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Construction**

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Engineering, University of KwaZulu-Natal**

Title:

**INVESTIGATION INTO THE DENITRIFICATION OF HIGH
STRENGTH LANDFILL LEACHATE USING PINE BARK AND
RAW AND COMPOSTED COMMERCIAL GARDEN REFUSE AS
A CARBON SOURCE: COLUMN STUDIES**

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Abstract

Landfill leachate, the liquid discharge from Municipal Solid Waste (MSW) landfills, is the combination of the surface runoff and ground water that percolates through the waste and the liquid contained in the waste itself and is considered to be toxic and presents a potential harm to the environment. Raw leachate contains high concentrations of biodegradable and non-biodegradable carbon as well as high concentrations of ammonia nitrogen. Traditionally, landfill leachate has been treated biologically through aerobic processes which reduce the biological carbon to carbon dioxide and biomass (bacterial growth) and ammonia nitrogen to nitrates. Unfortunately this is not sufficient to protect the environment from harm. It is necessary to further treat the leachate anaerobically to transform the nitrates to elemental nitrogen which is removed from the leachate as nitrogen gas. Biodegradable carbon is often the rate limiting substrate as carbon is consumed during the preceding nitrifying phase. Biodegradable carbon can be supplemented through the addition of methanol, at great expense

Leachate from the Mariannahill Landfill site is currently treated aerobically in a sequencing batch reactor where nitrification is achieved. The nitrified leachate is then used as a dust suppressant on the current site. It is anticipated that in 2012 the Land fill site would have reached capacity thereby eliminating the need to irrigate and leaving the site with an excess of nitrified leachate that will present an environmental risk.

The denitrifying performance of raw commercial garden refuse, pine bark and composted garden refuse as a growth medium and carbon source was investigated through the establishment of batch and column tests.

CGR Raw proved the most successful of the three growth media, achieving full denitrification at a loading rate of 1700 mg NO₃-N/kg of substrate/day

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1 INTRODUCTION

Landfill leachate, the liquid discharge from Municipal Solid Waste (MSW) landfills, is the combination of the surface runoff and ground water that percolates through the waste, the liquid contained in the waste itself and any re-circulated leachate (Crawford and Smith, 1985, Renou *et al*, 2007). The composition of landfill leachates varies significantly (Crawford and Smith, 1985, Renou *et al*, 2007, Lou *et al*, 2009). The factors that influence this variance include the nature of the waste within the landfill, the age of the landfill, climate and rainfall variations and the design and operation of the landfill site (Renou *et al*, 2007).

The landfill itself operates as an anaerobic reactor (Renou *et al*, 2007) and the anaerobic digestion model is a useful tool in illustrating the changes in composition of the leachate attributed to the age of the landfill. The leachate from young landfills is characterized by the products of acidogenesis (i.e. low pH and high Biological Oxygen Demand (BOD) load) while the leachate from older landfills is characterized by a low BOD: COD ratio and increased pH. Ammonium is produced at high concentrations throughout the life of the landfill. Table 1-1 below provides average leachate composition at various stages in the landfill life cycle.

Table 1-1: Typical Leachate characteristics at Various Landfill Ages (Tengrui *et al*, 2007)

Leachate Type	Young	Intermediate	Stabilized
Landfill age	< 5	5 – 10	> 10
pH	< 6.5	7	> 7.5
COD (g / L)	> 20	13 – 15	< 2
BOD : COD	> 0.3	0.1 – 0.3	< 0.1
TOC : COD	0.3	-	0.4
Organic Matter	70 – 90% VFA	20 – 30 % VFA	HMW
Nitrogen	100 – 2000 mg / L		
Metals (g / L)	2	< 2	< 2

Due to their reliability, simplicity and cost effectiveness, biological treatment processes are often selected to remove COD and TKN (Renou *et al*, 2007). Under aerobic conditions the organic carbon is degraded by micro-organisms to produce CO₂ and sludge (biomass). Ammonia-Nitrogen is oxidized by Nitrosomonas to nitrites (NO₂⁻-N) which in turn is oxidized by Nitrobacter to nitrates (NO₃⁻-N) during aerobic nitrification. Under anaerobic conditions the organic carbon is biologically degraded

to produce biogas (CO_2 & CH_4) and nitrates are denitrified by facultative bacteria to elemental nitrogen (N_2) (Metcalf and Eddy, 1995, Henze *et al*, 2002).

The Mariannhill Landfill in KwaZulu-Natal, South Africa, has been operating for approximately 10 years (Trois, 2009). The landfill receives between 550 and 700 tons of municipal solid waste (MSW) per day (Pisano, 2007) into 5 engineered landfill cells. Three of the five landfill cells have been closed with the final two currently in operation. There are no plans to add additional landfill cells and the landfill site is therefore expected to be closed in the medium term (Trois, 2009).

Currently the site operates a sequencing batch reactor (SBR) which is designed to achieve nitrification and denitrification (Trois, 2009, Strachan & Bowers, 2004). Although the plant can achieve denitrification with the addition of methanol as an additional carbon source, the plant is not operating the denitrification phase as all nitrified leachates are either irrigated or used as dust suppression on the site (Trois, 2009).

Although the site currently operates within the department of Water Affairs guidelines for disposal by irrigation and land treatment, the need for dust suppression will diminish as the landfill closes and a surplus of nitrified leachate will require disposal.

Recent laboratory scale experiments conducted by Plüg (2008) and Pisano (2007) at the University of KwaZulu-Natal have indicated that denitrification can be achieved with anaerobic submerged filters using various organic media as a growth medium and supplementary carbon source.

This research project aims to add to this body of research by investigating the suitability of raw commercial garden refuse, pine bark and composted commercial garden refuse as a growth medium and carbon source for denitrifying a synthetic landfill leachate with a nitrate concentration of 2000 mg/L. The nitrate concentration in the post nitrification treatment process varies between 500 and 2000 mg/L. Other studies have investigated 500 and 1000 mg/L concentrations.

The research conducted included three distinct steps. The chemical characterization of each of the proposed substrates in respect of the availability of carbon and biodegradable carbon and their carbon to nitrogen ratios, operating batch tests with each of the substrate and the nitrate solution and operating a column test aimed to simulate anaerobic submerged filter conditions.

It is anticipated that the outcomes from this research will indicate the relative suitability of each of the proposed substrates as well as the direction for any additional research. It is also expected that design data such as hydraulic and nitrate loading criteria will be determined to assist with the design of a pilot plant should one of the substrates prove suitable.

This report document has been set out as follows:

- Chapter 1: Introduction
- Chapter 2: Literature Review
- Chapter 3: Materials and Methods
- Chapter 4: Results and Discussion
- Chapter 5: Conclusion.

2 LITERATURE REVIEW

2.1 Mariannahill Landfill

The Mariannahill Landfill site is a municipal landfill that receives between 550 and 700 tones of waste per day and operates its own sorting operation prior to landfilling where recyclables and other materials are removed from the site prior to tipping. The site consists of 5 lined cells each with a leachate drainage collection system. The landfill is currently approximately 10 years old and three of the five cells have been closed up for good (Trois, 2009).

Mariannahill Landfill currently produces 50 m³ of leachate per day which is treated in a Sequencing Batch Reactor (SBR). The SBR has been designed to achieve both nitrification and denitrification (with the addition of methanol), but currently only operates as an aerobic process where BOD reduction and nitrification are achieved (Trois, 2009). From the SBR, flow is balanced in a reinforced concrete balancing tank, from where it is either passed through a 280 m² constructed lined reed bed, or is used for dust suppression (Strachan & Bowers, 2004). The reed beds act as polishing treatment where BOD is further reduced through aerobic process and suspended solids are settled and the effluent used for irrigation throughout the Mariannahill Conservancy.

2.2 Biochemistry of Landfills

2.2.1 Biodegradation in Landfills

The life of a landfill, pertaining to the microbiological activity, can be divided into three distinct phases. These three phases have been proposed by Crawford & Smith (1984), Lo (1996) and Renou *et al* (2007) to name a few. In the interests of simplicity, the model proposed by Renou *et al* (2007) (citing Lema *et al*, 1988) will be used to illustrate the microbiological degradation within a landfill cell. Renou *et al* (2007) proposed the anaerobic degradation model which is divided into three distinct phases. Phase 1 includes a combination of aerobic degradation and hydrolysis. During this phase, the free oxygen found in pockets within the landfill will promote the decomposition of readily biodegradable organic matter through the promotion of aerobic heterotrophic bacteria. The conversion of organic material to biomass will result in an increase in carbon dioxide (CO₂) production.

In addition to the aerobic oxidation, complex organic compounds (mainly polysaccharides, proteins and lipids) are reduced to simpler, more readily biodegradable organic compounds. In general polysaccharides are reduced to monosaccharides (sugars), proteins to amino acids and lipids to long chain fatty acids (LCFA).

Phase two involves the fermentation of the products formed in phase one under anaerobic conditions as all the available O_2 has been consumed. This acid forming phase occurs in two steps, the first being acidogenesis followed by acetogenesis. Acidogenesis includes the biodegradation of monosaccharides, Amino Acids and LCFA's to Volatile Fatty Acids (VFA) and acetic acid. Acetogenesis converts the remaining VFA's to acetic acid. Both the acidogenic and acetogenic steps produce biogas in the form of CO_2 and H_2 .

The third and final phase of the landfill prior to stabilization is referred to as methanogenesis. Predictably, methanogenesis is the process whereby the product of fermentation and acetogenesis are converted into Methane (CH_4) and CO_2 . It is important to note that a low pH (between 5 and 6) is characteristic of a landfill still in the acido / acetogenic phase. Further, pH values below 6.2 are likely to inhibit methanogenesis. It is therefore important that buffering is in existence within the waste material should methane production be a desirable outcome of the land filling process.

In general a transitional phase is established whereby equilibrium between acid formation and methanogenesis is established. This is because different conditions may occur simultaneously throughout the landfill.

Towards the end of the landfills life, a considerable percentage of the organic matter has been degraded and the production of methane ceases (Lo, 1996), allowing oxygen to diffuse into the landfill mass.

2.2.2 Landfill Leachates

Landfill Leachate can be defined as the liquid effluent that emanates from a landfill and is a result of both rainfall runoff that percolates through the waste and the liquid portion of the waste itself. The composition of landfill leachate varies significantly. The factors that influence the composition include the age of the landfill and the operation of the landfill.

2.2.2.1 Seasonal Climatic Variations

Seasonal variations in climate can have an effect on the composition of the leachate as both moisture content and temperature influence the extent of biological activity within the waste. The optimal moisture content of a landfill is reported to be approximately 40% (Crawford and Smith, 1985). A moisture content less than 40% has the effect of reducing biological activity (and hydrolysis) and hence reduces the BOD concentration within the leachate.

Temperature has a similar effect to that of moisture content in that it affects reaction rates. Anaerobic bacteria in general are mesophilic, enjoying temperatures between 20 and 40°C. A reduction in seasonal temperature has the effect of decreasing biological activity within the landfill waste.

2.2.2.2 Waste Composition

Landfill waste that is high in organic biodegradable carbon will increase the rate of decomposition (Hamoda *et al*). Additionally, a Carbon to Nitrogen (C/N) ratio of 25 : 1 or less will increase the rate of decomposition. When the C/N ratio increases above 25:1, nitrogen availability becomes the reaction limiting nutrient. The biodegradability will further be affected by the presence of toxins in the waste. The presence of hazardous organic compounds (phenolic wastes and tar bases) as well as heavy metals (cadmium, copper, lead, nickel, tin and zinc) can be toxic to certain bacteria and hence reduce the process of decomposition (Crawford & Smith 1985).

2.2.2.3 pH

pH - Methanogenic bacteria are sensitive to pH. Acidic conditions will inhibit methanogenesis with reactions ceasing at a pH of 6.2 and less (Henze et al, 2002).

2.2.2.4 Operational / Design Factors

As mentioned in section 2.2.2.1, moisture content plays an important role in the biodegradation of landfill waste. There are a number of operational procedures that have a significant effect on the moisture content of the landfill mass. Design and control of surface waters, the installation of landfill lining systems and leachate collection drains, capping waste after tipping, establishment of vegetation over capped fills and the recirculation of either leachate or partially treated leachate are a

few of the techniques available for managing landfill water / leachate (Crawford & Smith 1985).

2.2.2.5 Age of the Landfill

In section 2.2.1 we proposed the anaerobic digestion model as a means of explaining the lifecycle of a landfill in respect to the biological activity within the fill. In the same manner we can use this model to explain the variations in leachate composition produced over the life of the landfill.

The aerobic phase of the landfill is considered to be relatively short as oxygen is limiting. Some authorities report aerobic phases that last only three months. Given that this research project is focused on treatment of landfill leachates emanating from a mature landfill, it is considered not viable to place a heavy emphasis on the leachate during this phase of the landfill in this research project.

During the early years of a landfills life, once anaerobic conditions have been established, the dominant processes are that of hydrolysis and fermentation where by the complex organic matter is hydrolysed to simpler organic compounds, which in turn are fermented to volatile fatty acids and acetic acid. During this phase the leachate produced is characterised by a low pH as a result of the acid generation, high COD, often reported to be above 10 000 mg/L and a high BOD₅ : COD ratio. Renou *et al*, (2007) reports a BOD₅ : COD ration during this immature phase as high 0.7

As the landfill matures and methanogenesis becomes the dominant biological process, the VFA's and acetic acid are converted in CH₄ and CO₂. During the this phase, the biodegradable fraction of the leachate will diminish significantly. Leachates produced during methanogenesis are characterised by a pH of approximately 7.5, a low COD and low BOD₅ : COD ratio, often below 0.1. The low BOD₅ : COD ratio is a result of the consumption of VFA's and acetic acid leaving only refractory organic compounds, mainly humic and fulvic acid (Renou *et al*, 2007 and Crawford & Smith, 1985).

There is a very large intermediate phase where part of the landfill is dominated by acid fermentation and part by methanogenesis. During this phase the organic portion of the leachate consists of both VFA's and humic and fulvic acid. The proportions of each are determined by the operation of the landfill and the relative amount of each process taking place (Renou *et al*, 2007 and Crawford & Smith, 1985). Table 1-1 in the introduction provides a characterization of the typical landfill leachates that can be anticipated at various phases in the landfill process.

2.3 Alternatives for Leachate Treatment

As described above, landfill leachate can be a strong effluent with high BOD and NH₃-N concentrations as well as the presence of heavy metal salts. Traditionally treatment options have been divided into three categories; leachate transfer which includes the co-disposal of leachate with municipal wastewater and the recirculation of leachate within the landfill; biological treatment, both aerobic and anaerobic, and attached and suspended growth; and chemical and physical processes which include chemical oxidation, adsorption, air stripping and settling / flotation. In recent years more sophisticated, with regard to technology, approaches have been used. Among these is the range of filtrations, micro / nano / ultra and reverse osmosis, and biological membrane reactors (Renou *et al*, 2007).

The intention of this section of the literature review is to provide a brief description of a number of traditional treatment options, and in particular to focus on biological treatment including biological filters. Technologically intensive processes such as micro / nano / ultra filtration etc. have been omitted from this research as the aim is to develop a low cost low technology solution to the problems experienced at the Marianhill landfill. It is worth mentioning however that as discharge limits becoming increasingly stringent, these processes are adopted on a wider scale. Often these processes are used as either a primary treatment prior to biological treatment or as a polishing treatment after a biological treatment process.

2.3.1 Leachate Transfer

2.3.1.1 Co-disposal with at Municipal WwTW

Traditionally co-disposal was seen as an attractive method for the treatment of landfill leachates as it was considered to be simple and low in capital and operating costs. The disposal method was also considered beneficial as the leachate introduced nutrients to the treatment stream which then did not need to be added to the process. In recent years commentators have reconsidered this opinion and now consider the disposal method unsatisfactory as the leachate introduces compounds with low biodegradability and inhibitors such as ammonium and heavy metals. Strachan and Bowers (2004) commented on the co-disposal of leachate from the Mariannhill Landfill, saying that the disposal method amounted to no more than dilution with the municipal wastewater stream and that the transportation of leachate posed engineering problems related to corrosion of the pumping mains and elevated

methane levels within the municipal sewer system. Senior, E (1995) suggests that in particular cases, pre-treatment on-site prior to co-disposal may be more appropriate.

Renou *et al* (2007) report that a number of researchers have investigated co-disposal using sequencing batch reactors (and activated sludge) and have found that with a dilution of sewage to leachate of 9:1, 95% BOD and 50% nitrogen removal efficiencies can be achieved. They further note that the addition of Powered Activated Carbon (PAC) has demonstrated an improvement in treatment efficiencies, particularly when dilutions ratios are less than 9:1.

2.3.1.2 Recirculating Leachate

Recirculation of landfill leachate has been a popular treatment option as it is considered to be inexpensive (Lema *et al*, 1988). Recirculation of leachate promotes the development of anaerobic bacteria colonies (Crawford & Smith 1985) and accelerates the stabilization of the landfill (Crawford and Smith 1985, Bilgili *et al* 2008, Reinhart 1996 and Rodriguez *et al* 2004). Rodriguez *et al* reported the time to stabilization being reduced from several decades to between 2 & 3 years. In addition to the accelerated stabilization, the procedure can improve the quality of the effluent (leachate) but reducing COD (Rodriguez *et al*, 2004) and enhance methane production (Reinhart, 1996).

Despite the positive results reported above, the procedure does have some disadvantages. There is little research available that comments on appropriate recirculation rates. Crawford & Smith (1985) warn that the procedure can promote excessive acid formation (fermentation) and result in an increase in the landfills' pH and hence an inhibition of methanogenesis. This has the undesirable result of an increased organic content in the leachate and a decrease in the production of methane. Furthermore, Cossu *et al* (2001) warn that recirculation can result in a perched water table or an increased hydraulic gradient leading to seepage into the ground water, and has been linked to geotechnical instability.

2.3.2 Suspended Growth Processes

Biological treatment of landfill leachate is considered to be a reliable, easy to operate, cost effective method of treating landfill leachate. It is further considered to be efficient in both the removal of BOD and nitrogen in immature leachates with a BOD:COD ratio greater than 0.5 (Renou *et al* 2007).

There are a number of options available for biological treatment which can be classified as either aerobic or anaerobic and either of attached growth or suspended growth process. Aerobic biodegradation involves the biological reduction of organic matter, producing bacterial biomass (sludge) and CO₂, and can be operated in a manner that promotes the conversion of ammoniacal nitrogen to nitrates. Anaerobic digestion converts organic matter into biogas (CH₄ and CO₂). Anaerobic processes provide distinct advantages when compared to aerobic processes in that they produce valuable CH₄, they have a low biomass yield, low energy requirements and they can treat high strength wastewaters (Kettunen *et al*, 1996). The solid waste from the anaerobic process is also stabilized and can be used as a cover to waste placed on the landfill (Kennedy & Lentz, 1999).

A brief description of the treatment process and pros and cons relating to the treatment of landfill leachates for a number of processes is presented below.

2.3.2.1 Lagoons

Lagoons or stabilization ponds generally consist of a basin or a series of basins that are filled with wastewater. Ponds can be operated as aerobic or aerated ponds with surface aerators, as anaerobic ponds or as Aerobic-Anaerobic or facultative ponds. When operated as aerobic ponds that can also have a sludge return system and hence from a process perspective are no different from an Activated Sludge Plant (Metcalf & Eddy, 1995).

Lagooning is considered to be an effective low-cost method of removing pathogens and organic material, and is popular in developing countries as it does not require specialized skills to operate the plant (Maynard *et al*, 1999). Renou *et al* (2007), reports research conducted by Maehlum and Orupold *et al* (1999) in which treatment efficiencies of 70% and 55 – 64 % COD removal are achieved respectively.

Despite the simplicity and cost effectiveness of lagooning as a treatment option it is not considered to be a treatment option for the future as increasingly stringent discharge limits are likely to render the process unsatisfactory (Renou *et al*, 2007).

2.3.2.2 Activated Sludge

The activated sludge process was developed in 1914 by Arden and Lockett and involves the production of an activated mass of micro-organisms capable of stabilizing waste aerobically. There are many different configurations in operation currently which are fundamentally versions of the original process which include a completely mixed aeration tank with secondary settlement tank and recycle sludge for an increased solids retention time (sludge age). See Figure 2-1 below for a schematic of the basic process (Henze *et al*, 2002).

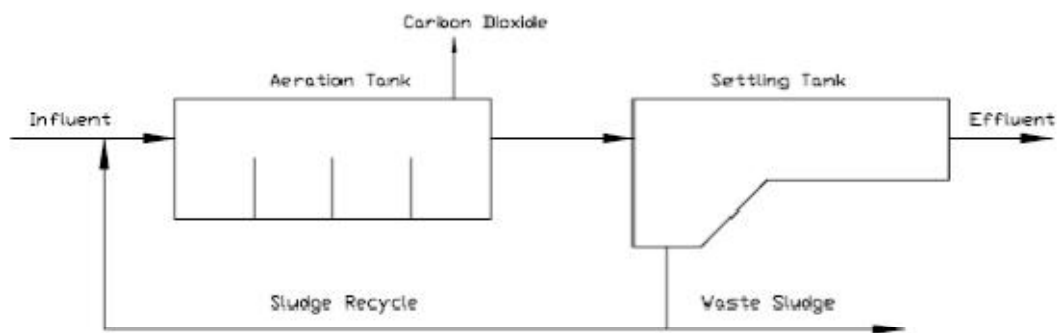


Figure 2-1: Standard Process Flow for Activated Sludge (Henze *et al*, 2002)

Renou *et al* (2007) report that activated sludge has been extensively used for the treatment of domestic wastewater and the co-treatment of leachate with domestic wastewater (refer to Section 2.3.1.1 for more on co-disposal), and that in recent times activated sludge has been shown to be inadequate for the treatment of landfill leachate (Lin *et al* 2000). It has been shown that despite the removal of organic matter, nutrients and ammonium, too many disadvantages exist, including the need for long aeration times and poor sludge settling characteristics (Loukidou *et al*, 2001) high energy demands and sludge bulking (Hoilijoki *et al*, 2000) and microbial inhibition owing to high ammonium concentrations (Lema *et al*, 1988).

2.3.2.3 Sequencing Batch Reactors (SBR)

The sequencing batch reactor is a modification of the activated sludge system using a single reactor and operating a fill and draw system. Aeration and clarification form the core treatment processes for both SBR and AS with the difference being that in AS, the aeration and clarification occur continuously in separate reactors and in the

SBR the two processes occur sequentially in a single reactor. There are five steps associated with the SBR system, viz. fill, react (aeration), settle, decant and idle. Since its inception however a number of variations on this process have been developed to allow for anaerobic and anoxic reaction steps which allow the plant to be designed for nitrification-denitrification and phosphorous removal in addition to BOD removal. The standard five step process is illustrated in Figure 2-2 below (Metcalf & Eddy, 1995)

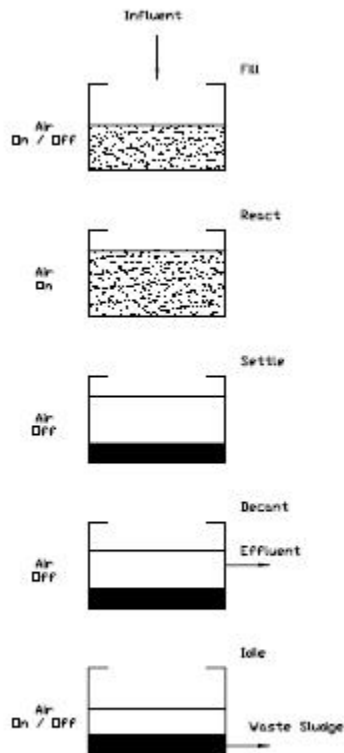


Figure 2-2: Process Flow for Conventional SBR Plant (Metcalf & Eddy (1995))

The sequencing batch reactor is considered ideal for the treatment of landfill leachates (Renou *et al*, 2007) as the process provides a process flexibility and ideal conditions for settling (Kennedy & Lentz, 1999). The flexibility of the process allows for the plant to provide concurrent carbon oxidation and nitrification (Renou *et al*, 2007) with COD removal efficiencies of 75% and ammonium nitrate removal of 99% (Lo, 1996) being witnessed.

2.3.2.4 Anaerobic Digestors

The anaerobic digester is a suspended growth process that is most commonly used for the treatment of high strength effluents such as primary sludge from primary settlers on municipal wastewater treatment works. Process advantages include the production of methane gas which can be used to heat the reactors and hence increase the reaction rate and the low sludge production rate. The anaerobic process is essentially an extension of the process that occurs within the landfill and is considered well suited to the treatment of landfill leachate, with BOD removal efficiencies of between 80 and 90 % being reported (Renou *et al*, 2008).

2.3.2.5 Up-flow Anaerobic Sludge Blanket Reactors (UASB)

The UASB is a combination of the anaerobic digester and a fluidized bed anaerobic filter (ref section 2.3.3) whereby the wastewater enters the reactor at the bottom and flows up through a sludge blanket. The sludge blanket is composed of biological granular particles (Metcalf & Eddy, 1995). The process allows for high treatment efficiencies with short hydraulic retention times (Renou *et al*, 2008) as a result of the sludge remaining in the sludge blanket. Metcalf & Eddy (1995) recommend up-flow velocities between 0.6 and 0.9 m/sec. In general anaerobic processes prefer high temperatures that aerobic processes, however, Renou *et al* (2008) citing Kettunen and Rintala (1998), reports results whereby the UASB have operated effectively for the treatment municipal landfill leachate at low temperatures. Treatment efficiencies or up 95 % of BOD was achieved at loading rates of 2-4 kg/m³.day.

2.3.3 Attached Growth Processes

In an attached growth process conditions are created that allow bacteria to establish themselves on a growth media (usually inert) in a thin layer referred to as a bio-film. The most common form of attached growth process is the trickling filter which is used extensively in municipal wastewater treatment. Other attached growth processes include the moving bed biological reactor (MBBR) and the rotating biological contactor (RBC). This research is focused on submerged filters and therefore will bias biological filters in the discussion on attached growth processes.

2.3.3.1 Biological Filters

Biological filters in general consist of a growth medium (usually inert; stone aggregate or crushed brick) over which an effluent passes. The bio-film which establishes on the media is responsible for removing the desired pollutant from the effluent. Biological filters can be configured to operate either as aerobic filters or anaerobic filters depending on the function that they are intended to fulfill.

The process kinetics involved in bio-filters are complex and as a result, a number of design criteria have been defined. For trickling filters Henze et al (2002) proposes the following:

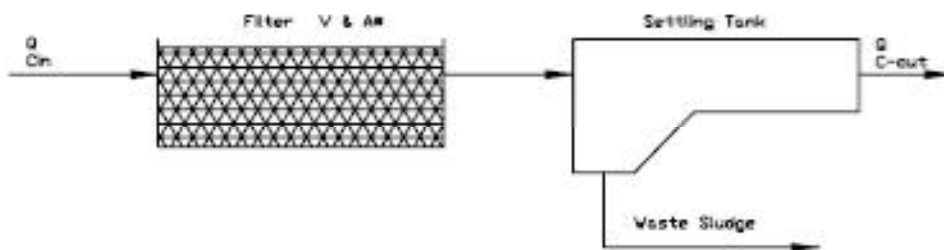


Figure 2-3: Simplified Process Flow Diagram for Fixed Media Filters

Treatment efficiency

$$E = (C_{in} - C_{out}) / C_{in}$$

Hydraulic Surface Loading Rate

$HLR = Q/A$ where $A =$ cross-sectional area of filter

Volumetric Loading Rate

$$B_V = Q \cdot C_{in} / V$$

Organic Surface Loading Rate

$$B_{A,C} = Q \cdot C_{in} / A_*, \text{ where } A_* \text{ is the actual area of filter media available}$$

For the design of nitrifying filters, Henze et al (2002) offer an additional parameter for the removal of ammonium nitrates.

Ammonia Removal Efficiency

$$r_{A,NH_4} = Q \cdot (C_{NH_4in} - C_{NH_4out}) / A_*$$

If full nitrification is to occur the above expression is equivalent to the Surface Loading Rate. Additionally, if the specific area of the media is known (that is the surface area per unit volume) or the area to mass ratio, the above can be expressed in terms of either the ammonia nitrogen per unit volume per day or per unit mass per day.

And for anaerobic denitrifying filters, Henze *et al* (2002) proposed a Nitrate removal rate definition, which can be seen as a Nitrate Loading Rate for full denitrification and can be manipulated to be expressed in terms of mass or volume of filter if no detailed specific area values are available.

Nitrate Removal Efficiency

$$r_{A,NO_3} = \frac{Q \cdot (C_{NO_3in} - C_{NO_3out})}{A_s}$$

It was mentioned earlier the reason for using the empirically determined design loading rates was that the process involved in biological filters are complex and were outside the scope of this research project. However, it is helpful to obtain a qualitative understanding of the transport and biological processes. The following discussion is a summary of the work presented by Henze *et al* (2002).

As described earlier, the bacteria form in a biomass on the surface of a medium, the wastewater passes over the bio-film which consumes the substrate. There are a number of transport processes here that effect the overall rate of the reaction. Firstly, the transport of substrate through the bio-film is controlled by molecular diffusion. Assuming that the substrate concentration in the liquid phase is uniform, and that there is no concentration gradient at the liquid bio-film interface influencing the reaction, the rate of the reaction is either controlled by the consumption of substrate or by the diffusion of substrate into the biomass, whichever is dominant. Additionally, the condition as to which is rate limiting (substrate availability or biomass uptake) is not necessarily the same throughout the bio-film. As diffusion and consumption occur, a concentration gradient is set across the bio-film. The result being that close to the bio-film / liquid interface, the diffusion is sufficiently fast to not affect the rate of uptake, where as close to the bio-film / filter media interface, diffusion may not have been able to transport the substrate sufficiently fast enough and substrate availability becomes rate limiting in this region.

Unfortunately the complexities do not stop there. Most biological reactions are redox by nature. This means that both the reductant and the oxidant need to be transported

through the bio-film by molecular diffusion. The process is now controlled by the diffusion of two components, each of which may or may not be available to the bacteria in sufficient concentrations as to avoid limiting the reaction rate, and at varying locations within the bio-film.

Adding to the complications, the conditions within the bio-filter itself are not always constant. Assuming a plug flow scenario through the filter, we find that the concentration at the inlet and outlet may vary sufficiently such that one or both of the substrates are limiting in one area of the filter and not in the other.

The design process therefore, if based on the full mathematical model, needs to be able to decipher the following:

- Is substrate concentration in the effluent rate limiting? If so, which substrate and where within the filter?
- Is diffusion rate limiting? If so, is it rate limiting throughout the depth of the bio-film and which of the substrates is rate limiting?

Biological filters have been used extensively in the treatment of leachates from municipal landfills. The attractiveness of the process is related to its cost effectiveness.

Jokela et al (2002) investigated various flow configurations and filter media for nitrification and denitrification, including an up-flow crushed brick aerated filter, a down flow mature compost aerated filter and a down-flow anaerobic filter using landfill waste as the filter media. The following results were noted:

- The up-flow aerated brick filters were capable of $\text{NH}_4\text{-N}$ removal efficiencies of 90% at loading rates between 100 and 130 mg $\text{NH}_4\text{-N/}$ (L.Day).
- The down-flow aerated mature compost filter achieved a removal efficiency of 90% at loading rates of between 100 and 125 $\text{NH}_4\text{-H /}$ (L.Day). The authors noted that TON removal occurred and postulated that this was either as a result of TON absorption by the compost or because denitrifying bacteria were present.
- The down-flow anaerobic landfill waste filters where loaded at between 0.36 and 0.6 mg TON / (L.Day). Over a 40 day duration the concentration in the effluent of TON reduced from 5.5 mg N/L to an undetectable level.

Hongjiang *et al* (2009) investigated the nitrifying efficiency of aged refuse aerobic trickling filters (full scale filters – 7000 m³ volume) and found that 87 - 96 % COD and 96 - 99 % NH₄-N removal efficiency can be achieved when loaded with 50 m³ of leachate with a COD and NH₄-N concentration of 5478-1082 and 811-1582 mg/L respectively.

2.3.3.2 Moving-Bed Biofilm Reactors (MBBR)

The Moving Bed Biofilm Reactor (MBBR), or suspended carrier biofilm reactor (SCBR) or fluidized bed reactor, process is based on the use of suspended carrier media upon which the biomass establishes. The main advantages, pertaining to the treatment of landfill leachate, when compared with the conventional suspended growth processes are higher biomass concentrations, reduced settling periods, better resistance to shock loadings and high ammonium removal efficiencies (Renou *et al*, 2007).

2.3.4 Wetlands

A number of wetland configurations are used for the treatment of municipal waste water, municipal landfill leachate and industrial wastewaters and include horizontal or vertical flow and subsurface or surface flow wetland. Both natural and constructed wetlands have been used for wastewater treatment, although natural wetlands are normally only used as a polishing treatment.

Pendleton *et al* (2005) reported 88% BOD and 98% NH₄-N removal efficiencies at one of their pilot plants in their presentation to the 10th International waste management and landfill symposium in Sardinia:

Connolly *et al* (2003) achieved 64.4% NH₄-N removal efficiency noting that some of the removal efficiency was attributed to adsorption into the bed matrix rather than biological nitrification.

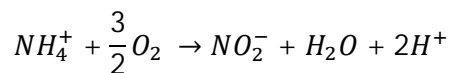
2.4 Biological Nitrification and Denitrification

The biological removal of nitrogen from an effluent stream requires two distinct phases. The first phase is the nitrification of ammonium to nitrates. This process occurs aerobically and is a two step process. The second phase is the denitrification of nitrates to elemental nitrogen and is a multi step process involving a number of intermediate products. Nitrification and denitrification are discussed in more detail in the proceeding sub-sections.

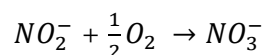
2.4.1 Nitrification

Nitrification is the two step process of converting ammonium into nitrates. The process is performed by autotrophic bacteria, which means that they use CO₂ as their sole carbon source. The oxidation of ammonia to nitrite is performed by bacteria called Nitrosomonas and the second phase, the oxidation of nitrite to nitrate, is done by organisms referred to as Nitrobacter. Other nitrifying bacteria are capable of performing these functions, but from an engineering perspective their performance is no different from the Nitrosomonas and Nitrobacter (Henze *et al*, 2002).

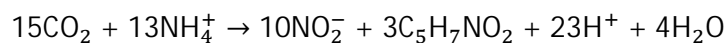
Ammonium Oxidation (Eq 1)



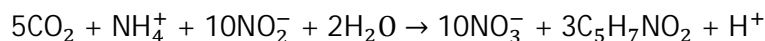
Nitrite Oxidation (Eq 2)



For oxidation of ammonium, the expression for biomass growth is (Eq 3)

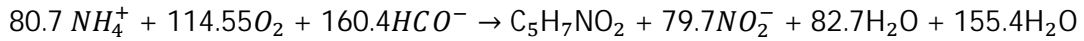


And for Nitrate oxidation the expression for biomass growth is (Eq 4)

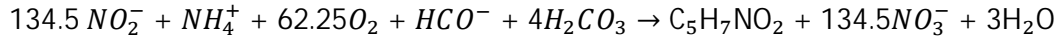


By combining equations 1 & 3 and 2 & 4 above, utilising the carbonate equilibrium system and by assuming observed yield constants $Y_{obs} = 0.1$ g VSS/g NH₄⁺-N and 0.06 g VSS/g NO₂⁻-N respectively we get the following overall reactions for each step in the nitrification process:

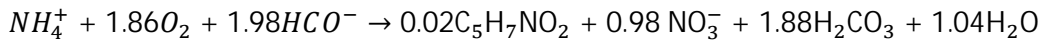
(Eq 5)



(Eq 6)



The overall reaction for nitrification can therefore be found to be:



It can be seen from equation 5 that for every mole of ammonium oxidised, approximately 2 mols of HCO⁻ are consumed thereby reducing the alkalinity of the solution.

2.4.1.1 Reaction Kinetics

A number of factors affect the kinetics of nitrification including substrate and oxygen concentration, temperature, pH and inhibiting substances.

For practical design purposes the nitrification process is often considered as a single step process and the double Monod expression is used to model the reaction kinetics in terms of ammonium and oxygen concentrations. This double Monod expression can be written as follows:

$$\mu_{obs} = \mu_{max} \frac{S_{\text{NH}_4}}{S_{\text{NH}_4} + K_{S_{\text{NH}_4}}} \cdot \frac{S_{\text{O}_2}}{S_{\text{O}_2} + K_{S_{\text{O}_2}}}$$

μ_{obs} = observed specific growth rate

μ_{max} = maximum specific growth rate

S_{NH_4} = NH₄ concentration

$K_{S_{\text{NH}_4}}$ = NH₄ saturation constant

S_{O_2} = oxygen concentration

$K_{S_{\text{O}_2}}$ = oxygen saturation constant

The effects of pH and temperature are modeled by allowing for a μ_{max} adjustment (Henze *et al*, 2002).

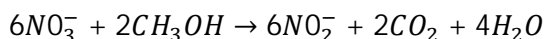
2.4.2 Denitrification

Biological denitrification is the biological conversion of nitrate-nitrogen (NO_3^- -N) to elemental nitrogen gas (N_2). The process has traditionally been referred to as anaerobic denitrification. This, however, is no longer considered appropriate as the biochemical pathways are not anaerobic, but rather a modification of the aerobic biochemical pathways as the facultative bacteria utilise NO_3^- as the electron donor in the absence of O_2 . The group of facultative heterotrophic bacteria capable of dissimilatory nitrate reduction include *Achromobacter*, *Aerobacter*, *Alcaligenes*, *Bacillus*, *Brevibacterium*, *Flavobacteria*, *Lactobacillus*, *Micrococcus*, *Proteus*, *Pseudomonas* and *Spirillum* (Metcalf & Eddy, 1995).

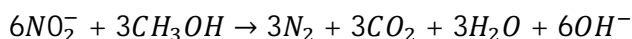
The conversion process is multi-step producing a number of intermediate product: Nitrite (NO_2^-), Nitric Oxide (NO) and Dinitrogen Oxide (N_2O). All of the intermediate products have toxic or inhibitory effects on the denitrification process. Nitrite is a micro-organism inhibitor and is used as a preservative. Nitric Oxide, which is converted to dinitrogen oxide in the atmosphere was used in World War I as a poison gas and can be found in the exhaust fumes from vehicles. Finally, dinitrogen oxide is used as an anaesthetic and is a greenhouse gas. Despite the toxic nature of the intermediate products, the concentrations are normally small and do not normally affect the process. Only when the process is stressed will the release of intermediate products occur. (Henze *et al*, 2002)

Metcalf and Eddy, citing McCarty *et al* 1969, propose the following stoichiometry using methanol as the carbon source.

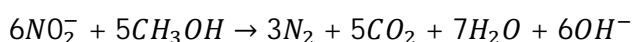
Step 1:



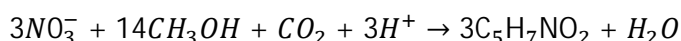
Step 2:



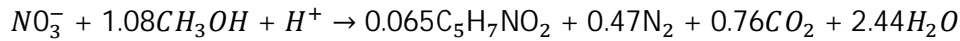
Combining steps 1 & 2 give the following overall reaction, without biomass synthesis



Step 3: Synthesis (McCarty *et al*, 1969)



Metcalf & Eddy, again citing McCarty *et al* (1969) suggest that in practise approximately a quarter of the required methonal provided will be utilised in synthesis, and that based on the laboratory experiments conducted, the following empirical equation can be used to describe denitrification with synthesis:



2.4.2.1 Factors Influencing Denitrification

Denitrifying bacteria can use wide range of carbon sources as an energy source including some inorganic materials. The denitrifiers are able to use organic matter from municipal wastewater as well as methanol, acetic acid, ethanol, glucose, molasses and hydrogen. The energy source used will affect the rate of the reaction.

In addition, temperature has an effect on reaction rates. Denitrifying bacteria prefer warmer temperatures and improve their removal efficiencies at temperatures above 35 °C.

Oxygen is an inhibitor to denitrifying bacteria as is a low pH. The bacteria thrive in an anaerobic environment with pH between 7 & 9 (Henze *et al*, 2002).

2.5 Motivation for Investigation

The objective of this research project was to investigate the efficiency of a low technology biological denitrification process for post treatment of landfill leachate (initially treated in an SBR) emanating from the Marianhill Landfill. From the above literature review it is evident that in order to achieve biological denitrification, both an external carbon source and an anaerobic environment are essential. The experiments that follow investigate the denitrification of a synthetic landfill leachate by simulating an anaerobic fixed film filter whereby the carbon required for denitrification is leached from the filter media itself. Similar research has been conducted by Pisano (2007) and Plugg (2008).

3 MATERIALS AND METHODS

3.1 Introduction

The series of experiments conducted and reported on in this research have been designed with the intention of investigating the viability of using commercial garden refuse, raw and after 10 weeks of composting, and pine bark as potential carbon sources and growth media for the denitrification of landfill leachates. As was mentioned in the introduction, this research project is intended to contribute towards a larger body of research. In this project, a synthetic leachate with a NO_3 concentration of 2000 mg/L was used as there is no previous work at this concentration.

There were three phases to the research:

- The first step involved the biochemical characterization of the three proposed substrates. For each substrate, the carbon to nitrogen ratio (C/N), biological degradability and chemical composition was established. Both the solid and liquid phases of the substrate were characterized. This characterization allowed us to determine whether or not the substrate was likely to support denitrification, i.e. is biologically degradable carbon available as a substrate and is it being leached into a readily utilizable form, and whether inhibitory conditions were present.
- Step two included anaerobic batch tests (refer to section 3,4) where optimum conditions were simulated allowing to determine the growth kinetics. A blank batch test was performed using tap water instead of a synthetic leachate for each substrate as a means of comparison. Understanding the reaction rates allows one to estimate a reasonable hydraulic retention period for the column tests which followed.
- During step three, laboratory scale column tests designed to simulate submerged anaerobic filters were performed on each of the substrates at two different flow rates. The intention was to assess the differences between the optimal conditions (batch tests) and those likely to be experienced in a full scale filter. The column tests were further designed to assist in providing design information for the development of full scale pilot plants should the need arise.

Figure 3-1 below provides a flow diagram which summarizes the rationale behind the research and highlights the research methodology, monitoring and analytical results.

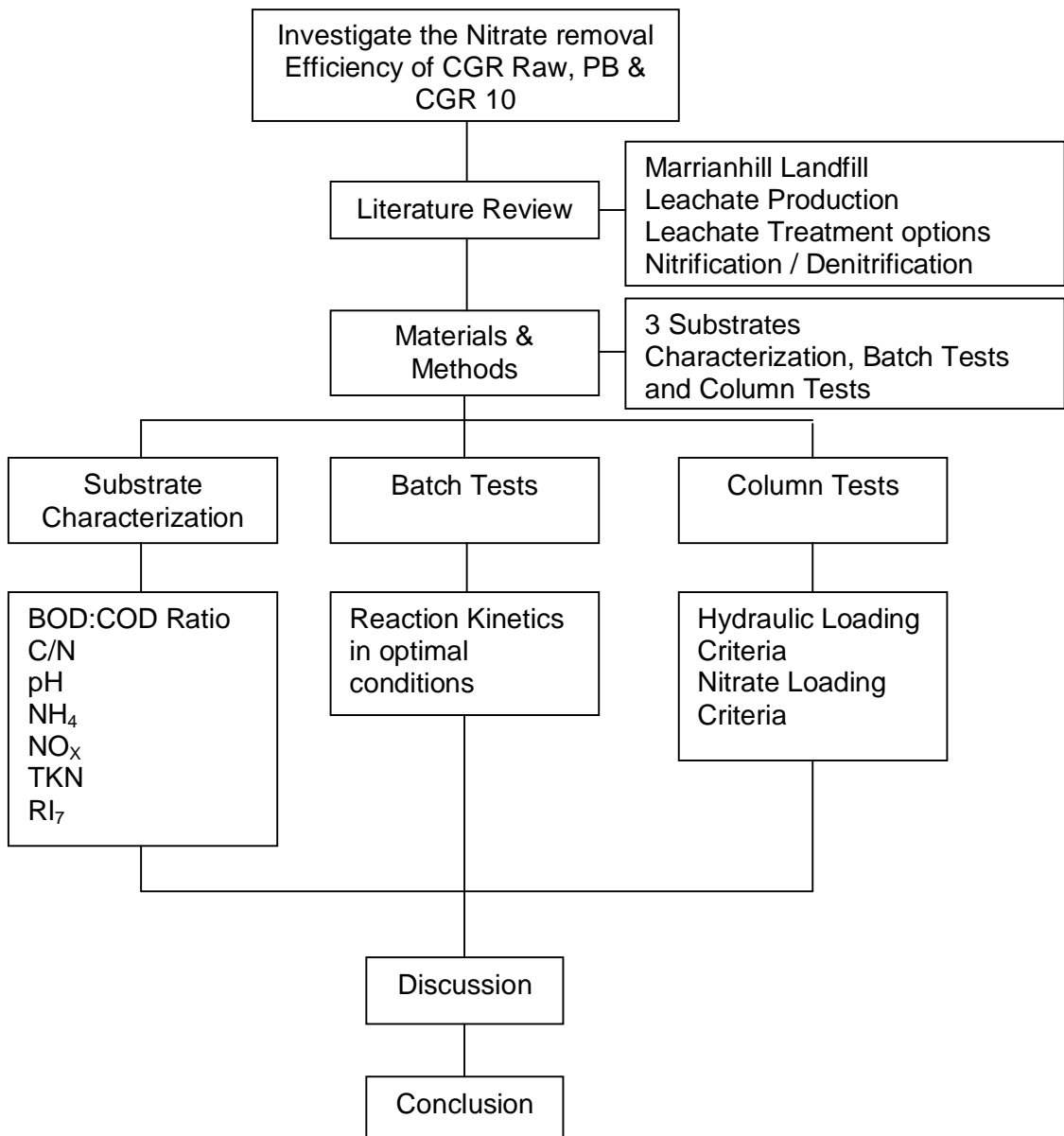


Figure 3-1: Research Layout

3.2 Materials

3.2.1 Synthetic Leachate

The purpose of the research performed in this study is to assess the suitability of three substrates as a carbon source for denitrification with a view to denitrifying a nitrified landfill leachate. It was decided that a nitrate solution would be used as opposed to a nitrified landfill leachate so that the effect of denitrifying inhibitors originating from within the nitrified leachate could be eliminated and the denitrifying process studied in isolation. A 2000 mg/L nitrate solution was prepared using Potassium Nitrate (KNO_3) and distilled water. The mass balance used is as follows:

$$1 \text{ mol } KNO_3 = 101.10 \text{ g}$$

$$1 \text{ mol } NO_3 = 62.005 \text{ g}$$

$$2,000 \text{ mg/L of } NO_3 \rightarrow 40,000 \text{ mg in } 20 \text{ L solution}$$

$$40 \times 101.10/62.005 = 65.2227 \text{ g of } KNO_3 \text{ per } 20 \text{ L tank of nitrate solution}$$

3.2.2 Substrates

3.2.2.1 Raw Commercial Garden Refuse (CGR Raw)

Garden refuse is produced daily throughout the eThekweni metro by the municipal parks and gardens teams and commercial landscaping companies and disposed of at the Bassar Road and Mariannhill landfills. The raw commercial garden refuse used in this investigation was taken from the Mariannhill landfill site [8].

3.2.2.2 Composted Commercial Garden Refuse (CGR 10)

Commercial garden refuse, as described above, was composted at the UKZN civil engineering departments workshop for a period of 10 weeks. The composting process used was forced aeration where air is continuously pumped through the contained compost heap (Trois, 2009).

3.2.2.3 Pine Bark (PB)

Large quantities of PB are produced as a by product of the paper and pulp industry in the KwaZulu-Natal region daily (Pisano, 2007). The sample used in this investigation was collected from the Sappi Paper Mill in Mandini.

Pisano (2007) reported that the term 'pine bark' refers to the tissue that is outside the vascular cambium, however the debarking process tends to remove the vascular cambium layer and some wood. Pisano (2007) cites the research done by Maggs (1994) and reports on the organic and elemental breakdown of PB and the finding that the major constituents included cellulose, lignin and tannins. These constituents contain high concentrations of carbon and contribute to a relatively high C/N ratio of PB. C/N ratios of 723:1, 580:1, 480:1, 300:1 and 150:1 were reported by Wilson (1989), Schliemann (1974), Lamb (1980) and Gartner (1979) respectively.

3.2.2.4 Sampling

All substrate samples were sorted by hand by Mr Plüg. During the sorting process foreign substances such as plastic bags and paper were removed and large pieces were cut to approximately 5 cm (max dimension) so as to render them easier to handle in the batch and column tests.

The standard quartering method was used to create eight representative piles of each substrate and each mixed to achieve homogeneity (Plüg, 2008).

3.3 Experimental Procedures

3.3.1 Substrate Characterization

Each substrate was characterized chemically by analyzing the solid and liquid (eluate) phases of each substrate. The eluates were produced by preparing a mixture of substrate and distilled water with a liquid to solid ratio of 10:1 and placing on the shaking tray for a period of 24 hrs to keep completely stirred. After the 24 hr shake down the samples were filtered through a 63 micron sieve producing a permeate. All testing was conducted at the Environmental Engineering Laboratory at the University of KwaZulu-Natal by Mr Plüg, and were in accordance with the standard procedures as published in the Standard Methods for the Examination of Water and Wastewater (Eaton *et al*, 2005) unless otherwise stated. A summary of the tests conducted is provided in the table below and in Sections 0 - 3.3.1.10. The results of the characterization are reported in Chapter 4.

Table 3-1: Summary of the Substrate Characterization Tests

	Test		Reference	Description
Solids	Moisture Content (%)	mc		Tests performed by Bem Laboratories
	Total Solids (%)	TS	2540 B	
	Volatile Solids (%)	VS	2540 E	
	Respirometric Index	RI7	5210 D	
	Total Carbon (%)	TC		
	Total Nitrogen (%)	TN		
	Carbon / Nitrogen Ratio	C/N		
Eluate	Total Solids (%)	TS	2540 B	Tests conducted by the Stewart Group in DBN South Africa Tests performed by Bem Laboratories
	Volatile Solids (%)	VS	2540 E	
	pH		4500 H	
	Conductivity (mS)		2520 B	
	COD (mg/L)	COD	5220 D	
	BOD ₅ (mg/L)	BOD ₅	5210 B	
	Ammonium (mg/L)	NH ₃		
	Combined Nitrated and Nitrites (mg/L)	NO _x		
	Total Carbon (%)	TC		
	Total Nitrogen (%)	TN		
	Carbon / Nitrogen Ratio	C/N		

3.3.1.1 *Moisture Content*

Plüg (2008) reported that the moisture content has been defined by Bedient *et al* (1999) as the ratio of the volume of water to the total volume of the sample.

A measured amount of each sample was weighed and then dried in an oven at 105°C for 24 hrs before being weighed again. The moisture content (ω) can be calculated as follows:

$$\omega = \frac{\text{mass wet sample} - \text{mass dry sample}}{\text{mass of wet sample}}$$

3.3.1.2 *Total Solids*

Standard method no. 2540 B, D, Clesceri et al, 2005

3.3.1.3 *Volatile Solids*

Standard method no. 2540 E, Clesceri et al, 2005

3.3.1.4 *Respirometric Index (RI₇)*

Standard method no. 5210 D, Clesceri et al, 2005

Qualitatively, the respirometric index is a 7 day test similar to that of the BOD₅ test and provides a measure of the biodegradability of the solids in the sample. The test is performed using the OxiTop ® system which measures variations in gas pressures resulting from biological oxidation and the production of CO₂ and correlates the results back to provide a measure with the units mg O₂ per g of Dry Mass.

3.3.1.5 *Carbon, Nitrogen and the C/N ratio*

Standard method no. 4500-N_{org} B & C, Clesceri et al, 2005

Total carbon, total nitrogen (TKN) and the carbon / nitrogen ratio tests were conducted by BemLab in the Western Cape.

3.3.1.6 *pH*

pH was measured using an Orion 410A pH meter.

3.3.1.7 Conductivity

Standard method no. 2540 E, Clesceri et al, 2005

The conductivity of a sample is an expression of the ability of the sample to carry an electric current and provides an indication of the amount of dissolved ions and total dissolved solids in the solution. Conductivity was measured using the a conductivity meter and has the units of mS

3.3.1.8 Chemical Oxygen Demand (COD)

Standard method no. 5220 D, Clesceri et al, 2005

The COD test is a measure of the amount of oxygen that is required to chemical oxidise an organic sample. The test is performed at 180°C for two hours, where an organic sample is added to a solution of potassium dichromate and sulphuric acid. At the end of the 2 hour digestion period the remaining potassium dichromate is measured and the consumption of the oxidant expressed in terms of oxygen equivalents. COD has the units of mg O₂ / l solution.

3.3.1.9 Biological Oxygen Demand (BOD)

Standard method no. 5210 B, Clesceri et al, 2005

The BOD is defined as the amount of oxygen consumed during the aerobic degradation of an organic substance by an established micro flora and provides a measure of the biodegradable matter contained within a sample (Pisano, 2007). BOD tests are usually carried out over a 5 day period and have the units O₂ / litre solution.

3.3.1.10 Ammonium and Nitrates

Standard method no. 4500 B & D, Clesceri et al, 2005

The ammonium-nitrogen and total nitrates tests were conducted by the Stewart Group in Durban.

3.4 Batch Tests

(Batch tests for the three substrates were conducted by Gareth Harper and Samista Jugwanth and Mr Plüg as part of their under graduate BSc Eng and MSc Eng dissertations)

The batch tests reported in this section were designed to simulate optimal conditions for the denitrification of a synthetic landfill leachate (2000 mg/L). The desired outcomes of the test are the establishment of the time required to achieve full denitrification and the determination of the kinetic constant for the denitrification process.

3.4.1 Test Preparation

The substrate samples are prepared as described in Section 3.2.2.4 with all alien substances removed and large pieces cut to allow them to fit into the 1500 ml Shcott bottle. Based on previous work (Pisano, 2007 and Plüg 2008), a liquid to solids ratio (L/S) of 10:1 based on the dry weight of the substrate was selected for all batch tests *(as mentioned earlier, the research reported in this research project contributes towards a greater body of research being conducted by the UKZN)*. To allow for the moisture that exists in the sample, the actual amount of solids, distilled water and potassium nitrate were calculated as follows:

Assume it is intended that a 750 ml sample is to be prepared. Based on the L/S ratio of 10:1, the required amount of substrate based on the dry weight is therefore 75g. Given that the TS (%) of the substrate is 51.15 % (this is the case for PB) we can therefore calculate the mass of moist substrate to be placed in the reactor as follows:

$$\frac{\text{Dry weight of the sample}}{\text{Wet weight of the sample}} = \frac{51.15}{100}$$

$$\text{Wet weight of sample required} = \text{dry weight of the sample} \times \frac{100}{51.15}$$

$$\text{Wet weight of sample required} = 75g \times \frac{100}{51.15}$$

$$\text{Wet weight of sample required} = 146.63g$$

We can therefore deduce that the volume of water within the sample is 146.63g – 75g = 71.63g of water \equiv 71.63 ml. Now in order to achieve a L/S ratio of 10:1, 750 ml – 71.63 ml = 678.37 ml needs to be added to the reactor.

Finally, to achieve a total concentration of 2000 mg/L of NO₃-N, 3602.09 mg of potassium nitrate needs to be added to a 1.0 L measure of distilled water. The mass of KNO₃ is calculated as follows:

$$\text{molecular mass of } KNO_3 = 101g$$

$$\text{molecular mass of } NO_3 = 62g$$

In order to achieve 2000 mg/L in 750 ml

$$2000 \text{ mg/L} \times 0.75 \text{ L} = 1500 \text{ mg } NO_3 \text{ needs to be added}$$

$$1500 \text{ mg } NO_3 \equiv 1500 \times \frac{101}{62} \text{ mg of } KNO_3$$

$$= 2443.55 \text{ mg of } KNO_3 \text{ added to } 678.37\text{ml of distilled water}$$

All nitrate solutions are prepared in 1000 ml batches. Therefore:

$$\text{mass of } KNO_3 = 2443.55 \times \frac{1000}{678.37} = 3602.09 \text{ mg of } KNO_3$$

A summary of the preparation of each of the samples is provided in Table 3-2.

Table 3-2: Summary of Potassium Nitrate required for batch tests

	CGR Raw	PB	CGR 10
L/S ratio	10:1	10:1	10:1
DM of solid	75 g	75 g	100 g*
TS (%)	62.86	51.15	32.97
Mass of Substrate	119.32 g	146.63 g	303.3 g
Mass of KNO₃ in 1.0 L solution	3465.9 mg	3602.09 mg	4093.4 mg

* Note that a large sample of the CGR 10 is required to achieve a similar sized sample (volumetric) as there is a different grain size distribution when compared with CGR Raw and PB.

Once the sample has been prepared and placed in the Shcott bottle, the container is sealed and deoxygenated with a light vacuum. Two samples for each substrate (four samples were prepared for the CGR Raw substrate) were prepared as well as a blank / zero NO₃ concentration sample for each substrate, and were placed on the shaker to ensure a completely stirred solution and good contact between the biomass (biofilm on the substrate) and the synthetic leachate solution and allowed to react until the nitrate concentration was undetectable. Figure 3-2 below shows four batch tests in place on the shaker.



Figure 3-2: Batch Test (Jugwanth, 2009)

3.4.2 Monitoring

The samples were monitored periodically and samples taken with a syringe and needle and tested for NO_3^- using the Merckoquant Nitrate Test. The test utilises nitrate sticks that change colour in relation to the concentration of $\text{NO}_3\text{-N}$ present. The testing regime was as follows:

Within the first hour, samples were drawn and tested after 5, 10, 15, 30 and 60 minutes. After the first hour samples were drawn and tested hourly throughout the duration of the first day. Between 3 and 4 samples were taken daily after the first day. The number of samples was a function of the relative change in $\text{NO}_3\text{-N}$ concentrations measured and the anticipated rate of change (as estimated by plotting previous measurements and extrapolating the graph).

Samples drawn from the batch tests are filtered to remove solids and diluted with distilled water to a known concentration. The purpose of diluting the sample is to ensure that an accurate reading is obtained from the NO_3^- test as above 50 mg/L the size of each graduation for each colour step increases steeply. Figure 3-3 below shows nitrate testing in action and shows the colour graduations for concentrations from 0 – 500 mg/L

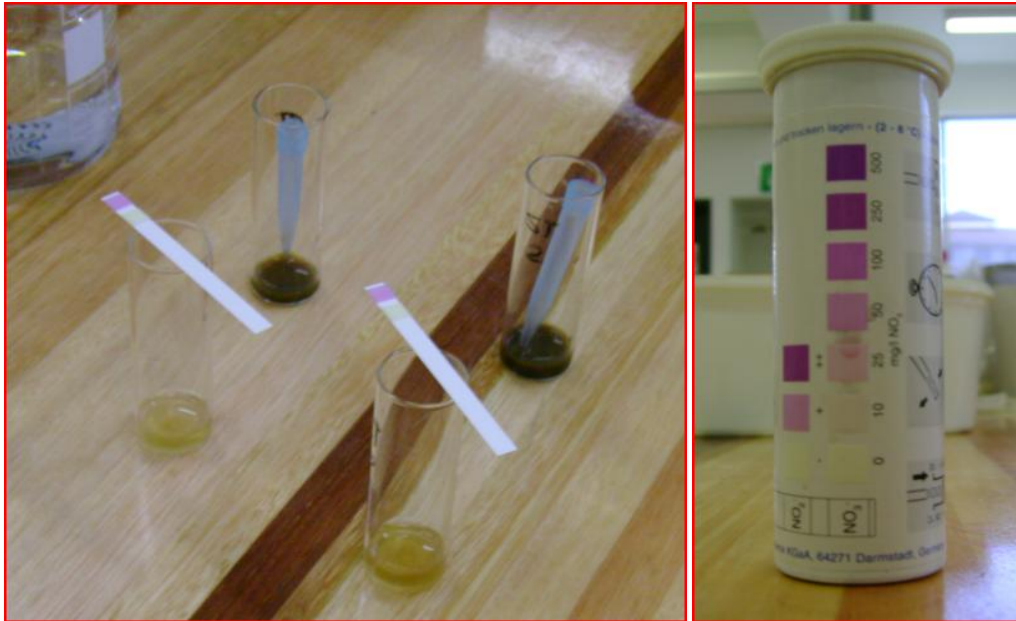


Figure 3-3: Nitrate Test (Jugwanth, 2009)

It should be noted that a procedure exists in the event that NO_2^- is identified in the sample. In such a case, the NO_2^- are removed from the solution by adding one drop of 10% amidosulfonic acid, bringing to the boil and allowing to cool before retesting.

The results of the batch tests are presented in chapter 4 with the raw data available in Appendix A

3.5 Column Tests

Anaerobic column tests were designed to simulate submerged anaerobic filters using three substrates, CGR Raw, CGR 10 and PB, as the carbon source and growth medium, for the purpose of investigating denitrification and determining the nitrate loading rate applicable to each substrate. In total, six experiments were conducted. Three columns, each with a different substrate, were run initially with a hydraulic retention time of 1 week for four weeks. After the initial four week trial, the hydraulic retention time was reduced from one week to two days.

3.5.1 Equipment

Each column was constructed from a 160 mm diameter transparent PVC cylinder approximately 1.0 m long and with a total volume of approximately 20 L. At either end of the cylinder is a plastic flange adaptor and blank flange, fitted with a rubber gasket and sealed with silicone gel.

The upper flange had three orifices. A 25 mm orifice with a plastic ball valve which served as the leachate inlet and two 12.5 mm orifices with silicon tubing attached. One of the silicon tubes was used to assist in flushing the air space above the substrate with nitrogen gas during a draw down procedure and for preventing an airlock during the filling procedure. The second silicon tube was connected to a gas collection system which was analysed periodically to provide a qualitative understanding of the biogas production.

The lower flange had a single orifice with a $\frac{1}{4}$ turn plastic ball valve which was used to extract leachate for sampling and drain down.

Along the length of the column were three ports which allowed for a small sample to be taken using a needle and syringe. The intention was to allow a concentration profile to be determined along the length of the column. This was based on the assumption that plug flow occurs.

During previous experiments with similar columns, the outlet became clogged as a result of decomposition of the substrate. In an attempt to avoid a similar problem, a drainage layer was created by placing a layer of marbles and a coarse filter on the bottom of the column prior to filling with substrate.

3.5.2 Preparation of Each Column

A bag with a known mass of each substrate (samples prepared as per Section 3.2.2.4) was used to fill the columns. The columns were filled by hand with care taken to achieve a reasonable degree of compaction to avoid large air voids forming in the column and ensure a good Solid / Liquid contact. Once the columns were filled, the bags of substrate were weighed and the mass of substrate in each column calculated.

The synthetic leachate was prepared as per Section 3.2.1 and the columns were filled until the substrate in each was submerged. The volume of synthetic leachate added into each column was noted allowing the L/S ratio to be calculated as well as the daily flow rate required to achieve the desired HRT. Figure 3-4 shows the column tests in operation.



Figure 3-4: Column Test (Photograph courtesy of B Plüg)

3.5.3 Operation of the Columns

Depending on the desired HRT and the initial input of synthetic leachate, a daily liquid turnover was calculated. An example of this is:

assume that the initial volume of liquid added was 10L

and that the desired HRT is one week operated over 5 days

then $10\text{ L}/5\text{ days} = 2\text{ L per day drawn and replaced}$

Every weekday morning at approximately 07:00 am the columns were drained of effluent and filled with required volume of synthetic leachate (2000 mg/L). During the draining process the airspace above the substrate was flushed with nitrogen gas to promote anaerobic conditions. Likewise, during the filling procedure care was taken to minimize the withdrawal of air by slowing down the intake to avoid the development of a vortex in the inlet funnel. Once drained and filled the column was left to react anaerobically until the following morning. Note that during the draining and filling procedures the gas collection system was isolated to minimize the capture of air or nitrogen gas. All orifices were isolated at the end of a procedure.

After a drain and fill procedure on a Friday, the columns remained stagnant until the Monday morning. Although the synthetic leachate is drawn and filled over a period of five days, the HRT is seven days.

Initially the three columns were operated with a HRT of 7 days. After four weeks the columns were drained and left to stand for four days before being refilled and operated with an HRT of 2 days. The same substrate was used in both sets of experiments. This was done as the columns had produced minor leaks and we did not want to risk worsening the situation and delaying the progress of the experiment.

3.5.4 Monitoring

On a daily basis, samples were taken and the effluent tested for NO_3^- concentrations, dissolved oxygen concentrations and pH. After a number of weeks operation it was noted that the dissolved oxygen concentration measurements were not providing reliable results and the process was ceased. It is believed the DO probe was improperly calibrated. An alternative explanation could be that the draw down process is relatively turbulent allowing oxygen to be dissolved into the effluent.

NO_3^- concentration tests were done using the Merckoquant Nitrate Test described in section 3.4.2. pH measurements were made using an Orion 410A pH meter.

At the end of each week, an additional sample was taken and the COD concentration in the effluent was analyzed.

Note that the intension of the three port along the length of the column was to gain an understanding of the concentration gradient should a zero nitrate concentration be measured in the effluent. This would allow one to gain an understanding of the time required to complete denitrification, i.e. if the concentration was zero halfway up the column, one might qualitatively suggest that the time to complete denitrification is half of the HRT. This qualitative understanding would assist in the design of future experiments.

The results of the column tests are presented in Chapter 4 with the raw data attached in Appendix B.

4 RESULTS AND DISCUSSION

4.1 Substrate Characterization

(All substrate classification tests were conducted by Björn Plüg in the Environmental Engineering Laboratory and the University of Kwa-Zulu Natal unless otherwise noted)

Table 4-1: Summary of Substrate Characterization

	Test	CGR Raw	PB	CGR 10
Solids	Moisture Content (%)	37.14	48.85	67.03
	Total Solids (%)	62.86	51.15	32.97
	Volatile Solids (%)	96.37	97.08	47.21
	RI ₇ (mg O ₂ / g DM)	7.77	17.77	8.58
	Total Carbon (%)	49.6	36.67	28.69
	Total Nitrogen (%)	0.55	0.59	1.2
	C/N ratio	90.19	62.15	23.91
Eluate	Total Solids (%)	4.08	3.66	2.40
	Volatile Solids (%)	3.04	3.35	1.62
	pH	5.45	4.18	6.98
	Conductivity (mS)	1.653	0.85	0.81
	COD (mg/L)	4253	4517	2764
	BOD ₅ (mg/L)	1101	297	155
	NH ₃ (mg/L)	12.74	8.54	9.80
	NO _x (mg/L)	6.86	15.12	7.14
	Total Carbon (%)	0.083	0.25	0.11
	Total Nitrogen (%)	0.018	0.07	0.06
	C/N ratio	4.54	3.57	1.83

In the following sections the suitability of each of the substrates will be discussed based on the results of the characterization tests reported in Table 4-1 above. It is worth bearing in mind that the purpose of the batch tests is to provide reaction rate / substrate utilization kinetics for denitrification in a submerged filter environment. The precursor to this is that optimal conditions are created such that nitrate removal can be investigated on its own. With regard to the physical / chemical composition of the substrate, the two most important factors are that sufficient organic carbon (BOD) is

available and that the concentration is unlikely to be limiting, and that the environment created is free from inhibitors.

Additional environmental factors which do not relate to the physical / chemical composition of the substrate but influence the efficiency of the biological reaction is the contact between the liquids and solid phases to ensure that substrate (OC and NH₃) is available for uptake at concentrations that are not rate limiting. This is addressed by operating the batch tests in submerged conditions and in a completely stirred fashion as a result of the shaker.

4.1.1 Commercial Garden Refuse (Raw)

4.1.1.1 Solids

Concentrating initially on the results from the tests done on the solid portion of the substrate, the VS test reveals that 97% of the total solids are volatile. A large portion of the volatile solids are likely to be organic carbon and suggests that significant OC is available as a carbon source for denitrification. This observation is confirmed by the Total Carbon test with a TC = 49.6%. A C/N ratio of 90.19 indicates that more carbonaceous material is likely to be made available as opposed to nitrogenous material. This is an important result as surplus carbon is required as a carbon source for the denitrification of nitrates added from the synthetic leachate solution.

A Respirometric Index of 7.77 indicates that biological decomposition is occurring (Gomez *et al*, 2005).

The organic carbon available in the solid form does not directly provide a food source for the denitrifying bacteria. Carbonaceous material will need to be hydrolyzed before it will be available as an energy source for denitrification (Henze *et al*, 2002 and Tsui *et al*, 2007).

4.1.1.2 Eluates

The eluates produced from the 24hr “blank” batch test contain a high carbon content. The results of the COD and BOD₅ test are; COD = 4253 mg/L and BOD₅ = 1101 mg/L, with a BOD₅/COD ratio of 0.259. This suggests that only a quarter of the COD is biodegradable which may result in an effluent with a high COD requiring further treatment prior to discharge. A mass balance on the carbon needs to be calculated to determine whether or not carbon concentration is limiting.

The pH of 5.45 is considered to be slightly acidic and may act as a denitrifying inhibitor. A pH above 6 is considered to be optimal for denitrification (Henze *et al*, 2002). NH_3^- and NO_x are present in concentrations that are unlikely to affect the process.

4.1.2 Pine Bark (PB)

4.1.2.1 Solids

A volatile solids content (VS) of 97.08 % indicates that significant organic material is present in the substrate. This is confirmed with by the fact that the total carbon content is 36.67%, equating to 73.65% of the total solids. The C/N ratio is 62.15 and it is therefore unlikely that carbon will be the rate limiting substrate if it is present as biodegradable carbon and leachates into solution efficiently (Lo Tsui *et al*, 2007).

4.1.2.2 Eluates

An eluate pH = 4.18 indicates an acidic environment which will inhibit the denitrifying bacteria. A COD of 4517 mg/L and BOD_5 of 297 mg/L suggests that despite their being an abundance available COD in the solid substrate, only a small portion is available as readily biodegradable carbon for the biological denitrification of nitrates after 24 hrs of leaching.

NH_3^- and NO_x are present in concentrations that are unlikely to affect the process.

4.1.3 Composted Commercial Garden Refuse (CGR 10)

4.1.3.1 Solids

Unlike the CGR Raw and PB, the VS test shows that approximately half of the TS (47.21%) is volatile, indicating that there is not an abundance of carbonaceous material available. The C/N ratio is appreciably lower than that for the CGR Raw and the PB. Both these results are not surprising as the significant degradation occurred during the composting process removing biodegradable carbon.

4.1.3.2 Eluates

The pH of the solution is favourable for denitrification (Henze *et al*, 2002). A very low BOD₅ (155 mg/L) suggests that biodegradable carbon will be the rate limiting substrate. The BOD₅:COD ration is 0.056. This is very low and is indicative of a substrate that has been extensively biodegraded. NH₃ and NO_x are present in concentrations that are unlikely to affect the process.

4.2 Batch Tests

4.2.1 Commercial Garden Refuse (CGR Raw)

Four batch tests were conducted with an initial nitrate concentration of 2000 mg/l and a single batch test conducted with a blank solution (i.e. 0 mg/L). The results of the batch tests are presented graphically below with the raw data attached in Appendix A.

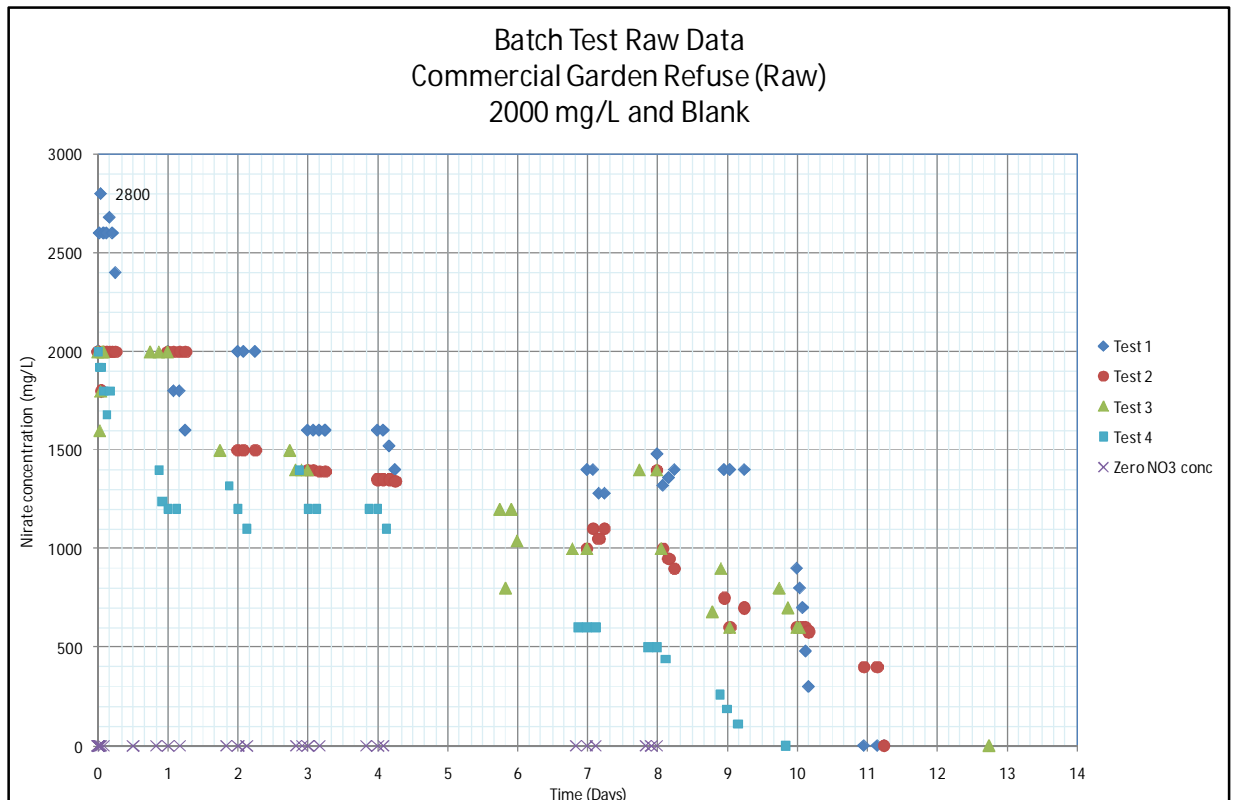


Figure 4-1: Raw data for CGR Raw Batch Tests

In addition to the characterization of the solid and eluate substrates prior to batch testing, the C/N ratio for the solids at the end of the test and the pH, COD, NH₃ and NO_x were determined for the eluate at the end of the test for each of the substrates.

Table 4-2 below provides a summary of the test results after the completion of the batch tests.

Table 4-2: Summary of batch test effluent tests

Parameter	Eluate Characterization at the start of the Batch test	Effluent Characterization at the then of the batch test	
		Blank	2000 mg/L
C/N	90.19	76.98	70.76
pH	5.45	6.01	7.04
COD (mg/L)	4253	9433	7956
NH ₃ (mg/L)	12.74	15.00	89.33
NO _x (mg/L)	6.86	8.00	8.70

The C/N ratio of the solid portion reduced slightly over the duration of the tests. This phenomenon indicated that carbon was leaching out of the solid matter into the liquid phase. It can also be seen that the C/N ratio for the Blank solution was slightly higher than for the 2000 mg/L solution. The 2000 mg/L tests ran for approximately 3 days longer allowing more time for carbon to leach into solution.

In both the input (24 hr blank batch) and the eight day blank batch, the pH is slightly acidic with the pH of the 2000 mg/L test rising from 5.45 at the start of the test to 7.04. In all batches with 2000 mg/L, denitrification did occur. The process produces alkalinity and explains the increase in the pH.

COD increases appreciably over the duration of the batch tests which correlates to the decrease in the C/N ratio. It can be seen that despite leaching more carbon (as noted by the relative changes to the C/N ratio), the 2000 mg/L tests show a final COD less than that of the blank test. Denitrification uses carbon as a energy source and this provides a feasible explanation for the lower COD.

Referring to the graph of nitrate concentration verses time (Figure 4-1);

Three phases of the process, an original start up phase, a steady state or constant denitrification phase between approximately day 2 and day 8 and a final accelerated denitrification phase can be identified.

Looking at the blank batch test we note that a zero nitrate concentration is measured consistently throughout the duration of the test. This indicates that nitrates are not being leached out of the solid substrate (at measurable concentrations using the

nitrate sticks) or being produced from some chemical reaction. This result is consistent with the literature for decomposition of organic matter. The conversion of ammonium to nitrates (nitrification) is an aerobic biological reaction. The batch was designed to be anaerobic and hence nitrate production by a biological reaction is unlikely.

The initial acclimation phase is characterized by an initial increase in the concentration of nitrates (sample 1) and then a rapid drop off. This start up phase can be explained by the fact that the actual solution added has a concentration greater than 2000 mg/L (this was to account for the moisture content introduced as part of the substrate sample). The drop off is explained through the dilution that occurs when the nitrate solution mixes with the moisture available in the substrate. The notion of an initial aerobic nitrification phase during start up is not supported as the $\text{NH}_3\text{-N}$ concentration where not sufficient at start up to increase the nitrate concentration as witnessed.

The denitrification phase appears to be steady between days 2 and 8 for all samples. The nitrate utilization kinetics for each batch have been modeled using a first order kinetic expression. The kinetic expression is of the form:

$$\begin{aligned} & \text{rate of change of nitrate concentration} = \text{nitrate utilisation (uptake)} \\ & \frac{dc}{dt} = -k \rightarrow C = C_0 - kt \end{aligned}$$

The trend lines are shown in Figure 4-2 - Figure 4-5 and summarized in Table 4-3 below:

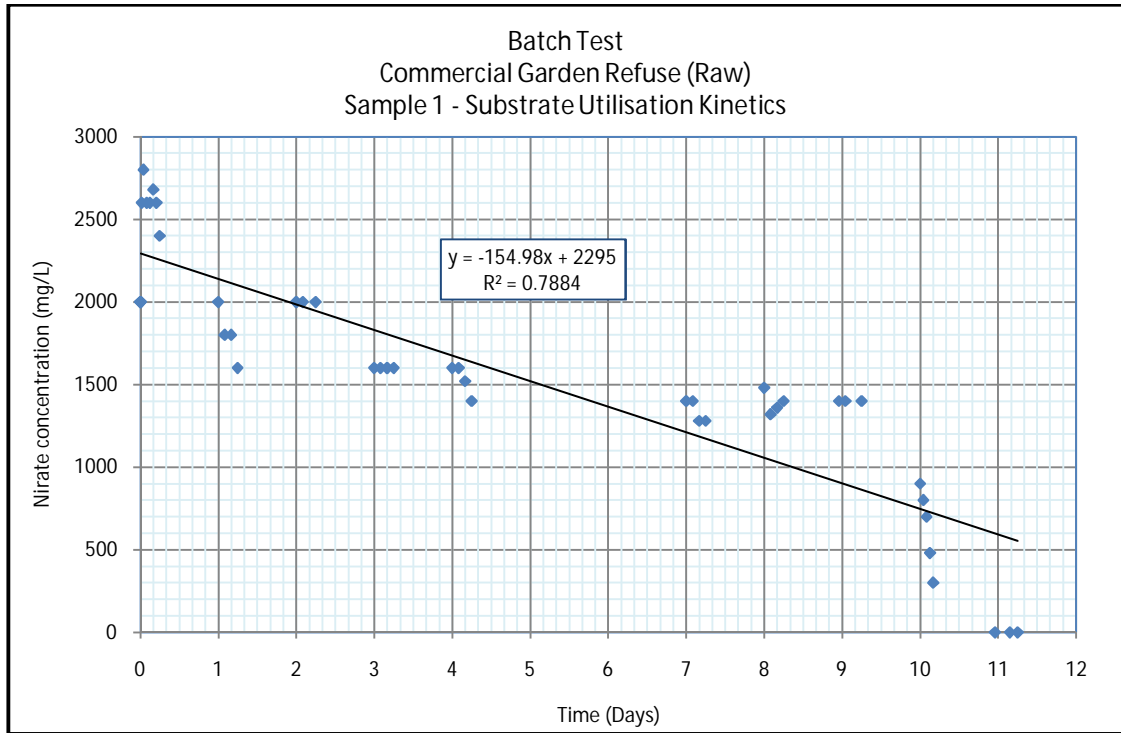


Figure 4-2: Estimation of the Nitrate Utilization Constant (CGR Raw Sample 1)

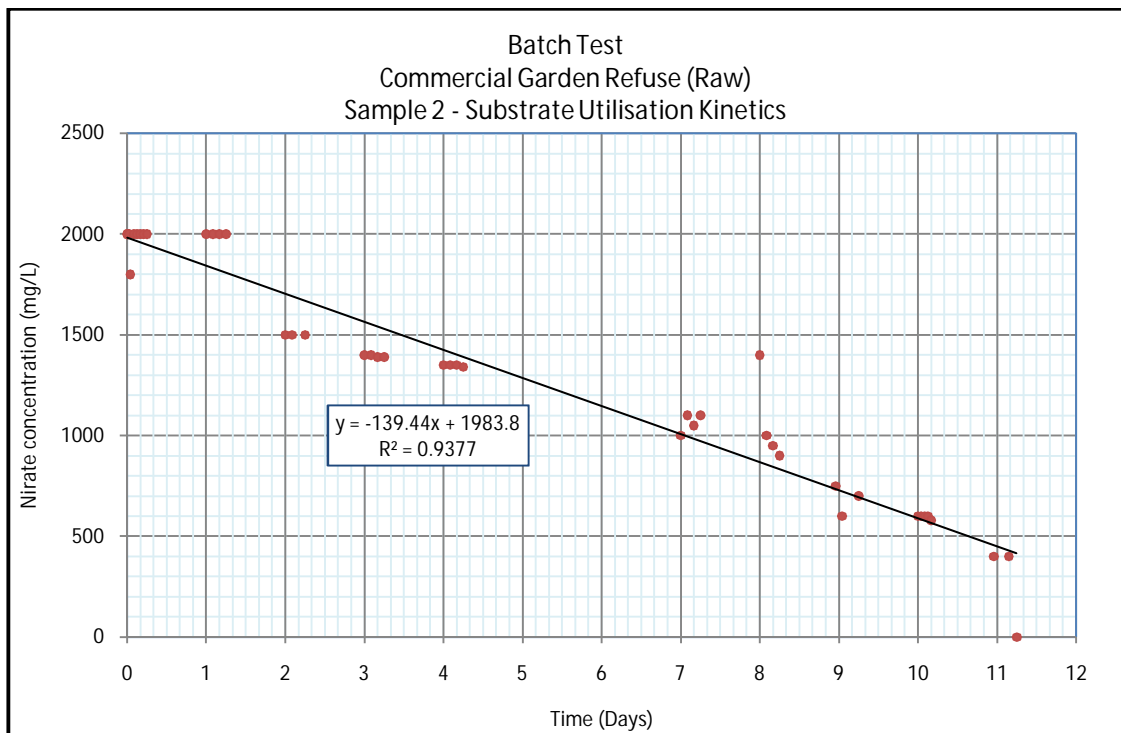


Figure 4-3: Estimation of the Nitrate Utilization Constant (CGR Raw Sample 2)

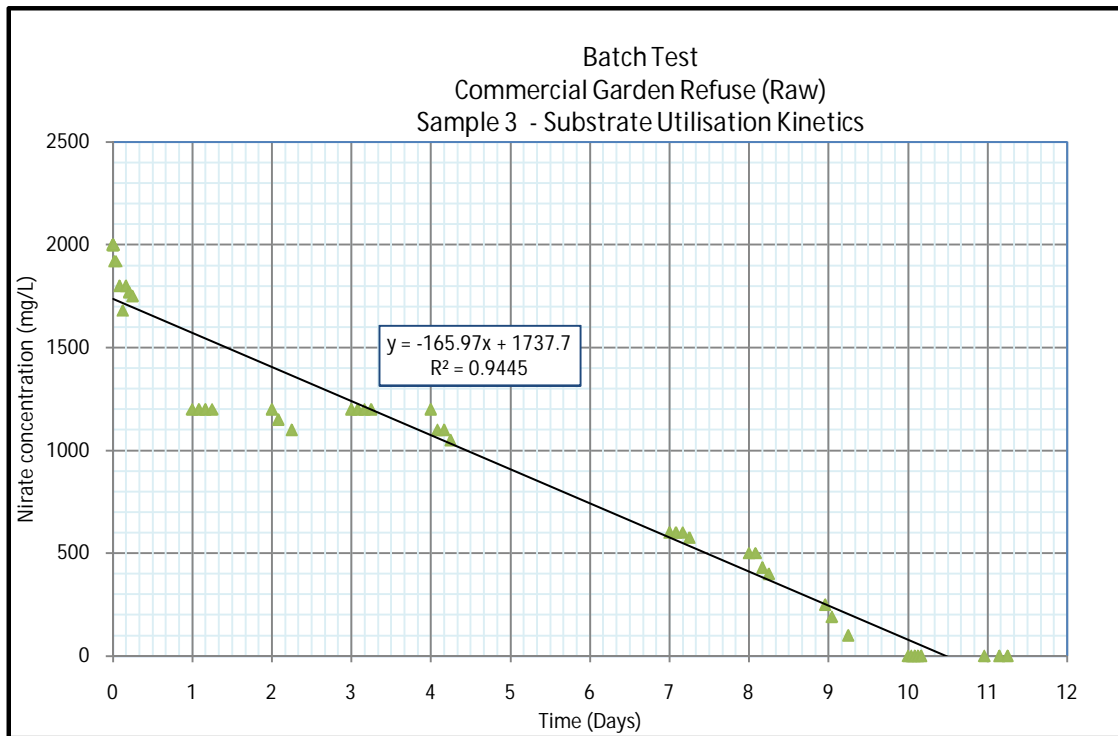


Figure 4-4: Estimation of the Nitrate Utilization Kinetic Constant (CGR Raw Sample 3)

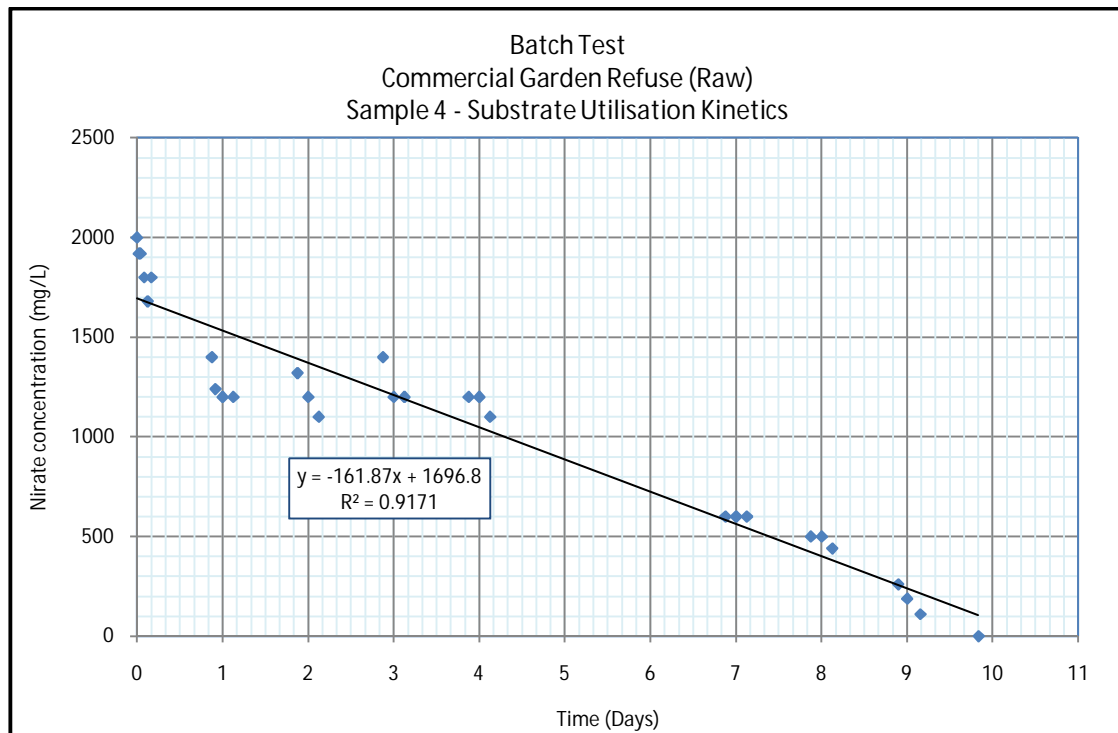


Figure 4-5: Estimation of the Nitrate Utilization Constant (CGR Raw Sample 4)

Table 4-3: Nitrate Utilization Constants

Sample	Nitrate Utilization Kinetic Constant
1	154.98 mg/(L x Day)
2	139.44 mg/(L x Day)
3	165.97 mg/(L x Day)
4	161.87 mg/(L x Day)
Average	155.57 mg/(L x Day)

4.2.2 Pine Bark (PB)

Two batch tests were conducted with an initial nitrate concentration of 2000 mg/l and a single batch test conducted with a blank solution (i.e. 0 mg/L). The results for the three batch tests are presented graphically below with the raw data attached in appendix A.

In addition to the characterization of the solid and eluate substrates prior to batch testing, the C/N ratio for the solids at the end of the test and the pH, COD, NH₃ and NO_x were determined for the eluate at the end of the test for each of the substrates.

Table 4-4 below provides a summary of the test results after the completion of the batch tests.

Table 4-4: Summary of batch test effluent tests (PB)

Parameter	Input	Output		
		Blank	Sample 1	Sample 2
TC (mg/L)	36.67		48.9	48.9
TN (mg/L)	0.59		0.28	0.29
C/N	62.15	85.9	174.64	168.62
pH	4.18	4.90	4.66	4.62
COD (mg/L)	4517	11192	13214	13275
NH ₃ (mg/L)	8.54	3.50	25	35
NO _x (mg/L)	15.12	1.50	325	275

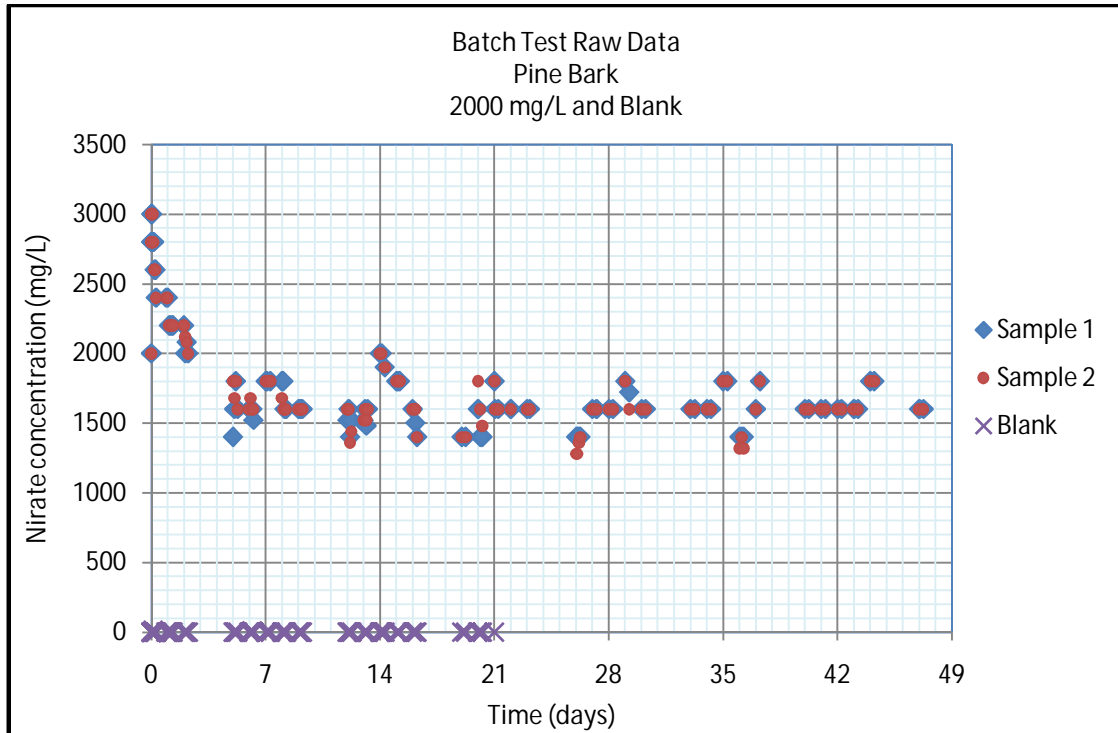


Figure 4-6: Raw Data for Pine Bark Batch Tests

The batch tests using Pine Bark as a substrate have not been successful as the bacteria were unable to denitrify all the available nitrate over the seven week duration of the experiment.

Refer to the data summarized in Table 4-4. The total carbon content of the solids has increased from 36.67% to 48.9%. This suggests that carbon has leached out of the solid at a slower rate than other constituents. This result appears to be supported by the increasing C/N ratio. The pH throughout the experiment remains in the range that is inhibitory to denitrification and it is likely to have had an effect on the poor performance of the denitrifying bacteria. COD concentrations in the liquid phase have increased dramatically over the duration of the experiment, again a confusing result given the increased C/N ratio of the solid substrate. In Section 4.1.2.2 a very low BOD/COD ratio was reported (0.066:1). So, despite the high COD concentrations measured at the termination of the experiment, it cannot be inferred that biologically degradable carbon is readily available, which may have contributed to the poor denitrification performance. The concentrations of ammonium in the eluate increased slightly, but not in a magnitude that is likely to have influenced the denitrification process. Nitrate concentrations of 325 and 275 mg/L are surprising low given that the final Nitrate concentration measurements from the batch tests themselves were 1600 mg/L.

Referring to the graphs showing nitrate concentration as a function of time (Figure 4-6) it is noticeable that both samples illustrate the initial start up phase described above for the CGR Raw samples. Again, providing an explanation for this result is difficult. Three possible mechanisms are at work here. The first being that in order to achieve a final concentration of 2000 mg/L in the solution, and synthetic leachate solution with a concentration of approximately 2211 mg/L was used to account for the moisture available in the substrate. A second explanation could be that initially oxygen was available in the void above the samples and that initially nitrification of ammonium to nitrates increased this nitrate concentration. Finally, we note that nitrates were present in the eluate which were not accounted for when preparing the synthetic leachate solution. Assuming that all three phenomena occurred, the initial nitrate concentration is still not fully explained. A rough mass balance (2211 mg/L synthetic nitrate, plus 8.54 mg/L of ammonium being converted to nitrates in a 71.63 ml liquid contribution and 15.12 mg/L of nitrates in the initial 71.63 ml eluate) does not result in a 3000 mg/L solution. A more plausible explanation may be that there was a high risk of error in the method used for measuring nitrate concentrations. Samples where the concentration was expected to be high were diluted to 40:1 to assist measurements. Graduations on the colour-metric system are 0, 10, 25, 50, 100 etc. Measurements in the range of 2000 mg/L at 40:1 dilution would be 50. Anything higher than 2000 mg/L would appear somewhere between 50 and 100 (one colour graduation) and the final reading would vary from 2000 – 4000 mg/L

Finally, nitrate utilization kinetics were not calculated for this test. The intention of the experiment was to determine the nitrate removal kinetics under optimal conditions. In the discussion above both pH inhibition and carbon limitations have been identified. Despite these postulations, the fact that denitrification ceased after day 5 is sufficient indication that optimal conditions were not achieved.

4.2.3 Composted Commercial Garden Refuse (CGR 10)

Two batch tests were conducted with an initial nitrate concentration of 2000 mg/l and a single batch test conducted with a blank solution (i.e. 0 mg/L). The results for the three batch tests are presented graphically below with the raw data attached in Appendix A.

In addition to the characterization of the solid and eluate substrates prior to batch testing, the C/N ratio for the solids at the end of the test and the pH, COD, NH₃ and NO_x were determined for the eluate at the end of the test for each of the substrates.

Table 4-5 below provides a summary of the test results after the completion of the batch tests.

Table 4-5: Summary of batch test effluent tests (CRG 10)

Parameter	Input	Output		
		Blank	Sample 1	Sample 2
C/N	23.91	48.09	Not available	Not available
pH	6.98	7.08	Not available	Not available
COD (mg/L)	2764	1944	Not available	Not available
NH ₃ (mg/L)	9.80	1.8	Not available	Not available
NO _x (mg/L)	7.14	<1	Not available	Not available

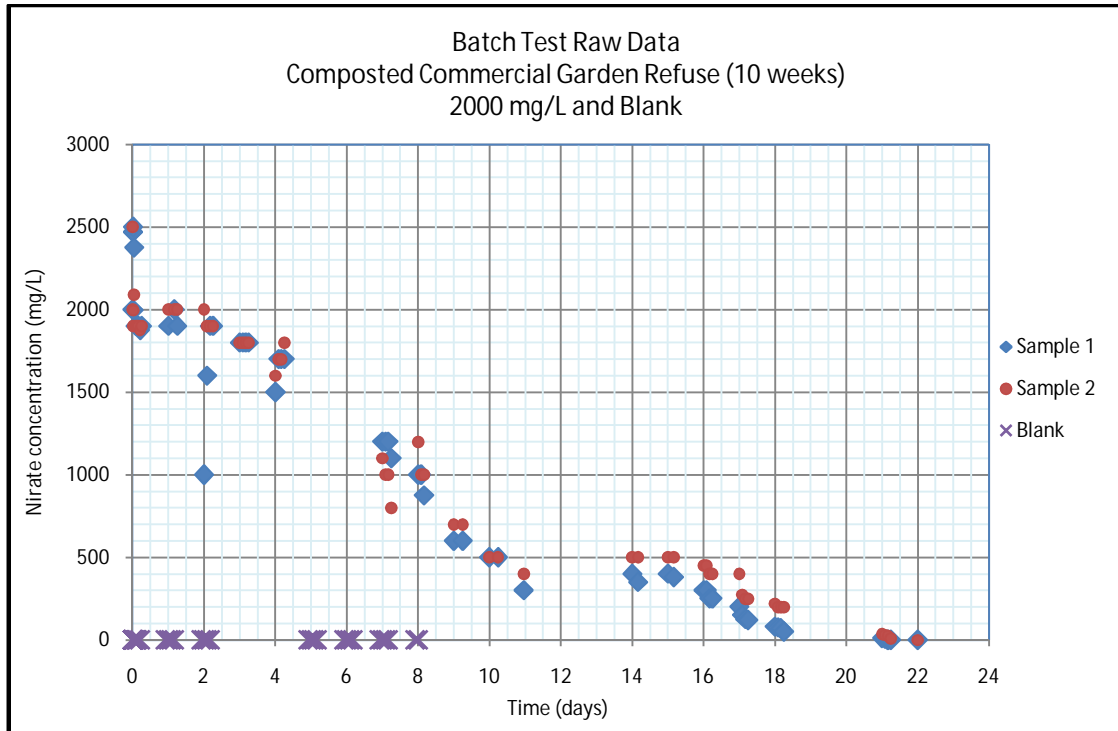


Figure 4-7: Raw Data for CGR 10 Batch Tests

A characterization of the substrates after the termination of the tests was not conducted.

It is evident that the initial start up phase that was discussed in the previous section appears in this test. The samples manage to fully denitrify within 22 days allowing us to calculate the utilization kinetic constant. Figure 4-8 and Figure 4-9 below show the estimation of the kinetic constant using a straight line graph for a zero order kinetic equation.

The fact that the blank test does not measure any nitrates over the duration of the experiment indicates that the substrate is not leaching nitrates.

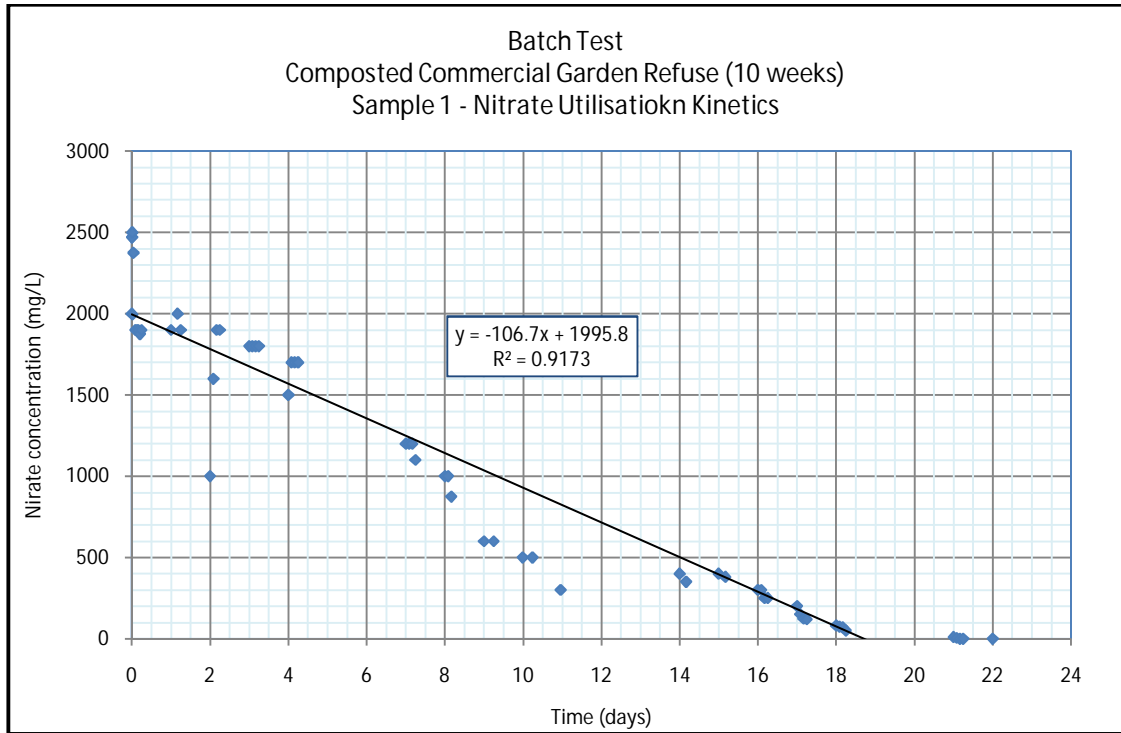


Figure 4-8: Estimation of the Nitrate Utilization Constant (CGR 10 Sample 1)

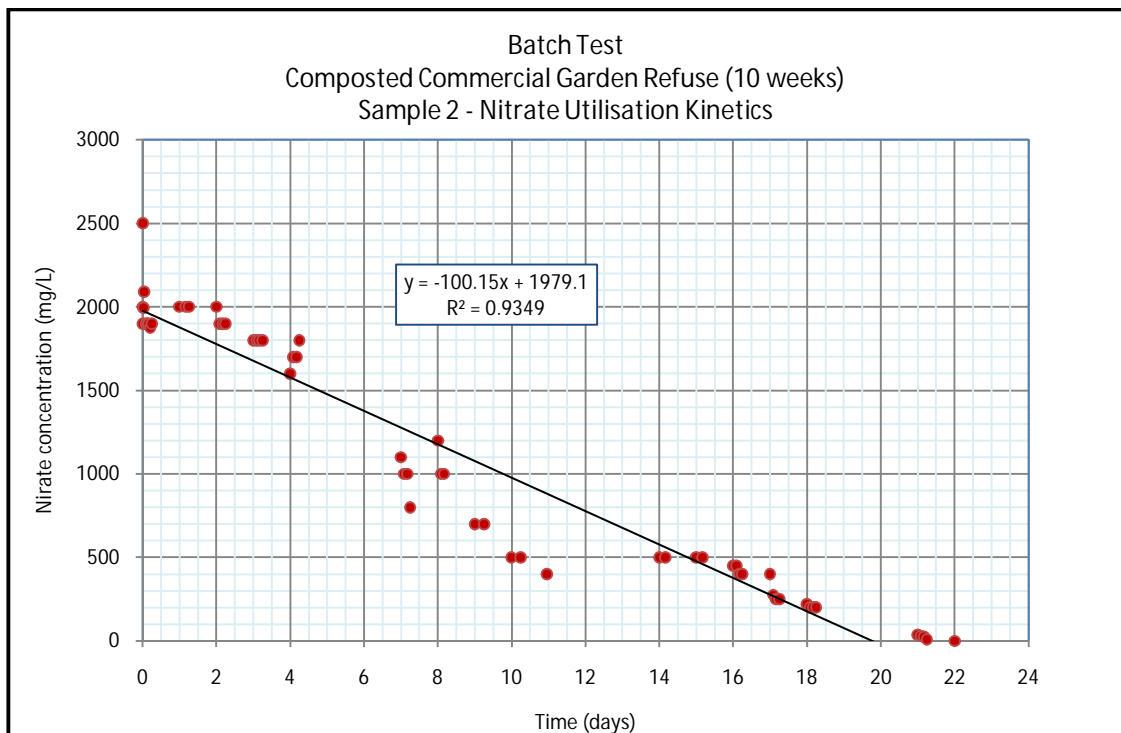


Figure 4-9: Estimation of the Nitrate Utilization Constant (CGR 10 Sample 2)

4.3 Column Tests

4.3.1 Experiment 1 (CRG Raw with HRT = 1 week)

Column 1 was filled with 2.8 kg of raw commercial garden refuse and 11.9 L of synthetic leachate with a nitrate concentration of 2000 mg/L was added until the solid substrate was completely submerged. This provided a L/S ratio of 4.25 : 1.

A hydraulic retention time of 1 week, operated over 5 days, was desired. This meant that 2.38 L of synthetic leachate need to be drawn from the column and replaced daily, Monday – Friday.

Figure 4-10 below provides a summary of the result of Experiment 1. The raw data is attached in Appendix B.

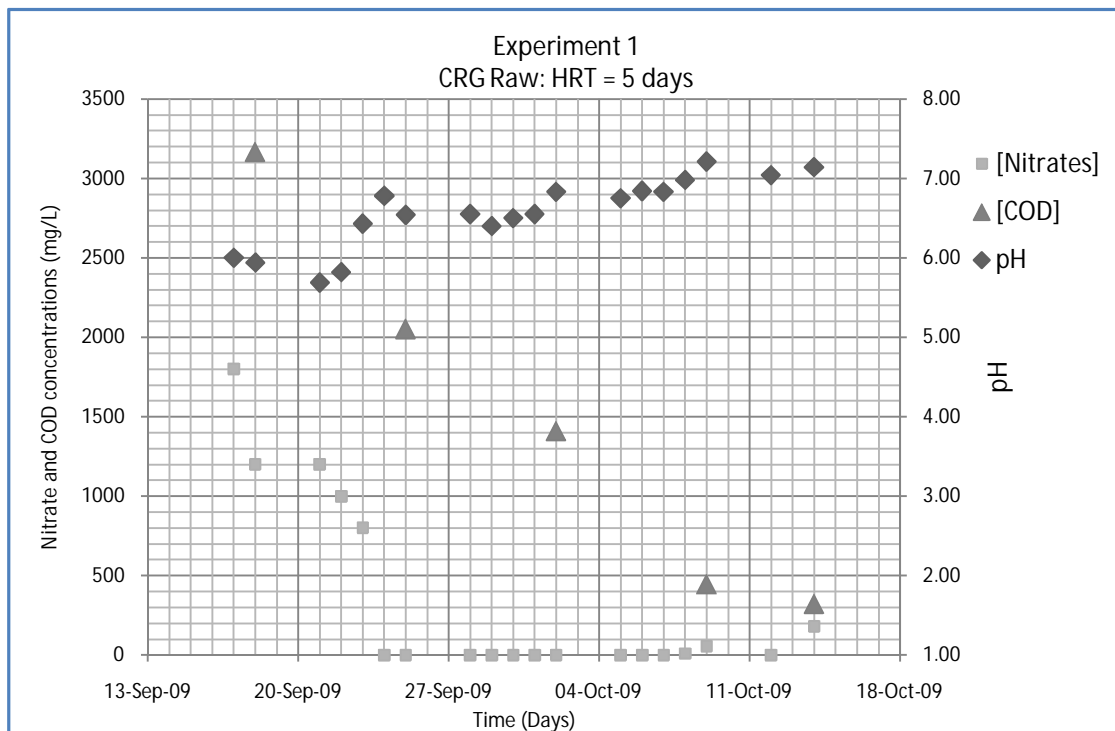


Figure 4-10: Raw Data for Experiment 1 (CRG Raw with HRT = 1 week)

Qualitatively it can be seen that full denitrification occurred within 8 days and the concentration of nitrates remained zero for the remainder of the experiment, barring two days where relatively low values of nitrate were detected. Initially the pH was measured as 6. This is considered within the range in which pH inhibition is unlikely to occur. Over the duration of the experiment the pH steadily increased to approximately neutral. This result was anticipated as denitrification produces alkalinity. The COD concentration steadily decreased over the duration of the

experiment. There are two mechanisms that affect the COD concentration. The first has to do with the relative rates of COD leaching into the liquid phase and the rate of COD being washed out of the reactor as a result of the filling and drawing process. The second mechanism is the COD utilization by micro-organisms for energy and cell assimilation. A possible explanation for there being minimal nitrate readings towards the end of the experiment is that given the low COD concentrations, COD became the limiting substrate in the denitrification process.

From a submerged filter design perspective there are two important design aspects that need to be discussed. The first is the Hydraulic loading per mass (or volume) of substrate and the second is the nitrate loading per mass (or volume)

The hydraulic loading rate can be defined as the flow per day per kg of substrate. This is calculated as follows:

Hydraulic Loading Rate

$$Q = 2.38L/Day$$

$$\text{mass of substrate} = 2.8 \text{ kg}$$

$$\text{Hydraulic loading} = 0.85L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 1700 \frac{mg}{kg \cdot Day}$$

Nitrate Removal

$$\begin{aligned} \text{mass of nitrate removed per day} &= (C_0 - C_{eff})Q \\ &= \frac{(2000 - 0)2.38L}{day} \end{aligned}$$

$$\text{Nitrate removal} = 4760 \text{ mg of Nitrate per } 2.8 \text{ kg of substrate per day}$$

$$= 1700 \text{ mg Nitrate/kg substrate} \cdot \text{Day}$$

Neither the actual volume or density of the packed substrate (media) is known; therefore it is not feasible to express the loading rates as a function of volume.

4.3.2 Experiment 2 (CGR Raw with HRT = 2 days)

Having completed Experiment 1, the column was drained down and allowed to stand for four days before Experiment 2 proceeded.

On day one of Experiment 2 the column, with the same medium as was used in Experiment 1, was filled until the medium was totally submerged. 11.33 L of the synthetic leachate solution (2000 mg/L) was added. Allowing for some of the moisture being absorbed onto the substrate, it was decided that 5L effluent would be drained daily and 5 L of the nitrate solution added.

Figure 4-11 below provides a summary of the result of experiment 2. The raw data is attached in Appendix B.

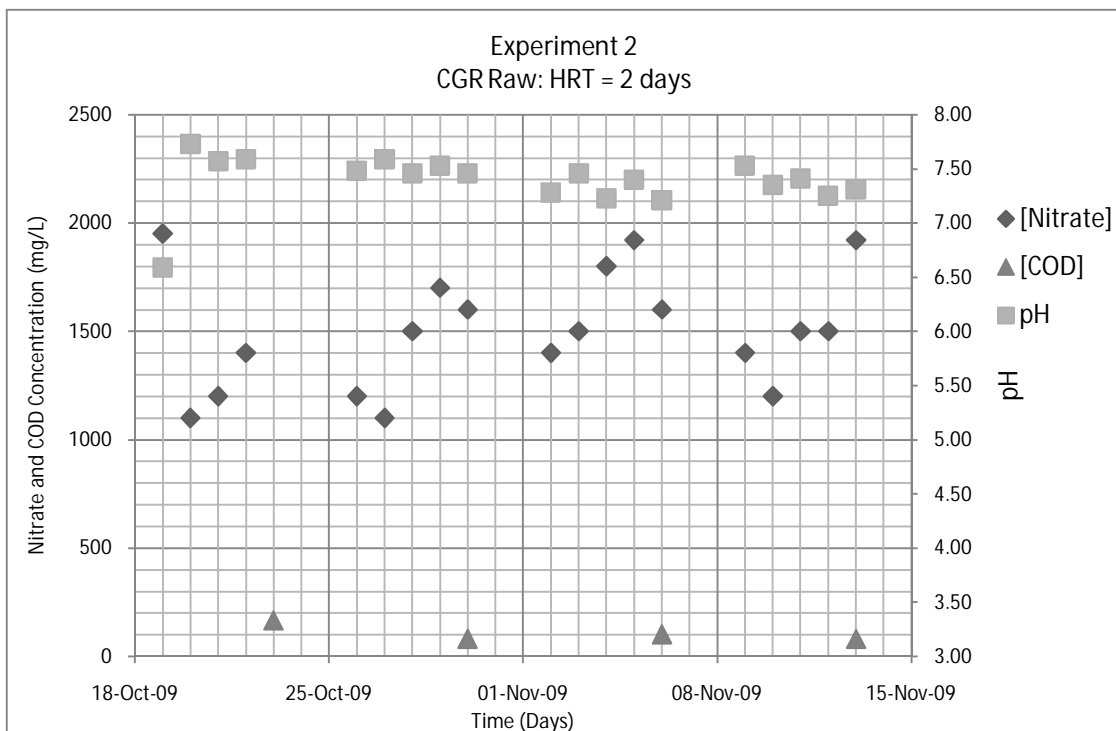


Figure 4-11: Raw Data for Experiment 2 (CRG Raw with HRT = 2 days)

pH remains between 6 and 8 throughout the experiment. This is within the range of pH values that are not likely to provide pH inhibitory behavior.

The COD concentrations in the effluent are considered fairly low throughout the duration of the experiment. In Section 4.1.1 it was noted that the BOD : COD ration was in the order of 1 : 4. This suggests that the BOD in the effluent was between 20 and 40 mg/L throughout the experiments. The notion of COD washout, when COD is drained from the system faster that it leaches out of the solid substrate, was

discussed in the previous section. It appears that this phenomenon may be occurring at a greater magnitude in this experiment and could be a rate limiting factor.

Full denitrification does not occur during this experiment suggesting that either the hydraulic loading rate or the nitrates loading rate have been exceeded. It appears that initially significant denitrification occurs (900 mg/L removed in the first day). For the remainder of the experiment we can see a pattern forming whereby the nitrification occurs over the 2 day weekend whilst the column sits dormant (effectively increasing the HRT to 4 days for that period) and slowly decreases during the course of the proceeding week. It is noticeable also that the efficiency of denitrification decreases as the experiment proceeds.

Calculating the loading rates as per the previous section and using an average nitrate concentration of 1475 mg/L as the effluent concentration we get the following:

Hydraulic Loading Rate

$$Q = 5L/day$$

$$\text{mass of substrate} = 2.8 \text{ kg}$$

$$\text{Hydraulic loading} = 1.79L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 3571.4 \text{ mg}/(\text{kg} \cdot \text{Day})$$

Nitrate Removal

$$\begin{aligned} \text{mass of nitrate removed per day} &= (C_0 - C_{eff})Q \\ &= (2000 - 1475) \cdot 5L/day \end{aligned}$$

$$\begin{aligned} \text{Nitrate removal} &= 2625 \text{ mg of Nitrate per } 2.8 \text{ kg of substrate per day} \\ &= 937.5 \text{ mg Nitrate/kg substrate} \cdot \text{Day} \end{aligned}$$

The rate of nitrate removal was not as high as that for the experiment with a HRT of one week. This is attributed to the limitation of COD as a carbon source for denitrification. It is believed that the optimal hydraulic loading rate at this nitrate concentration has been exceeded and that the rate of leaching of COD and BOD needs to be understood further before this can be escalated to a pilot scale project.

4.3.3 Experiment 3 (PB with HRT = 1 week)

Column 2 was packed with 3.48 kg of Pine Bark and 10 L of synthetic leachate with a nitrate concentration of 2000 mg/L was added until the solid substrate was completely submerged. This provided a L/S ratio of 2.87 : 1.

A hydraulic retention time of 1 week, operated over 5 days, was desired. This meant that 2.00 L of synthetic leachate need to be drawn from the column and replaced daily, Monday to Friday.

Figure 4-12 below provides a summary of the result of experiment 3. The raw data is attached in Appendix B.

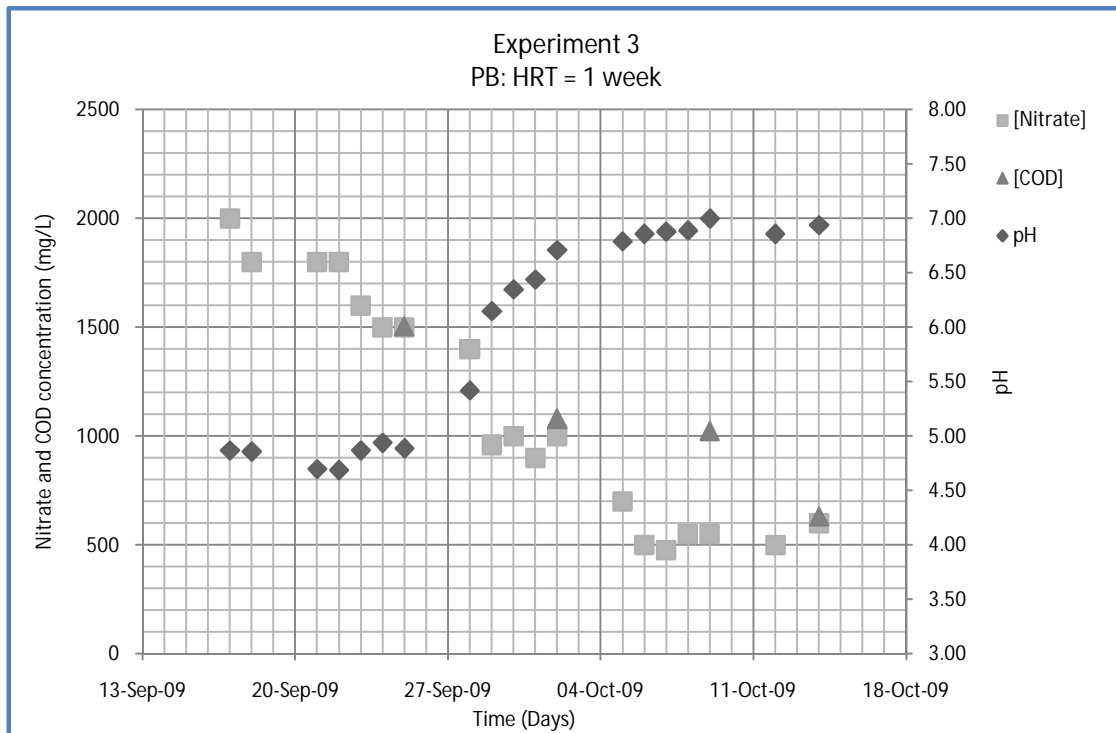


Figure 4-12: Raw Data for Experiment 3 (PB with HRT = 1 week)

Qualitatively it can be seen that denitrification occurs throughout the experiment and that the nitrate concentration decreases from 2000 mg/L on day 1 until it reaches a steady state of approximately 500 mg/L on day 20 of the experiment. The pH of the solution is initially marginally below 5 which is considered to be inhibitory for denitrification. Over the duration of the experiment the pH increases to around neutral and remains at neutral during steady state conditions. This neutral pH is not considered to be inhibitory. The increase in pH was an anticipated result as denitrification produces alkalinity.

COD concentrations decrease over the duration of the experiment but do not appear to reach a level that is considered to be carbon limiting. This observation is purely speculative as the fraction BOD available for denitrification would need to be investigated further along with a mass balance of the carbon in the system.

Calculating hydraulic loading rates and nitrogen loading rates we get the following:

Hydraulic Loading Rate

$$Q = 2L/day$$

$$\text{mass of substrate} = 3.48 \text{ kg}$$

$$\text{Hydraulic loading} = 0.57L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 1149.4 \text{ mg}/(\text{kg} \cdot \text{Day})$$

The nitrate loading rate has been calculated using an average nitrate concentration in the effluent of 530 mg/L. This average has been calculated for effluents measured after denitrification was deemed to have stabilized.

Nitrate Removal

$$\begin{aligned} \text{mass of nitrate removed per day} &= (C_0 - C_{eff})Q \\ &= (2000 - 530) \cdot 2L/day \end{aligned}$$

$$\begin{aligned} \text{Nitrate removal} &= 2940 \text{ mg of Nitrate per } 3.48 \text{ kg of substrate per day} \\ &= 844.8 \text{ mg Nitrate/kg substrate} \cdot \text{Day} \end{aligned}$$

4.3.4 Experiment 4 (PB with HRT = 2 days)

After concluding Experiment 3, the column was drained down and left to stand for four days. On day one of Experiment 4 the column 2, with the same substrate mass as was used in Experiment 3, was filled with synthetic leachate until all the substrate was submerged. 8.10 L of the nitrate solution was added. In order to achieve a HRT of 2 days, it was decided that 4 L of effluent would be drawn from the column daily and 4 L of nitrate added.

Figure 4-13 below provides a summary of the result of experiment 4. The raw data is attached in Appendix B.

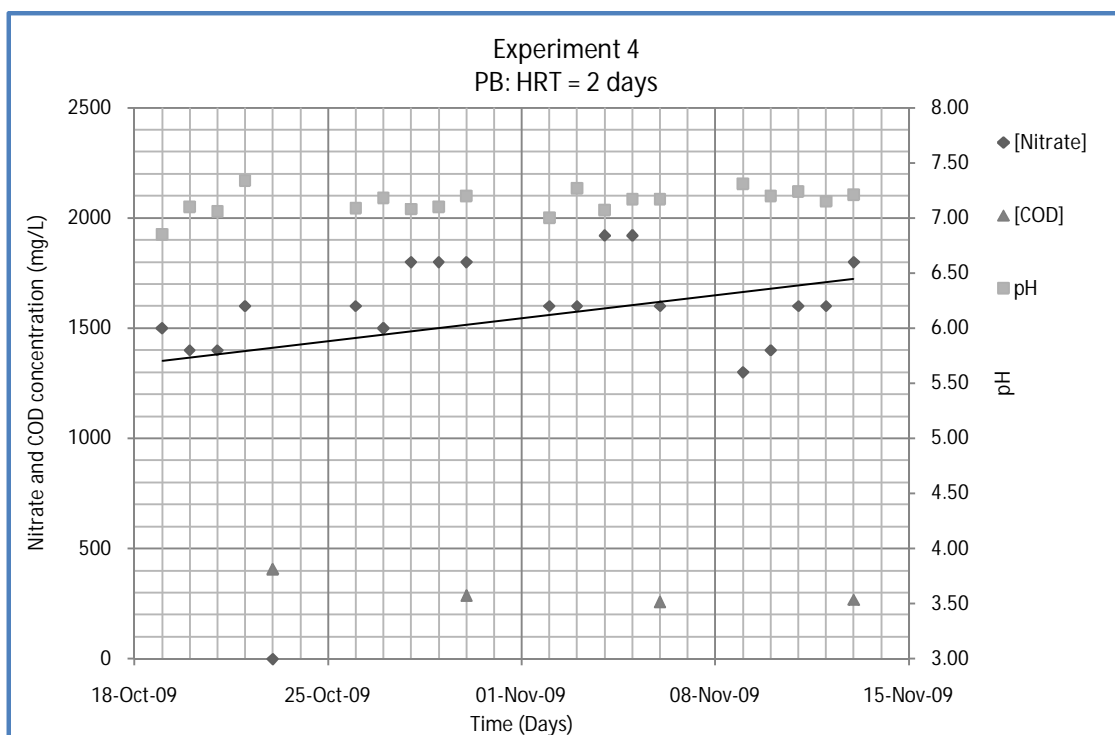


Figure 4-13: Raw Data for Experiment 4 (PB with HRT = 2 days)

The pH of the solution remains constant throughout the experiment at approximately 7 which is not considered to cause pH inhibition. COD concentrations decrease continuously which may be attributed to washout occurring as COD is discharged from the column faster than it is replaced by leaching from the solid substrate. This phenomenon needs to be investigated further and a mass balance on carbon established.

Initially it appears as though denitrification does occur, but the efficiency appears to decrease over the duration of the experiment. The same trend as was identified in

Experiment 2 whereby the nitrification efficiency decreased over the duration of any week was again identified. The increased level of denitrification in this case can be attributed to the increased HRT over this period.

For the purpose of calculating loading rates, a steady state nitrate concentration of 1712 mg/L was used. This is the average nitrate concentration measured for all Wednesdays, Thursdays and Fridays, when the HRT was 2 days. The design loading rates are therefore calculated as follows:

Hydraulic Loading Rate

$$Q = 4L/day$$

$$\text{mass of substrate} = 3.48 \text{ kg}$$

$$\text{Hydraulic loading} = 1.15L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 2298.85 \text{ mg}/(\text{kg} \cdot \text{Day})$$

The nitrate loading rate has been calculated using an average nitrate concentration in the effluent of 1712 mg/L. This average has been calculated for effluents measured after denitrification was deemed to have stabilized.

Nitrate Removal

$$\begin{aligned} \text{mass of nitrate removed per day} &= (C_0 - C_{eff})Q \\ &= (2000 - 1712) \cdot 4L/day \end{aligned}$$

$$\begin{aligned} \text{Nitrate Removal} &= 1152 \text{ mg of Nitrate per } 3.48 \text{ kg of substrate per day} \\ &= 331.0 \text{ mg Nitrate/kg substrate} \cdot \text{Day} \end{aligned}$$

4.3.5 Experiment 5 (CGR 10 with HRT = 1 week)

Column 3 was packed with 6.39 kg of CGR 10 and filled with 8.9 L of synthetic leachate with a nitrate concentration of 2000 mg/L until the solid substrate was completely submerged. This provided a L/S ratio of 1.39 : 1.

A hydraulic retention time of 1 week, operated over 5 days, was desired. This meant that 1.78 L of synthetic leachate need to be drawn from the column and replaced daily, Monday – Friday.

Figure 4-14 below provides a summary of the result of experiment 3. The raw data is attached in Appendix B.

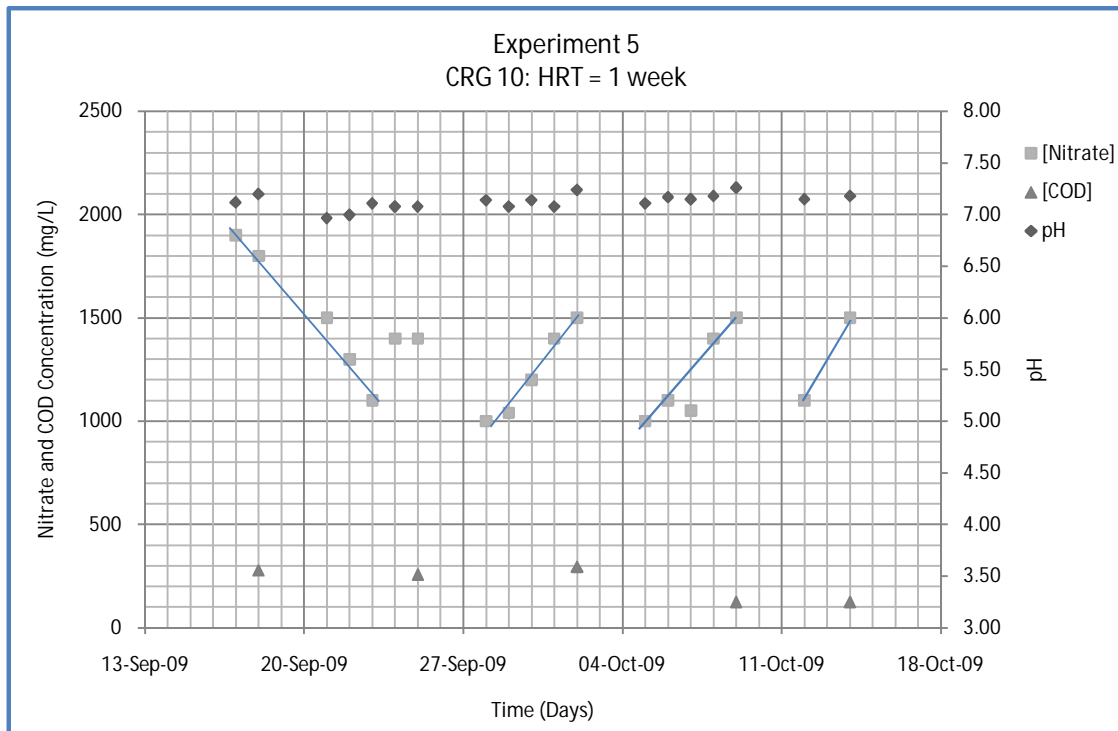


Figure 4-14: Raw Data for Experiment 5 (CGR 10 with HRT = 1 week)

The experiment does not reach a steady state making it difficult to comment on the nitrate removal efficiency. pH remains stable at approximately neutral which is not considered to be inhibitory for denitrifying bacteria. The COD concentration decreased slightly throughout the duration of the experiment. The concentrations in the effluent are lower than what was witnessed for the 24 hr blank batch test. The phenomenon of COD wash out could play a part in the poor denitrifying efficiency witnessed. Additionally, the BOD : COD ratio reported in the initial substrate classification (0.066:1) could play a part in inhibiting denitrification.

The trend of decreasing denitrification efficiency over the duration of a week, where the HRT is longer than 5 days over the weekend than during the week was again identified. Because steady state was not achieved it would be meaningless to calculate the nitrate removal rate as we can't establish an average effluent concentration that is representative of a steady state process. The hydraulic loading rate is however calculated as follows:

Hydraulic Loading Rate

$$Q = 1.78L/day$$

$$\text{mass of substrate} = 6.39 \text{ kg}$$

$$\text{Hydraulic loading} = 0.28L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 557.12 \text{ mg}/(\text{kg} \cdot \text{Day})$$

4.3.6 Experiment 6 (CGR 10 with HRT = 2 days)

After concluding Experiment 5, the column was drained down and left to stand for four days. On day one of Experiment 6 the column 3, with the same substrate mass as was used in Experiment 5, was filled with synthetic leachate until all the substrate was submerged. 6.00 L of the nitrate solution was added. In order to achieve a HRT of 2 days, it was decided that 3 L of effluent would be drawn from the column daily and 3 L of nitrate added.

Figure 4-15 below provides a summary of the result of experiment 4. The raw data is attached in Appendix B.

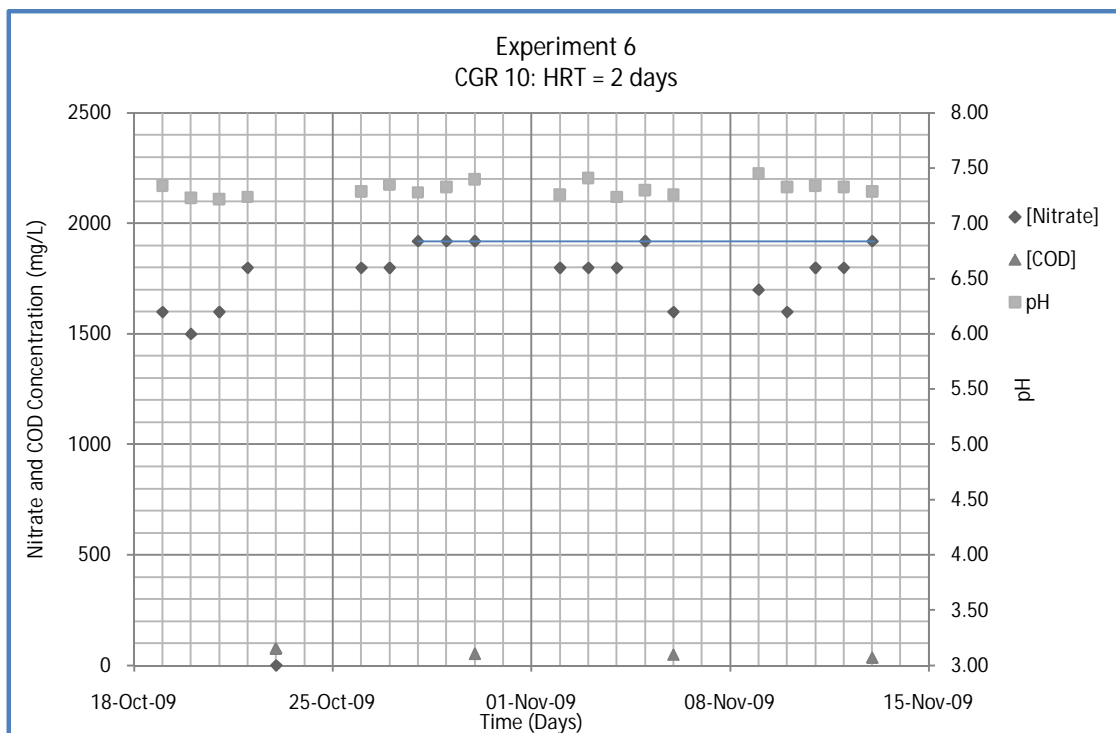


Figure 4-15: Raw Data for Experiment 6 (CGR 10 with HRT = 2 Days)

Throughout the duration of the experiment the pH remains constant in the range of 7.2 – 7.5 which is not likely to cause pH inhibition of the micro-organisms. The COD concentration on the other hand is relatively low ranging from 75 mg/L at the start of the experiment and decreasing constantly to 35 mg/L. The results of the initial eluate characterization showed that there was a low BOD : COD ratio (0.056:1). This low BOD : COD ratio coupled with the low COD concentration in the effluent suggests that carbon may be the limiting substrate for denitrification. Given the effects of the weekend and the increased HRT associated with not operating the columns over this period it appears that a steady state is achieved with a nitrate concentration of

approximately 1920 mg/L. Using this as the effluent concentration for the purpose of calculating the loading / removal rates produces:

Hydraulic Loading Rate

$$Q = 3L/day$$

$$\text{mass of substrate} = 6.39 \text{ kg}$$

$$\text{Hydraulic loading} = 0.47L/Day \cdot \text{kg of substrate}$$

Nitrate Loading Rate

$$NRL = Q \cdot C_{NO_3} / \text{mass of filter media}$$

$$NRL = 938.96 \text{ mg}/(\text{kg} \cdot \text{Day})$$

Nitrate Removal

$$\begin{aligned} \text{mass of nitrate removed per day} &= (C_0 - C_{eff})Q \\ &= (2000 - 1920) \cdot 3L/day \end{aligned}$$

$$\begin{aligned} \text{Nitrate Removal} &= 240 \text{ mg of Nitrate per } 6.39 \text{ kg of substrate per day} \\ &= 37.6 \text{ mg Nitrate/kg substrate} \cdot \text{Day} \end{aligned}$$

5 CONCLUSIONS

The primary focus of this project was to investigate the feasibility of using raw commercial garden refuse, pine bark or composted commercial garden refuse as a source of carbon and a growth media in an anaerobic denitrifying filter configuration.

The first phase of the experiment involved the characterization of the three substrates and the eluate produced from a 24 hr batch test with no added nitrates. The results of this phase of the experiment have suggested that of the three substrates investigated, only the CGR raw appears to leach sufficient biodegradable carbon to support denitrification. These results were based on a L/S ratio of 10:1, and other L/S ratios should be investigated before final conclusions can be drawn. An additional outcome is that both CGR raw and PB produce an eluate with a pH that will initially inhibit denitrifying bacteria.

The second phase of the project focused on batch tests, where each of the substrates were loaded with a 2000mg/L concentration and a L/S ratio of 10:1 until the sample either fully denitrified or the denitrification process stopped. Both the CGR raw and CGR 10 substrates denitrified fully whereas the PB sample ceased to denitrify after approximately 8 days. The CGR raw sample proved the most successful as full denitrification was achieved after 10 days as opposed to the 22 days that was required for denitrification using the CGR 10 substrate. In both the CGR 10 and PB batch tests it appears that availability of biodegradable carbon is the rate limiting factor. This comment is only speculative and further research needs to be done on the mechanisms governing the rate at which carbon is made available as a carbon source, and the associated ratio of BOD : COD.

The final phase of the research involved simulating anaerobic submerged filter conditions by operating columns packed with the substrate as a growth medium for two different hydraulic retention times. The results indicate that the CGR raw carbon substrate was the most successful where full denitrification was achieved for the slower HRT (1 week). In all experiments except for experiment 1, it appeared as though the rate at which carbon leached into solution when compared with the rate at which it was drawn from the column was a limiting factor in the denitrification process.

It is clear from this research that the CGR raw is the favourable substrate for the purpose of operating a fixed film submerged bio-filter for the purpose of denitrifying an effluent with high nitrate concentrations. The research has, however, not answered

all the questions posted, and it is believed that further research would be beneficial. The research in this report has not considered (quantitatively) the effects of carbon concentration, biomass concentration, pH and temperature on the rate of the nitrate utilization. These areas need to be further investigated if a biological model is to be established whereby the nitrate utilization (and carbon) as well and biomass growth can be predicted quantitatively for all filter and L/S configurations. Stressing the point made earlier regarding carbon availability, it is a recommendation as a result of this research that the processes governing carbon availability be further examined. Finally, a mass balance on carbon and nitrogen was not calculated in this research resulting in many of the comments being purely observational and to some degree speculative. It is recommended that any further experiments be designed in such a manner as to allow for the mass balances to be calculated.

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Appendix A: Raw Data – Batch Tests

Table 1: Raw Data – Batch Test - CGR Raw Samples 1 & 2

Time	(Days)			Sample 1	Sample 2
09:25	0.0000	50	50	2000	2000
09:30	0.0035	50	50	2000	2000
09:35	0.0069	50	50	2000	2000
09:40	0.0104	50	50	2000	2000
09:55	0.0208	65	65	2600	2600
10:25	0.0417	70	70	2800	2800
11:25	0.0833	65	65	2600	2600
12:25	0.1250	65	65	2600	2600
13:25	0.1667	67	64	2680	2560
14:25	0.2083	65	62	2600	2480
15:25	0.2500	60	60	2400	2400
09:25	1.0000	50	47	2000	1880
11:25	1.0833	45	47	1800	1880
13:25	1.1667	45	45	1800	1800
15:25	1.2500	40	42	1600	1680
09:25	2.0000	50	50	2000	2000
11:25	2.0833	50	50	2000	2000
15:25	2.2500	50	50	2000	2000
09:25	3.0000	40	42	1600	1680
11:25	3.0833	40	40	1600	1600
13:25	3.1667	40	40	1600	1600
15:25	3.2500	40	40	1600	1600
09:25	4.0000	40	40	1600	1600
11:25	4.0833	40	40	1600	1600
13:25	4.1667	38	38	1520	1520
15:25	4.2500	35	35	1400	1400
09:25	7.0000	35	38	1400	1520
11:25	7.0833	35	35	1400	1400
13:25	7.1667	32	35	1280	1400
15:25	7.2500	32	35	1280	1400
09:25	8.0000	37	38	1480	1520
11:25	8.0833	33	35	1320	1400
13:25	8.1667	34	36	1360	1440
15:25	8.2500	35	35	1400	1400
08:25	8.9583	35	47.5	1400	1900
10:25	9.0417	35	47.5	1400	1900
15:25	9.2500	35	47.5	1400	1900
09:25	10.0000	45	45	900	900
10:25	10.0417	40	80	800	1600
11:25	10.0833	35	95	700	1900
12:25	10.1250	48	80	480	1600

14:25	10.1667	30	80	300	1600
08:25	10.9583	0	80	0	1600
13:00	11.1493	-	75		1500
15:25	11.2500	-	75		1500
09:25	14.0000	-	30		1200
11:25	14.0833	-	30		1200
15:25	14.2500	-	30		1200
08:25	14.9583	-	32		1280
15:25	15.2500	-	33		1320
08:25	15.9583	-	70		1400
15:25	16.2500	-	70		1400
08:25	16.9583	-	40		1600
09:25	18.000	-	35		1400
13:25	18.167	-	35		1400
08:25	20.95833	-	0		0
09:25	21	-	0		0

Table 2: Raw Data – Batch Test - CGR Raw Samples 3 & 4

	Nitrites				Nitrites		
Time	(Days)		Sample 3	Time	(Days)		Sample 4
14:00	0.0000	50	2000	11:30	0.0000	50	2000
14:45	0.0313	40	1600	12:00	0.0208	48	1920
15:00	0.0417	45	1800	12:30	0.0417	48	1920
15:30	0.0625	50	2000	13:30	0.0833	45	1800
16:00	0.0833	50	2000	14:30	0.1250	42	1680
08:00	0.7500	50	2000	15:30	0.1667	45	1800
11:00	0.8750	50	2000	08:30	0.8750	35	1400
14:00	1.0000	50	2000	09:30	0.9167	31	1240
08:00	1.75	37.5	1500	11:30	1.0000	30	1200
08:00	2.7500	37.5	1500	14:30	1.1250	30	1200
10:00	2.8333	35	1400	08:30	1.8750	33	1320
12:00	2.9167	35	1400	11:30	2.0000	30	1200
14:00	3.0000	35	1400	14:30	2.1250	27.5	1100
08:00	5.7500	30	1200	08:30	2.8750	35	1400
10:00	5.8333	20	800	11:30	3.0000	30	1200
12:00	5.9167	30	1200	14:30	3.1250	30	1200
14:00	6.0000	26	1040	08:30	3.8750	30	1200
09:00	6.7917	25	1000	11:30	4.0000	30	1200
14:00	7.0000	25	1000	14:30	4.1250	27.5	1100
08:00	7.7500	35	1400	08:30	6.8750	15	600
14:00	8.0000	35	1400	11:30	7.0000	30	600
15:30	8.0625	25	1000	14:30	7.1250	30	600
09:00	8.7917	17	680	08:30	7.8750	25	500
12:00	8.9167	22.5	900	11:30	8.0000	25	500
15:00	9.0417	15	600	14:30	8.1250	22	440
08:00	9.7500	40	800	09:00	8.8958	26	260
11:00	9.8750	35	700	11:30	9.0000	37.5	187.5
14:00	10.0000	30	600	15:10	9.153	22	110
15:00	10.042	30	600	07:30	9.833	0	0
08:00	12.750	0	0				

Table 3: Raw Data – Batch Test - PB Raw Samples 1 & 2

PINE BARK 0 mg/L		PINE BARK 2000 mg/L					
Duration (days hr:min)	Blank	Duration (days hr:min)	DILUTED SAMPLES		CALCULATED ACTUAL		Average
			Sample 1	Sample 2	Sample 1	Sample 2	
00 00:00	0	0.0000	50	50	2000	2000	2000
00 00:05	0	0.0035	75	70	3000	2800	2900
00 00:10	0	0.0069	70	75	2800	3000	2900
00 00:15	0	0.0104	70	70	2800	2800	2800
00 00:30	0	0.0208	75	75	3000	3000	3000
00 01:00	0	0.0417	75	75	3000	3000	3000
00 02:00	0	0.0833	70	75	2800	3000	2900
00 03:00	12	0.1250	70	70	2800	2800	2800
00 04:00	0	0.1667	70	65	2800	2600	2700
00 05:00	0	0.2083	65	65	2600	2600	2600
00 06:00	0	0.2500	65	65	2600	2600	2600
00 07:00	0	0.2917	60	60	2400	2400	2400
00 22:00	0	0.9167	60	60	2400	2400	2400
01 00:00	0	1.0000	60	60	2400	2400	2400
01 02:00	0	1.0833	55	55	2200	2200	2200
01 04:00	0	1.1667	55	55	2200	2200	2200
01 06:00	0	1.2500	55	55	2200	2200	2200
01 08:00	0	1.3333	55	55	2200	2200	2200
02 00:00	0	2.0000	55	55	2200	2200	2200
02 02:00	0	2.0833	50	53	2000	2120	2060
02 04:00	0	2.1667	52	52	2080	2080	2080
02 06:00	0	2.2500	50	50	2000	2000	2000
05 00:00	0	5.0000	35	45	1400	1800	1600
05 02:00	0	5.0833	40	42	1600	1680	1640
05 04:00	0	5.1667	45	45	1800	1800	1800
05 07:00	0	5.2917	40	40	1600	1600	1600
06 00:00	0	6.0000	40	40	1600	1600	1600
06 02:00	0	6.0833	40	42	1600	1680	1640
06 04:00	10	6.1667	40	40	1600	1600	1600
06 06:00	0	6.2500	38	40	1520	1600	1560
07 00:00	0	7.0000	45	45	1800	1800	1800
07 02:00	0	7.0833	45	45	1800	1800	1800
07 07:00	0	7.2917	45	45	1800	1800	1800
08 00:00	0	8.0000	45	42	1800	1680	1740
08 02:00	0	8.0833	45	40	1800	1600	1700
08 04:00	0	8.1667	40	40	1600	1600	1600
08 06:00	0	8.2500	40	40	1600	1600	1600
09 00:00	0	9.0000	40	40	1600	1600	1600

09 02:00	0	9.0833	40	40	1600	1600	1600
09 04:00	0	9.1667	40	40	1600	1600	1600
09 06:00	0	9.2500	40	40	1600	1600	1600
12 00:00	0	12.0000	38	40	1520	1600	1560
12 02:00	0	12.0833	40	40	1600	1600	1600
12 04:00	0	12.1667	35	34	1400	1360	1380
12 06:00	0	12.2500	38	36	1520	1440	1480
13 00:00	0	13.0000	38	38	1520	1520	1520
13 02:00	0	13.0833	40	40	1600	1600	1600
13 04:00	0	13.1667	37	38	1480	1520	1500
13 06:00	0	13.2500	40	40	1600	1600	1600
14 00:00	0	14.0000	50	50	2000	2000	2000
14 02:00	0	14.0833	50	50	2000	2000	2000
14 07:00	0	14.2917	47.5	47.5	1900	1900	1900
15 00:00	0	15.0000	45	45	1800	1800	1800
15 02:00	0	15.0833	45	45	1800	1800	1800
15 05:00	0	15.2083	45	45	1800	1800	1800
16 00:00	0	16.0000	40	40	1600	1600	1600
16 04:00	0	16.1667	37.5	40	1500	1600	1550
16 06:30	0	16.2708	35	35	1400	1400	1400
19 00:00	0	19.0000	35	35	1400	1400	1400
19 06:00	0	19.25	35	35	1400	1400	1400
20 00:00	0	20.0000	40	45	1600	1800	1700
20 03:00	0	20.1250	35	40	1400	1600	1500
20 06:00	0	20.2500	35	37	1400	1480	1440
21 00:00	0	21.0000	45	45	1800	1800	1800
Stop	21 Days	21.0417	40	40	1600	1600	1600
		21.2500	40	40	1600	1600	1600
		22.0000	40	40	1600	1600	1600
		23.0000	40	40	1600	1600	1600
		23.1667	40	40	1600	1600	1600
		26.0000	35	32	1400	1280	1340
		26.0833	35	32	1400	1280	1340
		26.1667	35	34	1400	1360	1380
		26.2500	35	35	1400	1400	1400
		27.0000	40	40	1600	1600	1600
		27.2500	40	40	1600	1600	1600
		28.0000	40	40	1600	1600	1600
		28.2500	40	40	1600	1600	1600
		29.0000	45	45	1800	1800	1800
		29.2500	43	40	1720	1600	1660
		30.0000	40	40	1600	1600	1600
		30.2500	40	40	1600	1600	1600
		33.0000	40	40	1600	1600	1600
		33.2500	40	40	1600	1600	1600

34.0000	40	40	1600	1600	1600
34.2500	40	40	1600	1600	1600
35.0000	45	45	1800	1800	1800
35.2500	45	45	1800	1800	1800
36.0000	35	33	1400	1320	1360
36.1250	35	35	1400	1400	1400
36.2500	35	33	1400	1320	1360
37.0000	40	40	1600	1600	1600
37.2500	45	45	1800	1800	1800
40.0000	40	40	1600	1600	1600
40.2500	40	40	1600	1600	1600
41.0000	40	40	1600	1600	1600
41.2500	40	40	1600	1600	1600
42.0000	40	40	1600	1600	1600
42.2500	40	40	1600	1600	1600
43.0000	40	40	1600	1600	1600
43.2500	40	40	1600	1600	1600
44.0000	45	45	1800	1800	1800
44.2500	45	45	1800	1800	1800
47.0000	40	40	1600	1600	1600
47.2500	40	40	1600	1600	1600

Table 4: Raw Data – Batch Test – CGR 10 Raw Samples 1 & 2

CGR 10 - BLANK		CGR 10 - 2000mg/l					
Duration (days hr:min)	Blank	Duration (days hr:min)	Sample 1	Sample 2	Average	Minimum	Maximum
00 00:00	0	00 00:00	2000	2000	2000	2000	2000
00 00:05	0	00 00:05	2470	2500	2485	2470	2500
00 00:10	0	00 00:10	2470	1900	2185	1900	2470
00 00:15	0	00 00:15	2500	1900	2200	1900	2500
00 00:30	0	00 00:30	1995	1995	1995	1995	1995
00 01:00	0	00 01:00	2375	2090	2232.5	2090	2375
00 02:00	0	00 02:00	1900	1900	1900	1900	1900
00 03:00	0	00 03:00	1900	1900	1900	1900	1900
00 05:00	0	00 04:00	1900	1900	1900	1900	1900
00 22:00	0	00 05:00	1875	1875	1875	1875	1875
01 00:00	0	00 06:00	1900	1900	1900	1900	1900
01 02:00	0	01 00:00	1900	2000	1950	1900	2000
01 04:00	0	01 04:00	2000	2000	2000	2000	2000
01 22:00	0	01 06:00	1900	2000	1950	1900	2000
02 00:00	0	02 00:00	1000	2000	1500	1000	2000
02 02:00	0	02 02:00	1600	1900	1750	1600	1900
02 04:00	0	02 04:00	1900	1900	1900	1900	1900
04 22:00	0	02 06:00	1900	1900	1900	1900	1900
05 00:00	0	03 00:00	1800	1800	1800	1800	1800
05 02:00	0	03 02:00	1800	1800	1800	1800	1800
05 04:00	0	03 04:00	1800	1800	1800	1800	1800
05 22:00	0	03 06:00	1800	1800	1800	1800	1800
06 00:00	0	04 00:00	1500	1600	1550	1500	1600
06 02:00	0	04 02:00	1700	1700	1700	1700	1700
06 04:00	0	04 04:00	1700	1700	1700	1700	1700
06 22:00	0	04 06:00	1700	1800	1750	1700	1800
07 00:00	0	07 00:00	1200	1100	1150	1100	1200
07 02:00	0	07 02:00	1200	1000	1100	1000	1200
07 04:00	0	07 04:00	1200	1000	1100	1000	1200
07 22:00	0	07 06:00	1100	800	950	800	1100
08 00:00	0	08 00:00	1000	1200	1100	1000	1200
		08 02:00	1000	1000	1000	1000	1000
		08 04:00	875	1000	937.5	875	1000
		09 00:00	600	700	650	600	700
		09 06:00	600	700	650	600	700
		09 23:45	500	500	500	500	500
		10 05:45	500	500	500	500	500
		10 23:00	300	400	350	300	400
		14 00:00	400	500	450	400	500
		14 04:00	350	500	425	350	500

15 00:00	400	500	450	400	500
15 04:00	380	500	440	380	500
16 00:00	300	450	375	300	450
16 02:00	300	450	375	300	450
16 04:00	250	400	325	250	400
16 06:00	250	400	325	250	400
17 00:00	200	400	300	200	400
17 02:00	150	275	212.5	150	275
17 04:00	125	250	187.5	125	250
17 06:00	120	250	185	120	250
18 00:00	80	220	150	80	220
18 02:00	75	200	137.5	75	200
18 04:00	70	200	135	70	200
18 06:00	50	200	125	50	200
21 00:00	10	35	22.5	10	35
21 02:00	5	30	17.5	5	30
21 04:00	0	25	12.5	0	25
21 06:00	0	10	5	0	10
22 00:00	0	0	0	0	0

Appendix B: Raw Data – Column Tests

Table 5: Raw Data - Column Test 1 – CGR Raw HRT = 1 week

	Date	DO mg/L	NO ₃ mg/L				pH	temp
			sample	port 1	port 2	port 3		
Thurs	17-Sep-09	4.61	1800				6.00	21
Fri	18-Sep-09	4.33	1200				5.94	21
Mon	21-Sep-09	4.04	1200				5.69	21
Tues	22-Sep-09	0.75	1000				5.82	20
Wed	23-Sep-09	7.48	800				6.43	20
Thurs	24-Sep-09	-0.04	0				6.78	21
Fri	25-Sep-09	-0.04	0				6.54	21
Mon	28-Sep-09	-0.04	0	0	25*	2000	6.55	
Tues	29-Sep-09	8.59	0	200*	480*	2000	6.40	19
Wed	30-Sep-09	-0.04	0	0	0	1400	6.50	19
Thurs	01-Oct-09	-0.04	0	0	?	?	6.55	20
Fri	02-Oct-09	2.34	0	0	600	1400	6.83	21
Mon	05-Oct-09	5.72	0	0	0	600	6.75	21.00
Tues	06-Oct-09	0.67	0	0	0	1400	6.84	21
Wed	07-Oct-09	0.41	0	0	475	1600	6.83	22
Thurs	08-Oct-09	1.35	10	175	800	1600	6.98	21
Fri	09-Oct-09	0.80	55	400	900	1600	7.21	21
Mon	12-Oct-09	0.00	0	25	480	1000	7.04	21
Tues	13-Oct-09							
Wed	14-Oct-09	1.02	180	250	960	180	7.14	20
Thurs	15-Oct-09							
Fri	16-Oct-09							

Table 6: Raw Data - Column Test 2 – CGR Raw HRT = 2 days

	Date	OUT	IN	NO ₃ mg/L	NO ₂	pH	temp
Mon	19-Oct-09		11.33	1950		6.59	21
Tue	20-Oct-09	6.00	5.00	1100		7.73	21
Wed	21-Oct-09	5.00	5.00	1200		7.57	21
Thu	22-Oct-09	5.00	5.00	1400		7.59	20
Fri	23-Oct-09						
Mon	26-Oct-09	5.00	5.00	1200		7.48	21
Tue	27-Oct-09	5.00	5.00	1100		7.59	21
Wed	28-Oct-09	5.00	5.00	1500		7.46	22
Thu	29-Oct-09	5.00	5.00	1700		7.53	21
Fri	30-Oct-09	5.00	5.00	1600		7.46	20
Mon	02-Nov-09	5.00	5.00	1400		7.28	20
Tue	03-Nov-09	5.00	5.00	1500		7.46	21
Wed	04-Nov-09	5.00	5.00	1800		7.23	22.00
Thu	05-Nov-09	5.00	5.00	1920		7.40	21
Fri	06-Nov-09	5.00	5.00	1600	Yes	7.21	21
Mon	09-Nov-09	5.00	5.00	1400	Yes	7.53	23
Tue	10-Nov-09	5.00	5.00	1200	Yes	7.35	22
Wed	11-Nov-09	5.00	5.00	1500	Yes	7.41	21
Thu	12-Nov-09	5.00	5.00	1500	Yes	7.25	22
Fri	13-Nov-09	9.50		1920	Yes	7.31	21
				1474.44444			

Table 7: Raw Data - Column Test 3 – PB HRT = 1 week

	Date	DO mg/L	NO ₃ mg/L	NO ₂	pH	temp
			sample			
Thurs	17-Sep-09	5.33	2000	N/A	4.87	21
Fri	18-Sep-09	7.51	1800	N/A	4.86	21
Mon	21-Sep-09	3.17	1800	N/A	4.70	21
Tues	22-Sep-09	4.35	1800	Yes *	4.69	20
Wed	23-Sep-09	6.76	1600	N/A	4.87	20
Thurs	24-Sep-09	6.36	1500	Yes	4.94	21
Fri	25-Sep-09	2.60	1500	Yes	4.89	21
Mon	28-Sep-09	8.11	1400	Yes	5.42	
Tues	29-Sep-09	9.54	960	Yes	6.15	19
Wed	30-Sep-09	10.46	1000	Yes	6.35	19
Thurs	01-Oct-09	8.78	900	Yes	6.44	20
Fri	02-Oct-09	5.81	1000	Yes	6.71	20
Mon	05-Oct-09	8.64	700	Yes	6.79	21
Tues	06-Oct-09	1.06	500	N/A	6.86	21
Wed	07-Oct-09	1.78	475	N/A	6.88	22
Thurs	08-Oct-09	1.66	550	N/A	6.89	21
Fri	09-Oct-09	1.61	550	N/A	7.00	22
Mon	12-Oct-09	1.22	500	N/A	6.86	20
Tues	13-Oct-09					
Wed	14-Oct-09	0.85	600	N/A	6.94	20

Table 8: Raw Data - Column Test 4 – PB HRT = 2 days

	Date	OUT	IN	NO ₃ mg/L	NO ₂	pH	temp
Mon	19-Oct-09		8.10	1500		6.85	21
Tue	20-Oct-09	5.00	5.00	1400		7.10	21
Wed	21-Oct-09	5.00	5.00	1400		7.06	21
Thu	22-Oct-09	5.00	5.00	1600		7.34	20
Fri	23-Oct-09						
Mon	26-Oct-09	5.00	5.00	1600		7.09	21
Tue	27-Oct-09	5.00	5.00	1500		7.18	21
Wed	28-Oct-09	5.00	5.00	1800		7.08	22
Thu	29-Oct-09	4.00	4.00	1800		7.10	21
Fri	30-Oct-09	4.00	4.00	1800		7.20	20
Mon	02-Nov-09	4.00	4.00	1600		7.00	20
Tue	03-Nov-09	4.00	4.00	1600		7.27	20
Wed	04-Nov-09	4.00	4.00	1920		7.07	21
Thu	05-Nov-09	4.00	4.00	1920		7.17	20
Fri	06-Nov-09	4.00	4.00	1600		7.17	21
Mon	09-Nov-09	4.00	4.00	1300		7.31	22
Tue	10-Nov-09	4.00	4.00	1400		7.20	22
Wed	11-Nov-09	4.00	4.00	1600		7.24	21
Thu	12-Nov-09	4.00	4.00	1600		7.15	22
Fri	13-Nov-09	6.50		1800		7.21	21

Table 9: Raw Data - Column Test 5 – CGR 10 HRT = 1 week

	Date	DO mg/L	NO ₃ mg/L	NO ₂	pH	temp
			sample			
Thurs	17-Sep-09	7.95	1900	N/A	7.12	21
Fri	18-Sep-09	9.64	1800	N/A	7.20	21
Mon	21-Sep-09	5.75	1500	N/A	6.97	21
Tues	22-Sep-09	8.19	1300	N/A	7.00	20
Wed	23-Sep-09	9.31	1100	N/A	7.11	20
Thurs	24-Sep-09	7.42	1400	N/A	7.08	21
Fri	25-Sep-09	7.85	1400	N/A	7.08	21
Mon	28-Sep-09	8.26	1000	N/A	7.14	
Tues	29-Sep-09	5.43	1040	N/A	7.08	19
Wed	30-Sep-09	5.73	1200	N/A	7.14	19
Thurs	01-Oct-09	5.67	1400	N/A	7.08	20
Fri	02-Oct-09	8.11	1500	N/A	7.24	20
Mon	05-Oct-09	5.98	1000	N/A	7.11	21
Tues	06-Oct-09	1.07	1100	N/A	7.17	20
Wed	07-Oct-09	1.26	1050	N/A	7.15	22
Thurs	08-Oct-09	1.76	1400	N/A	7.18	21
Fri	09-Oct-09	1.93	1500	N/A	7.26	22
Mon	12-Oct-09	1.56	1100	N/A	7.15	20
Tues	13-Oct-09					
Wed	14-Oct-09	1.56	1500	N/A	7.18	20

Table 10: Raw Data - Column Test 6 – CGR 10 HRT = 2 Days

	Date	OUT	IN	NO ₃ mg/L	NO ₂	pH	temp
Mon	19-Oct-09		6.00	1600		7.34	21
Tue	20-Oct-09	4.00	4.00	1500		7.23	21
Wed	21-Oct-09	4.00	4.00	1600		7.22	21
Thu	22-Oct-09	3.00	3.00	1800		7.24	21
Fri	23-Oct-09						
Mon	26-Oct-09	3.00	3.00	1800		7.29	21
Tue	27-Oct-09	3.00	3.00	1800		7.35	21
Wed	28-Oct-09	3.00	3.00	1920		7.28	22
Thu	29-Oct-09	3.00	3.00	1920		7.33	21
Fri	30-Oct-09	3.00	3.00	1920		7.40	20
Mon	02-Nov-09	3.00	3.00	1800		7.26	20
Tue	03-Nov-09	3.00	3.00	1800		7.41	20
Wed	04-Nov-09	3.00	3.00	1800		7.24	21
Thu	05-Nov-09	3.00	3.00	1920		7.30	21
Fri	06-Nov-09	3.00	3.00	1600		7.26	21
Mon	09-Nov-09	3.00	3.00	1700		7.45	22
Tue	10-Nov-09	3.00	3.00	1600		7.33	22
Wed	11-Nov-09	3.00	3.00	1800		7.34	21
Thu	12-Nov-09	3.00	3.00	1800		7.33	22
Fri	13-Nov-09	4.70		1920		7.29	22