

## Simultaneous biofiltration of H<sub>2</sub>S, NH<sub>3</sub> and toluene using cork as a packing material

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**Abstract**—Simultaneous removal of ternary gases of NH<sub>3</sub>, H<sub>2</sub>S 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 *Nitrobacter* for nitrogen removal, *Thiobacillus thioparus* (ATCC 23645) for H<sub>2</sub>S 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<sub>3</sub>, 30-160 ppmv for H<sub>2</sub>S and 40-130 ppmv for toluene, respectively. The observed removal efficiency was 45-100% for NH<sub>3</sub>, 96-100% for H<sub>2</sub>S, and 10-99% for toluene, respectively. Maximum elimination capacity was 5.5 g/m<sup>3</sup>/hr for NH<sub>3</sub>, >20.4 g/m<sup>3</sup>/hr for H<sub>2</sub>S and 4.5 g/m<sup>3</sup>/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<sub>x</sub>, NO<sub>x</sub>, and CO<sub>2</sub> 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<sub>2</sub>S and NH<sub>3</sub> are the most typical odorous compounds often encountered in industrial or residential areas [14-16,18-27]. H<sub>2</sub>S and NH<sub>3</sub> 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<sub>2</sub>S [28]. According to the toxicity report, H<sub>2</sub>S can break down the central nervous system at the concentration level of 100 ppmv. Even more seriously, H<sub>2</sub>S is eventually a deadly toxic chemical above

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100 ppmv [29]. The threshold value of smelt level for  $\text{NH}_3$  is 50 ppmv in the open air [30].  $\text{NH}_3$  is known to irritate the throat and eyes. In Korea, the current regulation levels are 2-10 ppmv for  $\text{H}_2\text{S}$  and 50-100 ppmv for  $\text{NH}_3$  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- $\text{H}_2\text{S}$  containing waste air using bio-trickling beds. The  $\text{H}_2\text{S}$  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  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , the removal efficiency widely varied depending on the experimental conditions and the supporting media. The removal efficiency ranged from 80% to 100% for  $\text{NH}_3$  and from 90 to 100% for  $\text{H}_2\text{S}$ . Malhautier et al. [21] observed that elemental sulfur and sulfate were the products of  $\text{H}_2\text{S}$  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.,  $\text{NH}_3$  and  $\text{H}_2\text{S}$ ) have inhibitory effect on the removal efficiency when the concentrations of the  $\text{H}_2\text{S}$  and/or  $\text{NH}_3$  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  $\text{NH}_3$ - $\text{H}_2\text{S}$ -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  $\text{NH}_3$ - $\text{H}_2\text{S}$ -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

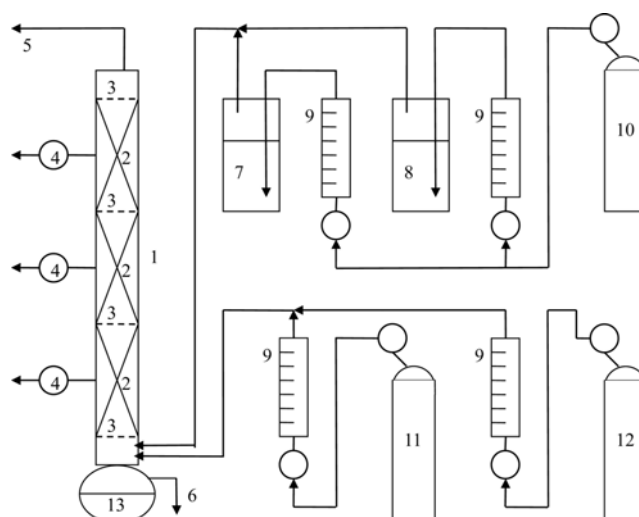


Fig. 1. Schematic diagram of the biofiltration system.

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.  $\text{H}_2\text{S}$  gas
12.  $\text{HN}_3$  gas
13. Water reservoir

Table 1. Characteristics of cork supporting media

| Property                       | Value                 | Unit                    | Remark                      |
|--------------------------------|-----------------------|-------------------------|-----------------------------|
| Surface area, $S_g$            | $2.30 \times 10^3$    | $\text{m}^2/\text{g}$   | BET                         |
| Bed porosity, $\epsilon_{bed}$ | 0.53                  | dimensionless           | measured                    |
| Particle size, $d_p$           | $3.30 \times 10^{-3}$ | m                       | measured                    |
| Specific surface area, $A_s$   | 806-940               | $\text{m}^2/\text{m}^3$ | $6(1 - \epsilon_{bed})/d_p$ |
| Bulk density, $\rho_b$         | $2.87 \times 10^5$    | $\text{g}/\text{m}^3$   | 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  $\text{H}_2\text{S}$  (Doekyang Energen Co., 1 mol% balanced with  $\text{N}_2$ ) and  $\text{NH}_3$  (Doekyang Energen Co., 1 mol% balanced with  $\text{N}_2$ ) 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 <sub>i</sub> , dimensionless) | Solubility (g/L) | Overall mass transfer coefficient <sup>a</sup> , (K <sub>L</sub> ·a, hr <sup>-1</sup> ) |
|------------------|------------------|------------------------------------------------------|------------------|-----------------------------------------------------------------------------------------|
| NH <sub>3</sub>  | 17.03            | 1,387                                                | 953.7            | 623-7,344                                                                               |
| H <sub>2</sub> S | 34.08            | 2.43                                                 | 3.34             | 15-24                                                                                   |
| Toluene          | 92.14            | 3.96                                                 | 14.74            | 54-72                                                                                   |

<sup>a</sup>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<sup>3</sup>/hr, which corresponds to 120 to 40 seconds of empty bed residence time (EBRT), respectively. The feed concentration of NH<sub>3</sub>, H<sub>2</sub>S 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<sup>3</sup>/hr for NH<sub>3</sub>, 1.27-20.4 g/m<sup>3</sup>/hr for H<sub>2</sub>S and 4.59-25.5 g/m<sup>3</sup>/hr for toluene, respectively. The initial pH was controlled at 7.0 by using NaOH and HNO<sub>3</sub>; 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<sup>3</sup>/hr), (ii) the elimination capacity (EC, g/m<sup>3</sup>/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:

$$EBRT = \frac{V_B}{q_0} \quad (1)$$

$$IL_i = \frac{C_{i,IN}^G}{EBRT} \quad (2)$$

$$EC_i = \frac{(C_{i,IN}^G - C_{i,OUT}^G)}{EBRT} \quad (3)$$

$$X_i = \frac{(C_{i,IN}^G - C_{i,OUT}^G)}{C_{i,IN}^G} = \frac{EC_i}{IL_i} \quad (4)$$

where C (g/m<sup>3</sup>) is the concentration in the gas phase, q<sub>0</sub> is the inlet volumetric gas flow rate (m<sup>3</sup>/hr) and V<sub>B</sub> is the packed-bed volume (m<sup>3</sup>). Superscript G represents physical properties observed in the gas phase, subscript i is the gas component (i.e., NH<sub>3</sub>, H<sub>2</sub>S 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<sub>3</sub>, H<sub>2</sub>S 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<sub>3</sub>, 1-120 ppmv for H<sub>2</sub>S, and 1-100 ppmv for toluene. The lowest detection limit was 0.5 ppmv for NH<sub>3</sub>, 0.2 ppmv for H<sub>2</sub>S, 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 °C and 100 rpm. The nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*, 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<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.080 g of KH<sub>2</sub>PO<sub>4</sub>, 0.020 g of MgSO<sub>4</sub> and 0.0085 g of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O in 1.0 L of double distilled water. A H<sub>2</sub>S 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<sub>2</sub>HPO<sub>4</sub>, 1.8 g of KH<sub>2</sub>PO<sub>4</sub>, 0.1 g of MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.1 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.03 g of CaCl<sub>2</sub>, 0.02 g of FeCl<sub>3</sub>, 0.02 g of MnSO<sub>4</sub>, and 10.0 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>4</sub>)<sub>2</sub>PO<sub>4</sub>, 1.20 g of KH<sub>2</sub>PO<sub>4</sub>, 5.0 g of NaCl, 0.20 g of MgSO<sub>4</sub>·7H<sub>2</sub>O, 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 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<sub>3</sub>, H<sub>2</sub>S 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 150<sup>th</sup> 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  $(\text{NH}_4)_2\text{SO}_4$ , 0.5 g of  $\text{KH}_2\text{PO}_4$ , 50 mg of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 4 mg of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 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 °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.

## 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  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and toluene. The volumetric air flow rate at the inlet was maintained at 0.030  $\text{m}^3/\text{hr}$  (from the 0<sup>th</sup> day to the 102<sup>nd</sup> day), increased to 0.060  $\text{m}^3/\text{hr}$  (from the 103<sup>rd</sup> day to the 130<sup>th</sup> day), and then further increased up

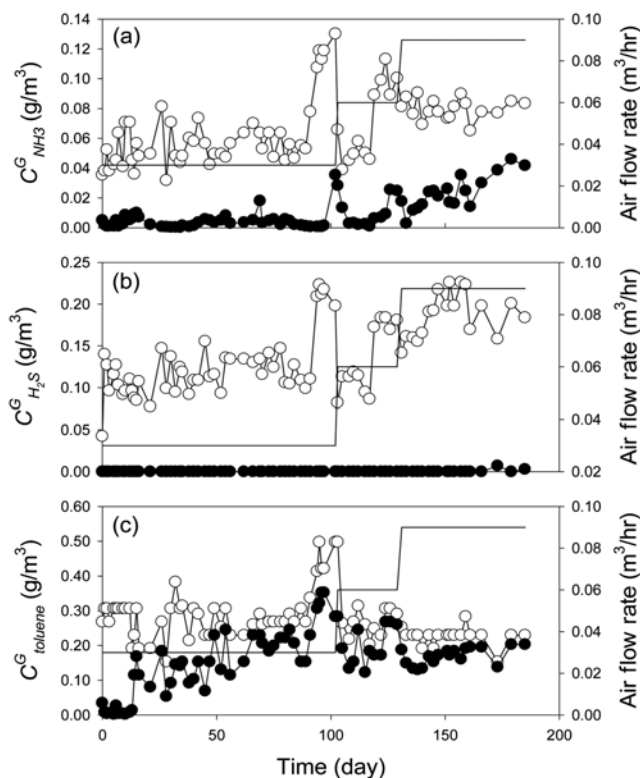


Fig. 2. Results of the long-term operation of the biofiltration using cork as supporting medium. (a)  $\text{NH}_3$ , (b)  $\text{H}_2\text{S}$ , and (c) toluene. Symbols:  $\circ$ =inlet concentration and  $\bullet$ =outlet concentration. Solid line indicates EBRT or inlet air flow rate.

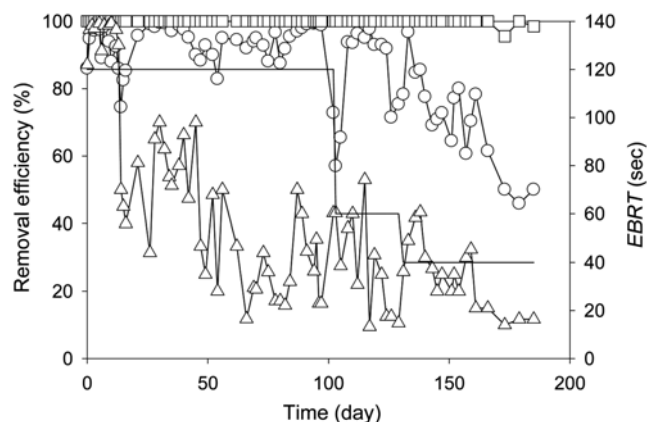


Fig. 3. Removal efficiency as a function of time. Symbols:  $\circ$ = $\text{NH}_3$ ,  $\square$ = $\text{H}_2\text{S}$ , and  $\triangle$ =toluene. Solid line indicates EBRT or inlet air flow rate.

to 0.090  $\text{m}^3/\text{hr}$  (from the 131<sup>st</sup> day to the 185<sup>th</sup> 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  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and toluene was about 50-184, 30-160, 40-130 ppmv, respectively. The corresponding inlet loadings (IL) for  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and toluene were 0.95-8.15  $\text{g}/\text{m}^3/\text{hr}$ , 1.27-20.4  $\text{g}/\text{m}^3/\text{hr}$  and 4.59-25.5  $\text{g}/\text{m}^3/\text{hr}$ , respectively.

In the very early stage of the biofiltration experiments (i.e., from the start to the 20<sup>th</sup> 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 20<sup>th</sup> day, the adsorption capacity of the biofilter column was under thermodynamic equilibrium with the pollutant gases.

Removal efficiency of ammonia,  $\text{H}_2\text{S}$ , and toluene as a function of time is shown in Fig. 3. Among the three gases,  $\text{H}_2\text{S}$  was completely removed during the 185 days of operation, even under different operating conditions. The removal efficiency of  $\text{NH}_3$  was maintained at nearly constant value (>95%) from the 20<sup>th</sup> to the 102<sup>nd</sup> day. On the 102<sup>nd</sup> day, the total inlet air flow rate increased from 0.03  $\text{m}^3/\text{hr}$  to 0.06  $\text{m}^3/\text{hr}$ . This change decreased the removal efficiency of  $\text{NH}_3$  for the following 5 days (from the 102<sup>nd</sup> to the 107<sup>th</sup> day), after which the removal efficiency was immediately recovered for the following periods (from the 108<sup>th</sup> day to 124<sup>th</sup> day). A very similar trend was observed when the flow rate increased again from 0.06  $\text{m}^3/\text{hr}$  to 0.09  $\text{m}^3/\text{hr}$  on the 131<sup>st</sup> day. The removal efficiency gradually decreased to 50% during the 131<sup>st</sup> to the 185<sup>th</sup> day. This is because the elimination capacity (EC) of  $\text{NH}_3$  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 21<sup>st</sup> day - the 100<sup>th</sup> day. As the air flow rate increased on the 102<sup>nd</sup> and 131<sup>st</sup> day, the removal efficiency slightly increased, but was followed by a slow and gradual decrease. Unlike 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**

| Column layer | Logarithmic counts for microbial populations, log(CFU/g) |             |             |                    |
|--------------|----------------------------------------------------------|-------------|-------------|--------------------|
|              | Nitrosomonas                                             | Nitrobacter | 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 131<sup>st</sup> day, dried at 105 °C, and then analyzed by XRD and an elemental analyzer (figure not shown). The residuals were mainly  $(\text{NH}_4)_2\text{SO}_4$  and elemental sulfur, which are known byproducts of  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  and  $\text{NH}_3$  were not influenced by the sulfur deposition (Fig. 3). According to Oyarzun et al. [28], elemental sulfur was an intermediate of  $\text{H}_2\text{S}$  metabolism and was further oxidized by *Thiobacillus thioparus* that was used for  $\text{H}_2\text{S}$  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  $\text{NH}_3$  removal, although the cork surface became partially hydrophobic, the solubility of  $\text{NH}_3$  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  $\text{H}_2\text{S}$  and  $\text{NH}_3$  were highly stable.

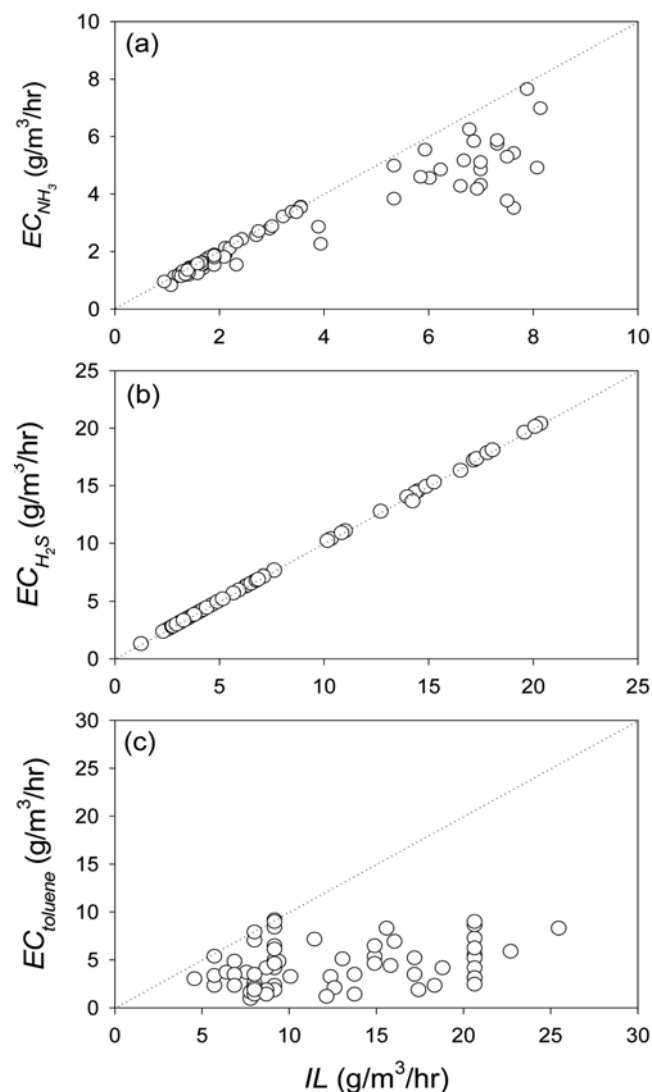
The lower removal efficiency of toluene, compared to the other two gases, may be explained by an inhibition effect caused by sulfur. Liu et al. [18] observed that at certain concentration level, the toluene removal was inhibited by presence of ethylacetate. Chung et al. [15] reported that that inhibition exists between the  $\text{NH}_3$  and  $\text{H}_2\text{S}$  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 ( $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and toluene), using three different microorganisms cultured in a single column biofilter: *Thiobacillus thioparus*, an autotroph for the oxidation of  $\text{H}_2\text{S}$ ; *Nitrosomonas* and *Nitrobacter*, autotrophs for the degradation of  $\text{NH}_3$ ; 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 inhibi-

tion 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 105<sup>th</sup> 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  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and toluene is shown in Fig. 4 and the results are summarized



**Fig. 4. Elimination capacities as a function of inlet loading. (a)  $\text{NH}_3$ , (b)  $\text{H}_2\text{S}$ , 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 <sup>3</sup> /hr) | X (%)  | EC (g/m <sup>3</sup> /hr) | EC <sub>max</sub> (g/m <sup>3</sup> /hr) |
|------------------|-------------------|--------------------|---------------------------|--------|---------------------------|------------------------------------------|
| NH <sub>3</sub>  | 50-184            | 0.25-65            | 0.95-8.15                 | 45-100 | 0.91-7.90                 | 5.5                                      |
| H <sub>2</sub> S | 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<sub>3</sub> (Fig. 4a), the elimination capacity (EC) of NH<sub>3</sub> (EC<sub>NH3</sub>) was almost linearly proportional to the inlet NH<sub>3</sub> loading and EC data were positioned near the diagonal line when the inlet loading (IL) was less than 4 g/m<sup>3</sup>/hr. Afterwards, for the inlet loadings from 4 to 8 g/m<sup>3</sup>/hr, the EC asymptotically approached a maximum elimination capacity of 5.5 g/m<sup>3</sup>/hr. The highest EC<sub>NH3</sub> was 7.6 g/m<sup>3</sup>/hr within the experimental conditions. For NH<sub>3</sub> removal, it should be noted that the experimentally measured elimination capacities by pure biological reaction might be overestimated because the solubility of NH<sub>3</sub> in water is extremely high (see Table 2).

In Fig. 4b, all data points of H<sub>2</sub>S 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<sub>2</sub>S loading into the biofilter. This also indicates that the inlet conditions for the H<sub>2</sub>S 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<sup>3</sup>/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<sub>3</sub> and H<sub>2</sub>S 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<sub>3</sub>, H<sub>2</sub>S and toluene) using cork chip as a supporting material, neither interactions nor competitive inhibitions were found among the three different microorganisms (*Thiobacillus thioautotrophicus*, *Nitrosomonas* and *Nitrobacter* 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 bio-

degradations of the ternary NH<sub>3</sub>, H<sub>2</sub>S 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<sub>3</sub> and H<sub>2</sub>S gases using a biotrickling bed. They reported that when the concentrations of the H<sub>2</sub>S and/or NH<sub>3</sub> substrates were relatively high, the substrates became inhibitory, influencing the removal efficiencies of NH<sub>3</sub> and H<sub>2</sub>S. 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<sub>2</sub>S 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<sub>2</sub>S 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<sub>2</sub>S.

## CONCLUSIONS

The biofiltration of three different gases (NH<sub>3</sub>, H<sub>2</sub>S 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<sub>3</sub>, H<sub>2</sub>S 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<sup>3</sup>/hr, 20.4 g/m<sup>3</sup>/hr or even higher, 4.5 g/m<sup>3</sup>/hr for NH<sub>3</sub> and H<sub>2</sub>S and toluene, correspondingly. The removal efficiencies of 45-100 and 96-100% have been observed for NH<sub>3</sub> and H<sub>2</sub>S, respectively. For toluene, however, the removal efficiency was very low, about 30%, because the tested inlet concentration was too high.

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