SIMULTANEOUS REMOVAL OF NITROGEN OXIDES AND VOLATILE ORGANIC COMPOUNDS IN FUNGAL VAPOR-PHASE BIOREACTORS

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ABSTRACT

Recent studies have shown that vapor-phase bioreactors containing the fungus *Exophiala lecanii-corni* can remove nitric oxide (NO) and volatile organic compounds efficiently from waste gas streams. However, when NH_4^+ accumulates in the bioreactor, the NO removal efficiency abruptly drops to 20 %. To achieve high NOx removals in the bioreactors, low NH_4^+ levels must be maintained, or a different nitrogen source needs to be provided. For VOCs removal, however, a proper nitrogen source should be available for the fungal growth at adequate level. In this study, two different nutrient supply methods were examined to control nitrogen levels in the bioreactors for attaining simultaneous removal of NOx and toluene. The influence of NO_3^- and NH_4^+ on NOx and toluene removal was also investigated. Two cylindrical bioreactors connected in series were operated at a 30 sec overall EBCT for 90 days. The spike nutrient addition method was proved to be inefficient regardless of the nitrogen species supplied. After the nutrient aerosol transfer method was employed, NH_4^+ level in the bioreactors was maintained at low level, and dramatic increase in NOx and toluene removal was observed. 119 $g/m^3/hr$ of toluene elimination rate was obtained at 136 $g/m^3/hr$ of toluene loading rate, and 31 $g/m^3/hr$ of NOx elimination capacity was achieved at 38 $g/m^3/hr$ of NOx loading rate. NO_3^- was found to be a less efficient than NH_4^+ for both NOx and toluene removal. Pressure drop in the bioreactors was effectively controlled by periodically exposing the bioreactors to NOx over 80 days.

INTRODUCTION

Since conventional nitrogen oxides (NOx) control technologies such as selective catalytic reduction (SCR), and selective non-catalytic reduction (SNCR) require high installation cost and energy consumption, and encounter operating problems like ammonia slip and catalyst deactivation [1, 2], several studies have recently been conducted that focus on NOx removal in vapor-phase bioreactors [3,4,5,6]. These studies have shown that vapor-phase bioreactors containing denitrifying and nitrifying microorganisms have the potential to be an effective treatment alternative for NOx removal in scrubbed flue gas streams although several problems such as a relatively long residence time and O_2 inhibition still remain to be resolved.

Recently, a fungal biofilter has been shown to remove NO efficiently under aerobic conditions at a 60 sec EBCT [7]. The biofilter was originally inoculated with a bacterial culture, but, after two weeks of operation, fungi became dominant in the bioreactor. The dominant species was identified as *Exophiala lecanii-corni* (CBS 102400). A maximum NO removal efficiency of 93 %, corresponding to an elimination capacity of 16.4 g $NO/m^3/hr$ at a 17.6 $g/m^3/hr$ of loading rate, was achieved at an O_2 concentration of 20%,

and a 60 sec EBCT. However, when NH_4^+ accumulated in the porous silicate packed bed (average 8.7×10^2 μg NH_4^+-N/g dry pellet), the NO removal efficiency dropped to 20 %. The reason for the loss of NO removal efficiency at high NH_4^+ levels in the packed bed was that the inhibitory effect of NO on fungal growth was enhanced at high NH_4^+ levels [8].

The primary purpose of the current study was to develop a vapor-phase bioreactor system for simultaneous removal of NOx and VOCs. To achieve high NOx removal, NH_4^+ concentration in the fungal bioreactors must be maintained at low levels, or other nitrogen sources must be provided since the inhibitory effect of NO on fungal metabolism is significantly enhanced at high NH_4^+ concentrations. However, limiting the ammonium supply or providing other nitrogen sources will likely compromise the VOC removal in the system [9]. Accordingly, in the current study, two different nutrient supply methods were examined at a 30 sec EBCT to develop a vapor-phase bioreactor system for simultaneous removal of NOx and toluene; a spike manual addition method and a periodic aerosol transfer method. At the same time, the influence of NO_3^- and NH_4^+ on NOx and toluene removal in the fungal bioreactors was investigated.

MATERIALS AND METHODS

Bioreactor Design and Fungal Inoculation Two cylindrical bioreactors made of stainless steel with a 5.5 cm I.D. were packed with Celite® R-635 (Celite Corporation, Lompoc, CA), a pelletized porous silicate media that have been autoclaved at 121°C for 20 min. A schematic of the bioreactors has been presented elsewhere [10]. Each reactor was equipped with several gas and pellet sampling ports, and was packed to an overall height of 17 cm. The two bioreactor columns had the same configuration, and were connected in series. Each bioreactor was operated at a 15 sec EBCT for 90 days. A 1.6 L/min air stream was filtered and passed through a humidifier. Each of the two bioreactors was inoculated with a pure culture (2.1 g dry biomass/L) of *E. lecanii-corni*(CBS 102400) previously isolated from a biofilter treating toluene [7]. Toluene (99.8 %, Fisher Scientific, Houston, TX) was continuously supplied for the entire operation period via a syringe pump (kd Scientific, Model KDS200, Boston, MA).

Nutrient Supply Two different nutrient delivery methods, a spike manual addition method (Days 1 to 33) and a periodic aerosol transfer method (Days 34 to 48, and Days 56 to 90) were evaluated to control the nitrogen level in the packed beds. When the spike manual method was used, 10 mL of nutrient solution were added manually through the nutrient injection port at the top of each reactor. On Days 34 to 48, and Days 56 to 90, an ultrasonic aerosol maker (Artistic Delights, Milpitas, CA) was used to generate a fine nutrient aerosol that was used to transfer nutrients via the air stream to the bioreactors. Approximately 80 mL of aqueous nutrient solution was ultrasonically vaporized per hour, and fed either into the first reactor for four hours or into each reactor for two hours as summarized in Table 1.

NOx experiments 1,003 ppm_v, of NO supply gas balanced with argon (certified by Air Liquid, Houston, TX) was used throughout this study. It was confirmed that 40 ppm_v of NO_2 were present in the NO supply gas. 0.4 L/min of NOx supply gas was delivered from a compressed gas cylinder to a mixing chamber where it was mixed with a toluene laden air stream. The flow rate of the combined air exiting the mixing chamber was 1.6 L/min and the O_2 concentration was 15.6 %. In each NOx removal experiment, the NOx stream was supplied to the bioreactors for a 4 hr period, prior to measuring the NOx

Days	Methods	Nitrogen Source	Quantity of Nitrogen Source Supplied Daily	Carrier Gas Flow Rate	
1~27	SMA[a]	KNO_3	10 mL of 7.23~ 28.9 g/L	-	To each reactor
28~33		$(NH_4)_2SO_4$	10 mL of 9.34 g/L	-	
34~48	PAT[b]	$(NH_4)_2SO_4$	5g/L for 4hrs	1.6 L/min	To the first reactor only
49~55	No addition	-	-	-	-
56~67	PAT[b]	$(NH_4)_2SO_4$	5 g/L for 4 hrs	1.6 L/min	To the first reactor only
68~77			5 g/L for 2 hrs	3.2 L/min	To each reactor
78~82		KNO_3	7.5 g/L for 2hrs		
83~90		$(NH_4)_2SO_4$	5 g/L for 2 hrs		

[a]: SMA (Spike Manual Addition) and [b]: PAT (Periodic Aerosol Transfer)

Table 1. Nutrient supply conditions examined in the fungal bioreactors

removal profile across the bioreactor.

Analytical Methods The concentration of toluene in the gas stream was analyzed using a Hewlett-Packard 6980 gas chromatograph (GC, Palo Alto, CA) equipped with a FID. NO, NO_2, and O_2, concentrations were determined using a Testo 350 flue gas analyzer (Testo Inc., Flanders, NJ). The flue gas analyzer was calibrated, and certified by the manufacture one week prior to the beginning of bioreactor operation. In addition, the response of the analyzer was recalibrated before each NOx experiment. NH_4^+ and NO_2^- concentrations in solution were analyzed using colorimetric methods [10, 11]. The moisture content of the pellets was determined gravimetrically. Pressure drop across the column was measured using an inclined vertical manometer (Dwyer Instrument Inc., Michigan City, IN).

RESULTS AND DISCUSSION

Toluene Removal

The toluene removal efficiencies observed in the bioreactors containing the fungus *E. lecanii-corni* are presented in Figure 1. The toluene loading rate was 45 g/m^3/hr. For the initial period of operation (Days 1 to 33) when a spike manual addition method was used to supply nitrogen to the packed beds, the toluene removal activity in the bioreactors was low regardless of the type of nitrogen or concentration of nitrogen supplied to the bioreactors. The highest toluene removal efficiency obtained in the bioreactor was 36 % when the nitrogen was supplied manually. These results indicate that the spike manual addition method is inefficient for maintaining bioreactor performance for toluene removal.

To improve the delivery of nitrogen to the column, a periodic aerosol transfer method was adapted on Day 33. Nutrient laden aerosol was generated ultrasonically, and transferred to the first reactor column (reactor A) for four hours (Table 1). As shown in Figure 1, the toluene removal efficiency dramatically increased, and, by Days 40 to 48, the overall removal efficiency was 82 to 89 %. However, only 50 to 58 % of the toluene was removed in the first reactor, and overall toluene removal efficiency was still less than 90 %.

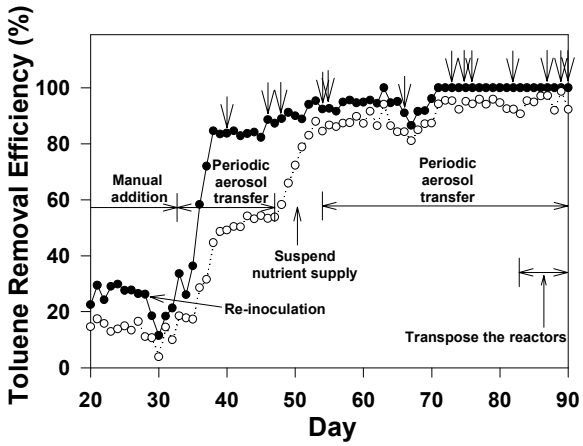

Figure 1. Toluene removal efficiency across both Reactors A and B (●) and across the first reactor (○) only as a function of operating time. The toluene loading rate was 45 $g/m^3/hr$. Symbol (↓) indicates the days when the NOx experiments were conducted.

Manual addition of nutrient media through over the top of the reactors caused uneven distribution of the fungus attached to the packed beds in the bioreactors by channeling and washing out. Since *E. lecanii-corni* is a dimorphic fungus which will form filaments when subjected to nitrogen limited conditions [12], the nutrient supply to the bioreactors was suspended on days 49 to 55 to enhance fungal distribution in the bioreactors, and improve pollutant removals. As a result, the overall pressure drop across the bioreactors increased to 15 mm H_2O (Figure 2), and the toluene removal efficiency in this reactor increased from 58 % to 88 % on days 49 to 54. Although the nutrient supply to the first reactor was resumed on Day 56, complete removal of toluene was not achieved. On Day 66, the NH_4^+ levels in the pellets in the second reactor were undetectable while relatively high NH_4^+ accumulation was observed in the first reactor (data not shown). Thus, most of the nitrogen supplied by the nutrient aerosol system was retained in the first reactor where most of the toluene was consumed. To boost nitrogen availability in the second reactor, the periodic

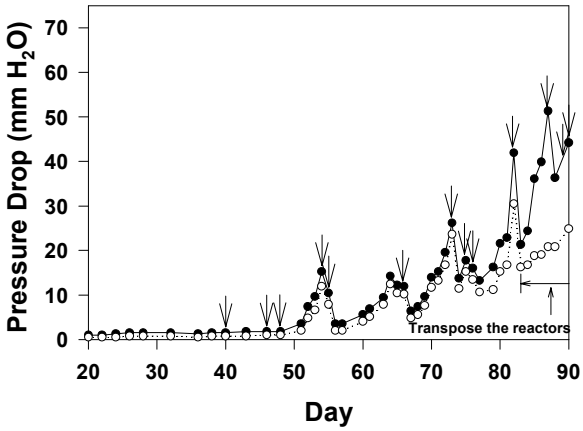

Figure 2. Pressure drop across the overall bioreactors (Reactors A and B) (●) and across Reactor A only (○) as a function of operating time. Symbol (↓) indicates the days when the NOx experiments were conducted.

aerosol transfer method was modified on Day 68. The air stream containing the nutrient laden aerosol was fed directly into each reactor for 2 hrs on Days 68 to 77 rather than just to the first reactor as had been done from Days 56 to 67. The flow rate of the carrier air stream used to deliver the nutrients was also increased to 3.2 L/min from 1.6 L/min on Days 68 to 77. By Day 77, the NH_4^+ level in the bioreactors increased to 1.27×10^2 μg NH_4^+-N /g dry pellet and 3.9×10 μg NH_4^+-N /g dry pellet in the first and second reactors, respectively. An overall toluene removal efficiency of greater than 99 % was achieved by Day 71. On day 83, a maximum elimination capacity of 119 g/m^3/hr was obtained for the 136 g/m^3/hr toluene loading rate (independent data).

Nitrogen Oxide Removal

The NOx ($NO+NO_2$) removal profiles achieved in the fungal bioreactors for inlet NOx concentrations of 250 (240 NO + 10 NO_2) ppm_v are shown in Figure 3. At a 30 sec EBCT across the bioreactors, a 250 ppm_v NOx feed concentrations correspond to a NOx loading rate of 38 g NOx/m^3/hr. On Days 55, a 42 % overall NOx removal efficiency was observed when the toluene removal efficiency was less than 90 %. After the toluene removal efficiency exceeded 99 %, the NOx removal efficiency increased to 73 % on Day 73. Thus, the increase of NOx removal activity coincides with the increase in the toluene removal activity in the bioreactors. Since nitrite (NO_2^-) is formed in aqueous media from NO reaction with O_2 under aerobic condition [11], residual NO_2^- level in the pellets pellet samples was measured. As the toluene removal activity increased (Figure 2), the residual NO_2^- level in the pellets decreased (data not shown).

In a previous study [7], a maximum elimination capacity of 16.4 g/m^3/hr was achieved for a NOx loading rate of 17.6 g/m^3/hr at a 60 sec EBCT. However, over time, the NO removal efficiency in the fungal bioreactor dropped to 20 % due to the accumulation of NH_4^+ (average 8.7×10^2 μg NH_4^+-N/g dry pellet) in the packed bed. In the current study, to maintain low NH_4^+ levels in the bioreactors, and prevent inhibition of NO removal, low levels of NH_4^+ were supplied to the bioreactor only periodically via the aerosol system described earlier. Using this nutrient supply method, the average NH_4^+ level in the pellets was maintained below 1.0×10^2 μg NH_4^+-N/g dry pellet throughout most of the operating period. In addition, to avoid accumulation of NH_4^+ in the packed

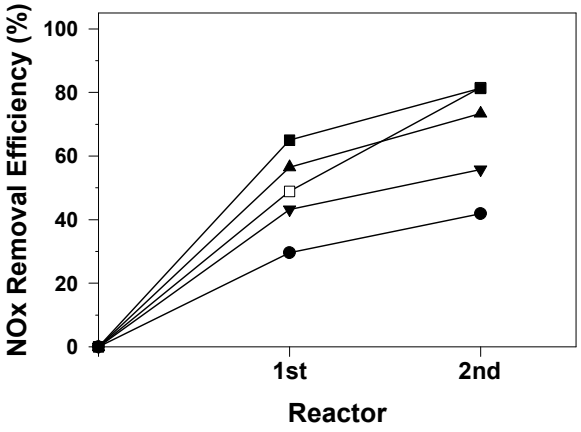

Figure 3. NOx removal efficiency (%) in the first reactor and the second reactor for a 250 ppm_v inlet NOx concentration on Day 55 (●), 66(▼), 73(▲), 82(□), and 87 (■).

bed, KNO_3 was supplied to the bioreactor instead of NH_4^+ on Days 78 to 82. The NOx removal efficiency in the first reactor significantly decreased as a result of this change although the overall NOx removal efficiency across both bioreactor columns slightly increased (Figure 3). These results imply that KNO_3 may not be an appropriate nitrogen source to achieve simultaneous removal of toluene and nitrogen oxides. On day 87, a maximum elimination capacity of 31 g NOx/m^3/hr was achieved for an inlet NOx concentration of 250 ppm_v at a 30 sec EBCT.

Pressure Drop and Nitrogen Oxides

Pressure drop caused by the biomass clogging in the vapor-phase bioreactors is a key operating parameter that must be controlled carefully to ensure stable bioreactor performance over long periods [13]. As shown earlier, briefly halting the nutrient supply to the bioreactors actually improved toluene removal activity. However, a relatively rapid rise in the pressure drop in the first bioreactor from Days 49 to 54 resulted and had the pressure drop continued to increase it would have been an obstacle to the long-term stability of the bioreactors. Unexpectedly, after the NOx ($NO+NO_2$) removal experiments were conducted on Days 54 and 55, the pressure drop across the bioreactors dramatically decreased (Figure 2). On Days 56 to 67, the pressure drop increased again across the first bioreactor, whereas the pressure drop in the second reactor did not change. On Day 66, NOx experiments were intentionally carried out for eight hours, and the pressure drop declined again. Despite the periodic declines in pressure drop following each NOx experiment, the baseline pressure drop in the first reactor continued to increase gradually indicating that biomass was accumulating in the bioreactor. The results suggest that fungal morphology is affected by the presence of NOx. However, further study needs to be conducted to delineate why the presence of NOx decreases the pressure drop across the bioreactor. Nevertheless, pressure drop across the bioreactor was effectively controlled by the periodic presence of NOx.

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