recirculation increases the rate of landfill gas generation and worsens the odor problem, which results from the landfilling operation. Recycling the leachate proves to be an effective tool in bioreactor landfill management and helps lessen the distinctive biological phase, which in return allows for the landfill to reach a state of stabilization rapidly (Warith, 2002). The enhanced biodegradation of waste promotes a faster reduction of the waste particles, which in turn clogged the available pores, thus reducing the leachate recirculation efficiency (Valencia et al., 2009). The settlement is a parameter that affects the design and maintenance of bioreactor landfills; therefore, it is very important to predict its settlement (Elagroudy et al., 2008). The variables as type of waste, organic and moisture contents, compaction density, porosity, compressibility, biodegradation rate, increased with the augment in the concentration of enzymes and with the presence of sludge in both aerobic and anaerobic stages. Therefore, increasing organic content of municipal solid waste have resulted in the enhancement of the biodegradation rate and settlement (Elagroudy et al., 2008).

In the landfill, the biodegradation is considered to be limited by low water content and slow leachate flow within the landfill, and thus leachate recirculation is a basic method derived from bioreactor practices which aims to control and enhance stabilization of the landfill. Sornumen et al. (2008) monitored and characterized internal leachate quality to provide information about its horizontal and vertical variation as well as effects of leachate recirculation on leachate quality using wells (Sormunen et al., 2008). The effect of leachate recirculation on internal leachate quality was hard to isolate due to variation caused by other factors during short-term leachate recirculation due to the fact that local conditions, waste management history, and landfill practices could have a considerable effect on the representativeness of leachate samples (Valencia et al., 2009).

A higher degree of waste stabilization towards the end of the experiment was found due to higher moisture content. Reaching neutral pH levels seemed to be the driving force that enhanced physical, chemical and biological characteristics (Valencia et al., 2009). Jiang et al. (2007) indicated the validity and feasibility of a bioreactor landfill to accelerate the stabilization of organic rich waste, enhance landfill gas generation, and achieve a degree of leachate pretreatment. However, they recommended to identify and resolve issues concerning full-scale design and/or operation of landfills, including landfill liners, temporary covers, leachate collection, and leachate recirculation systems before the leachate recirculation management strategy can be employed in modern sanitary landfills (Jiang et al., 2007).

2.2.1 *Removal of Heavy Metals*

The point of zero charge (PZC) is a concept relating to the phenomenon of adsorption and describes the condition when the electrical charge density on a surface is zero. When the pH is lower than the PZC, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions). Conversely, above the PZC the surface is negatively charged (attracting cations/repelling anions). The PZC is an important parameter to recognize the mechanism for removal of pollutants.

Cho et al. (2005) investigated the possibility of the utilization of coal fly ash as a low cost adsorbent (Cho et al., 2005). For this, batch experiments were performed to evaluate the removal of heavy metals from aqueous solutions by fly ash under various conditions of metal concentration, pH and fly ash dosage. The heavy metals used in this study were Zn, Pb, Cd and Cu. In the characterization for fly ash, scanning electron microscope (SEM) was used, which clearly showed that finer fly ash particles were primarily spherical, whereas the coarser particles were mainly composed of irregular and porous particles. In the experiments, real wastewater showed that fly ash was effective in the simultaneous removal of various heavy metals in metal industrial wastewater. Also, the percentage removal of heavy metals was dependent on the pH of the solution. However, at neutral pH conditions (pH 6 – 8), the removal was high even when small amounts of fly ash were used.

Wang et al. (2006) used the coal ash as effective adsorbents for removal of heavy metals and dyes from wastewater. The fly ash was modified by hydrothermal treatment using NaOH solutions under various conditions for zeolite synthesis. The results from XRD analysis indicated that the samples obtained after treatment were much different and the profiles revealed a number of new reflexes, suggesting that a phase transformation probably occurred. Modifying fly ash with NaOH solutions significantly enhanced the adsorption capacity for removal of heavy metals depending on the treatment temperature, time, and base concentration. For the heavy metals, the treated fly ashes showed effective adsorption with higher capacity for Ni than Cu (Wang et al., 2006).

Another example is the use of the coal fly ash as a low cost adsorbent material for the adsorption of heavy metal ions (Zn, Pb, Cd, Mn and Cu) present in the municipal solid waste leachate (Mohan and Gandhimathi, 2009). Batch experiments were conducted to determine the effect of contact time and fly ash dosage on adsorption of heavy metals. Mohan and Gandhimathi (2009) monitored the morphology of the adsorbent on the fly ash by SEM and Fourier Transform Infrared Spectroscopy (FTIR) analyses of fly ash samples after adsorption. The comparison of SEM between the raw fly ash and the fly ash after adsorption showed that there were morphological changes in the fly ash samples after adsorption. It was observed that the spherical balls of the fly ash particles were covered by precipitates and complexes formed by the heavy metal ions. They concluded that the fly ash was very effective as an adsorbent for Pb and Cd compared to other heavy metals. The use of fly ash in leachate treatment was recommended in order to remove the heavy metals before discharging the treated leachate into nearby water courses. The fly ash after its utilization for the adsorption of heavy metals could be disposed in the secured landfill along with hazardous waste (Mohan and Gandhimathi, 2009).

2.3 PHYSICAL AND BIOLOGICAL PARAMETERS, AND ORGANIC AND INORGANIC CONSTITUENTS IN A LANDFILL

The organic strength of the leachate, measured as BOD and COD (Warith, 2002), as well as pH were monitored to determine the effect of use of alternative daily cover in the composition of leachate and settlement. Table 1, lists the organic, inorganic, physical and biological parameters analyzed in a landfill. It is important to emphasize that the quality of leachate is principally the result of physical, chemical, and biological processes, and other additional variables are water movement, nutrients, and the presence of toxic or inhibitory elements and compounds (Yoshida et al., 2002).

Table 1 Physical Parameters, Organic and Inorganic Constituents and Biological Parameters.

Physical	Organic Constituents	Inorganic Constituents	Biological
Volume	COD	Nitrate	BOD
pH	Volatile Acids	Hardness	Dissolved Oxygen
Oxidation – Reduction Potential		Total Phosphorus	Gas Production
Color		Total Nitrogen	
Turbidity		Orthophosphate	
Conductivity		Alkalinity	
Settlement			

In a landfill, there are physical transformations (changes) in volume, size reduction and components. Chemical transformations that involve change of phase (e.g., solid to liquid, solid to gas, etc.) and biological transformations that involve decomposition of organic waste (Karthikeyan and Joseph, 2000). Leachate composition is complex, high and variable concentration of pollutants (Rong, 2009) and formed by many different organic and inorganic compounds that may be either dissolved or suspended and either biodegradable or non-biodegradable. Also, the characteristics of the leachate vary with regard to its composition, volume, and biodegradable matter present in the leachate with time. Therefore, characterization of leachate is complicated by its composition. The site specific nature of the leaching process is one of the most important characteristics that may vary as a function of landfill age (Bilgili et al., 2008; Munasinghe, 1997; Valencia et al., 2009). It is important to emphasize that water quantity of leachate relates to main factors such as: climate, surface hydrology and hydrogeology of the site, the amount of water entering and leaving a landfill, composition of solid waste, age of landfill and method of landfilling (Munasinghe, 1997; Rong, 2009). Landfill leachate characteristics vary from landfill to landfill because of the variety of specific conditions such as: moisture content, periodical variations in infiltration, waste composition, landfill microbiology, depth of the landfill, compaction density, use and composition of cover material, etc (Munasinghe, 1997). Also, landfill leachate strength varies considerably, like, for example, moisture content, periodical variations in infiltration through the refuse, wastes composition, landfill microbiology, depth of the landfill, density of compaction, use and composition of cover, etc, (Munasinghe, 1997).

Other important parameters in the analysis of landfill leachate are the nitrogen and phosphorus concentrations, because they are the main components of the inorganic pollution from the leachate. These concentrations are high when the landfill is processing wastes, but when the landfill is closed, the phosphorus is reduced slowly, and the nitrogen will rise step by step since waste decomposition is a slow process under the anaerobic conditions (Rong, 2009).

2.3.1 *Physical Parameters*

The important physical parameters in a landfill are the amount of leachate produced (volume), pH, oxidation-reduction potential (ORP), color, turbidity, conductivity and settlement.

2.3.1.1 *Volume*

The leachate composition is variable and the quantity of pollutants removed from solid waste is often attributed to the volume of water which infiltrates into the landfill and directly related to the natural processes occurring inside the landfill (support microbial activity). Simultaneously, in accordance to biochemical changes, physicochemical processes, including dissolution, precipitation, adsorption, dilution, volatilization and others, influence leachate quality (Valencia et al., 2009). The leachate is generated directly by inflow or rain infiltration, surface water and groundwater running into the waste. This liquid spends many years to infiltrate through the landfill. The water leaches and dissolves various constituents until it contains a load of heavy metals, chlorinated organic compounds and other substances. The intensity, quantity, frequency and duration of rainfall relate to quantity of leachate production (Rong, 2009), because the leachate production is a complex one since it depends on the landfill characteristics and the climate (Weerasekara et al., 2007): for example, the rainfall is an important factor for leachate; about 15%~50% of rainfall can become leachate (Fan et al., 2006;(Morris et al., 2003).

Also, the climate, surface hydrology, and hydrogeology of the site, all have a large influence on the amount of water entering and leaving a landfill which is important in the leaching process. In addition, the moisture content of the waste, seasonal variations in infiltration, landfill microbiology, waste compaction, and use and composition of the cover material have an influence on the characteristics of the resultant leachate. Therefore, the leachate characterization shows a relationship of water input patterns and hydraulics of the landfill to leachate strength and mass loading with respect to organic compounds (Munasinghe, 1997).

2.3.1.2 *pH*

The chemical composition of leachate varies greatly depending on the age of landfill and the time of sampling. For pH, if a leachate sample is collected during the acid phase of decomposition (Figure 2), the pH value is low and the concentrations of BOD_5, TOC, COD, nutrients, and heavy metals are high. While, if the leachate sample is collected during the methane fermentation phase (Figure 2), the pH are in the range from 6.5 to 7.5, and the BOD_5, TOC, COD, and nutrient concentration values will be significantly lower. The concentrations of heavy metals will be lower because most metals are less soluble at neutral pH values. Also, the pH of the leachate depend not only on the concentration of the acids that are present, but also on the partial pressure of the CO_2 in the landfill gas that is in contact with the leachate (Tchobanoglous and Kreith, 2002).

2.3.1.3 *Oxidation – Reduction Potential (ORP)*

The oxidation - reduction potential (ORP) is a parameter within a landfill that determines the mechanism of waste degradation (Bilgili et al., 2007; Shearer, 2001). The high ORP (aerobic conditions) causes accelerated degradation of waste, but air must be supplied, which increases operational costs. While, low ORP is related with the anaerobic degradation, in this mechanism methane is produced. The optimum ORP require for methanogenesis is found to be in the ranges from −100 to −300 mV (Bilgili et al., 2007).

2.3.1.4 *Color*

The color is a parameter due to dissolved and particulate material. The impurities can be deeply colored by the dissolved organic compounds. Color may be expressed as apparent or true color. The true color is measured after filtering the leachate sample to remove all suspended material.

2.3.1.5 *Turbidity*

Turbidity is caused by suspended matter or impurities that interfere with the clarity of the water. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble colored organic compounds, and plankton and other microscopic organisms (Clesceri et al., 1998). Turbidity is closely related to total suspended solids (TSS), but also includes plankton and other organisms.

2.3.1.6 *Conductivity*

Conductivity is the total concentration of ionic species in a solution and is a measure of the solution's ability to convey an electric current (Erses et al., 2008; Jun et al., 2009; Nikolaou et al., 2009). The conductivity of leachate reflects its total concentration of ionic solutes (Jun et al., 2009; Nikolaou et al., 2009) and it depends on the presence of ionic species; on their total concentration, mobility and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors (Clesceri et al., 1998).

2.3.1.7 *Settlement*

Landfills settle due to its weight and waste biodegradation (Hettiarachchi et al., 2007). Landfill settlement can be attributed to the following mechanisms: first, mechanical compression that can be divided into an initial compression, which ends rapidly as soon as the load is applied, and secondary compression, which continues over a long period of time. The initial settlement is caused mainly by the compression of void spaces filled with air; the compression of loose, resilient materials; and particle slippages and secondary compression is caused by long-term slippages, reorientation of particles, and delayed compression of some refuse constituents. The second mechanism is its response to the applied stress (Vaidya, 2002). The biodegradation induced settlement is a direct result of rearrangement of waste skeleton in response to the conversion of waste mass into landfill gases (Hettiarachchi et al., 2007) and lead to a decrease in landfill volume (Park and Lee, 2005).

Prediction of landfill settlement is an important parameter that affects the design and maintenance of bioreactor landfills (Elagroudy et al., 2008). But, there are a large number of variables involved in the settlement mechanisms including: the material and the thickness of the cover, solid waste composition, density achieved after compaction of the landfill, self-weight, overburden, climate, method of filling, mode of operation, etc., (Swati and Joseph, 2008) involving a challenge.

2.3.2 *Biological Parameters*

The biological parameters measured in a landfill are: biological oxygen demand (BOD_5), dissolved oxygen (DO), and gas production.

2.3.2.1 *Biological Oxygen Demand (BOD_5)*

Biological oxygen demand (BOD_5) is a measure of the amount of oxygen consumed in the biological processes that break down organic matter in water. BOD_5 is an empirical test used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 day. Dissolved oxygen is measured initially and after incubation, and the BOD_5 is computed from the difference between initial and final DO (Clesceri et al., 1998). Biodegradation is carried out by microorganisms, which can degrade organic compounds to carbon dioxide and biogas (CO_2 and CH_4) under anaerobic conditions (Renou et al., 2008).

The initial leachate from the acidic phase was characterized by high values of organic pollutants, where the large portion of the organic matter consists of volatile fatty acids which are easily biodegradable (Ozkaya et al., 2006). The BOD/COD ratio indicates the degree of biodegradation of the organic matter in leachate, understand the degree of landfill stabilization (Erses et al., 2008; Fan et al., 2006; Valencia et al., 2009; Warith, 2002) and gives information on the landfill age (Fan et al., 2006; Salem et al., 2008).

2.3.2.2 *Gas Production*

Landfills are complex systems where various biogeochemical interactive processes occur simultaneously. The most common issues related with landfills are the physical stability of the landfill, and the control of the gases and leachate from biochemical decomposition of the wastes. The gas generation as a result of biochemical waste decomposition changes the fill pressures in landfills, causing physical settlements. Biochemical waste decomposition accounts for a large part of the total landfill settlement. Since the organic wastes deposited in landfills are decomposed as a result of various stages of microbial activities, the landfills undergo a time-dependent settlement (Durmusoglu et al., 2005).

The leachate recirculation have positive effects that may be realized through increased moisture availability as they are significantly accelerated, decreases in the concentration of certain contaminants in leachate or accepted stability criteria, more rapid production of gas, and increased rates of settlement (Morris et al., 2003), and accelerate solid waste degradation, landfill stabilization (Jiang et al., 2007). Also, this may result in the washout of large amounts of organic matter before the methanogenic phase of the waste, thereby reducing the biological methane potential (Jiang et al., 2007). Higher rate of leachate recirculation can accelerate solid waste degradation, landfill stabilization and landfill gas generation (Jiang et al., 2007). The optimum leachate recirculation volume is important because it contributes to COD, decreasing volatile fatty acids, and effective methane gas productions. Also, leachate recirculation supplies reductions in organic matter; reduce waste quantity and volume. On the other hand, high recirculation volumes may deplete the buffering capacity and remove the activity of methanogens (Sponza and Agdag, 2004).

2.3.2.3 *Dissolved Oxygen (DO)*

Dissolved oxygen (DO) levels in natural and wastewaters depend on the physical, chemical, and biochemical activities in a water body. This analysis is a key in water pollution and waste treatment process control (Clesceri et al., 1998). Dissolved oxygen is a relative measure of the amount of oxygen that is dissolved or carried in a given medium.

2.3.3 *Organic Constituents*

The important organic constituents measured in the landfill are chemical oxygen demand (COD) and volatile acids.

2.3.3.1 *Chemical Oxidation Demand (COD)*

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Both organic and inorganic compounds of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest. COD is used as a measurement of pollutants in wastewater and natural waters (Clesceri et al., 1998). The ratio between COD and BOD provides an indication of the variation in the biodegradable organic fraction of the waste (Valencia et al., 2009; Warith, 2002) and to understand the degree of landfill stabilization (Erses et al., 2008).

The maximum value of COD concentration depends upon the amount of organics and whether they are readily degraded. The bioreaction occurs as the organic matter tends to degrade; the COD concentration of leachate decays steadily before achieving a stable concentration (Ozkaya et al., 2006). Also, the ratio of BOD/COD, which represents the proportions of biodegradable organics in leachate (Fan et al., 2006), decreased rapidly with the aging of the landfills due to the release of the large recalcitrant organic molecules from the solid wastes. For young landfills, where the biological activity corresponds to the acidogenic phase, the ratio BOD/COD reached the value of 0.83 and decrease up to 0.05. For old landfills in the last stage of fermentation the methanogenic phase is reached (Benson et al., 2007; Salem et al., 2008). Therefore, old landfill leachate is characterized by its low ratio of BOD/COD (Fan et al., 2006; Renou et al., 2008), and suggests that leachate was low in biodegradable organic carbon and relatively high in hard-to-biodegrade organic compounds such as humic compounds

(Erses et al., 2008).

2.3.3.2 *Volatile Fatty Acids*

The volatile fatty acids concentrations in leachate are very high and an optimum leachate recirculation volume contributes to decreasing volatile fatty acids, and effective methane gas productions (Sponza and Agdag, 2004). The decrease in the relationship of BOD and COD coincides with the decrease of volatile fatty acids which were converted into biogas (Valencia et al., 2009).

2.3.4 *Inorganic Constituents*

The inorganic constituents in a landfill measured are: nitrate, hardness, total phosphorus, total nitrogen, orthophosphate and alkalinity.

2.3.4.1 *Nitrate*

The landfill could be used as an anaerobic bioreactor for denitrification where nitrate is converted into N_2 gas. The use of nitrate instead of carbon dioxide as an electron acceptor for microbial metabolism induces a strong increase in the Gibb's free energy available for microorganisms' growth. Heterotrophic denitrification could therefore enhance decomposition rates and reduce the aftercare period, a critical issue for the landfill operators. This strategy enables the release of nitrogen outside of the system with concomitant consumption of organic carbon from the waste, thus possibly enhancing solid waste stabilization. Therefore, nitrate-enhanced leachate recirculation represents a promising strategy for more sustainable landfill management (Tallec et al., 2009).

Nitrate is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Nitrate in excessive amounts, contributes to the illness known as methemoglobinemia in infants and is an essential nutrient for many photosynthetic autotrophs and in some cases has been identified as the growth-limiting nutrient (Clesceri et al., 1998). Nitrate is a highly soluble form of nitrogen (Wolfe et al., 2000).

2.3.4.2 *Hardness*

Water hardness is a measure of high mineral contents that are represented by high concentrations of calcium and magnesium ions (Clesceri et al., 1998). Hard water is used by organisms as a skeletal strengthening compound.

2.3.4.3 *Total Phosphorus*

Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro, meta, and polyphosphates), and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms. Organic phosphates are formed primarily by biological processes (Clesceri et al., 1998).

2.3.4.4 *Total Nitrogen*

Nitrogen has the potential to pollute water (Bilgili et al., 2008). Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate generally occurs in trace quantities in surface water but may attain high levels in some groundwater. Nitrite can enter a water supply system through its use as a corrosion inhibitor in industrial process water (Clesceri et al., 1998). The total nitrogen in water is comprised of dissolved inorganic and organic nitrogen and particulate organic and inorganic nitrogen, minus N_2 gas. Bacterial denitrification converts nitrate to N_2 gas, hence the loss of some of the water's nitrogen.

2.3.4.5 *Orthophosphate*

Orthophosphate is the most stable kind of phosphate, and is the form used by plants. Orthophosphate is sometimes referred to as reactive phosphorus.

2.3.4.6 *Alkalinity*

Alkalinity of water is its acid neutralizing capacity (Clesceri et al., 1998). This measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. Other components that can contribute to alkalinity include borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulfide (Clesceri et al., 1998). Jun et al. (2009) conducted a study where they found that alkalinity addition had positive effects on the stabilization of solid waste that could accelerate the removal of leachate pollutants. The solid waste stabilization has a positive influence on the removal of total nitrogen. Therefore, the alkalinity addition could enhance the solid waste pH-buffering capacity, which could alleviate inhibition of methanogenesis. Alkalinity addition could also accelerate the degradation rate of pollutants (Jun et al., 2009).

2.4 MICROBIAL ACTIVITIES IN A LANDFILL

Microbial activities play an important role in organic matter decomposition, element cycling, and plant growth (Garau et al., 2007). Agricultural liming materials (as $CaCO_3$) increase soil pH and affect the activity and composition of microbial populations; therefore, the microbial and chemical responses to lime vary with soil type and management. When the pH increases, it enhances the deprotonation of organic substances and the bonding between organic compounds and soil particles decreases, making organic substances more available for microbial consumption. Furthermore, the formation of readily decomposable organic matter form more reactive pools and improve environmental conditions for microbial growth (Fuentes et al., 2006). Other parameters used to describe changes in soil microbial quality are the enzyme activities (Acosta-Martínez et al., 2007).

The appropriate conditions for microbial activity in a material used as a daily cover are (Chiemchaisri and Chiemchaisri, 2004):

- *Texture:* Soil void and aggregation are important because they relate to gas and water diffusion, which are also involved in the soil microbial activities. An optimum soil type using for design of landfill cover soil was silt or sandy loam soil.

- *Moisture Content*: Microorganisms and plants depend on water and nutrients soil to grow. For example, if there is a small amount of water, growing of microorganisms is interrupted. However, if there is too much water, it replaces the air in the soil and affects some microorganisms, especially aerobes. The fine textured soil (clay) can retain more water than lighter soil (sand) but clay soil is not a good habitat for aerobic microorganism (including methanotrophs) because clay absorbs more water than other soil types. The diffusion of atmospheric air through clay is less, when compare to sandy soil. However, high water content can cause starvation for methanotrophs; therefore, soil has a good proportion of water and air available to microorganisms which might enhance the growth of methanotrophs. Also, the moisture plays an important role in determining the extent of settlement (Swati and Joseph, 2008).
- *Temperature:* High temperature affects microorganisms much greater than low temperature. The cover soils temperature in landfills varies by atmospheric temperature during a day and a year and by plants covering the soil surface that affect soil temperature. The plants can protect from heat in soil surface, or retain heat in soil and water evaporation that reduced the temperature of the soil surface below that of the environmental air. The methanotroph activities have an optimum temperature for high methane oxidation rate found between 25 and 30°C.
- *Organic Matter*: Organic fraction of soil affects the physical, chemical and biological characteristics of soil. Organic matter supports suitable soil environments for growing microorganisms and when applied into soil mass it increases the activities of microorganisms that use organic compounds as energy source and increases the rate of mineralization. The application of large organic matters into the soil may have many adverse effects, the soil pores can be clogged because large consumption of oxygen by aerobic microorganisms, which might result in reduction of gas exchange and increases more aggregation of soil particles.

- *Nutrients*: Generally, nutrients are important factors to all organisms. However, each organism responds to each nutrient differently because their nutrient requirements are not alike.
- *Toxic Compounds*: The compounds often found to be toxic to all soil microorganisms are heavy metals and pesticides. These compounds affect the microorganisms living in deeper soil more than in top soil. Other toxic compounds detected in landfill gas are volatile organic compounds which might affect methanotrophic activities when they volatilize up to final landfill cover.
- *Oxygen to Methane Ratios*: The oxygen concentration is a significant factor in controlling the methane oxidation rate in landfill cover soil.

Microbial activity enhancement is possible using coal combustion byproducts like fly ash as a soil additive because it may improve physical, chemical and biological properties of the degraded soils and is a source of readily available plants micro and macro nutrients (Pandey and Singh, 2010). Pandey and Singh (2010) explored the possibility of fly ash addition into degraded soils for improving nutritional, physical and chemical properties. Fly ash can be used as a potential nutrient supplement for degraded soils thereby solving the solid waste disposal problem to some extent. However, the bioaccumulation of toxic heavy metals and their critical levels for human health in plant parts and soil should be investigated (Pandey and Singh, 2010). Consequently, Pandey et al. (2009) examined the influence of the application of fly ash into garden soil for *Cajanus cajan* L. cultivation on accumulation and translocation of hazardous metals from fly ash to the edible part. Incorporation of fly ash in garden soil increased the levels of pH, particle density, porosity, and water holding capacity (Pandey et al., 2009).

With regard to the reduction of contaminants in the leachate, Li et al. (2007) investigated Cr(VI) reduction in landfill leachate and identified whether correlations existed between Cr(VI) reduction and concentrations of Cr(VI), bacterial biomass and organic matter (Li et al., 2007). Bacterial growth and biomass concentration were monitored by optical density (OD) readings, measured at 600 nm using a spectrophotometer. The results showed that Cr(VI) underwent reduction in municipal landfill leachate. The reduction in medium inoculated with bacteria and the lack of Cr(VI) reduction in sterilized landfill leachate demonstrated the microbial activity of bacteria in landfill leachate was responsible for Cr(VI) reduction. The bacterial growth rate was believed to relate to the content of leachate recirculation, bacterial species, organic matter and exposed Cr(VI) concentration. The study also illustrated that microbial Cr(VI) reduction was a first order reaction with respect to bacterial biomass concentration. The reduction rate was a function of the initial Cr(VI) concentration and type of organic matter (Li et al., 2007).

2.5 COAL COMBUSTION BYPRODUCTS

Coal combustion byproducts are materials produced from coal combustion in power plants. Coal combustion byproducts are categorized in four groups, each based on physical and chemical forms derived from coal combustion methods and emission controls: fly ash is captured after coal combustion by filters, electrostatic precipitators and other air pollution control devices; flue gas desulfurization materials are produced by chemical "scrubber" emission control systems that remove sulfur and oxides from power plant flue gas streams; bottom ash and boiler slag can be used as a raw feed for manufacturing portland cement clinker. The AES power plant facility in Guayama, Puerto Rico mainly produces two types of coal combustion byproducts: fly ash and bottom ash. These two products are mixed with water and solidified to produce CCAs. A description of the fly ash, bottom ash and CCAs produced at the AES facility will be reviewed in the following sections:

2.5.1 *Fly Ash*

Fly ash is the finely divided mineral that results from the combustion of pulverized coal produced during the steam generation process in the power plant. The fly ash particles solidify while suspended in the exhaust gases and are collected by electrostatic precipitations. The physical and chemical characteristics of fly ash can vary greatly and mainly depend on the combustion method and coal properties used at a particular power plant. This material consists mainly of silica, aluminum, iron, and calcium oxides. Other elements such as magnesium, potassium, sodium, titanium and sulfur; are also present to a lesser degree (Pando and Hwang, 2006).

According to the American Society for Testing and Materials (ASTM Standard C 618), fly ash can be classified in two main types: Class C (high calcium content, >20% by weight), and Class F (a low calcium fly ash, <10% by weight). The principal factors that influence the classification of fly ash are the percentages of silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3) and calcium oxide (CaO) (Pando and Hwang, 2006).

Mostly, fly ash consists of spherical silt-sized particles ranging between 10 and 100 microns (Pando and Hwang, 2006). Fly ash is usually dark gray in color, but this depends on its chemical composition and mineral constituents. Approximately 80% of fly ash consists of tiny glass spheres and the other 20% is composed of quartz, mullite, hematite and magnetite (Pando and Hwang, 2006).

Coal ashes have been used to remediate heavy-metal-contaminated wastewater by precipitation in the form of metal hydroxides (Erol et al., 2005) or by adsorption (Lin and Yang, 2002). Erol et al. (2005) reported the removal of Cu^{2+} and Pb^{2+} ions by precipitation from aqueous solutions by using six fly ashes with different compositions. Results indicated that both Cu^{2+} and Pb^{2+} removal capacities of the fly ash samples were directly proportional to their CaO contents. The formation of metal hydroxide precipitation was found by scanning electron microscopy (SEM) investigations, and X-ray diffraction (XRD) analysis revealed the $Cu(OH)_2$, $Cu(OH)_2.H_2O$ and $Pb(OH)_2$ peaks in the treated fly ash samples. The cementitious and adsorbing characteristic of fly ash reduced the leaching of heavy metals from the wastes by precipitation (Erol et al., 2005). Lin and Yang (2002) studied the adsorption capacity of bed ash (bottom ash) for heavy metals, nitrogen, phosphorus, and COD, and concluded that bed ash could be used as an efficient adsorption material for pollutant removal from wastewater (Li et al., 2002).

Mollamahmutoglu and Yilmaz (2001) used fly ash mixed with binding material (bentonite) to obtain less permeable liner material that may be used for waste disposal areas. They found that 20% bentonite fly ash was suitable as a liner or cover material. Sivapullaiah and Lakshmikantha (2004) found that coal fly ash-bentonite mixtures were a promising material for landfill liners because the hydraulic conductivity meets the common regulatory specifications of 1×10^{-7} cm/s for its use as a liner material (Sivapullaiah and Lakshmikantha, 2004). With respect to use in construction, Reyes (2007) obtained results to suggest that circulating fluidized bed combustion byproduct fly ash may improve the strength and stiffness of clay but cause some expansion which is critical for roads and buildings. Therefore, they recommended to evaluate the expansion potential using similar loads to those the soil will be experimenting (Reyes R., 2007). Other applications for fly ash is it utilization as a soil conditioner in pellets through a reaction with aqueous KCl solutions, producing in the process a slow release potassium fertilizer becoming a product with a great potential value for agricultural purposes (Castañeda Muñoz, 2006).

Coal combustion byproducts (fly ash or bottom ash) have been utilized in many different environmental applications, including the removal of substances and use in the landfills. Wang et al. (2005) used fly ash and red mud for removal of methylene blue from aqueous solution (Wang et al., 2005). They found that fly ash generally exhibits higher capacity than red mud. Physical and chemical treatment can significantly change the adsorption capacity. Heat treatment adversely influences the dye adsorption while acid treatment by nitric acid can greatly enhance the adsorption capacity of fly ash due to the enhanced rate of intraparticle diffusion of the adsorbate, as diffusion is an endothermic process (Wang et al., 2005).

2.5.2 *Bottom Ash*

Bottom ash is a coal combustion byproducts consisting of coarse grained particles that fall to the bottom of the furnace as a result of the coal combustion procedures. It is usually the smaller portion of the total ash produced during the coal combustion process. Similar to fly ash, the physical and chemical characteristics of bottom ash will mainly depend on the combustion method and coal properties used at a given power plant (Pando and Hwang, 2006).

The chemical composition of bottom ash is similar to fly ash. However, bottom ash is more inert than fly ash, and as a result, bottom ash particles have a greater tendency to fuse together (Pando and Hwang, 2006). Bottom ash is composed principally of silica (SiO_2), alumina (Al_2O_3), and iron with smaller percentages of calcium, magnesium, sulfates and other compounds. The main components of the AES bottom ash are silica + alumina + ferric oxide ($SiO_2 + Al_2O_3 + Fe_2O_3$), lime (CaO), and sulfur trioxide (SO_3), representing 47%, 36%, and 12.8% by weight, respectively (Pando and Hwang, 2006).

The physical properties of bottom ash are similar to those of natural sand, with particle sizes ranging from gravel to fine sand with low percentages of silt and clay-sized particles. Bottom ash is typically grey to black in color and has a large particle size (diameter between 0.08 and 4.9 mm), angular shape, and high porous surface resulting in a higher water requirement and lower compressive strength (Pando and Hwang, 2006). Bottom ash is commonly used as a replacement for construction aggregate because it is well-graded in size which avoids the need for blending with other fine aggregates to meet construction gradation requirements (Pando and Hwang, 2006).

Lin and Yang (2002) studied coal bottom ash produced from a thermal power plant that was used in a batch experiment to investigate the adsorption characteristic of this bottom ash. The adsorbate solutions were synthetic wastewaters that contained copper (Cu^{2+}) or COD and a sanitary landfill leachate. The experimental results showed that coal bottom ash had a good adsorption capacity for copper and COD and could reduce the concentrations of various pollutants in the leachate (Ling et al., 1998).

Compacted soil barriers are one of the most important components of municipal waste landfills (Tchobanoglous and Kreith, 2002). The material used to construct a landfill liner must prevent the flow of fluids through them. Soils with low values of permeability are often used to construct landfill barriers. Natural sands and other materials with less cohesion are used to construct hydraulic barriers by adding mixtures to modify their properties. Most scientists and researchers have concluded that bottom ash has geotechnical characteristics similar to those of sands (Kumar and Stewart, 2003). However, information on the use of bottom ash, with or without admixtures, in the construction of landfill barriers is limited.

Kumar and Stewart (2003) tests were performed to determine the feasibility of the use of bottom ash to construct compacted landfill barriers. They found that the addition of bentonite decreased the hydraulic conductivity of bottom ash–bentonite mixtures tested in triaxial flexible wall permeability apparatus, and showed that the hydraulic conductivity of bottom ash with 15% bentonite content was close to the acceptable value required for its use as hydraulic barrier. (REF)

2.5.3 *Coal Combustion Byproducts Aggregates (CCAs)*

Coal combustion byproducts (CCAs) are an agglomerate of fly and bottom ash particles. This material gains strength with time due to cementitious reactions (Pando and Hwang, 2006). The main components of the AES aggregates (CCAs) are silica + alumina + ferric oxide (SiO_2 + Al_2O_3 + Fe_2O_3), lime (CaO), and sulfur trioxide (SO_3), representing 51%, 30%, and 14.7% by weight, respectively.

The physical properties of the CCAs were realized for Kochyil and Little (2004). The CCAs have a similar gradation as a natural gravel, with particle sizes ranging from gravel (diameter between 4.90 and 50.00 mm) to fine sand (diameter between 0.075 and 0.43 mm) with very low percentages of silt and clay-sized particles; the average specific gravity for the coarse fraction was found to be about 1.16 (larger than 2.36 mm), while the fine fraction had a specific gravity of about 2.69 (smaller than 2.36 mm). The low specific gravity of the coarse aggregate is due to the high void content of this fraction and the high void ratio content of the coarse aggregate was found to be related to a structure of an agglomerate of particles. These large particles are actually agglomeration of finer particles that were found to be susceptible to abrasion and breakdown. The specific gravity value obtained for the fine fraction is consistent with typical values found in natural aggregates (Kochyil and Little, 2004).

Due to the mechanical properties of the CCAs, they make an excellent substitute for virgin natural materials with a variety of applications within the construction industry: development of roads, parking lots, sidewalks and parks; filling private estates and commercial developments; stabilization of land and material base; and light aggregate (AES-PR, 2010). It has also been found that CCAs had sorption capacity and its feasible to remove contaminants: Hernandez Ramos (2009) demonstrated an effective TNT removal using a sequencing batch sorption reactor with a contact time of one hour and complete TNT sorption in the third sequence resulting in total 14.4 mg TNT removal per kg CCAs (Hernández, 2009b).

In a research of phyto-viability on restored land with CCAs as backfilling amendments, the CCAs enhanced germination and growth of the plants (beans, pumpkins, papayas, and botellas). Also, no negative impacts of the CCAs to the plant germination and growth were observed (Hernández, 2009a). CCAs reduced more phosphate concentrations when high dosage, big size CCAs and low flow was applied. Furthermore, the temperature did not affect significantly on reduction capacity of CCAs. Therefore, the water quality parameters did not show any detrimental effects on groundwater quality through CCAs amendment and promotes its utilization for open pit restoration as a subsoil substitute (Latorre, 2010).

2.6 REMOVAL OF HEAVY METALS

Heavy metals are actually the most important pollutants in source and treated water, and are becoming a severe public health problem (Wang and Wu, 2006). Important studies have been conducted to accomplish an efficient treatment method to reduce the concentration of heavy metals found in landfill leachate (Fan et al., 2006). Safari and Bidhendi (2007) proposed an in situ treatment where the daily cover as the main component of the system is considered a major requirement for isolating waste from the surrounding environment and the use of daily cover as a medium for the reduction/elimination of certain constituents in leachate. Safari and Bidhendi (2007) indicated that the effect of lime in increasing the pH of the leachate in the pore spaces of the soil could be considered the predominant mechanism for removal of metals (Zn and Mn) by precipitation reactions. But, an extensive increase in the pH values of the effluents can be inappropriate in terms of any biological activity (Safari and Bidhendi, 2007).

The removal of heavy metal is possible by different techniques such as chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption. Coal combustion byproduct (fly ash) was studied as a potential adsorption material for the treatment of wastewater containing heavy metals. Mohan and Gandhimathi (2009) did adsorption experiments in alkaline pH (around 8.1) greater than the point of zero charge of the fly ash used (6.9) so that the fly ash was adsorption mechanism. They concluded that the fly ash was very effective as an adsorbent for lead and cadmium compared to other heavy metals and the use of fly ash was recommended before discharging the treated leachate into nearby water courses (Mohan and Gandhimathi, 2009). González et al. (2010) concluded that the main involved mechanism could be precipitation during Cu^{2+} removal, corroborated by the formation of the posnjakite mineral phase. For the removal of Pb^{2+}, due to the high pH values, it was possible to attribute a precipitation process, although a precipitated mineral phase was visually not detected (González et al., 2010). In the fly ash, both precipitation and/or adsorption would be involved in the removal of heavy metals because precipitation of the heavy metals resulted from the presence of calcium hydroxide, and adsorption was due to the presence of silica and alumina available in the fly ash (Wang and Wu, 2006).

Hong et al. (2009) evaluated coal fly ash and synthetic coal fly ash aggregates as low cost reactive media for the remediation of groundwater contaminated with zinc. The material called synthetic coal fly ash aggregates were prepared by mixing coal fly ash, sodium silicate, and deionized water. These materials have strong capacities for the removal of zinc from water by adsorption and precipitation but the elevated pH of the effluent and variable leaching characteristics of the materials generate negative environmental impacts. Therefore, its use as a reactive media that needs to be evaluated below the groundwater table (Hong et al., 2009). Calcium oxide (CaO) content is effective in determining the alkalinity of the solution than their total basic constituents content and the removal of the cadmium and lead is found directly proportional to their CaO contents (Erol et al., 2005). The results of the SEM showed that the metal hydroxides were precipitated on the fly ash samples (Erol et al., 2005).

Similarly, Lin and Yang (2002) made experiments using coal bottom ash as an adsorbent for the removal of pollutants in wastewater and landfill leachate. In the experiments copper and COD were used and they concluded that high pH solutions increased copper removal efficiency but decreased COD removal efficiency. Also, in treating landfill leachate, the removal efficiency was dependent on pollutant type (Lin and Yang, 2002).

2.6.1 *Point of Zero Charge*

The pH where the net total particle charge is zero is called the point of zero charge (PZC), which is one of the most important parameters used to describe variable charge surfaces (Appel et al., 2003). The PZC is achieved when the charge by the positive surface groups is equal to that by the negative ones. The PZC value characterizes surface acidity: when particles are introduced in an aqueous environment their surface charge is positive if solution pH is less than PZC, whereas it is negative if solution pH is greater than PZC (Reymond and Kolenda, 1999).

The point of zero charge is a very important parameter that plays a crucial role in many chemical phenomena such as adsorption, interactions between particles in colloidal suspensions, coagulation, dissolution of mineral, and electrochemical phenomena (Bourikas et al., 2003). The PZC is a very useful parameter for several applications; therefore several methods have been developed so far for determining it. Methods such as: the classical potentiometric titration technique, the mass titration technique, and the immersion technique have been used widely (Bourikas et al., 2005).

The mass titration method allows evaluating the PZC for aqueous suspensions of an oxide by increasing mass fractions of solid. The pH of suspensions tends towards the

PZC of the solid when the oxide concentration tends towards an infinite value. Therefore, the method is based on the postulation that PZC value is associated with the pH of minimal solubility that allows to deduce PZC value from pH at equilibrium of a concentrated suspension (Reymond and Kolenda, 1999).

3. MATERIALS AND METHODOLOGY

The primary goal of this research was to develop and evaluate the performance of landfills with CCAs as an ARDC material. The goal of this research has been accomplished through a methodology involving laboratory experiments with the development of lab-scale physical landfill models (PLMs) and the comparison of biochemical characteristics of leachate to establish relationships between biological decompositions of solid wastes and subsequent physical settlement. Smaller physical landfill models (SPLMs) with CCAs as daily cover were also evaluated in terms of CCA application rate and packing density. Also, point of zero charge of CCA was determined to better understand mechanisms involved with heavy metal removal. Enhanced microbial activity in the presence of CCAs was also verified in a separate experiment.

In this chapter, the materials and methods used for the corresponding laboratory experiments are discussed. Specifically, detailed discussion made on the methodology applied to determine the significant differences in leachate quality of different experiments, settlements, biogas production, and other important variables in the performance of landfills with CCAs as an ARDC employed in this research.

3.1 MATERIALS

This section describes the materials used in this research: CCAs, sand, gravel, and artificial solid wastes. Also, it details the consideration related to the design, construction, and development of the PLMs, SPLMs, and the environmental chamber.

3.1.1 *Coal Combustion Byproducts Aggregates (CCAs)*

Coal combustion byproducts aggregates are a solidified mixture of fly and bottom ashes with water. This material gains strength with time due to cementitious reactions (Pando and Hwang, 2006). CCAs were obtained from a local coal-burning power plant (AES Puerto Rico). AES Puerto Rico is a company that uses the combustion of coal in circulating fluidized bed (CFB), which is considered one of the cogenerators of the world's cleanest coal to meet the social needs of electricity production at the lowest cost in the market because this technology has the ability to reduce air emissions and other pollutants (cleanest combustion) and contributing to the diversification of energy sources (Siberón, 2005). The CFB technology for coal combustion adds limestone to capture sulfur and reduce emissions of sulfur dioxide (Siberón, 2005). The company uses coal with low sulfur (<1%) and the byproduct of the process is a waste composed of non-reacted coal ash that has not calcined, various minerals and high limestone quality. AES PR mainly produces two types of coal ash: fly ash and bottom ash. By mixing these two products with water, AES PR also produces a third by-product referred to as manufactured aggregate (CCAs) (Pando and Hwang, 2006).

The AES PR has a facility to manufacture CCAs located in Guayama (Puerto Rico). In this facility, the ashes are mixed with treated effluent from a wastewater treatment plant to produce a solution of 74% solids known as conditioned ash which is transported by belt to an area where conditioned ash is compacted and cured for a period of 7 to 14 days to form CCAs. The shredded CCAs are loaded onto cargo trucks for sale in the island or in barges for export (Siberón, 2005). Results of CCAs chemical analyses are summarized in Table 2 (Kochyil and Little, 2004).

To determine possible hazardous characteristics of CCAs an analysis for toxicity characteristics leaching procedure (TCLP) was made by an EPA-certified analysis laboratory (EQLAB, 2005) in Puerto Rico. The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. In the TCLP analysis simulates landfill conditions. Over time, water and other liquids percolate through landfills. The percolating liquid often reacts with the solid waste in the landfill, and may pose public and environmental health risks because of the contaminants it absorbs. In the TCLP procedure the pH of the sample material is first established, and then leached with an acetic acid/sodium hydroxide solution at a 1:20 mix of sample to solvent (US-EPA, 1992). Results of the TCLP demonstrated that chemical concentrations are well below maximum contaminant levels (MCLs) (Table 3).

Table 2 Chemical Composition of CCAs (Kochyil and Little, 2004).

CCA Components	% Weight
Silica, SiO_2	34.79
Alumina, Al_2O_3	11.97
Ferric Oxide, Fe_2O_3	4.19
$SiO_2 + Al_2O_3 + Fe_2O_3$	**50.95**
Titania, TiO_2	0.51
Lime, CaO	29.67
Magnesia, MgO	1.11
Potassium Oxide, K_2O	0.76
Sodium Oxide, Na_2O	1.52
Sulfur Trioxide, SO_3	14.66
Phosphorus Pentoxide, P_2O_5	0.32
Strontium Oxide, SrO	0.23
Barium Oxide, BaO	0.24
Manganese Oxide, Mn_3O_4	0.03
Undetermined	0
Alks, As Na_2O, Dry Coal Basis	1.76
Base: Acid Ratio	0.79

Table 3 Concentrations of Trace Elements from CCAs (EQLAB, 2005)

Elements	EPA MCL (mg/L)	Lab Results (mg/L)
Arsenic	-	< 0.005
Barium	100	0.230
Cadmium	1	< 0.002
Chromium	5	0.028
Lead	5	< 0.005
Selenium	1	< 0.005
Silver	5	< 0.002
Mercury	0.2	< 0.0004
pH	2 < pH < 12.5	11.9

The physical properties of the CCAs were determined by Kochyil and Little (2004). The CCAs have a similar gradation as a natural gravel, with particle sizes ranging from gravel (diameter between 4.90 and 50.00 mm) to fine sand (diameter between 0.075 and 0.43 mm) with very low percentages of silt and clay-sized particles; the average specific gravity for the coarse fraction was found to be about 1.16 (larger than 2.36 mm), while the fine fraction had a specific gravity of about 2.69 (smaller than 2.36 mm). The low specific gravity of the coarse aggregate is due to the high void content of this fraction and the high void ratio content of the coarse aggregate was found to be related to a structure of an agglomerate of particles. These large particles are actually agglomeration of finer particles that were found to be susceptible to abrasion and breakdown. The specific gravity value obtained for the fine fraction is consistent with typical values found in natural aggregates (Kochyil and Little, 2004). Results from their gradation experiment (Figure 3) are presented in Table 4. From the gradation results it can be seen that the AES CCAs has a gradation similar to sandy gravel.

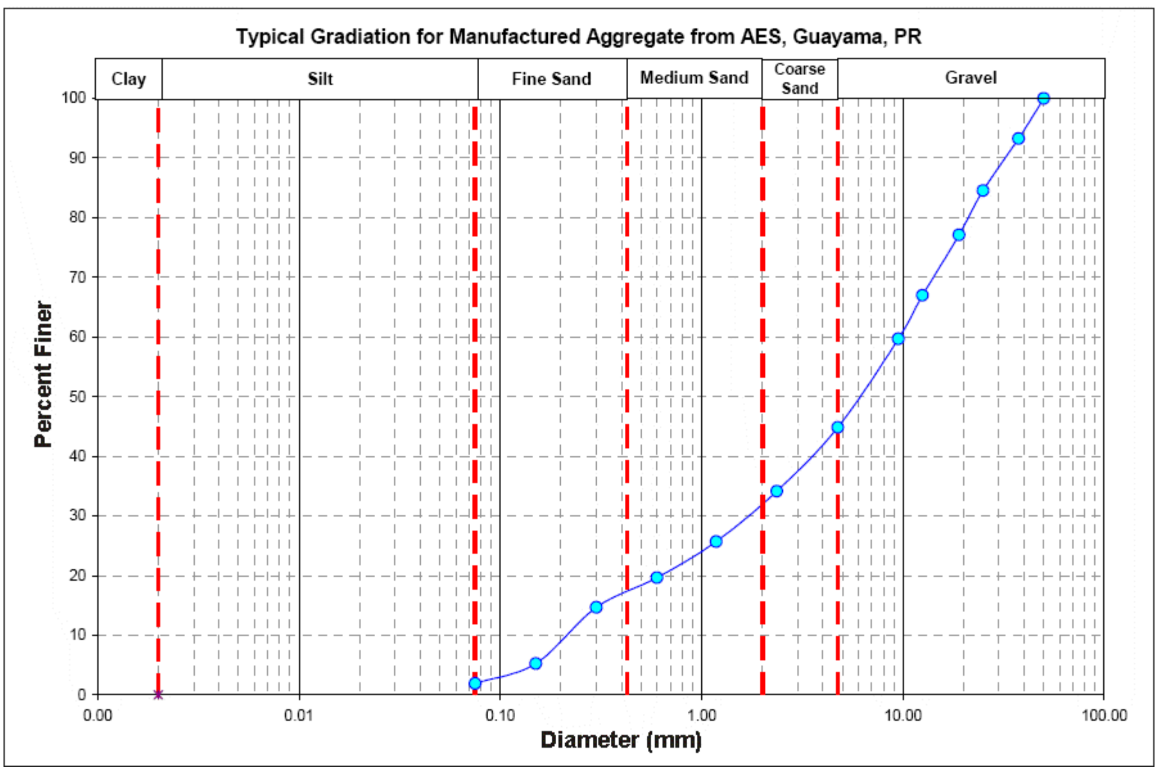

Figure 3 Gradation curve for the AES CCAs (Kochyil and Little, 2004).

Table 4 Gradation for the AES CCAs (Kochyil and Little, 2004).

Sieve Identification	Sieve Size (mm)	Total % passing
2 in	50.8	200
1.5 in	37.5	93.27
1 in	25.4	84.55
0.75 in	19	77.12
0.5 in	12.5	66.99
3/8 in	9.5	59.7
#4	4.75	44.84
#8	2.36	34.16
#16	1.18	25.72
#30	0.6	19.65
#50	0.3	14.66
#100	0.15	5.24
#200	0.075	1.92
P-200	0	0.00

Raw aggregates with various sizes were first oven-dried at 105^{o}C overnight and then crushed using a mechanical crusher. Sieving was performed to collect the CCAs sizes of 2.36 ~ 9.53 mm for facilitating the laboratory-scale experiment (Figure 4).

Figure 4 Sand and CCAs Used for Daily Covers in this Study.

3.1.2 *Sand and Gravel*

Natural clean sand sampled from Isabela, PR was used as the daily cover of the control PLM. Its physicochemical properties were previously characterized in the Environmental Laboratory of the Department of Civil Engineering and Surveying (Molina et al., 2006) in accordance to the methods recommended by the Soil Science Society of America (Dane, 2002; Sparks, 1996). It was determined that the sand was composed of 92.6% sand and 7.4% of fines (silts and clays). The sand properties are listed in Table 5 and Table 6:

Table 5 Physical Parameters of Isabela Sand (Molina et al., 2006).

Physical Parameters	
USCS Classification	SP
Specific Gravity	2.83
Specific Surface Area (m^2/g)	16.87
Mineralogy	Quartz/calcite

Table 6 Chemical Composition of Isabela Sand (Molina et al., 2006).

Chemical Composition	
Ca (ppm)	275.00
Mg (ppm)	36.40
Na (ppm)	36.40
HCO_3^-(mg/kg)	2.00
CO_3(mg/kg)	< 1.00
Cl^- (ppm)	59.00
Organic Carbon (%)	0.07
Soil Organic Matter (%)	0.47
TFe (mg/kg)	6125.70
TN (mg/kg)	< 713.00
pH	8.83
Cation Exchange Capacity (mg/100g)	2.10

Gravel was used as the supporting materials on the bottom of the PLMs and SPLMs was purchased from a local hardware store. They was sized from 1/2" (12.5 mm) to #8 mesh (2.36 mm) and washed prior to use.

3.1.3 *Artificial Solid Wastes*

Artificial solid wastes simulating real solid wastes produced in Puerto Rico were prepared in accordance to the "Final Report Waste Characterization Study," prepared by Autoridad de Desperdicios de Sólidos (ADS, 2003). This report contains the characterization of solid wastes for the months of June and September 2003 in Puerto Rico (Table 7). The final composition of the artificial solid wastes used in this research was determined based on the average values given in Table 7.

Table 7 Waste Characterization Results of Solid Waste Discards in Puerto Rico: June and September 2003 (ADS, 2003).

Component	Description	% Weight (June 2003)	% Weight (Sept 2003)	%Average
Plastic	Type 1-Polyethylene	1.10	0.80	0.95
	Type-HDPE	2.90	3.00	2.95
	Type 3-7 (PVC, LDPE, PP, PS, Mixed)	6.50	6.70	6.60
Paper Cardboard	High quality paper	1.30	1.00	1.15
	Low quality paper	8.70	8.70	8.70
	Corrugated	9.30	8.80	9.05
Metals	Ferrous Metals	9.40	9.40	9.40
	Non- Ferrous Metals	1.10	0.70	0.90
Yard	Yard waste	20.40	22.10	21.25
Organic	Organic waste	12.90	12.80	12.85
C&D	Construction debris	17.10	14.90	16.00
Glass	All types glass	2.40	2.40	2.40
HHW	Household Hazardous Waste	0.50	0.50	0.50
Other	Not Otherwise Defined	6.30	9.0	7.65

Raw materials were collected to prepare artificial mixtures solid wastes. They included: plastic (types 1 to 7), paper, cardboard, metals, glass, and organics (Figure 5 to Figure 8). The organic materials were replaced with composts which were obtained from a composting plant in the municipality of Mayagüez. The raw materials were cut into smaller pieces (area = 1 cm^2) to accommodate in a lab-scale PLMs.

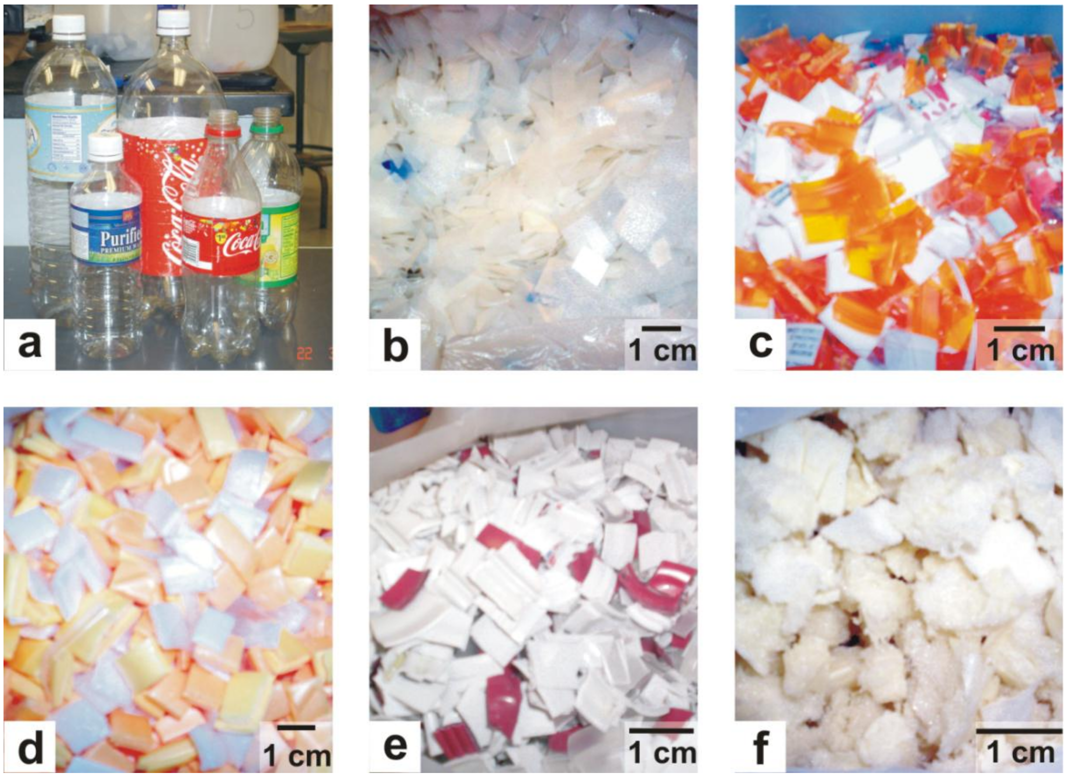

Figure 5 Plastics: Type 1 (a), Type 2 (b), Type 5 (c), Type 6 (d) and Type 7 (e and f).

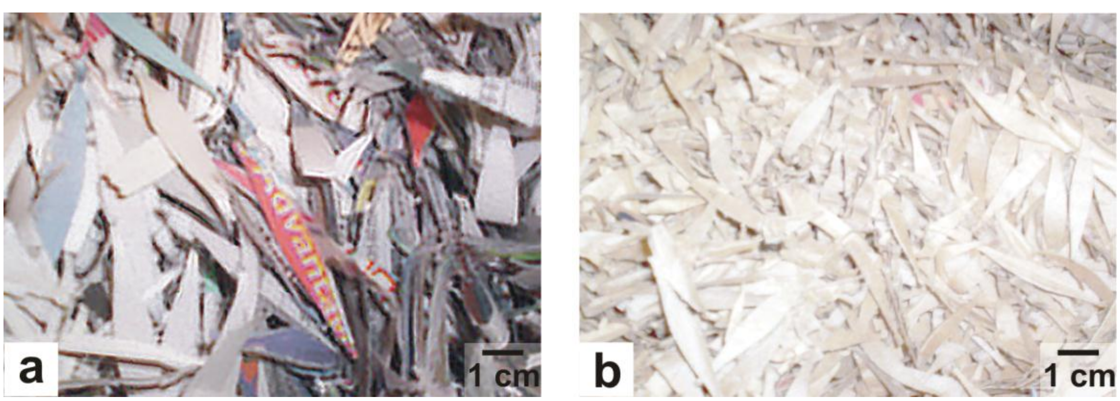

Figure 6 High and Low Quality Paper (a) and Corrugated (b).

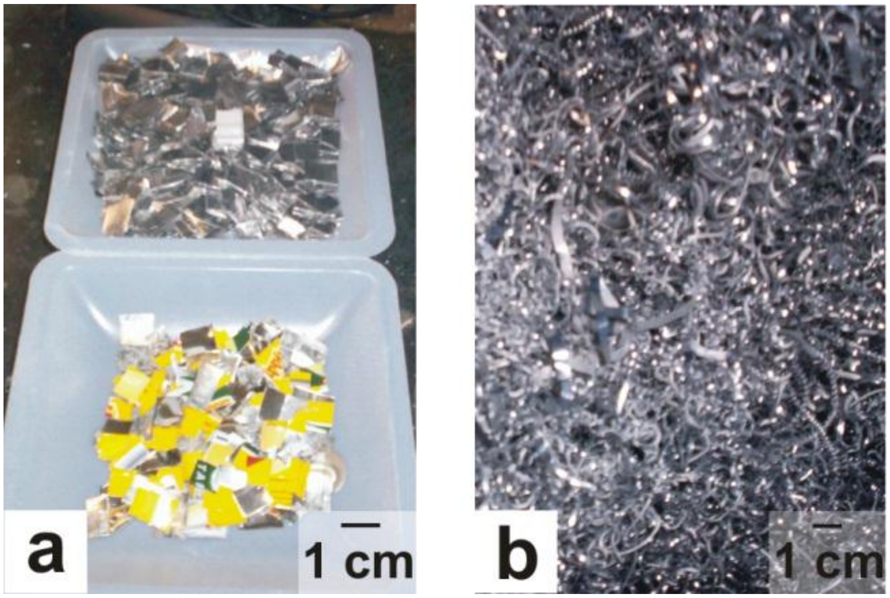

Figure 7 Ferrous (a) and No Ferrous Metals (b).

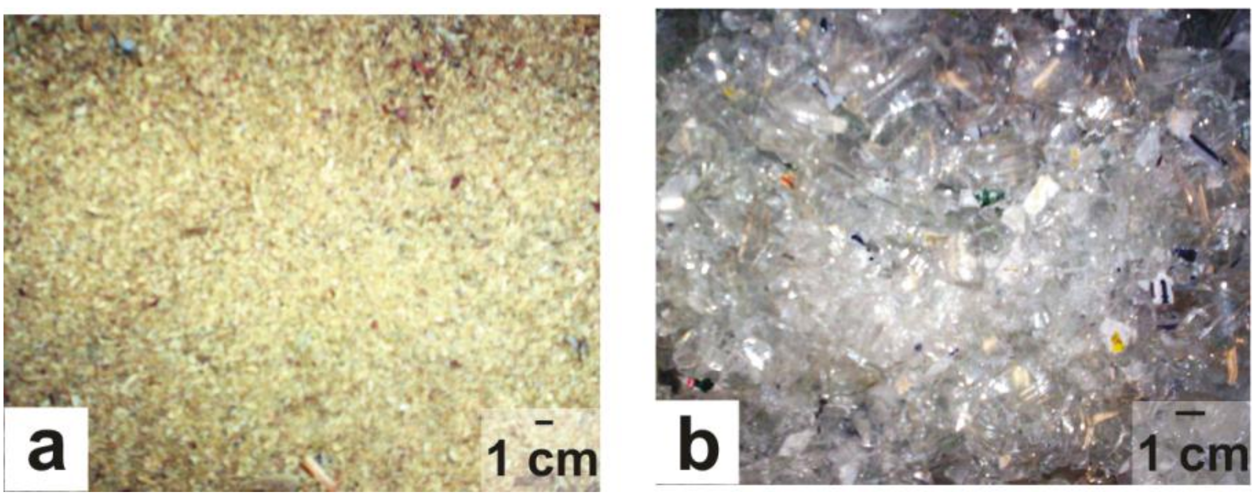

Figure 8 Construction Debris (a) and Glass (b).

The above listed materials were mixed according to the compositional fractions shown in Table 7, incubated for a week and then packed in the PLMs and SPLMs (Figure 9).

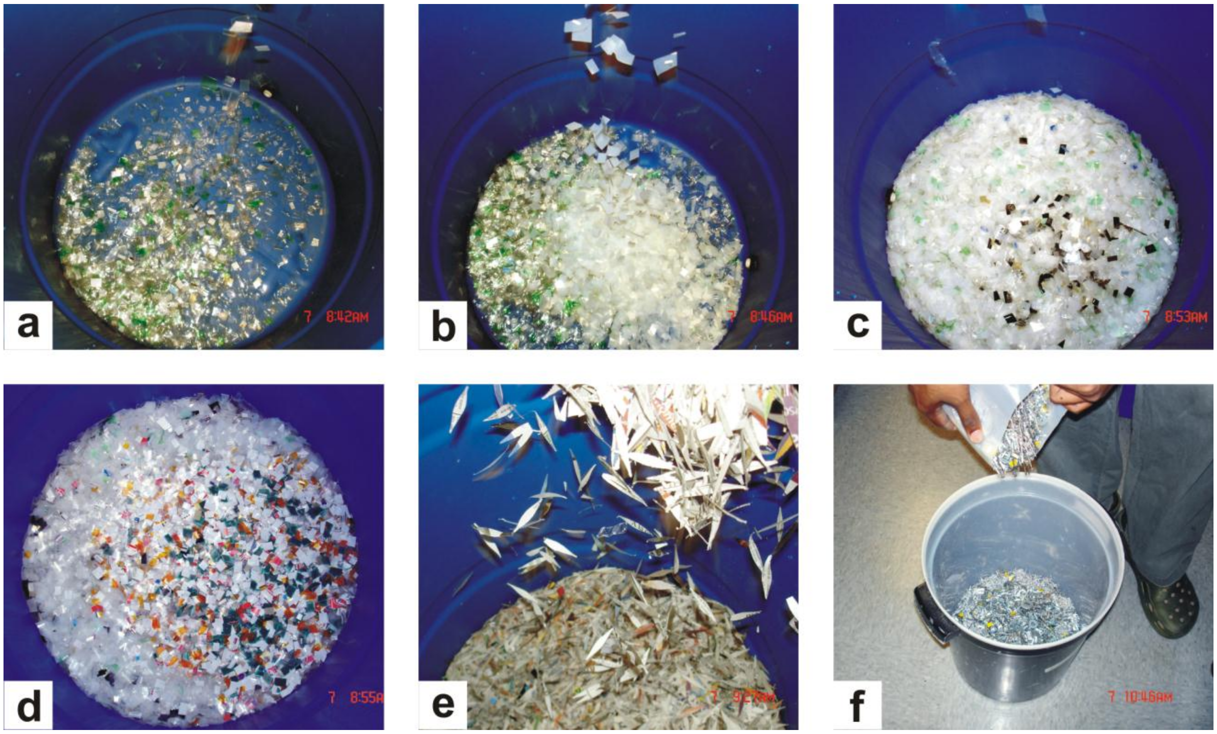

Figure 9 Mixing Synthetic Solid Waste Materials: Plastic Type 1 (a), Type 2 (b), Type 6 (c), Type 7 (d), Low Quality Paper (e), and No Ferrous Metals (f).

3.1.4 *Environmental Chamber*

An environmental chamber (Figure 10) was constructed to house the PLMs and SPLMs and to facilitate hydrologic events and gas collection. The environmental chamber was isolated and equipped with a thermal circulator in order to maintain a constant temperature at 30°C (Figure 12), to enhance landfill biochemical processes so as to facilitate the quantification of the effectiveness of CCAs as an alternative reactive daily cover (ARDC) in a shorter period of time. The chamber also has a simulation system of the tropical water spray and gas collection (Figure 11). The tropical water spray was used to simulate precipitation events and was composed of a pump connected to a PVC pipe and a filter reaches the cap of the top in the PLMs to be connected with the nozzle (Model: PJ-10 in steel stainless, size 1/8”) located within each of the PLMs. The gas collection system consisted of flexible tubing exiting the top of the PLMs connected to the gas flowmeter which measures the velocity of the gas produced and accumulated volume was measured by the totalizer, then the gas is in a pickup tedlar bag. For the

SPLMs experiment, the reactors were located inside the chamber to maintain the same conditions of the PLMs.

Figure 10 Environmental Chamber and Physical Landfill Model.

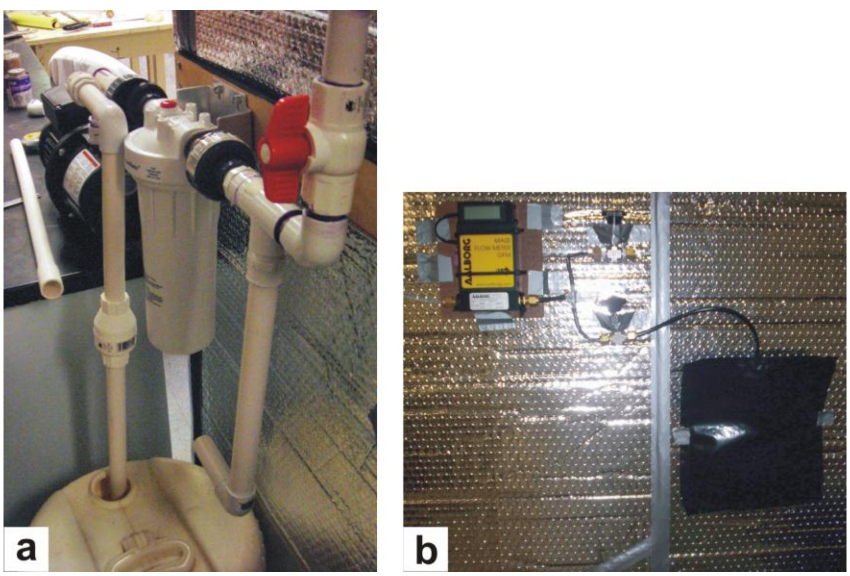

Figure 11 Water Spraying System (a) and Gas Collection System (b).

Figure 12 Thermal Circulator inside the Environmental Chamber.

3.1.5 *Physical Landfill Models*

Biochemical decomposition and settlement were simulated using PLMs in a temperature-controlled environmental chamber (Figure 10). The PLMs were constructed using PVC tubes with a diameter (d) of the 30.48 cm (12 in) and 99.06 cm (39 in) length (L). The PLMs were equipped with a gas extraction port and a water spraying system on the top and a leachate drain port on the bottom (Figure 11). The gas extraction port consisted of a 0.635 cm (1/4 in) teflon tube. For settlement monitoring, the PLMs had a side-wall window of transparent Plexi-glass.

One PLM used a soil cover (Isabela sand) over compacted waste, whereas another PLM used CCAs as an alternative daily cover (ARDC). The orders of the layers in the PLMs were (from bottom to top): gravel, sand, solid wastes, daily cover (CCAs or Sand), solid wastes, daily cover (CCAs or Sand), solid wastes, daily cover (CCAs or Sand), and sand as the final layer. Table 8 and Table 9 show the packing density of each layer of the PLMs.

After packing (filling), the reactors with each of the layers were sealed inside the environmental chamber at a constant temperature before they were subjected to different hydrological cycles explained later in the experimental methods section.

Table 8 Configuration of Control PLM.

	Layer Thickness (cm)	Mass (kg)	Density (kg / m^3)
Sand	14.5	21.62	2043.29
MSW	20.0	5.99	410.29
Sand	4.0	3.60	1233.97
MSW	19.1	5.99	429.62
Sand	3.6	3.60	1371.08
MSW	20.8	5.99	394.13
Sand	3.1	3.60	1,618.32
Gravel	2.0	7.38	5,057.65

Table 9 Configuration of CCAs PLM.

	Layer Thickness (cm)	Mass (kg)	Density (kg / m^3)
Clean Sand	10.4	15.61	2057.42
CCAs	3.5	1.47	575.47
MSW 1	20.0	5.99	410.29
CCAs	3.6	1.47	559.48
MSW	19.0	5.99	431.88
CCAs	3.2	1.47	629.42
MSW 3	20.8	5.99	394.51
Sand	3.2	3.59	1,536.64
Gravel	2.0	7.38	5,057.65

3.1.6 *Smaller Physical Landfill Models (SPLMs)*

Three reactors were built to scale with respect to the original PLMs (Figure 13). One of the reactors used densities to the CCAs PLM (ρ_{SPLM-1} = 742.65 Kg/m^3), the other used densities similar to the control PLM (ρ_{SPLM-2} = 1551.00 Kg/m^3), and the third had a density greater than CCAs PLMs (ratio 1:1.44 and ρ_{SPLM-3} = 849.65 Kg/m^3). The daily cover used for the SPLMs was CCAs with the objective to determine the quality of the leachate in them. The order of the layers in the SPLMs were (from bottom to top): gravel, sand, solid wastes, daily cover (CCAs), solid wastes, daily cover (CCAs), solid wastes, daily cover (CCAs), and sand as the final layer.

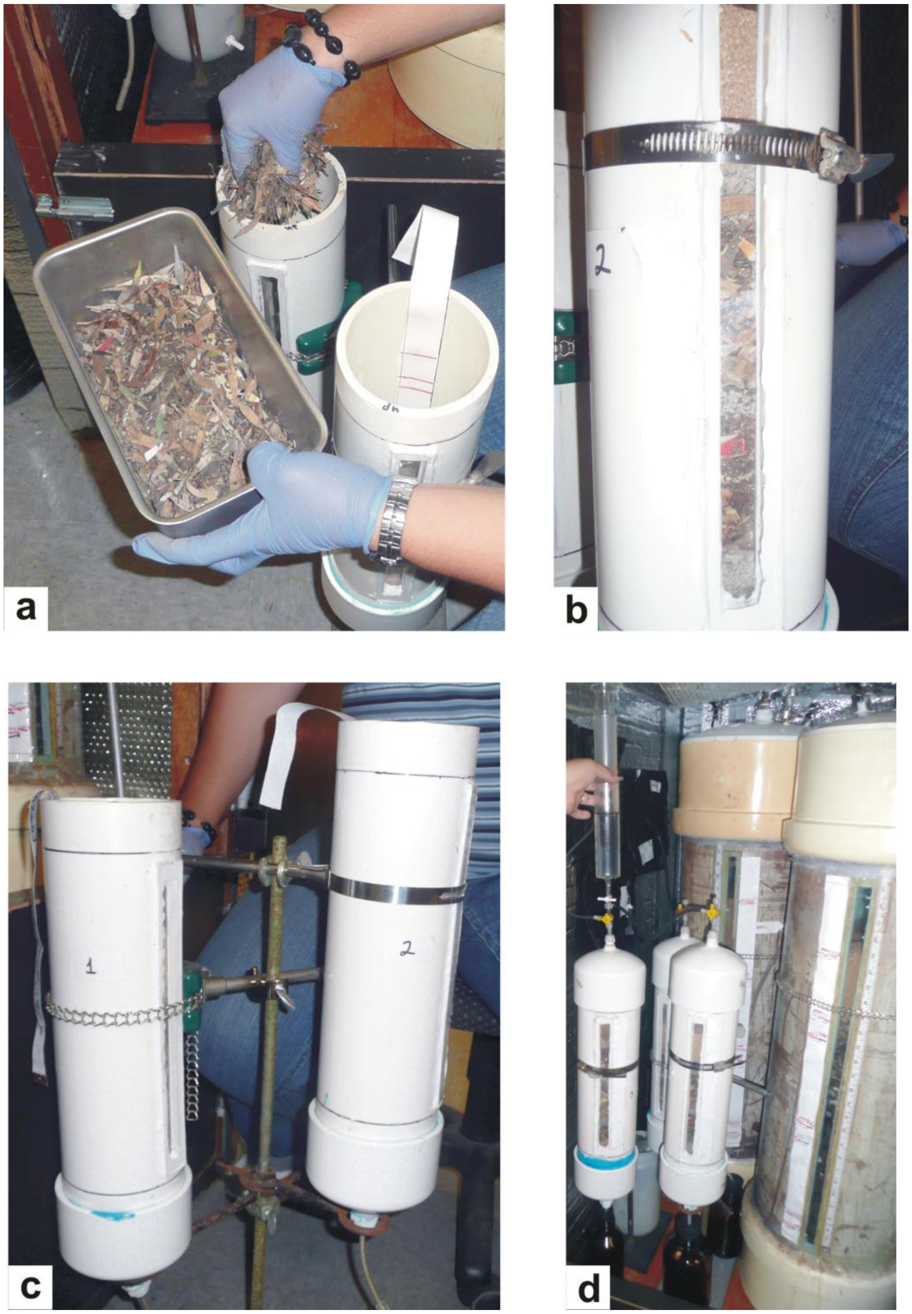

Figure 13 Construction of SPLMs.

The dimensions of the SPLMs were 40.0 cm (15.7 in) of high and 10.2 cm (4.0 in) in radius. The packing densities of the three small reactors are found in Table 10 to Table 12 as follows:

Table 10 Configuration of SPLM-1.

	Layer Thickness (cm)	Mass (kg)	Density (kg / m^3)
Sand	3.47	0.58	2,057.96
CCAs	1.17	0.05	727.38
MSW	6.67	0.22	410.18
CCAs	1.20	0.05	706.15
MSW	6.33	0.22	431.97
CCAs	1.07	0.05	794.42
MSW	6.93	0.22	394.59
Sand	1.07	0.13	3,851.83
Gravel	5.08	2.08	1,444.93

Table 11 Configuration of SPLM-2.

	Layer Thickness (cm)	Mass (kg)	Density (kg / m^3)
Sand	3.50	0.58	2,043.30
CCAs	1.33	0.22	2,037.97
MSW	6.67	0.22	410.18
CCAs	1.33	0.13	1,238.69
MSW	6.37	0.22	429.51
CCAs	1.20	0.13	1,376.33
MSW	6.94	0.22	394.21
Sand	1.02	0.13	5,261.78
Gravel	5.10	2.09	1,266.10

Table 12 Configuration of SPLM-3.

	Layer Thickness (cm)	Mass (kg)	Density (kg / m^3)
Sand	3.50	0.87	2,058.10
CCAs	1.20	0.08	825.38
MSW	6.70	0.33	502.03
CCAs	1.20	0.08	825.38
MSW	6.30	0.33	534.30
CCAs	1.10	0.08	898.18
MSW	6.90	0.33	488.73
Sand	1.10	0.20	3,916.77
Gravel	7.60	3.14	1,155.87

3.1.7 *Instruments for Leachate Quality Analysis*

The leachate from each of the PLMs and SPLMs was collected and analyzed for: physical parameters (volume of leachate produced, pH, oxidation-reduction potential, color, turbidity, conductivity and settlement), organic constituents (chemical oxygen demand and volatile acids), inorganic constituents (nitrate, hardness, total phosphorus, total nitrogen, orthophosphate and alkalinity) and biological parameters (biological oxygen demand, dissolved oxygen, and biogas production). The instruments used for leachate quality analysis are listed in Table 13.

The recollection of the leachate in a container was realized using an output port in the bottom of the each PLM. Then, the volume of leachate was measured and homogenized to begin the analysis. Samples of leachate from a volume of 10.0 mL were used to measure: pH, ORP, heavy metals, hardness, specific conductivity, nitrate, and dissolved oxygen, which are made using selective electrodes, thus placing the electrode and an expected time of three minutes and the measurement was taken. In the case of total phosphorus, orthophosphate, total nitrogen, COD and heavy metals, HACH products were used, therefore, the methods: HACH 8190, HACH 8178, HACH 10071, HACH 8000 and HACH 8317, were followed correspondingly.

The Atomic Absorption Spectrometer, model Perkin Elmer AAnalyst 400 was used to measure the heavy metals concentrations (Cd and Pb) with LDL of the 0.2 mg/L. The turbidity used was a model 2020 Turbidimeter (La Motte code 1799), an equipment easy and reliable, where the sample is taken in a cell and then measure. For biochemical oxygen demand (BOD), the standard method 5210 B (5-day BOD Test) of the EPA was used. For the alkalinity, EPA method 310.2 was used; it is a standard method of the titration. The Membrane Filtration Heterotrophic Plate Count Method is a fast, simple way to estimate bacterial populations in water, the Method 8242 of the HACH was used.

Table 13 Physiochemical and Biological Water Quality Parameters Monitored for Leachate Collected.

Parameter	Instrument/Method	Detection Limit Range
pH	2- Wire Transmitter pH/ORP (Eutech Instruments) Model: Alpha pH 500	0 to 14.00 pH
Oxidation Reduction Potential (ORP)	2- Wire Transmitter pH/ORP (Eutech Instruments) Model: Alpha pH 500	-1,000 to 1,000 mV
Heavy Metals (Pb, Cd)	Cole Parmer Combination Ion Selective Electrodes, Pb^{2+*} Model: EW-27504-20 Cole Parmer Combination Ion Selective Electrodes, Pb^{2+*} Model: EW-27504-04 HACH Lead Track (Pb) (HACH 8317) Atomic Absorption Spectrometer Perkin Elmer AAnalyst 400	LDL 0.2 mg / L LDL 5 µg / L as Pb
Total Phosphorus	PhosVer[3] with Acid Persulfate Digestion Test'N Tube Procedure (HACH 8190)	0 to 3.50 mg / L PO_4^{3-}
Orthophosphate	Amino Acid Method (HACH 8178)	0.23 to 30.00 mg / L PO_4^{3-}
Hardness	Cole Parmer Combination Ion Selective Electrode, Water Hardness Model: EW-27504-34	LCL 0.4 mg / L Ca^{+2}
Turbidity	2020 Turbidity meter (La Motte code 1799)	0 to 1,100 NTU
Specific Conductivity	EC Test 11 + Multi Range (Oakton Instruments) Model: DO-35634-30	0 to 2000 µS 0 to 20.00 mS
Nitrate	Cole Parmer Combination Ion Selective Electrode, Nitrate Model: EW-27504-22	LCL 0.6 mg / L as NO_3^-
Total Nitrogen	Test'N Tube (HACH 10071)	0.0 to 25.0 mg / L as N
Chemical Oxidation Decomposition (COD)	Reactor Digestion Method (HACH 8000)	0 to 1,500 mg / L COD
Biological Oxygen Demand (BOD)	5-Day BOD Tests	N/A
Dissolved Oxygen	Oakton, Waterproof PD 650 Meter only Model: EW-35432-02	0 to 20.0 mg / L
Alkalinity	Titration Method	N/A
Heterotrophic Bacteria Counts	Membrane Filtration (0.45 um)	> 50 too many to count
Optical Density	UV/VIS Spectrometer Perkin Elmer Lambda 20	N/A

Note: Lower Detection Limit (LCL).

Table 14 Parameters Measured for Generated Gases and Waste Bed Physical Settlement.

Phase	Parameter	Instrument/Method
Gas	Volume	Gas Flow meter AALBORG Model: EW-32661-10 Totalizer AALBORG Model: EW-32661-11
Solid Waste	Settlement	Scaled Plexi-glass

In order to measure the optical density, the UV/VIS Spectrometer Perkin Elmer Lambda 20 at wavelength 600 nm with glass cells of the 1.0 mL was used. Optical densities were used to represent an indirect measurement of biomass concentration (Griffiths et al., 2011). For the gas phase samples, the gas velocity at an instant and the accumulated volume was measured with the totalizer the. For solid waste settlement, the measurements were made using a metric scale placed in the window of each PLM.

3.2 EXPERIMENTAL METHODS

This section describes the methodology used throughout this research for the development of the PLMs and SPLMs, microbial activities, the point of zero charge and the removal of heavy metals.

3.2.1 *Evaluation of Physical Landfill Models (PLMs)*

For the simulation of environmental conditions in a landfill, the PLMs were subject to four stages with respect to hydrological sequences. The first two sequences represented rainfall simulations. In these stages, the rainfall conditions of Mayagüez were simulated, highly intense (2 inches per hours). The third sequence represented a dry period and the last sequence was leachate recirculation. A detailed description of each sequence is shown below:

- First Sequence: This stage represented a wet period; the rainfall was applied at an intensity of 2 inches per hour on two different days. Water was sprayed with a nozzle installed on the top cover of the PLMs on Mondays for an hour and Fridays for a half hour. The nozzle used was a stainless steel male pipe size 1/8" (Model: PJ – 10 Bete). This stage lasted for five weeks, and was defined as the wet period (WP).

- Second Sequence: The rainfall was applied only one day at an intensity of 2 inches per hour for half hour. This period lasted four weeks, representing a moderate period (MP).
- Third Sequence: This stage represents dry period (DP), therefore, no rainfall. This stage was run for three weeks.
- Fourth Sequence: This stage was leachate recirculation. This stage corresponded to five weeks, where the collected leachate in the other of sequence was recirculated to the PLMs. The recirculation rate used was 800 mL/min for 4 minutes and at the last recirculation it lasted for 12 minutes.

The hydrologic simulation was repeated in different cycles: the first cycle was composed of wet, moderate, dry, and recirculation periods; second and third cycles were composed of dry, moderate, and recirculation periods; and the last cycle was composed of dry and recirculation periods (in this recirculation period, the duration was more time and more volume of leachate). The leachate samples were collected weekly and leachate quality parameters were monitored as shown in Table 13. Biogas production was also monitored using the totalizer flowmeter and physical settlement was assessed through the side-wall window on the PLMs (Table 14). The hydrologic simulation was important for the determination of the effects hydrologic cycles had the on behavior of landfill biochemistry.

3.2.2 *Evaluation of Smaller Physical Landfill Models (SPLMs)*

For SPLMs the environmental conditions simulated were similar to PLMs. They were subject to three stages with respect to hydrological sequences. First sequence represented rainfall simulations. In this stage, the rainfall condition was represented with a volume of 200 mL (value represents the condition of 2 in/h) of distilled water. The second sequence represented a recirculation leachate period. And the third sequence was the dry stage (no rainfall). The three stages: moderate, recirculation and dry period were chosen for the most significant quality of leachate in PLMs. A detailed description of each sequence is shown below:

- First Sequence: This stage represented a moderate period; the rainfall was applied inside of the SPLMs in one day. Water was sprayed with a nozzle installed on the top cover of the SPLMs. This stage lasted for four weeks.
- Second Sequence: This stage was leachate recirculation. In this stage, which lasted five and ten weeks, the collected leachate was recirculated to the corresponding PLM.
- Third Sequence: This stage was for a dry period (no rainfall). This stage ran for three weeks.

For the SPLMs the sequence of hydrologic simulation was repeated in two cycles: the first cycle was composed of moderate, recirculation, and dry period; and the last cycle was composed of recirculation and dry period. The leachate samples were collected weekly and leachate quality parameters were monitored as shown in Table 13. Biogas production was also monitored daily.

3.2.3 *Removal of Heavy Metals*

An important aspect in the use of CCAs as an ADC is the possibility of using it as a reactive daily cover for heavy metals removal. The main mechanisms of the removal of heavy metals in aqueous solution are ion exchange, surface precipitation, bulk solution precipitation and adsorption. Usually, the pH value is the most important parameter that determines the predominant mechanism (Erol et al., 2005). Therefore, various experiments were conducted to explore this aspect, such as: smaller physical landfill models with heavy metals solution injection, batch reactors and estimation of point of zero charge. These experiments are explained below:

3.2.3.1 *Smaller Physical Landfill Models with Heavy Metals Solution Injection*

For this experiment, aqueous solutions of Cd^{2+} and Pb^{2+} were prepared from analytical reagent grade (Brand: Orion) with a concentration of 100 mg/L. SPLM-1 and SPLM-2, which were injected with a solution, composed of leachate, and cadmium and lead. The total volume injected was 100 mL: 60 mL of leachate, 20 mL of the cadmium solution and 20 mL of the lead solution; this was mixed and injected in the SPLMs (1 and 2). The leachate in the SPLM-1 and SPLM-2 was analyzed for heavy metals and other parameters (leachate volume, pH, turbidity, conductivity, COD, BOD, and biogas production). The heavy metals (Cd^{2+} and Pb^{2+}) were determined by an Atomic Absorption Spectrometer Perkin Elmer AAnalyst 400.

3.2.3.2 *Batch Reactors*

For the bath reactor a volume of 200 mL of the aqueous solution of Cd^{2+} and Pb^{2+} (concentration of 100 mg/L) was mixed with 200 grams of CCAs in an Erlenmeyer and placed in a Reciprocal Shaking Bath Model 50 at 150 rpm and constant temperature, 25^{o}C. The mixture was then allowed to separate by gravity and the supernatant liquor was analyzed for pH (Erol et al., 2005), and heavy metals were measured using an Atomic Absorption Spectrometer Perkin Elmer AAnalyst 400.

3.2.3.3 *Estimation of Point of Zero Charge (PZC)*

The point of zero charge (PZC), is a concept relating to the phenomenon of adsorption, and describes the condition when the electrical charge density on a surface is zero. The PZC is an important parameter to recognize the mechanism of removal of pollutants. The experimental method used to calculate the PZC was mass titration. This method increases amounts of the CCAs added to solution in order to obtain suspensions with the following solid content percentage: 0.01 %, 0.1 %, 1 %, 5 %, 10 %, 15 %, 20 %, 25 %, 30 %; 40 %, 50 % and 60 %. In each case, the solid concentration was calculated from the mass of dry solid. The solution used was made of monovalent ions (NaCl and KCl) at different concentrations (0.01 M, 0.1 M and 1.0 M) (Reymond and Kolenda, 1999). Bottles containing CCAs and 100 mL of the monovalent ions solution were sealed and placed in a Reciprocal Shaking Bath Model 50 at a constant temperature of 25^{o}C and 150 rpm.

The pH of suspensions was measured after 24 hours of contact time, time for which equilibrium pH was reached in all the cases. The curves giving the suspension pH value as a function of solid content were plotted. The PZC is the constant pH value achieved in each of the curves of the monovalent ions solution (Reymond and Kolenda, 1999).

3.2.4 *Determination of Microbial Activities*

Experiments were held to verify that the presence of CCAs help increase microbial biomass and consisted of five reactors (Figure 14), the difference between them was the amount of CCAs. Jar test was used at 100 revolutions per minute (rpm) (Figure 14), pH and optical density (OD) in wavelength of the 600 nanometers (nm) were measured at different sampling time (Fang et al., 2009; Juneson et al., 2001; Li et al., 2007). Optical densities were used to represent an indirect measurement of biomass concentration in microbial cell suspensions (Griffiths et al., 2011). The nutrient solutions were prepared as follow: 0.2505 g of $FeCl_2$, 27.5218 g of $CaCl_2$, 22.5553 g of $MgSO_4{\cdot}7H_2O$, and 8.5526 g of KH_2PO_4 more 33.4353 g $Na_2HPO_4{\cdot}7H_2O$ per liter (Clesceri et al., 1998).

Figure 14 Jar Test Used in the Experiment.

The reactors were built in the following way: a control reactor did not have CCAs. The other reactors, 1 to 4 had 5, 10, 15, and 20 grams of CCAs, respectively. The reactors contained 10 mL of each nutrient solution, deionized water (1,958 mL), 5 grams of glucose, bacteria (BOD Seed Inoculum Polyseed, 2 mL) were added; and the line that corresponded to total volume was marked.

Samples with a volume of 5 mL were withdrawn at different times. Microbial biomass were monitored by optical density (OD) (Fang et al., 2009; Juneson et al., 2001; Li et al., 2007), at 600 nm using UV/VIS Spectrometer Lambda 20, then measured the pH and the samples were returned to each of the reactors. For the measures of the optical density, the sample in the glass cells was placed in the UV/VIS Spectrometer. Every twenty-four hours 5.0 grams of glucose were added, and the liquid level was maintained with deionized water.

3.3 STATISTICAL ANALYSIS

Two types of statistical analysis were performed: ANOVA and Pearson correlation. The ANOVA was performed in order to find significant differences between parameters and concentrations of compounds in the leachate of each of the PLMs. The level of significance for the ANOVA was of 5%. The ANOVA null hypothesis (H_0) was to prove if there was no significant difference between the PLMs results.

$$H_o\colon \mu_1 = \mu_2 \qquad (1)$$

And, the ANOVA alternative hypothesis (H_a) was to prove if there was a significant difference

$$H_a\colon \mu_1 \neq \mu_2 \qquad (2)$$

If the p-value calculated is lower than the value of 0.05 (α); H_0 is rejected and the hypothesis H_a (are not equal).

$$p - value < 0.050 \qquad (3)$$

Therefore, H_1 proves that a significant difference exists. The analysis was conducted for each of the parameters in each of the stages.

To statistically compare the concentrations of compounds in the leachate of each of the PLMs and SPLMs, the MINITAB® computer software for quality improvement was used. The MINITAB® is a statistical software package that has a wide range of basic and advanced data analysis capabilities. In comparison of significant differences in leachate quality between PLMs and SPLMs, important variables in the performance of landfills with CCAs as an ARDC were identified.

For statistical analyses it was necessary to test for data normality by making a probability plot for each parameter measured in the experiments. The normality assumption was checked using normal probability plot. The normal distribution was expected when the data in the probability plot fall in a linear trend within the 95% confidence intervals. When the p-value was larger than an alpha of 0.05, the data was normally distributed and two samples T-test could be used to compare replicates of data for significance differences and an analysis variance (ANOVA) could be conducted.

The ANOVA null hypothesis H_0 was met if there were no significant difference between the results. If the Fisher value (F) calculated was higher than the value of $F_{critical}$, H_0 was rejected and the hypothesis H_1 (are not equal) was accepted. Therefore, H_1 proved that a significant difference exists.

The Pearson correlation is a statistical relationship between two random variables or two sets of data. Correlation refers to any of a broad class of statistical relationships involving dependence. A Pearson correlation is a number between -1 and +1 that measures the degree of association between two variables. A positive value for the correlation implies a positive association. A negative value for the correlation implies a negative or inverse association. These relationships may provide a useful mean for estimating leachate strength and characteristics on each period (Fan et al., 2006).

4. EVALUATION OF PHYSICAL LANDFILL MODELS (PLMs)

The land availability for waste disposal has been a limiting factor for the operation and development of landfills. This research aimed to assess the feasibility of using coal combustion byproducts aggregates (CCAs) as an alternative reactive daily cover, expecting to facilitate solid waste management and to enhance landfill operational quality.

To meet this end, biochemical decomposition and settlement were simulated using laboratory-scale physical landfill models (PLMs) in a temperature-controlled environmental chamber. The control PLM used sandy soil as the daily cover, whereas the treatment PLM used CCAs. Both PLMs were subject to different periods of hydrological sequences: the first two sequences represented wet and moderate weather periods (WP and MP), the third simulated a dry period (DP), and the last one was performed with leachate recirculation period (RP). The hydrological sequence simulation was repeated. The quality of leachate produced during the periods was analyzed for chemical oxygen demand (COD), and biological oxygen demand (BOD), pH, total nitrogen and total phosphorus (TP) over the 400-day experimental period. The extent of landfill settlement was monitored as well.

In general, the results showed that the hydrological sequences had substantial effect on the physiochemical characteristics of landfill leachate. The CCAs PLM presented a reduction in the organic and inorganic compounds compared to those of the control PLM. Specifically, in the moderate hydrological sequences, lower concentrations of COD and TP by 57.4% and 37.1%, respectively, were produced from the CCAs PLM than the control PLM. In the leachate recirculation sequences, the CCAs PLM behaved as a bioreactor landfill, resulting in an increase of biogas production and an earlier settlement that were attributed to enhanced waste biodegradation.

4.1 RESULTS

Below are the results of the physical parameters, and the biological, inorganic and organic compounds measured from each of the PLMs.

4.1.1 *Physical Parameters*

Among the physical parameters, measured were the amount of leachate produced (volume), pH, oxidation-reduction potential (ORP), color, turbidity, conductivity and settlement.

4.1.1.1 *Volume*

The leachate production in the PLMs depended on the hydrological periods. For example, the rainfall is an important factor for leachate; about 15 - 50 % of rainfall can become leachate (Fan et al., 2006). In this experiment, the leachate was collected in amber glass bottles; the volume was measured weekly using a graduated cylinder. Figure 15 shows the leachate volume collected from of the PLMs. The amount of leachate produced in the PLM with CCAs as daily cover was very similar to the control PLM with sand as daily cover. This is attributed to similar void fractions controlling the flow through the control and CCA PLMs.

Figure 15 shows the volume collected weekly from each PLM. There were differences in the amount collected because hydrological variations greatly affected leachate generation rates. Also, leachate generation was greatly influenced by the volume of rainwater infiltration permitted by the landfill's daily cover (Morris et al., 2003).

Accumulated leachate volumes are shown in Figure 16. The rainfall intensity simulated was 2 inches per hour. In the WP, the rainfall volume added was approximately between 4,000 and 6,000 mL, in the MP the volume was between 1,000 and 2,000 mL, and during the dry period (DP), no rain simulation was performed. Water collected during the dry periods corresponded to water flowing out of storage in the porous media. In the RP, leachate collected in the previous periods was added; the volume was between 2,000 and 4,000 mL. For the last recirculation period (RP4) the leachate quantity was increased to accelerate the process of solid waste decomposition. Graphically, there was no significant difference between the PLMs. Hydraulically this means that the PLM with CCAs as daily cover produced very similar amount of leachate compared to the control PLM with sand as shown in Figure 16, due to similar void fractions controlling the flow through the PLMs.

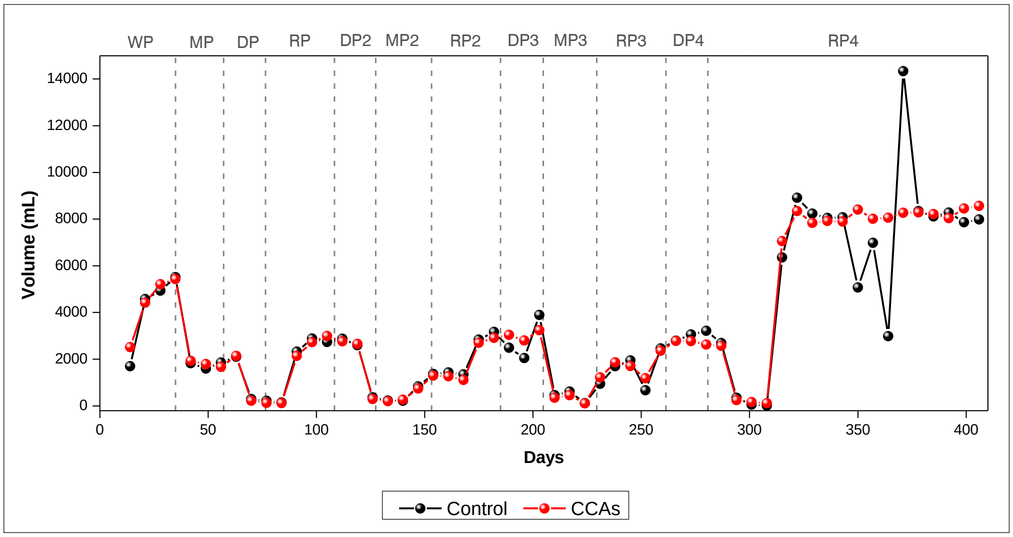

Figure 15 Volume of Leachate Produced in PLMs (WP – Wet Period, MP – Moderate Period, DP – Dry Period and RP – Recirculation Period).

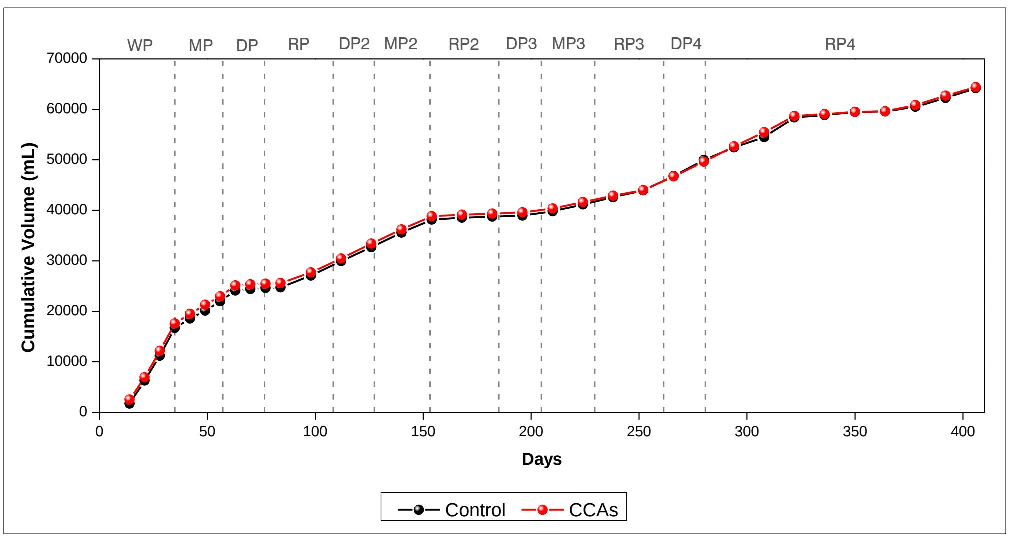

Figure 16 Accumulated Volume of Leachate Produced in PLMs.

4.1.1.2 *pH*

The pH profile is shown in Figure 17. The pH values were found lower in the control PLM with sand as daily cover than the PLM with CCAs as daily cover.

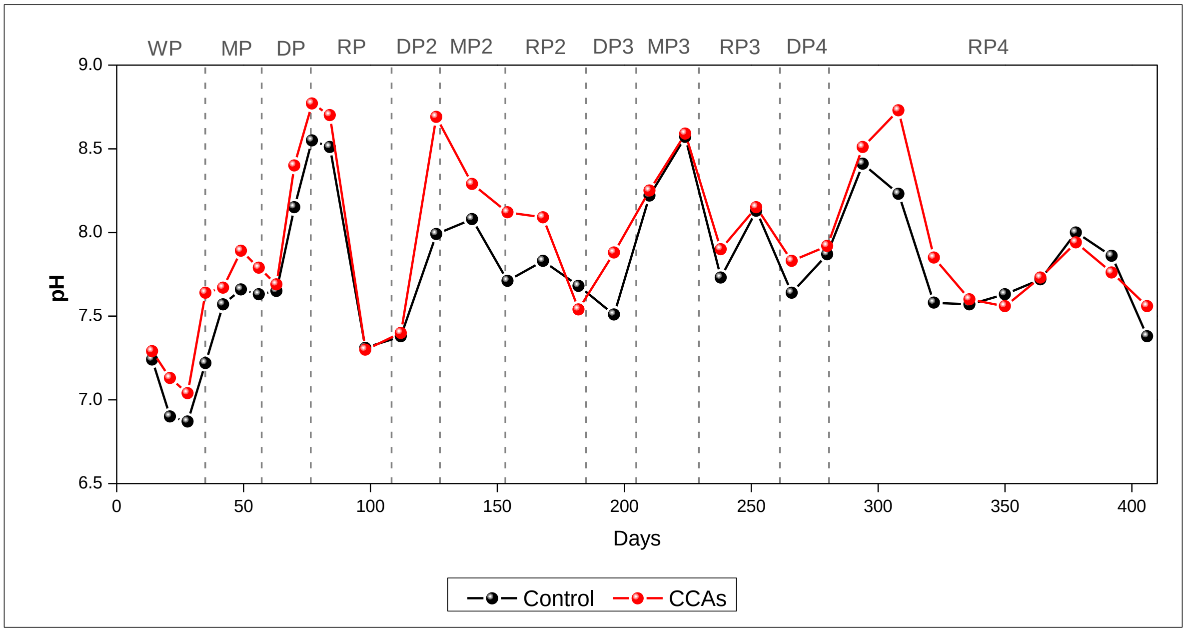

Figure 17 pH Values of Leachate Produced in PLMs.

In the first period (WP), both PLMs started with in neutral conditions at the beginning of the experiment, the initial pH was approximately 7.3. This value decreased slightly due to the accumulation of acids from the hydrolyzation of solid wastes to organic acids and end products by acidogenic bacteria (Elagroudy et al., 2009; Lo et al., 2009). Also, this behavior represents the initial adjustment and transition of solid waste degradation in the PLMs. The pH increased in moderate period 1 (MP) and dry period 1 (DP) (corresponding to days 29 – 84). In this phase, the biogas production most likely started, whereas hydrogen, carbon dioxide and volatile fatty acid concentrations decreased. The conversion of fatty acids causes the pH to increase and alkali metal are released associated with OH^{-} and CO_3^{-2}, that could provide alkalinity buffer and neutralize the volatile fatty acid produced (Lo et al., 2009).

The pH ranges between 7.3 and 8.1 for the RP2 and RP3 periods, respective, for accelerated biogas production, while decelerated biogas production in 308 days decreased the pH. In the last recirculation period (RP4), the pH decreased and gasses are likely to be produced again. The pH peak found in the DP may be due to the conversion of the fatty acids and the release alkali metals associated with OH^{-} and CO_3^{-2}. This can also be a consequence of the delayed leachate release. Low values in the RP suggest that the microbial population in the recirculation landfill is able to recover from the production of soluble organic matter induced by recirculation period. The leachate recirculation can lead to the inhibition of methanogenesis due to high concentrations of organic acids (low pH), which are toxic for the methanogens. This problem may occur in this case of having high levels of recirculation volumes due to the imbalance between acidogenesis and methanogenesis (Sponza and Agdag, 2004).

4.1.1.3 *Color*

In this research, true color was measured. It was measured after filtering the leachate sample to remove all suspended material using filter paper. Similar color values were found regardless of the type of daily cover. These results are shown in Figure 18:

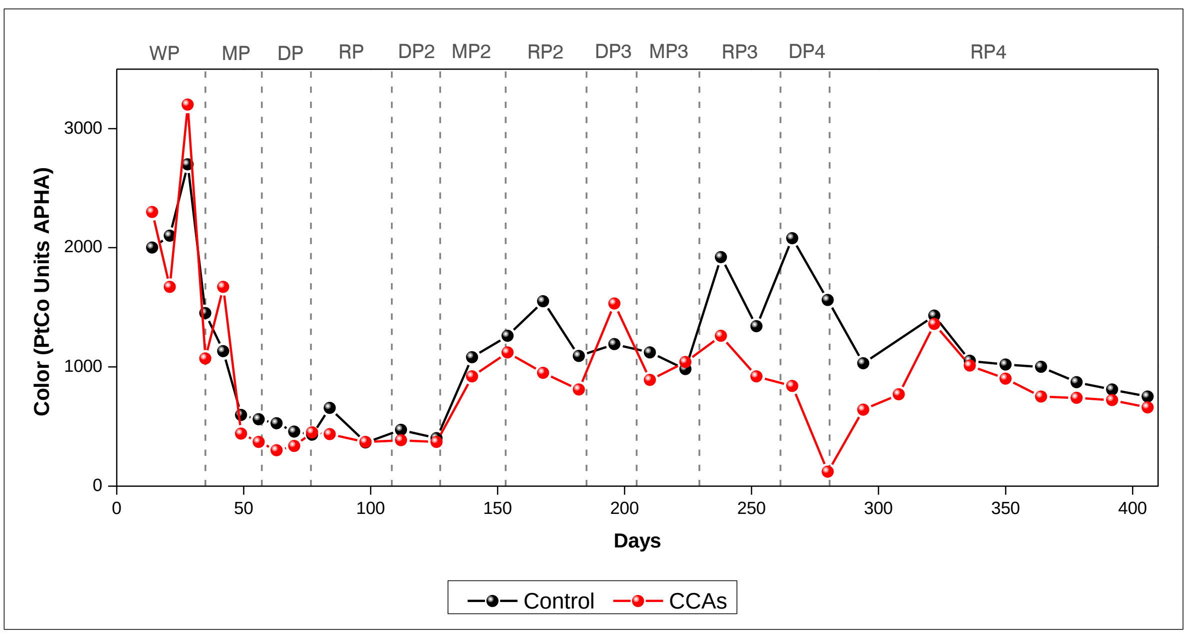

Figure 18 Color Intensity of Leachate Produced in PLMs.

The color of leachate was orange-brown or dark-brown, associated with malodorous smell; mainly due to the presence of organic acids, which came from the high concentrations of organic matter decomposed. The dark color and malodor disappeared slowly due to the increasing age of PLMs. These changes can be due to the nature of precipitation or quality or quantity of solid waste (Rong, 2009).

The high values of color, corresponding to the WP in the beginning of the experiment, were 2,000 and 2,300 PtCo Units APHA in the control and CCAs PLMs, respectively. These values increased and then decreased in the dry period 2 (DP2) to 400 PtCo Units APHA. The values showed some variations: dry period values were low and the values increased during recirculation but decreased in the last recirculation due to the volume of leachate used.

4.1.1.4 *Turbidity*

The results for turbidity are shown in Figure 19. Similar turbidity values were found regardless of the type of daily cover.

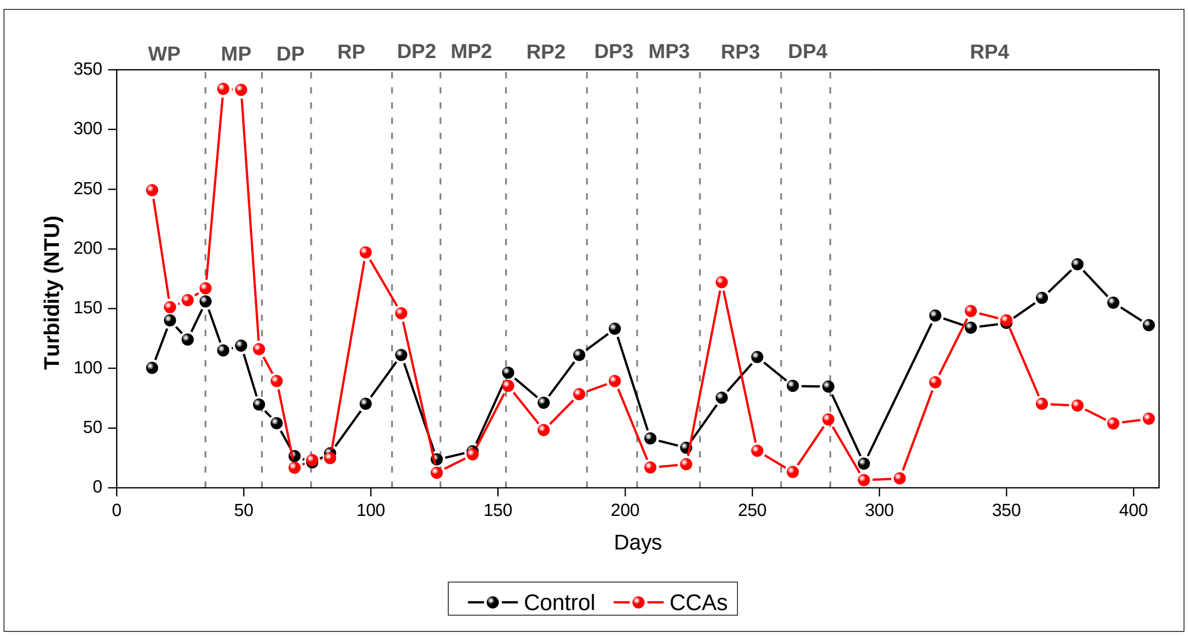

Figure 19 Turbidity of Leachate Produced in PLMs.

In the beginning of the experiment (WP), turbidity was greater in the CCAs PLM (249 NTU) than in the control PLM (100 NTU). At the end of the experiment, the turbidity of the control PLM (136 NTU) was greater than the CCAs PLM (58 NTU). Therefore, the turbidity of the CCAs PLM decreased by 76.8% while the control PLM increased by 36.0%. During the different stages, it can be noted that in the DP, the turbidity values were the lowest for both PLMs while in the RP it increased but the CCAs PLM had the lowest values (660 NTU) and the control PLM corresponded to 750 NTU. Therefore, the CCAs PLM had better turbidity response in the RP.

4.1.1.5 *Conductivity*

The results for conductivity are shown in Figure 20. The conductivity values were found lower in the control PLM with sand as daily cover than the PLM with CCAs as daily cover.

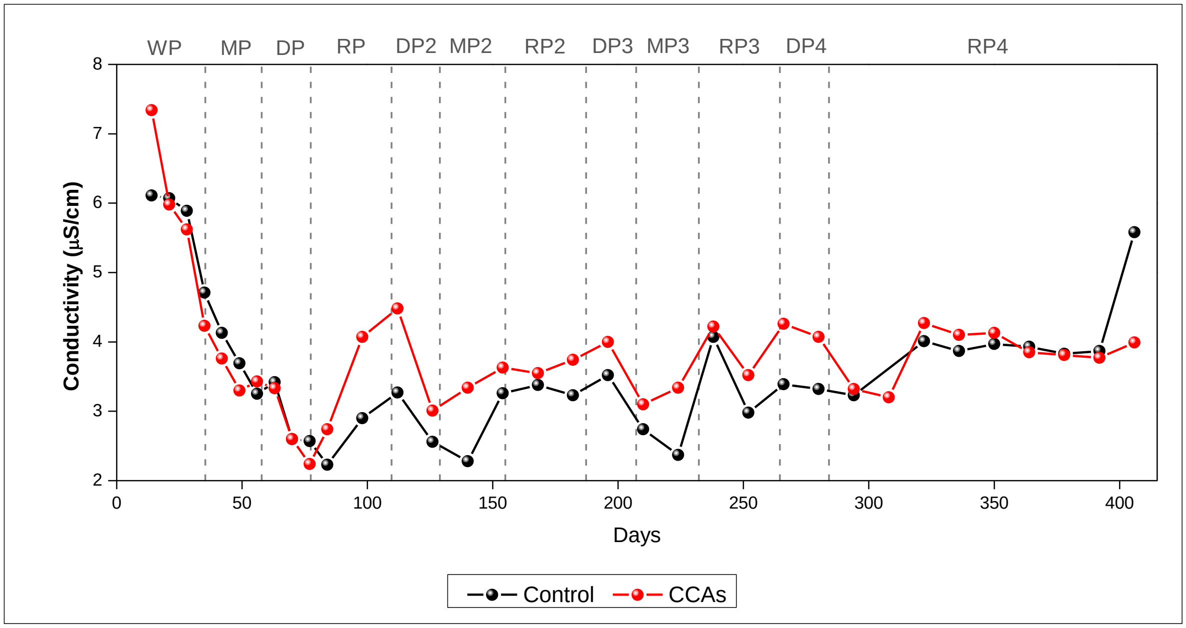

Figure 20 Conductivity of Leachate Produced in PLMs.

Higher conductivity values corresponded to the WP. The maximum conductivity (initial conditions) of CCAs and control PLMs were 7.3 and 6.1 µS/cm, respectively. This may be attributed to the ions washed out by the infiltration water in the WP. The conductivity in the CCAs PLM was higher because the CCAs as daily cover, sand and solid waste released more ions resulting in a higher conductivity.

After the WP, the conductivity decreased to values between 2.0 and 4.5 µS/cm. The behavior of this variable was similar to that of turbidity. Low values were observed in DP. Recirculation produced higher conductivity values due to the dissolution of some chemicals that did not degrade or transform. Thereby, the conductivity was higher in the last RP. At the end of the experiment, the conductivity decreased to 4.0 and 5.6 µS/cm for CCAs and control PLMs, respectively.

4.1.1.6 *Settlement*

For an absolute settlement, the control PLM achieved better settlement (Figure 21). Therefore, the extent of settlement was normalized to the density of daily covers (Figure 22 and Figure 23). To have a comparison of the settlement of the solid waste in each PLM, the normalization of the settlement consisted of dividing the length of the layer of solid waste by the compaction density average daily cover. The PLM with CCAs as daily cover showed much greater settlement. Figure 22 shows the normalized settlement measured weekly. The settlement immediately began with the WP but, in general, the CCAs PLM produced greater settlement.

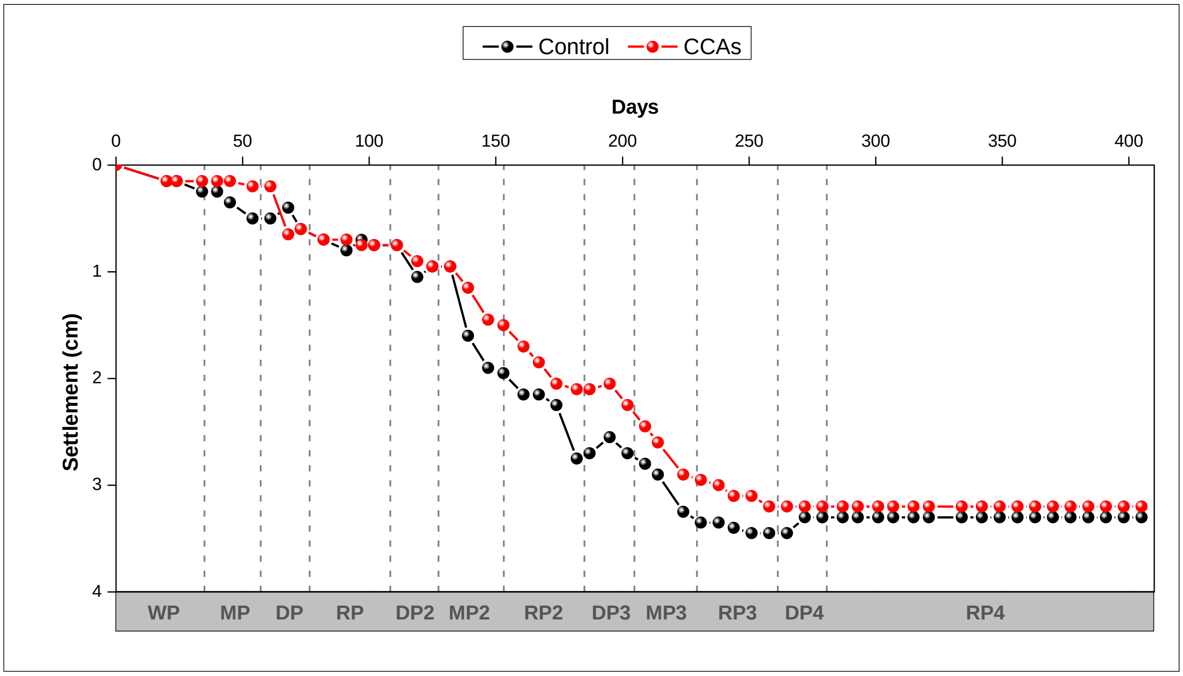

Figure 21 Settlement in PLMs.

The normalized settlement was higher in the PLM with CCAs than in the control. In the first period (WP and MP), there was not a marked difference between both PLMs. The initial settlement was due to the immediate impact of the overlying multiple cover layers and primary settlements were due to primary compressions of solid waste due to dissipation of pore water and air from voids, as previously noted by Swati and Joseph (2008). But, after the DP, the difference was noticeable in both PLMs and the dominant settlement was the secondary settlement due to decomposition. The stability of the settlement was reached in the third period of recirculation (RP3). The high settlement coincided with the accelerated biogas generation. Also, the biogas generation as a result of biochemical waste decomposition changed the fill pressures in landfills, which caused physical settlements. The settlement in the PLM with CCAs is advantageous for the conservation of landfill space and soil resource.

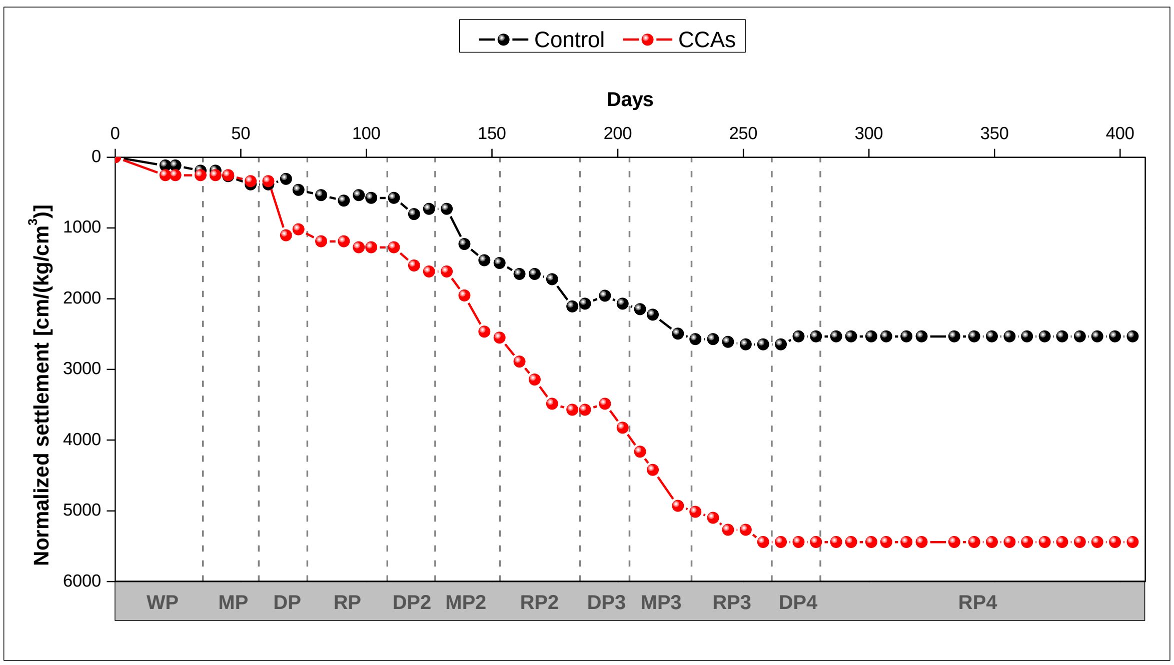

Figure 22 Weekly Normalized Settlement in PLMs.

Similar to observations made by Swati and Joseph (2008), the difference in the settlement of the PLMs was marked in the RP periods due to enhanced microbiological activity that transformed and stabilized the decomposable organic waste. The results for the improvement of biodegradation was achieved by recirculating the leachate collected from other periods because it helped to maintain a wet environment in addition to supplying the nutrients needed for the biodegradation as reported by Hettiarachchi et al. (2007) and Swati and Joseph (2008). The water content is not the only essential condition to promote rapid hydrolysis of the waste. It is also essential to know the field capacity in order to maintain the appropriate moisture levels in a landfill and also to control leachate production in time and magnitude (Vaidya, 2002). In the last recirculation period (RP4), the volume used was more when compared with the others and presented a new biogas production period in the experiment but the settlement was maintained.

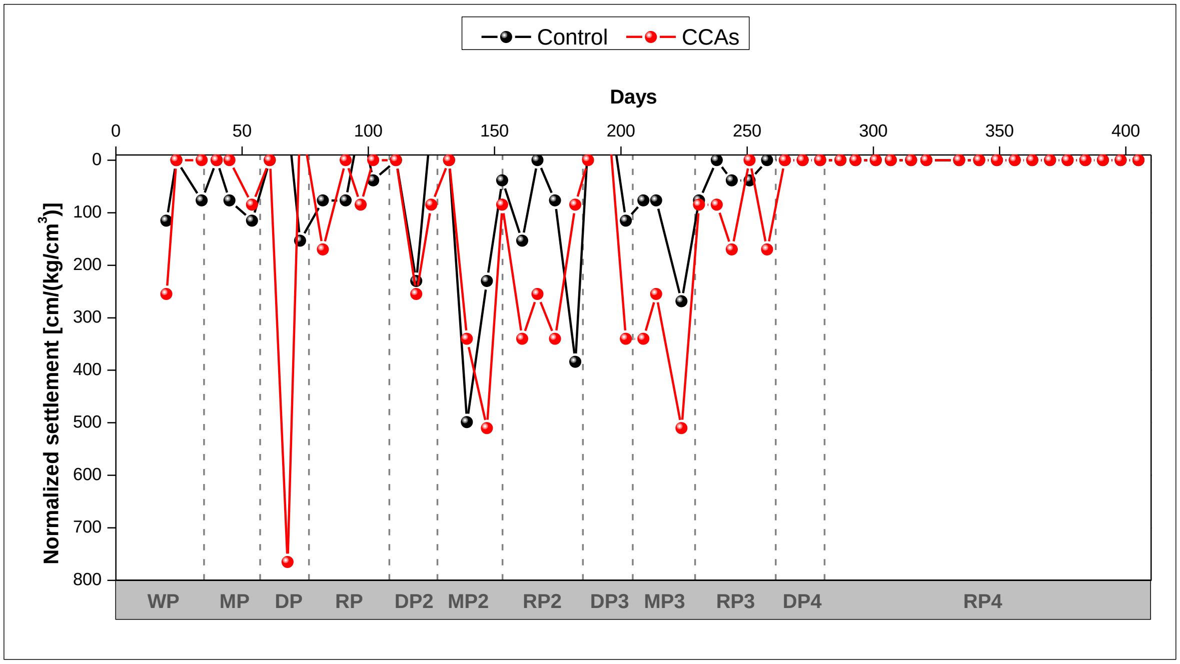

Figure 23 Cumulative Normalized Settlement in PLMs.

It is important to know that enhanced decomposition increased the rate of solid waste settlement which provided an additional airspace prior to closure and limited the potential for settlement-induced damage of the final cover. The CCAs PLM enhanced the rate and extent of decomposition, increased the rate of landfill biogas production, and improved the viability of gas-to-energy options.

The results found in the PLMs with respect to the settlement are expressed in the Figure 24.

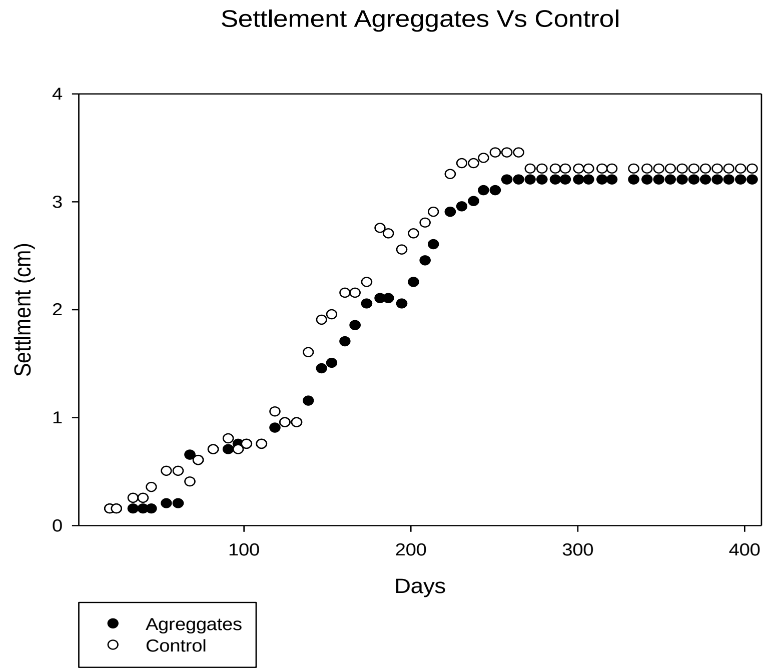

Figure 24 Settlement Data for PLMs CCAs and Control (Sand).

For the settlement data, a mathematical function was sought to predict the behavior in each of the PLMs. The functions (***f***) used were power, logarithmic, and sigmoidal, the variable '***x***' represent the settlement, the variable '***a***', '***b***' and 'x_0' are specific for each functions. The results for the correlation coefficient and equations are tabulated in the Table 15.

Table 15 Comparison of Numerical Parameters among Different Regressions.

Function	**Equation**	**Parameters**						**R^2**	
		Aggregate			**Control**				
		a	**b**	**X_0**	**a**	**b**	**X_0**	**Aggregate**	**Control**
Power	$f = a \cdot x^b$	0.019	0.8844	NA	0.0341	0.7928	NA	0.8973	0.8572
Logarithmic	$f = a + b \cdot ln(abs(x))$	-5.4492	1.4672	NA	-5.4648	1.5066	NA	0.8811	0.8702
Exponential	$f = a \cdot (1 - exp(-b \cdot x))$	7.1135	0.0018	NA	5.4785	0.0029	NA	0.9120	0.8860
Sigmoidal	$f = \frac{a}{(1 + exp(-(x - x_0)/b))}$	3.2899	41.8668	157.7570	3.3788	35.4449	144.1916	0.9905	0.9858

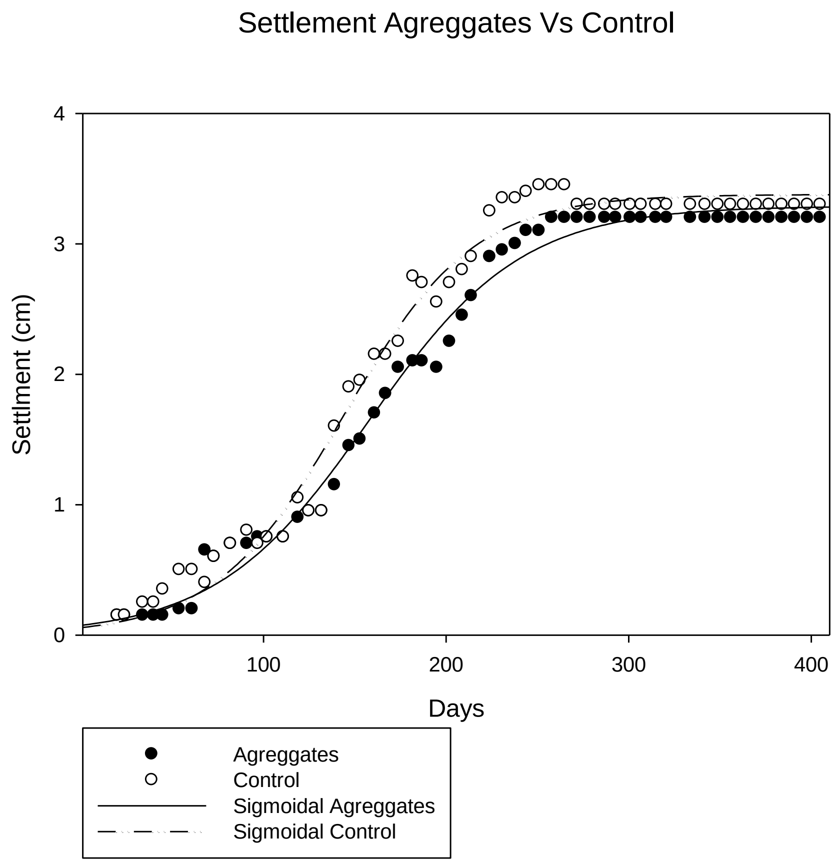

Figure 25 Correlation Between Settlement and Time Using a Function.

As shown (Figure 25), the best data fit was obtained with a sigmoidal function for the settlement with respect to the time. A very high correlation coefficient (R^2) was observed ($R^2 > 0.99$). The parameters represents: maximal amplitude (***a***), maximal slope ($\boldsymbol{X_0}$), and the midpoint intensity where amplitude is half maximum (***b***).

4.1.2 *Organic Constituents in the Leachate*

The organic constituents measured in the experiment were COD and volatile acids.

4.1.2.1 *Chemical Oxidation Demand (COD)*

COD concentrations were found lower in the PLM with CCAs as daily cover than in the control PLM. These results are shown in Figure 26

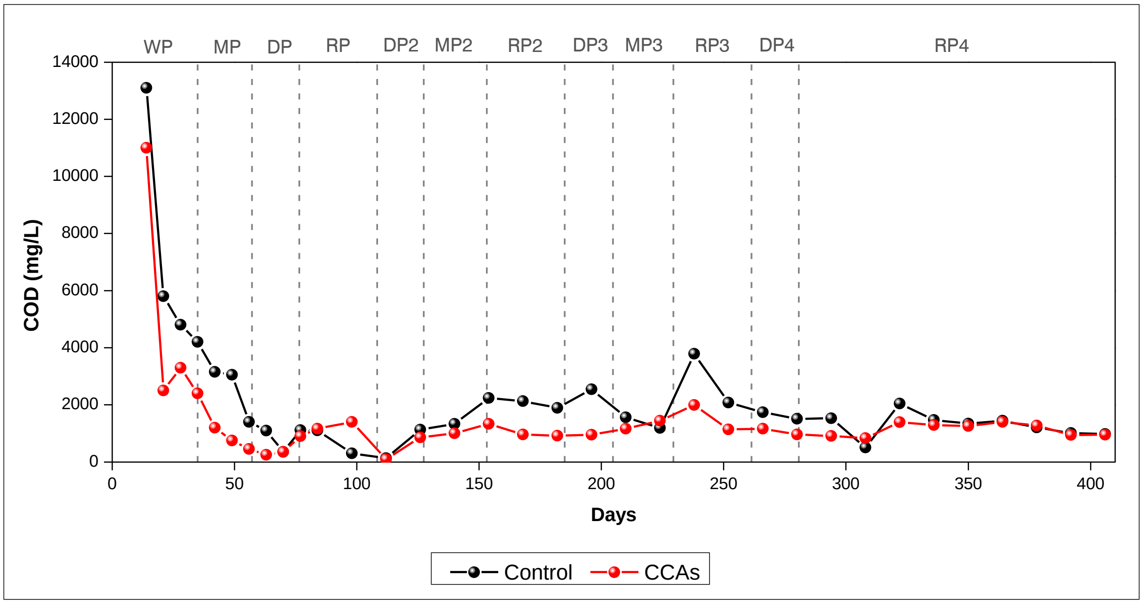

Figure 26 Chemical Oxygen Demand of Leachate Produced in PLMs.

COD (organic strength) was very high during the wet period, when it reached a maximum of 13,000 mg/L for the control PLM and 11,000 mg/L for CCAs PLM. These values were consistent with the literature: leachate from young landfills were characterized by high COD and BOD_5 (Sarubbi and Sanchez, 2009) even several thousands of mg/L, while in leachate from old landfills, COD and BOD_5 concentrations are below a few hundred mg/L (Kulikowska and Klimiuk, 2008).

COD decreased significantly during the MP, 1,400 and 750 mg/L for the control PLM and CCAs PLM, respectively. COD was degraded by microorganisms resulting in a gradual decrease in digestion period (Lo et al., 2009). Therefore, COD concentrations decreased as daily biogas generation raised (Elagroudy et al., 2009). The trend of the COD concentration in the RP decreased due to the fact that leachate recirculation improves leachate quality, especially in terms of COD. Also, lower COD values suggest a faster organic matter degradation process in the CCAs PLM during this period and was consistent with the greater settlements presented in the PLM. When leachate presented the highest values of pH and the lowest values of COD, it suggests that the delay in releasing the leachate influenced the process of organic matter degradation, as also observed by Junqueira et al., (2006).

COD continued to decrease in both PLMs during the recirculation period 4 (RP4); they decreased to achieve similar concentrations (980 and 950 mg/L for the control and CCAs PLMs, respectively). High recirculation volumes (RP4) may deplete the buffering capacity and remove the activity of methanogens. Therefore, an optimum leachate recirculation volume contributes to decreases in COD and volatile fatty acids, and increase methane biogas productions as was also reported by Bilgili et al., (2007).

4.1.2.2 *Volatile Fatty Acids*

The volatile acid concentrations were only calculated for the last recirculation stage. They were found similar regardless of the type of daily covers. The results are shown in Figure 27.

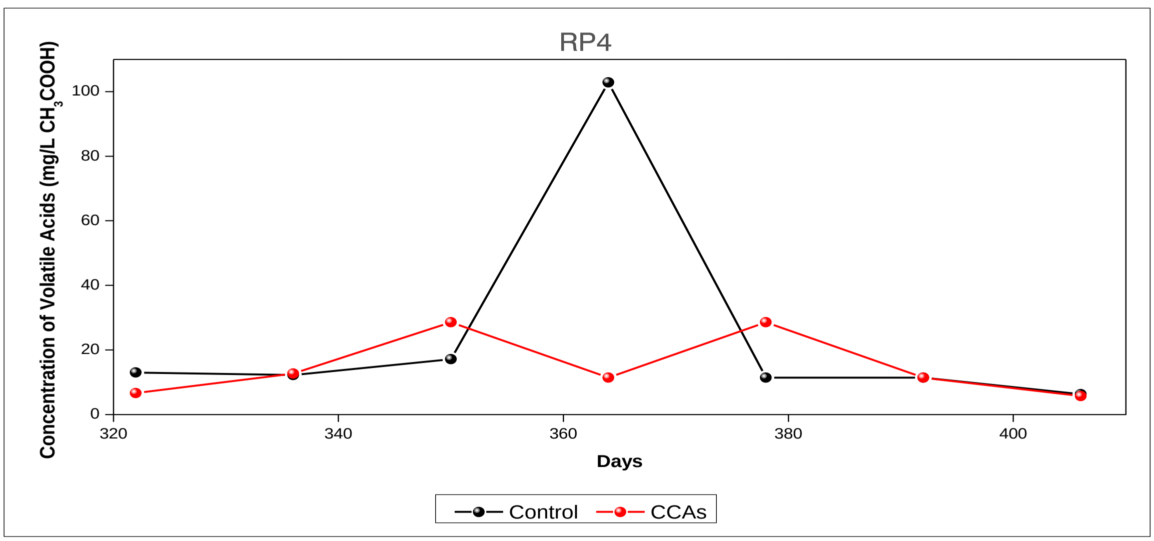

Figure 27 Volatile Acids of Leachate Produced in PLMs.

No notable differences were observed between the PLMs. A data point showing > 100 mg/L volatile acids was believed to be an outlier due probably to an experimental error resulted from a failure of homogenization of the sample. The volatile fatty acids concentration was low at the end of the experiment due to: first the organic waste hydrolyzed into aqueous organic acids and then they were consumed by acidogenic bacteria to produce volatile fatty acids and carbon dioxide. A drop of volatile fatty acids concentration was reported by Elagroudy et al. (2009) as the daily methane production increased, because the methanogenic bacteria used the volatile fatty acids as a substrate to produce methane and carbon dioxide.

4.1.3 *Inorganic Constituents in the Leachate*

The inorganic constituents measured were: nitrate, hardness, total phosphorus, total nitrogen, orthophosphate and alkalinity.

4.1.3.1 *Nitrate*

The changes of nitrate in the PLMs are shown in Figure 28. The nitrate concentration in leachate maintain the same behavior over time, but present two outliers points (DP and RP3 periods), which are due to experimental errors. For nitrate concentrations a similar trend was found regardless of the type of daily covers.

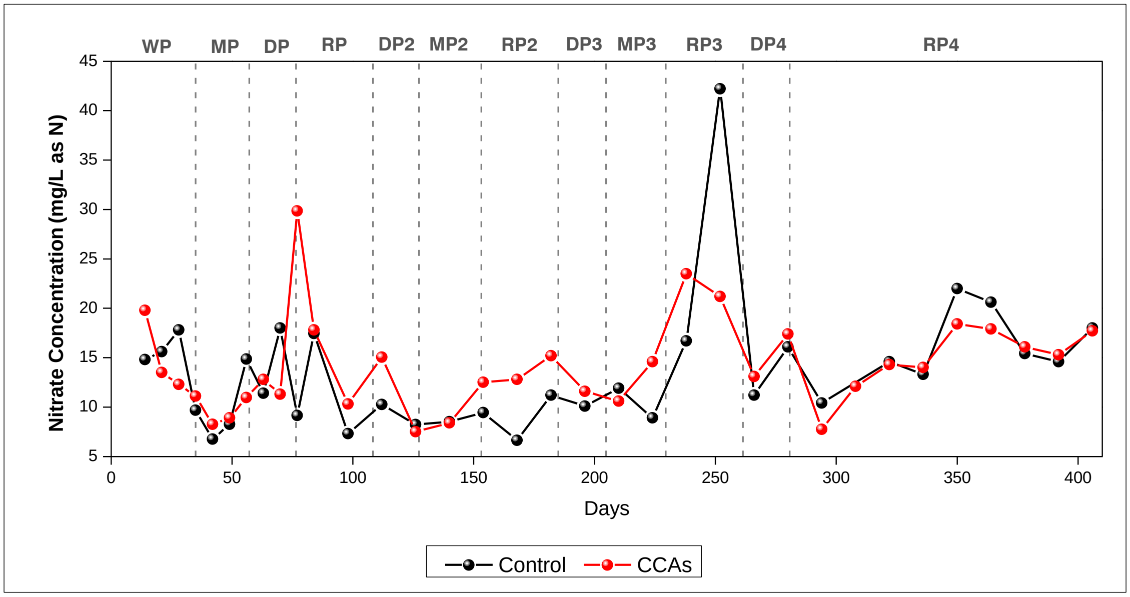

Figure 28 Nitrate Concentrations of Leachate Produced in PLMs.

In the process of decomposition, nitrate is among the end products. For the control and CCAs PLM, the initial value was 14.8 and 19.8 mg/L as nitrogen, respectively. These values decreased a little in WP, and increased in the MP and DP. However, they were in a range of 8.0 to 15.0 mg/L in period 3. The concentrations increased slightly in the last recirculation period (RP4) due to recirculated leachate. Both

PLMs had a similar behavior, but the lowest nitrate concentrations occurred in dry period and the highest in moderate period.

4.1.3.2 *Hardness*

Hardness was measured as the concentration of calcium (mg/L). This parameter was found similar in the PLM with CCAs as daily cover and the PLM with sand as daily cover. These results are shown in Figure 29:

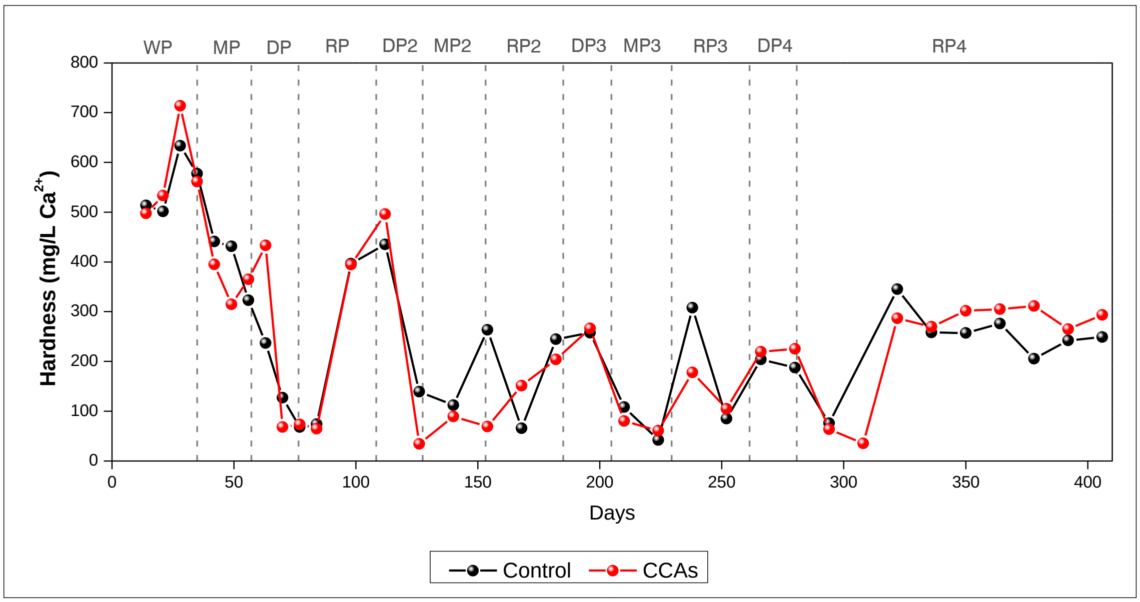

Figure 29 Hardness of Leachate Produced in PLMs.

The WP produced high values of hardness (713.8 mg/L as Ca^{2+} for CCAs and 633.6 mg/L as Ca^{2+} for sand). These values are due to the high calcium content component of the CCA daily covers. Then, these values decreased in the MP and DP (73.8 mg/L as Ca^{2+} for control and 64.8 mg/L as Ca^{2+} for CCAs). Lower hardness values are attributed to the continuous washing of the PLMs during the hydrological periods.

4.1.3.3 *Total Phosphorus*

Lower total phosphorus concentrations were found in the PLM with CCAs as daily cover than the control PLM. These results are shown in Figure 30:

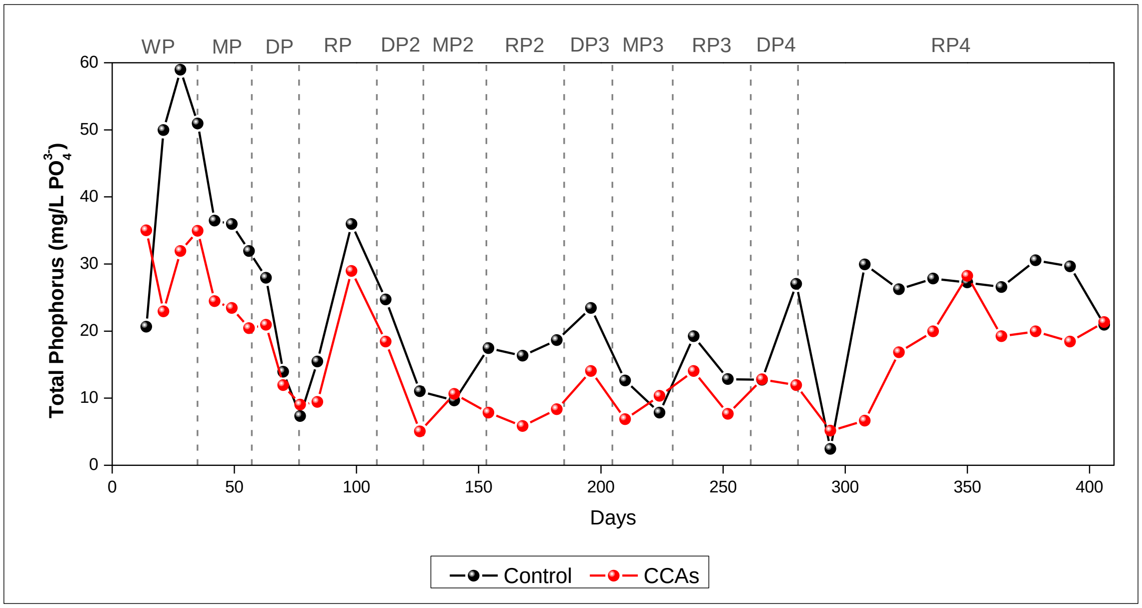

Figure 30 Total Phosphorus of Leachate Produced in PLMs.

In the WP, the total phosphorus concentration in the control PLM was 20.6 mg/L PO_4^{-3}. This value increased, then decreased in both the DP and the RP Overall, the phosphorus concentrations were lower in the leachate from the CCAs PLM than from the control PLM, implying potential of phosphorus reduction due to the use of CCAs as daily covers.

4.1.3.4 *Total Nitrogen*

The results for total nitrogen concentrations are shown in Figure 31. For total nitrogen concentrations, a similar trend was found regardless of the type of daily covers.

Total nitrogen in the leachate decreased over time, but the concentrations in the control PLM was greater in all hydrological periods compared with the CCAs PLM. The maximum value in total nitrogen ocurred in the WP, 500 mg/L as N, in both PLMs, then the concentration decreased until the RP where it increased and maintained values between 100 - 200 mg/L as N. Similar to the phosphorus concentrations, the nitrogen concentration were lower in the leachate from CCA PLM than the control PLMs. These findings indirectly indicated that CCAs enhanced biological activities in the CCA PLM, for which nitrogen and phosphorus were utilized more as macronutrients for mirobial metabolism.

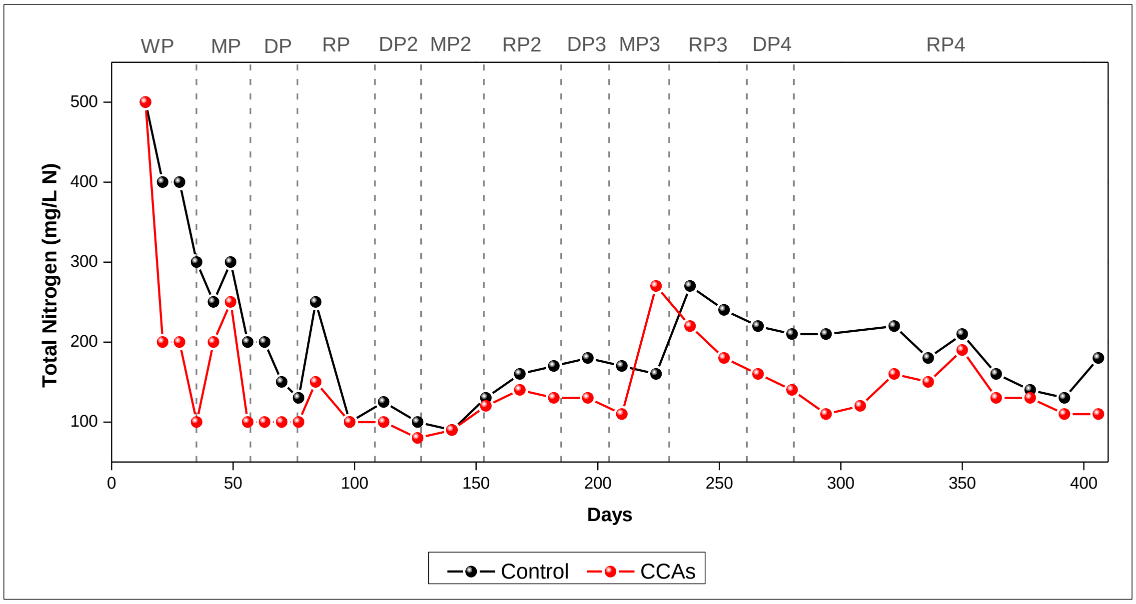

Figure 31 Total Nitrogen of Leachate Produced in PLMs.

4.1.3.5 *Orthophosphate*

Orthophosphate concentrations were found to be lower in the PLM with CCAs as daily cover than the control PLM. These results are shown in Figure 32:

The orthophosphate concentrations in the WP in the CCAs and control PLMs were 4.1 and 15.3 mg/L, respectively. These values increased and decreased in the wet period. The orthophosphate concentrations were high in the control PLM compared to the CCAs PLM and were maintained throughout the experiment. The decrease in orthophosphate concentration may have been from the assimilation of orthophosphate by microorganisms in the decomposition process and dilution in the leachate as reported by Erses et al., (2008). In the other periods, the orthophosphate concentration was fluctuated. In the last recirculation period (RP4), orthophosphate concentrations were increased probably due to hydrolysis of organic phosphorus compounds.

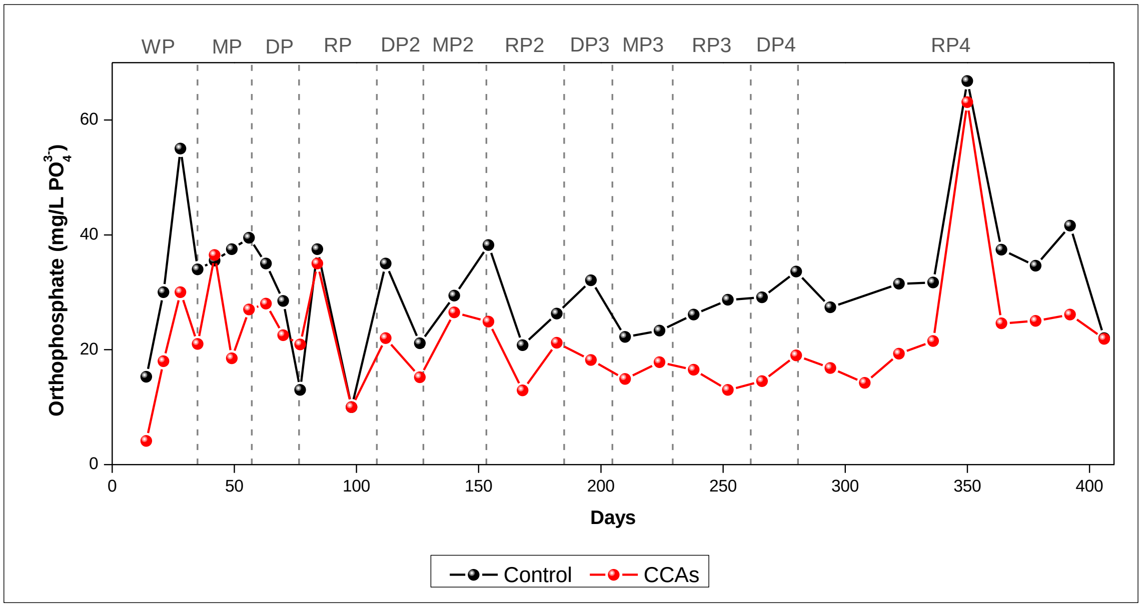

Figure 32 Orthophosphate of Leachate Produced in PLMs.

4.1.3.6 *Alkalinity*

Alkalinity concentrations were found to be lower in the PLM with CCAs as daily cover than in the control PLM. These results are shown in Figure 33.

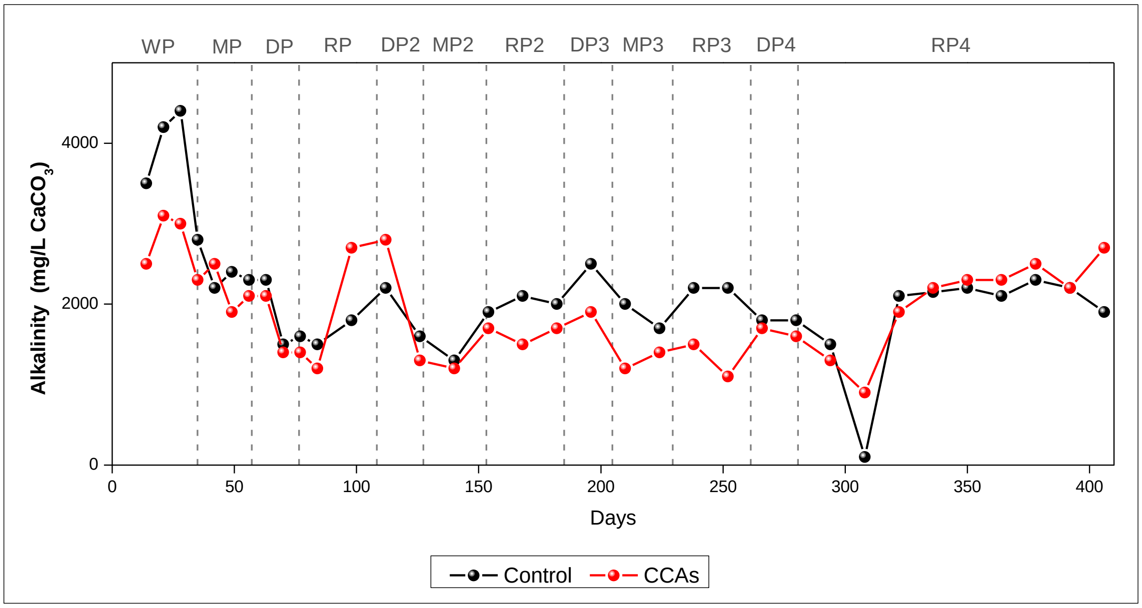

Figure 33 Alkalinity of Leachate Produced in PLMs.

Researchers suggested an alkalinity of at least 2,000 mg/L is necessary to maintain an optimum methanogenesis (Bilgili et al., 2007). In the WP, the alkalinity began at 2,500 and 3,500 mg/L $CaCO_3$ corresponding the CCAs and control PLMs, respectively. These values increased and then decreased in the moderate and dry period until 1,200 and 1,500 mg/L $CaCO_3$. It may be noted that the highest alkalinity concentration was found in the RP. This may be due to the recirculated leachate concentration as response and low values in the dry period. The recirculated leachate can take advantage of adapted microflora and high alkalinity of effluent to buffer pH and inoculate, thus providing optimal environmental and nutrient conditions for acidogenic bacteria and methanogens, and improve the landfill performance (i.e. PLMs) coinciding in the research done by Clesceri et al. (1998, 2009).

It is important to point out that the high values of alkalinity measured could be attributed to the presence of ions such as bicarbonate, carbonate, hydroxide, borates, silicates, phosphates, ammonium, sulfides, and organic ligands in inorganic soils and CCAs. Sites where limestone and carbonate-rich soils are predominant, waters often have high alkalinity. Although alkalinity highly depends on pH and hardness, a direct correlation between them was not observed during this experiment.

4.1.4 *Biological Parameters in the Leachate*

Among the biological parameters measured were: BOD_5, dissolved oxygen (DO), and biogas production.

4.1.4.1 *Biological Oxygen Demand*

BOD_5 concentrations were found to be similar regardless of the type of daily covers. The results are shown in Figure 34.

BOD_5 showed a similar trend to COD. Biological oxygen demand was very high during the WP, when it reached a maximum of 2,450 mg/L for the control and 2,100 mg/L for CCAs. The initially high BOD concentration in the leachate was followed by a quick BOD decline similar to the results of Warith (2002). The high values corresponds to a period in which the microbial population is still low (i.e., in lag phase). After population growth there is higher microbial activity and greater BOD decomposition, occurring lower BOD values. Biological oxygen demand decreased significantly during the MP and DP, from 250 to 200 mg/L. In these periods the pH values started to increase, which in turn resulted in a decline in the BOD concentrations in PLMs. Also, the onset of methanogenic conditions, as suggested by the increasing pH and decreasing BOD concentrations and BOD/COD ratio has similarly been reported by Morris et al. (2003). BOD continued to decrease significantly during the other periods, until it reached values in a range of 400 - 100 mg/L.

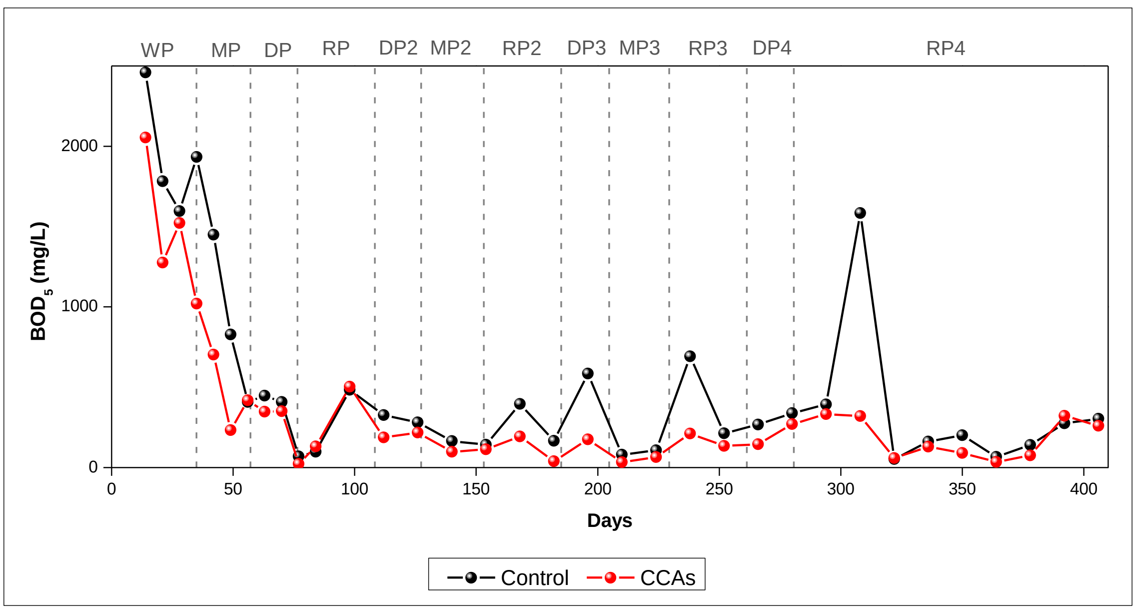

Figure 34 Biological Oxygen Demand of Leachate Produced in PLMs.

4.1.4.2 *Biogas Production*

Daily and cumulative biogas productions of the PLMs are shown in Figure 35 and Figure 36. It is notable that the larger production of gases occurred in the PLM with CCAs as daily cover than the control PLM. Besides, an early start of biogas production was found for the PLM with CCAs as daily cover, specifically, in the RP. More biogas production indicates that more biological activity occurred in the PLM with CCAs as daily cover.

In the recirculation periods (RP1 and RP2), an accelerated biogas production was observed in both PLMs, but the CCAs PLM produced more biogas than the control PLM. In the beginning of the experiment (WP, MP and DP), organic matter in the PLMs were hydrolyzed and organic acids were produced that ceased biogas production. While in the RP, methanogenic bacteria slowly started to appear and biogas volume increased (Erses et al., 2008). This is evidence that leachate recirculation can shorten the transitional period for active methane production and boost the methanogenesis of a landfill cell, as also subjected by Chan et al., (2002). Figure 35 and Figure 36 suggest that biogas production be significantly enhanced in the RP as a result of both accelerated biogas production rates and the return of organic materials in the leachate to the landfill for biogas conversion as suggested by Jiang et al., (2007). Also, leachate recirculation reduced waste stabilization time and improved leachate quality, especially in terms of COD which depends on the portions of nutrients, minerals or organics being attenuated by the waste and cover, and if effective attenuations are high, a lower strength of leachate is expected (Chan et al., 2002).

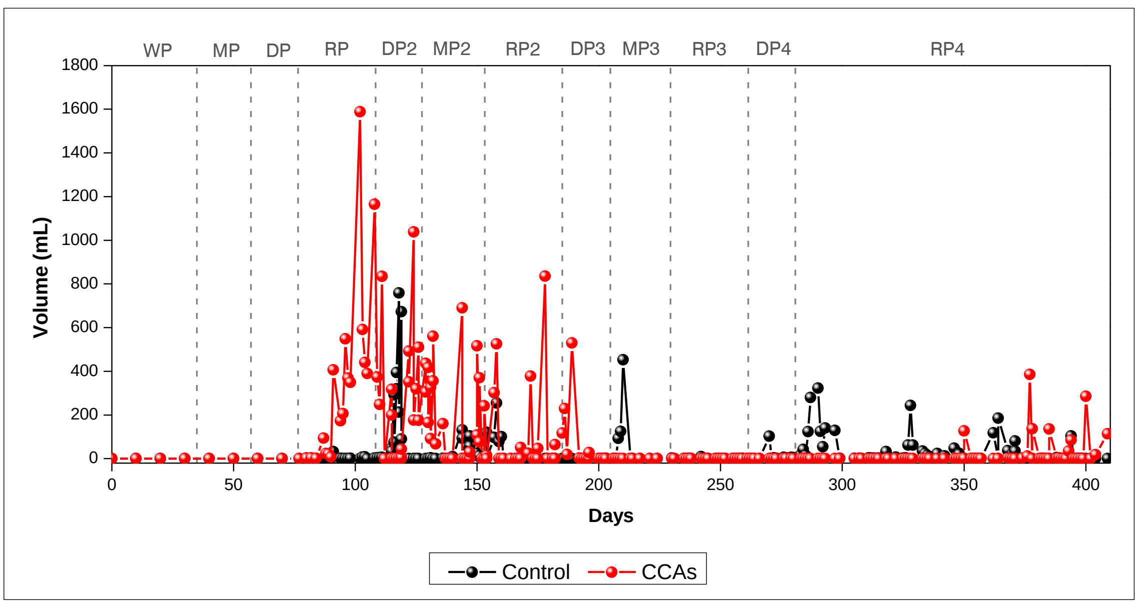

Figure 35 Daily Biogas Production in PLMs.

Figure 36 shows that cumulative biogas production in the PLM with CCAs was higher than in the control PLM. This indicates a possible further biodegradation of solid waste due to microbial activity. The cumulative biogas production in both PLMs began in the first RP, but for the PLM with CCAs it increased to recirculation period 2 (RP2), and then remained stable and again increased in the recirculation period 4 (RP4). Additional moisture stimulates microbial activity by providing better contact between insoluble substrates, soluble nutrients, and microorganisms and enhances the biodegradation of the waste. For the control PLM, the increase in biogas production was in the moderate period 2 (MP2), dry period 3 (DP3) and 4 (DP4), and in the final RP. It is possible that when the rate and extent of decomposition is enhanced, the rate of landfill biogas production is increased this may improve the viability of gas-to-energy options (Benson et al., 2007) because much of the biogas generated in landfills can be captured and used in a gas engine or turbine to generate electricity as suggested Haaren (2010).

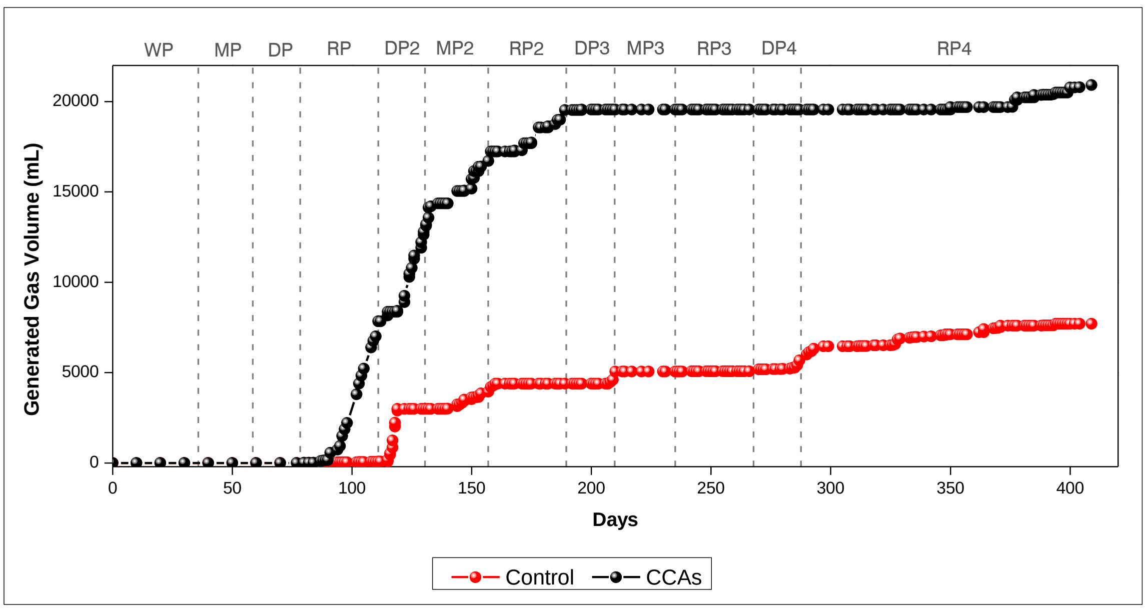

Figure 36 Cumulative Biogas Production in PLMs.

4.1.5 *Statistical Comparison*

Table 33 through Table 40 (Appendix 1) show all the parameters measured in each of the PLMs, with their respective average values, standard deviation, maximums, minimums and the number of samples taken for each period. To statistically compare the parameters and concentrations of compounds (pH, ORP, heavy metals, phosphorus, turbidity, nitrate, total nitrogen, COD, BOD, dissolved oxygen, alkalinity, and hardness shown in Table 16 - Table 21 in the leachate of each of the PLMs, an analysis of variance

(ANOVA) was used. Below are the results:

4.1.5.1 *Wet Period*

For the first sequence (WP), the statistical analyses were performed for each of the measured parameters, and results are summarized in Table 16:

Table 16 Statistical Analysis for Wet Period.

Parameter	F	p - value	Parameter	F	p - value
Volume (mL)	0.04	0.847	DO (mg/L O_2)	4.06	0.091
pH	1.72	0.237	COD (mg/L COD)	0.55	0.486
ORP (mV)	0.62	0.462	Total Phosphorus (mg/L PO_4^{-3})	2.46	0.168
NO_3^- (mg/L as N)	0.01	0.914	Total Nitrogen (mg/L N)	2.45	0.168
Hardness (mg/L as Calcium)	0.13	0.736	Orthophosphate (mg/L PO_4^{-3})	2.44	0.170
Color (Pt Co Units APHA)	0.00	0.996	Alkalinity (mg/L $CaCO_3$)	5.9	0.050
Turbidity (NTU)	3.9	0.096	BOD_5 Average (mg/L)	2.72	0.150
Conductivity (μS/cm)	0.02	0.897	Normalized Settlement (cm/(kg/cm^3))	1.30	0.297

The only parameter that showed a significant difference was alkalinity:

$$\mu_{CONTROL} > \mu_{CCA} \quad (4)$$

$$3{,}725\ mg/L\ CaCO_3 > 2{,}725\ mg/L\ CaCO_3 \quad (5)$$

The average of the control PLM with sand as daily cover was greater than the one with CCAs as daily cover. This was due to the chemical characteristics of the Isabela sand (HCO_3^- and CO_3) used in the construction of control PLM, which contributed the alkalinity in the first period.

4.1.5.2 *Moderate Period*

In the second sequence (MP), the statistical analyses for each of the measured parameters (Table 17):

Table 17 Statistical Analysis for Moderate Period.

Parameter	F	p - value
Volume (mL)	0.02	0.894
pH	3.58	0.079
ORP (mV)	0.41	0.534
NO_3^- (mg/L as N)	0.02	0.887
Hardness (mg/L as Calcium)	0.06	0.803
Color (Pt Co Units APHA)	0.87	0.368
Turbidity (NTU)	2.06	0.173
Conductivity (µS/cm)	0.15	0.700
DO (mg/L O_2)	0.21	0.652

Parameter	F	p - value
COD (mg/L COD)	13.13	0.003
Total Phosphorus (mg/L PO_4^{-3})	4.58	0.050
Total Nitrogen (mg/L N)	3.73	0.074
Orthophosphate (mg/L PO_4^{-3})	7.72	0.015
Alkalinity (mg/L $CaCO_3$)	5.89	0.029
BOD_5 Average (mg/L)	2.87	0.112
Cumulative Biogas Volume (mL)	309.72	0.000
Normalized Settlement (cm/(kg/cm^3))	3.54	0.073

The parameters that showed a significant difference were COD, total phosphorus, orthophosphate, alkalinity and cumulative biogas production (Table 18).

The averages of the PLM with CCAs as daily cover for COD, total phosphorus, orthophosphate, and alkalinity were smaller than the control PLM with as sand daily cover. Biodegradation was faster in the reactor of CCA representing a decrease in these parameters. Cumulative biogas production was more in the CCAs PLM possibly due to the enhancement of microbial activity

Table 18 Comparison of Parameters with Significant Difference for Moderate Period.

Parameter	Averages CCAs PLM	Averages Control PLM
COD (mg/L COD)	1,009 ± 545.0	2,368 ± 910.0
Total Phosphorus (mg/L PO_4^{-3})	15.6 ± 7.7	24.8 ± 9.4
Orthophosphate (mg/L PO_4^{-3})	22.2 ± 8.3	32.7 ± 6.7
Alkalinity (mg/L $CaCO_3$)	1,800 ± 441.0	2,200 ± 151.2
Cumulative Biogas Volume (mL)	16,258 ± 4,615.0	3,986 ± 182.0

4.1.5.3 *Dry Period*

For the third sequence (DP), the statistical analyses are summarized in table 19.

Table 19 Statistical Analysis for Dry Period.

Parameter	F	p - value
Volume (mL)	0.30	0.587
pH	6.48	0.022
ORP (mV)	0.16	0.695
NO_3^- (mg/L as N)	0.39	0.544
Hardness (mg/L as Calcium)	5.44	0.034
Color (Pt Co Units APHA)	0.71	0.412
Turbidity (NTU)	9.56	0.007
Conductivity (µS/cm)	5.79	0.029
DO (mg/L O_2)	0.86	0.367

Parameter	F	p - value
COD (mg/L COD)	0.61	0.447
Total Phosphorus (mg/L PO_4^{-3})	2.1	0.167
Total Nitrogen (mg/L N)	1.39	0.257
Orthophosphate (mg/L PO_4^{-3})	2.06	0.172
Alkalinity (mg/L $CaCO_3$)	0.81	0.380
BOD_5 Average (mg/L)	1.17	0.296
Cumulative Biogas Volume (mL)	131.72	0.000
Normalized Settlement (cm/(kg/cm^3))	7.24	0.013

The parameters with a significant difference found in the DP were pH, hardness, turbidity, conductivity and cumulative biogas production (Table 20). The averages of the

PLM with CCAs as daily cover for hardness and turbidity were smaller than the control PLM. While the averages of the CCAs PLM for pH, conductivity and cumulative biogas production were greater than the control PLM due to the enhancement of microbial activity.

Table 20 Comparison of Parameters with Significant Difference for Dry Period.

Parameter	Averages CCAs PLM	Averages Control PLM
pH	8.6 ± 0.2	8.3 ± 0.2
Hardness (mg/L as Calcium)	63.2 ± 18.5	93.2 ± 33.3
Turbidity (NTU)	17.3 ± 7.4	28.2 ± 7.0
Conductivity (μS/cm)	3.0 ± 0.4	2.6 ± 0.3
Cumulative Biogas Volume (mL)	14,202 ± 870.0	1,539 ± 945.0

4.1.5.4 *Recirculation Period*

For the third sequence (RP), the statistical analyses are summarized in Table 21:

Table 21 Statistical Analysis for Recirculation Period.

Parameter	F	p - value
Volume (mL)	0.02	0.900
pH	0.5	0.486
ORP (mV)	0.27	0.607
NO_3^- (mg/L as N)	0.43	0.518
Hardness (mg/L as Calcium)	0.53	0.475
Color (Pt Co Units APHA)	2.66	0.116
Turbidity (NTU)	4.07	0.055
Conductivity (μS/cm)	2.41	0.134
DO (mg/L O_2)	1.56	0.224

Parameter	F	p - value
COD (mg/L COD)	1.79	0.193
Total Phosphorus (mg/L PO_4^{-3})	9.77	0.005
Total Nitrogen (mg/L N)	8.25	0.008
Orthophosphate (mg/L PO_4^{-3})	3.74	0.065
Alkalinity (mg/L $CaCO_3$)	0.76	0.392
BOD_5 Average (mg/L)	2.13	0.158
Cumulative Biogas Volume (mL)	0.54	0.478
Normalized Settlement (cm/(kg/cm^3))	393.59	0.000

The parameters that showed a significant difference were turbidity, total phosphorus, total nitrogen, cumulative biogas volume and cumulative normalized settlement (Table 22):

Table 22 Comparison of Parameters with Significant Difference for Recirculation Period.

Parameter	**Averages CCAs PLM**	**Averages Control PLM**
Turbidity (NTU)	92.9 ± 50.5	126.8 ± 33.2
Total Phosphorus (mg/L PO_4^{-3})	18.3 ± 6.0	25.5 ± 5.8
Total Nitrogen (mg/L N)	133.9 ± 26.3	171.2 ± 38.7
Cumulative Biogas Volume (mL)	16,125 ± 6,284.0	4,747 ± 2,685.0
Normalized Settlement (cm/(kg/cm^3))	4,372 ± 1,618.0	2,103 ± 739.0

The averages of the PLM with CCAs as daily cover for parameters such as turbidity, total phosphorus and total nitrogen were smaller to those of the control PLM with sand as daily cover. The difference in these parameters may be due to a faster biodegradation in the CCA PLM. This assumption is also supported with greater cumulative biogas production and cumulative normalized settlement, indicating more biodecomposition of waste by enhanced microbial activity.

5. EVALUATION OF SMALLER PHYSICAL LANDFILL MODELS (SPLMs)

In this experiment, three smaller physical landfill models (SPLMs) were constructed using coal combustion byproducts aggregates (CCAs) as daily cover, with the objective to evaluate the behavior of CCAs with respect to the packing density. The first SPLM had the similar packing density as the CCAs PLM had. The second one was constructed with the similar packing density of the control PLM and the third one had a higher packing density than the CCAs PLM's (1.23). Therefore, the hydraulic and biochemical properties of CCAs as alternative reactive daily cover (ARDC) were compared in the three SPLMs.

The SPLMs configuration was (from bottom to top): gravel, sand, solid wastes, daily cover (CCAs), solid wastes, daily cover (CCAs), solid wastes, daily cover (CCAs), and sand as the final layer (packing density and configuration of the SPLMs are in the methodology). The results of the CCAs PLM showed that using CCAs as an ARDC had the following advantages: lower concentrations of inorganic and organic compounds in leachate, more settlement and more biogas production as consequence of the microbial activity. The same behavior was expected in the SPLMs.

5.1 RESULTS

Below are the results of the physical parameters, as well as the biological, and inorganic and organic compounds measured in each of the SPLMs.

5.1.1 *Physical Parameters*

The physical parameters measured were the amount of leachate produced (volume), pH, color, turbidity, and conductivity.

5.1.1.1 *Volume*

The volume of the leachate was collected in the bottom of each SPLM and measured weekly using a graduated cylinder. Figure 37 shows the hydraulic conditions of the SPLMs.

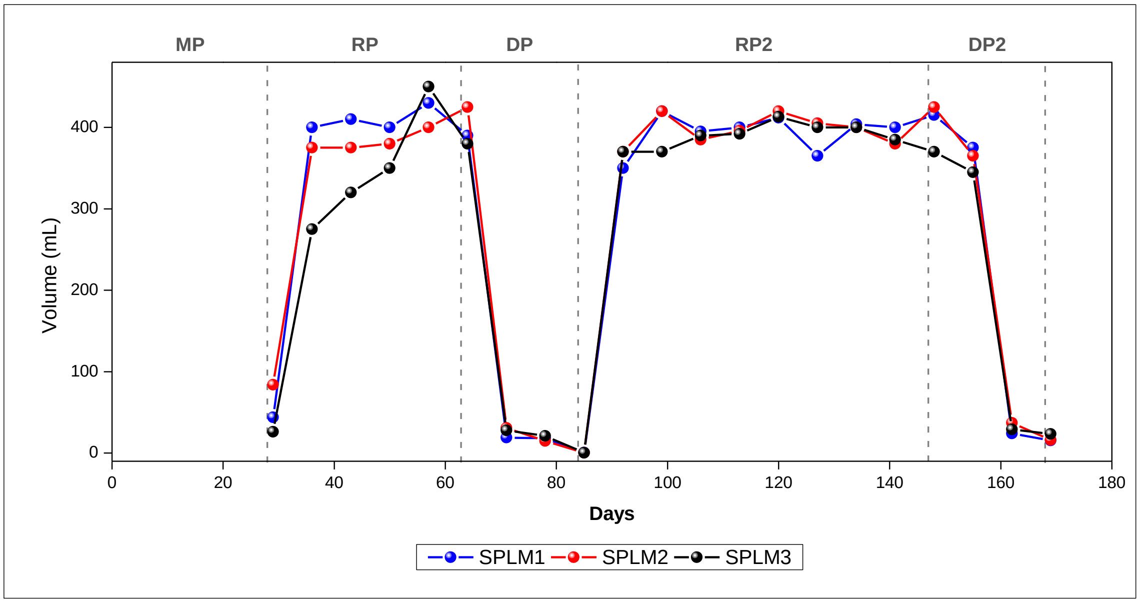

Figure 37 Volume of Leachate Produced in SPLMs.

The first simulated period was the MP. The rainfall volume added was 200 mL to each SPLM; in this period there was no production of leachate in the SPLMs (Figure 37). Then, in the recirculation period, the volume of leachate added to the SPLMs was 400 mL and in the DP no rain simulation was performed. Therefore, water collected during the dry periods corresponded to water flowing out of storage in the porous media in the SPLMs. Graphically and statistically, there was no significant difference between the SPLMs; this means they were hydraulically equivalent. With these results, it was found that, hydraulically, the SPLMs produced very similar amounts of leachate with CCAs as daily cover (Figure 37). This was due to the great void fractions in the CCAs particles, especially small-sized ones, where the water could be held at a greater extent than in sand (Escobar et al., 2009; Fonseca et al., 2007).

5.1.1.2 *pH*

In this research, the pH in the SPLMs (Figure 38) had the same behavior as the CCA PLM. The only difference was that in the first RP since the SPLM-2 started with a pH of 6.7, increased and then continued with the same behavior as the others SPLMs. At the beginning of the experiment, the pH decreased for SPLM-1 and SPLM-2 possibly due to the accumulation of acids from the hydrolyzation of solid waste into organic acids and the end products of acidogenic bacteria as mentioned for Elagroudy et al. (2009). This leads to high levels of volatile acids and lower pH values (Lo et al., 2009). In general, during periods of recirculation (RP and RP2), low values of pH were obtained in the range of 7.4 - 8.0 while for dry period (DP and DP2) the values was greater (~ 8.9). It is important to note that the condition for onset of methanogenic conditions suggests an increase in pH and a decrease in BOD concentrations and BOD/COD ratio (Morris et al., 2003). Also, the high values in the dry periods (DP and DP2) could be a consequence of the delayed leachate release (Junqueira et al., 2006).

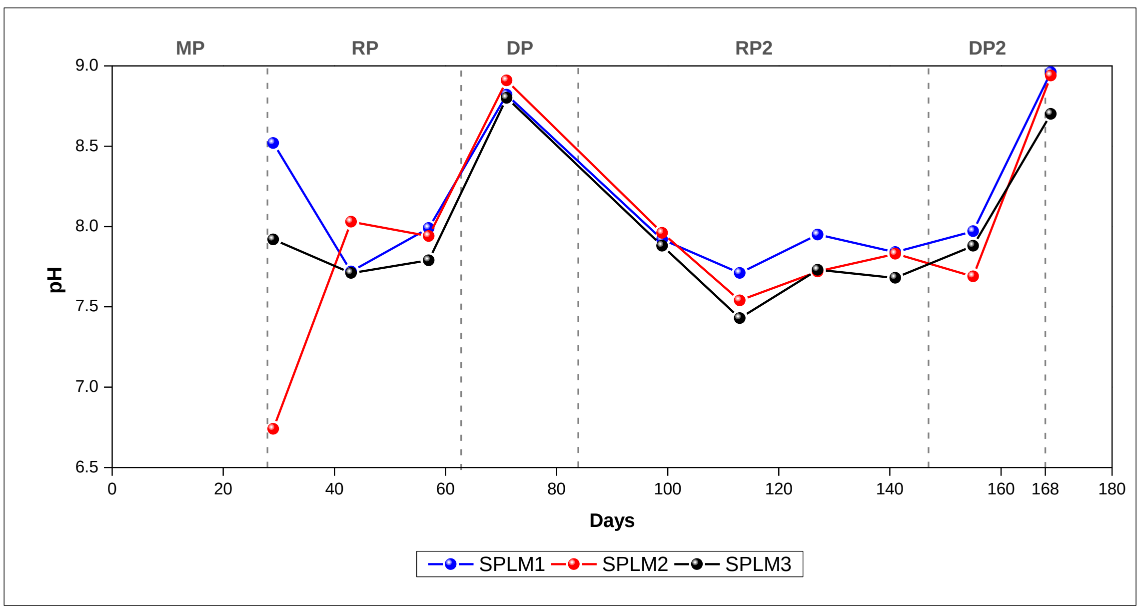

Figure 38 pH Values of Leachate Produced in SPLMs.

The pH in the recirculation period (RP and RP2) of the experiment suggests that the microbial population in the recirculation landfill be able to recover from the production of soluble organic matter induced by recirculation.

5.1.1.3 *Color*

The color of leachate was orange-brown or dark-brown, the same manner as in the PLMs. The dark color disappears due to the increasing of the time in the SPLMs. The color results in the SPLMs are shown in Figure 39:

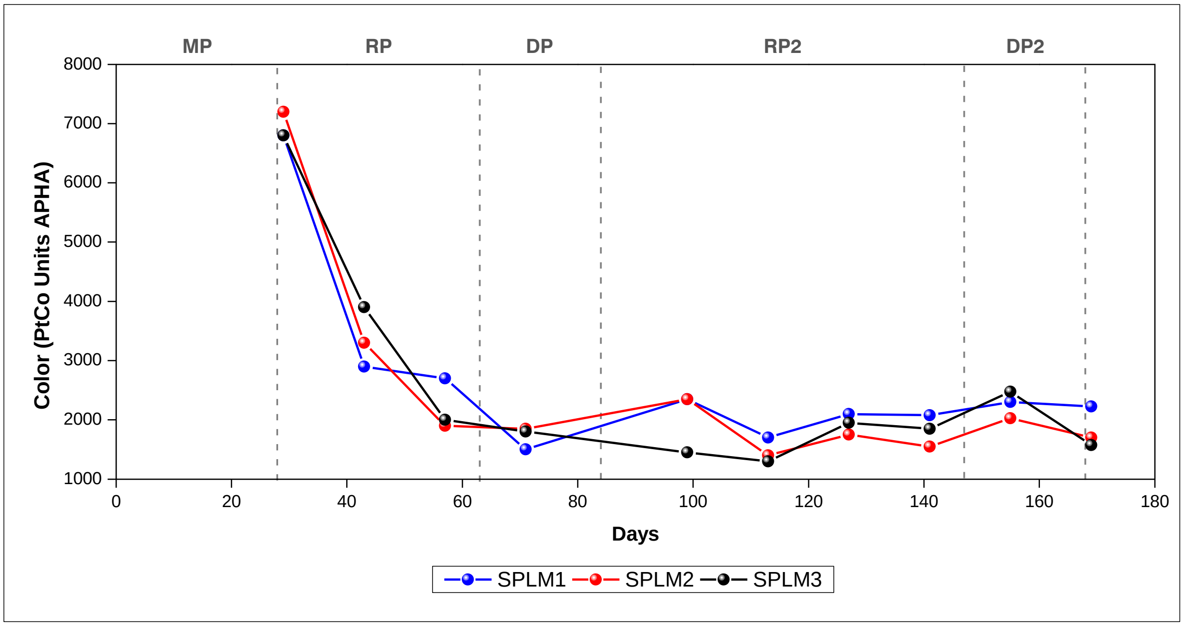

Figure 39 Color Intensity of Leachate Produced in SPLMs.

The first recirculation period (RP) had high values of color, the range of values were 6,800 – 7,200 Pt Co Units APHA, due to the presence of organic acids, which came from the high concentrations of decomposed organic matter. But, starting from the first dry period (DP), the values were maintained between the range 1,575 – 2,225 Pt Co Units APHA in the three SPLMs, showing no significant difference between them.

5.1.1.4 *Turbidity*

The results for turbidity are shown in Figure 40. Turbidity similarities were found regardless of the type of SPLMs

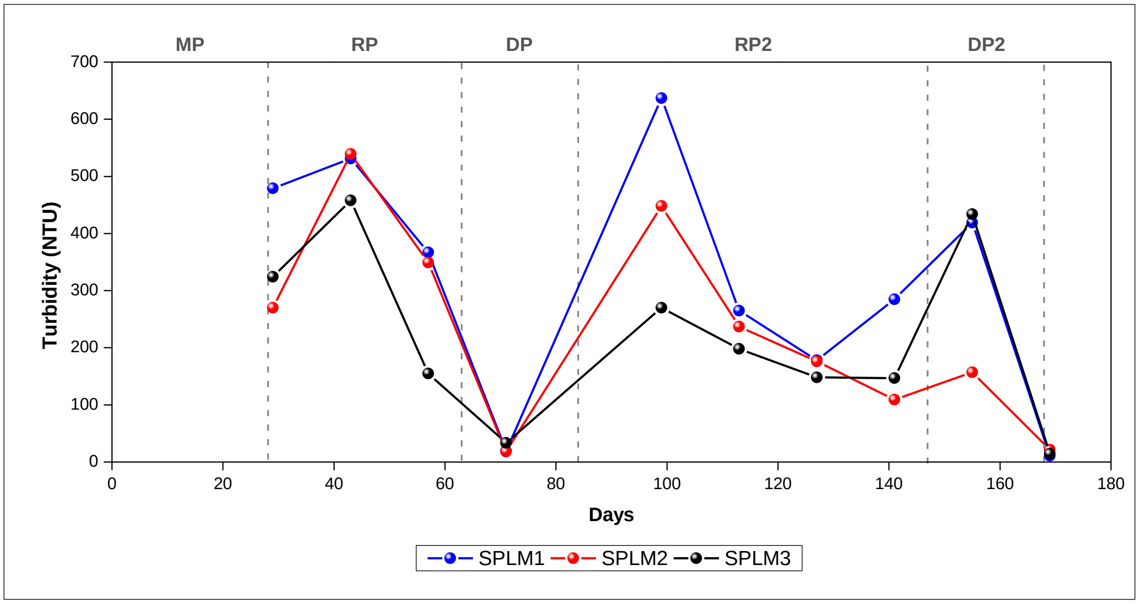

Figure 40 Turbidity of Leachate Produced in SPLMs.

In the experiment, recirculation periods (RP and RP2) increased leachate turbidity and then values decreased until dry periods (DP and DP2), this behavior corresponded to decrease in the suspend particles in the SPLMs. In the experiment, leachate samples of dry periods which contained less volume had lower concentrations of suspended particles than the samples from the recirculation periods which contained more volume and more suspend particles added in the leachate recirculation.

5.1.1.5 *Conductivity*

In the experiment, the conductivity values were due to precipitation and the washout of easily mobilized ions such as metals, chloride and sulfate as a result of rainfall simulation and sampling, which were concurred with Erses et al. (2008). These components may come from solid waste and their decomposition, daily cover and sand used in the construction of the SPLMs.

The results for conductivity are shown in Figure 41. The conductivity behaved similarly in the SPLMs. However, SPLM-2 began the recirculation period with a high conductivity of 23.8 μS/cm, while for the SPLM-1 and SPLM-3 were 11.2 and 13.0 μS/cm, respectively. The high conductivity in the beginning of the experiment may be attributed to the ions washed out by the leachate recirculation. In the first period of recirculation (RP) the values declined but in the dry period it decreased slightly. At the end of the experiment, the SPLMs conductivities were similar, in the range of 2.6 - 3.2 μS/cm.

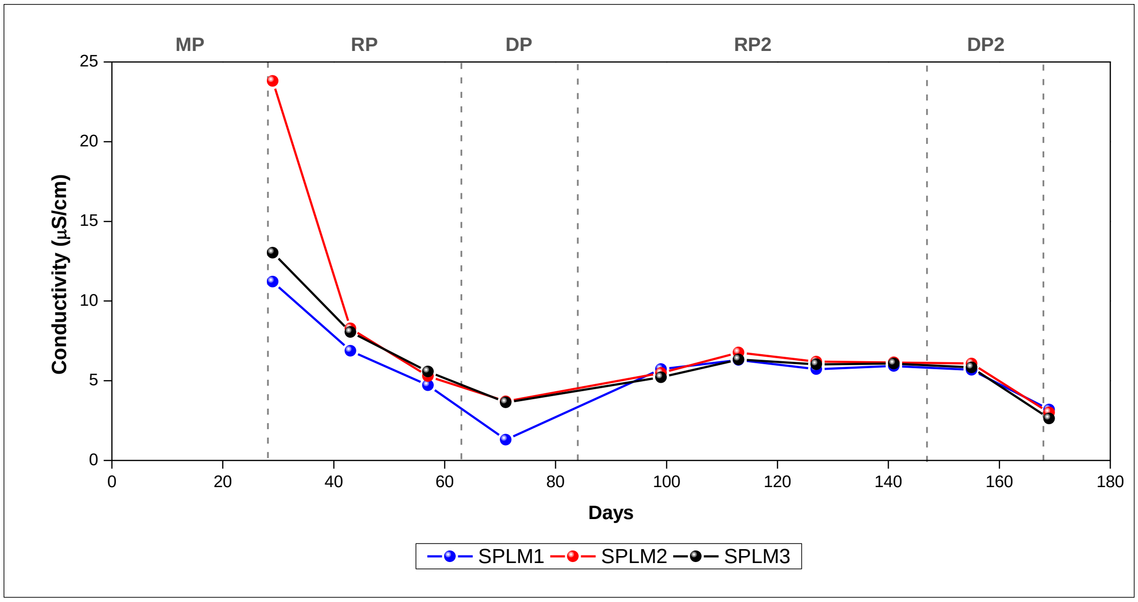

Figure 41 Conductivity of Leachate Produced in SPLMs.

5.1.2 *Organic Constituents in the Leachate*

The organic constituents measured in the SPLMs COD and volatile fatty acids.

5.1.2.1 *Chemical Oxidation Demand*

The results of COD concentrations in the SPLMs are shown in the following Figure 42.

The SPLMs had the same behavior with respect to COD. In the beginning of the experiment, specifically in the RP, the highest values of COD were found since leachate from young landfill is characterized by high COD, even several thousands of mg/L. After, the COD decreased rapidly in the same period because COD was degraded by microorganisms, resulting in a gradual decrease during the digestion period as indicated Lo et al., (2009). The leachate recirculation improves leachate quality, especially in terms of COD.

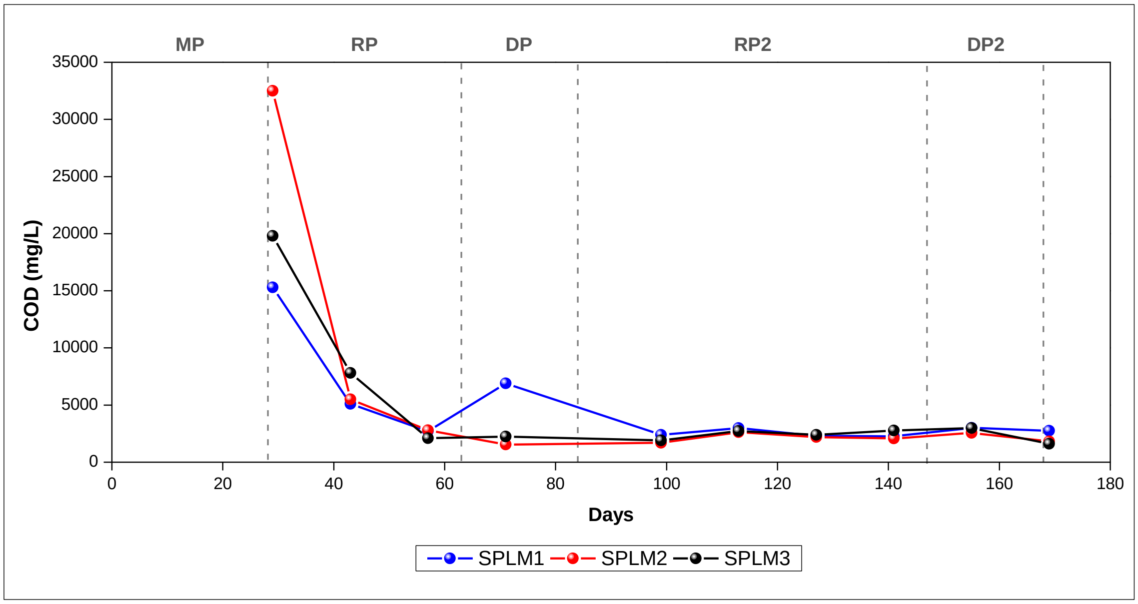

Figure 42 Chemical Oxygen Demand of Leachate Produced in SPLMs.

The maximum value of COD concentration depends on the amount of organics and whether they are readily degraded. SPLM-2 had the highest COD concentration of 32,500 mg/L when compared to SPLM–1 and SPLM–3. The concentrations were 15,300 and 19,800 mg/L, respectively, reaching the DP with concentrations of 6,900, 1,550 and 2,250 mg/L for SPLM-1, SPLM-2 and SPLM-3, respectively. Then, the SPLMs maintained similar concentrations in the range of 1,600 – 2,750 mg/L as COD. The lower COD values suggest a faster organic matter degradation process. Overall, COD values from SPLMs showed a similar trend that observed with the PLMs.

5.1.2.2 *Volatile Fatty Acids*

The volatile acids concentrations were calculated for the SPLMs and the results are shown in Figure 43.

The volatile fatty acids concentrations in the SPLMs had the same behavior in the first RP presenting high values, the concentrations were 331.4, 470.4 and 497.1 mg/L as CH_3COOH corresponding to SPLM-1, SPLM-2 and SPLM-3. These concentrations decreased dramatically at the end of the experiment and the values were 18.9, 14.3 and

74.3 mg/L as CH_3COOH for SPLM-1, SPLM-2 and SPLM-3, respectively. This decrease in the concentration of volatile acids may be due to: the organic waste hydrolyzed into aqueous organic acids consumed by acidogenic bacteria to produce volatile fatty and carbon dioxide. Then the volatile fatty concentration dropped as the daily biogas production increased, because the methanogenic bacteria used the volatile fatty as a substrate to produce methane and carbon dioxide coincide with those reported by Elagroudy et al. (2009).

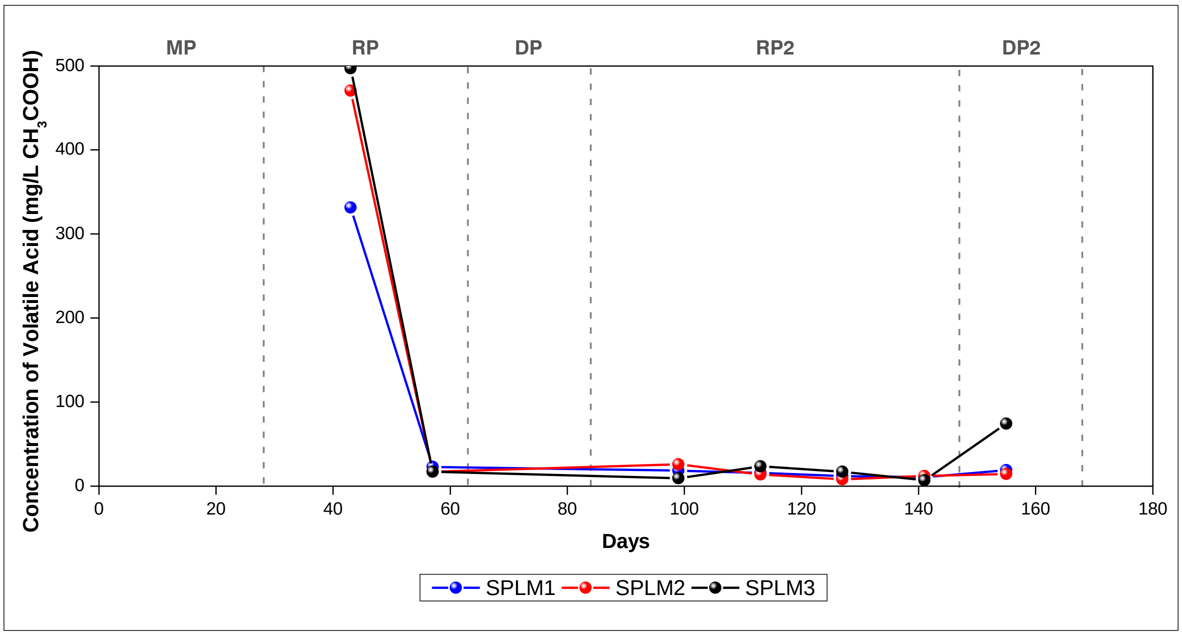

Figure 43 Volatile Fatty Acids of Leachate Produced in SPLMs.

5.1.3 *Inorganic Constituents in the Leachate*

The inorganic constituents measured in the SPLMs, in order to know the quality of the leachate were: nitrate, hardness, total phosphorus, total nitrogen, orthophosphate and alkalinity.

5.1.3.1 *Nitrate*

Figure 44 shows the nitrate concentrations in the SPLMs. Similar trends are observed for all reactors. the total removals of nitrate were 72.0, 80.4 and 84.1% for SPLM-1, SPLM-2 and SPLM-3, respectively. It is remarkable, the highest percentage of removal was found in the SPLM with the most amounts of CCAs as daily cover. In dry periods (DP and DP2), nitrate concentrations were lower compared with the periods of recirculation, this corresponds to the behavior seen in the CCAs PLM. Therefore, the difference in packing density of the SPLMs appears to represent a difference in the behavior of the nitrates, the only difference is in the SPLM-3, becoming an outlier point may be due to experimental error by taking the sample (time or lack of homogenization).

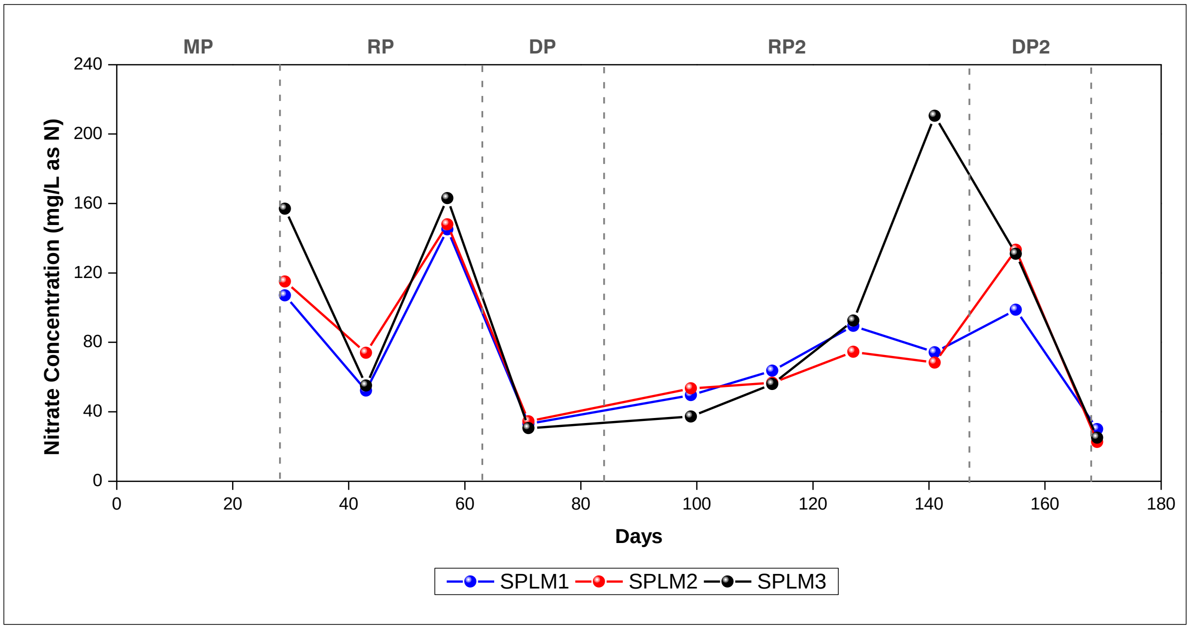

Figure 44 Nitrate Concentrations of Leachate Produced in SPLMs.

5.1.3.2 *Hardness*

In the SPLMs, high hardness concentrations were found due to high lime concentration present in the CCAs which directly contribute to increments in hardness by ions dissolution in presence of water as was found in Latorre (2010). Initially, hardness concentrations were found lower in the PLM with CCAs as daily cover than the PLM with sand as daily cover. The results of hardness for SPLMs are shown in Figure 45:

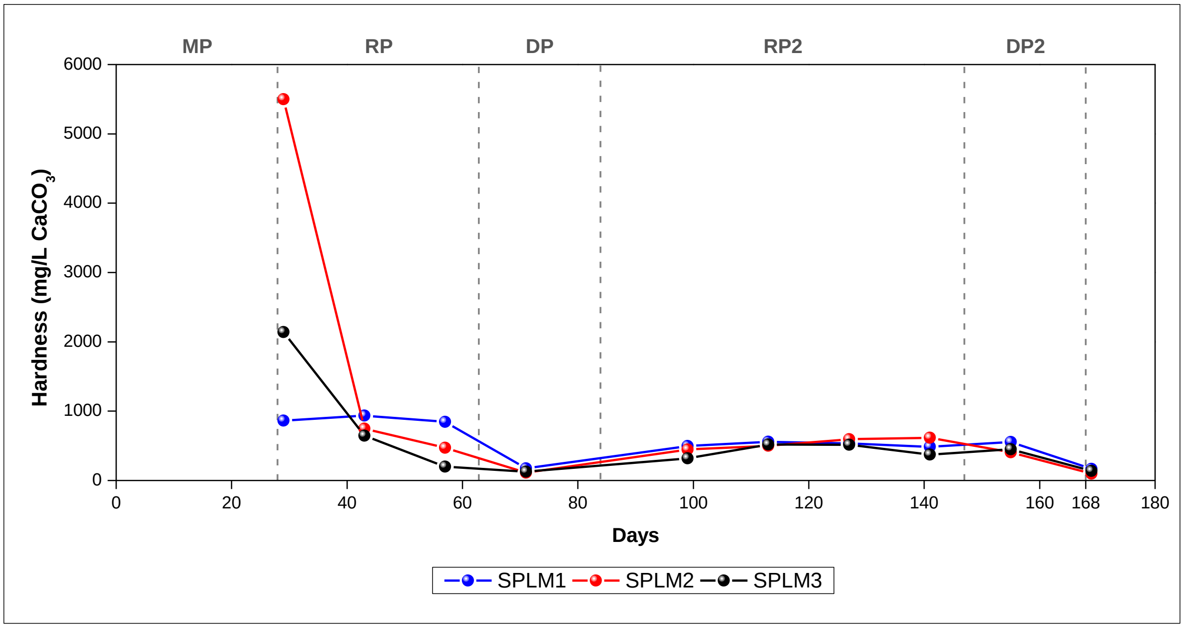

Figure 45 Hardness Leachate Produced in SPLMs.

The highest values of hardness were found in the first recirculation period (RP), where SPLM-2 had the highest value of hardness (5,500 mg/L $CaCO_3$) followed by SPLM-3 with 2,140 mg/L $CaCO_3$ and 863 mg/L $CaCO_3$ for SPLM-1. These results indicate that the SPLM with higher packing density (i.e., higher amount of CCA) contributed a greater amount of lime (CaO) and (MgO). Hardness decreased after the initial RP and stabilized during the later periods of the experiment due possibly to washing of the SPLMs as a result of the infiltration periods. The values at the end of the experiment were similar: 168, 99 and 138 mg/L $CaCO_3$ corresponding to SPLM-1, SPLM-2 and SPLM-3.

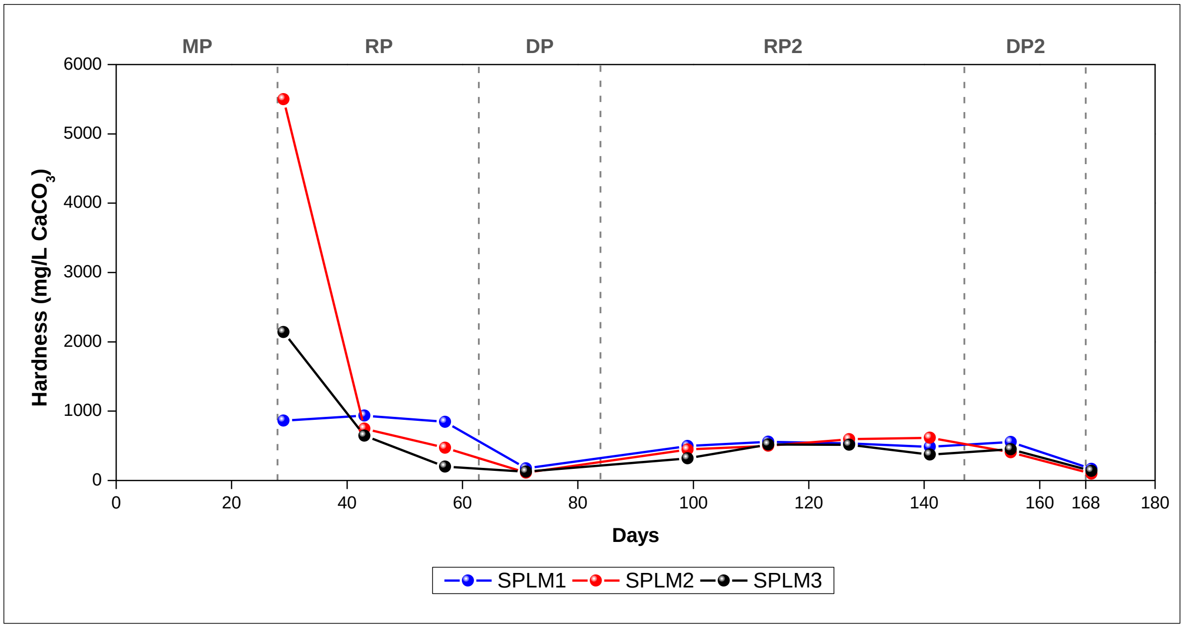

Figure 46 Hardness of Leachate Produced in SPLMs.

5.1.3.3 *Total Phosphorus*

The total phosphorus results are shown in Figure 47. At the beginning of the experiment, high concentrations occurred in the first RP (55.9, 70.9 and 93.9 mg/L as PO_4^{-3}, corresponding to SPLM-1, SPLM-3 and SPLM-2) due to increased loads of phosphorus in the leachate recirculation and these values decreased until they reached a similar concentration in the DP (between 8.9 - 11.4 mg/L as PO_4^{-3}). Then in the other recirculation period (RP2), the concentrations increased slightly and then decreased to a low concentration. The final phosphorous concentrations were 33.7, 17.4 and 10.7 mg/L as PO_4^{-3}, corresponding to SPLM-1, SPLM-3 and SPLM-2, respectively.

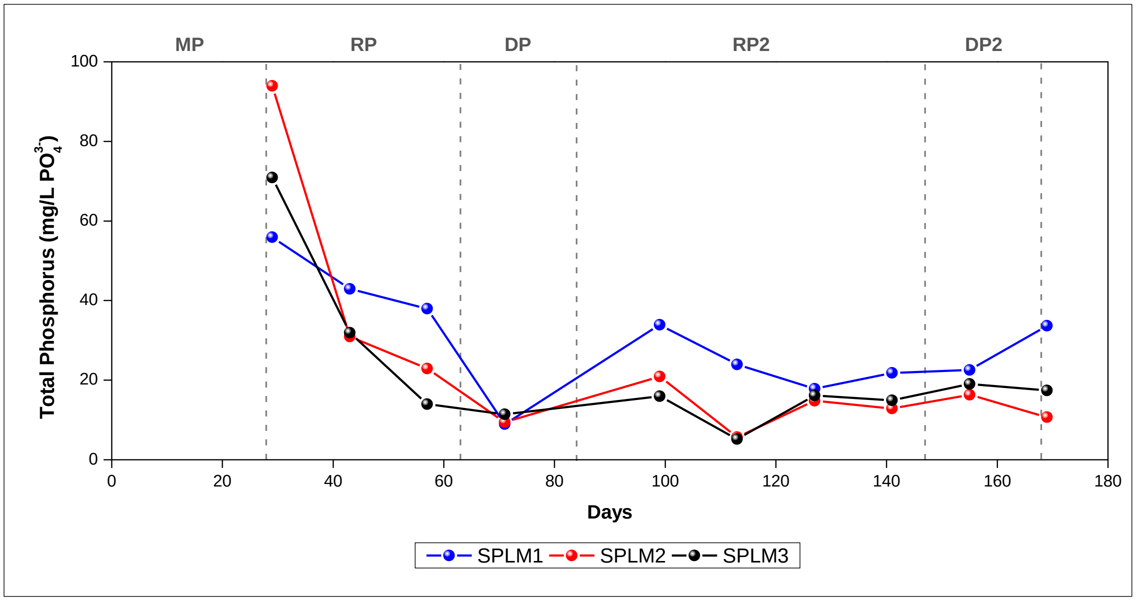

Figure 47 Total Phosphorus of Leachate Produced in SPLMs.

5.1.3.4 *Total Nitrogen*

The results for total nitrogen concentrations are shown in Figure 48 where it is shown that total nitrogen concentrations were found similar regardless of the CCAs PLM.

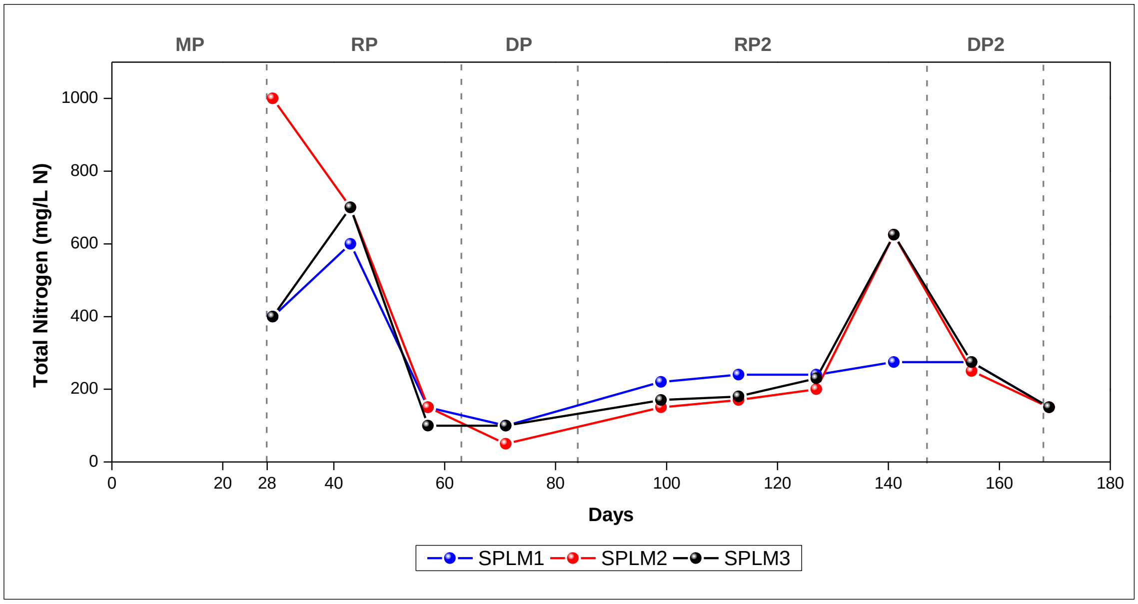

Figure 48 Total Nitrogen of Leachate Produced in SPLMs.

Nitrate and total nitrogen in refuse decreased with time (Figure 48). For the

SPLM-1 and SPLM-3, the concentrations were 400 mg/L as N (initial concentrations were similar, indicating uniformity in waste composition) and increased to 600 and 700 mg/L as N respectively while for SPLM-2 was 1,000 mg/L as N. Decreases and increases in the concentrations in the RP were due to leachate recirculation up to a concentration of 150 mg/L as N in the DP. Total nitrogen concentrations were high when the SPLMs were in the initial stages in the processing wastes, but they were low due probably to the use of the total nitrogen as a nutrient for microorganisms in the role of decomposition and growth.

5.1.3.5 *Orthophosphate*

Orthophosphate concentrations in the SPLMs with CCAs as an ARDC showed the following behavior in Figure 49. The SPLM-2 and SPLM-3 followed the same behavior, starting with a concentration for orthophosphate of 71 and 99 mg/L as PO_4^{-3} then these concentrations decreased slowly and in the second period of recirculation (RP2) it increased and then decrease in the DP to a concentration of 16 and 17 mg/L as PO_4^{-3}. Orthophosphate concentration increased as a result of the hydrolysis of organic phosphorus compounds and the decline in orthophosphate concentrations that may have been the result of orthophosphate assimilation by microorganisms and dilution. While the SPLM-1 began with an orthophosphate concentration of 57 mg/L as PO_4^{-3} which increased to 202 mg/L (this point is possible outlier due to experimental error in the sample) and then decreased slowly to finally increase in the dry period to 42 mg/L as PO_4^{-3}.

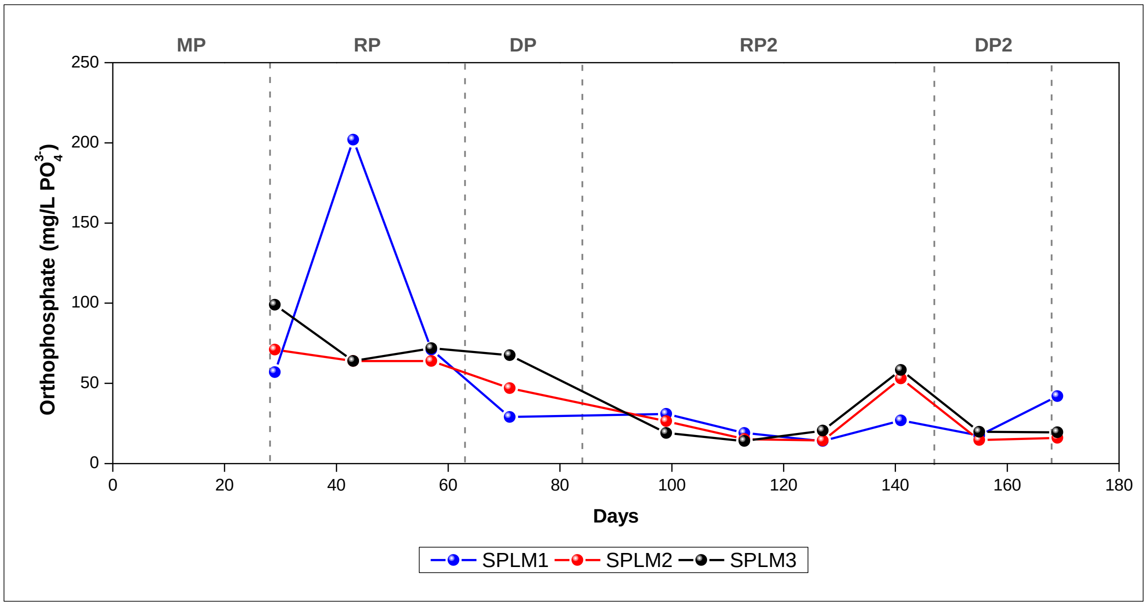

Figure 49 Orthophosphate of Leachate Produced in SPLMs.

5.1.3.6 *Alkalinity*

At the beginning of the experiment, high alkalinity concentrations were produced. These values are attributed to the presence of ions such as bicarbonates, carbonates, hydroxides, borates, silicates, phosphates, ammonium, sulfides, and organic ligands in soils and CCAs. It is important and necessary to maintain adequate alkalinity, or buffer capacity, to maintain a stable pH in the digester for optimal biological activity, this value must be at least 2,000 mg/L to maintain an optimum methanogenesis as reported by Bilgili et al., (2007). The results for the alkalinity concentrations in the SPLMs are shown in Figure 50:

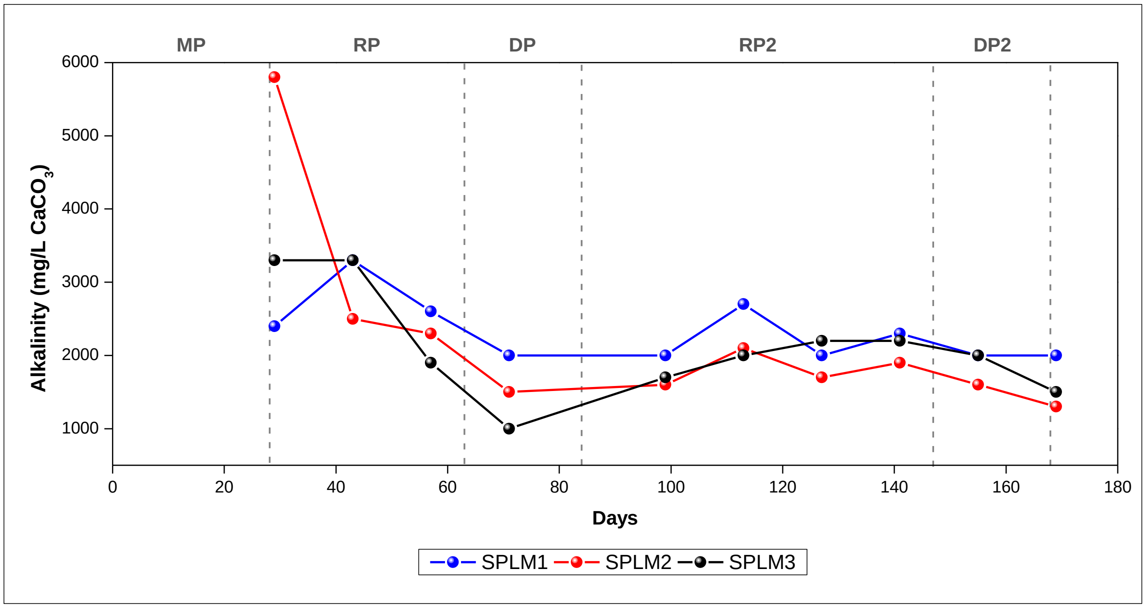

Figure 50 Alkalinity of Leachate Produced in SPLMs.

For SPLM-2, the concentration of alkalinity was the highest at 5,800 mg/L $CaCO_3$ and decreased in the RP slowly to a concentration of 1,300 mg/L $CaCO_3$. In the recirculation, advantage can be taken of adapted microflora and high alkalinity of effluent in the methanogenic reactor to buffer pH and inoculate, thus providing optimal environmental and nutrient conditions for acidogenic bacteria and methanogens, and improve the performance of the landfill system as suggested by Jun et al. (2009). While the concentrations for SPLM-1 and SPLM-3 were 2,400 and 3,300 mg/L $CaCO_3$ in the beginning of the experiment, these values increased and then decreased slightly to 2,000 and 1,500 mg/L $CaCO_3$. Alkalinity values in the recirculation periods helped to improve microbial activity reflected in the biogas production in the SPLMs.

5.1.4 *Biological Parameters in the Leachate*

Among the biological parameters measured were: BOD_5, dissolved oxygen (results is found in the Appendix 4), and biogas production.

5.1.4.1 *Biological Oxygen Demand*

BOD_5 concentrations in SPLMs had the same behavior (Figure 51); the difference was in the first RP. In the experiment, the high BOD_5 concentration in the leachate was followed by a quick BOD_5 decline caused by the leachate recirculation and moisture content were reasonably high to allow material solid waste biodegradation as reported by Elagroudy et al. (2009). The initial concentrations were 351, 1,055 and 1,061 mg/L for SPLM-1, SPLM-2 and SPLM-3, respectively. Then SPLM-2 increased its concentration 2,635 mg/L and decreases dramatically (106.4 mg/L), SPLM-1 also increases its concentration to 878 mg/L and then decrease to 126 mg/L. Initially, the BOD_5 concentration increased in SPLM-1 and SPLM-2 as a result of low methanogenic activity, which facilitated the accumulation of organic acids from the hydrolysis and acidogenesis steps. Then as the methanogenic bacteria became active, the BOD_5 decreased. By contrast, SPLM-3 concentration decreased to 126 mg/L. The reductions were part of the recirculation period, and then the concentrations of SPLMs followed the same behavior up to a final concentration range of 212 - 357 mg/L.

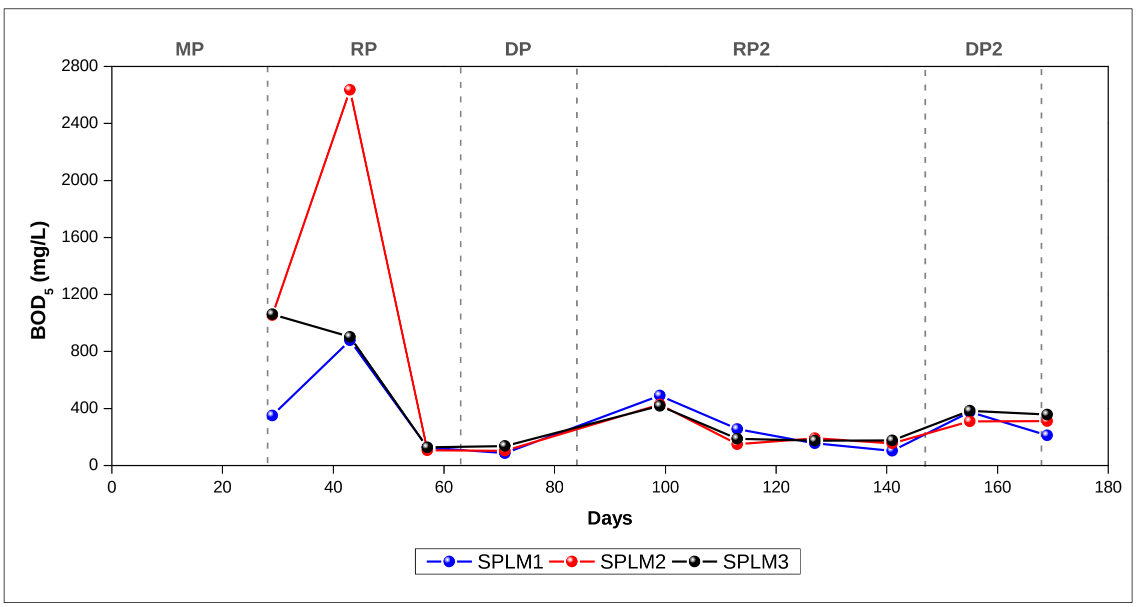

Figure 51 Biological Oxygen Demand of Leachate Produced in SPLMs.

5.1.4.2 *Biogas Production*

With respect to biogas production in the SPLMs, it was only measured on SPLM-1 and SPLM-3. Figure 52 shows the daily biogas production while Figure 53, shows the cumulative biogas production. The biogas production due to more biological activity occurred in the SPLMs. The leachate recirculation shortened the period of the methanogenic stage and lowered the leachate strength, which depended on the portions of nutrients, minerals or organics being attenuated by the waste and soil as mentioned Chan et al. (2002). The daily biogas production began in the recirculation period.

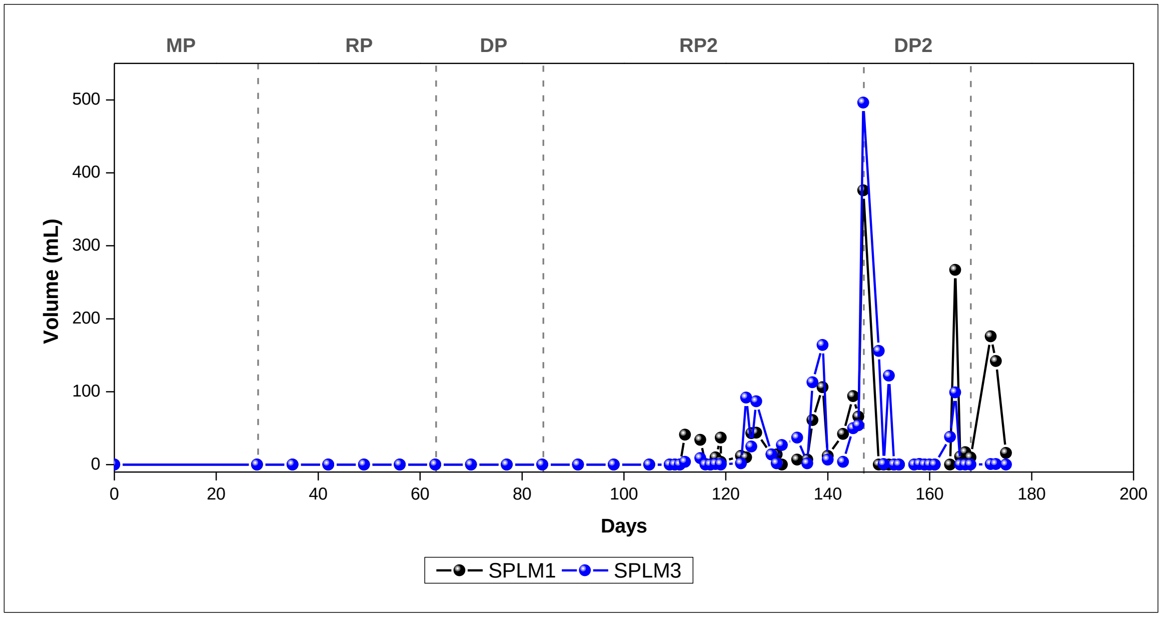

Figure 52 Daily Biogas Production in SPLMs.

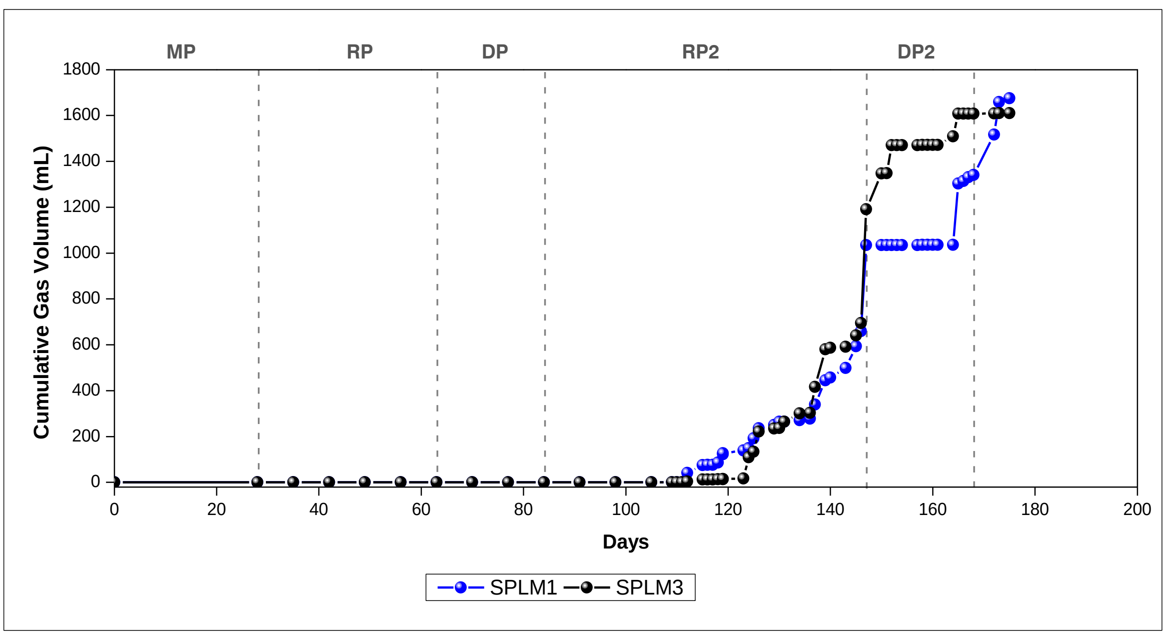

Figure 53 Cumulative Biogas Production in SPLMs.

The biogas production in both SPLMs (1 and 3) began in the second recirculation period (RP2), this indicates a possible further biodegradation of solid waste, since leachate recirculation reduced waste stabilization time and was effective in enhancing biogas production and improving leachate quality. But for the SPLM-3 cumulative biogas production present more biogas production, especially in the dry period (DP2). Therefore, in this research the results showed that leachate recirculation was effective in enhancing the degradation rate of the waste, and biogas production. Figure 53 showed that biogas production was significant in both SPLMs, enhanced the bioreactor as a result of both accelerated biogas production rates and the return of organic materials in the leachate to the landfill for conversion to biogas, in the RP. It is unlikely that the packing density interfered with the production of biogas in the reactors as evidenced by the microbial activity and decomposition of solid waste.

5.1.5 *Statistical Comparison*

Table 41 – Table 46 (Appendix 2) summarize the parameters measured in the SPLMs at each period, with their respective average values, standard deviations, maximums and minimums, as the number of samples taken. Statistical analyses were performed to compare the parameters and concentrations of compounds (pH, ORP, heavy metals, phosphorus, turbidity, nitrate, total nitrogen, COD, BOD, dissolved oxygen, alkalinity, and hardness) in the leachate of each of the SPLMs. Therefore, an ANOVA was used to find significant differences between compounds in the leachate, the level of significance for the ANOVA was of 5%.

5.1.5.1 *Dry Period*

The statistical analysis for each SPLM in the DP is summarized in Table 23. In the comparison of the p-value calculated with value of α (0.05), it was found that none of the parameters show significant difference in them, therefore, the behavior of the variables was the same for all the SPLMs.

Table 23 Statistical Analysis for Dry Period in the SPLMs.

Parameter	F	p - value	Parameter	F	p - value
Volume (mL)	0.00	0.999	DO (mg/L O_2)	1.03	0.413
pH	0.03	0.968	COD (mg/L COD)	2.16	0.197
ORP (mV)	0.03	0.97	Total Phosphorus (mg/L PO_4^{-3})	1.14	0.381
NO_3^- (mg/L as N)	0.03	0.973	Total Nitrogen (mg/L N)	0.07	0.932
Hardness (mg/L as Calcium)	0.18	0.838	Orthophosphate (mg/L PO_4^{-3})	0.17	0.844
Color (Pt Co Units APHA)	0.12	0.892	Alkalinity (mg/L $CaCO_3$)	2.94	0.129
Turbidity (NTU)	0.21	0.817	BOD_5 Average (mg/L)	0.21	0.819
Conductivity (µS/cm)	0.18	0.839			

The packing densities of the SPLMs were: one SPLM used the same densities that the CCAs PLM used (ρ_{SPLM-1} = 742.65 Kg/m^3), the other used densities similar to the control PLM (ρ_{SPLM-2} = 1551.00 Kg/m^3), and the third had a density greater than CCAs PLMs (ρ_{SPLM-3} = 849.65 Kg/m^3). And, the results indicated that packing density of the CCA did not significantly alter the production and composition of leachate in the dry period.

5.1.5.2 *Recirculation Period*

In the RP, the statistical analysis of the measured parameters performed to the SPLMs is summarized in Table 24

Table 24 Statistical Analysis for Recirculation Period in the SPLMs.

Parameter	F	p - value
Volume (mL)	2.67	0.082
pH	1.76	0.206
ORP (mV)	3.05	0.077
NO_3^- (mg/L as N)	0.45	0.649
Hardness (mg/L as Calcium)	2.74	0.097
Color (Pt Co Units APHA)	2.74	0.097
Turbidity (NTU)	1.36	0.287
Conductivity (µS/cm)	0.42	0.665
DO (mg/L O_2)	0.1	0.903
COD (mg/L COD)	0.13	0.88
Total Phosphorus (mg/L PO_4^{-3})	**3.8**	**0.046**
Total Nitrogen (mg/L N)	0.08	0.924
Orthophosphate (mg/L PO_4^{-3})	0.38	0.688
Alkalinity (mg/L $CaCO_3$)	1.44	0.268
BOD_5 Average (mg/L)	0.39	0.681
Volatile Acids (mg/L as CH_3COOH)	0.04	0.959

Table 25 Comparison of Parameters with Significant Difference for Recirculation Period in the SPLMs.

Parameter	Average SPLM-1	Average SPLM-2	Average SPLM-3
Total Phosphorus (mg/L PO_4^{-3})	29.7	18.0	16.4

In the recirculation period, the total phosphorus was the only parameter found with a significant difference, by comparing the average concentration of total phosphorus in the SPLMs (Table 25): SPLM-1 (ρ_{SPLM-1} = 742.65 Kg/m^3) had the highest concentration, 29.7 mg/L PO_4^{-3}; for the SPLM-2 (ρ_{SPLM-2} = 1551.00 Kg/m^3) was 18.0 mg/L PO_4^{-3}; while the lowest concentration was found in the SPLM-3 (ρ_{SPLM-3} = 849.65 Kg/m^3), 16.4 mg/L PO_4^{-3}. It is important to emphasize that no significant difference between SPLM-2 and SPLM-3.

6. REMOVAL OF HEAVY METALS

The purpose of this study was to investigate the possibility of heavy metal uptake by coal combustion byproducts as a low cost adsorbent material when used as an alternative daily cover. Three experiments were conducted: injection of heavy metals to smaller physical landfill models (SPLMs), batch experiments to determine the effect of contact time and pH in the removal of heavy metals, and an estimation of point of zero charge of CCAs.

The smaller physical landfill models SPLM-1 and SPLM-2 were injected with a solution composed of leachate, cadmium and lead. In the batch reactors, a volume of 200 mL of the aqueous solution of Cd^{2+} and Pb^{2+} was mixed with CCAs in an Erlenmeyer and placed in a Reciprocal Shaking Bath Model 50 at 150 rpm. Point of zero charge of CCAs was investigated using a mass titration method in order to understand the process for the removal of heavy metal. The applied solid/liquid ratio ranged from 0.01 to 60 g with a volume of 100 mL aqueous solution. The aqueous solution of NaCl and KCl was used to provide constant and adequate ionic strength. In the chapter of Materials and Methods (Section 3.2.3) has more details of the development of these experiments.

6.1 RESULTS

Below are the results found in each of the experiments that evaluated the CCAs capacity for the removal of heavy metals and the point of zero charge.

6.1.1 *Smaller Physical Landfill Models with Heavy Metals Solution Injection*

For this experiment, the SPLM-1 and SPLM-2 were injected with a solution composed of leachate (60 mL), and cadmium (20 mL) and lead (20 mL) (concentration of cadmium and lead was 100 mg/L). The measured parameters were: pH, volume of leachate produced, turbidity, conductivity, chemical oxygen demand, biological oxygen demand, volume of biogas produced, and concentration of heavy metals. In this section, the results of heavy metal and pH are shown, while the results of other parameters are found in Appendix 5.

Heavy metals were measured using Cole Parmer Combination Ion Selective Electrodes, (Cd^{2+} and Pb^{2+}) and Atomic Absorption Spectrometer Perkin Elmer AAnalyst 400 and no heavy metals were found, is possible that concentrations of heavy metals are below detection levels 0.2 mg/L. Therefore, two samples collected after 4 weeks of the experiment were subject to an Inductively Coupled Plasma-Mass Spectrophotometer (ICP-MS) to detect heavy metals concentrations. The results are shown in Table 26.

Cadmium and lead leachate concentrations from the smaller physical landfill models (Table 26) show a strong metal removal by the CCA. Considering the higher cadmium and lead concentrations in the recirculated leachate, very low concentrations were found, approximately at 100 µg/L. Therefore, it is construed that spike heavy metals in the recirculated leachate was removed by CCAs in the SPLMs. For the determination of the mechanism, it was necessary to conduct a batch experiment where CCAs was in contact with solutions contain similar concentrations of heavy metals and also the point of zero charge was calculated.

Table 26 Concentrations of Cadmium and Lead in the SPLMs in the Leachate During the Experiment of the Heavy Metals.

Name	**Concentration Cd (µg/L)**	**Concentration Pb (µg/L)**
SPLM-1	100.8	107.1
SPLM-2	100.8	110.5

The pH is an important parameter to determine the mechanism of removal of heavy metals. Analyzing the values of the pH in the experiment (Figure 54) disclosed that the range of the first SPLMs was 7.7 – 9.0 while for the second SPLMs the range was 8.1 - 8.6. Therefore, it can be concluded with these pH values and the solubility of heavy metals that the possible main mechanisms for removal of heavy metals were precipitation or adsorption.

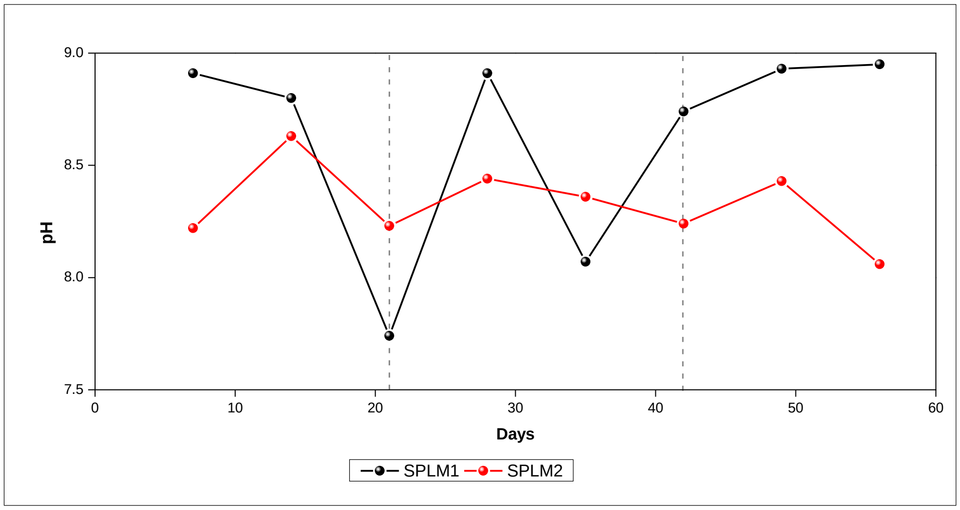

Figure 54 pH Values of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

Batch ReactorsFigure 55 shows the removal kinetics of cadmium and lead concentrations versus time in the batch reactors. Importantly, the initial concentration of heavy metals was 100 mg/L, after mixing the CCAs with the solution in a time of 12 minutes (0.2 hours), the concentrations fall to 29.6 mg/L for cadmium and 17.3 mg/L for lead, showing that the material quickly removes the heavy metals. After 4.0 hours, lead concentrations were below detection limit of the equipment (0.05 mg/L), while that of cadmium was 1.77 mg/L. The behavior the pH as a function of the time is presented in the Figure 56, where it is notable that the remotion was greater in the first 0.5 hours of the experiment, where the pH of the solution increased to 5.8 and stabilized after four hours to 7.2.

The results of the batch kinetic tests are shown in Figure 57 to Figure 58. The removal of heavy metals represents the percentage of heavy metals removed in the batch kinetic tests to that of the initial heavy metals concentration in the solution. It is notable the removal of heavy metals was increased with increasing reaction time. In the first twelve minutes (0.2 hours), the concentrations of heavy metals decreased rapidly, 70.4 and 82.7% removal for cadmium and lead, respectively. Figure 57 shows the percentages of removal as a function of time. For lead, the removal increased with increasing reaction time and the greatest removal occurred in 1.5 h and then it became stable thereafter (100% Pb^{2+} removal). The removal of cadmium increased gradually with increasing of time and the highest percentage of removal was achieved in 4.0 hours (98.2% Cd^{2+} removal).

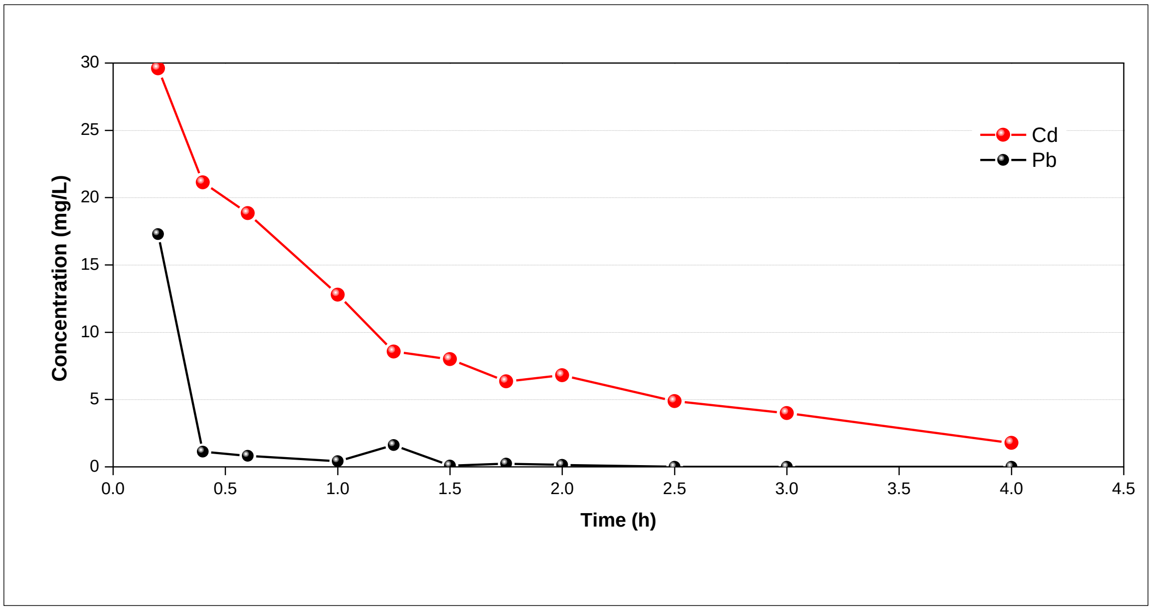

Figure 55 Concentration of Cadmium and Lead as a Function of Time.

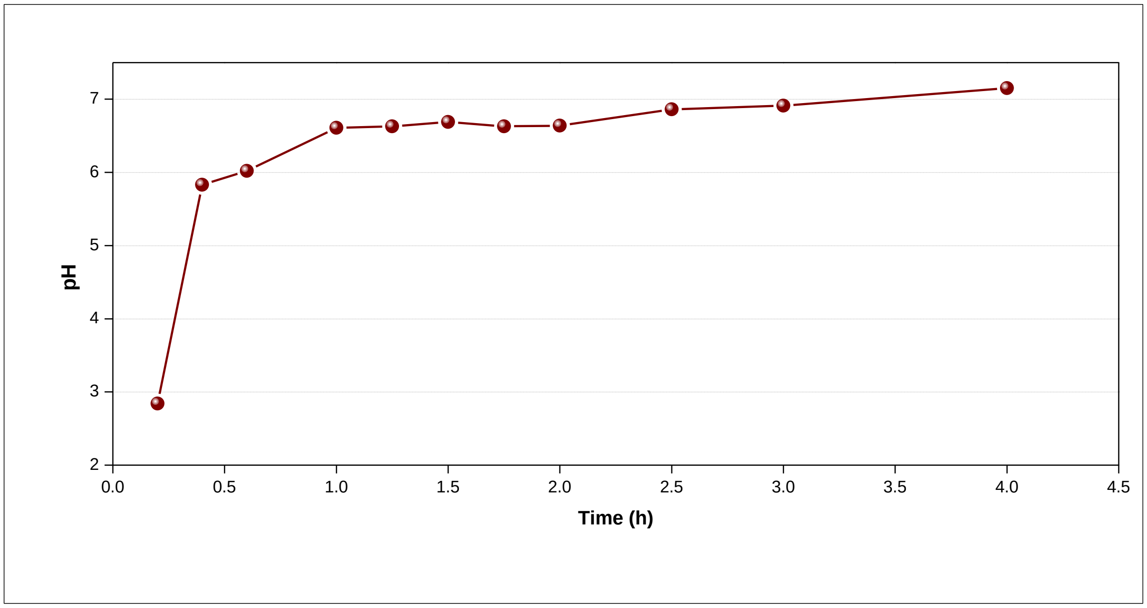

Figure 56 pH of the Solution as a Function of Time.

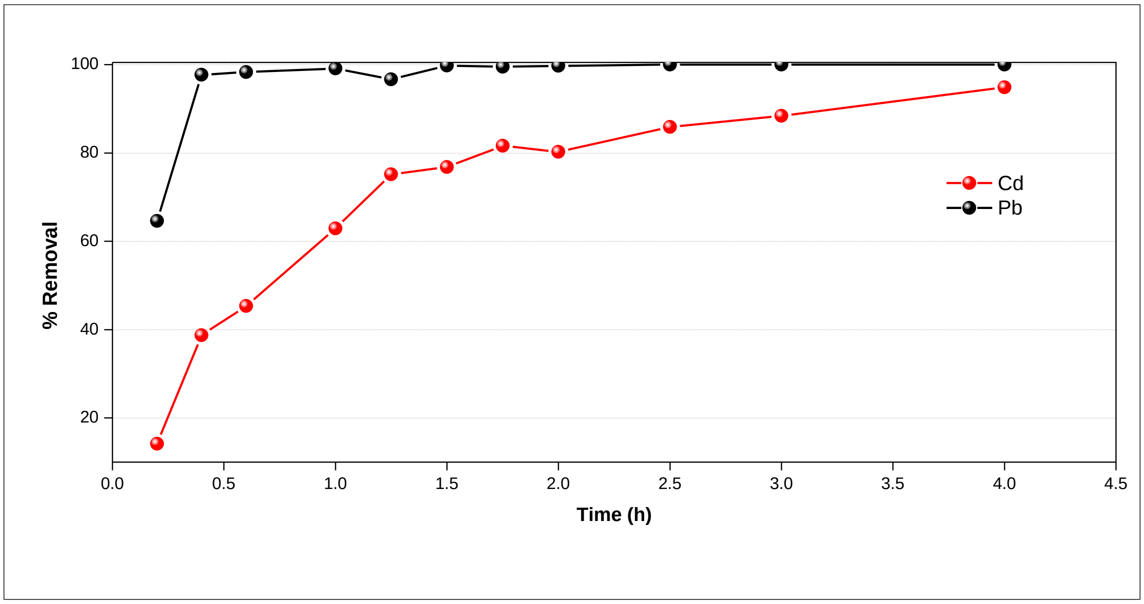

Figure 57 Reduction of Cadmium and Lead as a Function of Time.

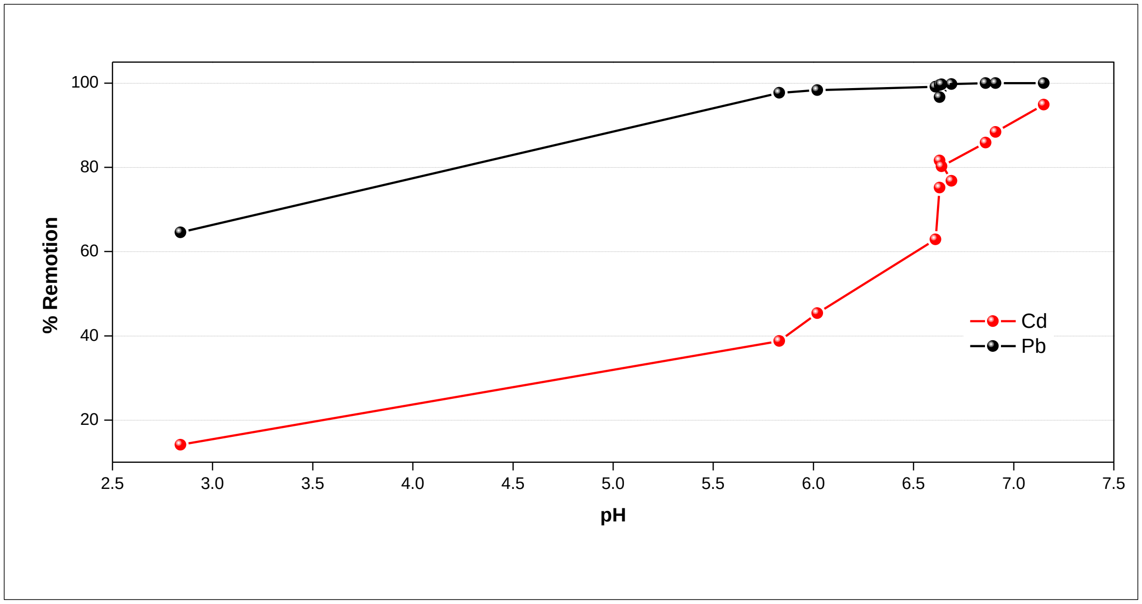

Figure 58 Reduction of Cadmium and Lead as a Function of pH.

Figure 58 shows the behavior of the solution's pH with respect to percentage removal of heavy metals. The range of the pH was 2.8 – 7.2. The value of the final pH affects the tendency for the removal of heavy metals (Cd and Pb), as shown in Figure 58. For lead the increase in the pH was more significant because their removal increased due to precipitation. The precipitation is based on the low solubility of the heavy metal hydroxides as mentioned in Erol et al., (2005).

6.1.2 *Estimation of Point of Zero Charge of CCAs*

This section presents the results of the calculated PZC with the mass titration method. Additionally, the results are divided by the solution used, deionized water, KCl and NaCl.

6.1.2.1 *Point of Zero Charges Calculated Using Deionized Water*

As a first approximation of the calculation of the PZC, deionized water with a very high resistivity (18.3 MΩ/cm) was used. The results of the deionized water suspensions with very low solid contents showed a very low ionic strength. The measurements of pH were taken for duplicates and the results are shown in the Figure 59.

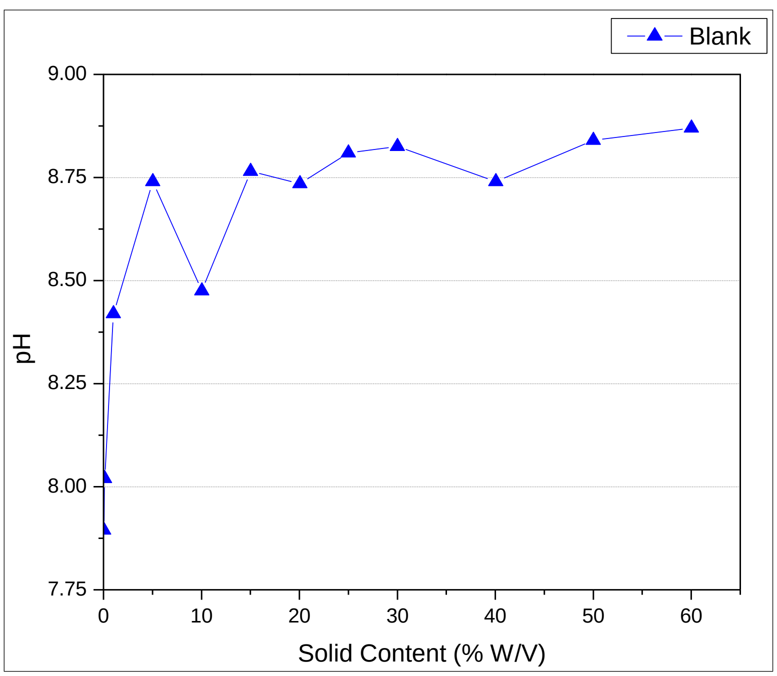

Figure 59 Determination of the Point of Zero Charge of CCAs Using Deionized Water.

The constant pH in Figure 59 represents the value of the PZC in the deionized water: 8.9. It is important to corroborate this value using aqueous solutions containing monovalent ions because the added ions were not specifically adsorbed on the solid surface and the presence of these ions could modify mass titration curves because of a screen effect on the surface charge, but the PZC value was not altered (Bourikas et al., 2003; Reymond and Kolenda, 1999).

6.1.2.2 *Point of Zero Charges Calculated Using Potassium Chloride*

It is necessary to calculate the PZC using an electrolyte solution with constant and adequate ionic strength, such as: NaCl, KCl, $NaNO_3$ and $CaCl_2$. In this study the solution of indifferent monovalent electrolytes, NaCl and KCl, was used (Reymond and Kolenda, 1999). The concentrations of the electrolyte solutions used were 1.0, 0.1, and 0.01 M and their corresponding results were compared.

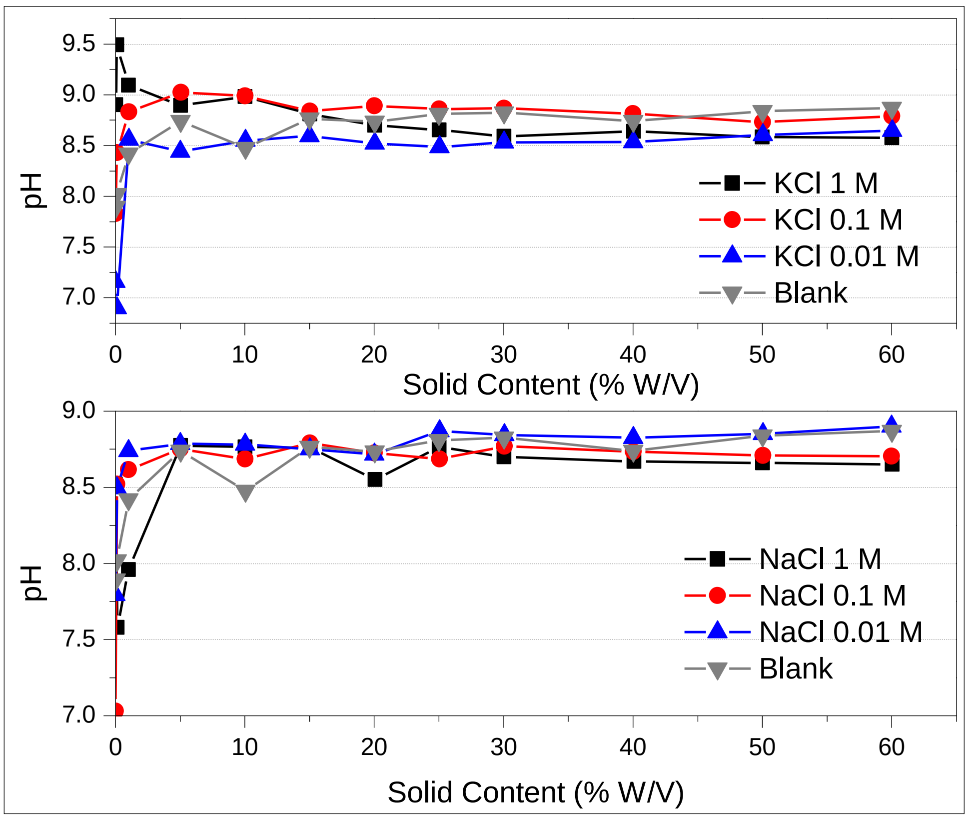

Figure 60 Determination of the Point of Zero Charge of CCAs Using KCl and NaCl.

The results of the measured PZC using potassium chloride solutions are found in Figure 60. In this case, the measured PZC value for CCAs was between 8.6 - 8.8.

6.1.2.3 *Point of Zero Charges Calculated Using Sodium Chloride*

The other approximation realized was using a sodium chloride solution at different concentrations: 1.0, 0.1 and 0.01 M. The behavior (Figure 60) was similar to the one shown by potassium chloride (Figure 60), but the PZC value found was between: 8.7 - 8.9.

6.1.2.4 *Point of Zero Charges Calculated for CCAs*

The PZC was found to be independent on the electrolyte concentration. Therefore, it can be concluded that the presence of these reactive ions does not modify the surface of the CCAs (Bourikas et al., 2003; Reymond and Kolenda, 1999). Figure 61 and Table 27 summarize the values of PZC quantified from the current study.

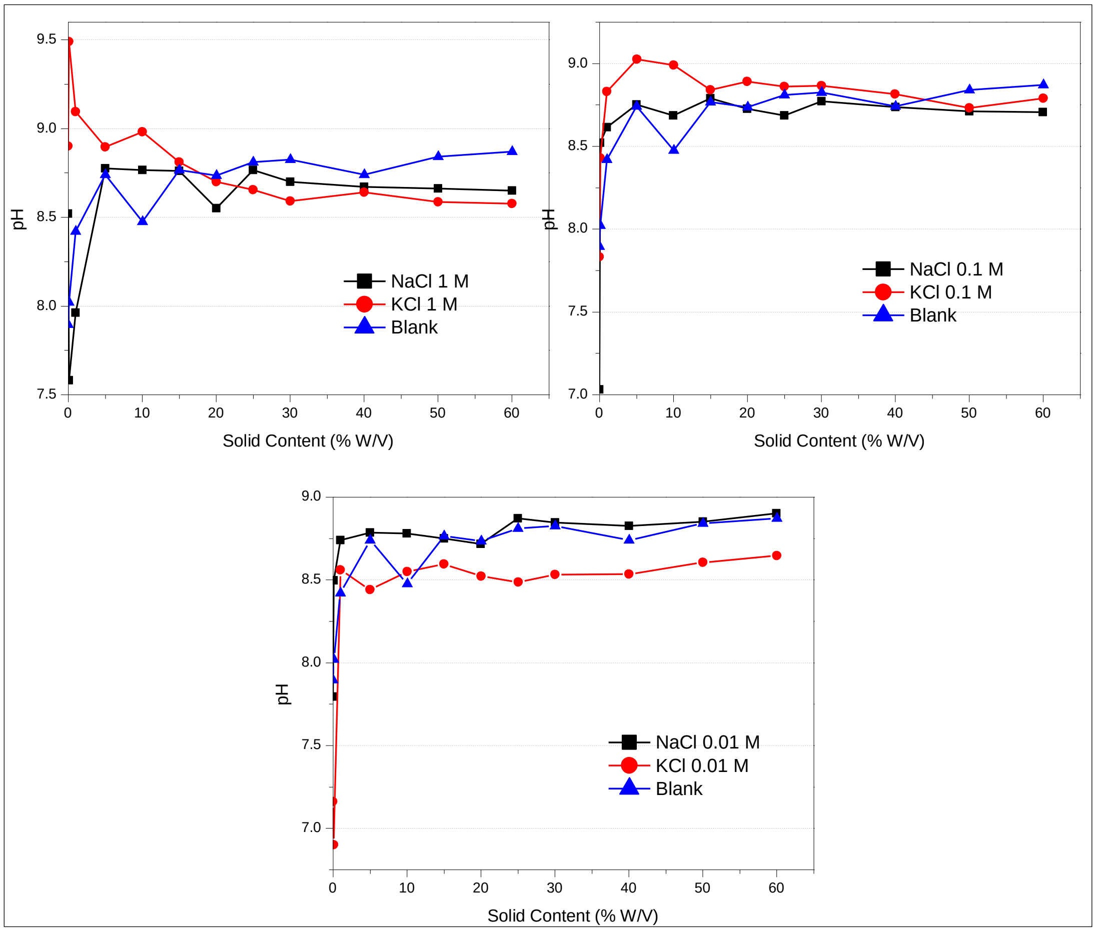

Figure 61 Determination of the Point of Zero Charge of CCAs

Table 27 Calculation of the Point of Zero Charge of CCAs.

Solution	**Concentration**	**PZC**
Deionized Water		8.7
KCl	1.0, 0.1 and 0.01 M	8.6 - 8.8
NaCl	1.0, 0.1 and 0.01 M	8.7 - 8.9

The CCA's point of zero charge was found at 8.7 ± 0.2. The PZC value characterizes surface acidity: when particles are introduced in an aqueous environment their surface charge is positive if solution pH is less than PZC, whereas it is negative if solution pH is greater than PZC. In the current experiments conducted with CCAs, the removal of heavy metals occurred and the relevant pH values was below the PZC, suggesting that the mechanism for heavy metals is precipitation.

7. DETERMINATION OF MICROBIAL ACTIVITIES

An important process in a landfill is the biodegradation, process in which organic substances are broken down into smaller compounds by the enzymes produced by living microbial organisms. This transformation is through metabolic or enzymatic processes. In the biodegradation processes the final product is carbon dioxide or methane. The degradation of organic material can be achieved aerobically (with oxygen), or anaerobically (without oxygen) (ENSO, 2010).

The microbial growth can be explained in four different phases: lag phase, log phase, stationary phase and death phase, whose characteristics are as follows (Musabj, 2011):

- Lag phase: corresponds to a phase of adaptation. In this phase the bacteria multiply slowly. The period of extension of the lag phase depends upon the nature of the medium and size of inoculum.
- Log phase: is the growth phase, because bacteria find favorable conditions, the bacterial growth starts significantly. The favorable conditions for bacterial growth are: oxygen presence, optimum temperature, neutralized pH and nutrients.
- Stationary phase: in this phase the bacterial growth stabilizes because the growth rate is slow. The stabilization is due to depletion of resources, loss of carrying space of a medium or environment. Equilibrium is reached in this phase since the growth rate and the death rate are the same.
- Death phase: in this phase, the conditions of bacterial growth changes to unfavorable conditions, eventually the bacteria start to die. Also, the waste material changes the medium or environment. Therefore the favorable conditions are lost and bacteria start to die.

Different mathematical models can be used to describe the microbial growth. The logistic function model describes the growth of microbial populations as a function of population density, time and growth rate (Wachenheim et al., 2003). The logistic function model has the following advantages in the analysis of growth data: predict when a given cell density will be reached and correlate the growth rate to the concentration of a nutrient, and the nutrient at a low concentration.

The optical density was used as an indirect measurement of biomass in microbial cell suspensions. This parameter is a non-destructive measurement of biomass in cultures of bacteria and other unicellular microorganisms where the amount of light absorbed by a suspension of cells is related directly to cell mass or cell number (Griffiths et al., 2011). The microbial biomass is determined by measuring optical density at 600 nm (OD_{600}) using an UV spectrophotometer (Fang et al., 2009; Wachenheim et al., 2003).

With respect to microbial activity in a landfill, it is important to recall that the application of coal combustion byproducts in soil affects the bioavailability (refers to how much of a chemical is available to a living biota including plants and soil microorganisms) of nutrients and heavy metals by both acting as their source and sink in soils. Between the major nutrients elements included are silicon (Si), aluminum (Al), iron (Fe), calcium (Ca) and sulphur (S), together with lesser amounts of sodium (Na), magnesium (Mg), boron (B), strontium (Sr) and potassium (K). Some of the coal combustion byproducts are rich in S and Ca thereby acting as a source of these nutrients. They also control the transformation of nitrogen (N) and phosphorus (P) through immobilization and mineralization reactions. Therefore, the coal combustion byproducts can be used to manage the bioavailability of nutrients and heavy metals, thereby enhancing soil chemical fertility and mitigating metal contaminated soils (Seshadri et al., 2010).

The purpose of this experiment is to support the potential of the CCAs for enhancement of microbial activities in the landfills when used as an ADC. Enhancement of microbial activity in landfills was assessed with PLMs where CCAs were utilized as a reactive ADC. Microbial activity enhancement due to CCAs was confirmed with a separate experiment, where the greater colony forming unit (CFU) was observed in the system having CCAs than in the control system without CCAs (30~150 x 10^{10} CFU/100 mL vs. 140 x 10^6 CFU/100 mL).

7.1 RESULTS

7.1.1 *Optical Density*

Figure 62 and Figure 63 are representations of the first-day and last-day appearance of the reactors. The difference seen in Figure 62 was due to the amount of CCAs in each reactor, while in the fourteenth day of the experiment, the difference in color intensity was due to microbial activity present (Figure 63). Figure 64 and Figure 65 show the results of daily OD and pH measurements. The general trends showed no significant changes in the beginning and began to increase in the optical density values. This suggests the growth of microbial activity with an adaptation period in the beginning. Importantly are the results of the microbial growth curve in the definition of its phases. The lag phase was found between 0.5 and 48 hours, while the log phase was between 51 and 197 hours and the stationary phase between 214 and 264 hours, after that time would begin the phase of death for microbes. When comparing the reactors, control and reactor 3 showed a notable difference. In reactor 3, the microbial biomass was higher.

Figure 62 Visual Comparisons of the Reactors at the First Day of the Experiment.

Figure 63 Visual Comparisons of the Reactors at the Fourteenth Day of the Experiment.

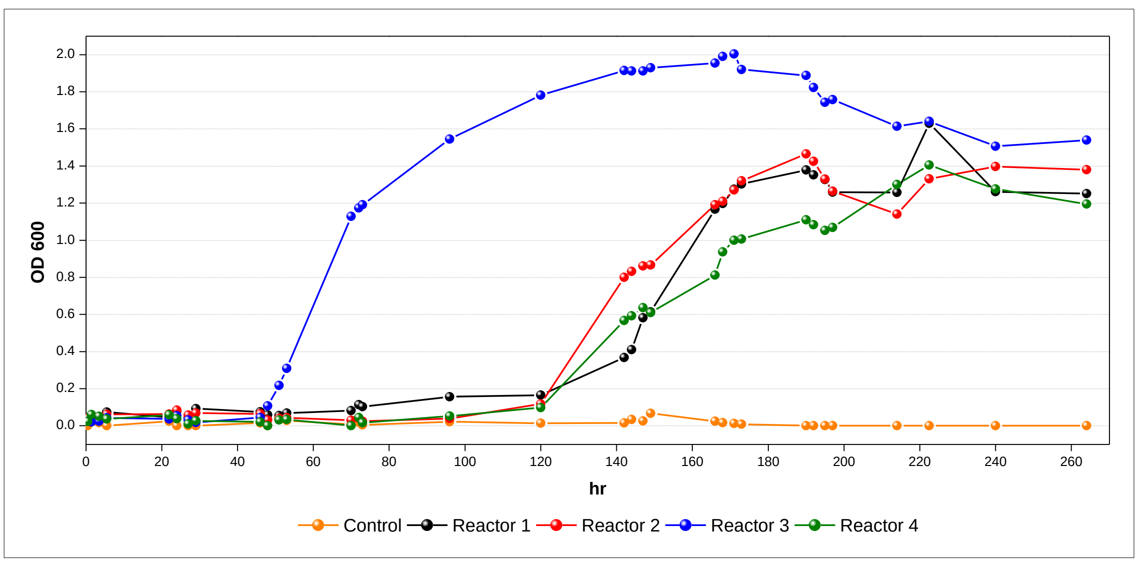

Figure 64 Optical Density Measured at 600 nm from Five Reactors During the Experiment.

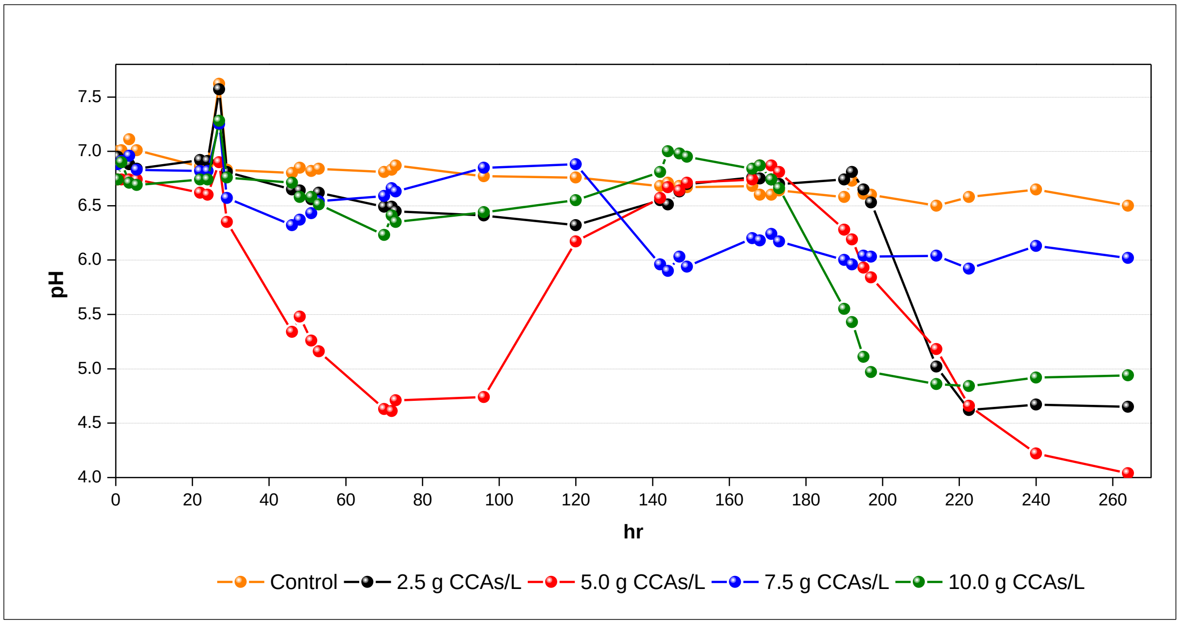

Figure 65 pH of Five Reactors During the Experiment.

It was necessary to perform a statistical analysis to find if there were significant differences between the reactors. The analysis was realized per stages as follows (Figure 66 and Figure 67):

- In lag phase, the differences in microbial growth were among the control and the reactors with CCAs, and there were no difference between them. With respect to pH, it was found that a higher average value of 7.0 was presented in the control while the reactor 2 (5.0 g CCAs/L) showed the lower average value of 6.4, and for others it was found to be in a range of 6.8 - 6.9.
- In the exponential phase, there was a significant difference between the reactors, reactor 3 (7.5 g CCAs/L) presented an increase in microbial growth, and the pH decreased slightly compared with the lag phase.
- In the stationary phase, the reactor 3 maintained the difference compared to other reactors and their pH values were declining and the range was found to be between 4.5 – 6.6.

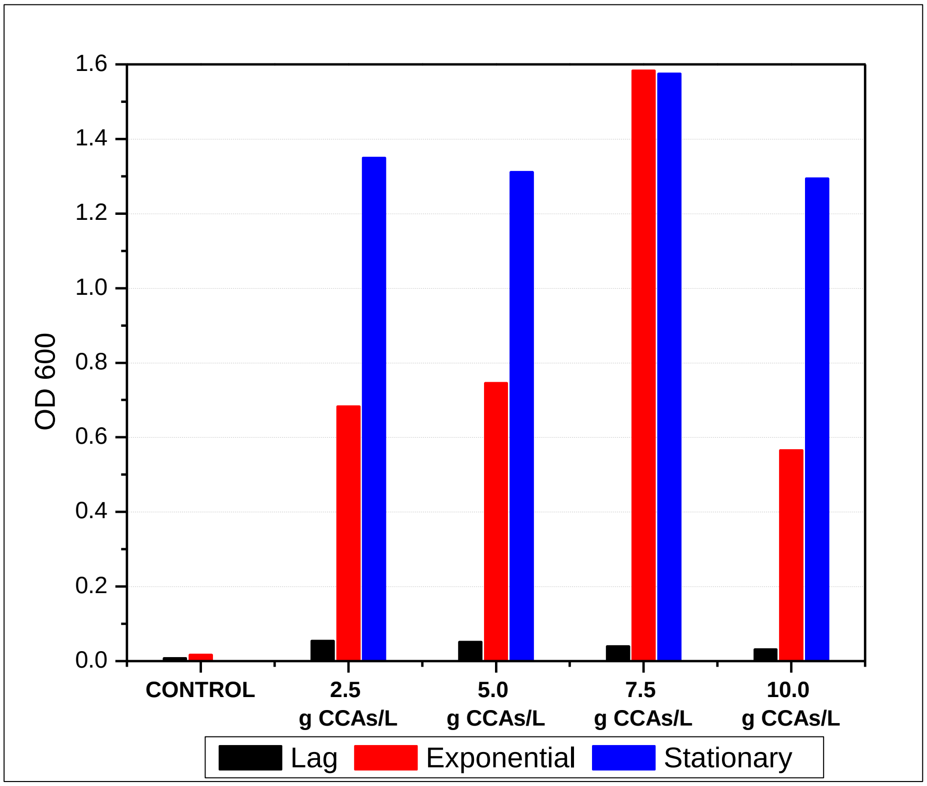

Figure 66 Comparison of Optical Density in the Reactors During the Microbial Growth Phase.

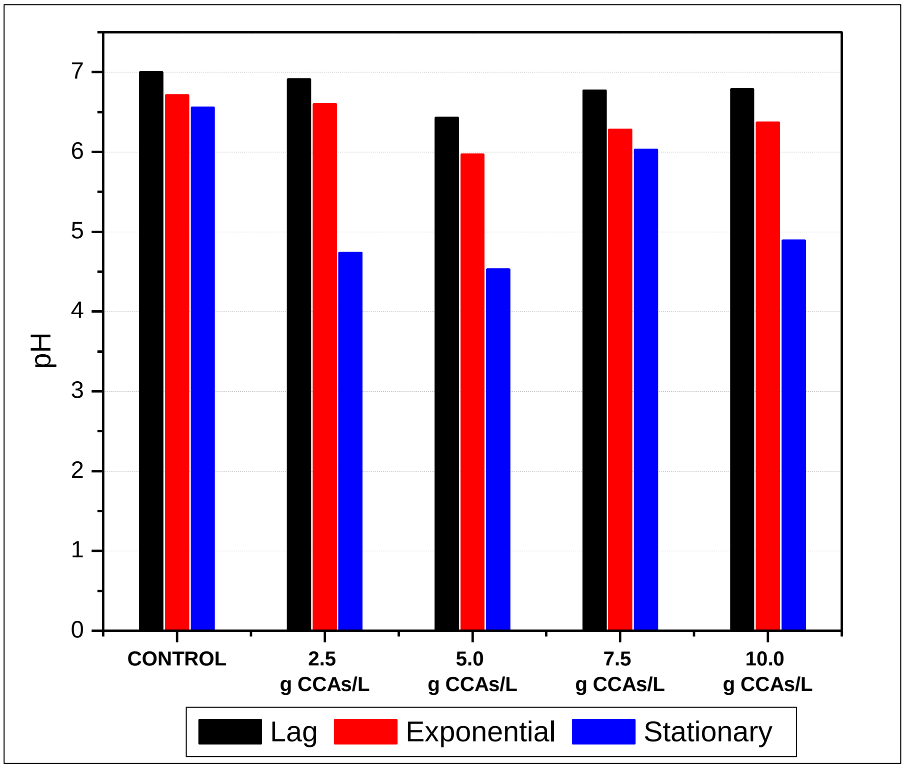

Figure 67 Comparison of pH in the Reactors During the Microbial Growth Phase.

In Figure 68, the values for OD were plotted with respect to the pH values.

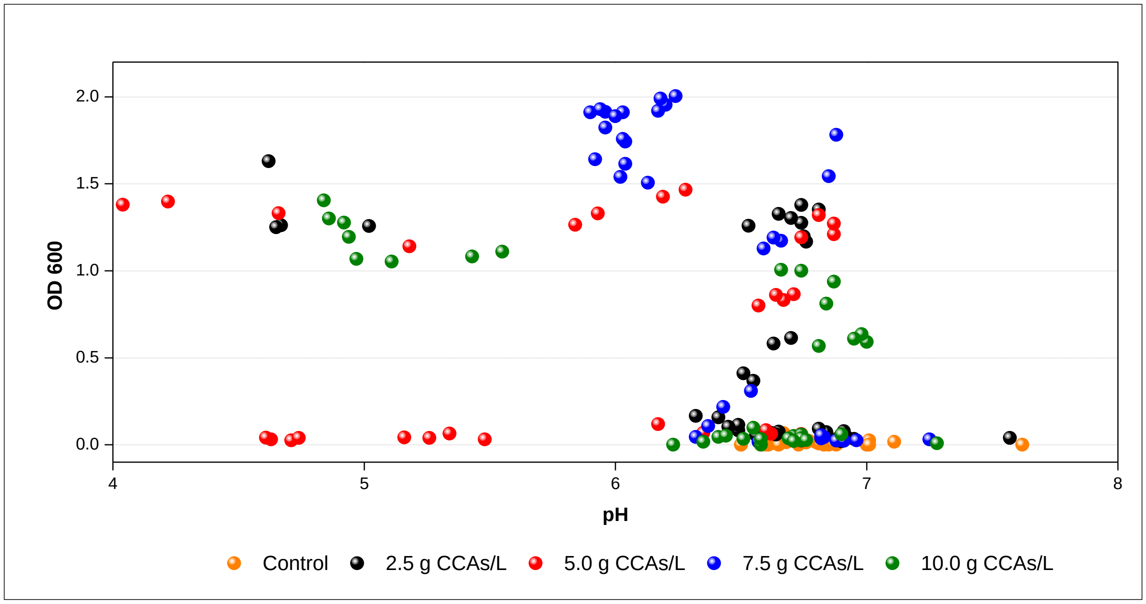

Figure 68 Relationship between Optical Density and pH in the Four Reactors During the Experiment.

To find a relationship between the variables (CCAs, OD and pH), the Pearson correlation was used. The Pearson correlation was calculated for these parameters and it was found that the CCAs were positively correlated with OD (0.319) while pH was negatively (-0.295). This indicates that when the amount of CCAs increased the pH values decreased while the OD increased due to increased microbial activity. The following is an analysis for each of the reactors using the Sigma Plot ® to estimate an equation which represents the trend of the data. For the control reactor, the data apparently has no clear trend (Figure 69). The best fit for the other reactors was with a sigmoid function (Logistic Model) with three parameters$\left(f = a/1 + e^{\left(\frac{-(X-X_0)}{b}\right)}\right)$. The parameters represents: maximal amplitude (a), maximal slope (X_0), and the midpoint intensity where amplitude is half maximum (b).

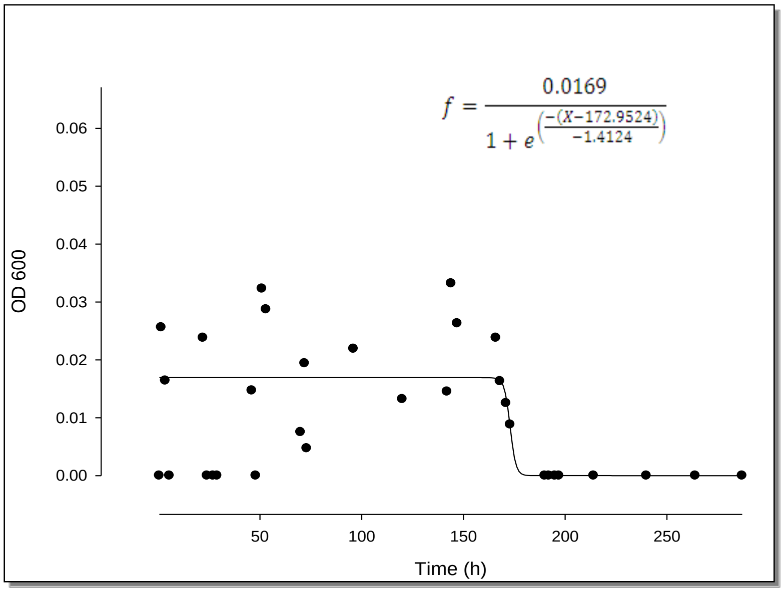

Figure 69 Sigmoidal Data Fitting for the Control Reactor (0.0 g/L CCAs).

Figure 70 to Figure 73 show the fitting results of the treatment reactors with CCA addition.

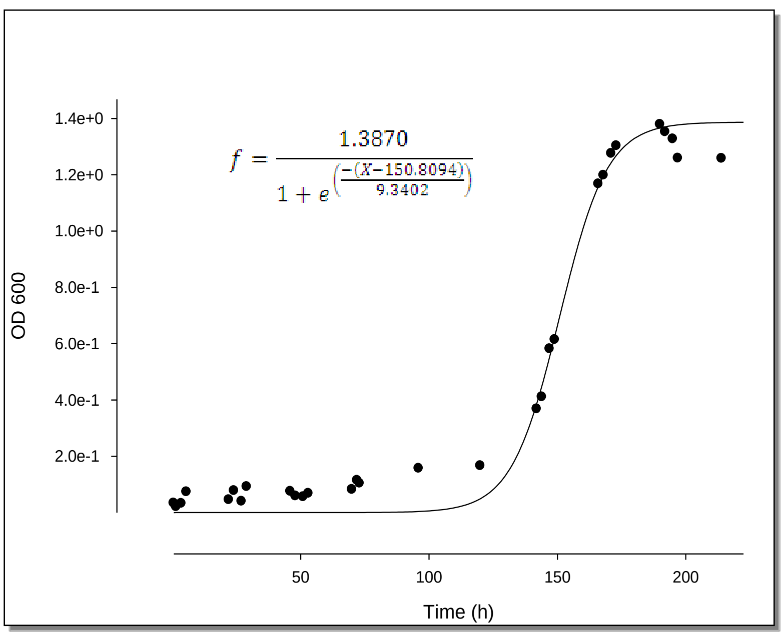

Figure 70 Sigmoidal Data Fitting for the Reactor 1 (2.5 g/L CCAs).

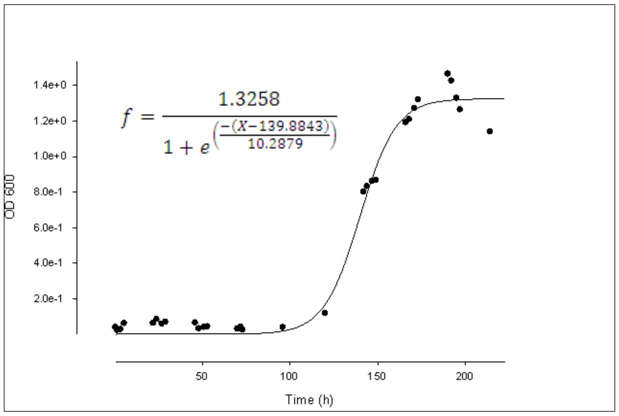

Figure 71 Sigmoidal Data Fitting for the Reactor 2 (5.0 g/L CCAs).

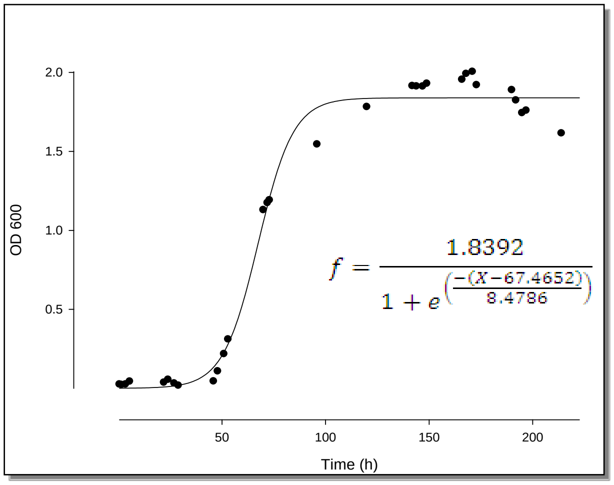

Figure 72 Sigmoidal Data Fitting for the Reactor 3 (7.5 g/L CCAs).

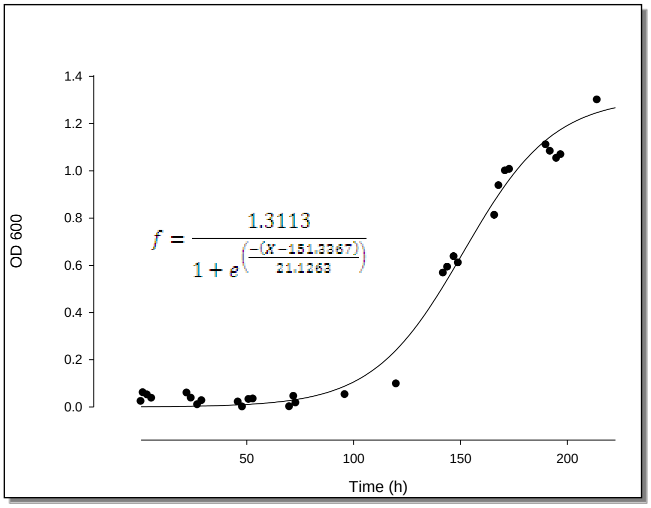

Figure 73 Sigmoidal Data Fitting for the Reactor 4 (10.0 g/L CCAs).

Table 28 summarizes the R^2 values for each reactor. The control reactor is the only one that does not fit due to the random behavior of the data.

Table 28 Values of R^2 for Each Reactor.

Reactor	R^2
Control	0.24
R1	0.98
R2	0.99
R3	0.99
R4	0.99

Using the equation calculated it is possible to obtain the optical density values on steady state for each reactor. Table 29 relates it with S/L ratio (g CCAs/Volume of the reactor).

Table 29 Values of Optical Density in Steady State for Each Reactor.

Reactor	Application Rate (g CCAs/L)	OD_{600} SS	S/L Ratio (g/L)
Control	0.0	0.00	0.0
R1	2.5	1.40	2.5
R2	5.0	1.33	5.0
R3	7.5	1.84	7.5
R4	10.0	1.25	10.0

The polynomial adjustment was done with the values of OD on steady state of five reactors (Table 29) plotted against the solid-to-liquid (S/L) ratio (g CCAs/L reaction volume) (Figure 74).

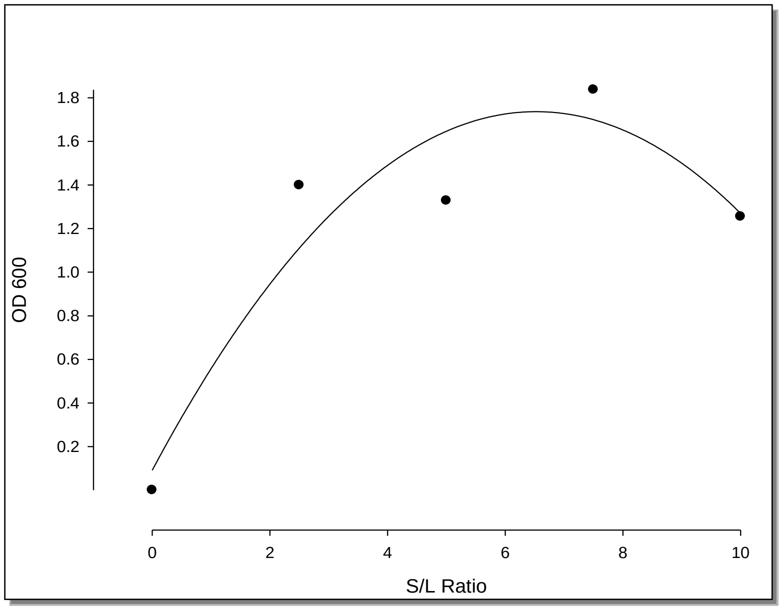

Figure 74 Relationship between the Steady State Value of OD 600 and the Solid/Liquid Ratio (S/L).

As shown in Figure 74, the optimal value corresponds to reactor 3 (15 g CCAs), with a steady state value for OD of 1.84 and with S/L ratio (mass CCAs/volume of the reactor) of 7.5 g/L. This value represents the optimal amount of the CCA for enhancing microbial activity in the conditions of this experiment.

7.1.2 *Heterotrophic Bacteria*

The heterotrophic plate count was made via membrane filtration, count for enumeration of total heterotrophic bacteria (THB) in each reactor. For the control reactor, dilutions of 10^4 and 10^6 were made, and for the other reactors the dilutions were 10^8 and 10^{10}. In this first dilution, the THB was too many to count (TMTC). More THB were counted in the reactors with aggregate compared with the control reactor. Besides, more THB were counted in the reactor with 15 g of CCAs, implying a better microbial environment provided by the aggregates (i.e., surface area, intra-particle pores, etc.). These results show the benefits of CCAs in the improvement of microbial activities which is an important factor in the operation of a landfill. Figure 75 to Figure 80 show the microbial activity in the plate:

Figure 75 Heterotrophic Plate Count with a Membrane Filtration (Dilution was 10^4 for Control and 10^6 for others).

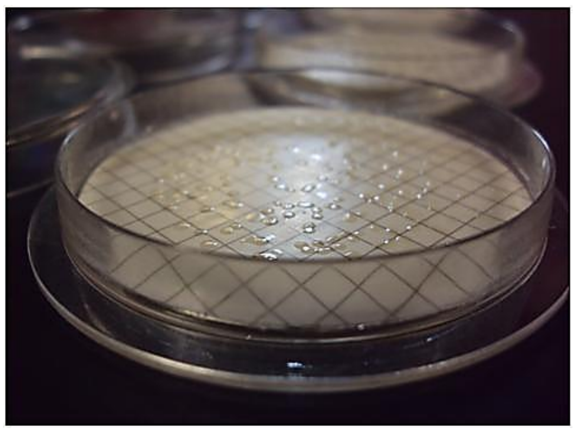

Figure 76 Heterotrophic Plate Count with a Membrane Filtration for the Control Reactor (10^6 dilution).

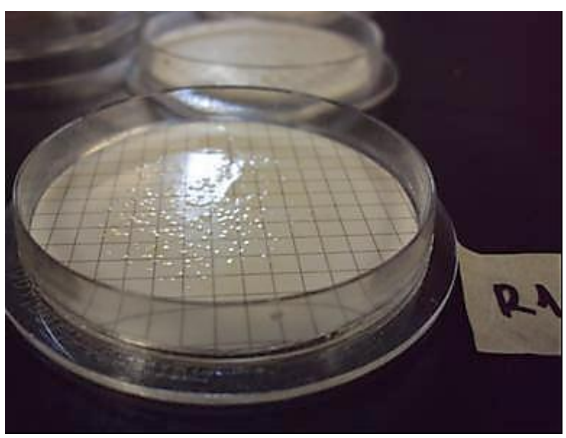

Figure 77 Heterotrophic Plate Count with a Membrane Filtration for the Reactor 1 (2.5 g CCAs/L) (10^{10} Dilution).

Figure 78 Heterotrophic Plate Count with a Membrane Filtration for the Reactor 2 (5.0 g CCAs/L) (10^{10} Dilution).

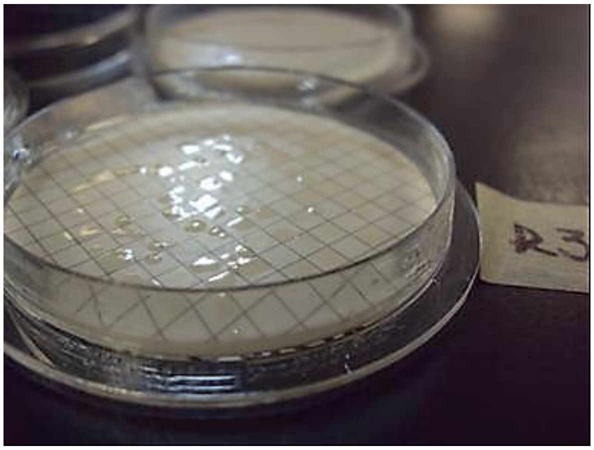

Figure 79 Heterotrophic Plate Count with a Membrane Filtration for the Reactor 3 (7.5 g CCAs/L) (10^{10} Dilution).

Figure 80 Heterotrophic Plate Count with a Membrane Filtration for the Reactor 4 (10.0 g CCAs/L) (10^{10} Dilution).

Table 30 and Table 31 contain the numerical results from the THB analysis.

Table 30 Total Heterotrophic Count for Control Reactor.

	Dilution	
	10^4	10^6
Control	TMTC	140 CFU/100 ml

Table 31 Total Heterotrophic Count for Reactors with CCAs.

	Dilution	
	10^8	10^{10}
R1 (2.5 g/L)	TMTC	150 CFU/100 ml
R2 (5.0 g/L)	TMTC	30 CFU/100 ml
R3 (7.5 g/L)	TMTC	53 CFU/100 ml
R4 (10.0 g/L)	TMTC	74 CFU/100 ml

NOTE: Colony Forming Unit (CFU) and too many to count (TMTC).

These results corroborate the preliminary landfill simulations, where reactors were made in form of columns with wastes and daily covers (Fonseca et al., 2007). These reactors were constructed with a porcelain funnel on the bottom and a PVC pipe on the top. The dimensions of the column reactors were 20.3 cm in diameter and 30 cm long. A total number of four reactors were built. Table 32 shows the configuration of each reactor. For the reactors 1 and 3 the same amount and type of materials were used, but the reactor 3 had higher organic and inorganic concentrations in the waste surrogate than in the reactor 1. The reactor 2 had a 50% more CCAs than the reactor 1. While the reactor 4 was the control reactor which contained only inorganic sand layers as the daily cover (Fonseca et al., 2007).

Sponges soaked with glucose were used as the surrogates of wastes. Glucose ($C_6H_{12}O_6$) was chosen as representative organic. A mixture of $C_6H_{12}O_6$ was prepared at the concentration of 10 mg/L. For the reactors 1, 2 and 4, 10 mL of the mixture were evenly spiked on the sponges resulting in 0.006 mg $C_6H_{12}O_6$/g sponge. A mixture having 50% higher concentration was applied to the sponge in the reactor 3 (Fonseca et al., 2007).

Table 32 Configuration of Preliminary Landfill Reactors.

	Reactor 1		Reactor 2		Reactor 3		Reactor 4 (Control)	
Materials	**Depth (cm)**	**Weight (grams)**	**Depth (cm)**	**Weight (grams)**	**Depth (cm)**	**Weight (grams)**	**Depth (cm)**	**Weight (grams)**
Sand	2.5	750	1.25	375	2.5	750	2.5	750
Aggregates	2.5	380	3.75	570	2.5	380	2.5*	750*
Sponge	5.0	16.8	5.0	16.8	5.0	16.8	5.0	16.8
Aggregates	2.5	380	3.75	570	2.5	380	2.5*	750*
Sand	2.5	750	1.25	375	2.5	750	2.5	750
Gravel	2.5	900	2.5	900	2.5	900	2.5	900

Note *: sand

To complete the configuration of the reactors, the top was covered with sand to facilitate even distribution of water percolation throughout the reactor cross-sectional surface area (324.3 cm^2), and the bottom was covered with sand on top of gravel in order to prevent the solid materials from escaping the system and also to facilitate leachate collection. Each week, 100 mL of tap water was evenly sprayed onto the top layers of the reactors and the percolated water were collected for one week and analyzed (Fonseca et al., 2007).

At the end of this experiment, microbial properties of the reactors were examined. The CFU was counted after a five-day, room-temperature incubation in the dark. Duplicate plates were used for each dilution (10^4 - 10^6) and then averaged to obtain the final populations. Total heterotrophic bacteria counts were assessed from the water percolated from each reactor. Results indicated that greater than $1x10^6$ CFU were present regardless of the reactor types as shown in Figure 81. However, more THB were counted in the percolated water from the aggregate-amended reactors compared to those from the control reactor. Besides, more CFU were counted in the reactor which had more aggregates (i.e., reactor 2 vs. reactor 1), implying a better microbial environment provided by the aggregates (i.e., surface area, intra-particle pores, etc.). The CFU of the reactor 2 was not much different from that of the reactor 3 (Fonseca et al., 2007).

Nutritionally is important, the concentrations of macro (Ca, Mg, K and S) and micro-nutrients (B, Fe, Mn, Cu, Zn, among others) available from the CCAs that are known to enhance microbial growth (Lin and Yang, 2002). These results showed the benefits of CCAs to improve the microbial activity, an important feature in the operation of a landfill.

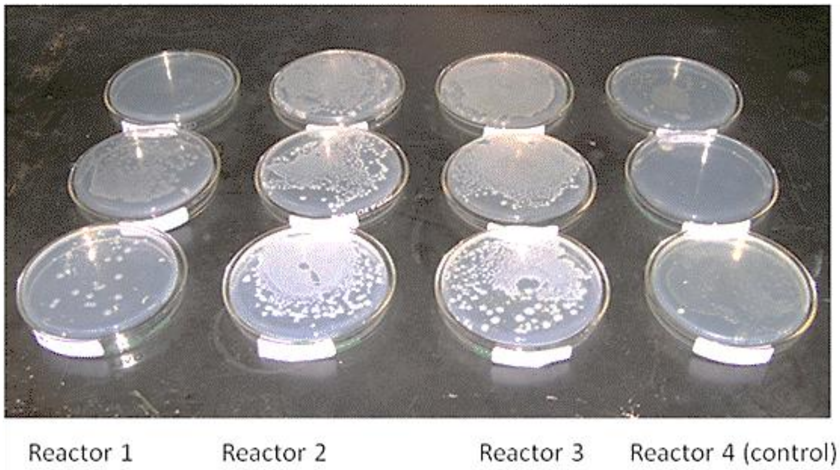

Figure 81 Total Heterotrophic Bacteria Counts in the Percolated Water.

8. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Experimental results showed that the CCAs can be beneficially utilized as an alternative reactive daily cover in landfills because:

✓ ***In the Physical Landfill Models (PLMs):***

- Very similar hydraulic characteristics (leachate quantity): PLM with CCAs as daily cover produced very similar amount of leachate when compared to the control PLM with sand as daily cover. This was attributed to similar void fractions controlling the flow through the sand and CCA.
- Better leachate quality: In the wet period, the alkalinity concentration was lower than in the control PLMs; in the moderate period significant lower concentration of COD, total phosphorus, orthophosphate, and alkalinity found in the CCAs PLM than in the control PLM, while cumulative biogas production was more in the CCAs PLM; in dry period hardness and turbidity were smaller in the CCAs PLM than in the control PLM and pH, conductivity and cumulative biogas production were greater in the CCAs PLM than in the control PLM; and in the recirculation period, the turbidity, total phosphorus and total nitrogen, were smaller in the CCAs PLM than in the control PLM and cumulative biogas production and cumulative normalized settlement were greater in the CCAs PLM (more biodecomposition and more settlement, enhanced microbial activity).
- Better settlement (53.4% more settlement was found in the CCAs PLM in comparison with control PLM) and earlier settlement to a greater extent. The largest settlement was found in the recirculation stages due to improvement of the microbiological activity in the process of biodecomposition which generated a more settlement in the PLM and higher biogas production.
- The CCAs PLM generated 63.0% more biogas production the control PLM. Also, biogas production from the CCAs PLM started earlier due to more active biodecomposition and enhanced biological decomposition of solid waste.
- Leachate recirculation seemed advantageous as it increased moisture necessary for biological decomposition of solid waste, decreased the concentrations of

contaminants in leachate (leachate strength), produced more biogas, increased settlement, and therefore enhanced landfill stabilization.

✓ ***In the Smaller Physical Landfill Models (SPLMs):***

- SPLMs were hydraulically equivalent despite different packing densities of CCAs. Also, leachate water quality was similar.
- Lower concentrations were found in the CCAs SPLMs for: NO^{3-}, hardness, color, turbidity, conductivity, total nitrogen, BOD_5, COD, total phosphorus and orthophosphate. Therefore, a better leachate quality was produced. The SPLMs did not show significance differences between them. Only the concentration of total phosphorus presented a significant difference in the recirculation period: the highest total phosphorus concentration was found in the SPLM-1, whereas the lowest concentration was in the SPLM-3 (greater packing density).

✓ ***Removal of Heavy Metals:***

- The CCA is possible using as a reactive daily cover for heavy metals removal. The results showed an increase of pH due to CCAs, resulting in a higher heavy metals removal capacity. Also, the quantification of the CCA's point of zero charge (8.7 ± 0.2) suggests that removal is mainly caused by precipitation processes.

✓ ***Microbial Activities:***

- Microbial activity was enhanced due to CCAs where the greater CFU was observed from the system having CCAs than the control system without CCAs ($30 - 150 \times 10^{10}$ CFU/100 mL vs. 140×10^{6} CFU/100 mL). More total heterotrophic bacteria were counted in the percolated water from the aggregate-amended reactors compared to those from the control reactor. In addition, more CFU was counted in the reactor which had more aggregates, implying a better microbial environments provided by the aggregates (i.e., surface area, intraparticle pores, etc.).

- Based on the greater microbial populations and activity found in the CCAs amended systems, enhanced biological waste decomposition is expected to occur in landfills. This will, in turn, provide extra space for more wastes to be disposed of in the landfill. This resource recovery will also lead to significant soil resource conservation which otherwise would have had to be excavated.

However, due to the limitations inherent in the laboratory-scale research, the following topics are recommended for further studies in the performance of landfill with CCAs as an alternative reactive daily cover:

✓ To analyze the composition of biogas produced from the CCAs PLM as biogas can be utilized as an alternative energy source.

✓ To define the stage of biological decomposition and settlement with respect to aerobiosis and anaerobiosis in order to better understand the mechanisms that govern leachate characteristics.

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LIST OF APPENDIXES

APPENDIX 1. SUMMARY OF LEACHATE CHARACTERISTICS IN THE PLMS

Table 33 - Table 40, show all the parameters measured in each of the PLMs, with their respective average values, standard deviation, maximums, minimums and the number of samples taken for each period.

- ***Characteristics of Leachate for CCAs PLM***

Parameters measured during the wet, moderate, dry and recirculation period in the PLM used CCAs as alternative daily cover.

Table 33 Characteristics of Leachate in Wet Period for PLM with CCAs.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	4	4,395.0	1,323.0	2,520.0	5,430.0
pH	4	7.28	0.264	7.04	7.64
ORP (mV)	4	-106.5	39.0	-140.0	-58.0
NO_3- (mg/L as N)	4	14.18	3.88	11.10	19.80
Hardness (mg/L Ca)	4	576.4	95.3	497.2	713.8
Color (Pt Co Units APHA)	4	2,060.0	911.0	1,070.0	3,200.0
Turbidity (NTU)	4	181.0	45.8	151.0	249.0
Conductivity (μS/cm)	4	5.79	1.28	4.23	7.34
DO (mg/L O_2)	4	3.03	0.211	2.81	3.31
COD (mg/L)	4	4,800.0	4,153.0	2,400.0	11,000.0
Total Phosphorus (mg/L PO_4^{-3})	4	31.2	5.7	22.9	35.0
Total Nitrogen (mg/L N)	4	250.0	173.2	100.0	500.0
Orthophosphate (mg/L PO_4^{-3})	4	18.3	10.7	4.1	30.0
Alkalinity (mg/L $CaCO_3$)	4	2,725.0	386.0	2,300.0	3,100.0
BOD_5 (mg/L)	4	1,468.0	441.0	1,020.0	2,054.0
Cumulative Normalized Settlement (cm/(kg/cm^3))	4	191.3	127.5	0.0	255.0

Table 34 Characteristics of Leachate in Moderate Period for PLM with CCAs.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	12	1,492.0	414.0	740.0	2,140.0
pH	8	7.91	0.19	7.67	8.15
ORP (mV)	8	-49.1	140.5	-256.0	93.0
NO_3- (mg/L as N)	8	13.86	5.55	8.25	23.50
Hardness (mg/L Ca)	8	251.3	141.8	69.0	433.1
Color (Pt Co Units APHA)	8	879.0	481.0	300.0	1,670.0
Turbidity (NTU)	8	151.1	120.4	30.9	334.0
Conductivity (µS/cm)	8	3.59	0.30	3.30	4.22
DO (mg/L O_2)	8	2.30	1.28	0.44	4.88
COD (mg/L)	8	1,009.0	545.0	250.0	1,990.0
Total Phosphorus (mg/L PO_4^{-3})	8	15.58	7.68	5.84	24.44
Total Nitrogen (mg/L N)	8	163.80	57.10	100.0	250.0
Orthophosphate (mg/L PO_4^{-3})	8	22.2	8.3	12.9	36.5
Alkalinity (mg/L $CaCO_3$)	8	1,800.0	441.0	1,100.0	2,500.0
BOD_5 (mg/L)	8	294.5	194.5	113.2	703.5
Cumulative Biogas Volume (mL)	47	16,258.0	4,615.0	0.00	19,552.0
Cumulative Normalized Settlement (cm/(kg/cm^3))	12	2,742.0	2,083.0	255.0	5,271.0

Table 35 Characteristics of Leachate in Dry Period for PLM with CCAs.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	12	222.4	107.80	110.0	460.0
pH	9	8.55	0.20	8.25	8.77
ORP (mV)	9	132.89	17.22	107.00	163.00
NO_3- (mg/L as N)	9	13.32	7.05	7.50	29.85
Hardness (mg/L Ca)	9	63.17	18.49	34.17	89.02
Color (Pt Co Units APHA)	9	650.0	264.8	335.0	1,040.0
Turbidity (NTU)	9	17.29	7.43	6.33	28.00
Conductivity (μS/cm)	9	3.00	0.39	2.24	3.34
DO (mg/L O_2)	9	5.41	1.12	3.78	6.94
COD (mg/L)	9	957.3	299.4	352.0	1,440.0
Total Phosphorus (mg/L PO_4^{-3})	9	8.34	2.51	5.04	11.94
Total Nitrogen (mg/L N)	9	125.6	57.7	80.0	270.0
Orthophosphate (mg/L PO_4^{-3})	9	20.4	6.8	14.2	35.0
Alkalinity (mg/L $CaCO_3$)	9	1,255.6	159.0	900.0	1,400.0
BOD_5 (mg/L)	9	174.4	133.3	22.6	350.9
Cumulative Biogas Volume (mL)	48	14,202.0	870.0	0.0	19,554.0
Normalized Settlement (cm/(kg/cm^3))	12	3,195.0	1,913.0	1,020.0	5,441.0

Table 36 Characteristics of Leachate in Recirculation Period for PLM with CCAs.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	29	5,325.0	2,743.0	2,140.0	8,560.0
pH	13	7.68	0.20	7.30	7.94
ORP (mV)	13	81.2	61.9	-78	158
NO_3- (mg/L as N)	13	15.104	2.466	10.3	18.4
Hardness (mg/L Ca)	13	295.2	77.5	204.1	496.2
Color (Pt Co Units APHA)	13	784.0	382.0	120.0	1,530.0
Turbidity (NTU)	13	92.9	50.5	13.2	197.0
Conductivity (μS/cm)	13	4.04	0.22	3.74	4.48
DO (mg/L O_2)	13	4.21	1.65	1.02	6.9
COD (mg/L)	13	1,076.2	350.4	100.0	1,400.0
Total Phosphorus (mg/L PO_4^{-3})	13	18.34	5.90	8.34	28.94
Total Nitrogen (mg/L N)	13	133.85	26.31	100.00	190.00
Orthophosphate (mg/L PO_4^{-3})	13	23.57	12.65	10.00	63.10
Alkalinity (mg/L $CaCO_3$)	13	2,192.0	409.0	1,600.0	2,800.0
BOD_5 (mg/L)	13	176.2	134.7	34.4	503.9
Cumulative Biogas Volume (mL)	142	16,125.0	6,284.0	102.0	20,902.0
Cumulative Normalized Settlement (cm/(kg/cm^3))	28	4,372.0	1,618.0	1,190.0	5,441.0

- ***Characteristics of Leachate for Control PLM***

Parameters measured during the wet, moderate, dry and recirculation period in the PLM that used inorganic sand as alternative daily cover.

Table 37 Characteristics of Leachate in Wet Period for Control PLM.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	4	4,179.0	1,697.0	1,700.0	5,510.0
pH	4	7.06	0.20	6.87	7.24
ORP (mV)	4	-87.8	27.5	-111.0	-49.0
NO_3- (mg/L as N)	4	14.47	3.44	9.67	17.80
Hardness (mg/L Ca)	4	556.4	61.4	501.3	633.6
Color (Pt Co Units APHA)	4	2,063.0	512.0	1,450.0	2,700.0
Turbidity (NTU)	4	130.0	23.9	100.0	156.0
Conductivity (μS/cm)	4	5.70	0.66	4.71	6.11
DO (mg/L O_2)	4	5.79	2.74	3.42	8.56
COD (mg/L)	4	6,975.0	4,136.0	4,200.0	13,100.0
Total Phosphorus (mg/L PO_4^{-3})	4	45.12	16.81	20.64	58.94
Total Nitrogen (mg/L N)	4	400.0	81.6	300.0	500.0
Orthophosphate (mg/L PO_4^{-3})	4	33.57	16.40	15.28	55.00
Alkalinity (mg/L $CaCO_3$)	4	3,725.0	727.0	2,800.0	4,400.0
BOD_5 (mg/L)	4	1,943.0	371.0	1,596.0	2,459.0
Normalized Settlement (cm/(kg/cm^3))	4	105.6	79.1	0.0	191.9

Table 38 Characteristics of Leachate in Moderate Period for Control PLM.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	12	1,468.0	460.0	670.0	2,100.0
pH	8	7.74	0.18	7.57	8.13
ORP (mV)	8	-14.1	65.8	-120.0	7.08
NO_3- (mg/L as N)	8	14.53	11.76	6.63	42.20
Hardness (mg/L Ca)	8	269.2	139.7	65.4	441.1
Color (Pt Co Units APHA)	8	1,110.0	512.0	525.0	1,920.0
Turbidity (NTU)	8	88.73	24.33	54.00	119.00
Conductivity (µS/cm)	8	3.52	0.41	2.98	4.13
DO (mg/L O_2)	8	2.0	1.5	0.1	4.3
COD (mg/L)	8	2,368.0	910.0	1,100.0	3,790.0
Total Phosphorus (mg/L PO_4^{-3})	8	24.77	9.41	12.84	36.44
Total Nitrogen (mg/L N)	8	218.8	56.9	130.0	300.0
Orthophosphate (mg/L PO_4^{-3})	8	32.7	6.7	20.8	39.5
Alkalinity (mg/L $CaCO_3$)	8	2,200.0	151.2	1,900.0	2,400.0
BOD_5 (mg/L)	8	572.0	421.0	142.0	1,450.0
Cumulative Biogas Volume (mL)	47	3,986.0	182.0	0.00	5,066.0
Cumulative Normalized Settlement (cm/(kg/cm^3))	12	1,491.0	982.0	192.0	2,649.0

Table 39 Characteristics of Leachate in Dry Period for Control PLM.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	12	255.0	174.3	3.5	615.0
pH	9	8.30	0.22	7.99	8.57
ORP (mV)	9	137.0	25.6	112.0	200.0
NO_3- (mg/L as N)	8	11.57	3.98	8.22	18.00
Hardness (mg/L Ca)	8	93.2	33.3	41.7	139.1
Color (Pt Co Units APHA)	8	769.0	315.0	400.0	1,120.0
Turbidity (NTU)	8	28.15	6.99	20.10	41.20
Conductivity (μS/cm)	8	2.57	0.32	2.23	3.23
DO (mg/L O_2)	8	4.92	1.06	3.30	6.27
COD (mg/L)	9	1,090.0	415.0	350.0	1,560.0
Total Phosphorus (mg/L PO_4^{-3})	9	12.25	7.70	2.44	29.94
Total Nitrogen (mg/L N)	8	157.5	53.7	90.0	250.0
Orthophosphate (mg/L PO_4^{-3})	8	25.3	7.2	13.0	37.5
Alkalinity (mg/L $CaCO_3$)	9	1,422.0	531.0	100.0	2,000.0
BOD_5 (mg/L)	9	354.0	480.0	70.1	1,584.0
Cumulative Biogas Volume (mL)	48	3,754.0	1,861.0	0.00	1,861.0
Normalized Settlement (cm/(kg/cm^3))	12	1,539.0	945.0	307.0	2,534.0

Table 40 Characteristics of Leachate in Recirculation Period for Control PLM.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	29	5,228.0	3,068.0	2,046.0	14,330.0
pH	13	7.63	0.21	7.31	8.00
ORP (mV)	13	93.3	56.2	-72.0	149.0
NO_3- (mg/L as N)	13	14.2	4.3	7.3	22.0
Hardness (mg/L Ca)	13	273.6	74.4	187.3	435.1
Color (Pt Co Units APHA)	13	1,053.0	454.0	365.0	2,080.0
Turbidity (NTU)	13	126.78	33.24	70.20	187.00
Conductivity (μS/cm)	13	3.75	0.65	2.90	5.58
DO (mg/L O_2)	13	3.36	1.85	0.50	6.96
COD (mg/L)	13	1,354.0	661.0	130.0	2,540.0
Total Phosphorus (mg/L PO_4^{-3})	13	25.50	5.77	12.74	35.94
Total Nitrogen (mg/L N)	13	171.2	38.7	100.0	220.0
Orthophosphate (mg/L PO_4^{-3})	13	33.21	12.77	10.00	66.80
Alkalinity (mg/L $CaCO_3$)	13	2,080.8	213.6	1,800.0	2,500.0
BOD_5 (mg/L)	13	259.1	154.4	52.3	585.6
Cumulative Biogas Volume (mL)	142	4,747.0	2,685.0	4.00	7,705.0
Normalized Settlement (cm/(kg/cm^3))	28	2,103.0	739.0	537.0	2,649.0

APPENDIX 2. SUMMARY OF LEACHATE CHARACTERISTICS IN THE SPLMS

The following tables (Table 41 to Table 46) summarize the parameters measured in the SPLMs at each period, with their respective average values, standard deviations, maximums and minimums, as the number of samples taken.

- ***Characteristics of Leachate for SPLM-1***

In this section are found the parameters measured during dry and recirculation period in the SPLM-1, which used a daily cover with a density equivalent to the CCAs PLM (Table 41 and Table 42).

Table 41 Characteristics of Leachate in Dry Period for SPLM - 1.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	6	75.40	147.00	0.63	375.00
pH	3	8.58	0.54	7.97	8.96
ORP (mV)	3	83.0	84.7	-14.0	142.0
NO_3^- (mg/L N)	3	53.9	38.9	30.0	98.8
Hardness (mg/L Ca)	3	120.1	88.7	67.4	222.6
Color (Pt Co Units APHA)	3	2,008.0	442.0	1,500.0	2,300.0
Turbidity (NTU)	3	150.0	233.0	11.2	419.0
Conductivity (μS/cm)	3	3.4	2.2	1.3	5.7
DO (mg/L as O_2)	3	4.20	0.35	3.80	4.50
COD (mg/L)	3	4,220.0	2,325.0	2,750.0	6,900.0
Total Phosphorus (mg/L PO_4^{-3})	3	21.7	12.4	8.9	33.7
Total Nitrogen (mg/L N)	3	175.0	90.1	100.0	275.0
Orthophosphate (mg/L PO_4^{-3})	3	29.5	12.3	17.5	42.0
Alkalinity (mg/L $CaCO_3$)	3	2,000.0	0.0	2,000.0	2,000.0
BOD_5 (mg/L)	3	225.0	145.4	86.4	376.4
Volatiles Acids (mg/L CH_3COOH)	1	18.86	*	18.86	18.86

Table 42 Characteristics of Leachate in Recirculation Period for SPLM - 1.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	14	399.4	433.0	350.0	430.0
pH	6	7.86	0.0142	7.71	7.99
ORP (mV)	6	-218.0	27,234.0	-336.0	107.0
NO_3^- (mg/L N)	6	79.0	1,262.3	49.5	145.0
Hardness (mg/L Ca)	6	257.8	6,151.0	194.9	374.9
Color (Pt Co Units APHA)	6	2,304.0	194,604.0	1,700.0	2,900.0
Turbidity (NTU)	6	377.2	30,405.0	178.0	637.0
Conductivity (μS/cm)	6	5.88	0.52	4.71	6.88
DO (mg/L as O_2)	6	3.6	8.0	0.1	8.4
COD (mg/L)	6	2,960.0	1,174,840.0	2,260.0	5,100.0
Total Phosphorus (mg/L PO_4^{-3})	6	29.7	99.2	17.8	42.9
Total Nitrogen (mg/L N)	6	287.5	25157.5	150.0	600.0
Orthophosphate (mg/L PO_4^{-3})	6	60.7	5203.2	14.0	202.0
Alkalinity (mg/L $CaCO_3$)	6	2,483.0	245,667.0	2,000.0	3,300.0
BOD_5 (mg/L)	6	335.0	91,166.0	103.0	879.0
Volatiles Acids (mg/L CH_3COOH)	6	68.4	16,626.6	10.3	331.4

- ***Characteristics of Leachate for SPLM-2***

Parameters measured during dry and recirculation period in the SPLM-2, which used a daily cover with a density equivalent to the control PLM (Table 43 and Table 44).

Table 43 Characteristics of Leachate in Dry Period for SPLM - 2.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	6	77.4	141.5	0.46	365.0
pH	3	8.51	0.71	7.69	8.94
ORP (mV)	3	94	56.3	29.0	127.0
NO_3^- (mg/L N)	3	63.4	60.8	22.5	133.3
Hardness (mg/L Ca)	3	82.3	69.4	39.7	162.4
Color (Pt Co Units APHA)	3	1,858.3	162.7	1,700.0	2,025.0
Turbidity (NTU)	3	65.6	79.2	18.4	157.0
Conductivity (µS/cm)	3	4.26	1.60	3.01	6.07
DO (mg/L as O_2)	3	3.67	0.89	2.80	4.40
COD (mg/L)	3	1,982.0	528.0	1,550.0	2,570.0
Total Phosphorus (mg/L PO_4^{-3})	3	12.16	3.68	9.44	16.34
Total Nitrogen (mg/L N)	3	150.0	100.0	50.0	250.0
Orthophosphate (mg/L PO_4^{-3})	3	25.9	18.3	14.6	47.0
Alkalinity (mg/L $CaCO_3$)	3	1,466.7	152.8	1,300.0	1,600.0
BOD_5 (mg/L)	3	242.0	120.1	103.4	312.3
Volatiles Acids (mg/L CH_3COOH)	1	14.29	*	14.29	14.29

Table 44 Characteristics of Leachate in Recirculation Period for SPLM - 2.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	14	396.9	394.4	370.0	425.0
pH	6	7.84	0.033	7.54	8.03
ORP (mV)	6	-145.5	25,326.7	-301.0	121.0
NO_3^- (mg/L N)	6	79.1	1,214.9	53.5	148.0
Hardness (mg/L Ca)	6	225.6	2,017.6	179.3	299.2
Color (Pt Co Units APHA)	6	2,042.0	487,417.0	1,400.0	3,300.0
Turbidity (NTU)	6	309.7	27,314.2	109.3	539.0
Conductivity (μS/cm)	6	6.34	1.17	5.29	8.29
DO (mg/L as O_2)	6	4.2	5.1	1.3	8.0
COD (mg/L)	6	2,817.0	1,881,827.0	1,700.0	5,500.0
Total Phosphorus (mg/L PO_4^{-3})	6	18.04	77.60	5.69	30.94
Total Nitrogen (mg/L N)	6	333.0	66,238.0	150.0	700.0
Orthophosphate (mg/L PO_4^{-3})	6	39.52	554.45	14.40	64.00
Alkalinity (mg/L $CaCO_3$)	6	2,017.0	121,667.0	1,600.0	2,500.0
BOD_5 (mg/L)	6	611.0	996,865.0	106.0	2,636.0
Volatiles Acids (mg/L CH_3COOH)	6	0.378	0.104	0.106	0.987

- ***Characteristics of Leachate for SPLM-3***

In this section the parameters measured during dry and recirculation period in the SPLM-3 are found, this SPLM used a daily cover with a density ratio equal to 1.23 of the CCAs PLM (Table 45 and Table 46).

Table 45 Characteristics of Leachate in Dry Period for SPLM - 3.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	6	74.5	132.9	0.48	345.0
pH	3	8.46	0.505	7.88	8.80
ORP (mV)	3	95.3	57.5	29.0	130.0
NO_3^- (mg/L N)	3	62.2	59.6	25.0	131.0
Hardness (mg/L Ca)	3	95.4	73.7	50.5	180.5
Color (Pt Co Units APHA)	3	1,950.0	468.0	1,575.0	2,475.0
Turbidity (NTU)	3	161.0	237.0	14.5	434.0
Conductivity (μS/cm)	3	4.04	1.64	2.63	5.84
DO (mg/L as O_2)	3	3.37	0.81	2.5	4.1
COD (mg/L)	3	2,280.0	695.0	1,600.0	2,990.0
Total Phosphorus (mg/L PO_4^{-3})	3	15.97	4.01	11.44	19.04
Total Nitrogen (mg/L N)	3	175.0	90.1	100.0	275.0
Orthophosphate (mg/L PO_4^{-3})	3	35.6	27.6	19.5	67.5
Alkalinity (mg/L $CaCO_3$)	3	1,500.0	500.0	1,000.0	2,000.0
BOD_5 (mg/L)	3	292.7	136.1	136.4	384.4
Volatiles Acids (mg/L CH_3COOH)	1	74.29	*	74.29	74.29

Table 46 Characteristics of Leachate in Recirculation Period for SPLM - 3.

Variable	Total Count	Mean	Standard Deviation	Minimum	Maximum
Volume (mL)	14	376.1	1,743.6	275.0	450.0
pH	6	7.70	0.023	7.43	7.88
ORP (mV)	6	-2.17	18,589.4	-263.0	107.0
NO_3^- (mg/L N)	6	102.4	4,823.2	37.2	210.5
Hardness (mg/L Ca)	6	172	4,175.5	79.4	258.2
Color (Pt Co Units)	6	2,075.0	878,750.0	1,300.0	3,900.0
Turbidity (NTU)	6	229.3	14,768.7	147.0	458.0
Conductivity (μS/cm)	6	6.21	0.968	5.22	8.05
DO (mg/L as O_2)	6	3.83	2.90	1.5	6.4
COD (mg/L)	6	3,285.0	5,010,790.0	1,900.0	7,800.0
Total Phosphorus (mg/L PO_4^{-3})	6	16.35	75.12	5.19	31.94
Total Nitrogen (mg/L N)	6	334.0	66,964.0	100.0	700.0
Orthophosphate (mg/L PO_4^{-3})	6	41.3	685.1	14.0	72.0
Alkalinity (mg/L $CaCO_3$)	6	2,217.0	317,667.0	1,700.0	3,300.0
BOD_5 (mg/L)	6	331.0	88,806.0	126.0	902.0
Volatiles Acids (mg/L CH_3COOH)	6	95.1	38,820.7	6.86	497.1

APPENDIX 3. PHYSICAL LANDFILL MODELS (PLMS)

In the evaluation of PLMs a physical parameter measured was the oxidation-reduction potential (ORP), and biological parameter was dissolved oxygen. But, due to the collected conditions of the leachate, the results do not correspond to actual behavior of the PLMs. The results of these parameters are presented below:

- ***Oxidation – Reduction Potential (ORP)***

For the oxidation–reduction potential, the values found were similar regardless the type of daily cover used. The results of ORP are plotted in Figure 82.

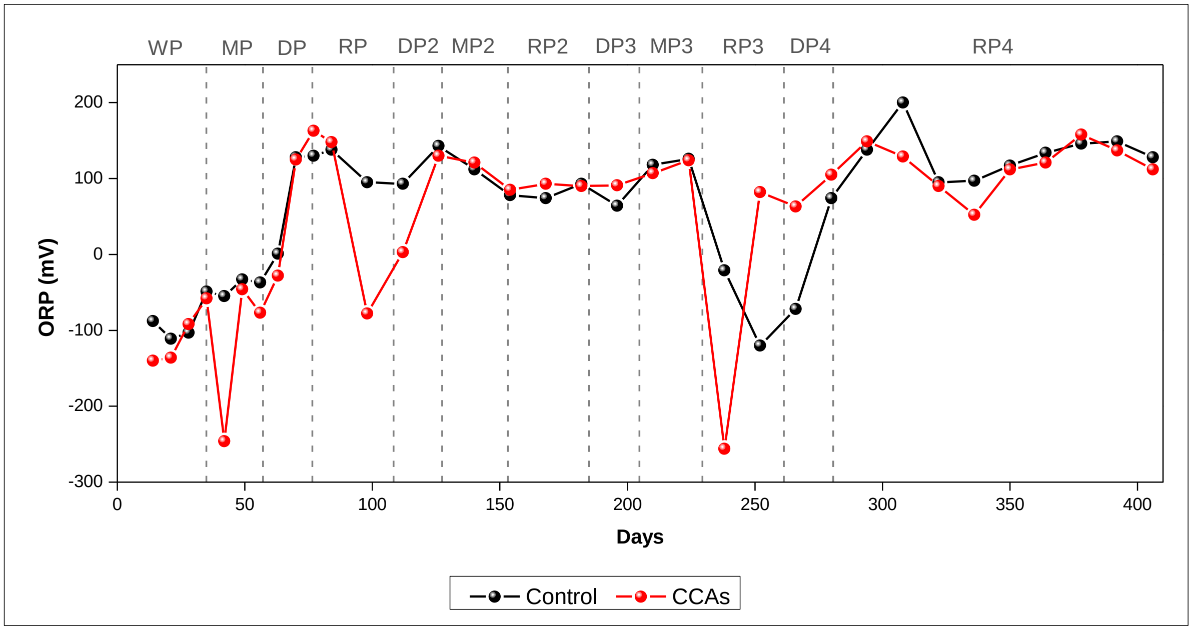

Figure 82 ORP Values of Leachate Produced in PLMs.

The high ORP (aerobic conditions) causes accelerated degradation of waste, and low ORP is related with the anaerobic degradation. High positive values of ORP are given in the first DP while the lowest values occurred in MP. The behavior did not show differences between the PLMs. The CCAs PLM showed the lowest values of ORP in the MP. The ORP tests are very sensitive to sample storage time and the measure may rise fairly rapid and become a lot more positive when it is tested only hours after sampling (Bilgili et al., 2007). The ORP results did not correspond to the behavior found in each of the PLMs because the leachate collection system was open to the environment interfering with the measurement (ion exchange).

- ***Dissolved Oxygen (DO)***

For dissolved oxygen, similar values were found regardless of the type of daily covers. The results are shown in Figure 83:

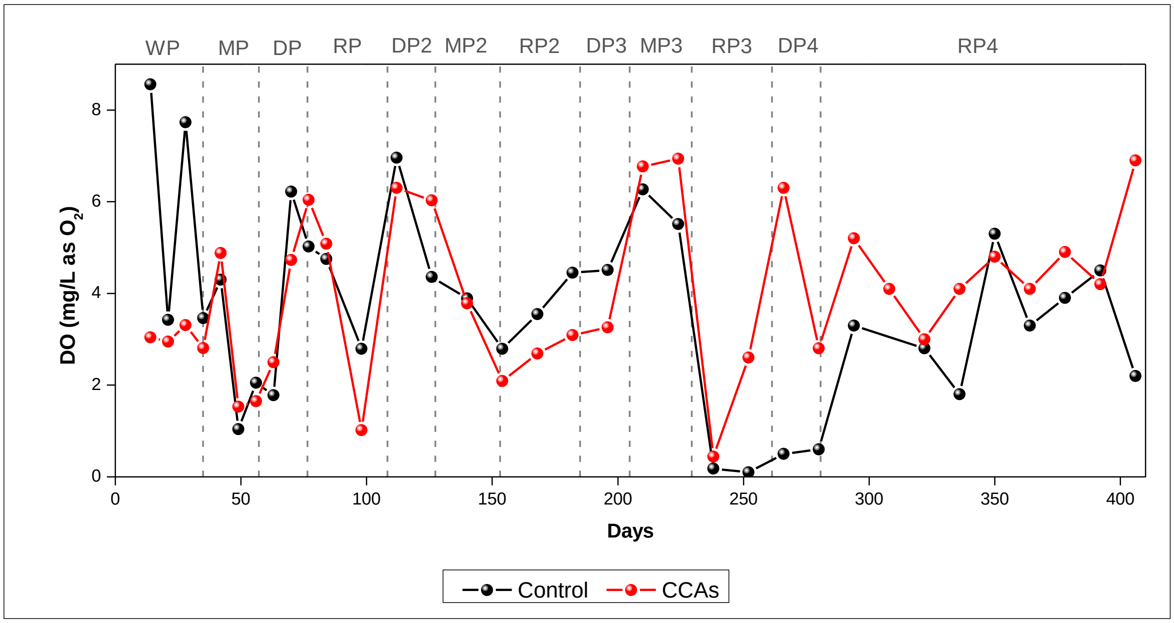

Figure 83 Dissolved Oxygen of Leachate Produced in PLMs.

In the WP, the control PLM presented high DO concentration 8.6 mg/L O_2 and the CCAs PLM low concentration of 3.0 mg/L O_2, while at the end experiment concentrations of 2.2 and 6.9 mg/L O_2 were found for control and CCAs PLM, respectively. The trend of DO concentration was the variable in the other periods in both PLMs: in the MP, the concentrations were high while in periods of recirculation were low. In the last recirculation period (RP4), the concentrations were variable and at the end of the experiment, CCAs PLM had a higher DO concentration compared with the control PLM. The result of the DO showed a random tendency and did not reflect the actual behavior of PLMs because the leachate collection system was open to the atmosphere so this interferes with the measurements.

APPENDIX 4. SMALLER LANDFILL MODELS (SPLMS)

In the evaluation of SPLMs, other parameter measured was dissolved oxygen (DO). But, due to the collected conditions of the leachate, the results do not correspond to actual behavior of the PLMs. The results of these parameters are presented below:

- ***Dissolved Oxygen (DO)***

The results of the dissolved oxygen are shown in Figure 84. In the first RP, the SPLM-1 had the highest concentration of DO (5.0 mg/L O_2), while for SPLM-2 and SPLM-3, concentrations were 0.3 and 1.6 mg/L O_2. In the case of the SPLM-1, the concentration decreased dramatically and then increased gradually in the second recirculation period (RP2) (8.4 mg/L O_2), SPLM-2 increased the concentration (8.0 mg/L O_2), while for SPLM-3 increased (3.7 mg/L O_2).

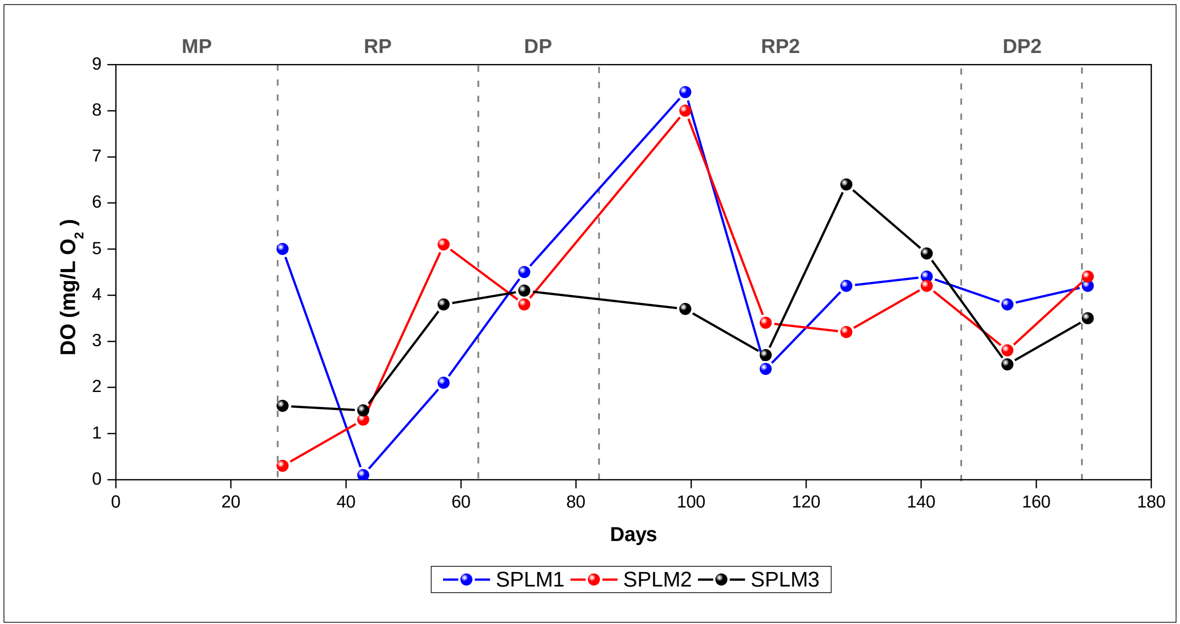

Figure 84 Dissolved Oxygen of Leachate Produced in SPLMs.

At the end of the experiment, final concentrations were in the range of 3.5 - 4.2 mg/L O_2. High values of dissolved oxygen in the SPLMs coincide with periods of recirculation this is probably due to oxygen entering through the system recirculated. It should be emphasized that the measurements of dissolved oxygen does not represented the actual values of the SPLMs because the containers that collected the leachate remained open to the atmosphere affecting the measurements.

APPENDIX 5. SMALLER LANDFILL MODELS WITH HEAVY METALS SOLUTION INJECTION

Possibility of heavy metal uptake by coal combustion byproducts as a low cost adsorbent material when used as an alternative daily cover was tested. One experiment was done: a heavy metals solution was injected in smaller physical landfill models. Results of heavy metals removal tests indicated that CCAs were able to remove Cd^{2+} (cadmium) and Pb^{2+} (lead). Also, other parameters were measured: volume of leachate produced, turbidity, conductivity, chemical oxygen demand, biological oxygen demand and volume of biogas produced. Below are the results found in each of the parameters:

For this experiment we used the SPLM-1 and SPLM-2, which were injected with a solution composed of leachate (60 mL), and cadmium (20 mL) and lead (20 mL) (concentration of cadmium and lead was 100 mg/L). In Figure 85, shows the volume of leachate collected weekly. It is notable that there was no significant difference between the SPLMs because they were hydraulically similar. The dotted lines represent the time when the injections were made in the SPLMs.

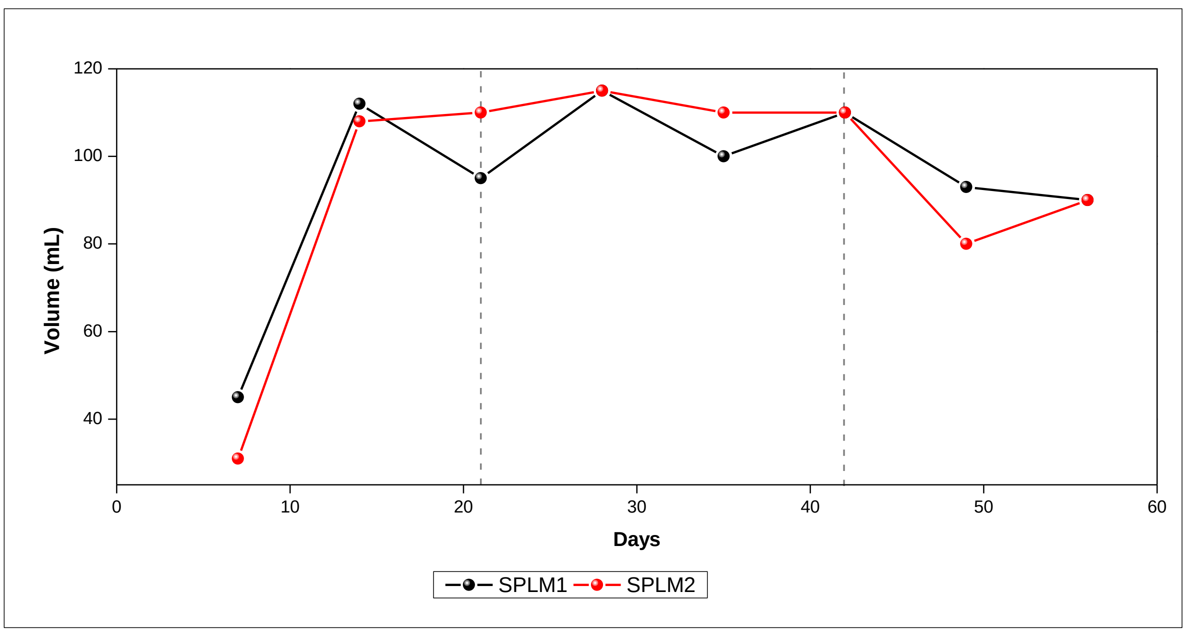

Figure 85 Volume of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

In these experiments, parameters such as the turbidity and conductivity were not significantly different between the SPLMs. The initial turbidity (Figure 86) for SPLMs was 16.3 and 24.1 NTU, respectively; these values increase rapidly but after the second and third injection they reduced and maintained the same trend. This was due to the reduction of suspended particles through the recirculation of the solutions. An opposite behavior was observed the conductivity (Figure 87) since it increases with the injections of the leachate and heavy metals, due to the increase of cations and anions, but after the last injection, the conductivity reduced to similar values of the 4.0 and 4.2 µS/cm for SPLM-1 and SPLM-2.

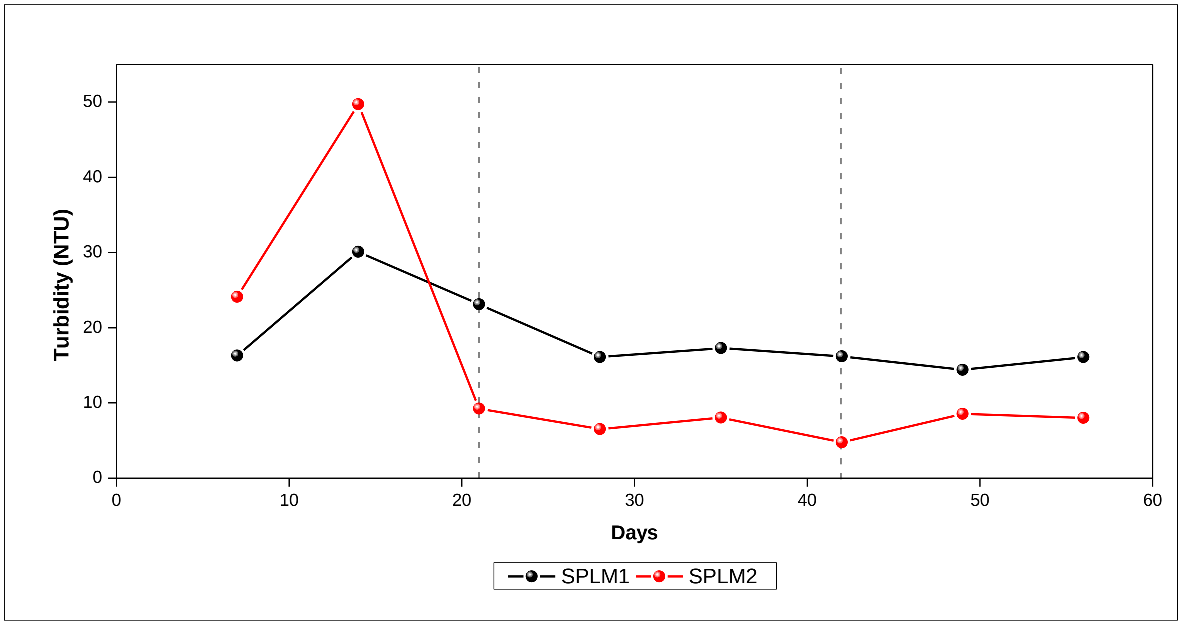

Figure 86 Turbidity of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

Other parameters analyzed were the COD (Figure 88) and the BOD (Figure 89), there was no significant difference between the SPLMs. COD remarkably decreased with time due to the decline of all organic material in the SPLMs (Figure 88), while BOD (Figure 89) fluctuated; the first phase had a high value which declined rapidly and the second phase increased and decreased again in the third phase. These fluctuations were the response to the injections with leachate and heavy metals realized to the SPLMs

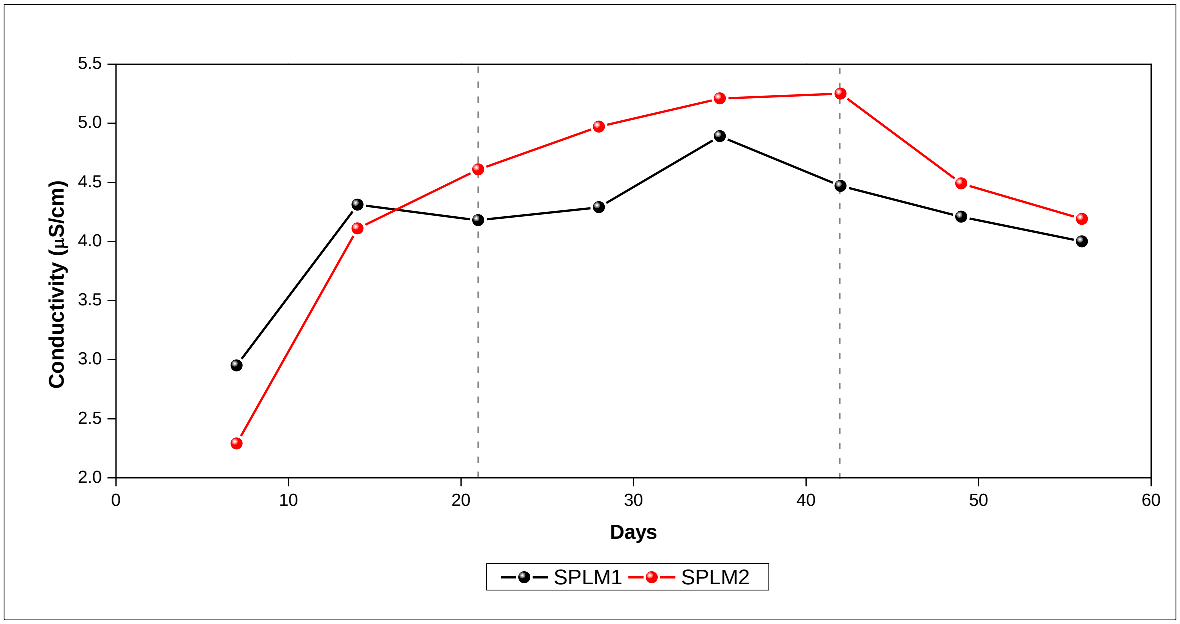

Figure 87 Conductivity of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

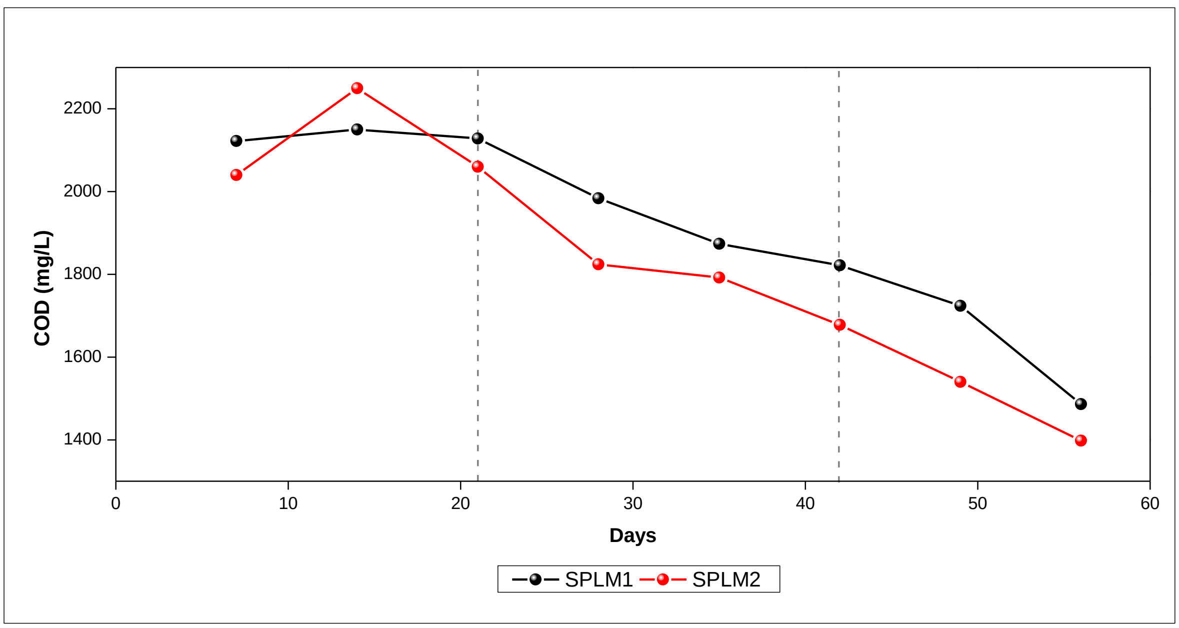

Figure 88 Chemical Oxygen Demand of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

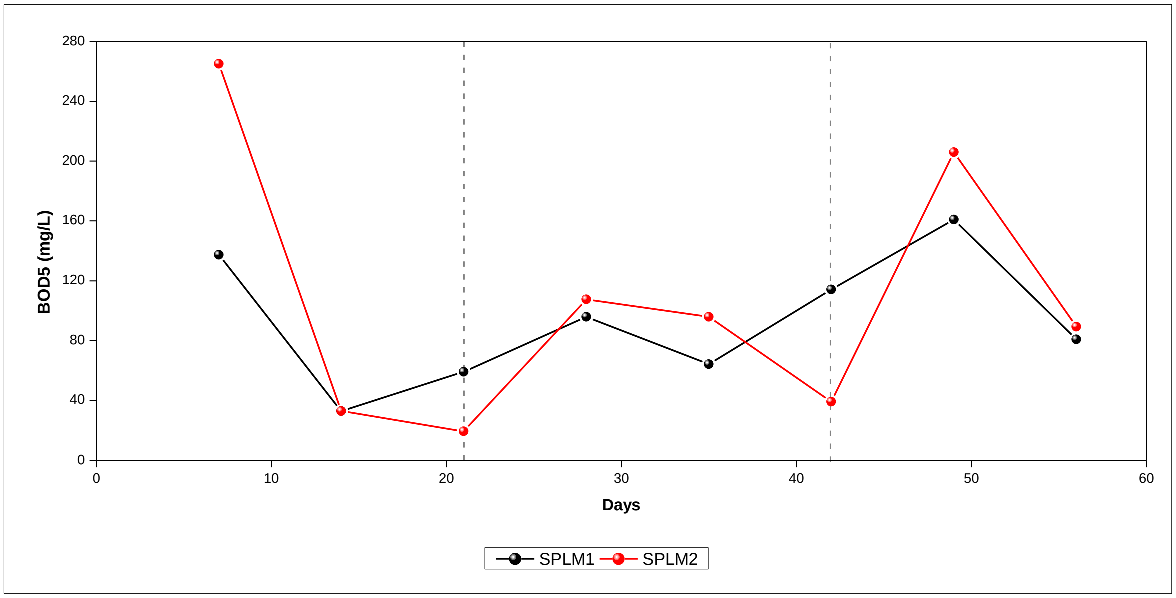

Figure 89 Biological Oxygen Demand of Leachate Produced in SPLMs During the Experiment of the Heavy Metals.

The biogas production was measured in the SPLM-1 (Figure 90). It can be noticed that the biogas production increased over time as the result of microbial activity due to the recirculation of leachate. Furthermore, the increased in microbial activity was not affected by the heavy metals added in the injections, possibly because they were removed by the CCAs through a specific mechanism (adsorption or precipitation).

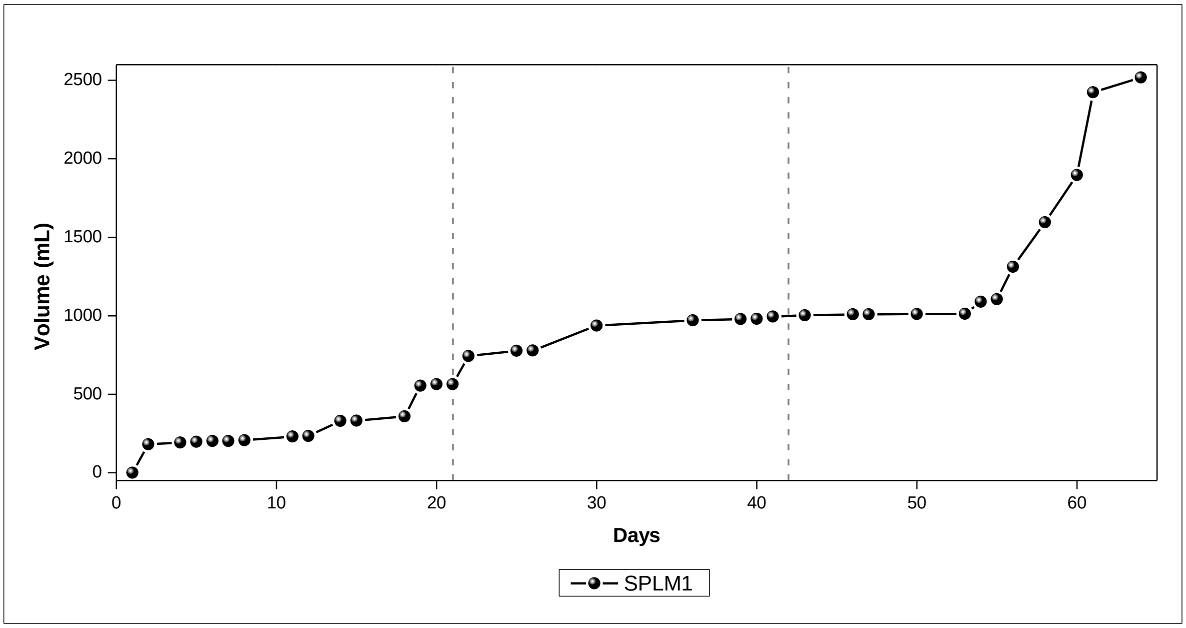

Figure 90 Biogas Production in SPLM-1 During the Experiment of the Heavy Metals.