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Comparison of Three Bed Packings for the Biological Removal of Nitric Oxide From Gas Streams

Brady D. Lee[1], William P. Flanagan[2], Joni M. Barnes[1], Karen B. Barrett[1], L. Bryan Zaccardi[1] and William A. Apel[1]

ABSTRACT

Environmental and health issues coupled with increasingly stringent nitrogen oxide (NO_X) emission standards indicates a need for the development of alternative low-cost technologies for the removal of NO_X from gas streams. Biological NO_X conversion offers promise as a novel treatment method. Thermophilic denitrifying bacteria indigenous to composts and soils are capable of converting NO_X to environmentally benign nitrogen via a dissimilatory reductive pathway. The present study compares the performance of three bioreactor packing materials (compost, perlite, and biofoam) for the removal of nitric oxide (NO) from a simulated wet-scrubbed combustion gas. Although all three materials performed well (>85% NO removal) at residence times of 70-80 seconds, the compost performed better than the other materials at shorter residence times (13-44 seconds). The perlite and biofoam materials, however, both offer long-term thermal stability and lower pressure drop compared with compost. The feasibility of biological NO_X conversion processes will depend on the combined factors of NO_X removal ability and pressure drop. The results presented here suggest that the compost, perlite and biofoam systems, subject to further optimization, offer potential for the biological removal of NO_X from gas streams.

INTRODUCTION

Nitrogen oxides (NO_X) are hazardous air pollutants that lead to the formation of acid rain and tropospheric ozone. Approximately 24 million tons of NO_X were released to the atmosphere from U.S. sources during 1998.[1] Titles I and IV of the 1990 Clean Air Act Amendments regulate NO_X emissions from major stationary sources.[2] The overall goal of these programs is to achieve NO_X reductions of 2 million tons per year below 1980 levels by the year 2000.

Biological treatment of fuel combustion gases using gas phase bioreactors such biofilters or biotrickling filters offers a number of unique challenges. Many coal combustion streams are scrubbed with a water/limestone slurry to reduce sulfur dioxide emissions. Gases exiting the scrubbers typically exhibit temperatures between 50°C and 60°C. The bioreactor packing materials should therefore exhibit long-term thermal stability within this temperature range and must contain suitable concentrations of thermophilic denitrifying bacteria. Blower operating costs for coal-fired power plants can be significant, thus the treatment system must operate with minimal back pressure. Many fuel combustion applications generate flue gas streams with very large volumetric flow rates. The bioreactor must therefore operate with a short gas residence time in order to achieve a competitive capital cost and a reasonable footprint area. Finally, combustion streams typically contain oxygen at levels ranging from 3-8%, therefore the biological treatment process must be capable of operating under such oxidative conditions.

Substantial prior work has been conducted regarding the use of compost-based biofilters for the removal of NO_X from gas streams.[3,4] The objective of the present study was to identify alternative bioreactor packing materials that exhibit long-term thermal stability and can achieve biological NO_X

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removal with reduced back pressure. Various ratios of compost to inert material (i.e., lava rock and perlite) in the bed medium were also compared. The effect of oxygen on the biological NO_x -removal process was not considered in this study, but is the subject of on-going research at the Idaho National Engineering and Environmental Laboratory (INEEL).[5,6]

EXPERIMENTAL METHODS

Biofilter Packings

The three types of bed packings compared during this study included wood compost, perlite and biofoam. Compost is the most common biofilter packing material used in Europe and North America. Perlite and biofoam were chosen as potential alternatives to compost since both materials potentially offer a lower resistance to gas flow and greater long-term thermal stability.

Compost was obtained from an unfinished wood chip compost pile (courtesy of Browning Excavation, Pocatello, ID). Unfinished compost was used during this phase of the study to capitalize on thermophilic microorganisms dominant in the interior of a compost pile where temperatures are elevated during active composting. For initial experiments the compost was amended with 30% w/w crushed lava rock (4-6 mm) to improve moisture retention and bed porosity and 20% w/w ground calcite as a means of internal pH control.

Horticultural expanded perlite is an inert, porous ceramic material of volcanic origin.[7] Perlite has been used as a thermostable biofilter packing for thermophilic ethanol degradation[8] and as a packing for fungal biofilters treating styrene-contaminated air.[9] The perlite used in this study had an average aggregate diameter of approximately 2-4 mm and was manufactured by A.H. Hoffman, Inc. (Landisville, PA).

Biofoam is a non-compressible, macroporous ceramic material manufactured by Cercona, Inc. (Dayton, OH). The biofoam is made by encapsulating refractory materials in a sodium aluminosilicate hydrogel that is formed by reacting sodium silicate and sodium aluminate. Typical densities of this material range from 0.3-0.8 g/cm^3. The material has three average porosity ranges: a cell wall porosity of 2-10 microns, a porosity between cells of 20-100 microns, and an average cell size from 100-600 microns. Monolithic biofoam structures have been used as biofiltration matrices for the treatment of volatile organic compounds in air.[10] For this study, the biofoam material was manufactured as non-uniform spheres with an average particle diameter of approximately 12 mm.

Biofilter Design and Maintenance

Bench scale biofilters (Figure 1) were constructed of 7.62 cm i.d. × 30.48 cm length glass process pipe coupled on both ends with 7.62 cm × 5.08 cm straight reducers.[3,4] The biofilters were fitted with Teflon end caps that provided vents for gas inlet and outlet streams, manometer ports, thermocouple ports, a liquid effluent port, and a headspace pressure release valve. A perforated Teflon plate situated between the pipe and the bottom reducer supported the biofilter packing material. Four Teflon-fitted ports were spaced vertically along the biofilters to allow delivery of a liquid nutrient medium. The biofilters were wrapped with heat tape and covered with a 1 cm thick layer of fiberglass insulation. The heat tape was controlled by a Thermolyne Type 45500 Input Controller and a Cole-Parmer Digi-Sense Temperature Controller using a thermistor inserted into the biofilter packing as the input signal. The temperature of the biofilters was maintained at 53-55^{o}C.

A nitrogen carrier gas (flow rate 0.5 to 8 L/min) was humidified and preheated by passing upflow through a humidification column constructed of 7.62 cm i.d. × 60.96 cm length glass process pipe coupled on both ends with 7.62 cm × 5.08 cm straight reducers. The humidification column was filled with demineralized water and contained 0.68 kg of 8 mm × 8 mm glass Raschig rings to provide greater dispersion of nitrogen gas bubbles. The column was wrapped with heat tape, insulated with 1 cm thick fiberglass insulation, and controlled at a temperature of 65^{o}C using a control system similar to that

described for the biofilters. Nitrogen gas exiting the column contained 99.7+ percent relative humidity over the range of gas flow rates studied.

The humidified, preheated nitrogen gas was delivered to the biofilter apparatus through heat-traced 3.18 mm o.d. (0.125 in o.d.) stainless steel tubing. NO was metered into the nitrogen upstream of the biofilter to provide a nominal biofilter inlet concentration of 500 ppmv. The combined gas stream was fed through the biofilter in downflow, continuous one-pass operation.

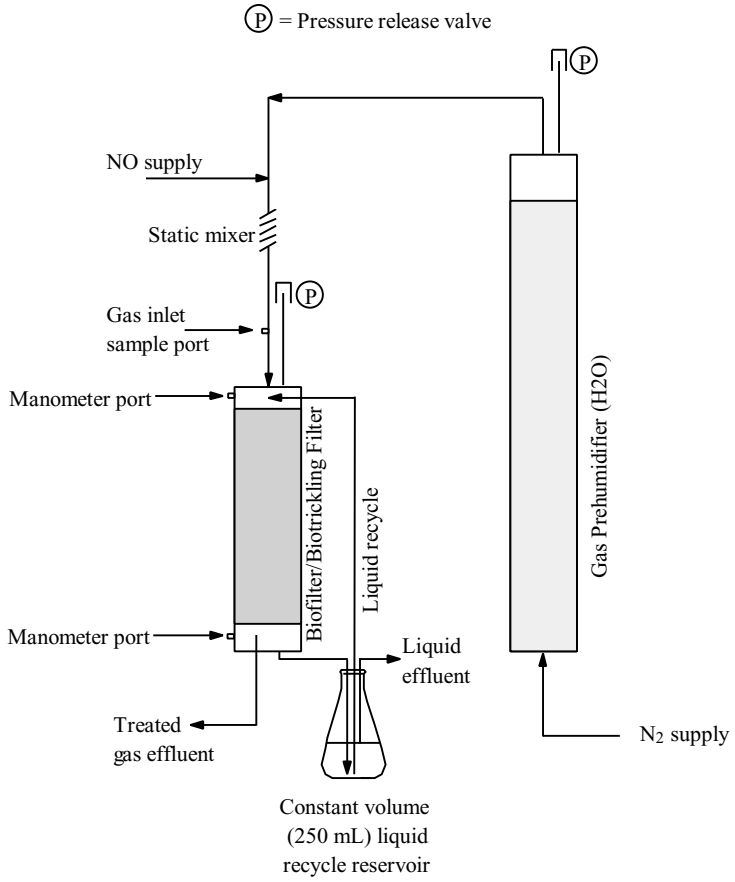

Figure 1. Diagram of biofilter/biotrickling filter apparatus. The liquid recycle loop was only used to keep the packing wetted during operation of the biofoam system, and was not included during operation of the compost or perlite-based systems.

Unlike the compost and perlite biofilter packings, the biofoam material had very little moisture retention capacity. A liquid recycle stream was therefore incorporated into the reactor design to keep the biofoam packing wetted during operation (Figure 1). This configuration is typically referred to as a biotrickling filter rather than a biofilter.[11] The liquid recycle rate was set at a nominal 37.5 mL/min for a gas influent rate of 1 L/min, plus an additional 13 mL of recycle/min for each additional liter of gas influent/min. The effect of liquid recycle rate on NO removal was not characterized during this study.

Inoculum Preparation

The perlite and biofoam materials were inoculated with thermophilic denitrifying bacteria enriched from compost. The inoculum cultures were prepared by adding 5 g of compost from Schenectady, NY to 40 mL of denitrifying medium in serum vials. The vials were crimp-sealed and the headspaces replaced with nitrogen, followed by stationary incubation at 55°C for 48-72 hours. Active inoculum cultures were mixed with prewetted perlite or biofoam packing material just prior to biofilter loading. Three serum vial cultures were used to inoculate each biofilter. Biofilters containing compost as the packing material were not inoculated.

Nutrient Delivery

A liquid nutrient medium was supplied to the biofilter to provide a source of carbon, inorganic nutrients, and supplemental moisture. The medium entered the biofilter either at the top of the biofilter or through four coiled soak hoses that distributed the liquid nutrients within the biofilter packing. The nutrient delivery rate was set at a nominal 288 mL/day for a gas influent rate of 1 L/min, plus an additional 100 mL of nutrient/day for each additional liter of gas influent/min. Note that the liquid delivery rate was based on empirical experience with compost-based biofilters and may not have been optimal for the perlite or biofoam reactors.

The nutrient medium used for the perlite and biofoam reactors contained (per liter of demineralized water): 4.76 g KH_2PO_4, 2.61 g K_2HPO_4, 1 g $(NH_4)_2SO_4$, 0.098 g $MgSO_4$, 10mL of the trace salts stock solution described earlier, and lactate as the carbon source. Lactic acid was added to demineralized water and neutralized with 4N NaOH prior to the addition of other nutrient constituents.

Analytical Methods

Nitric oxide levels in the influent and effluent gas streams were measured using a Model 42H Chemiluminescent NO-NO_2- NO_X Analyzer (Thermo Environmental Instruments Inc., Wilmington, DE). The voltage output from this instrument was connected to a standard laboratory integrating recorder. A linear calibration curve was prepared prior to each sampling event by injecting several different volumes of a 1000 ppmv NO (in nitrogen) calibration gas. Sample and standard injections were performed in quadruplicate.

End-point biomass concentrations within the perlite and biofoam reactors were determined using a modified total suspended solids (TSS) procedure. Biomass was calculated as the dry weight difference between the digested and non-digested samples. Perlite and biofoam control samples were used to account for possible weight loss due to attrition of packing material during the procedure. All biomass determinations were performed in duplicate. Surface area measurements of each packing material was also determined.

RESULTS AND DISCUSSION

Compost

NO removal results from a biofilter containing compost receiving acetate as the carbon source are presented in Figure 2. The experiments were conducted to determine the effect of gas residence time in the biofilter on NO removal efficiency. Over a 7 week test period the biofilter was operated at gas flow rates of 1, 2, 3, and 5 L/min, corresponding to empty bed residence times of 78, 39, 26, and 15.6 seconds, respectively. The pH of the liquid effluent remained near 7 for the duration of the test. During the first 5 weeks of operation the biofilter performed well; however, during the sixth week of the experiment (4 days after the flow rate was increased to 5 L/min), NO removal dropped to near 10%. Since the pH of the bed was within the optimum operating range the decrease in NO removal may have been caused by the build-up of inhibitory metabolic end products in the bed. For this reason the bed medium was washed for 72 hours with deionized water. Following the washing the NO removal increased to an average of 67% over the subsequent 11 day period.

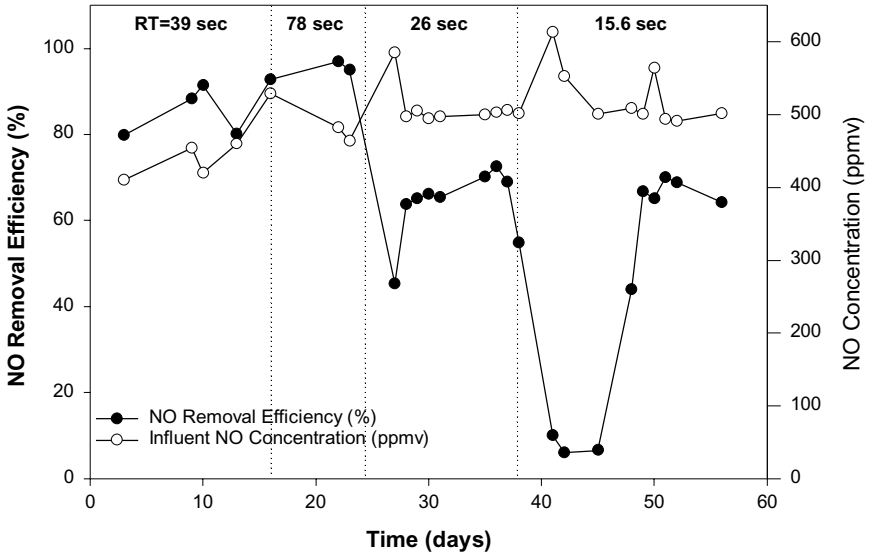

Figure 2. Influent NO concentration and NO removal efficiency for the compost biofilter.

Perlite

Results from the biofilter containing perlite as the bed packing material are given in Figure 3. This system was operated over a 70 day period at gas flow rates of 1.1, 1.9, 2.5 and 4 L/min (corresponding to empty bed residence times of 71, 41, 31 and 19.5 seconds). The NO removal efficiencies ranged from 94 to 56% at the longest and shortest residence times, respectively. The pH of the liquid effluent ranged from 6.9 to 9.0.

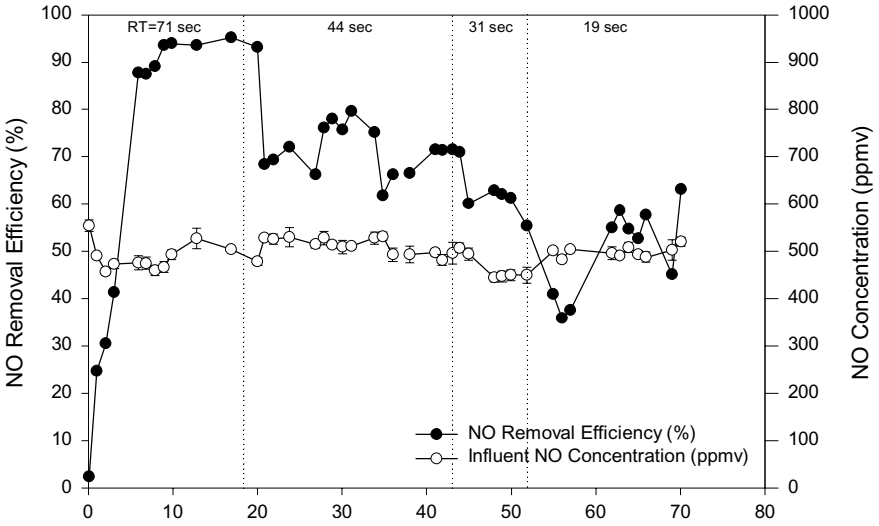

Figure 3. Influent NO concentration and NO removal efficiency for perlite biofilter.

To assess potential abiotic losses of NO in the perlite system, a biofilter containing autoclaved, uninoculated perlite was operated for 8 days (data not shown). The effluent NO concentration matched the influent NO concentration within 5 minutes or less of start-up. The observed loss of NO throughout the control experiment averaged 0.2%, which was less than the standard deviation associated with the analytical procedure.

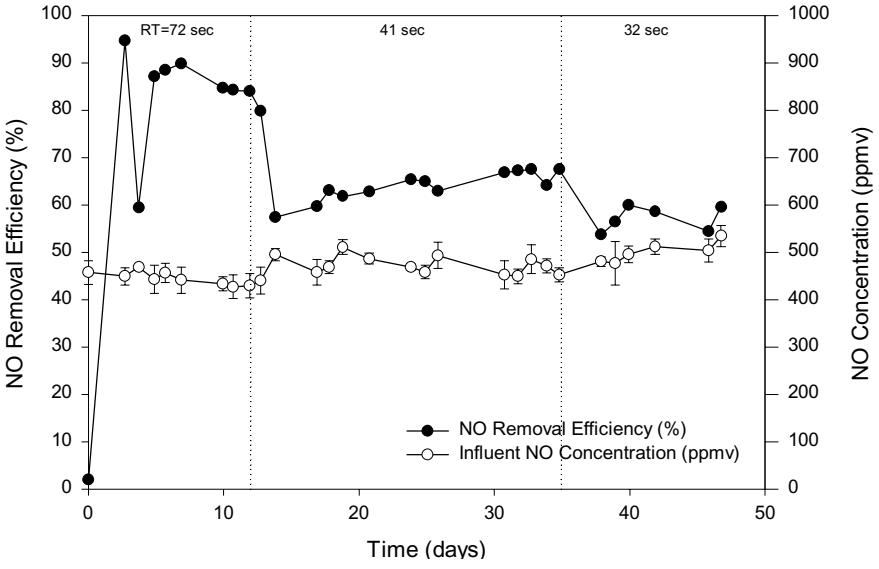

Figure 4. Influent NO concentration and NO removal efficiency for biofoam biotrickling filter.

Biofoam

Results from the biotrickling filter containing biofoam as the bed packing material are given in Figure 4. This system was operated over a 47 day period at gas flow rates of 1.1, 1.9 and 2.5 L/min (corresponding to empty bed residence times of 71, 41 and 31 seconds). The NO removal efficiencies ranged from 58 to 85.5% at the shortest and longest residence times, respectively. The pH of the liquid effluent ranged from 7.1 to 8.5.

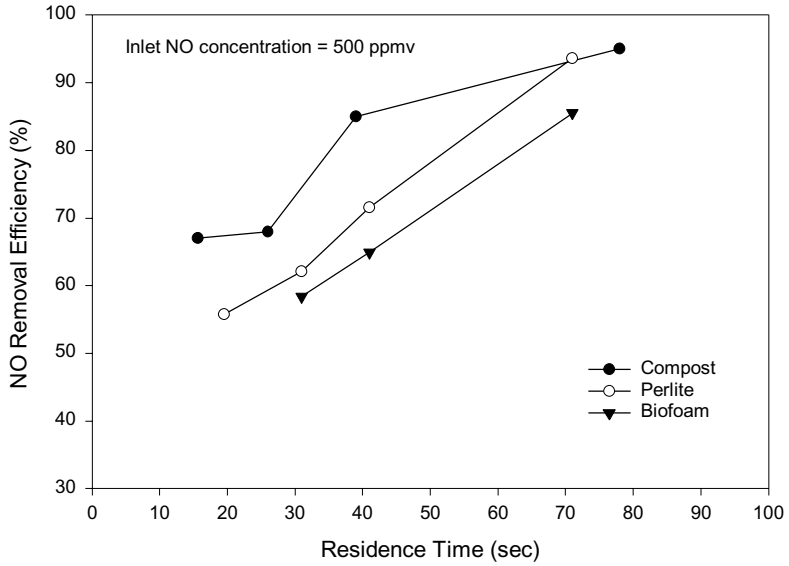

Figure 5. Packing comparison: NO removal efficiency vs. gas residence time.

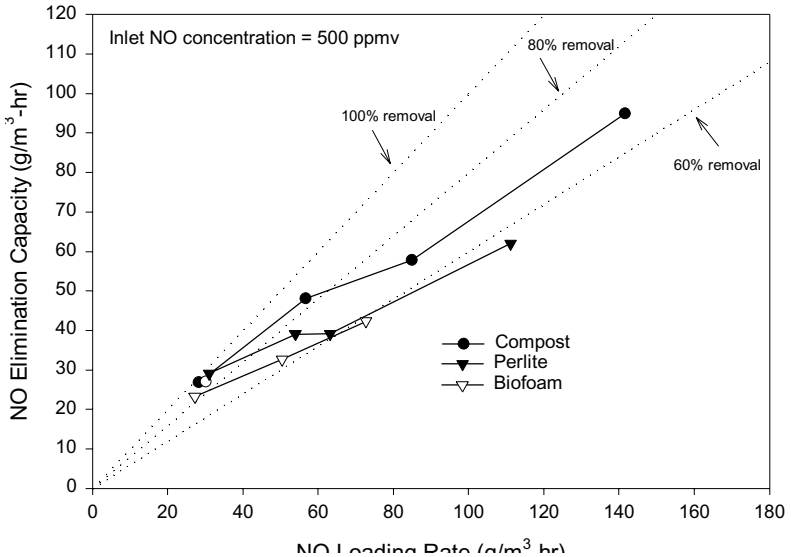

Figure 6. Packing comparison: NO elimination capacity vs. NO loading rate.

Packing comparison

The performance of the compost, perlite and biofoam systems are compared in Figures 5 and 6. Each data point represents the average performance of a system at each residence time setpoint following a several day acclimation period.

The compost biofilter consistently provided the best performance over the range of residence times studied (Figures 5 and 6). The NO elimination capacities ranged from 27 to 95 g NO/m^3 bed•hr at residence times from 78 to 16 seconds, respectively.

The NO removal efficiency remained greater than 80% for residence times of 39 seconds or longer. The perlite biofilter exhibited performance comparable to the compost biofilter at a residence time of 71 seconds, but did not perform as well at shorter residence times. The biotrickling filter containing biofoam was the least effective of the systems studied, although this reactor configuration was nevertheless able to achieve a reasonable NO removal efficiency (85.5%) at a residence time of 71 seconds.

The observed performance differences among the various packings may be due to a variety of factors. Biological removal of NO in compost-based biofilters has been studied extensively,[3-6] thus many of the operating conditions, including moisture delivery rate, have been empirically developed. In contrast, the effect of moisture delivery rate on the performance of the perlite and biofoam systems has not yet been investigated.

Differences also exist regarding the amount and distribution of biomass in each packing material. Compost inherently contains a wide variety of indigenous microflora, including thermophilic denitrifying bacteria, thus compost biofilters do not require inoculation. In contrast, perlite and biofoam systems must be inoculated with appropriate cultures derived from compost or other sources. For best results, the inoculum should be mixed evenly into the packing material, although this is often difficult to achieve in practice. Furthermore, a suitable biofilm must form within and throughout the host packing material in

order for efficient biodegradation to occur. Biofilm development often occurs more slowly in alternate reactor configurations than in compost-based biofilters.[12]

End-point biomass concentration measurements revealed that the perlite packing contained a much higher concentration of biomass than the biofoam packing (Table 1). This is consistent with the

Table 1. **Biomass profiles in perlite and biofoam reactors.**

	TSS* (mg biomass/g packing)		TSS* (mg biomass/L empty bed volume)	
Bed Depth (cm from top)	Perlite	Biofoam	Perlite	Biofoam
0-7.5	91.3±20.4	16.1±10.8	9,934±2,219	2,707±1,825
7.5-15	299.5±1.7	38.9±8.9	32,577±187	6,552±1,492
15-22.5	175.1±19.3	49.8±8.7	19,045±2,095	8,381±1,471
22.5-30	97.3±13.1	43.7±6.2	10,585±1,422	7,360±1,040

*TSS = total suspended solids

higher NO removal efficiencies observed in the perlite system. Determination of biomass concentrations in compost-based biofilters is difficult via standard methods, and was therefore not performed in this study.

For biodegradation to occur, gas-phase NO must first diffuse through a thin aqueous layer surrounding the biofilm. Since NO is poorly soluble in water, mass transfer limitation may play an important role during biological treatment. A packing material with a large surface area would theoretically exhibit better gas/liquid mass transfer properties, and would potentially support a greater concentration of utilizable biomass. Surface area measurements for each of the packing materials are shown in Table 2. As expected, the surface area results were qualitatively correlated with NO removal ability.

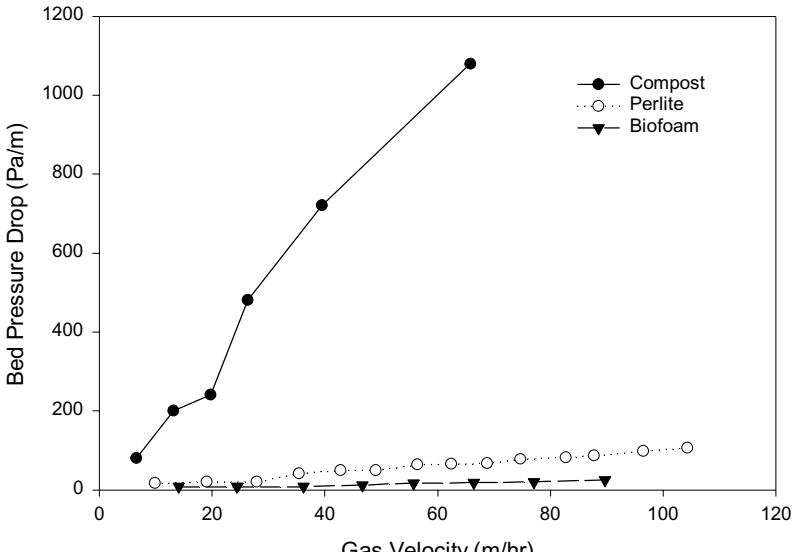

Figure 7. Packing comparison: bed pressure drop vs. gas velocity.

Pressure drop

A pressure drop comparison for each packing type is shown in Figure 7. The perlite and biofoam packings exhibited significantly lower pressure drops than compost for gas influent flow rates ranging from 0.5 to 8 L/min. These results appear to correlate with the surface area measurements reported in Table 2. Note that the pressure drops observed for each packing material remained fairly constant throughout the course of this study.

Table 2. Surface area analyses.

Sample	Surface Area (m^2/g)	Std. Dev. (m^2/g)
Compost	7.10	0.036
Perlite	0.298	0.121
Biofoam	0.119	0.059

For long-term operation, some bioreactor configurations have been known to experience significant pressure drop increases or even plugging as a result of excess biomass accumulation. This is typically experienced in biotrickling filters using inert packing materials rather than in compost-based biofilters,[13,14] and has indeed been observed in previous studies with biofoam material used for the treatment of volatile organic compounds.[15] It is not known whether excess biomass accumulation would occur during long-term operation of the presently discussed biofoam or perlite systems for the biological treatment of NO_x.

CONCLUSIONS

This study has identified two alternative bioreactor packing materials that may be suitable for the biological treatment of NO_x in gas streams. The research presented here evaluates three biofilter bed packing materials and compares NO_x removal efficiencies, gas residence times, and pressure drop characteristics. The perlite and biofoam packings both offer long-term thermal stability and reduced back pressure compared with compost. The NO_x removal ability of the alternative packings was comparable to compost at the longer residence time of 71 seconds, although the compost biofilters performed significantly better at the shorter residence times. These performance differences may be due to a variety of factors: (1) the perlite and biofoam systems have not yet been optimized with respect to moisture delivery rate or inoculation procedure; (2) biomass concentrations and the time required for biofilm development within the various packings may differ substantially; (3) the packings exhibit different amounts of surface area, which may affect gas/liquid mass transfer properties as well as the amount of utilizable biofilm within each packing.

The overall performance and economic assessment of biological NO_x reduction will depend on the combined factors of NO_x removal ability, gas residence time, and pressure drop characteristics. The results presented here suggest that the compost, perlite and biofoam systems, subject to further optimization, could offer potential for the biological removal of NO_x from gas streams.

ACKNOWLEDGMENTS

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