한국환경과학회지 제17권(제1호), 7~17, 2008
Journal of the Environmental Sciences

Simultaneous Removal of H_2S, NH_3 and Toluene in a Biofilter Packed with Zeocarbon Carrier

Byoung-Gi Park, Won Sik Shin*, Yong-Shik Jeong** and Jong-Shik Chung

Department of Chemical Engineering, POSTECH San-31, Hyoja-Dong, Pohang, Gyeongbuk 790-784, Korea
**Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, Korea*
***Environment & Energy Department, POSCO 1 Goedong-dong, Namgu, Pohang, Gyeongbuk 790-785, Korea*

(Manuscript received 14 September, 2007; accepted 4 December, 2007)

Abstract

Simultaneous removal of NH_3, H_2S and toluene in a contaminated air stream was investigated over 185 days in a biofilter packed with Zeocarbon granule as microbial support. In this study, multi-microorganisms including *Nitrosomonas* and *Nitrobacter* for nitrogen removal, *Thiobacillus thioparus* (ATCC 23645) for H_2S removal, and *Pseudomonas aeruginosa* (ATCC 15692), *Pseudomonas putida* (ATCC 17484) and *Pseudomonas putida* (ATCC 23973) for toluene removal were used simultaneously. The empty bed residence time (*EBRT*) was 40-120 seconds and the feed (inlet) concentrations of NH_3, H_2S and toluene were 0.02-0.11, 0.05-0.23 and 0.15-0.21 ppmv, respectively. The observed removal efficiency was 85%-99% for NH_3, 100% for H_2S, and 20-90% for toluene, respectively. The maximum elimination capacities were 9.3, 20.6 and 17 $g/m^3/hr$ for NH_3, H_2S and toluene, respectively. The results of kinetic model analysis showed that there were no particular evidences of interactions or inhibitions among the microorganisms, and that the three biodegradation reactions took place independently within a finite area of biofilm developed on the surface of the Zeocarbon carrier.

Key Words : Ammonia, Biofilter, Hydrogen sulfide, Odor, Toluene, Zeocarbon

1. Introduction

Biofiltration has become one of the most suitable alternative processes to high temperature incineration, i.e. thermal or catalytic processes in treating low-level airborne pollutants. Compared to incineration, biofiltration has many advantages: emissions of secondary pollutants such as SO_x, NO_x, and CO_2 are avoided and maintenance and operation costs are lower. Due to these advantages, malodorous or volatile organic compounds (VOCs) emitted from various industrial sources have been treated by biofiltration systems in commercial scales[1~8].

Among the sources of air pollutions, H_2S and NH_3 are colorless, corrosive, toxic, and can cause malodorous nuisances, while toluene is a suspected carcinogen. The threshold of the smelt level for H_2S is as low as 0.00047 ppmv[9]. According to a toxicity report, H_2S is known as a breakdown chemical of the central nervous system below 100 ppmv and is eventually deadly toxic above 100 ppmv[10]. NH_3 is known to irritate eyes and throat. The threshold value for NH_3 is 50 ppmv in air[11]. The current regulation level in Korea is 2-10 ppmv for H_2S and 50-100 ppmv for NH_3. Toluene is regulated as a part of the total VOCs or benzene derivatives and the legally allowed level is 30 ppmv[12]. Therefore, the actual emission level for toluene is much lower than that for the total VOCs.

Corresponding Author : Jong-Shik Chung, Department of Chemical Engineering, POSTECH San-31, Hyoja-Dong, Pohang, Gyeongbuk 790-784, Korea
Phone: +82-54-279-2267
E-mail: jsc@postech.ac.kr

Toluene is a Title III toxic compound of the 1990 Clean Air Act Amendment proposed by the US EPA[13].

Most of researches on the biofiltration system have focused on the treatment of a single component gas, but this is impractical for real industrial applications as most emission sources, especially emissions with malodorous gases, contain multi-components including sulfur- and nitrogen-containing mixed compounds[4,9,10,14-21].

Recent studies have focused on the removal of binary gases (e.g., toluene/H_2S or NH_3/H_2S). According to Cox and Deshusses[22], for the treatment of binary gases of toluene and H_2S in a waste air stream, the removal efficiencies measured in bio-trickling beds were nearly 100% for H_2S, however, the toluene removal efficiency was much less; only 75% at pH 7.0 and 25% at pH 4.5. For NH_3 and H_2S, the removal efficiency was 80% to 100% for NH_3 and 90% to 100% for H_2S, respectively. Chung et al.[21] reported that when the concentrations of the H_2S and/or NH_3 substrates were relatively high, the substrates became inhibitory influencing the removal efficiencies of NH_3 and H_2S. Liu et al.[5] also reported on the inhibition effect in a biofilter that treats the binary gases of toluene and ethylacetate. Kim et al.[4] reported a similar decreasing trend in removal efficiency in H_2S/NH_3 removal, due to the accumulation of sulfur in packing materials during a long-term operation of packed-bed system. Malhautier et al.[3] observed that elemental sulfur and sulfate were the major products of H_2S oxidation reducing the void fraction of the biotrickling bed in H_2S/NH_3 removal. Several attempts were reported on the simultaneous removal of binary gases, however, biofiltration for the removal of ternary gases especially for a mixture of toluene, H_2S and NH_3 were not investigated.

In this study, the simultaneous removal of ternary gases containing 10-250 ppmv of NH_3/H_2S/toluene in a biofilter was investigated using Zeocarbon as a packing material. The Zeocarbon carrier has been used in water and wastewater treatment facilities. Main components of this packing material are activated carbon and zeolite. A more detailed information are available from the manufacturer (Zeobuilder Co., Korea, http://www.zeobuilder.co.kr). The Zeocarbon can provide sufficient adsorptive property to contaminant gases as well as habitats to microorganisms. The packing material showed no pressure-drop, while it keeps the same level of removal activities observed from the conventional packing materials during a long-term operation of biofiltration systems. The removal efficiency and elimination capacity were measured at various inlet loadings and gas concentrations during unsteady and steady-state operations. Microbial counting was also performed in order to investigate the existence of any inhibitory effects among the substrates and/or microorganisms during long-term operations of biofiltration systems.

2. Materials and Methods

2.1. Biofiltration system

A lab-scale biofiltration system used for the simultaneous removal of ternary NH_3/H_2S/toluene mixtures in the air stream was depicted in Fig. 1. The biofilter column was made of a 4-cm-id and 110-cm-long transparent Pyrex glass. The column was packed with a commercial Zeocarbon carrier (ZC-100, Zeobuilder Co., Korea). The physical properties of the Zeocarbon are summarized in Table 1. The actual packing length of the Zeocarbon was 0.8 m and was equally divided into three layers. A spacer (5-cm-long) made of a

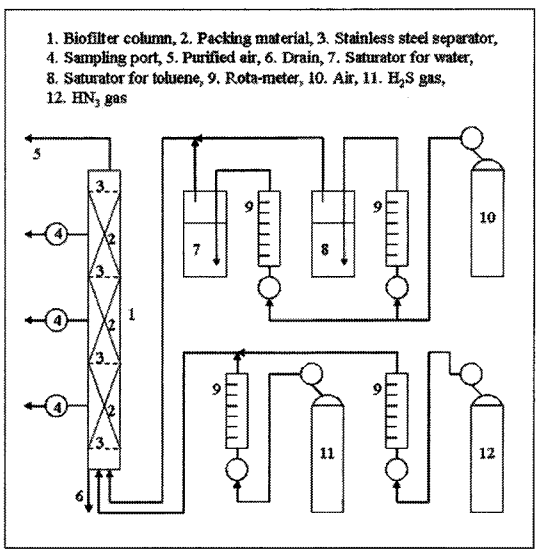

Fig. 1. Schematic diagram of the biofiltration system.

Table 1. Physical properties of Zeocarbon (ZC-100)

Property	Value	Unit	Remark
Surface area, S_g	292	m^2/g	BET
Bed porosity, e_{bed}	0.66	-	measured
Particle size, d_p	0.6×10^{-3} - 1.18×10^{-3}	m	measured
Specific surface area, A_s	1,730-3,400	m^2/m^3	$6(1-e_{bed})/d_p$
Bulk density, r_b	6.5×10^5	g/m^3	measured

stainless steel mesh screen was inserted between the layers to support the Zeocarbon pellets. The total bed volume of the Zeocarbon packing was 1.0 liter. A sampling port was installed at the middle point of each layer in order to sample the microbial support materials and to measure gas concentration. At the bottom of the biofilter column, a 100-mL water reservoir was placed through which inlet feed gas was bubbled. Any water collected and remaining excess were continuously drained out of the reservoir. A portion of the feed air was passed through a water saturator containing double-distilled water to provide moisture and the other portion through a toluene (J. T. Baker, 99.7%) saturator. The two streams were mixed together before being introduced into the bottom of the biofilter column. The relative humidity was maintained above 95%. The H_2S (Doekyang Energen Co., 1 mol% balanced with N_2) and NH_3 (1 mol% balanced with N_2, Doekyang Energen Co.) gases were separately fed into the biofilter column from the gas cylinders. The physical properties of the contaminant gases are summarized in Table 2. The volumetric flow rates of all gas streams were controlled by pressure regulators and rotameters. Finally, the treated air was released from the top of the biofilter column.

2.2. Operation of the biofiltration system

The biofiltration system was continuously operated for 185 days at room temperature (22±3°C) and atmospheric pressure. During the biofiltration experiments, the packed Zeocarbon was washed using a nutrient solution when the column showed a pressure drop due to the accumulation of elemental sulfur along the biofilter column. The total volumetric air flow rate varied from 0.030 to 0.090 m^3/hr that corresponds to from 40 to 120 seconds of empty bed residence time (*EBRT*), respectively. The concentration of NH_3, H_2S and toluene gas in the feed was about 0.02-0.11 g/m^3 (32-156 ppmv), 0.05-0.23 g/m^3 (48-160 ppmv) and 0.15-0.21 g/m^3 (40-56 ppmv), respectively. The inlet loading (*IL*) was 1-10 g/m^3/hr for NH_3, 2-21 g/m^3/hr for H_2S and 3-24 g/m^3/hr for toluene. The initial pH was controlled at 7.0 using NaOH and HNO_3.

2.3. Measurement of the performance of the biofiltration system

Conventionally, the performance of the biofiltration system can be characterized by several factors. They are (i) the inlet mass load of the pollutant gas component (*IL*, g/m^3/hr), (ii) the elimination capacity (*EC*, g/m^3/hr), (iii) the empty bed residence time (*EBRT*, seconds), and (iv) the removal efficiency (*X*, %). Among the factors, *IL* (g/m^3/hr), an actual burden applied on the system, is defined as the total volumetric flow rate of the feed multiplied by the inlet concentration of the pollutant gas. *EC* (g/m^3/hr) is the actual removal capacity of the contaminant gas within the biofilter bed. It is usually less than *IL*, but is equal to *IL* when 100% removal is achieved. The *EBRT* (seconds) is an imaginary residence time, assuming

Table 2. Physical properties of gas components in pure water at 298.15 K and 1 atm

Component	Molecular weight	Henry's law constant, H_i (-) [a]	Solubility (g/m^3)	Overall mass transfer coefficient (K_La, hr^{-1}) [b]
NH_3	17.03	1,387	953,680	623 - 7,344
H_2S	34.08	2.43	3,340	15 - 24
Toluene	92.14	3.96	14,740	54 - 72

Note: [a] $H_i=C_{i,liquid}/C_{i,gas}$ and [b] data reported by references 17, 30-32

that the packed column is empty. X(%) is the conversion of the target gas component that shows how much of the pollutant gas is removed in the biofilter bed. The factors are defined as:

$$EBRT = \frac{V_B}{q_0} \tag{1}$$

$$IL_i = \frac{C^G_{i,IN}}{EBRT} \tag{2}$$

$$EC_i = \frac{\left(C^G_{i,IN} - C^G_{i,OUT}\right)}{EBRT} \tag{3}$$

$$X_i = \frac{\left(C^G_{i,IN} - C^G_{i,OUT}\right)}{C^G_{i,IN}} = \frac{EC_i}{IL_i} \tag{4}$$

where C (g/m^3) is the concentration in the gas phase, q_0 is the inlet volumetric gas flow rate (m^3/hr) and V_B is the packed-bed volume (m^3). Superscript G represents the gas phase, subscript i is the gas component (i.e., NH_3, H_2S and toluene) and subscripts IN and OUT indicate the inlet and outlet conditions, respectively.

2.4. Analytical methods

Both the inlet and outlet concentrations of NH_3, H_2S and toluene gases were measured by using the gas detection tubes (Model 3La, 4L and 122L, Gastec Co., Japan). The effective detection range of the tube was 2.5-200 ppmv for NH_3, 1-20 ppm_v for H_2S, and 1-100 ppmv for toluene. The lowest detection limit was 0.5 ppmv for NH_3, 0.2 ppmv for H_2S, and 0.5 ppmv for toluene. The residuals, pale yellow colored cakes, formed on the Zeocarbon surface and in the drain water, were analyzed using X-ray powder diffraction (XRD, MAC Science Co., Model M18XHF, CuK) and an elemental analyzer (LECO Co., Model CHNS 932). The bed porosity of the Zeocarbon support was measured by a mercury porosimeter (Microstructure Lab, Carlo Erba Strumentazione). The BET surface area was measured by nitrogen adsorption using Micromeritics (Model *ASAP 2021C*).

2.5. Microorganisms

Three different types of microorganisms were independently cultivated in aqueous minerals solutions using a shaking incubator (Jeio Tech, SI-900R) at 30°C and 100 rpm. The nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*, were isolated from the activated sludge in a sewage water treatment facility located at Pohang University of Science and Technology, Pohang, Korea. The nitrifying bacteria were grown in a mineral nutrient medium prepared by dissolving 0.2357 g of $(NH_4)_2SO_4$, 0.080 g of KH_2PO_4, 0.020 g of $MgSO_4$ and 0.0085 g of $Fe_2(SO_4)_2{\cdot}H_2O$ dissolved in 1.0 L of double-distilled water. A H_2S degrading bacterium, *Thiobacillus thioparus* (ATCC 23645), was obtained from the Korean Collection for Type Cultures (KCTC). The organism was cultivated in a mineral medium (ATCC medium 290 S6) prepared by dissolving 1.2 g of Na_2HPO_4, 1.8 g of KH_2PO_4, 0.1 g of $MgSO_4{\cdot}7H_2O$, 0.1 g of $(NH_4)_2SO_4$, 0.03 g of $CaCl_2$, 0.02 g of $FeCl_3$, 0.02 g of $MnSO_4$, and 10.0 g of $Na_2S_2O_3$ in 1.0 liter of double-distilled water. For the toluene degradation, *Pseudomonas aeruginosa* (ATCC 15692), *Pseudomonas putida* (ATCC 17484) and *Pseudomonas putida* (*Pseudomonas arvilla*, ATCC 23973) were also purchased from the Korean Collection for Type Cultures (KCTC). The *Pseudomonas aeruginosa* was grown in ATCC medium 129, i.e., a nutrient agar containing 0.5% NaCl, 3.0 g of beef extract and 5.0 g of peptone in 1.0 L of double-distilled water. The *Pseudomonas putida* (ATCC 17484) was incubated in ATCC medium 3, i.e., a nutrient agar at pH 6.8 containing 3.0 g of beef extract, 5.0 g of peptone and 15.0 g of agar in 1.0 L of double-distilled water. The *Pseudomonas putida* (*ATCC 23973*) was cultivated in ATCC medium 1271 containing a benzoate nutrient medium containing 3.0 g of $(NH_4)_2PO_4$, 1.20 g of KH_2PO_4, 5.0 g of NaCl, 0.20 g of $MgSO_4{\cdot}7H_2O$, 0.50 g of yeast extract, 3.0 g of sodium benzoate (filter-sterilized) and 20 g of agar noble (Difco 0142) in 1.0 L of double-distilled water. All culture media were autoclaved at 121°C for 15 minutes prior to use.

After cultivation, the microorganisms were mixed together immediately before inoculation. The mixed microorganisms were sprayed over the Zeocarbon carriers in an open vessel with aeration for several hours. The inoculated Zeocarbon carriers were then packed into the biofiltration column and acclimated for two weeks. The *ILs* of NH_3, H_2S and toluene, were kept

at a quarter of those used for normal operating conditions.

2.6. Microbiological analysis

In order to count the microbial populations, the colony-forming unit (CFU) was measured on the 105th day of operation by the conventional most probable number (MPN) method[23,24]. Subsamples of Zeocarbon carriers were collected through the upper, middle and lower sampling ports attached to the biofilter column. The Zeocarbon samples were homogenized with a basal salt medium and then centrifuged at 10,000 rpm for 20 min. The medium was prepared by dissolving 2.5 g of $(NH_4)_2SO_4$, 0.5 g of KH_2PO_4, 50 mg of $MgSO_4 \cdot 7H_2O$, 4 mg of $CaCl_2 \cdot 2H_2O$, and 0.1 mg of Fe-EDTA in 1.0 L of double-distilled water at pH 8.0-8.2. The homogenized suspensions were diluted with the medium. 0.5 mL of aliquots of the suspension with different dilution ratios were then transferred into test tubes or plates containing 4.5 mL of the basal salt medium. Subsequently, the samples were incubated for 21 days at 30°C in a shaking incubator (Jeio Tech, SI-900R). After 21 days, the test tubes were counted after color-changing indicators were added. Values for the microbial populations were finally obtained by referring to the MPN table.

3. Results and Discussion

3.1. Experimental results for the long-term tests

Fig. 2 shows the results of the long-term operation of the biofiltration system for the simultaneous removal of NH_3, H_2S and toluene. The inlet volumetric air flow rate was maintained at 0.030 m^3/hr (from the 0th day to the 102nd day), increased to 0.060 m^3/hr (from the 103rd day to the 130th day) and then further increased up to 0.090 m^3/hr (from the 131st day to the 185th day), and the corresponding *EBRT* was 120 sec, 60 sec and 40 sec, respectively. As summarized in Table 1, bed porosity was 0.66 and the feed concentration of NH_3, H_2S and toluene was about 0.02-0.15 g/m^3, 0.05-0.25 g/m^3 and 0.15-0.35 g/m^3, respectively. The corresponding *IL* for NH_3, H_2S and toluene was 1-10 g/m^3/hr, 2-21 g/m^3/hr and 3-24 g/m^3/hr, respectively.

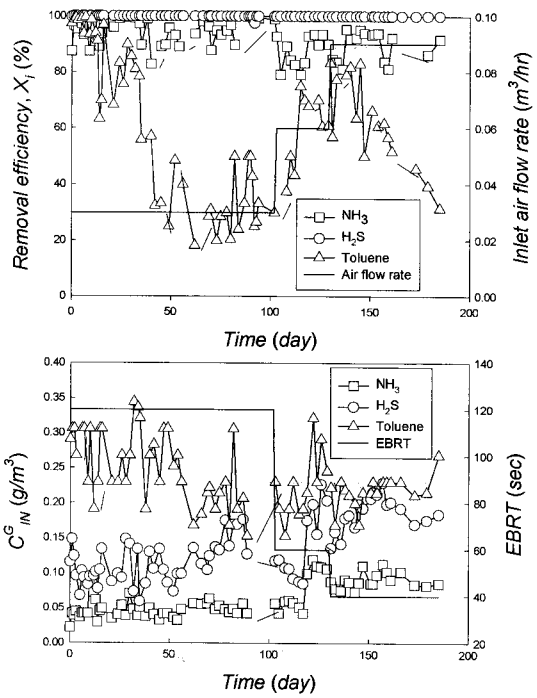

Fig. 2. Results of the long term operation of a biofilter. Symbols: open squares=NH_3, open circles=H_2S, and open triangles=toluene. Solid line represents EBRT or inlet air flow rate.

In the very early stages of the biofiltration experiments (i.e., from the start to the 20th day), above 95% of all gases were removed. According to Kim[4] and Zilli et al.[13], the high removal in the early stage was mainly due to the adsorptive effect of the biofilter system, but not due to the biodegradation activities of the microorganisms. After the 20th day, the adsorption capacity of the biofilter column was under thermodynamic equilibrium with the pollutant gases. A detailed discussion on adsorption is available elsewhere[4].

Among the three gases, H_2S was completely removed during the 185 days of operation, even under different experimental conditions (Fig. 2). The removal efficiency of NH_3 was maintained at near 90% from the 20th day to the 102nd day during which the biofiltration system reached a steady state for the NH_3 removal. On the 102nd day, the total inlet air flow rate increased from 0.03 m^3/hr to 0.06 m^3/hr. This change decreased the removal efficiency for the following 13 days (i.e., from the 102nd day to the 125th day), after

which a new steady state was observed. A very similar trend was observed when the flow rate increased on the 131st day. The removal efficiency further decreased from the 131st day to the 150th day, followed by a new steady state. At steady states, the NH_3 removal efficiency was maintained at 90% regardless of changes in the flow rate.

Toluene showed a rather complicated and abnormal trend in the removal efficiency upon the change in the flow rate. The removal efficiency was over 90% during the first 20 days due to absorption and adsorption. After this, the removal efficiency gradually decreased and then, it reached a steady state of about 30% of the removal efficiency (i.e., from the 21st day to the 100th day). As the air flow rate increased between 102nd day and 131st day, the removal efficiency increased, but followed by a slow and gradual decrease. Similar pattern was observed for between the 132nd day and 185th day. Zilli et al.[13] reported that toluene needs at least 50 days to obtain a new steady state after changing the reaction conditions, which is in agreement with our observations. At present, the abnormal increase in the toluene removal efficiency upon the increase in the flow rate is not clearly understood.

To investigate the reason of poor removal efficiency of toluene, both the residuals of drain water in the bottom reservoir and the pale yellow colored cake deposited on the Zeocarbon surface were sampled on the 131st day, dried at 105°C, and then analyzed by XRD and an elemental analyzer (Figure not shown). The residuals are mainly $(NH_4)_2SO_4$ and elemental sulfur, which are known byproducts of H_2S oxidation[4,9]. It appeared that the Zeocarbon surface was covered by the elemental sulfur and became more and more hydrophobic. Furthermore, relatively small sized elemental sulfur particles were continuously accumulated on the Zeocarbon surfaces and were highly difficult to remove by washing. In other part, biofilm formation on the Zeocarbon surface may also be hindered by the elemental sulfur deposition. However, the removal efficiencies of H_2S and NH_3 were not influenced by the sulfur deposition (Fig. 2). According to Oyarzun et al.[9], elemental sulfur was an intermediate of H_2S metabolism and was further oxidized by *Thiobacillus thioparus* that is used for H_2S removal in this study. Generally, *Thiobacilli* species can withstand very well and survive when they are exposed to elemental sulfur and/or sulfur-containing compound environments. In the case of NH_3 removal, although the Zeocarbon surface became partially hydrophobic, solubility of NH_3 in water was too high to be affected by the hydrophobic Zeocarbon surface (see Table 2). This is the main reason why the toluene removal efficiency continuously decreases, while those for H_2S and NH_3 were highly stable.

The lower removal efficiency of toluene, compared to the other two gases, may be explained by an inhibition effect. Liu et al.[5] observed that at a certain concentration level, toluene removal was inhibited by the presence of ethylacetate. Chung et al.[6] also reported that inhibition exists between the NH_3 and H_2S substrates when the substrate concentrations were relatively high. The Andrews-Haldane biokinetic model was introduced in order to account for the inhibition effect of binary substrates in the biofiltration system[25]. In this work, we intended to treat a mixture of three substrates (i.e., NH_3, H_2S and toluene), using three different microorganisms cultured in a single column biofilter: *Thiobasillus thioparus*, an autotroph for the oxidation of H_2S; *Nitrosomonas* and *Nitrobactor*, autotrophs for the degradation of NH_3 and *Pseudomonas putida*, a heterotroph for the oxidation of toluene. Accordingly, competitive inhibition among the three substrates may exist in this system. Therefore, we performed a biokinetic study using the Andrews-Haldane biokinetic model. Through the kinetic study, however, we were not able to find any evidence regarding the competitive inhibition effect on toluene removal. A more detailed discussion on the biokinetic study is provided in the following section. Detailed discussions on the model equations are available elsewhere[21,25,26].

3.2. Effect of inlet feed condition on the elimination capacity

The plot of the *EC* vs. the inlet concentration of each pollutant gas, with the inlet flow rate as a parameter, was shown in Fig. 3-5. For NH_3, the highest value for the *EC* was 9.3 $g/m^3/hr$ when the inlet air flow rate

was 0.09 m^3/hr and the NH_3 concentration was 0.11 g/m^3. The highest value of the *EC* for H_2S was 20.6 g/m^3/hr at a concentration of 0.23 g/m^3, and for toluene it was 15.2 g/m^3/hr at 0.21 g/m^3. The *EC*s were linearly proportional to the inlet concentrations for all three gases (Fig. 3-5).

The inhibition effect between the ternary substrates was analyzed by the Andrews-Haldane biokinetic model. The model is given as [21,25,27,33]:

$$r_i = \frac{\mu_{m,i} C_i}{K_{S,i} + C_i + \frac{C_i^2}{K_{I,i}}} \quad (5)$$

where r_i (g/m^3/hr) = the apparent removal rate of pollutant component, *i*, $\mu_{m,i}$ (g/m^3/hr) = the maximum removal rate of a pollutant component, *i*, C_i (g/m^3) = the concentration of component, I, $K_{S,i}$ (g/m^3) = the half saturation coefficient for removal of component, *i*, and $K_{I,i}$ (g/m^3) = the inhibition coefficient for component, *i*.

Our previous report showed that this linear relationship is generally observed at low levels of the substrate concentration region, where the substrate concentration (C_i) is much smaller than the half saturation constant ($K_{S,i}$) in biokinetics[27]. In addition, the Andrews-Haldane biokinetic model equation can be reduced to the pseudo-first order reaction[27]. In this kinetic regime, only the ratio of the maximum removal rate to the half saturation constant can be obtained. This concentration range is even far below the concentration range where the competitive inhibition occurs[27]. The trends of the *EC*s (Fig. 3-5) indicate that neither reaction nor inhibition is limiting in the biofiltration system within the tested conditions. In addition, these results are consistent with those of others[6,27] regarding the H_2S removal kinetic study that uses the Andrews-Haldane biokinetic model. According to their observations[6,27], the *EC* increased as both the inlet flow rate and concentration increased, even at ten to hundred times higher flow rate and concentration than those used in this

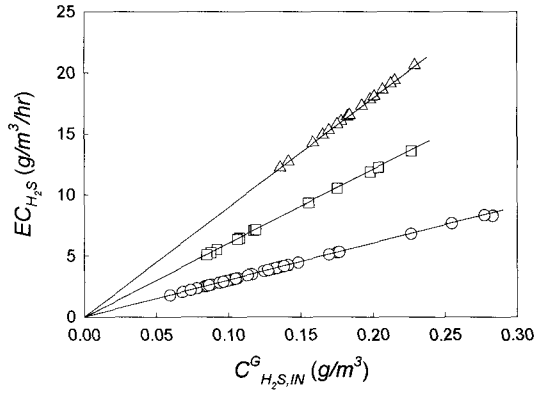

Fig. 4. Elimination capacity of H_2S as a function of the inlet concentration at various inlet flow rates of the gas stream. Symbols: open circles=0.03 m^3/hr, open triangles=0.06 m^3/hr and open squares=0.09 m^3/hr.

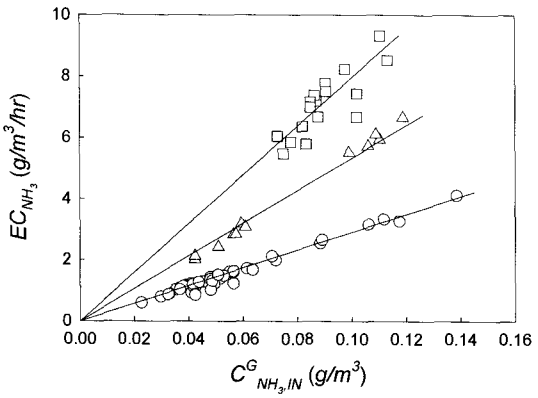

Fig. 3. Elimination capacity of NH_3as a function of the inlet concentration at various inlet flow rates of the gas stream. Symbols: open circles=0.03 m^3/hr, open triangles=0.06 m^3/hr and open squares=0.09 m^3/hr.

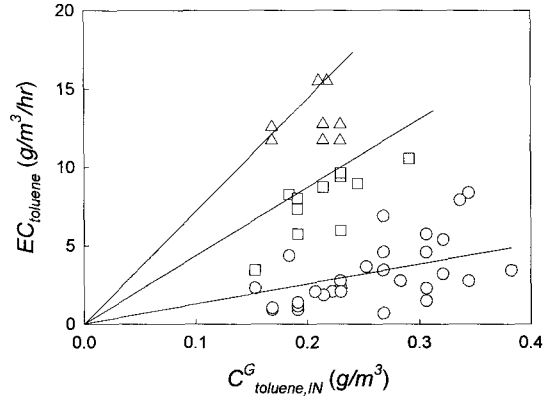

Fig. 5. Elimination capacity of toluene as a function of inlet concentration at various inlet flow rates of the gas stream. Symbols: open circles=0.03 m^3/hr, open triangles=0.06 m^3/hr and open squares=0.09 m^3/hr.

Table 3. Microbial populations in the biofilm fixed on the Zeocarbon supporting media

	Logarithmic counts for microbial populations, log(CFU/g)			
Column Section	*Nitrosomonas*	*Nitrobacter*	*Thiobasilli*	*Pseudomonas putida*
Upper	4.4	3.2	4.1	5.1
Middle	5.0	5.2	5.5	5.7
Lower	7.5	5.5	6.2	7.5

study (H_2S concentration = 0.28 g/m^3 up to 1.12 g/m^3). The *EC* value increased asymptotically as the inlet H_2S concentration increased from 1.12 g/m^3.

On the 105th day, the microbial populations were measured by the conventional MPN method[23,24] and the results were summarized in Table 3. At the three sampling points, the populations of the all microorganisms were similar indicating that there was no superior species among the different microorganisms. The microbial populations in the bottom layer were two to three orders of magnitude higher than those in the middle and upper layers. This is simply because more substrates are available in the bottom layer of the biofilter.

The *EC*s of the biofilter, as a function of the *IL* of NH_3, H_2S and toluene, were shown in Figs. 6-8, respectively and the results were summarized in Table 4. In the Figs., the squares denoting the adsorption effect were measured during the first 20 days (except H_2S in Fig. 7). As discussed previously, the adsorption onto the Zeocarbon supporting media and absorption into the aqueous solution are the main reasons for the high initial *EC*. Due to adsorption and absorption, the EC values lied on the dotted diagonal line that corresponds to 100% removal efficiency for all gases. In Fig. 6, at an *IL* of less than 4 g/m^3/hr, the *EC* for NH_3 was linearly proportional to the inlet NH_3 loading;

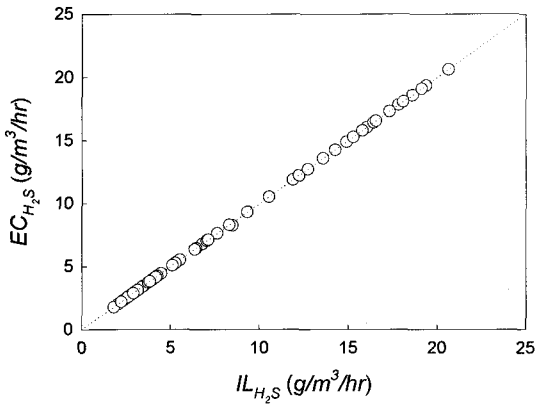

Fig. 7. Elimination capacity of H_2S as a function of inlet loading. Symbols: open circles=experimental data.

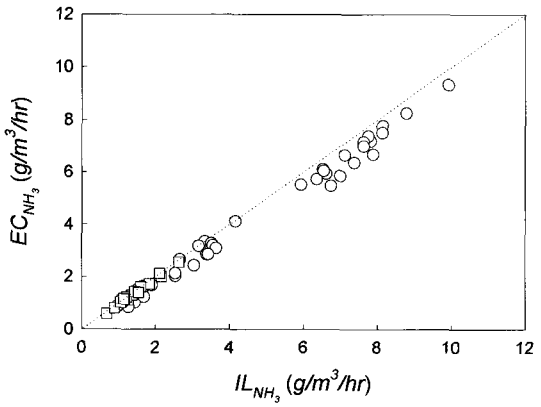

Fig. 6. Elimination capacity of NH_3 as a function of inlet loading. Symbols: open circles=experimental data and open squares=adsorption onto Zeocarbon carrier.

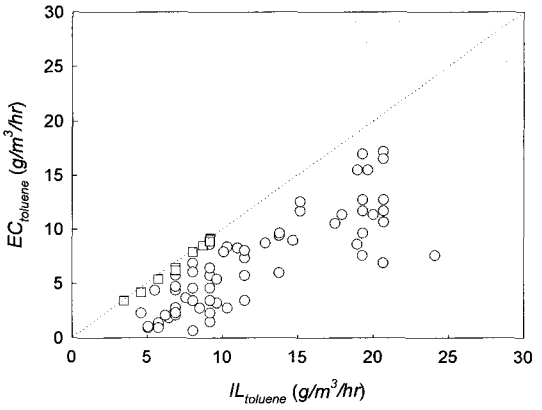

Fig. 8. Elimination capacity of toluene as a function of inlet loading. Symbols: open circles=experimental data and open squares=adsorption onto Zeocarbon carrier.

Table 4. Summary of the results on the long-term tests for the bench scale biofiltration system

	Inlet concentration		Inlet loading	Removal efficiency[a]	Elimination capacity	Outlet concentration
Component	$C^G_{i,IN}$ (g/m^3)	$C^G_{i,IN}$ (ppmv)	IL (g/m^3/hr)	X (%)	EC (g/m^3/hr)	$C^G_{i,OUT}$ (ppmv)
NH_3	0.02-0.11	20-300	1-10	80-95	9.3	0-20
H_2S	0.05-0.23	40-200	2-21	100	206	0
Toluene	0.15-0.21	30-100	3-24	30-90	15.2	7-67

Note: a=the highest value observed under the experimental conditions.

therefore, the experimental values were near the diagonal line. For the *IL*s of 6 to 10 g/m^3/hr, the *EC*s were positioned slightly below the diagonal line (100% removal). For the NH_3 removal, however, the experimentally measured *EC*s might be overestimated. This is because the solubility of NH_3 in water is extremely high (953.7 g NH_3/L at 298.15K and 1 atm), as listed in Table 2. As shown in Fig. 7, the *EC*s of H_2S were positioned on the diagonal line. This confirms that the removal efficiency is nearly 100% within the entire experimental conditions, regardless of the H_2S loading into the biofilter, however, the *EC*s of toluene were well below the diagonal line (Fig. 8). The lower *EC*s for toluene were because most of the data were taken under unsteady state conditions due to a very long transient time (i.e., 30 - 50 days were needed to reach a steady state) as depicted in Fig. 2. Considering inlet concentration ($C^G_{i,IN}$) of toluene was higher than those of NH_3 and H_2S (Table 4), the microbial activities and the population of toluene degrading bacteria (*Pseudomonas aeruginosa* and *Pseudomonas putida*) was less (Table 3). Relatively weaker microbial activities and a lower population growth rate of the heterotrophs (toluene degrading bacteria) compared to those for the autotrophs (NH_3 and H_2S degrading bacteria) could be another reason.

Overall, during the simultaneous biofiltration of the relatively low concentrations of three substrate gases, (NH_3, H_2S and toluene) using Zeocarbon as a supporting material, neither interaction nor competitive inhibition was found among the different microorganisms (i.e., *Thiobasillus thioparus*, *Nitrosomonas* and *Nitrobacter* and *Pseudomonas putida*). Biodegradations of the three gases were parallel processes where the three different reactions occurs simultaneously in a finite area (at the same sites) of the microbial fixing carrier materials. Although there were chances for competitions among the three different microorganisms in terms of nutrients and byproducts for the metabolisms, simultaneous biodegradations of the ternary NH_3, H_2S and toluene substrates took place independently. This observation was in contrast to those reported by others[6,21,28,29] regarding the removal on the binary NH_3 and H_2S gases. This observation, however, is in agreement with the results of Cox and Deshusses[22] who reported that there was no interaction between the two microorganisms during the simultaneous removal of binary H_2S and toluene. Although toluene removal was relatively low due to a long recovery time after shock loading, our results showed that multiple gaseous contaminants can be simultaneously treated in a single-stage biofiltration system. There was no clear evidence of the inhibition on toluene removal influenced by the presence of H_2S.

4. Conclusions

In this study, the biofiltration of three different gases (i.e. NH_3, H_2S and toluene) that are widely different in physicochemical properties was investigated using Zeocarbon granules as a supporting material of the microorganisms. The results of Andrews-Haldane biokinetic model showed that neither interaction nor competitive inhibition exist among the different kinds of microorganisms. The population densities of the microorganisms on the surface of the Zeocarbon carriers were about the same at each sampling point. The microbial populations increased along the height of the biofilter column and were in the order of bottom > middle > upper layer. This is attributed to the avail-

ability of substrates to the microorganisms (i.e., more inlet gases were available in the bottom layer). There was no evidence of the inhibition on toluene removal by the presence of H_2S and NH_3, however, toluene removal was highly sensitive to a shock loading. Although our results showed that a single-stage biofiltration system could be used for the simultaneous removal of low concentration levels of ternary NH_3, H_2S and toluene mixtures in a waste gas stream, further research work is needed to improve the toluene removal.

References

1) Lim K. H., 2005, The treatment of waste-air containing mixed solvent using a biofilter 2. Treatment of waster-air containing ethanol toluene in a biofilter, Korean J. Chem. Eng., 22, 228-233.
2) Lim K. H., Park S. W., 2004, The treatment of waste-air containing mixed solvent using a biofilter 1. Transient behavior of biofilter to treat waste-air containing ethanol, Korean J. Chem. Eng., 21, 1161-1167.
3) Malhautier L., Gracian C., Roux J., Fanlo J., Cloirec P. L., 2003, Biological treatment process of air loaded with an ammonia and hydrogen sulfide mixture, Chemosphere, 50, 145-153.
4) Kim H. S., 2002, Biofiltration for Removal of Odor Gases, Ph.D. Dissertation, Pohang University of Science and Technology, Pohang, Korea.
5) Liu Y., Xie Q., Sun Y., Chen J., Xue D., Chung J. S., 2002, Simultaneous removal of ethyl acetate and toluene in air stream using compost-based biofilters, J. Hazard. Mater., 95, 199-213.
6) Chung Y., Huang C., Tseng C., 2001, Biological elimination of H_2S and NH_3 from waste gases by biofilter packed with immobilized heterotrophic bacteria, Chemosphere, 43, 1043-1050.
7) Kim S. H., Oh K. J., Moon J. H., Kim D., 2000, Simultaneous removal of H_2S and NH_3 using *Thiobacillus sp.* IW in a three-phase fluidized-bed bioreactor, J. Micorbiol. Biotechnol., 10, 419-422.
8) Park S. J., Cho K. S., Hirai M., Shoda M., 1993, Removability of malodorous Gases from a night soil treatment by a pilot-scale peat biofilter inoculated with *Thiobacillus thioparus* DW44, J. Ferment. Bioeng., 76, 55-59.
9) Oyarzun P., Arancibia F., Canales C., Aroca G. E., 2003, Biofiltration of high concentration of hydrogen sulphide using *Thiobacillus thioparus*, Process Biochem., 39, 165-170.
10) Shojaosadati S. A., Elyasi S., 1999, Removal of hydrogen sulfide by the compost biofilter with sludge of leather industry, Resour. Conserv. Recycl., 27, 139-144.
11) Busca G., Pistarino C., 2003, Abatement of ammonia and amines from waste gases: A summary, J. Loss Prevent Proc., 16, 157-163.
12) Korean Ministry of Environment, 2007, Permissible air pollutant emission standards, Korean Ministry of Environment Printing Office: Seoul, Republic of Korea.
13) Zilli M., Palazzi E., Sene L., Converti A., Borghi, M. D., 2003, Toluene and styrene removal from air in biofilter, Process Biochem., 37, 423-429.
14) Delhomenie M., Bibeau L., Gendron J., Brzezinski R., Heitz M. A., 2003, Study of clogging in a biofilter treating toluene vapors, Chem. Eng. J., 94, 211-222.
15) Acuna M. E., Villanueva C., Cardenas B., Christen P., Revah S., 2002, The effect of nutrient concentration on biofilm formation on peat and gas phase toluene biodegradation under biofiltration conditions, Process Biochem., 38, 7-13.
16) Elias A., Barona A., Arreguy A., Rios J., Aranguiz I., Penas J., 2002, Evaluation of a packing material for the biodegradation of H_2S and product analysis, Process Biochem., 37, 813-836.
17) Shinabe K., Oketani S., Ochi T., Kanchanatawee S., Matsumura M., 2002, Characteristics of hydrogen sulfide removal in a carrier-packed biological deodorization system, Biochem. Eng. J., 5, 209-217.
18) Yoon I. K., Kim C. N., Park C. H., 2002, Optimum operating conditions for the removal of volatile organic compounds in a compost-packed biofilter, Korean J. Chem. Eng., 19, 954-959.
19) Hirai M., Kamatomo M., Yani M., Shoda M., 2001, Comparison of biological H_2S removal characteristics among four inorganic packing materials, J. Biosci. Bioeng., 91, 396-402.
20) Cho K., Ryu H. W., Lee N. Y., 2000, Biological deodorization of hydrogen sulfide using porous lava as a carrier of *Thiobacillus thiooxidans*, J. Biosci. Bioeng., 90, 25-31.
21) Chung Y., Huang C., Tsen, C., Pan J. R., 2000, Biotreatment of H_2S- and NH_3-containing waste gases by co-immobilized cells biofilter, Chemosphere, 41, 329-336.
22) Cox H. H. J., Deshusses M. A., 2002, Co-treatment of H_2S and toluene in a biotrickling filter, Chem. Eng. J., 87, 101-110.
23) Row R., Toff R., Waide J., 1977, Microtechnique for most-probable-number analysis, Appl. Environ. Microbiol., 33, 675-680.
24) Schmidt W. L., Belser L. W., 1994, Autotrophic ni-

trifying bacteria, p. 159-197. In: Weaver R. W., Angle S., Bottomley P., Bezdiecek D., Smith S., Tabatabai A., Wollum A., Mickelson S. H., Bigham J. M. (ed), Methods of Soil Analysis. Part 2. Microbiological and Biochemical Properties (Soil Science Society of America Book, No 5), 2nd ed., Soil Science Society of America, Madison, WI.

25) Edwards V. H., 1970, The influence of high substrate concentrations on microbial kinetics, Biotechnol. Bioeng., 7, 679-712.

26) Zarook S. M., Shaikh A. A., Ansar Z., Baltzis B. C., 1997, Biofiltration of volatile organic compound (VOC) mixtures under transient conditions, Chem. Eng. Sci., 52, 4135-4142.

27) Park B. G., Chung J. S., 2006, Biokinetics on simultaneous biofiltration of H_2S, NH_3 and toluene in waste air, Korean J. Chem. Eng., 23(3), 428-434.

28) Kim H. S., Xie Q., Kim Y. J., Chung J. S., 2002a, Biofiltration of ammonia gas with sponge cube coated with mixtures of activated carbon and zeolite, Environ. Technol., 23, 839-847.

29) Kim H. S., Kim Y. J., Chung J. S., Xie Q., 2002b, Long-term operation of a biofilter for simultaneous removal of hydrogen sulfide and ammonia, J. Air Waste Manage. Assoc., 52, 1389-1398.

30) Kang Y. T., Nagano T., Kashiwagi T., 2002, Mass transfer correlation of NH_3-H_2O bubble absorption, Int. J. Refrig. 25, 878-886.

31) Cesario M. T., Beverloo W. A., Tramper J., Beefink H. H., 1997, Enhancement of gas-liquid mass transfer rate of apolar pollutants in the biological waste gas treatment by a dispersed organic solvent, Enzyme Microb. Technol., 21, 578-588.

32) Terasaka K., Oka J., Tsuge H., 2002, Ammonia absorption from a bubble expanding at a submerged orifice into water, Chem. Eng. Sci., 57, 3757-3765.

33) Bailey J. E., Ollis D. F., 1986, Biochemical Engineering Fundamentals, 2nd. ed., McGraw-Hill, Inc., 928pp.