

Nitrogen and sulfate attenuation in simulated landfill bioreactors

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Abstract The characteristics of leachate from landfills vary according to site-specific conditions. Leachates from old landfills are often rich in ammonia nitrogen, posing potential adverse environmental impacts in the case of uncontrolled discharge. At landfills where leachate recirculation is practiced, leachate ammonia concentrations may accumulate to higher levels than during the single pass leaching. Using leachate recirculation with system modifications, separate aerobic and anoxic zones for nitrification and both autotrophic and heterotrophic denitrification can be provided. Results from simulated landfill bioreactors indicated that both nitrogenous and sulfur compounds can be attenuated through autotrophic denitrification, and leachate nitrate concentrations of 750 mg/L reduced to less than 1 mg/L by denitrification to nitrogen gas promoting this very common process in a landfill environment results in the reduction of both leachate ammonia and sulfate concentrations.

Keywords Autotrophic denitrification; landfill bioreactor; landfill stabilization; leachate treatment; recirculation; sulfur removal

Introduction

Leachate, with a high concentration of organic and inorganic compounds, represents a potential source of contamination of surrounding soil, underlying groundwater aquifers, as well as nearby surface water resources. Moreover, high leachate ammonia concentrations could be toxic to aquatic life, and a potential exists for dissolved oxygen consumption through ammonia oxidation and eutrophication as a result of nitrate accumulation (Dedhar and Mavinic, 1986).

Landfill leachate treatment prior to ultimate discharge is generally required. Two major management strategies are employed; single pass leaching with leachate containment, collection, and *external* treatment, and *in situ* leachate containment, collection, and recirculation back into the landfill. Compared to external treatment, leachate recirculation has been demonstrated as an economical way of pretreating leachate and accelerating waste stabilization processes occurring in landfill (Pohland, 1980).

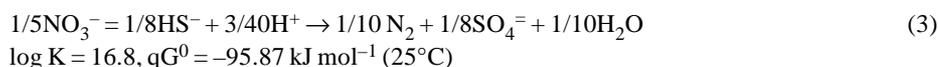
It has been shown that residual concentrations of leachate nitrogen generated during leachate recirculation were greatly reduced with attenuation by nitrification-denitrification processes within the landfill system (Onay and Pohland, 1998). While observing the behavior of nitrogenous compounds in simulated landfill bioreactors, the attenuation potential of sulfur compounds as a result of autotrophic denitrification was also observed. As a consequence, experiments were conducted using KNO_3 as a nitrogen source, and the interaction between the reduced sulfur compounds and nitrate was recorded.

Reaction mechanisms

Sulfur compounds are present in refuse and landfill leachate principally as soluble sulfate and precipitated sulfide forms (Rees, 1980). Sulfides are produced during anaerobic decomposition by the reduction of sulfates and other sulfate-containing inorganic compounds as well as conversion of proteins. Previous researches identified two different

mechanisms for the natural attenuation of sulfur in landfills (Batchelor and Lawrence, 1978). The first one, dissimilatory microbial sulfate reduction, is a process in which certain bacteria use sulfate as an electron acceptor in the oxidation of organic matter. Sulfate, with sulfur in the +6 oxidation state, is reduced to sulfide in a -2 oxidation state. Organic compounds are also simultaneously oxidized with the concurrent release of energy for microbial growth and cell maintenance. Miller and Hughes (1968) and Lens *et al.* (1995) indicated that *Desulfovibrio* and *Desulfotomaculum* are two genera of sulfate-reducing bacteria analogous to methane-fermenting bacteria because they can use and compete for end products from the acid fermentation phase of anaerobic decomposition. The most important implication of sulfate reduction to sulfide in landfills is the immobilization of toxic heavy metals. Since sulfide is a powerful precipitant, it can form heavy metal sulfides that are insoluble and precipitate or are filtered from solution.

The second process for sulfur attenuation in landfills that also promotes nitrogen removal from leachate is autotrophic denitrification. In spite of many heterotrophic bacteria which are capable of denitrification using external carbon sources, an autotrophic bacteria, *Thiobacillus denitrificans*, was also shown to be able to carry out denitrification using inorganic sulfur compounds (H_2S , S , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, SO_3^{2-}) as its energy source and inorganic carbon compounds (e.g. CO_2 , HCO_3^-) as its carbon source. The principle of autotrophic denitrification by *Thiobacillus denitrificans*, is well-established, and can be illustrated by the following equations (Claus and Kutzner, 1985):



Trisch and Jennings (1978) and Bisogli and Driscoll (1977) investigated autotrophic denitrification of domestic wastewater using various sulfur compounds, including sulfide and thiosulfate, and obtained high nitrate removal efficiencies in completely mixed suspended growth systems. On the other hand, Sikora and Keeney (1976) made an evaluation of a sulfur-nitrate removal system for septic tank seepage bed effluent with an average nitrate concentration of 40 mg/L by using elemental sulfur as the inorganic electronic donor. Complete nitrate removal was achieved with an effluent sulfate concentration of 90 mg/L. Claus and Kutzner (1985) studied the physiology and kinetics of autotrophic denitrification by *Thiobacillus denitrificans* and indicated that denitrification was inhibited by sulfate concentrations (the reaction product) above 5 g/L. On the other hand, Aminuddin and Nicholas (1973) showed both substrate and intermediate compound inhibitions on *Thiobacillus denitrificans* at concentrations of 6.5 g NO_3^-/L and 100 mg NO_2^-/L , respectively.

Materials and methods

A three-reactor laboratory system was designed to simulate the landfill environment and to investigate the potential for *in situ* removal of nitrogenous compounds in landfills with leachate recirculation of Figure 1. The simulated landfill reactors were operationally similar to the overall system, consisting of two 57 litre reactors as nitrification and denitrification units, and one 113 litre reactor as a main methanogenic unit. Compost was utilized as the waste matrix because of its similarity to the stabilized waste mass present in landfills after accelerated stabilization with leachate recirculation and during the final maturation phase of landfill stabilization, i.e., lower carbon and higher nitrogen content when compared to the

typical values given for Municipal Solid Waste (Table 1). In order to simulate conditions during the final maturation phase of landfill stabilization, and to better understand the potential for conversion of nitrogenous compounds, the experiment was divided into two operational stages: separate reactor operation and combined reactor operation. The main purpose of conducting the separate reactor operation stage was to ensure the initiation and development of desirable microbial populations and activity under feed solutions loadings of potassium nitrate and ammonium chloride to the denitrification and nitrification reactors, respectively. After establishing active microbial populations, the combined reactor operation was initiated to simulate the typical flow patterns in an actual landfill utilizing leachate recirculation and promoting separate bonds for *in situ* nitrification and denitrification.

In order to facilitate evaluation of the extent of nitrification, denitrification and methanogenesis, leachate samples were analyzed for: chemical oxygen demand (COD); volatile organic acids (VOAs) including acetic, propionic, iso-butyric, butyric, iso-valeric, valeric, and caproic acids; pH; oxidation-reduction potential (ORP); ammonia nitrogen; anions (chloride, nitrite, nitrate, phosphate, and sulfate); and metals (Ca, Mg, Mn, K, Fe),

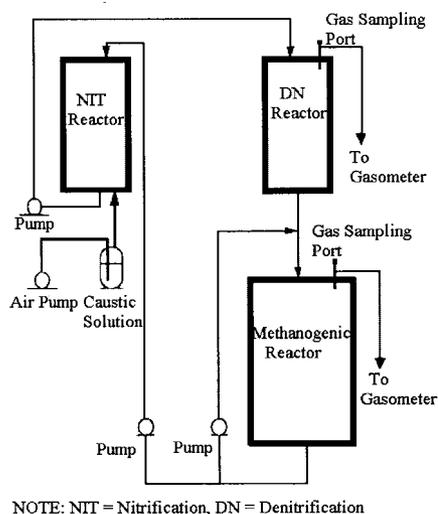


Figure 1 Operational features of Landfill Bioreactor System

Table 1 Comparison of characteristics of compost and municipal refuse

Parameter	Results	Typical data of Municipal Refuse***
Total Kjeldal Nitrogen (TKN)	1.31	0.94**
Ammonia Nitrogen (NH ₃ -N)	0.16	
Nitrate Nitrogen (NO ₃ -N)	<0.01	
Phosphorus (P ₂ O ₅)	1.15	
Calcium (Ca)	2.1	
Magnesium (Mg)	0.37	
Manganese (Mn)	0.065	
Iron (Fe)	1.4	
Potassium (K ₂ O)	0.28	
Carbon (C)	33.2	49.1
Alkalinity (CaCO ₃)	5.58	
Total Solids	72.5	80
Volatile Solids	60	52
Wet Density (kg/m ³)	502	295

*Results are expressed in percent by weight of waste matrix added, unless an alternative unit is given

**Total nitrogen

***Tchobanoglous *et al.* (1993)

and gas production and composition from the denitrification and methanogenic reactors were monitored. All leachate and gas analyses were performed according to *Standard Methods* (1992).

Results and discussion

While investigating the transformations of nitrogenous compounds in landfill bioreactors, the presence of autotrophic denitrification was detected when the reactors were under combined operation. In order to confirm the presence of autotrophic denitrification, with oxidation of reduced sulfur compounds to sulfate and reduction of nitrate to nitrogen gas, 1.56 g KNO_3 was added to the denitrification reactor. Gas samples from the head space of the denitrification reactor were analyzed for hydrogen sulfide and nitrogen. The hydrogen sulfide gas concentrations were then converted to corresponding liquid concentrations according to Henry's Law. Figure 2 indicates the change in hydrogen sulfide and sulfate concentrations with time, with hydrogen sulfide concentrations reaching a minimum when the leachate sulfate concentration was maximum. Analysis of the reactor head space content for hydrogen sulfide revealed that a hydrogen sulfide concentration of 1.2 mg/L was completely converted by Day 13. Figure 3 indicates the relationship between leachate nitrate concentrations and nitrogen gas with nitrate being exhausted when nitrogen gas was highest. These two graphs clearly illustrate the interaction between sulfur species when nitrate is available as a substrate. It appears that after the reduction of nitrate to nitrogen gas was completed, sulfate reduction to sulfide again became the dominant process.

Using the relationships given by Equations 1 through 3, 0.967 g of sulfate should be produced per gram of nitrate reduced to nitrogen gas. However, the measured sulfate produced from the nitrate that was introduced into the reactor was always lower than the expected stoichiometrical amounts. This was possibly due to the utilization of nitrate by the heterotrophic denitrifiers. Moreover, by examining the same equations, 3.0 grams of sulfate should theoretically be produced per gram of sulfide oxidized. However, sulfide precipitation with heavy metals, all of the sulfide present in the reactor was not available for oxidation to sulfate. Therefore, the measured amount of sulfide oxidized was lower than the stoichiometrical relationship between sulfate and sulfide. Retrieval and visual examination of the final compost matrix also confirmed sulfide precipitation with iron indicated by black deposits on the surface of compost.

The comparison of the first stage of operation to the second stage of operation in terms of sulfate generation from the mass of nitrate added revealed that the mass of sulfate generated during the first stage of operation was smaller than the sulfate generated during the

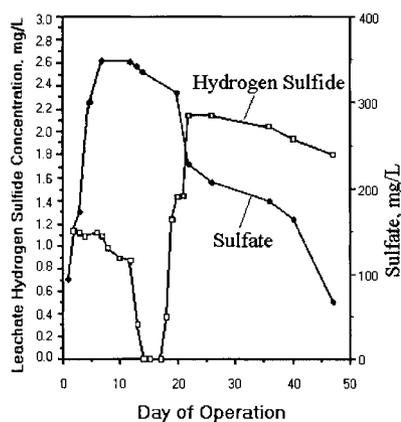


Figure 2 Change in sulfur concentrations

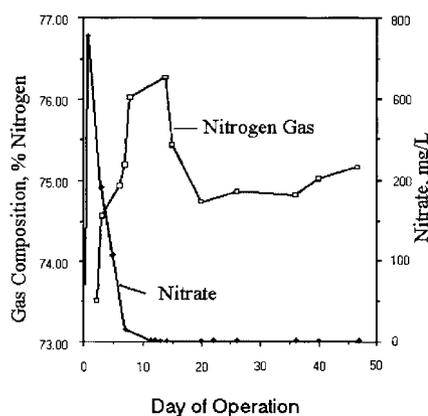


Figure 3 Change in nitrogen concentrations

second stage of operation. Correspondingly, the overall autotrophic denitrification increased from 15% up to 55% during the combined reactor operations. This was most likely attributable to the consumption of readily biodegradable organic matter during the first stage of operation necessary for proliferation of the heterotrophic denitrifiers. After the utilization of the readily available organic carbon sources necessary for the heterotrophic denitrification, conditions for the autotrophic denitrifiers became more favorable and denitrification proceeded using reduced sulfur compounds as electro donors.

Conclusions

Bioreactor landfills employing leachate recirculation for *in situ* leachate treatment and accelerated waste stabilization can be modified to enhance overall operational control and to attenuate specific leachate constituents.

The results indicate the successful removal of leachate concentrations by the application of autotrophic denitrification process. The rate of nitrate removal was rapid, and complete conversion of leachate nitrate concentrations of 750 mg/L to nitrogen gas occurred within 10 days.

Utilization of reduced sulfur compounds originally available in landfill environments is an important attenuation mechanism that promotes *in situ* denitrification without the addition of external carbon sources. Furthermore, autotrophic denitrification can utilize sulfur compounds, prevent their accumulation in landfills and decrease their potential for inhibition of methanogenic bacteria by sulfate-reducing bacteria in competition for substrate.

These findings are also important to the operation of landfills where reduction of leachate ammonia and sulfate concentrations can be accomplished without any need for external leachate treatment.

The further development and application of this attenuation potential in full scale landfill bioreactors necessary so that its full benefits can be realized in practice.

Acknowledgement

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