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Removal of nitrogen oxides from gas streams using biofiltration

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Abstract

Nitrogen oxides (NO_x) are primary air pollutants, and as such, there is considerable interest in the development of efficient, cost effective technologies to remediate NO_x containing emissions. Biofiltration involves the venting of contaminated gas streams through biologically active material such as soil or compost. This technology has been used successfully to control odors as well as volatile organic compounds from a variety of industrial and public sources. The purpose of this study was to evaluate the feasibility of using biofiltration as a means to remediate NO_x containing gas streams. Biofiltration studies measuring nitric oxide (NO) removal by bacteria indigenous to wood compost were conducted. Vertical biofilters (2 l volume) constructed from glass process pipe (3 in i.d. × 12 in) were loaded with 11 of compost bed medium. Compaction of compost in the biofilters was minimized by the addition of wood chips (15% w/w). A nitrogen gas stream, containing various concentrations of NO (100–500 μl/l), was purged (1 l min^{-1}) through the biofilter under single pass, continuous flow conditions. Adsorption studies comparing NO removal in autoclaved and non-autoclaved biofilters indicated that approximately 3% NO removal was attributed to abiotic uptake. Control of pH in the biofilter was a critical variable for maximum nitric oxide removal. Optimum denitrifying activity occurred at pH levels ranging between 6 and 7. Nitric oxide removal rates increased in biofilters treated with an external carbon and energy source. Biofilters treated with phosphate buffer containing either lactate or dextrose were capable of removing more than 90% of the NO from a 500 μl/l NO gas stream flowing at 1 l min^{-1}.

1. Introduction

The burning of fossil fuels is a major source of atmospheric nitrogen oxides (NO_x). Although low levels of nitrous oxide (N_2O) are emitted, nitric oxide (NO) and nitrogen dioxide (NO_2) are the major NO_x components released during combustion processes [1]. Nitrogen oxides are hazardous pollutants which adversely affect human

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health; exposure to NO_2 at concentrations of 100 ppm or greater can result in respiratory failure or death [2]. Nitrogen oxides are also detrimental to the environment. In the atmosphere, NO and NO_2 react with moisture in the air to form nitrous acid, which in turn, leads to the formation of acid rain. In addition, NO_x contributes to stratospheric ozone depletion and global warming [3,4].

During combustion, nitrogen and oxygen react to produce nitrogen oxides. Two main mechanisms are involved; thermal NO_x is produced from molecular nitrogen in the combustion air and fuel NO_x forms as nitrogen is released from the fuel [5]. Although NO_x production can be significantly reduced by combustion control methods (modification of burning temperatures and reduction of gas residence time in the high temperature zone of the boiler); post combustion treatment is required to achieve current regulatory air standards [5]. One such treatment to reduce NO_x levels is the use of an ammonia-based selective catalytic process [6]. Although this is an effective technique, the catalysts are easily poisoned and pose a hazardous waste disposal problem. Biofiltration, a biological process, may offer an alternative technology to remediate NO_x containing emissions.

Biofiltration involves the venting of contaminated gas streams through biologically active material such as soil or compost. This technology has been used successfully to control odors as well as volatile organic compounds from a variety of industrial and public sources [7,8]. The use of biofiltration to treat NO_x containing emissions relies on the activity of denitrifying organisms which are indigenous to the bed medium. Denitrifying bacteria are ubiquitous in nature and include a variety of physiologic and taxonomic groups. The majority of denitrifying bacteria which occur naturally in soil and water are members of the Genus *Pseudomonas*; second in number are species of *Alcaligenes* [9]. Denitrifyers have the ability to reduce oxides of nitrogen when oxygen levels become limited [4, 10–14]. Denitrification is a dissimilatory reductive process which occurs according to the following simplified order:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Thus, microbial denitrification results in the formation of environmentally benign nitrogen gas from toxic nitrogen oxides.

In the present study, the ability of indigenous denitrifying bacteria to remove and degrade NO_x within a compost biofilter was assessed.

2. Experimental

2.1. Compost

The biofilters used in this study contained a wood compost bed medium. The compost, which was derived from a mixture of both coniferous and deciduous trees, was obtained from the Schenectady County Soil and Water Conservation District (Scotia, NY). No exogenous microbial inoculum was added; however, small (15–20 mm diameter) wood chips were blended (15% w/w) into the compost to serve as a bulking agent.

2.2. Batch studies

Batch studies were set up in 120 ml serum bottles containing 30 g of wood compost. To remove oxygen, each bottle was flushed with helium and then sealed with a Viton septum. Using a syringe, a specific volume of helium was removed from the headspace (100 ml) of each bottle and replaced with an equal volume of either N_2O or NO. Abiotic control bottles were prepared in the same manner using autoclaved compost. The bottles were incubated statically at 37 °C. Periodically, headspace samples (100 µl) were removed from the bottles and analyzed for NO_x content.

2.3. Biofilter design and maintenance

Bench scale biofilters (2 l) were constructed from glass process pipe (3 in i.d. × 12 in) coupled on both ends with 3 in × 2 in straight reducers (Fig. 1). The reducers were fitted with Teflon end caps equipped with gas inlet and outlet vents. To provide access to the compost, holes were drilled in the sides of the columns and fitted with Teflon sample ports. Each biofilter was loaded with 1 l of bed medium. Various concentrations of nitric oxide (100–500 µl/l) were metered into a stream of nitrogen and delivered to the biofilters at a flow rate of $1\,l\,min^{-1}$ under single pass conditions. Using volumetric water displacement, the void volume of the biofilter was found to be approximately 1.4 l. To provide moisture to the bed medium and maintain a neutral pH within the system, the biofilters were treated daily, via the sample ports, with 60 ml of phosphate buffer solution.

2.4. Adsorption studies

Autoclaved compost was used to assess abiotic removal of nitric oxide. Compost was autoclaved for 30 min (120 °C) and then incubated at 37 °C for 24 h to allow

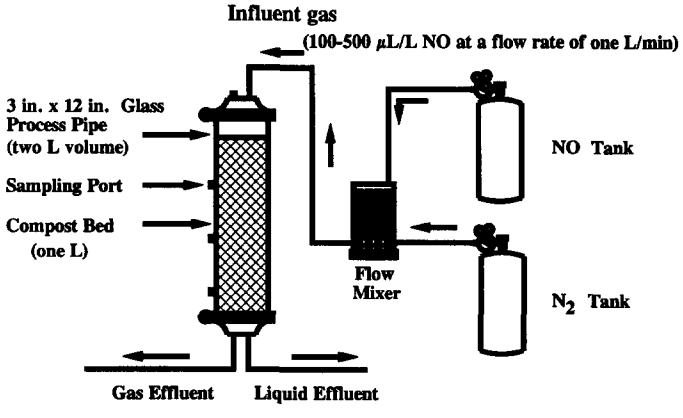

Fig. 1. Schematic of NO_x biofilter.

vegetation of heat resistant spores. This process was repeated a minimum of three times. A biofilter was assembled, loaded with the autoclaved compost, and autoclaved again. A parallel biofilter containing biologically active compost was also assembled and both biofilters were then brought on line.

2.5. Analytical methods

Nitrous oxide (N_2O) was analyzed using a Gow-Mac (Bridgewater, NJ) Series 550 P gas chromatograph (GC) equipped with a thermal conductivity detector and a HayeSep-Q (Alltech, 80/100 mesh) stainless steel packed column (8 ft × 1/8 in). Helium was used as carrier gas at a flow rate of 30 ml min^{-1}. The GC oven temperature was maintained at 30 °C, the injector at 75 °C and the detector at 85 °C. Using these parameters, the column retention time of N_2O was approximately 3.5 min.

A Bendix Model 8101-C Oxides of Nitrogen Analyzer (Dasibi Environmental Corp., Glendale, CA), using a flow injection type of analysis, was used to monitor NO_x levels in the influent and effluent gas streams. The voltage output signal from the instrument was connected to a standard integrating laboratory recorder. This type of instrument is capable of determining both nitric oxide (NO) and nitrogen dioxide (NO_2), either separately or together as NO_x. The instrument uses a chemiluminescence-type detection system.

3. Results and discussion

3.1. Screening studies

Initially, screening studies were conducted to assess the ability of indigenous compost bacteria to remove and degrade NO_x. In batch experiments, the bacteria were found capable of rapidly reducing headspace N_2O. As shown in Fig. 2, within 96 h, 0.48 m*M* N_2O was completely removed from the headspace (100 ml) of serum bottles containing 30 g of compost. At that time, the bottles were spiked with a second dose of N_2O (0.5 m*M*), which again was depleted within 96 h. Two additional N_2O spikes were added to the bottles and each time the same pattern of N_2O removal was observed. During this experiment N_2O levels in serum bottles containing autoclaved compost remained high (0.46 m*M* N_2O), clearly indicating that N_2O reduction was due to microbial activity. In a similar experiment, 0.34 m*M* NO was added to serum bottles containing biologically active compost; within 48 h, NO was no longer detected in the headspace. These preliminary data indicated that biofiltration of NO_x was feasible; hence, biofilter studies were initiated. Since NO is the predominant form of NO_x in combustion gas streams, all future biofiltration experiments focused on the removal and degradation of NO.

3.2. Abiotic adsorption of nitric oxide

The removal of NO in a biofilter involves both biological and physical mechanisms. Adsorption studies were conducted comparing NO removal in autoclaved and

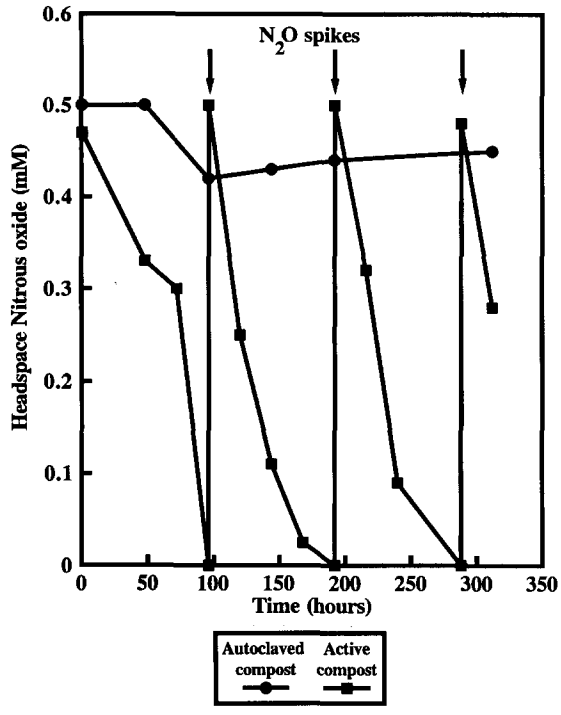

Fig. 2. Removal of N_2O by indigenous compost bacteria. The compost (30 g) was contained in sealed serum bottles (120 ml) and incubated under helium at 37 °C. The experiment was started by injecting 15 ml N_2O (0.5 m*M*) into the headspace (100 ml) of each bottle.

non-autoclaved biofilters. As shown in Fig. 3, approximately 3% NO removal was attributed to abiotic uptake.

3.3. *Effect of dextrose on nitric oxide removal*

A series of experiments were conducted to assess NO removal in compost biofilters and, concurrently, to determine if the bed medium provided adequate carbon and energy for optimum biodegradation of NO. Two biofilters were assembled and brought on line. Biofilter I was maintained at 37 °C and treated daily with 60 ml of phosphate buffer (0.6 m*M* K_2HPO_4). Biofilter II was maintained at 37 °C and treated daily with 60 ml phosphate buffer containing 0.6 g dextrose. During the first 20 d of the experiment, the biofilters were purged with a stream of nitrogen (1 l min^{-1}) containing 100 µl/l NO; on day 20, the influent NO concentration was increased to 275 µl/l. As shown in Fig. 4, bed ripening was observed within 3 d of operation and at steady state, both biofilters effectively removed 100 µl/l NO from the influent gas stream. As influent NO levels were increased, NO conversion in the non-dextrose-treated biofilter decreased. However, in the dextrose amended biofilter a temporary

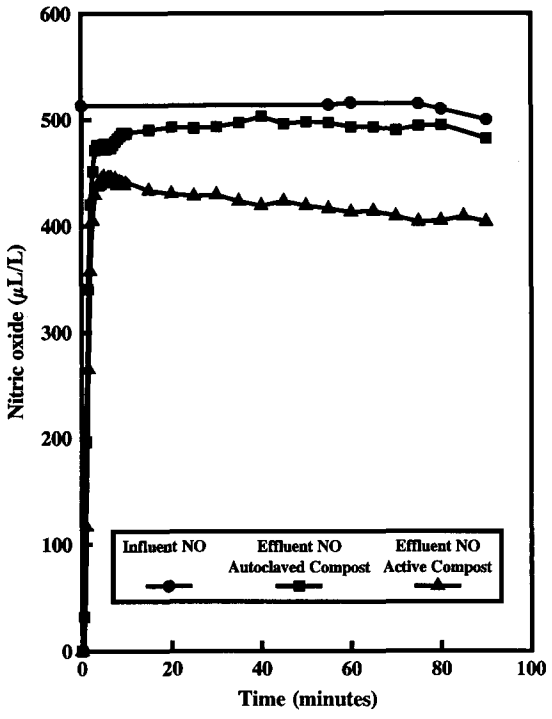

Fig. 3. Removal of NO by autoclaved and non-autoclaved compost biofilters at 22 °C. A nitrogen gas stream containing 510 μl/l NO was continuously purged (1 l min^{-1}) through the biofilters under single pass conditions.

decrease in NO removal was observed, presumably as bacteria acclimated to the higher NO level (days 21–23), followed by a rebound (i.e. recovery of efficient NO removal). On day 30 of the experiment, the dextrose treated biofilter removed 94% of the influent NO, whereas the non-dextrose treated column removed 58% NO. These data suggest that at least for short periods of operation, the quantity of compost used in these studies provided adequate carbon and energy for the removal and degradation of low NO levels. At higher NO concentrations, however, substrate became limited and the addition of an exogenous carbon source was required to maintain efficient NO reduction.

To evaluate further the effects of NO concentration and dextrose treatment on NO removal, the concentration of influent NO to the above biofilters was increased to 500 μl/l. After one week of operation, Biofilter I (phosphate buffer treated) removed 38% of the influent NO; whereas, Biofilter II (treated with phosphate buffer plus dextrose) removed 74% NO. At that time, in order to determine if substrate levels in Biofilter II were adequate, the concentration of dextrose was increased from 0.6 to 1.2 g per day.

Twenty-four hours after the dextrose level was augmented, 98% of the influent NO was removed in the biofilter (Fig. 5). On day 2 and 3 of the experiment, 99% NO

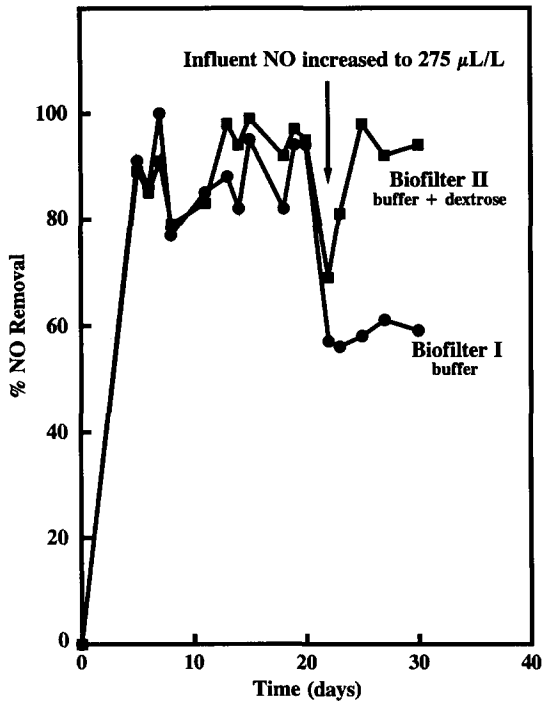

Fig. 4. Effect of dextrose on NO removal in a compost biofilter. Biofilter I was treated daily with 60 ml of phosphate buffer (0.6 mM K_2HPO_4). Biofilter II was treated daily with 60 ml phosphate buffer containing 0.6 g dextrose. Both biofilters were maintained at 37 °C. During the first 20 d of the experiment the influent gas stream (1 l min^{-1}) contained 100 μl/l NO. On day 20, the influentNO concentration was increased to 275 μl/l.

removal was measured. However, on day 6, NO removal dropped to 25%. Throughout these studies, the pH of liquid draining from the biofilters was monitored on a regular basis. Prior to this experiment, the pH typically ranged between 6.3 and 6.5. As shown in Fig. 5, after the dextrose level was increased, the pH of the compost initially remained stable; however, between day 3 and day 6 of the study, the pH dropped from 6.0 to 5.0. At that time, to determine if the dramatic decrease in NO removal was due to low pH, the biofilter was treated with a stronger buffer solution (1.2 mM K_2HPO_4). Twenty-four hours after the phosphate level was raised, an increase in both pH and NO removal was observed (Fig. 5). Within 48 h, the pH of the liquid draining from the biofilter measured 6.0, and NO removal was found to be 70%.

To confirm the effect of pH on NO removal, a biofilter containing fresh compost (not previously exposed to NO) was brought on line and maintained at pH 6.5 by daily treatment (60 ml) with the stronger buffer solution (1.2 mM K_2HPO_4). The biofilter was operated at ambient temperature, treated with 1.2 g of dextrose per day and purged with a nitrogen gas stream (1 l min^{-1}) which contained approximately 500 μl/l NO. Within 6 days, NO levels in the effluent gas stream decreased from 457 to

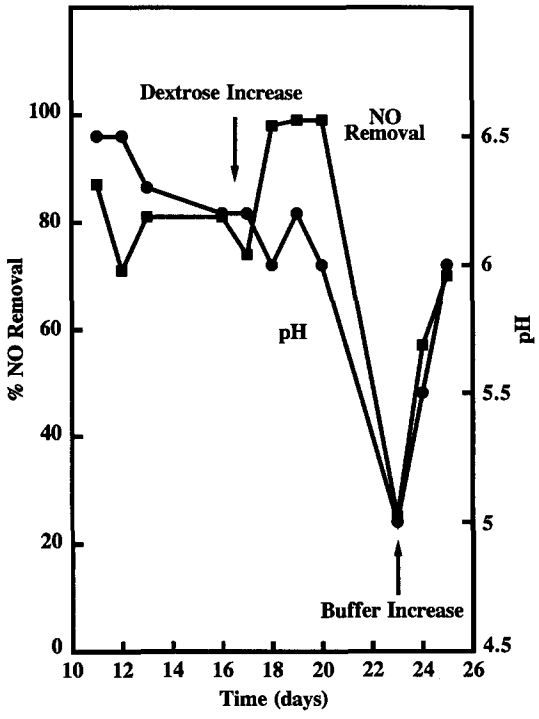

Fig. 5. Effect of increased dextrose concentration on NO removal and pH of a compost biofilter. A nitrogen gas stream containing 500 μl/l NO was continuously purged (1 l min^{-1}) through the biofilter under single pass conditions. The biofilter was maintained at 37 °C and treated daily with 60 ml phosphate buffer (0.6 m*M* K_2HPO_4) containing 0.6 g dextrose. On day 17 of the experiment, the concentration of dextrose was increased to 1.2 g/d. On day 23, in an effort to raise the pH, the concentration of phosphate buffer was increased from 0.6 to 1.2 m*M* K_2HPO_4.

96 μl/l and after 19 days of operation, 95% NO removal was measured (Fig. 6). The conversion of NO to N_2 in the biofilter is due to the activity of naturally occurring denitrifying bacteria. Although the majority of denitrifying bacteria are non-fermenters, numerous other indigenous compost bacteria anaerobically ferment dextrose. Metabolic end products of fermentation include lactic acid, acetic acid, and formic acid. The decrease in pH in the presence of high levels of dextrose may reflect the accumulation of these organic acids. Although denitrifyers can tolerate some pH variance, they are most active when the pH of their environment ranges from pH 6 to 8 [15]. Consequently, as shown in these studies, pH control in the biofilter is a critical parameter in the optimization of nitric oxide removal.

3.4. Effect of lactate on nitric oxide removal

To avoid pH changes due to the accumulation of fermentative end products, use of sodium lactate, a non-fermentable carbon source, was evaluated. A biofilter containing fresh compost was brought on line (37 °C) and treated daily with 60 ml phosphate

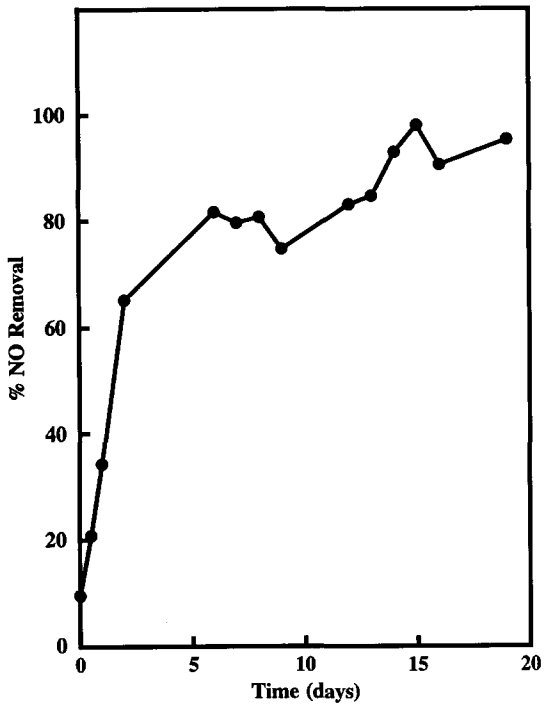

Fig. 6. NO removal by a compost biofilter treated with dextrose and maintained at pH 6.5. The biofilter was operated at 22 °C and treated daily with 1.2 m*M* K_2HPO_4 (60 ml) containing 1.2 g dextrose. A nitrogen gas stream containing 500 μl/l NO was continuously purged (1 l min^{-1}) through the biofilter under single pass conditions.

buffer (0.6 m*M* K_2HPO_4) containing 0.25 *M* lactate. Over a 14 d test period, 80–94% of the influent NO (510 μl/l) was removed in the biofilter and the pH ranged between 6.0 and 6.9 (Fig. 7). The pH stability observed during this experiment was encouraging; therefore, the effects of treating compost biofilters with lactate over a longer time course were assessed.

New biofilters were brought on line and treated daily (60 ml) with either a phosphate buffer solution (0.04 *M* Na_2HPO_4, 0.02 *M* KH_2PO_4) or phosphate buffer plus lactate. The carbon equivalents (CH_2O) required by bacteria to convert completely the level of NO present in the influent gas stream to nitrogen, carbon dioxide, and water were calculated. Theoretically, 2 mol of NO are biologically converted for every mole of CH_2O. Based upon this calculation, to provide adequate substrate for denitrification, lactate levels were adjusted as inlet NO concentrations changed. Initially, the biofilters were purged with an influent gas stream containing 100 μl/l NO; this was increased to 250 μl/l NO on day 10, and to 500 μl/l NO on day 25 of the experiment. NO levels, present in the influent and effluent gas streams of the biofilters, were measured over a 42 day test period. As shown in Fig. 8, removal of NO in lactate and non-lactate treated biofilters was compared at 37 °C. At an influent nitric oxide

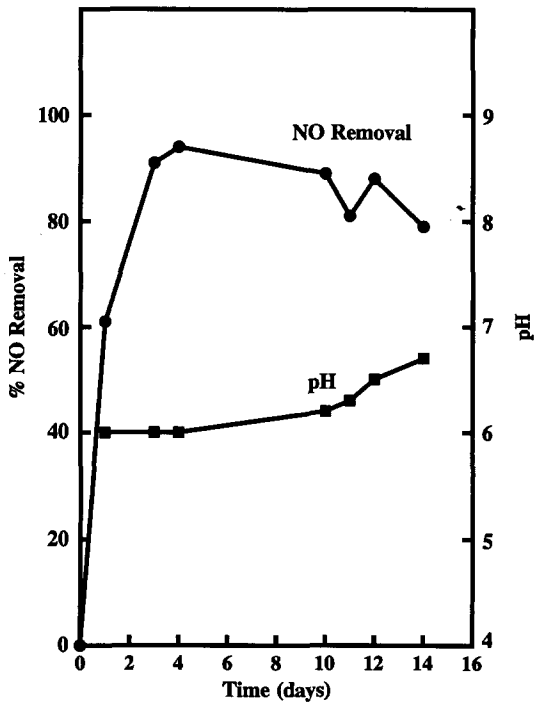

Fig. 7. NO removal and pH in a compost biofilter treated with lactate. The biofilter was maintained at 37 °C and treated daily (60 ml) with 0.6 m*M* phosphate buffer (K_2HPO_4) containing 0.25 *M* sodium lactate. The influent gas stream, which contained 510 µl/l NO, was purged through the biofilter at a flow rate of $1\,l\,min^{-1}$.

concentration of 100 µl/l, NO removal in the biofilters reached steady state within 10 d of operation. During this time, addition of exogenous carbon did not result in a notable increase in NO degradation. As the NO concentration was increased to 250 µl/l, lactate treatment significantly enhanced NO removal. Following acclimation to the higher NO level (day 21), 94% NO removal was measured in the lactate treated biofilter and 58% NO removal was measured in the non-lactate treated biofilter. As in previous dextrose studies, the need for exogenous carbon was amplified at an influent NO level of 500 µl/l. On day 42 of the experiment, 83% NO removal was measured in the lactate treated biofilter, whereas the non-lactate treated biofilter removed 22% NO. During this test period, pH levels in the biofilters ranged between 6.5 and 8.0.

3.5. Effect of temperature on nitric oxide removal

The effect of temperature on NO removal in lactate treated biofilters was measured at 22 and 37 °C. Initially, higher NO removal occurred at 37 °C; however, microbial activity in the 22 °C biofilter increased with time. By day 3, approximately 85% of the influent NO was removed by both the 22 and 37 °C biofilter. As shown in Fig. 8, at

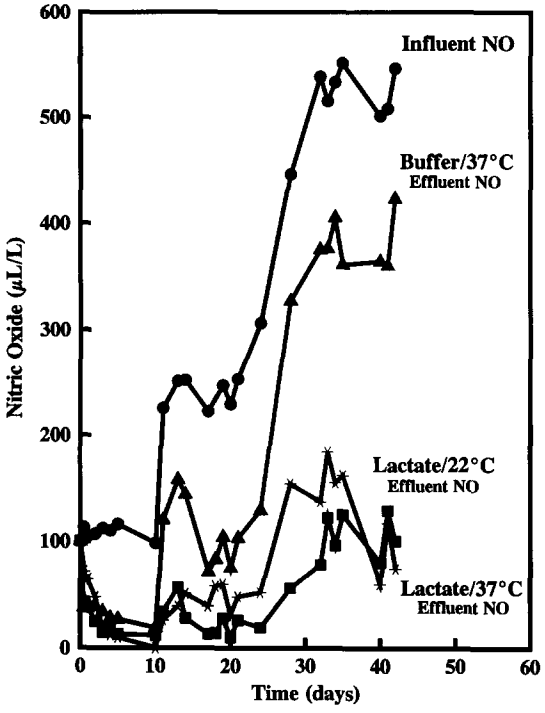

Fig. 8. NO levels measured in the influent and effluent gas streams of continuous flow compost biofilters. Nitrogen carrier gas, containing various concentrations of NO (100–500 μl/l), was directed through the biofilters at a flow rate of 1 l min^{-1}. The biofilters were treated daily (60 ml) with either a phosphate buffer solution (0.04 *M* Na_2HPO_4, 0.02 *M* KH_2PO_4) or phosphate buffer plus lactate. As influent NO levels changed, lactate levels in the buffer were adjusted to provide adequate substrate for denitrification.

influent concentrations of 250 μl/l NO (day 10–21) and 500 μl/l NO (day 31–42) NO removal by both biofilters was comparable. Although ripening of the biofilter appeared to occur more quickly at 37 °C, once the biofilters became biologically active, operating at 37 °C was not required for optimal NO removal.

3. Conclusions

(1) These studies have demonstrated that biofiltration is a viable technology for the removal of NO_x from gas streams.

(2) Biological removal of NO_x in a biofilter is significantly enhanced by the addition of an exogenous carbon and energy source.

(3) Control of pH in the biofilter is a critical parameter for optimum denitrifying activity.

(4) Combustion gas streams typically contain various amounts of oxygen and fluctuate in temperature depending upon post combustion treatment. An industrial

NO_x biofilter designed for flue gas remediation must be capable of operating under these variable conditions. In addition, commercial application of a NO_x biofilter will require an inexpensive carbon and energy source. Additional work related to these variables will be necessary to determine the ability of biofiltration to compete with existing technologies.

Acknowledgements

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