Korean J. Chem. Eng., **26**(1), 79-85 (2009)

Simultaneous biofiltration of H_2S, NH_3 and toluene using cork as a packing material

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

*Current address: R&D Center, LG Petrochemical Co., Ltd., 754 Chungheung-dong, Yeosu 555-805, Korea
**Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, Korea
***Department of Chemical Engineering, POSTECH, San-31, Hyoja-dong, Pohang, Gyeongbuk 790-784, Korea
(*Received 31 July 2007 • accepted 24 July 2008*)

Abstract−Simultaneous removal of ternary gases of NH_3, H_2S and toluene in a contaminated air stream was investigated over 185 days in a biofilter packed with cork as microbial support. Multi-microorganisms including *Nitrosomonas* and *Nitrobactor* 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 inlet feed concentration was 50-180 ppmv for NH_3, 30-160 ppmv for H_2S and 40-130 ppmv for toluene, respectively. The observed removal efficiency was 45-100% for NH_3, 96-100% for H_2S, and 10-99% for toluene, respectively. Maximum elimination capacity was 5.5 g/m^3/hr for NH_3, >20.4 g/m^3/hr for H_2S and 4.5 g/m^3/hr for toluene, respectively. During long-term operation, the removal efficiency of toluene gradually decreased, mainly due to depositions of elemental sulfur and ammonium sulfate on the cork surface. The results of microbial analysis showed that nearly the same population density was observed on the surfaces of cork chips collected at each sampling point. Kinetic model analyses showed that there were no particular evidences of interactions or inhibitions among the microorganisms.

Key words: Ammonia, Biofilter, Cork, Hydrogen Sulfide, Odor, Carrier, Toluene

INTRODUCTION

Biofiltration technology has promising potential as an effective and economical treatment technology than the traditional treatment technologies for treating contaminated air stream with low concentration of odorous compounds and/or volatile organic compounds (VOCs). The fundamental principle of biofiltration of polluted air is that gaseous pollutants are destroyed in the process being converted into carbon dioxide, water and biomass by microbial metabolic reactions. During biofiltration, polluted air is passed through the biofilter medium where the pollutant is transferred from the gas to the liquid-solid phase where they are degraded by biofilm [1].

The concept of biofiltration to treat waste gases is similar to other forms of biological wastewater treatment. In biofiltration, a fan or blower forces gases containing biodegradable odorous compounds and VOCs through a packed bed that contains an unsaturated solid medium that supports a biologically active aqueous layer. As contaminated air flows through the support medium and past the aqueous biofilm, contaminants partition to the aqueous or solid phases where they are transformed by microorganisms into products such as carbon dioxide, water, and biomass.

Biofiltration primarily depends on the choice of the packing material. A proper packing material should have favorable conditions such as high porosity, appropriate pore size and suitable surface area for microbial growth and lower clogging effect that involves biofilter systems operated for long periods of time [2,3]. While packing media used in conventional biofilter beds consist mostly of peat or compost, a wide variety of other materials have been used. These include soil, wood chips, bark, sawdust, activated carbon, ceramic, ground tires, polystyrene beads and polyurethane foam [2,4-11]. In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms [12].

High porosity, appropriate pore size, low density, and the ability to sorb water are features important to the proper operation of packed bed biofilters. High porosity permits the uniform gas flow distribution needed for maximum contact between the gas stream contaminants and the microbial population. Pore size is directly related to head loss and clogging problems that often result from microbial growth. Low density, an obvious advantage in construction, helps minimize compaction of the bed due to the weight of the packing material itself [13]. Because microorganisms grow best on wet surfaces, the ability of filter material to absorb water is also an important factor in medium selection. In spite of their increasing popularity, three problems such as clogging due to excessive microbial growth, inadequate moisture control and difficulty to control in nutrient content of filter beds are commonly cited for conventionally designed and operated biofilter systems.

Biofiltration generates the least amount of secondary pollutants such as particulates, dioxin, SO_x, NO_x, and CO_2 and requires minimum efforts for operation and maintenance [14-24]. Deodorization and detoxification of volatile organic compounds (VOCs) in the air stream are the typical application of the biofiltration.

Among the sources of air pollution, H_2S and NH_3 are the most typical odorous compounds often encountered in industrial or residential areas [14-16,18-27]. H_2S and NH_3 are toxic and can cause malodorous nuisances, while toluene is a suspected carcinogen. Remarkably, 0.00047 ppmv is the lowest value of smelt level for H_2S [28]. According to the toxicity report, H_2S can break down the central nervous system at the concentration level of 100 ppmv. Even more seriously, H_2S is eventually a deadly toxic chemical above

†To whom correspondence should be addressed.
E-mail: jsc@postech.ac.kr

100 ppmv [29]. The threshold value of smelt level for NH_3 is 50 ppmv in the open air [30]. NH_3 is known to irritate the throat and eyes. In Korea, the current regulation levels are 2-10 ppmv for H_2S and 50-100 ppmv for NH_3 depending on the regions and sources of the pollutants. Toluene is not yet exclusively controlled; nevertheless, it is controlled as a part of total VOCs or benzene derivatives, and their legally allowed level is 30 ppmv in the open air [31]. Toluene is a toxic chemical regulated by the 1990 Clean Air Act Amendments (CAA) [32].

Recently, a number of research works have focused on the removal of malodorous gases. However, up to now, most researches on biofiltration have dealt with only single or binary gas, which seems to be impractical for real industrial application. This is because most of the emission sources contain multiple contaminants including sulfur and nitrogen compounds as well as VOCs, but limited to single or binary contaminants [16,17,20,33-38]. Cox and Deshusses [20] investigated the treatment of the binary toluene-H_2S containing waste air using bio-trickling beds. The H_2S removal efficiency was nearly 100%; however, the toluene removal was much less: only 75% at pH 7.0 and 25% at pH 4.5. For the simultaneous removal of NH_3 and H_2S, the removal efficiency widely varied depending on the experimental conditions and the supporting media. The removal efficiency ranged from 80% to 100% for NH_3 and from 90 to 100% for H_2S. Malhautier et al. [21] observed that elemental sulfur and sulfate were the products of H_2S oxidation and subsequently reduced the void fraction of the biotrickling bed. Kim et al. [16] reported that microbial activity decreased due to accumulation of sulfur on the surface of packing materials during the long-term operation of packed-bed biofilter system. Chung et al. [17] also reported that the substrates (i.e., NH_3 and H_2S) have inhibitory effect on the removal efficiency when the concentrations of the H_2S and/or NH_3 are relatively high. Liu et al. [18] also reported on the inhibitory effect of a biofilter system treating binary gases of toluene and ethylacetate.

In this study, we investigated the simultaneous removal of ternary gases of NH_3-H_2S-toluene in a biofilter packed with cork. Cork was selected due to its physical characteristics: high surface area and porosity, low density and ability to sorb water providing habitats for microbial growth. The removal efficiency and elimination capacity were examined 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 interactions and inhibitory effects among the three substrates and/or microorganisms during long-term operations of a single packed-bed biofiltration system.

MATERIALS AND MATHODS

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 Is 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 cork chips. The physical properties for the cork chips are summarized in Table 1. The actual packing length of the cork was 80 cm and was equally divided into three layers. A spacer (5-cm-long) made of a stainless steel mesh screen was inserted between the layers to support the cork chips. The total bed volume of the cork packing was

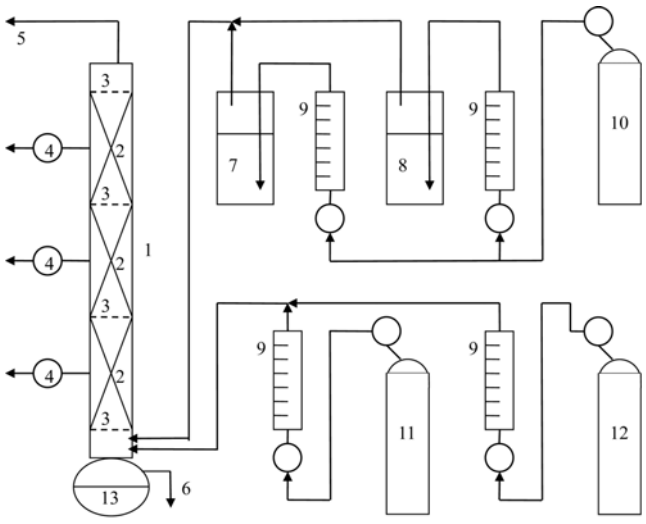

Fig. 1. Schematic diagram of the biofiltration system.

1. Biofilter column
2. Packing
3. Stainless steel separator
4. Sampling port
5. Purified air
6. Drain
7. Saturator for water
8. Saturator for toluene
9. Rotameter
10. Air
11. H_2S gas
12. HN_3 gas
13. Water reservoir

Table 1. Characteristics of cork supporting media

Property	Value	Unit	Remark
Surface area, S_g	2.30×10^3	m^2/g	BET
Bed porosity, ε_{bed}	0.53	dimensionless	measured
Particle size, d_p	3.30×10^{-3}	m	measured
Specific surface area, A_s	806-940	m^2/m^3	$6(1-\varepsilon_{bed})/d_p$
Bulk density, ρ_b	2.87×10^5	g/m^3	measured

1.0 liter. A sampling port was installed at the middle point of the each section in order to sample the microbial support materials and to measure gas concentrations. 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 was 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 (Doekyang Energen Co., 1 mol% balanced with N_2) 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. Operation of the Biofiltration System

The biofiltration system was continuously operated for 185 days at room temperature and atmospheric pressure. During the biofiltration experiments, the packed cork was washed with a nutrient

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

Gas	Molecular weight	Henry' law constant (H_i, dimensionless)	Solubility (g/L)	Overall mass transfer coefficient[a], ($K_L \cdot a$, hr^{-1})
NH_3	17.03	1,387	953.7	623-7,344
H_2S	34.08	2.43	3.34	15-24
Toluene	92.14	3.96	14.74	54-72

[a]Data reported by Shinabe et al. [43]; Cesario et al. [44]; Kang et al. [45]; Terasaka et al. [46]

solution when the column showed a significant pressure drop due to accumulation of microorganisms, elemental sulfur and ammonium sulfate along the biofilter column. The total volumetric air flow rates increased from 0.030 to 0.090 m^3/hr, which corresponds to 120 to 40 seconds of empty bed residence time (EBRT), respectively. The feed concentration of NH_3, H_2S and toluene gas was about 50-184 ppmv, 30-160 ppmv and 40-130 ppmv, respectively. The inlet loading (IL) was 0.95-8.15 g/m^3/hr for NH_3, 1.27-20.4 g/m^3/hr for H_2S and 4.59-25.5 g/m^3/hr for toluene, respectively. The initial pH was controlled at 7.0 by using NaOH and HNO_3; however, the pH was quickly changed after the biological reaction started. During the biofiltration experiments, the measured pH in the drain water was in the range of 8 to 9.

3. Measurement of the Performance of the Biofiltration System

Conventionally, the performance of the biofiltration system can be characterized by several measuring 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, the 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 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 is an imaginary residence time, assuming 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:

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

$$\mathrm{IL}_i = \frac{C^G_{i,IN}}{\mathrm{EBRT}} \tag{2}$$

$$\mathrm{EC}_i = \frac{(C^G_{i,IN} - C^G_{i,OUT})}{\mathrm{EBRT}} \tag{3}$$

$$X_i = \frac{(C^G_{i,IN} - C^G_{i,OUT})}{C^G_{i,IN}} = \frac{\mathrm{EC}_i}{\mathrm{IL}_i} \tag{4}$$

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 physical properties observed in 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.

4. Analytical Methods

Both the inlet and outlet concentrations of NH_3, H_2S and toluene gases were measured by using 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, 1-120 ppmv 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, which formed on the cork surface and in the drain water, were characterized by X-ray powder diffraction (XRD, MAC Science Co., Model M18XHF, CuK) and an elemental analysis (LECO Co., Model CHNS 932). The bed porosity of the cork support was measured by a mercury porosimeter (Microstructure Lab, Carlo Erba Strumentazione). The BET surface area was measured by nitrogen adsorption with Micromeritics (Model ASAP 2021C).

5. Microorganisms

Three different types of microorganisms were independently cultivated in aqueous minerals solutions by using a shaking incubator (Jeio Tech, SI-900R) at 30 ºC and 100 rpm. The nitrifying bacteria, *Nitrosomonas* and *Nitrobactor*, were isolated from the activated sludge in a sewage 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 $Fe_2(SO_4)_2 \cdot H_2O$ 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 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 containing a nutrient agar with 0.5% NaCl, 3.0 g of beef extract and 5.0 g of peptone. 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 ºC for 15 minutes prior to use.

After cultivation, the microorganisms were mixed together immediately before inoculation. The mixed microorganisms were sprayed over the cork carriers in an open vessel with aeration for several hours. The inoculated cork carriers were then packed into the biofiltration column and acclimated for the next two weeks. The inlet loadings (IL) of NH_3, H_2S and toluene, were kept at a quarter of those used for normal operating conditions.

6. Microbiological Analysis

To count the microbial populations, the colony-forming unit (CFU) was measured at the 150th day of operation by the conventional most probable number (MPN) method [39,40]. Subsamples of cork carriers were collected through the upper, middle and lower sampling ports attached to the biofilter column. The cork 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 medium. Subsequently, the samples were incubated for 21 days at 30 ºC 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.

RESULTS AND DISCUSSION

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 volumetric air flow rate at the inlet 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

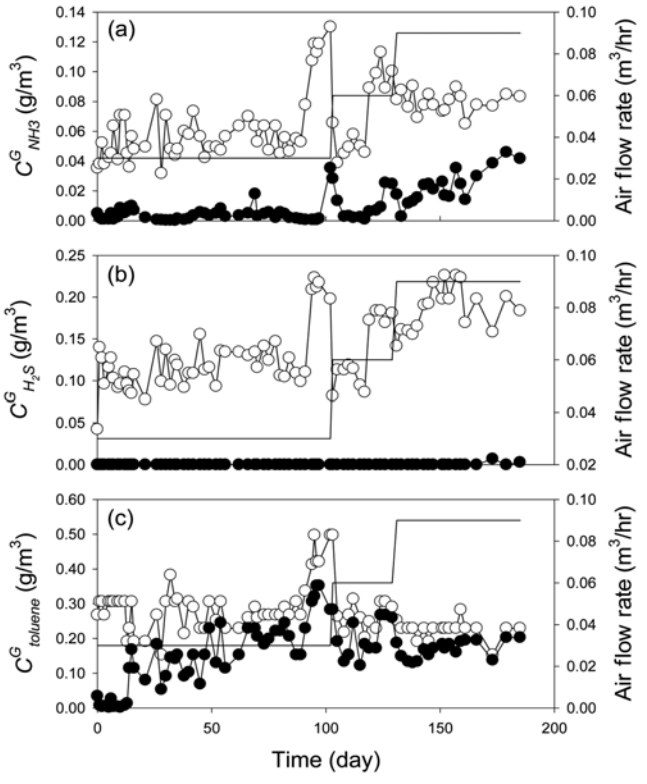

Fig. 2. Results of the long-term operation of the biofiltration using cork as supporting medium. (a) NH_3, (b) H_2S, and (c) toluene. Symbols: ○=inlet concentration and ●=outlet concentration. Solid line indicates EBRT or inlet air flow rate.

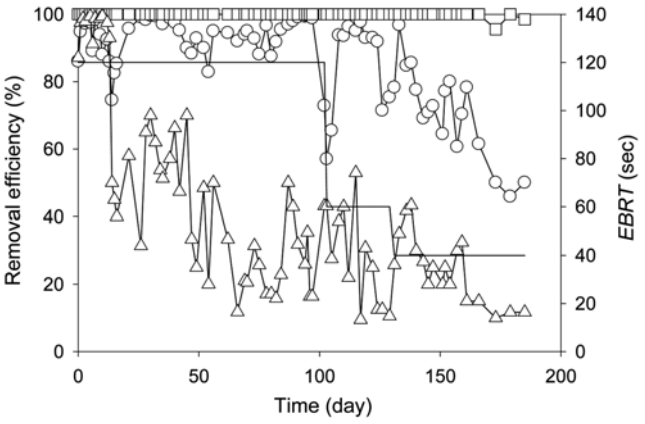

Fig. 3. Removal efficiency as a function of time. Symbols: ○=NH_3, □=H_2S, and △=toluene. Solid line indicates EBRT or inlet air flow rate.

to 0.090 m^3/hr (from the 131st day to the 185th day); the corresponding empty bed residence time (EBRT) was 120 sec, 60 sec and 40 sec, respectively. As summarized in Table 1, the bed porosity was 0.53 and the feed concentration of NH_3, H_2S and toluene was about 50-184, 30-160, 40-130 ppmv, respectively. The corresponding inlet loadings (IL) for NH_3, H_2S and toluene were 0.95-8.15 g/m^3/hr, 1.27-20.4 g/m^3/hr and 4.59-25.5 g/m^3/hr, respectively.

In the very early stage of the biofiltration experiments (i.e., from the start to the 20th day), above 95% of all gases were removed. According to Zilli et al. [22] and Kim et al. [16], the high removal in the early stage was mainly due to adsorption onto the packing material and mass transfer into aqueous phase, but not due to biodegradation activities of the microorganisms. After the 20th day, the adsorption capacity of the biofilter column was under thermodynamic equilibrium with the pollutant gases.

Removal efficiency of ammonia, H_2S, and toluene as a function of time is shown in Fig. 3. Among the three gases, H_2S was completely removed during the 185 days of operation, even under different operating conditions. The removal efficiency of NH_3 was maintained at nearly constant value (>95%) from the 20th to the 102nd day. 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 of NH_3 for the following 5 days (from the 102nd to the 107th day), after which the removal efficiency was immediately recovered for the following periods (from the 108th day to 124th day). A very similar trend was observed when the flow rate increased again from 0.06 m^3/hr to 0.09 m^3/hr on the 131st day. The removal efficiency gradually decreased to 50% during the 131st to the 185th day. This is because the elimination capacity (EC) of NH_3 already reached the maximum value.

Toluene exhibited a rather complicated and abnormal trend in the removal efficiency upon the change in the flow rate. The removal efficiency of toluene was above 95% for the first 20 days due to absorption and adsorption. After this, the removal efficiency gradually decreased from 99% to 10% during the 21st day - the 100th day. As the air flow rate increased on the 102nd and 131st day, the removal efficiency slightly increased, but was followed by a slow and gradual decrease. Unlikely the other two gases, the trend in toluene removal was not directly related to the change in the total inlet

Table 3. Counts for microbial populations in the biofilm fixed on the cork supporting media

	Logarithmic counts for microbial populations, log(CFU/g)			
Column layer	Nitrosomonas	Nitrobactor	Thiobasilli	Pseudomonas putida
Upper	7.3	5.0	7.6	6.9
Middle	7.3	3.1	8.0	7.4
Lower	7.8	4.5	6.5	6.8

flow rate and no recovery in microbial activity was observed. The irregular behavior in toluene removal efficiency was not fully understood. Zilli et al. [22] reported that microbial activity for toluene removal needs at least 50 days to obtain a new steady state after changing the reaction conditions, which is in agreement with our observations.

To investigate the reason for poor removal efficiency of toluene, both the residuals of drain water in the bottom reservoir and the pale yellow colored cake deposited on the cork 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 were mainly $(NH_4)_2SO_4$ and elemental sulfur, which are known byproducts of H_2S oxidation [16,28]. It appeared that the cork surface was covered by the elemental sulfur and became more and more hydrophobic. Furthermore, relatively small-sized elemental sulfur particles were continuously accumulated in the cork pores and were highly difficult to remove by washing. In other part, biofilm formation on the cork surface may also have been hindered by the elemental sulfur deposition. However, the removal efficiencies of H_2S and NH_3 were not influenced by the sulfur deposition (Fig. 3). According to Oyarzun et al. [28], elemental sulfur was an intermediate of H_2S metabolism and was further oxidized by *Thiobacillus thioparus* that was 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 cork surface became partially hydrophobic, the solubility of NH_3 in water was too high to be affected by the hydrophobic cork 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 caused by sulfur. Liu et al. [18] observed that at certain concentration level, the toluene removal was inhibited by presence of ethylacetate. Chung et al. [15] reported that that inhibition exists between the NH_3 and H_2S substrates when the substrate concentrations are relatively high. The Andrews-Haldane biokinetic model was introduced in order to account for the inhibition effect of binary substrates in the biofiltration system [41]. In this work, we intended to treat a mixture of three substrates (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. Detailed discussions on the model equations are available elsewhere [27,41,42].

Microbial populations were measured by the conventional MPN method [39,40] on the 105th day and the results are summarized in Table 3. At the three sampling points, the populations of the all microorganisms were similar, indicating that there is no superior species among the different microorganisms.

2. Effects of Inlet Feed Condition on the Elimination Capacity

The plot of elimination capacity vs. the inlet loadings of NH_3, H_2S and toluene is shown in Fig. 4 and the results are summarized

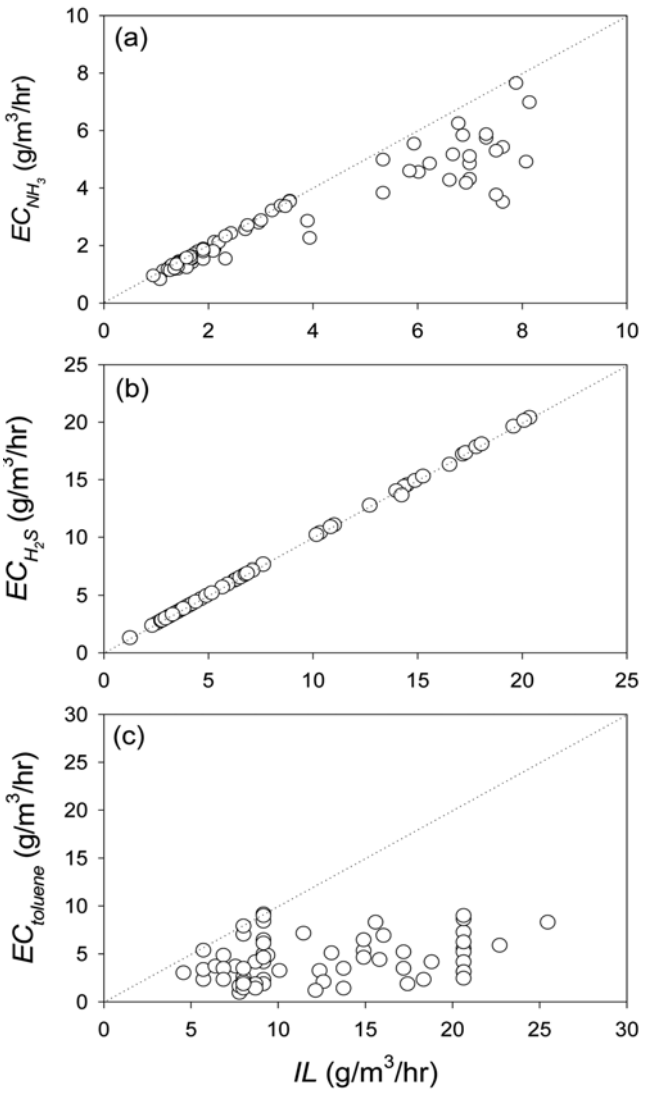

Fig. 4. Elimination capacities as a function of inlet loading. (a) NH_3, (b) H_2S, and (c) toluene.

Table 4. Summary of the results of long-term operation of biofilter

Component	C_{IN}^{G} (ppmv)	C_{OUT}^{G} (ppmv)	IL (g/m^3/hr)	X (%)	EC (g/m^3/hr)	EC_{max} (g/m^3/hr)
NH_3	50-184	0.25-65	0.95-8.15	45-100	0.91-7.90	5.5
H_2S	30-160	0-5	1.27-20.4	96-100	1.50-20.4	N/A
Toluene	40-130	0.5-110	4.59-25.5	10-99	0.92-9.13	4.5

in Table 4. Almost 100% removal efficiency within the relatively low inlet loadings was observed during the first period of 20 days. As mentioned previously, the absorption by the cork supporting media and dissolution into aqueous phase were the main reason for the high initial elimination capacity during the very early stage of biofilter operation.

For NH_3 (Fig. 4a), the elimination capacity (EC) of NH_3 (EC_{NH3}) was almost linearly proportional to the inlet NH_3 loading and EC data were positioned near the diagonal line when the inlet loading (IL) was less than 4 g/m^3/hr. Afterwards, for the inlet loadings from 4 to 8 g/m^3/hr, the EC asymptotically approached a maximum elimination capacity of 5.5 g/m^3/hr. The highest ECNH3 was 7.6 g/m^3/hr within the experimental conditions. For NH3 removal, it should be noted that the experimentally measured elimination capacities by pure biological reaction might be overestimated because the solubility of NH3 in water is extremely high (see Table 2).

In Fig. 4b, all data points of H_2S elimination capacity were positioned on the diagonal line, which confirms that the removal efficiency is nearly 100% within the entire experimental conditions, regardless of H_2S loading into the biofilter. This also indicates that the inlet conditions for the H_2S removal are still far below maximum elimination capacity.

For toluene removal (Fig. 4c), however, most of the elimination capacities were positioned below the diagonal line except only a few points. A few data points positioned on the diagonal line that correspond to 100% of elimination capacity were observed for the first 20 days of biofilter operation. As mentioned previously, these were mainly due to the absorption onto cork surface and the dissolution into aqueous phase. In spite of wide variation in EC of toluene, the EC was maintained at a constant value of 4.5 g/m^3/hr within experimental error, which was assumed to be the maximum elimination capacity.

The lower elimination capacities for toluene were attributed to (i) high inlet loading above the maximum elimination capacity, (ii) relatively lower microbial activities and a slow growth rate of the heterotrophs (i.e., toluene-degrading bacteria) compared to the other autotrophs (NH_3 and H_2S degrading bacteria), (iii) a long recovery time compared to other gases upon shock loading, and (iv) inhibition of toluene removal activity by the elemental sulfur deposition on the cork surface.

During the simultaneous biofiltration of the relatively low concentrations of ternary gases (NH_3, H_2S and toluene) using cork chip as a supporting material, neither interactions nor competitive inhibitions were found among the three different microorganisms (*Thiobasillus thioparus*, *Nitrosomonas* and *Nitrobactor* and *Pseudomonas putida*). Biodegradations of the three gases were parallel processes where the three different reactions occurred simultaneously at the same sites of the packing 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 is in contrast to those reported by Chung et al. [27] for the removal on the binary NH_3 and H_2S gases using a biotrickling bed. They 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. [18] also reported on the inhibition effect in a biofilter that treats the binary gases of toluene and ethylacetate. Kim et al. [16] reported a similar decreasing trend in removal efficiency, due to the accumulation of sulfur in packing materials during a long-term operation of packed-bed system. Malhautier et al. [21] observed that elemental sulfur and sulfate were the major products of H_2S oxidation reducing the void fraction of the biotrickling bed. This observation, however, is in agreement with the results of Cox and Deshusses [20] who reported that there was no interaction between the microorganisms during the simultaneous removal of the binary H_2S and toluene gases in a biotrickling filter. 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 inhibition on toluene removal by the presence of H_2S.

CONCLUSIONS

The biofiltration of three different gases (NH_3, H_2S and toluene) that are widely different in physicochemical properties was investigated by using cork chips as a supporting material of microbial growth. The results of the Andrews-Haldane biokinetic model showed that neither interaction nor competitive inhibition exists among the different kinds of microorganisms. However, the toluene removal was highly affected by the sulfur deposition on cork surface and the relatively high feed concentration of toluene. The microbial populations on the surface of the cork carriers were about the same at each sampling point. 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. In the design and stability aspects, this system can be operated up to inlet loading of 5.5 g/m^3/hr, 20.4 g/m^3/hr or even higher, 4.5 g/m^3/hr for NH_3 and H_2S and toluene, correspondingly. The removal efficiencies of 45-100 and 96-100% have been observed for NH_3 and H_2S, respectively. For toluene, however, the removal efficiency was very low, about 30%, because the tested inlet concentration was too high.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support of this research provided by the Korean Ministry of Science and Technology (MOST).

REFERENCES

1. J. S. Devinny, M. A. Deshusses and T. S. Webster, *Biofiltration for air pollution control*, CRC Press, Boca Raton, FL, USA (1998).
2. W. M. Moe and R. L. Irvine, *J. Env. Eng.*, **126**, 826 (2000).
3. A. Torkian, R. Dehghanzadeh and M. Hakimjavadi, *J. Chem. Technol. Biotechnol.*, **78**, 795 (2003).
4. J. O. Kim, *Environ. Eng. Res.*, **2**, 9 (1997).
5. R. J. Abumaizar, W. Kocher and E. H. Smith, *J. Hazard. Mater.*, **60**, 111 (1998).
7. W. M. Moe and R. L. Irvine, *Wat. Res.*, **35**, 1407 (2001a).
8. W. M. Moe and R. L. Irvine, *Wat. Sci. Technol.*, **43**, 35 (2001b).
9. A. Amarsanaa, W. S. Shin, J.-H. Choi and S.-J. Choi, *Env. Eng. Res.*, **11**, 1 (2006).
10. A. Amarsanaa, W. S. Shin, J.-H. Choi and S.-J. Choi, *J. Environ. Sci.*, **15**, 513 (2006).
11. M. Delhomenie, L. Bibeau, N. Bredin, S. Roy, S. Broussau, R. Brzezinski, J. L. Kugelmass and M. Heitz, *Adv. Environ. Res.*, **6**, 239 (2002).
12. K. A. Kinney, W. Wright, D. P. Chang and E. D. Schroeder, *Biodegradation of vapor phase contaminants*, in Bioremediation: principles and practice, S. K. Sikdar and R. L. Irvine Eds., Technomic Press, Lancaster, PA, USA (1997).
13. S. J. Ergas, E. D. Schroeder, D. P. Y. Chang and R. L. Morton, *Water Environ. Res.*, **67**, 816 (1995).
14. S. H. Kim, K. J. Oh, J. H. Moon and D. Kim, *J. Micorbiol. Biotechnol.*, **10**, 419 (2000).
15. Y. Chung, C. Huang and C. Tseng, *Chemosphere*, **43**, 1043 (2001).
16. H. S. Kim, Y. J. Kim, J. S. Chung and Q. Xie, *J. Air Waste Manage. Assoc.*, **52**, 1389 (2002).
17. H. S. Kim, Q. Xie, Y. J. Kim and J. S. Chung, *Environ. Technol.*, **23**, 839 (2002).
18. Y. Liu, Q. Xie, Y. Sun, J. Chen, D. Xue and J. S. Chung, *J. Hazard. Mater.*, **95**, 199 (2002).
19. M. E. Acuna, C. Villanueva, B. Cardenas, P. Christen and S. Revah, *Proc. Biochem.*, **38**, 7 (2002).
20. H. H. J. Cox and M. A. Deshusses, *Chem. Eng. J.*, **87**, 101 (2002).
21. L. Malhautier, C. Gracian, J. Roux, J. Fanlo and P. L. Cloirec, *Chemosphere*, **50**, 145 (2003).
22. M. Zilli, E. Palazzi, L. Sene, A. Converti and M. D. Borghi, *Process Biochem.*, **37**, 423 (2003).
23. K. H. Lim and S. W. Park, *Korean J. Chem. Eng.*, **21**, 1161 (2004).
24. K. H. Lim, *Korean J. Chem. Eng.*, **22**, 228 (2005).
25. S. J. Park, K. S. Cho, M. Hirai and M. Shoda, *J. Ferment. Bioeng.*, **76**, 55 (1993).
26. A. H. Wani, R. M. R. Branion and A. K. Lau, *J. Hazard. Mater.*, **60**, 287 (1998).
27. Y. Chung, C. Huang, C. Tseng and J. R. Pan, *Chemosphere*, **41**, 329 (2000).
28. P. Oyarzun, F. Arancibia, C. Canales and G. E. Aroca, *Process Biochem.*, **39**, 165 (2003).
29. S. A. Shojaosadati and S. Elyasi, *Resour. Conserv. Recycl.*, **27**, 139 (1999).
30. G. Busca and C. Pistarino, *J. Loss Prevent Proc.*, **16**, 157 (2003).
31. Korean Ministry of Environment, *Permissible air pollutant emission standards*, Korean Ministry of Environment Printing Office: Seoul, Republic of Korea (2005).
32. A. B. Neal and R. C. Loehr, *Waste Manage.*, **20**, 59 (2000).
33. K. Cho, H. W. Ryu and N. Y. Lee, *J. Biosci. Bioeng.*, **90**, 25 (2000).
34. M. Hirai, M. Kamatomo, M. Yani and M. Shoda, *J. Biosci. Bioeng.*, **91**, 396 (2001).
35. A. Elias, A. Barona, A. Arreguy, J. Rios, I. Aranguiz and J. Penas, *Process. Biochem.*, **37**, 813 (2002).
36. K. Shinabe, S. Oketani, T. Ochi, S. Kanchanatawee and M. Matsumura, *Biochem. Eng. J.*, **5**, 209 (2002).
37. I. K. Yoon, C. N. Kim and C. H. Park, *Korean J. Chem. Eng*, **19**, 954 (2002).
38. M. Delhomenie, L. Bibeau, J. Gendron, R. Brzezinski and M. A. Heitz, *Chem. Eng. J.*, **94**, 211 (2003).
39. R. Row, R. Toff and J. Waide, *Appl. Environ. Microbiol.*, **33**, 675 (1977).
40. W. L. Schmidt and L. W. Belser, *Autotrophic nitrifying bacteria*, in Methods of Soil Analysis. Part 2. Microbiological and Biochemical Properties (Soil Science Society of America Book, No 5), R. W. Weaver, S. Angle, P. Bottomley, D. Bezdiecek, S. Smith, A. Tabatabai, A. Wollum, S. H. Mickelson and J. M. Bigham Eds., 2nd ed., Soil Science Society of America, Madison, WI, USA, pp. 159-197 (1994).
41. V. H. Edwards, *Biotechnol. Bioeng.*, **7**, 679 (1970).
42. S. M. Zarook, A. A. Shaikh, Z. Ansar and B. C. Baltzis, *Chem. Eng. Sci.*, **52**, 4135 (1997).
43. K. Shinabe, S. Oketani, T. Ochi and M. Matsumura, *J. Ferm. Bioeng.*, **80**, 592 (1995).
44. M. T. Cesario, W. A. Beverloo, J. Tramper and H. H. Beefink, *Enzyme Microb. Technol.*, **21**, 578 (1997).
45. Y. T. Kang, T. Nagano and T. Kashiwagi, *Int. J. Refrig.*, **25**, 878 (2002).
46. K. Terasaka, J. Oka and H. Tsuge, *Chem. Eng. Sci.*, **57**, 3757 (2002).