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Sustainable landfill leachate treatment using refuse and pine bark as a carbon source for bio-denitrification

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Abstract: Raw and 10-week composted commercial garden refuse materials and pine bark mulch were evaluated for their potential use as alternative and sustainable sources of carbon for landfill leachate bio-denitrification. Dynamic batch tests using synthetic nitrate solution of 100, 500 and 2000 mg NO_3 L^{-1} were used to investigate the substrate performance at increasing nitrate concentrations under optimal conditions. Further to this, sequential batch tests using genuine nitrified landfill leachate with a concentration of 2000 mg NO_3 L^{-1} were carried out to evaluate substrates behaviour in the presence of a complex mixture of chemicals present in leachate. Results showed complete denitrification occurred in all conditions indicating that raw and composted commercial garden refuse and pine bark can be used as sustainable and efficient media for landfill leachate bio-denitrification. Of the three substrates, raw garden refuse yields the fastest denitrification rate followed by 10-week composted commercial garden refuse and pine bark. However the efficiency of raw commercial garden refuse was lower when using genuine leachate, indicating the inhibitory effect of components of the leachate on the denitrification process. 10-week composted commercial garden refuse performed optimally at low nitrate concentrations, while poor nitrate removal ability was found at higher nitrate concentrations (2000 mg L^{-1}). In contrast pine bark performance was 3.5 times faster than the composted garden refuse at higher nitrate concentrations. Further to this, multi-criteria analysis of the process variables provided an easily implementable framework for the use of waste materials as an alternative and sustainable source of carbon for denitrification.

Keywords: denitrification; leachate treatment; carbon source; pine bark; commercial garden refuse.

1. Introduction

South Africa produces 108 million tonnes of waste per annum, of which 98 million tonnes are sent to landfill sites. [1] This significant amount of waste contains a large proportion of bioreactive wastes, which produce mainly gas and wastewater known as leachate. [2-3] Leachate treatment and disposal is one of the biggest issues during solid waste management practices. Leachate has very high strength regarding to pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), ammonia, chloride, colour, odour, and heavy metals. If it is not collected carefully and not discharged safely, leachate has the ability to cause major environmental impacts as well as affect human health due to its high toxicity. The major concern associated with leachate is its ammonia content, which can reach levels of up to 1000 mg L^{-1}. [3-6] Leachate can contaminate ground and surface water resources, which can consequently affect potable water supply. Furthermore, it can affect biological systems and ecological communities of many fauna and flora exposed to contaminated water. [4,7,8] There are typically few wastewater treatment facilities in developing countries due to the high cost of treatment and lacking environmental pollution control laws and enforcement. [8] The ammonia in leachate can be treated by biological nitrification. [9,10] Such a process approach has been adopted at the Mariannhill landfill site (LFS) (Durban, South Africa), which receives between 550-700 tonnes of municipal solid waste per day [10] and produces and nitrifies approximately 30 m^3 of leachate per day. The leachate treatment plant operates by aerobically converting ammonia to nitrites, and then to nitrates.

Nitrates can still have significant environmental and human health implications. Nitrates can lead to adverse eutrophication in aquatic environments. [11] Nitrate levels > 45 mg L^{-1} can also affect human health [12] through ingestion of nitrate-

containing water or vegetables, causing among others; abdominal pains, diarrhoea, vomiting, diabetes, birth defects, infant mortality, hypertension and respiratory tract infections. [13] Therefore a denitrification step is required to reduce nitrate levels to acceptable discharge limits. In South Africa, the nitrate discharge limit set by the Department of Water Affairs and Forestry is 15 mg NO_3 L^{-1}. [14] The nitrate concentration of the effluent from the nitrification sequencing batch reactor (SBR) installed at the Mariannhill landfill site ranged between 285 and 1425 mg L^{-1} in 2011/12. The SBR effluent is currently recirculated into the landfill through use as a dust suppressant. Closure of the landfill site is expected in 2022 at which point recirculation will no longer be a viable treatment option. [15] The use of biological denitrification, in the form of a biological anaerobic filter bed operated in a flowing system, will be adopted at the landfill site as this is believed to be one of the most promising methods of nitrate removal. [3]

Biological denitrification is the process by which oxidised nitrogenous compounds such as nitrates or nitrites are reduced to nitrogen gas under anoxic conditions through the assistance of a diverse group of bacteria. [3,16,17] The biological denitrification process typically follows a nitrification step whereby ammonia and much of the organics are removed. [18] There is thus a deficiency of carbon essential for denitrification. As a result, an external carbon source is required as an electron donor in order for microorganisms to survive. [18]

Typically methanol, glucose, ethanol, propionic and acetic acid are commonly used as they are easily biodegradable. [19-21] These carbon sources, however, are expensive which consequently restricts their viability in full-scale application. [21]

The use of waste materials as a carbon source in denitrification has been researched for over 20 years. [3,20,22-25] It has the dual benefit of removing wastes from the waste stream, diverting it from landfill sites, and use as an

alternative carbon source. It is therefore an economically and environmentally sustainable carbon source alternative. Alternative carbon sources from waste materials that have been found to successfully denitrify leachate include tree barks, sawdust, corncobs, wood chips, newspapers, yeast, whey and compost. [20,23]. Many of these alternative carbon sources have shown denitrification rates and chemical oxygen demand:nitrogen ratios (COD:N) comparable to traditional chemicals such as methanol and acetic acid. [26] There is, however, still a need to continue identifying feasible alternative carbon sources in terms of cost, availability and denitrification efficiency in order to continue the development of sustainable nitrate removal solutions. [26] Trois et al. [3,21] previously investigated the use of composted garden waste and pine bark (PB) as an alternative and low-cost carbon source for supporting biodenitrification as they are found in high quantities in South African landfills. They demonstrated that complete nitrate removal was achievable and provided insights into the key microbes involved in the biodenitrification process. However, little information on the chemical characterisation during the denitrification process was provided. Therefore, the main objectives of this study were to (1) investigate the feasibility of using raw commercial garden refuse (raw CGR), 10 week composted commercial garden refuse (CGR 10) and pine bark as sustainable alternative carbon sources for the denitrification of treated landfill leachate at an initial nitrate concentration of up to 2000 mg NO_3 L^{-1}; (2) characterise the substrates performance against the nitrate concentrations load using synthetic and genuine leachate and (3) provide a decision support tool to inform future treatment strategies.

2. Materials and Methods

2.1. Substrate selection

Substrates tested were raw CGR, CGR composted for 10 weeks and PB. The CGR substrate was sourced from the waste stream of the Bisasar Road Landfill site in Durban, South Africa. The CGR substrate, which was made up of mainly thin twigs and leaves, went through an onsite chipper which reduced the chip size to smaller than 5 cm in length. It was subsequently stored in an onsite pile and collection of sample happened within days of the chipping process. To obtain the CGR 10, composting of the raw CGR was conducted on site for 10 weeks through a turned windrow technology. The PB was obtained from the MONDI paper company in South Africa. They were prepared as wood chips with a length approximately 3-5cm in size.

2.2. Substrate and leachate characterisation

Substrate and leachate characterisation methodology was conducted according to standard analytical methods as published by the American Public Health Association. [27]

Characterisation was conducted on both the solid and eluate fractions of the substrate. The eluate was attained by immersing the substrate in distilled water for 24 hours at a liquid:solid (L/S) ratio of 10:1 by weight. This enabled optimal liquid to solid contact.

Characterisation tests which were conducted on the solid substrates included moisture content (w), total solids (TS), volatile solids (VS), respiration index (RI_7), total carbon (TC), total nitrogen (TN) and carbon to nitrogen ratio (C/N). Characterisation tests which were conducted on the eluate samples and leachate included: TS, VS, pH, soluble chemical oxygen demand (sCOD), biochemical oxygen demand (BOD_5), TC, TN, C/N, ammoniacal nitrogen (NH_3-N) and total oxidised nitrogen (NO_x-N). Total carbon and total nitrogen were determined

through total combustion using a Leco Truspec® CN analyser. Respiration index (RI_7) was tested by adding 5 drops of allylthiourea (ATH) to 25 g of substrate in a 1.5 L glass bottle. 5 drops of 45% potassium hydroxide (KOH) was placed into a rubber cylinder situated below a pressure sensor lid. Samples were incubation at 20°C for 7 days and measurements were recorded using an OxiTop® respirometric apparatus. NH_3-N and NO_x-N was measured using UV-VIS spectroscopy according to standard methods (4500-NO_2^- and 4500-NO_3^-).

2.3. Batch tests set-up and analysis

Denitrification of both synthetic leachate containing 100, 500 and 2000 mg NO_3 L^{-1} respectively and treated (nitrified) leachate sourced from the Mariannhill LFS containing 2000 mg NO_3 L^{-1} was carried out in triplicate batch reactors. Batch tests were conducted using raw CGR, CGR 10 and PB as a carbon source.

All batch tests were conducted in one L anaerobic bottles equipped with two airtight silicone septa that allow for continuous sampling while avoiding air ingress. Each substrate (S) was mixed with the leachate solution (L) at L/S=10/1, by weight, to ensure full saturation and optimal liquid-solid contact in the batch reactors. [3] A control test replacing nitrate solution/leachate with distilled water was also carried out for each batch test. Optimal environmental conditions and full liquid to solid transfer were obtained by performing the experiments at a controlled temperature of 25 ºC and shaking speed of 150 rpm. The batch systems were flushed with N_2 to set anoxic conditions. Nitrate concentration was measured at regular intervals daily using nitrate test sticks (type Merckoquant). pH, NH_3-N, NO_x-N and C/N ratio were measured in triplicate at regular time intervals. The intervals between sampling were dependent on the substrate and initial nitrate load

of the batch test, which are presented in Figure 1. pH, NH_3-N and NO_x-N were tested on the eluate fraction of the batch test while C/N ratio was tested on the solid fraction. sCOD was measured at the start and end of the 2000 mg NO_3 L^{-1} batch tests. Variability in results was less than 5%.

Batch tests incorporating the use of treated leachate was conducted subsequent to the synthetic leachate batch tests, and were designed to assess the effect of genuine leachate on the denitrification process. The genuine leachate batch tests were further used to determine the substrate longevity in terms of denitrification efficiency. This was done by replacing denitrified leachate, after denitrification was complete, with fresh pre-treated (nitrified) leachate at a concentration of 2000 mg NO_3 L^{-1}, while keeping the same substrate. Pre-treated leachate was obtained from the Mariannhill landfill site, South Africa. Leachate was collected after nitrification was conducted in an on-site sequencing batch reactor (SBR).

3. Results and Discussion

3.1. Substrate and leachate characterisation

Substrate characterisation shows that the RI_7 value of raw CGR, an indication of the extent to which readily biodegradable organic matter has been decomposed, [28] was the highest (Table 1). This indicated that raw CGR was the least decomposed and consequently the most readily biodegradable. The C/N, sCOD and BOD_5 values of raw CGR were high, displaying a high level of organic strength. Due to these chemical characteristics, raw CGR was identified as the substrate that would best promote the action of denitrifying bacteria by providing the highest amount of biodegradable carbon in the shortest time while depositing little nitrogenous compounds back into the system (Table 1).

PB showed a high C/N and a high RI_7 as it is a relatively fresh material having not undergone any stabilisation. The C/N in this study was approximately three times higher than found in Trois et al. [3] This finding suggests that the heterogeneous character of the PB composition influences directly the amount of carbon available to sustain the denitrification process.

Furthermore, the eluate characterisation showed that TS and sCOD were low, suggesting that carbon from PB was not immediately released into the system, and therefore had a poor leaching ability. The poor leaching ability of PB, particularly in the leaching of organic compounds, was also reported by Ribe et al. [29]

The use of CGR 10 was evaluated, as it is a theoretically more biologically stable substrate, possessing a lower organic strength than raw CGR, due to the composting process. This would ideally result in low COD effluent, requiring less COD management of the effluent. Results confirmed that CGR 10 possessed a lower sCOD than raw CGR and the lowest RI_7 of the three substrates. The substrate showed good potential as a carbon source as it still possessed a sufficient organic load to promote bio-denitrification. The optimum C/N for stabilised compost to promote denitrification ranges between 13 and 16. [20] The C/N of the CGR 10 was 21, which was 2.4 and 9 times lower than the raw CGR and PB respectively, similar to the findings of Trois et al. [3] CGR 10 showed good potential to desorb its available carbon adequately as indicated by the significant TS and sCOD in the eluate fraction.

The pH for all substrates was below the optimum pH, which ranges normally between 6 and 8. pH was expected to increase to optimal levels at the onset of denitrification as carbonate alkalinity increases during nitrate reduction. [20]

3.2. Simulated leachate batch tests

An initial lag phase was observed in most batch tests, where no denitrification took place (Table 2). Microbial populations require time to acclimate to environmental conditions, and reach sufficient densities to initiate the denitrification process. The occurrence of microbial acclimatisation is a well-documented process. [30,31] CGR 10 showed the shortest lag phase of the substrates at one, three and two hours for the 100, 500 and 2000 mg NO_3 L^{-1} batch tests respectively (Table 2). It is possible that composting promoted the rapid establishment of a specialised microbial consortium. [32] Lag phase for raw CGR was 5, 2 and 22 hours for the 100, 500 and 2000 mg NO_3 L^{-1} batch tests, respectively and the lag phase for PB was between 23 and 24 hours in all batch tests.

A possible reason for the short lag phases observed is due to the low pH variation during acclimatisation (Figure 1). Findings from Trois et al. [3] confirmed a short lag phase when using CGR substrates, however they found a longer lag phase when using PB (20-80 hours), particularly at higher nitrate concentrations. They accounted this to pH buffering and microbial competition. Since results from this study showed less pH variation during the lag phase when compared to Trois et al. [3], it is likely that this contributed to the shorter lag phases observed.

Complete denitrification was achieved in all batch tests using synthetic leachate solution, indicating that raw CGR, CGR 10 and PB can all adequately be used as alternative carbon sources to facilitate denitrification at a nitrate concentration of up to 2000 mg L^{-1} under optimal conditions.

Raw CGR was the most efficient substrate in facilitating biological denitrification in batch tests at all nitrate concentrations. Raw CGR and CGR 10 showed similar rates of denitrification at lower nitrate concentrations (Table 2). In contrast, PB completed denitrification for the 100 and 500 mg NO_3 L^{-1} batch tests four and 1.3 times slower, respectively.

Batch tests containing synthetic leachate at 2000 mg NO_3 L^{-1} showed a different trend in that raw CGR facilitated an extremely rapid denitrification rate completing full denitrification in less than 1.4 days. In contrast denitrification was 5.1 and 18 times slower when PB and CGR10 were used respectively, compared to raw CGR (Table 2).

In the absence of lag time, which was not taken into account when calculating the removal rate, raw CGR showed a consistently high removal rate compared to CGR 10 and PB (Figure 2). At high nitrate concentrations, the raw CGR showed a low R^2 and an extremely steep removal rate gradient indicating a rapid, non-uniform reduction of nitrates over time (Figure 2). The raw CGR substrate promoted a denitrification rate in the 2000 mg NO_3 L^{-1} batch test that was almost three times faster than that of the 500 mg NO_3 L^{-1} batch test.

While our understanding for this behaviour is limited, it is possible that at high nitrate concentration, the rapid rate of nitrate reduction was either due to concomitant chemical denitrification and biological denitrification, [33] or exclusively by microbial biomass growth at increasing nitrate concentration. The former is more likely as ammonia/ammonium (only ammoniacal nitrogen tested) leached from the raw CGR (Figure 1) will react with nitrite (formed during the reduction of nitrate during denitrification) to form nitrogen gas. [33]

The potential increase in microbial growth at higher nitrate concentrations is less likely because a higher initial nitrate concentration would result in a higher production of nitrites in the system (formed from the reduction of nitrates during denitrification) and nitrite ions are considered inhibitors of bacterial growth. [34]

Batch tests using PB showed a relatively linear reduction of nitrates over time (Figure 2). The removal rate gradient became steeper at increasing nitrate concentrations indicating an increasing rate of nitrate removal at higher nitrate

concentrations. This finding was likely due to the leaching dynamics of PB. Approximately 2.5 and 3.5 times longer was needed to complete denitrification during the 500 and 2000 mg NO_3 L^{-1} batch tests respectively, compared to the 100 mg NO_3 L^{-1} batch test. The longer contact time between the substrate and the surrounding environment at higher nitrate concentrations (Figure 2) ensured that PB was able to leach an adequate amount of carbon required for denitrification.

The CGR 10 substrate showed a decreasing removal rate at increasing nitrate concentrations and furthermore showed extremely slow denitrification rates at a high nitrate concentration (Figure 2). One possible reason for this may be due to the high amount of NO_x-N observed in the system (Figure 1). Considering that a major constituent of NO_x-N is nitrite-N, and at high concentration nitrites are toxic to denitrifiers, it is possible that this would influence denitrification rates [34]. However further research, in particular on the effect of nitrogenous oxides on microbial dynamics, is required to better elucidate this issue.

It is expected that these observed trends in denitrification rates when using raw CGR, CGR 10 and PB at the various nitrate concentrations will consistently show the same trend, with the potential exception of raw CGR at 2000 mg NO_3 L^{-1}. It is likely that the denitrification rates observed in this batch test were a result of conditions favourable towards the dominance of chemical denitrification over biological denitrification, such as high nitrate concentration and approximately neutral pH. [33] These conditions may not always be prevalent. It is however conclusive that denitrification rates when using raw CGR will always occur at a faster rate than CGR 10 and PB while denitrification rates when using CGR 10 will always occur at the slowest rate at high initial nitrate concentrations.

It is also acknowledged that, apart from biological denitrification, the adsorption of nitrates by the substrates is also a process which may have contributed to the

removal of nitrates from the system. [35-37] Studies reported that the maximum adsorption potential of agricultural waste ranged between 1.32-1.41 mmol g^{-1} [35] which is slightly higher than PB (1.06 mmol g^{-1}). [36,37] Considering 210 g raw CGR, 235 g CGR 10 and 196 g PB was used in each batch test, it was calculated that the maximum nitrate adsorption capacity was 18.4, 20.5 and 12.9 g, respectively. This means the influence of substrate adsorption decreases with increasing nitrate concentration, showing a maximum nitrate removal potential of ≤ 1 % in the 2000 mg NO_3 L^{-1} batch tests.

3.3. Chemical characterisation of batch tests

The amount of several influential chemical compounds was monitored throughout each batch test in order to determine the limiting/promoting variables associated to the denitrification system. This information provided fundamental insight to the potential application of these substrates.

3.3.1. pH

pH for PB was below the optimal 6-8 at lower nitrate concentrations and only increased to the optimal range in the 2000 mg NO_3 L^{-1} batch test (Figure 1). Sufficient time was given for PB to release hydroxyl ions (OH), at higher nitrate concentrations, resulting in an increase in pH during denitrification. [3] The pH for the CGR substrates largely increased between the start and end points and showed optimal pH at between 6 and 8. The finding supports the hypothesis of increased pH at the onset of denitrification. [3,20,38] It is therefore concluded that pH is not an inhibiting factor affecting denitrification rates in the CGR substrates. However, it is possible that low pH affected optimal efficiency in the PB substrate. It is

recommended that pH be monitored if PB is used at the primary carbon source, particularly in fast flow rates or low nitrate concentrations.

3.3.2. C/N

Raw CGR and PB maintained the highest C/N in all batch tests while CGR 10 contained the lowest (Table 3). The latter was due to substrate stabilisation during composting. Results indicated that the C/N at the end of denitrification, regardless of substrate or nitrate concentration, was still adequate to promote denitrification, according to adequate C/N for stabilised compost proposed by Tsui et al. [20] PB and raw CGR at the end of the 2000 mg NO_3 L^{-1} batch test were both substantially high, with a C/N of 88 and 36, respectively. In contrast CGR 10 showed a substantially lower C/N at the end of the 2000 mg NO_3/L batch test (Table 3). Nevertheless this was still adequate to facilitate denitrification.

3.3.3. COD and Carbon source demand

The sCOD was determined at the start and end of the 2000 mg NO_3 L^{-1} batch tests (Table 4). Results indicated that all batch tests showed a depletion of sCOD during the course of denitrification process, indicating that COD was utilised by microorganisms to facilitate denitrirification. The amount of COD utilised per unit nitrate differed between the carbon sources. The carbon source demand for the raw CGR 2000 mg NO_3 L^{-1} batch test was the highest per unit nitrate removed (Table 4). This indicates that raw CGR provided a readily biodegradable source of carbon which was easily and rapidly utilised by microorganisms. This may partially account for the rapid rate of denitrification observed, in conjunction with the occurrence of chemical denitrification. The CGR 10 batch test showed a carbon source demand almost five times lower than the raw CGR batch test. Combined

with the lower sCOD in the system (Table 4), this suggests that the CGR 10 substrate possessed a lower amount of biodegradable carbon available for utilisation by microorganisms. This consequently may have contributed to the significantly longer amount of time required for complete denitrification.

The PB batch test showed the lowest carbon demand per unit nitrate removed, which was less than half of the CGR 10 carbon demand (Table 4). Considering it facilitated complete denitrification three times faster than CGR 10 and poses the lowest risk to producing high COD effluent (Table 4), it shows high commercial potential.

Results indicate that the stoichiometric relationship between COD and nitrate removal between the carbon sources in non-linear. The amount of COD utilised per unit nitrate removed is substrate dependent, and therefore should be an important determinant when considering carbon loading, in order to maximise microbial carbon utilisation while minimising COD residue in the treated effluent.

The amount of nitrate that was removed per unit mass of total sample when using raw CGR, CGR 10 and PB was also calculated (Table 2). Results indicated that 153.2, 137.1 and 164.5 μmol NO_3 L^{-1} were removed per gram total sample respectively (Table 2). This indicated that PB required the least amount of sample per unit nitrate removed, followed by raw CGR then PB. The amount of carbon source required to facilitate denitrification is an important commercial consideration. Since this value was attained from a single batch test with a maximum nitrate concentration of 2000 mg NO_3 L^{-1}, it is important for future tests to evaluate the maximum amount of nitrates that can be removed per unit substrate. This can be done by either increasing the initial nitrate load or testing substrate longevity until no denitrification occurs.

3.3.4. Nitrogenous compounds

Analysis of the amount of nitrogen in the form of NO_x-N and NH_3-N was investigated to determine the amount of nitrogenous compounds that would leach over time (Figure 1). The leaching of nitrogenous oxides was found to be highest in the CGR 10 substrate at all nitrate concentrations. This finding is in accordance with Trois et al. [3] Considering raw CGR and CGR 10 denitrification rates were similarly efficient at lower nitrate concentrations, it is inferred that the release of nitrogenous compounds does not affect the system's ability to remove nitrates at low nitrate concentrations (short period of time). There was a general increase in the amount of nitrogenous oxides desorbed into the system at increasing nitrate concentrations. This was expected as the substrates interacted with the liquid environment for an extended period. Furthermore, higher nitrate concentrations would lead to an increase in nitrogenous oxides due to the reduction of nitrates through the denitrification process. The use of CGR 10 as a carbon source is therefore not recommended at high nitrate concentrations or in systems with a low flow rate, as the increased levels of nitrogenous compounds is detrimental to the systems efficacy.

The release of NH_3-N and NO_x-N by the PB, particularly at lower nitrate concentrations was negligible (Figure 1), due to its poor leaching ability over a short period. The leaching of nitrogenous compounds when using raw CGR and PB also increased at increasing nitrate concentrations, however, the extent of which did not affect the system's efficiency.

3.4. Genuine leachate batch tests

Results from genuine leachate batch tests (Table 5) did not parallel the synthetic leachate batch tests (Table 2). The main differences observed were as follows: i)

genuine leachate had a slight inhibitory effect on raw CGR and PB while it had a favourable effect on CGR 10 with regards to denitrification efficiency and ii) raw CGR showed a significantly lower lag phase compared to the synthetic leachate batch test, while CGR 10 showed a significant increase in its lag phase. In contrast PB remained consistent.

The feasibility of using the same substrate without replenishment to facilitate denitrification was tested by running the batch tests twice, without renewing the substrates. Results presented in Table 5 indicate that there was a complete elimination of a lag phase in the raw CGR and PB substrates after Phase 1. It is likely that this was due to the establishment of an adapted microbial community during Phase 1. [31] The denitrification efficiency also increased significantly from Phase 1 to Phase 2 as a result. There was a 27% increase in denitrification efficiency with the raw CGR substrate and a 12% increase with PB.

While CGR 10 showed an increase in denitrification rates between the synthetic and genuine leachate batch tests, it showed a decrease in denitrification efficiency between Phase 1 and Phase 2. There was a 2.5 times increase in the lag phase and an over 3 times reduction in denitrification rate. This is likely a result of a decrease in the amount of biodegradable carbon available to the microorganisms and an increase in the desorption of nitrogenous and other toxic compounds into the system as suggested by Trois et al. [3]

3.5. Decision support tool for use of raw CGR, CGR 10 and PB.

The potential value of each substrate depends on the process variables. Table 6 presents a comparative analysis of the process variables, which when combined with a matrix to evaluate the Strengths, Weaknesses, Opportunities and Threats (SWOT) involved with using raw CGR, CGR10 and PB (Table 7), serves as a

decision support tool. The carbon source is fundamentally important to a denitrification system. [19] The choice of carbon source should be case specific and should account for cost, amount of sludge produced, potential denitrification rate, carbon utilisation capacity, effluent characteristics, ease of handling, storing safety and toxicity. [19]

An important determinant for the choice of carbon source is the frequency at which each substrate is required to be replaced. Factors that could influence rate of substrate renewal include: chemical environment of the system, COD availability and excessive biomass growth. [26] Results suggested that both raw CGR and PB could be used over a long period of time without the need for frequent renewal as they maintained a suitable chemical environment with sufficient carbon to support microbial communities.

The accumulation of excessive biomass on the surface of the substrate could also lead to the need for substrate renewal. Trois et al. [21] enumerated microbial biomass when using CGR 10 and PB during the denitrification process. Their results indicated that that when CGR 10 was used, biomass decreased by five orders of magnitude in the first two days, and thereafter maintained a constant level until denitrification was complete. Biomass present when using PB was initially ten times higher than biomass present when using CGR 10. A logarithmic decrease of biomass was observed over the first seven days, reducing by one order of magnitude. While this indicates that biomass growth for both CGR 10 and PB was limited for the duration of the denitrification process, an investigation of biomass over a longer denitrification period of time is necessary.

Results from this study are being used towards the development of an innovative low-cost and low-energy biological denitrification reactor in the form of a flowing anaerobic filter bed at the Mariannhill landfill site, in Durban. Further research is

required to investigate the longevity of raw CGR, CGR 10 and PB and the chemical and biological influences of nitrate removal.

The use of raw CGR seems to be the most promising of these alternative carbon sources as: low levels of ammoniacal nitrogen and nitrogenous oxides at all nitrate concentrations were leached into the system, there was a short lag phase and there was sufficient carbon to be used sustainably over a long period of time. A drawback of the use of raw CGR is the production of high COD effluent. It is therefore recommended that a COD polishing plant should be attached to the denitrification reactor, such as an aerobic reed bed.

4. Conclusions

Overall this study demonstrated that raw CGR, CGR 10 and PB, could be used as an effective and sustainable carbon source for biological denitrification. The substitution of conventional carbon sources for alternative waste carbon sources provides a more integrated treatment option than conventional treatment. No work has previously been conducted investigating the feasibility of using CGR and PB as a carbon source in such detail. This information allowed for the generation of a novel decision support tool, and added fundamental insight for the development and implementation of a biological anaerobic filter bed at the Mariannhill Landfill Site, Durban, South Africa.

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Table Captions

Table 1: Characterisation tests conducted on solid and eluate phases of raw CGR, CGR 10 and PB and on nitrified leachate obtained from the Mariannhill landfill site in Durban, South Africa.

Table 2: Batch test performance for the 100, 500 and 2000 mg NO_3 L^{-1} batch tests conducted using raw CGR, CGR 10 and PB. Removal rate excludes acclimatisation phase

Table 3: C/N ratio change in the batch tests

Table 4: Carbon source demand for nitrate removal when using raw CGR, CGR 10 and PB at 2000 mg NO_3 L^{-1}

Table 5: Lag, reduction and total time of denitrification for 2000 mg NO_3/L MSW nitrified leachate batch tests conducted when using raw CGR, CGR 10 and PB.

Table 6: Comparative analysis of denitrification system process variables for raw CGR, CGR 10 and PB

Table 7: SWOT analysis for raw CGR, CGR 10 and PB

Figure Captions

Figure 1: NH_3-N and NO_x-N leached from substrates and pH at intermittent points throughout the 100 (A), 500 (B) and 2000 (C) mg NO_3 L^{-1} batch tests

Figure 2: Nitrate removal rate curves during the reduction phase when using raw CGR, CGR 10 and PB at 100 (A), 500 (B) and 2000 (C) mg NO_3 L^{-1}