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The Fate of Nitrogen in Bioreactor Landfills

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Although bioreactor landfills have many advantages associated with them, challenges remain, including the persistence of ammonia-nitrogen in the leachate. It has been suggested that ammonia-nitrogen is one of the most significant long-term pollution problem in landfills and is likely a parameter that will determine when landfill postclosure monitoring may end. The fate of nitrogen in bioreactor landfills is not well understood. As more landfills transition operation to bioreactors, more attention must be paid to how operating the landfill as a bioreactor may affect the fate of nitrogen. Processes such as sorption, volatilization, nitrification, denitrification, anaerobic ammonium oxidation, and dissimilatory nitrate reduction may all occur.

KEY WORDS: aerobic treatment, ammonia-nitrogen, denitrification, leachate, nitrification

I. INTRODUCTION

A new and promising trend in solid waste management is to operate the landfill as a bioreactor. Bioreactor landfills are controlled systems in which moisture addition (often leachate recirculation) and/or air injection are used to create a solid waste environment capable of actively degrading the readily biodegradable organic fraction of the waste. Several researchers have documented the benefits associated with bioreactor technology.[79,90,98,101,126] One

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advantage is that increased waste degradation rates characteristic of bioreactor landfills permit the life of a bioreactor landfill to be expanded beyond that of conventional landfills through recovery of valuable airspace. As leachate is recirculated, it is treated in situ, decreasing its organic strength and thus potential impact to the environment. In situ treatment potentially reduces the length of the postclosure care period and associated costs.[90,99,101] Additionally, bioreactor landfills stimulate gas production; the majority of the methane is produced earlier in the life of the landfill, allowing for more efficient capture and subsequent use.

Although the organic strength of the leachate is significantly reduced in bioreactor landfills, ammonia-nitrogen remains an issue. The ammonia-nitrogen concentrations found in leachate from bioreactor landfills are greater than those found in leachate from conventional landfills.[7,82] Ammonia-nitrogen tends to accumulate in both systems because there is no degradation pathway for ammonia-nitrogen in anaerobic systems. However, in bioreactor landfills, moisture addition and/or recirculating leachate increases the rate of ammonification, resulting in accumulation of higher levels of ammonia-nitrogen, even after the organic fraction of the waste is degraded.[7,17,82,93] The increased ammonia-nitrogen concentrations intensifies the toxicity of the leachate to aquatic species,[125] potentially inhibiting the degradation process and necessitating leachate treatment before ultimate disposal to protect receiving waters.[17] It has been suggested that ammonia-nitrogen is one of the most significant long-term pollution problem in landfills,[7] and it is likely that the presence of ammonia-nitrogen will determine when the landfill is biologically stable and when postclosure monitoring may end.[93] Thus an understanding of the fate of nitrogen in bioreactor landfills and possible mechanisms for ammonia-nitrogen removal is critical to both a successful and economic operation.

As more and more landfills transition operation to bioreactors, more attention must be paid to how operating the landfill in such a manner may affect the fate of nitrogen. The in situ physical, chemical, and biological processes in bioreactor landfills differ from those typically observed when operating a landfill conventionally, potentially resulting in different nitrogen transformation and removal processes. The fate of nitrogen in bioreactor landfills is not well understood. Because of the adverse impact ammonia-nitrogen has on the environment, an understanding of nitrogen transformation processes in bioreactor landfills is necessary to ensure adverse environmental impacts and/or treatment costs are minimized by expanding the current use of landfills to include in situ leachate treatment.

This article discusses the nitrogen transformation and removal processes that may occur in bioreactor landfills. Little research has been conducted evaluating the fate of nitrogen in bioreactor landfills, or in conventional landfills for that matter. However, it is suspected that processes that typically occur in wastewater treatment and in soils will also occur in bioreactor landfills, but in a much less controlled fashion, as the inherent variability and heterogeneities in bioreactor landfills do not allow for them to be operated with the high level of control possible in wastewater treatment processes. Using wastewater and soil literature, as well as landfill-related literature, nitrogen removal and transformation processes that may occur in bioreactor landfills are discussed and evaluated in this review.

II. BIOREACTOR LANDFILL OPERATION

Traditionally, landfills have been thought of as storage and containment systems, functioning primarily to entomb the waste. Recently, however, the focus of solid waste management has changed to regarding the landfill as a complex biological system capable of managing solid waste in a more proactive manner, acting to degrade the readily biodegradable material.[88,100,101] Because bioreactor landfill environments are different from conventional landfills, there is potential for a greater number of nitrogen transformation and removal processes to occur and for them to occur to a greater extent than in conventional landfills. System design of bioreactor landfills provides the flexibility in the location and duration of liquid and air injection, allowing for adjustment of pH, oxidation–reduction potential (ORP), and moisture content to create an environment conducive to microbial degradation and biological nitrogen removal. System design is rigid with respect to parameters such as waste composition and age (i.e., organic carbon content); waste components cannot be controlled and vary from landfill to landfill, while waste age varies from location to location within a landfill. Thus, in a landfill, the active control of in situ reactions and nitrogen removal/transformation is generally restricted by the location and volume of injected liquid and air.

Liquid addition to landfills has many advantages associated with it. Leachate recirculation involves the collection and redistribution of leachate through the landfill. Moisture addition and movement are important factors affecting waste biodegradation, resulting in an increase in the moisture content of the waste and distribution of nutrients throughout the landfill, respectively. Optimal levels of moisture content have been found to be between 40 and 70%, on a wet-weight basis.[6] Much research has been conducted evaluating the benefits associated with increasing the moisture content of solid waste and can be found elsewhere.[101] At times, insufficient leachate is available and it is necessary to supplement with other liquids such as groundwater, stormwater, wastewater, or surface water.

Achieving uniform liquid distribution is difficult. Waste heterogeneities and differences in compaction within landfills create distribution challenges. Injected liquid will flow around areas with lower hydraulic conductivities and channel through the waste following preferential flow pathways formed by areas of higher hydraulic conductivites; the areas of higher hydraulic conductivity may be due to waste heterogeneity or differences in compaction ratios.[73] The nonuniform distribution that occurs results in portions of the landfill (on both a micro and macro level) having various moisture contents and thus different waste degradation rates; therefore, several microbial consortiums will be present, potentially in close proximity to one another, allowing for different types of microbial degradation and thus nitrogen removal/transformations to occur simultaneously. Differential settlement may also occur as a result of the changes in waste degradation with respect to location. There are different methods that can be used to reinject leachate or add liquid to landfills, including horizontal trenches and vertical injection pipes. These recirculation methods have been reviewed elsewhere.[98,99] Reintroduction rates, for horizontal trenches, vary from 0.15 to 0.30 gpm/ft trench, while vertical injection rates in wells are generally from 0.5 to 2.5 gpm.[101]

Air addition has also been used as an enhancement and has been shown to enhance degradation processes in landfills at both the field and laboratory scale.[4,36,68,74,79,96,112] Adding air uniformly throughout the waste is also a challenge. Not only do waste heterogeneities and compaction affect the air distribution, the presence of moisture does as well. Air will take the path of least resistance; thus, there will likely be areas of an aerobic landfill in which air does not reach, resulting in anoxic or anaerobic pockets within the waste mass.

Generally, bioreactor landfills undergo the same degradation processes as conventional landfills, just at a faster rate and to a greater extent because of the optimization of in situ conditions. However, degradation pathways may vary depending on the operation of the bioreactor landfill. Compared with conventional landfills, bioreactor landfills have shown a more rapid and complete waste conversion and stabilization process.[46,90,98,126] Increased waste degradation rates characteristic of bioreactor landfills may allow for the life of a bioreactor landfill site to be expanded beyond that of a conventional landfill, potentially allowing for the reuse of one site rather than construction of many. Because waste degradation rates increase in bioreactor landfills, airspace may be created by settlement and filled prior to closure. Moisture injection increases the rate of initial settlement due to additional unit weight, and, over time, increases the extent of waste degradation, all resulting in the recovery of a significant volume of airspace. For example, Reinhart and Al-Yousfi[99] reported that for one landfill 13–15% settlement occurred over a 4-year period when recirculating leachate; a dry control cell at the same site settled only 8–12%. Bioreactor landfills also provide a means to store and/or treat leachate. As leachate is recirculated, it is treated in situ via naturally occurring processes such as adsorption, ion exchange, and mechanical filtration,[91] significantly decreasing both the organic strength (i.e., chemical oxygen demand [COD] and biochemical oxygen demand [BOD] by almost 50%) and heavy metal content, thus reducing impact to the environment were the leachate to reach the groundwater or surface water.[90,99] Not only can leachate be treated within bioreactor landfills, but it may also be stored by adsorption by the waste, rather than stored external to the landfill. Perhaps the biggest advantage of bioreactor landfills is the reduction of landfill biological stabilization time.[99] This reduction in time has been repeatedly proven through the reduction of COD half-lives in landfills utilizing leachate recirculation;[101] COD half-lives in leachate from conventional landfills have been calculated to be around 10 years, whereas for bioreactor landfills, the COD half-life of the leachate is closer to 230 to 380 days.[99,101]

Four types of bioreactor landfills have been explored, each with different operating schemes to obtain optimal results: anaerobic, aerobic, facultative, and hybrid systems. Each bioreactor type is a patented process.[43,47,48,53]

A. Anaerobic Bioreactor Landfills

Anaerobic bioreactor landfills are those in which moisture addition is practiced. Sources of liquid addition may include groundwater, stormwater, infiltrating rainfall, or leachate. Moisture content adjustment results in enhanced methane production, which has been repeatedly demonstrated in several laboratory, pilot, and field-scale studies.[27,36,84,88,98,117,118] Because waste degradation is enhanced in anaerobic bioreactors and organic material is returned to the landfill via leachate recirculation,[99] methane is produced at a much faster rate. The total volume of gas produced also increases, as organics in the leachate are recycled and then biodegraded within the landfill. The majority of gas production may be confined to a few years, earlier in the life of the landfill, than traditionally occurs in conventional landfills, allowing for more efficient capture and subsequent use.[99] Gas production time frames are highly dependent on the moisture content of the waste. Modeling of gas production from bioreactor landfills requires different parameters than used for conventional landfills.[7,33] As the parameters are fitted for wet landfills, the time for 99% of the methane to be produced may decrease by almost 14-fold.[33] Although the vast majority of the gas will be produced relatively early after closing the landfill (within 20 years), limited methane production may continue over long periods of time due to wetting of previously unreached dry areas.

Anaerobic bioreactor landfills are more effective at degrading the solid waste than conventional landfills. However, when compared to other types of bioreactor landfills, anaerobic systems tend to have lower temperatures and slower degradation rates.[74,112] A disadvantage to operating the landfill as an anaerobic bioreactor is the accumulation of ammonia-nitrogen. In anaerobic bioreactor landfills, the ammonia-nitrogen present in the leachate is continually returned to the landfill, where there is no degradation pathway for ammonia in anaerobic environments. An advantage of operating the bioreactor anaerobically when compared to other bioreactor landfill types is that air is not added; therefore the operational costs are less than what would be incurred aerobically and methane can be captured and reused.

B. Aerobic Bioreactor Landfills

Adding air to landfills has been shown to enhance degradation processes in landfills, as aerobic processes tend to degrade organic compounds typically found in municipal solid waste (MSW) in shorter time periods than anaerobic degradation processes.[5,68,79,96,112] Reported advantages of operating the landfill aerobically rather than anaerobically include increased settlement, decreased metal mobility, reduced ex situ leachate treatment required, lower leachate management and methane control costs, and reduced environmental liability.[30,96] Both laboratory and field-scale studies have been conducted showing the effectiveness of the aerobic bioreactor landfill system.[68,74,110]

Many of the nitrogen transformation/removal process are favored by aerobic processes, including nitrification and ammonia air stripping or volatilization. Air stripping and volatilization may be favored in aerobic bioreactor landfills because of higher pH levels and temperatures that are inherent in an aerobic environment. The additional gas flow associated with air injection may also induce greater masses of ammonia-nitrogen removal.

During aerobic degradation of MSW, biodegradable materials are converted mostly to carbon dioxide and water. Little, if any, methane is produced, which may be viewed as either an advantage or disadvantage, depending on whether methane collection and use as an energy source is desired or required. Methane is a potent greenhouse gas; thus, if it cannot be efficiently controlled and collected in anaerobic landfills, its production can be a local environmental concern. Further, the solid waste environment during aerobic degradation has a fairly neutral pH,[44,74,96,112] which decreases metal mobility. Volatile organic acid production is decreased in aerobic bioreactors because the anaerobic fermentation processes are limited. However, volatile acid and methane production may still occur in anaerobic pockets within the landfill.

The aerobic process generates a considerable amount of heat, leading to elevated in situ temperatures as high as 66°C.[4,74,112] The elevated temperatures increase evaporation, which results in a significant loss of leachate. As a consequence, there is less leachate to manage.[30] The high temperatures may limit certain biological nitrogen transformation processes from occurring, although no data regarding temperature effects are available. Additionally, the combination of the high temperatures and presence of air may create a fire potential. However, by minimizing methane production and ensuring proper moisture contents, fire potential is lessened.

Odors often associated with anaerobic systems, such as from hydrogen sulfide and volatile acids, are reduced in aerobic bioreactor landfills. Aerobic processes do have some odor associated with them; however, it is an earthy smell. Some odorous compounds emitted by aerobic composting include methanethiol, which has a pungent sulfide odor.[77]

C. Hybrid Bioreactor Landfills

Another, less studied type of bioreactor landfill that shows promise is the hybrid bioreactor. This type of bioreactor landfill is still in the early stages of development. Hybrid bioreactor landfills involve the combination of both aerobic and anaerobic conditions. Two types of these aerobic/anaerobic systems have been explored: short-term cycling of air injection into the landfill, and sequencing of aerobic and anaerobic conditions.

Cycling of air injection into the landfill is defined as a pattern of alternating in situ aerobic and anaerobic conditions that is repeated throughout the life cycle of the landfill, while sequencing of air injection into the landfill involves an initial aerobic phase, followed by a final anaerobic phase. Because there are many advantages associated with both aerobic and anaerobic degradation processes, researchers see combining the processes as a way to maximize the potential of a bioreactor landfill. There are some components in both the waste and the leachate that are recalcitrant in anaerobic conditions but degradable in aerobic environments, such as lignins and aromatic compounds. Utilizing one of these hybrid techniques may allow for the leachate and/or waste to be treated more completely.[10,86,100] Operating a bioreactor landfill as a hybrid system may serve to combine several nitrogen transformation and removal processes, such as nitrification and denitrification, potentially resulting in complete in situ removal of nitrogen from landfills.

A few laboratory studies have been completed evaluating the effect of cyclic air injection on the performance of bioreactor landfills.[10,86,132] Each cyclic air injection system evaluated achieved a more biologically stable leachate with respect to COD in a shorter period of time than that experienced by purely aerobic systems. Ziehmann and Meier[132] conducted both laboratory and pilot-scale studies evaluating this technique. Three bioreactor systems were operated for 180 days. Anaerobic and aerobic conditions were cycled based on the methane concentration measured; once the methane concentration reached 2.5% by volume, air was added. Results from the laboratory study showed that the leachate from the reactor in which aerobic and anaerobic conditions were alternated had lower concentrations of total organic carbon and COD than those from either the anaerobic or aerobic reactors. However, when operating the pilot-scale study, there was little difference between the cyclic and continuously aerobic reactors, suggesting that the advantages of the cyclic system seen in the small-scale studies may not be realized at field scale. Each study was conducted over short time periods, so additional long-term studies are needed to evaluate this process further.

A few studies have also evaluated the effect of a sequencing air-injection system.[12,111] In this system, waste is placed in lifts. The first lift is aerated for a period of time; when the second lift is placed, aeration of the first layer stops and aeration of the second layer commences. Leachate is continuously recirculated. This process continues until the landfill is filled.[47] It is hypothesized that this system acts to speed typical anaerobic degradation processes, specifically the onset of methanogenesis. By initially aerobically degrading the waste, the temperature of the waste is increased and the extent of the acidogenic phase is reduced, thus allowing for the early onset of methanogenesis. Fletcher et al.[35] conducted a study that demonstrated the effect of increasing temperatures on methane production. Air was briefly added to an older landfill using vertical injection wells to promote aerobic activity. As a result of the air addition, local temperatures increased by 17°C. Methane production was stimulated as a result of the increase in temperature.

Stegmann and Spendling[111] conducted lysimeter tests evaluating sequencing of air addition. In their studies, waste was loosely placed in thin layers (from 0.4 to 2 m) with no cover to allow natural air diffusion into the waste; leachate was also recirculated. In the lysimeters with the 0.4-m lifts, a new loosely placed lift of waste was applied every 6 weeks. Another lysimeter was operated with waste placed in 2-m lifts; after 2 years, another 2-m layer of loose waste was placed. The addition of waste lifts prevented air intrusion into the lower layers of waste, resulting in the lower layers becoming anaerobic. The investigators found that the waste placed in thinner layers resulted in the production of methane earlier. Because of the initial aerobic degradation of the readily biodegradable organics, it was hypothesized that the organic acid production was reduced and did not reach concentrations inhibitory to methane production. Methane production rates were not measured.

D. Facultative Bioreactor Landfills

Facultative bioreactor landfills are operated with the intent of actively degrading the waste mass and, at the same time, controlling high ammonia-nitrogen concentrations typically found in the leachate from bioreactor landfills. In facultative systems, leachate is removed from the bioreactor landfill and nitrified in an external treatment system prior to recirculation.[48] Thus, the ammonia-nitrogen concentrations of the treated leachate are low to nonexistent, while the nitrate levels are high. As the nitrate-rich leachate is recirculated and passes through the landfill, denitrification occurs, since several microorganisms, including facultative microorganisms, use the nitrate for respiration. Although this type of bioreactor has not been evaluated in many studies, there is laboratory evidence suggesting that implementation of such a system is plausible.[92,93,119] Price et al.[93] conducted a laboratory-scale study demonstrating the ability of this process to denitrify nitrified leachate as it passed through the waste. The Outer Loop Landfill in Louisville, KY, is in the process of using this approach for controlling nitrogen discharges.[119] A disadvantage of this technique is that external treatment of leachate for ammonia-nitrogen removal must occur, which adds an extra step to the bioreactor landfill process and can be both difficult and costly because of high levels of ammonia-nitrogen in the leachate. Additionally, while denitrification of the leachate is occurring, methane production may be halted until the nitrate is consumed. It has been shown that methane production quickly resumes after nitrate is depleted.[93]

III. AMMONIA-NITROGEN IN LEACHATE

The ammonia-nitrogen in leachate is derived from the nitrogen content of the waste; the concentration is dependent on the rate of solubilization and/or leaching from the waste. The nitrogen content of MSW is less than 1%, on a wet-weight basis,[113] and is composed primarily of the proteins contained in yard wastes, food wastes, and biosolids.[17] As the proteins are hydrolyzed and fermented by microorganisms, ammonia-nitrogen is produced. This process is termed ammonification. Researchers report concentrations range from less than detection levels to over 5000 mg/L.[28,39,95,101]

Leachate composition is quite variable, depending highly on waste composition, moisture content of the waste, and age of the landfill. Table 1 provides ammonia-nitrogen concentration ranges for both conventional and bioreactor landfills as a function of waste age as summarized by Reinhart and Townsend.[101]

Removal of ammonia-nitrogen from leachate to low levels is necessary because of its aquatic toxicity and oxygen demand in receiving waters. Several researchers have conducted tests to measure the toxicity of leachate, concluding that ammonia-nitrogen significantly contributed to the toxic nature of the leachate.[7,61,125] In landfill leachate, the vast majority of the ammonia-nitrogen species will be in the form of the ammonium ion (NH_4^+) because pH levels are generally less than 8.0.[96,100,119] Figure 1 provides the distribution of ammonia and ammonium as a function of pH. Dissolved unionized ammonia (predominant at pH levels above 10) is more toxic to anaerobic degradation processes than ammonium ions but should not be present in significant concentrations in a landfill. Ammonia-nitrogen concentrations greater than

TABLE 1. Ammonia-Nitrogen Concentrations in Both Conventional Bioreactor Landfills with Respect to Degree of Landfill Biological Stabilization[101]

	Concentration (mg/L as N)	
Stabilization phase	Conventional landfills	Bioreactor landfills
Transition	120–125	76–125
Acid formation	2–1030	0–1800
Methane fermentation	6–430	32–1850
Final maturation	6–430	420–580

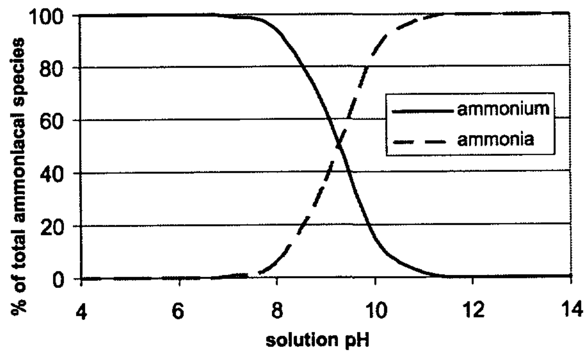

FIGURE 1. Dominant form of ammoniacal nitrogen in solution at 25°C at various pH levels.

500 mg/L as N are inhibitory to the degradation process.[66] Ammonium concentrations between 50 and 200 mg/L have been shown to be beneficial to anaerobic degradation processes in wastewater treatment, while ammonium concentrations between 200 and 1000 mg/L have been shown to have no adverse effect. Concentrations ranging from 1500 to 5500 mg/L have been shown to have inhibitory effects at higher pH levels, and concentrations above 5800 mg/L have been shown to be toxic to some microorganisms.[66] However, the effect of ammonium concentrations on landfilled waste degradation has not been reported.

IV. NITROGEN TRANSFORMATION AND REMOVAL PROCESSES

Currently, ammonia-nitrogen is treated in leachate ex situ to the landfill.[21,52,54,70,109,127] Ammonia-nitrogen removal methods often include complex sequences of physical, chemical, and/or biological processes, including chemical precipitation, nanofiltration, air stripping, and biological nitrification/denitrification via various reactor configurations (i.e., rotating biological filters, suspended and attached growth reactors). However, operating the landfill as a bioreactor provides opportunities for in situ nitrogen transformation and removal processes. Little research has been conducted evaluating the fate of nitrogen in bioreactor landfills; however, understanding the possible nitrogen transformations is important when considering potential leachate management options. When adding air to landfills, biological processes such as nitrification traditionally found and expected only in landfill cover soils as a result of air diffusion may now occur within the waste mass. Additionally, recirculating nitrified leachate allows for denitrification processes to occur in anoxic areas found in both anaerobic and aerobic bioreactor landfills. Figure 2 illustrates the potential nitrogen transformation and/or removal pathways that may occur in bioreactor landfills.

The heterogeneous nature of solid waste complicates the nitrogen cycle in bioreactor landfills. Because the waste is heterogeneous, portions of the

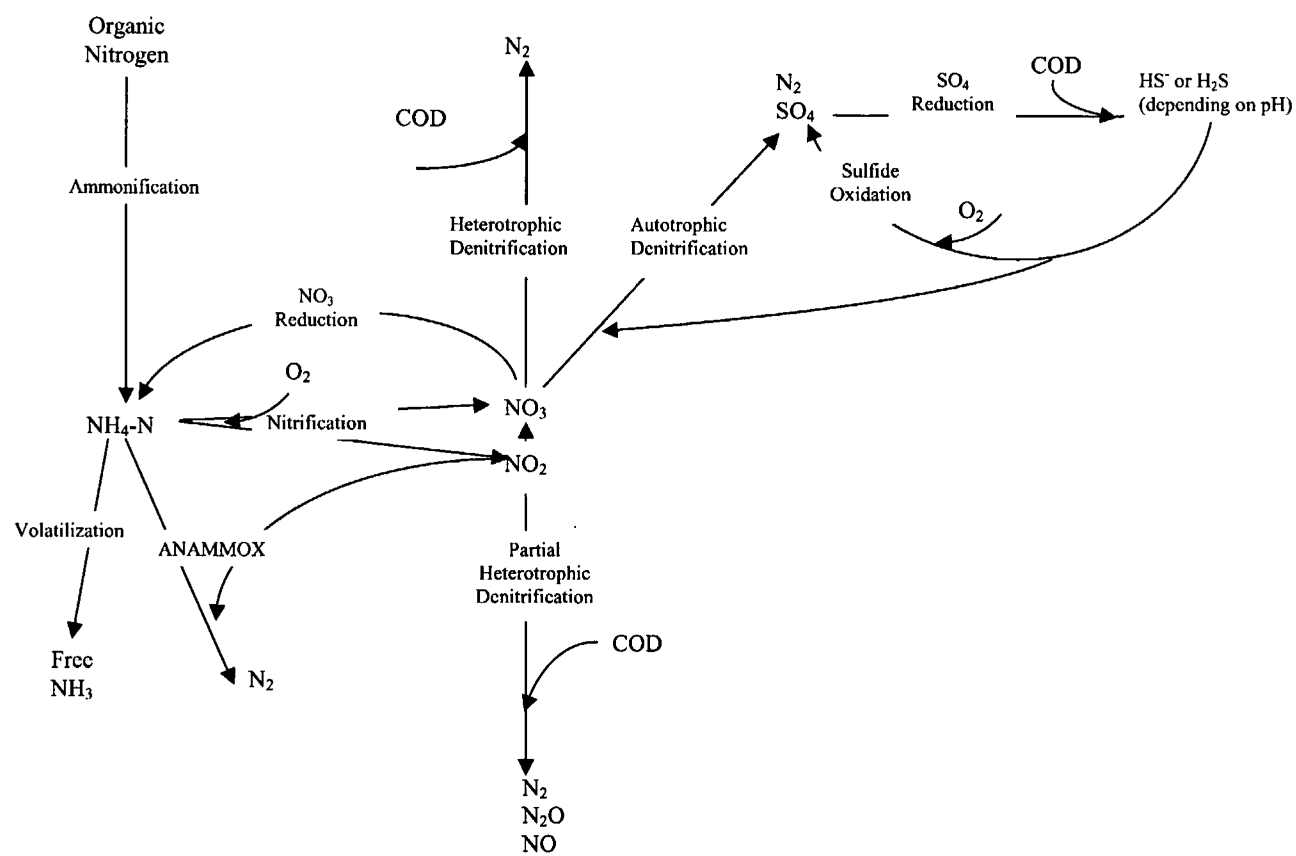

FIGURE 2. Potential pathways of nitrogen transformation and/or removal in bioreactor landfills.

landfill may contain different amounts of nutrients, be at different temperatures, have different moisture levels, and may be at different ORPs. Environmental conditions greatly affect the transformation and removal of nitrogen. Thus, within one landfill cell, there may be many nitrogen transformation processes occurring simultaneously or sequentially. Processes commonly found in wastewater treatment processes and in soils, such as ammonification, sorption, volatilization, nitrification, denitrification, anaerobic ammonium oxidation (ANAMMOX), and nitrate reduction, may all occur in bioreactor landfills. This section discusses how the nitrogen transformation and removal processes found in wastewater and/or soils may also occur in bioreactor landfills based on the current knowledge associated with each process.

A. Ammonification

Proteins present in the waste are the major source of ammonia-nitrogen. This conversion of organic nitrogen to ammonia-nitrogen by heterotrophic bacteria is termed *ammonification*. Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids.[17] During deamination, amine groups are liberated to form ammonia or ammonium, depending on the pH, and alkalinity is slightly elevated.[17] The deamination process is illustrated in Figure 3. Once ammonification occurs, the

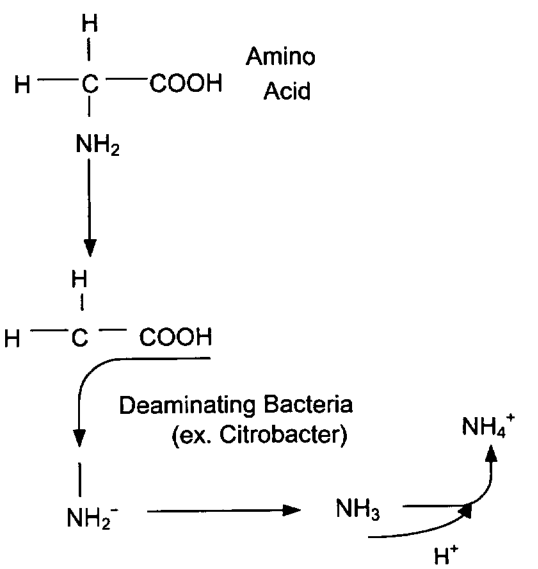

FIGURE 3. The deamination process.

ammonia-nitrogen is dissolved in the leachate and is ready to be transformed and/or removed via volatilization, sorption, or biological processes when in an aerobic environment. The pH also increases during ammonification. Any free ammonia that is present is highly reactive and has been found to combine with organic matter (i.e., carboxyls, quinine hydroxls), making them more biodegradable.[85] Thus, in landfills, any ammonia that is produced within the landfill may redissolve and react with organic matter before exiting the landfill.

Little research has been conducted evaluating the rate of ammonification in landfills. However, ammonia-nitrogen release from wastes has been evaluated in both solid waste digestion and composting studies.[25,107] Ammonification rates were not quantified, although the generation trends appear to follow first-order reaction kinetics. Additionally, ammonification occurs during the organic hydrolysis phase of landfill stabilization, which is also often represented by first-order kinetics.[3,42] In compost, ammonification has been found to be optimal between 40 and 50°C.[104]

B. Ammonium Flushing

The mass of ammonia-nitrogen that can be leached from the waste is controlled by the volume of water passed through the landfill, the nitrogen content of the waste, and the ammonia-nitrogen concentration in the bulk liquid. Reducing ammonia-nitrogen concentrations by washout and dilution to acceptable levels within a landfill requires the addition of large volumes of water. The Institute of Waste Management Sustainable Landfill Working Group[55] reported that at a solid waste moisture content of 30% (wet weight basis) and an initial liquid-phase ammonia-nitrogen concentration of 5833 mg/L as N, a flushing volume of approximately 2.4 m^3/tonne of waste was necessary to reduce the nitrogen concentration to 2 mg/L as N. It was also noted that other studies had been conducted suggesting that flushing volumes between 5 and 7.5 m^3/tonne of waste were needed to adequately reduce nitrogen concentrations in the landfill. No time frames for this reduction to occur were given. The effectiveness of flushing will be dependent on hydraulic conductivity of the waste, as it will be harder to introduce liquid in areas of lower permeability. As the hydraulic conductivity decreases, the time required for leaching to occur increases, as does the ammonification process.

Purcell et al.[94] conducted a laboratory-scale study evaluating the flushing of ammonia-nitrogen from landfills. It was found that as flushing rates increased from 435 mm/year to 2195 mm/year, the release of ammonium-nitrogen from the waste and thus overall removal from the reactors increased. The main mechanisms of ammonia-nitrogen removal were found to be washout and dilution from the incoming water.

Flushing results in the removal of ammonia-nitrogen from landfills by adding large volumes of water, which must be treated externally. When operating the landfill as a bioreactor, leachate is recycled, and hence ammonia-nitrogen is continually reintroduced to the landfill while additional ammonia is solubilized into the leachate.

C. Ammonium Sorption

Sorption of ammonia-nitrogen to waste may be significant in bioreactor landfills because of the high ammonium concentrations present. Ammonium is known to sorb onto various inorganic and organic compounds.[65] The amount of ammonium sorbed on some organics has been reported to exceed the mass found in the bulk liquid.[81] Sorption of ammonium to the waste will allow for temporary storage of ammonium prior to it being used in other processes, such as nitrification and volatilization, and may also result in the slow dissolution of ammonium over time.[50]

Sorption is dependent on pH, temperature, ammonium concentration, and ionic strength of the bulk liquid. For ammonia to sorb to waste particles, it must be in the form of ammonium (NH_4^+). At pH levels expected in a landfill, the dominant form of the ammonia species is the ammonium ion,[75] as depicted in Figure 1. As ionic strength of the bulk liquid increases, sorption of ammonium tends to decrease[50,81] due to ion-exchange effects. The sorbed ammonium is released and exchanged with other ions present in the bulk liquid, especially those with higher selectivity or concentration. A common procedure used to extract sorbed ammonium from solid particles involves the addition of a sodium or potassium sulfate solution. The sodium or potassium ions exchange with the ammonium, allowing for the ammonium to desorb from the waste. The conductivity of landfill leachate is generally high (approximately 7000 μmho/cm)[61] and thus may influence ammonium sorption. The effect of the ionic strength in leachate on the sorption of ammonium needs to be evaluated.

In marine sediments, sorption of ammonium has been shown to follow a Langmuir-type isotherm.[65] However, Nielson[81] conducted a study of ammonium sorption to activated sludge and found the data did not fit well to that isotherm type. Little work has been conducted evaluating ammonium desorption, which is important to predict the amount of ammonium that will be available for treatment over time.[81] Nielson[81] found that a portion of sorbed ammonium on activated sludge flocs was oxidized and used during the nitrification processes; however, a significant portion of the sorbed ammonium remained unoxidized, even when the ammonium in the bulk water was almost completely removed via nitrification. Ammonium desorption kinetics may be dependent on ammonium removal in the bulk liquid; as the ammonium concentration in the bulk liquid decreases, potentially due to flushing or other removal processes, ammonium is likely to be desorbed from the waste to regain equilibrium.[50] Ionic strength affects were not evaluated in this study; however, they were noted to potentially impact the sorption and desorption properties of ammonium.

Ammonium sorption in soils has also been measured. Kwok and Loh[64] conducted a laboratory-scale study evaluating the cation-exchange capacity of different soil types in Singapore. In each isotherm study, ammonium sorption followed a Freundlich isotherm; sorption increased with increasing exchange capacity. Van Raaphorst and Malchaert[122] conducted ammonium sorption studies on various sea sediments and found the sorption data to also follow a Freundlich isotherm. Additionally, Van Raaphorst and Malchaert[122] conducted a study in which they measured the mass of ammonium that could be extracted from a sediment using a potassium chloride solution over a 40-h time period. They found that exchange of ammonium was initially rapid (during the first 10 h), but declined significantly after 10 h. During the 40-h test, not all of the ammonium was recovered, suggesting that some of it was tightly bound to the soil particles.

Studies evaluating the sorptive capacity of fresh waste have not been conducted; however, the sorptive capacity of peat and soil has been studied. Heavey[50] found that peat (which may simulate well-oxidized waste) could sorb 18 to 27 mg NH_4^+/g dry peat. It seems probable that more sorption occurs in older solid waste than in younger waste because older waste has a smaller particle size and thus a larger surface area, yielding more available reactive sites for sorption. Additionally, older waste contains more recalcitrant organic particles (predominantly humic and fulvic acids) to which ammonium may sorb. Further, as waste ages, there may be changes in the surface charges of the waste, resulting in higher levels of sorption. The presence of complex organics has been shown to influence ammonium sorption; the ammonium ions may fix irreversibly to these molecules. He et al.[49] found that approximately 15% of the radiolabeled ammonium they added to soil samples was associated with the humic fractions; however, the ammonium was recoverable using a series of several different types of extraction media. Reinhart[97] conducted long-term desorption isotherms with various organic pollutants and MSW and found that as time increased, the mass of sorbed compound increased. It was suggested that sorption may be time dependent; the compound may sorb deeper into the solid phase over time, ultimately allowing for sorption of more mass over time. A similar phenomenon of irreversible sorption in soils has been observed[14,78,120] and will likely occur with ammonium. More research on the sorption and desorption of ammonia-nitrogen on MSW is necessary.

D. Volatilization

In conventional landfills, ammonia makes up approximately 0.1 to 1.0% (dry volume basis) of landfill gas exiting the landfill.[113] Ammonia is not a greenhouse gas, so its impact on the environment is not as harmful as methane; however, there are some adverse health effects that may result from exposure to the gas. Ammonia has a pungent odor and is a respiratory-tract irritant.

Also, ammonia gas can dissolve in the moisture on skin and form ammonium hydroxide, a corrosive chemical that can cause skin irritation.[72]

Volatilization only occurs when free ammonia is present. At pH levels above 10.5 to 11.5, the majority of the ammonia-nitrogen present in solution is in the form of free ammonia gas (NH_3), as depicted in Figure 1. The free ammonia concentration at a particular pH level may be computed via Eq. (1).

$$[\mathrm{NH_3\text{-}N}] = \frac{[\mathrm{NH_4^+\text{-}N}] \times 10^{\mathrm{pH}}}{\frac{K_a}{K_w} + 10^{\mathrm{pH}}} \tag{1}$$

where NH_3-N is the free ammonia concentration, (mass/volume), NH_4^+-N the ammonium concentration (mass/volume), K_a the acid dissociation constant, and K_w the water ionization fraction (10^{-14}).

As temperature increases, more of the ammonia is converted to free ammonia gas because of the temperature dependence of the acid dissociation constant. At a pH level of 7, under standard conditions (i.e., temperature is 25°C and pressure is 1 atm), 0.56% of ammonia present is in the form of free ammonia. When the temperature increases to 60°C, a temperature commonly found in aerobic landfills, the percentage of free ammonia present at pH 7 increases to 4.90%. Ammonia volatilization has been measured in numerous compost studies. Results have shown that as temperature increases, the dominant ammonia removal mechanism becomes volatilization. Sanchez-Monedero et al.[105] found that at temperatures above 40°C, the only ammonia removal mechanism observed in compost was volatilization. Tiquia and Tam[116] also found that at temperatures above 40°C and at pH levels of 7 and above, the majority of nitrogen removed from compost is via volatilization.

Air flow also plays an important role in ammonia-nitrogen volatilization. As air is introduced, it begins to agitate the leachate, creating a removal pathway for dissolved free ammonia to volatilize and leave the landfill. Air flow also dilutes the concentration of gas-phase ammonia-nitrogen above the leachate, increasing the driving force for dissolved ammonia-nitrogen to partition to the gaseous phase.[51,114]

Ritzkowski and Stegmann[103] conducted a laboratory-scale study in which the mass of ammonia-nitrogen volatilized from the waste mass was measured. All gas emissions from a simulated aerobic bioreactor landfill exited through an acid scrubber to capture any ammonia-nitrogen that may have been volatilized. It was found that at a pH of 7.4 and a temperature of 35°C, 50% of the ammonia-nitrogen initially present in the leachate was volatilized. The air flow rate was not reported.

E. Nitrification

Nitrification has been successfully used in wastewater treatment processes as a means to convert ammonium-nitrogen to nitrite and nitrate for decades, and the mechanisms in which it is conducted and operated have been thoroughly studied.[1,41,106,121] The purpose of this section is not to thoroughly review the nitrification process, but rather to discuss how nitrification may occur in bioreactor landfills. More detailed information about nitrification can be found elsewhere.[38,106]

Nitrification is a two-step aerobic process in which ammonia-nitrogen/ammonium is microbially oxidized to nitrite and nitrate via obligate aerobe, autotrophic, chemolithotrophic microorganisms. Because nitrification is an aerobic process, it is almost nonexistent in conventional landfills and in bioreactor landfills in which air is not added. In those systems, nitrification is restricted to upper portions of the landfill or the cover where air may infiltrate.[17] In landfills in which air is purposely added, nitrification can be a significant nitrogen removal pathway.

During the first step of nitrification, *Nitrosomonas* bacteria oxidize ammonia-nitrogen to nitrite, according to the following reaction[102]:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \tag{2}$$

The second step of the nitrification process is the oxidation of nitrite to nitrate by *Nitrobacter* bacteria (or the more recently implicated *Nitrospira*) according to the following reaction[102]:

$$NO_2^- + 0.50O_2 \rightarrow NO_3^- \tag{3}$$

Nitrifiers must fix and reduce inorganic carbon to use as their carbon source,[102] resulting in low cell yields and thus small maximum specific growth rates. Additionally, nitrification results in the consumption of alkalinity as nitrous acid is formed. The first step of nitrification is often the limiting step, as the *Nitrosomonas* bacteria grow more slowly than *Nitrobacter* or *Nitrospira*.[38] Some heterotrophic microorganisms are able to nitrify; however, their specific nitrifying rates are considered generally three to four orders of magnitude lower than that of the autotrophs.[40,106] Thus, heterotrophic nitrification is generally considered to be a minor pathway. Some of the heterotrophic nitrifiers are able to denitrify (reduce nitrate) aerobically as well.

Nitrification has also been documented to naturally occur in soils.[9,16,124] Nitrification processes in soil generally result from the addition of nitrogen fertilizers and the diffusion of oxygen.

Nitrification may occur in bioreactor landfills in which air is added. Although the metabolic processes associated with nitrification may be essentially the same in landfills and wastewater treatment processes, the operation, control, and potential extent of such processes are not the same. Nitrification in landfill environments is complicated by oxygen and temperature limitations, heterotrophic bacteria competition, and potentially pH inhibition. Oxygen is a required element for nitrification. Adding air to a landfill would be dual-purpose: to nitrify, removing the ammonia-nitrogen, and to enhance the degradation of solid waste. However, maintaining and controlling sufficient oxygen levels within the landfill, especially considering the heterogeneous nature of solid waste and the high temperatures characteristic of aerobic landfills, may be difficult and may result in oxygen limitations (dissolved oxygen concentration declines with temperature increases) and thus reduced nitrification rates. Additionally, oxygen may become limiting to nitrifiers in areas within the landfill containing large amounts of organic carbon (newly placed waste) due to competition with heterotrophs. Under oxygen-limiting conditions, autotrophic ammonia-oxidizing bacteria may produce nitric and nitrous oxides, which would be a distinct disadvantage of this technique as they are potent greenhouse gases.[17] Heterotrophic nitrifiers are also capable of producing nitrous oxide.

Cheng et al.[20] measured the production of both nitric and nitrous oxides in Chinese agricultural soils in which high levels of fertilizer were added. Different types of soils were tested to determine which conditions resulted in higher gas production. Both nitric and nitrous oxide production from nitrification was observed. Production could be correlated with the pH of the system; soils that were more basic (pH > 8) resulted in the highest concentrations of nitrous oxide, while the more acidic soils produced the least. Khalil et al.[60] also conducted a study evaluating the production of nitrous oxide in soils, paying particular attention to the influence of oxygen on nitrous oxide production. They found that as oxygen decreased, the mass of nitrous oxide from nitrification increased. In landfills, there may be areas in which oxygen concentrations are limiting; thus, nitrous oxide production via nitrification may result. However, long residence times are expected, so the nitrous oxide may be converted to nitrogen gas before exiting the landfill.

When air is added to landfills, in situ temperatures generally increase, often as high as 55 to 66°C,[4,74] which is a temperature range potentially inhibitory to nitrification.[69,80,128] Willers et al.[128] reported that pure *Nitrosomonas* cultures have a thermal death point between 54 and 58°C. In landfills, there may be pockets of lower temperatures, allowing for the nitrifiers to be protected. Additionally, nitrifiers that may be present within biofilms on waste particles may be temporarily protected from high temperatures. At these high temperature levels, volatilization may become the predominant ammonia-nitrogen removal mechanism. Sanchez-Monedero et al.[105] completed studies evaluating the dynamics of nitrogen transformations during organic waste composting. They reported that nitrification did not occur when temperatures rose above 40°C. Several studies evaluating nitrification in thermophilic wastewater processes have been conducted.[59,69,80] Juteau et al.[59] found that nitrification did not occur under thermophilic conditions. However, Lubkowitz-Baily and Steidel[69] and Willers et al.[128] found that nitrification was achievable at temperatures as high as 44°C in wastewater and 50°C in veal-calf slurry, respectively, although the rate of nitrification was decreased significantly at both temperature levels. In higher temperature environments, other types of bacteria may be responsible for conversion of ammonium to nitrite.[76] Methanotrophs have been shown to oxidize ammonium to nitrite under thermophilic conditions (53°C); however, nitrification by the methanotrophs was highly dependent on oxygen and methane concentrations; at methane concentrations above 84 μM, nitrification was inhibited.[76] In hydrothermal vents, thermophilic heterotrophic nitrifiers have been isolated and found to convert ammonium to nitrite at temperatures as high as 65°C, thus conversion of ammonium to nitrite at high temperatures is possible.[76] Heterotrophic nitrifiers generally have lower ammonium conversion rates than autotrophic nitrifiers, but in environments in which autotrophic processes are inhibited, heterotrophic processes may occur and be the dominant nitrogen conversion process.

It is suspected that in situ nitrification may be optimized when operated in landfill cells containing older waste, because, as in composting, as the age of the waste increases, the temperature of the system decreases due to reduced biological activity.[113,123] Additionally, since older waste contains fewer biodegradable organics, less competition with heterotrophs for oxygen will occur. Sanchez-Monedero et al.[105] also reported that nitrification did not occur in compost processes until the majority of the organic matter was degraded, something also seen in wastewater treatment processes.[19,67] Additionally, in older waste, more recalcitrant organics, such as humic acids, are present. In leachate collected during the methanogenic stage of degradation, almost 60% of the dissolved organics present were in the form of high molecular weight compounds (i.e., humic and fulvic acids).[61] Humic acid has been shown to inhibit nitrification, resulting in the buildup of nitrite concentrations. Bazin et al.[8] conducted a study in which humic acid was added to columns containing glass beads and pure cultures of nitrifying microorganisms. At input levels of 100 $\mu g/cm^3$, the humic acid additions had no adverse effect on nitrification rates and aided in buffering the pH of the system. However, when humic acid was added at rates above that level, nitrification was inhibited. The mechanism of inhibition was not stated. It is suspected that in landfills humic acids may affect nitrification, although more work needs to be conducted evaluating the extent of such effects.

pH may also be a complication during nitrification processes in landfills. The pH of leachate in aerobic landfills is generally near neutral, or slightly above.[96,112] The alkalinity of leachate is generally in the range of 1000 to 10000 mg/L as calcium carbonate.[113] Because nitrification destroys alkalinity, there may not be sufficient alkalinity present to buffer pH changes that would result from nitrification of high ammonia-nitrogen leachates. It is possible that alkalinity may need to be added to the landfill to buffer the leachate.

1. NITRIFICATION CASE STUDIES IN LANDFILLS

Several researchers have evaluated the potential use of in situ, or partially in situ, nitrification processes in landfills. Youcai et al.[131] conducted a study in which a biofilter consisting of old waste (8 to 10 years old) was used to treat leachate. Aerobic portions existed at the top and bottom of the system (air was not supplied, rather was drawn in from the atmosphere via convection), while the middle of the system was anaerobic. It is important to note that these conditions (aerobic and anaerobic) were never shown experimentally, nor was the ORP measured. A removal of 99.5% of the ammonia-nitrogen in leachate was observed. Elevated concentrations of nitrate and nitrite were measured, indicating the ammonia-nitrogen was converted biologically. Additionally, 20–30% of total nitrogen in the leachate was removed, suggesting in situ nitrification and denitrification occurred sequentially in the landfill.

Incidental treatment of nitrogen in aerobic or semiaerobic landfills has also been observed. Hanashima[44] described lysimeters operated under aerobic and semiaerobic conditions over a three to 20-year period. Aerobic test cells were continuously supplied with air via a feed pipe to the bottom of the cell. The semiaerobic cell was constructed with a large drainage pipe in contact with the atmosphere to provide aeration to the bottom of the cell while maintaining the upper portion of the landfill under anaerobic conditions. Leachate was recycled to both cells. Comparison with the performance of conventional anaerobic cells suggested that nitrogen removal under both semiaerobic and aerobic conditions was significantly greater than under anaerobic conditions.

The most efficient method evaluated to date is complete in-situ removal of nitrogen using dedicated zones. Onay and Pohland[82] completed an in-situ nitrification/denitrification laboratory study in which a three-component system was used to facilitate the process. A laboratory study was conducted to evaluate a conceptual idea of an anoxic denitrification zone located near the surface of the reactor, an anaerobic zone to simulate methanogenic conditions in the middle, and at the bottom an aerobic nitrification zone. When utilizing leachate recirculation among the zones, approximately 95% nitrogen removal was achieved. Onay and Pohland[82] completed another study during which the reactors were connected in series, but with no leachate recycle, just a single pass. Nitrogen removal was observed with this set of experiments as well; however, only 30 to 52% removal of nitrogen in the leachate was achieved. Onay and Pohland[82] suggested application of this type of system in the field by having different portions of the landfill serving as treatment zones: The upper portion of the landfill would be anoxic, the middle anaerobic, and the bottom aerobic (air naturally added via convection through leachate collection pipes).

2. NITRIFICATION KINETICS

Traditional nitrification kinetics in wastewater systems are derived from the net growth rates of both *Nitrosomonas* and *Nitrobacter*, with the growth rate of *Nitrosomonas* considered as the rate-limiting step and thus the most critical from a design perspective. Monod kinetics are often used, as they describe first-order substrate-limiting growth at low ammonia-nitrogen concentrations and zero-order at higher concentrations.[38,102] Because ammonia oxidation is the rate-limiting step, it is often used as the overall rate of nitrification. Several environmental factors influence the rate and must be accounted for in the rate expression, including pH, dissolved oxygen (DO) concentrations, and temperature. These factors are included in the rate expression of ammonia oxidation in a multiplicative Monod manner.[26] The Monod relationship can also be modified to account for substrate inhibition, which could be relevant at high ammonia-nitrogen concentrations.

The nitrification process in solid waste environments may be better approximated by fixed-film theory rather than suspended, as the waste may act as an attachment surface for the microorganisms.[85,108] In fact, a bioreactor landfill may contain both suspended and fixed-film populations, but it seems likely that in most cases the greater portion of the biomass will be associated with biofilms. This means that diffusion of electron acceptors and donors and other mass transfer limitations become significant. In landfills, mass transfer of ammonium and/or oxygen may be a bigger factor than in wastewater treatment because of the large particle sizes of the waste and because the liquid to solid ratio is much smaller than in typical wastewater treatment processes. Mass transfer limitations would likely become apparent in the value of the half-saturation constant in the Monod model.[89] The half-saturation constants in wastewater for nitrification are generally 1 to 2 mg/L as N; a much larger value may indicate mass transfer limitations. In addition, the presence of biofilms increases the possibility of multiple microenvironments (e.g., even an aerobic region may contain biofilms with anoxic depths and thus possibly simultaneous denitrification). Thus, it is unlikely the kinetics of in situ nitrification will fit well to strict Monod or biofilm kinetic models; rather, an expression including both types of consortia may be appropriate.

F. Denitrification

Denitrification has been applied in many wastewater treatment processes. The intent of this section is not to review the denitrification process, rather to discuss how denitrification may occur in bioreactor landfills. Information regarding denitrification processes may be found elsewhere.[11,29,31,37,38,71,106] In situ denitrification is also complicated in solid waste systems, although it may be easier to implement than nitrification. Denitrifiers are more robust than nitrifiers; however, they require a sufficient organic carbon source for high nitrate removal rates. Because of the carbon needs, denitrification may occur most efficiently in young waste, rather than in older, partially oxidized waste. Price et al.[93] evaluated the potential need for an external carbon source in the laboratory and noted that a fresh layer of refuse contained sufficient carbon to stimulate significant nitrate consumption. If a sufficient organic carbon source is not readily available, partial denitrification may occur, which may lead to the production of harmful intermediates (N_2O and NO), which are potent greenhouse gases.[20,60]

Typically, in situ denitrification occurs in anoxic bioreactor landfills. However, because of the potential for anoxic pockets to be present in aerobic systems, denitrification may also occur in portions of aerobic bioreactor landfills that air does not reach.

1. HETEROTROPHIC DENITRIFICATION

Denitrification is an anoxic process that reduces nitrate to nitrite, nitric oxide, nitrous oxide, and finally nitrogen gas, as shown in reactions (4)–(7)[102]:

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \tag{4}$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \tag{5}$$

$$2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O \tag{6}$$

$$N_2O + 2e^- + 2H^+ \rightarrow N_2(g) + H_2O \tag{7}$$

Typically, denitrifying bacteria are heterotrophic, facultative aerobes, which use nitrate as an electron acceptor when oxygen is absent or limiting. A potential advantage of denitrification is the simultaneous carbon and nitrate destruction without requiring oxygen input.[38] Denitrification also recovers half of the alkalinity consumed during nitrification. It is important to note that processes in which nitrate is used as a terminal electron acceptor are energetically favored over acetogenic, sulfate reduction, and methanogenic processes. Thus in landfills in anaerobic/anoxic environments in which nitrate reduction occurs, inhibition of such processes may occur.

Researchers have evaluated in situ, or partially in situ, denitrification at both laboratory and field scale. Burton and Watson-Craik[18] operated a landfill test cell designed to denitrify externally nitrified leachate. Nitrate returned to the landfill cell was efficiently consumed under the anoxic/anaerobic landfill conditions, confirmed using labeled isotopic nitrate. Both Waste Management[119] and Aljarallah and Atwater[2] have completed similar studies at field and laboratory scale, respectively. Aljarallah and Atwater[2] noted that denitrification was feasible in a bioreactor landfill; however, methane production and waste degradation were hindered. A carbon balance was conducted on the leachate and solid waste in their study and found that as the nitrate concentration increased, less carbon was released in either the liquid or gas form, suggesting that waste degradation was inhibited by high nitrate concentrations (i.e., 800 mg/L as N). Additionally, it was noted that poor leachate quality was produced (high organic strength). Jokela et al.[58] conducted a similar laboratory study demonstrating that in situ denitrification is possible and can result in the elimination of nitrogen. Ammonia was detected in the effluent from the solid waste column, which was attributed to either release from the waste or high leachate COD to nitrate ratio, which may promote the reduction of nitrate to ammonia-nitrogen (see Figure 1). It was also concluded that at an oxidized nitrogen loading rate below 3.8 g N/total solids-day, methanogenesis was not inhibited. High leachate COD concentrations inhibited nitrification in the ex-situ process, presumably due to competition for available oxygen.

Price et al.[93] also conducted studies evaluating the ability of older waste (with low organic carbon) to denitrify nitrified leachate. It was shown that the landfill does have the capacity to denitrify, as significant nitrate consumption was observed, and that fresh waste contained enough organic carbon to support denitrification, while older waste required the addition of an external carbon source. Additionally, it was observed that methanogenic activity was inhibited during denitrification, but quickly resumed following nitrate removal.

2. AUTOTROPHIC DENITRIFICATION

Nitrate removal in wastewaters containing high sulfur concentrations or reduced sulfur sources, such as hydrogen sulfide, may occur via autotrophic denitrification. Thiobacillus denitrificans use an inorganic sulfur source (i.e., H_2S, S, SO_3^{2-}) rather than an organic carbon source when reducing nitrate to nitrogen gas[83] according to reaction (8).

$$2NO_3^- + 1.25HS^- + 0.75H^+ \rightarrow N_2 + 1.25SO_4^{2-} + H_2O \tag{8}$$

This nitrate removal mechanism produces sulfate. At low carbon to nitrogen ratios this removal mechanism is favored over heterotrophic denitrification.[62] Autotrophic denitrification may occur in landfills, especially in older landfills or older portions of landfills where the carbon to nitrogen ratio may be low. The increased sulfate concentrations may have an adverse effect on methane production rates by limiting the amount of organic carbon available to the methanogens due to competition with sulfidogens.

While operating their reactors, Onay and Pohland[83] observed the presence of autotrophic denitrification. To confirm their findings, a spike of nitrate was added and gas samples from the headspace of the reactor were measured for nitrogen and hydrogen sulfide. It was found that 13 days after the nitrate spike, the hydrogen sulfide present in the gas phase disappeared. After the nitrate source was exhausted, the sulfate was converted back to hydrogen sulfide. Onay and Pohland[83] concluded that autotrophic denitrification accounted for between 15% and 55% of the nitrate conversion to nitrogen gas, with the variation being attributed to the mass of organics present in the system. Additionally, it was stated that autotrophic denitrification is advantageous, as it converts nitrate to nitrogen gas in the absence of an organic carbon source and can utilize inorganic sulfur compounds. High sulfate concentrations (increased to approximately 350 mg/L sulfate) were produced; however, the impact of sulfate on methanogenesis was not quantified.

3. DENITRIFICATION KINETICS

Traditionally, Monod kinetics are used to describe denitrification in wastewater systems. The nitrate removal rate is dependent on several factors that must be accounted for in the rate expression. Because an organic carbon source is desirable for rapid denitrification, the amount present in the system affects the rate, as does the biodegradability of the carbon source. Additionally, pH and dissolved oxygen (DO) levels affect the denitrification rate and can be accounted for in a Monod expression in a multiplicative manner.

As in nitrification, the denitrification process in solid waste may be better approximated by fixed-film theory rather than suspended, as the waste may act as an attachment surface for the microorganisms.[85,108] Mass transfer effects may also be severe in denitrification processes and may be reflected in higher half-saturation values when fitting the data to the Monod model.[89] It is unlikely the kinetics of in situ denitrification will fit well to either strict Monod or biofilm kinetic models; rather, an expression combining both types of consortia may be appropriate.

G. ANAMMOX

Biological oxidation of ammonia-nitrogen may also occur under anaerobic conditions and is termed the ANAMMOX process (anaerobic ammonium oxidation). Bacteria capable of ANAMMOX use ammonium as the electron donor and nitrite as the electron acceptor, as shown in reaction (9)[56,57]:

$$\begin{aligned} &NH_4^+ + 1.26NO_2^- + 0.085CO_2 + 0.02H^+ \rightarrow \\ &\quad N_2 + 0.017H^+ + 0.24NO_3^- + 1.95H_2O \end{aligned} \tag{9}$$

There has been little research concerning ANAMMOX in solid waste environments; however, studies conducted in wastewater have shown that ANAMMOX readily occurs.[45,56,57,106] Researchers have determined that the microorganisms most often responsible for the ANAMMOX process are from the Planctomycetales group.[56,129] This process is generally favorable in environments in which retention time is long, operation is stable, nitrite is present, and electron donors that would cause nitrite reduction via denitrification are absent. Because of the potential for anaerobic regions located within an aerobic landfill, this biological ammonia-nitrogen removal mechanism may incidentally occur simultaneously with nitrification. However, the growth rates of the ANAMMOX bacteria are extremely slow; thus, ammonia-nitrogen removal is slow as well. It is questionable whether or not the ANAMMOX microorganisms will be able to compete with denitrifiers for nitrate and nitrite within landfills.[17] Removal rates have been shown to be less than half that of aerobic nitrification.[129]

H. Dissimilatory Nitrate Reduction to Ammonium

Dissimilatory nitrate reduction to ammonium (DNRA) in anaerobic or anoxic environments may also occur in landfills according to reaction (10).

$$NO_3^- + 2H^+ + 4H_2 \rightarrow NH_4^+ + 3H_2O \tag{10}$$

As shown, ammonium is produced as a result of nitrate reduction. This pathway is generally favored when the microbes are electron acceptor (nitrate) limited in high organic carbon environments[92,115] and has been shown to occur readily in anaerobic digestion and anoxic sediments where the redox potential is low.[115] DNRA is favored over denitrification in anaerobic and anoxic environments in environments with a high COD to nitrate ratio because in an electron acceptor limiting environment it is more advantageous for the microorganisms to metabolize nitrate to ammonium and gain 8 electrons per mole of nitrate than denitrify and only gain 5 electrons per mole of nitrate.[115] In electron acceptor rich environments (higher COD to nitrate ratios), denitrification is usually the favored nitrate reduction process because the greatest need by the microorganisms is to gain energy. The microbes responsible for the DNRA process differ from denitrifiers in that they are generally fermentive (obligate anaerobes, facultative anaerobes, and aerobes), using nitrate as electron sink, rather than being respiratory and using nitrate as a terminal electron acceptor.[22,115]

DNRA depends highly on redox conditions and the amount of labile carbon available.[13,34,130] Yin et al.[130] conducted experiments in Chinese and Australian paddy soils and found that the partitioning of nitrate that was reduced to ammonium and to that being denitrified was greatly dependent on the amount of labile carbon present, which was demonstrated by an increase in ammonium production with increasing carbon. Buresh and Patrick[15] conducted an experiment on estuarine sediment and found that approximately 15% of the nitrate was converted to ammonium at a redox potential of 0 mV. When decreasing the redox potential to −200 mV, approximately 35 to 42% of the nitrate was reduced to ammonium, while an increase in redox potential (300 mV) resulted in a significant decline of ammonium production, supporting the theory that DNRA is optimal in low redox environments. When nitrate is added to systems, a general increase in the redox potential occurs. If nitrate is added to environments with a sufficiently low redox potential, DNRA may be favored. However, if the nitrate addition results in an increase in redox above 0 mV, denitrification of the nitrate is more likely. Oxygen also impacts DNRA; however, it is less sensitive to changes in oxygen than denitrification.[34]

In anaerobic or anoxic areas within the bioreactor landfill in which low nitrate concentrations are present in areas containing young waste (high degradable organic carbon) and low redox potentials, DNRA may be favored over denitrification.[115] The dissimilatory nitrate reduction pathway is not desired because it results in an increase in ammonium concentration. However, this removal mechanism may be limited because of competition from the denitrifiers for nitrate. The nitrate-reducing bacteria require a tenfold greater population than denitrifiers to reduce 50% of the nitrate.[93] Bonin[13] reported that a ratio of 1.8:1.0 denitrifiers to DRNA microbes is generally present in an environment. In landfills, there is generally adequate denitrifying populations naturally present to out-compete any DNRA capable microorganisms. Price et al.[93] conducted laboratory studies in solid waste evaluating the denitrification capacity of the waste and found that there was no noticeable increase in ammonium due to DNRA. However, the redox potential of the laboratory reactors was not measured. Because there had been several additions of nitrate to each reactor, it is possible the redox potential was high enough to inhibit DNRA activity.

I. Simultaneous Nitrogen Removal Processes

Simultaneous nitrification and denitrification has been observed in wastewater processes, particularly in trickling filter and other biofilm processes. Because the potential for anoxic pockets in aerobic landfills is high, simultaneous nitrification and denitrification may occur in aerobic bioreactor landfills. Pochana and Keller[87] conducted experiments evaluating the factors that may affect simultaneous processes in activated sludge flocs. They determined that the most influential parameters are DO, particle size, and carbon source. Of particular interest is that as the floc size increases, the potential for anoxic zones around the particles increases due to oxygen flux limitations. Solid waste particles are large compared to activated sludge flocs; thus the probability of oxygen flux limitations is high, supporting the likelihood of simultaneous processes.

Because landfills are heterogeneous and may support several different microenvironments simultaneously (i.e., aerobic, anaerobic, and anoxic), several combinations of nitrogen transformation processes mentioned may be present. In aerobic bioreactor landfills, it is possible that partial nitrification (only resulting in the production of nitrite) followed by either ANAMMOX or denitrification will occur naturally because of the heterogeneous nature of the in situ environment. There will be portions of the landfill that are aerated well, some only partially aerated, and others not aerated at all. As leachate flows from one section of the landfill to another, it is possible that it will come into contact with aerobic, anoxic and anaerobic regions, leading to multiple nitrogen transformation processes. For example, leachate ammonium may be converted only to nitrite before the leachate flows to an anaerobic pocket.

In that anaerobic pocket, the nitrite may then be converted to nitrogen gas. The hydraulic conductivity of the landfill will be a factor, as the time during which the leachate remains in each type of environment will ultimately determine the extent of the reactions that may occur. The ability to predict which nitrogen transformations will occur allows for more strategic design and operation of bioreactor landfills.

J. Other Nitrate Processes

Nitrate may also have an abiotic fate in landfills. Leachate generally does not have high nitrate concentrations; however, nitrate may be present if nitrification has occurred in situ, or if the leachate is nitrified externally and then reinjected to the landfill. Nitrate sorption has been shown to occur in soils, although not to the extent that ammonium sorption has been observed. Kwok and Loh[64] measured nitrate sorption in six different soils. Sorption was detected, but in small amounts (average for all soils was 0.004 mol/kg). Kowalenko and Yu[63] also evaluated the sorption of nitrate on soils and found that up to 34% of additional nitrate was removed from soils when performing an extraction using potassium chloride. Sorption of nitrate by waste is probable. Because of the large variability of waste types, there is bound to be particles with negative charges that would allow for anion exchange.

Another fate of nitrate is the abiotic transformation via iron. Davidson et al.[24] proposed a method of abiotic nitrate removal called the "ferrous wheel hypothesis" in which reduced iron [Fe(II)] abiotically converts nitrate to nitrite in anaerobic environments; nitrite then reacts with the dissolved organic matter to produce dissolved organic nitrogen. No evidence of this occurring in compost or solid waste has been reported; however, because leachate typically contains large amounts of iron(II) (3–5500 mg/L),[61] the possibility exists. Iron(II) has also been shown to reduce nitrate in basic solutions to ammonia-nitrogen. Fanning[32] reported that a pH of 8 was optimal for the reduction; however, the reduction proceeded at lower pH levels, just at slower rates. Additionally, it was suggested that the reaction may be influenced or catalyzed by the presence of silver and copper. Silver is not generally found in leachates, but copper can be found at levels ranging from 0.005 to 10 mg/L.[61]

Studies in acid forest soil have observed the disappearance of nitrate via an abiotic mechanism. Dail et al.[23] conducted a radiolabeled study attempting to determine the fate of nitrate. They found that nitrate was incorporated into an insoluble organic nitrogen form in both live and sterile soils, suggesting abiotic fate attenuation. Additionally, in their study, there was more attenuation of nitrate in soils with larger amounts of organic carbon, suggesting the abiotic conversion is related to the soil carbon content. Because of the large organic carbon content found in landfills, this nitrate transformation mechanism could easily occur.

V. FUTURE RESEARCH DIRECTIONS

An understanding of the fate of nitrogen and possible mechanisms for ammonia-nitrogen removal in bioreactor landfills may significantly increase the capability of bioreactor landfills to more completely treat leachate in situ. Bioreactor landfills are currently one of the most advantageous methods available for solid waste management, but still have significant undeveloped potential with respect to in situ leachate and waste treatment. An understanding of the fate of nitrogen, and thus the ways in which nitrogen can be removed/treated allows for this undeveloped potential to be better developed. Additionally, understanding the fate of nitrogen may aid in developing methods to remediate old landfills.[103]

Little research has been conducted evaluating the potential processes of nitrogen transformation and removal in bioreactor landfills and is needed before an in-depth understanding of the processes can be achieved and used to optimize the operation of bioreactor landfills. Both laboratory- and full-scale studies should be completed to evaluate the hypothesized, but untested, nitrogen transformation processes. To date, no controlled full-scale studies purposely evaluating in situ nitrification as a nitrogen transformation process have been conducted. Additionally, laboratory-scale studies need to be conducted to gain a better understanding of the rates and kinetics of the nitrogen transformation processes, as well as to develop design requirements for an in situ nitrogen removal system to facilitate full-scale testing.

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