Simultaneous Biofiltration of H$_2$S, NH$_3$ and Toluene using an Inorganic/Polymeric Composite Carrier

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Abstract

Simultaneous removal of ternary gases of NH$_3$, H$_2$S and toluene in a contaminated air stream was investigated over 180 days in a biofilter. A commercially available inorganic/polymeric composite chip with a large void volume (bed porosity > 0.80) was used as a microbial support. Multiple microorganisms including Nitrosomonas and Nitrobactor for nitrogen removal, Thiobacillus thioparus (ATCC 23645) for H$_2$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) ranged from 60 - 120 seconds and the inlet feed concentration was 0.0325 g/m$^3$ - 0.0651 g/m$^3$ for NH$_3$, 0.0636 g/m$^3$ - 0.141 g/m$^3$ for H$_2$S, and 0.0918 g/m$^3$ - 0.383 g/m$^3$ for toluene, respectively. The observed removal efficiency was 2% - 98% for NH$_3$, 2% - 100% for H$_2$S, and 2% - 80% for toluene, respectively. Maximum elimination capacity was about 2.7 g/m$^3$/hr for NH$_3$, > 6.4 g/m$^3$/hr for H$_2$S and 4.0 g/m$^3$/hr for toluene, respectively. The inorganic/polymeric composite carrier required 40 - 80 days of wetting time for biofilm formation due to the hydrophobic nature of the carrier. Once the surface of the carrier was completely wetted, the microbiological activity became stable. During the long-term operation, pressure drop was negligible because the void volume of the carrier was two times higher than the conventional packing materials.

Keywords: Biofiltration, BioM$^{TM}$, Carrier, Microorganism, Odor, VOC

1. Introduction

Biofiltration technology has a 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 the 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.

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 odoriferous 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 the aqueous biofilm, contaminants partition to the aqueous or solid phases where VOCs are transformed by microorganisms into inert 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. 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. In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms.

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.

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Deodorization and detoxification of volatile organic compounds (VOCs) in the air stream are the typical application of the biofiltration.

Among the sources of air pollutions, H₂S and NH₃ are the most typical odorous compounds often encountered in industrial or residential areas. H₂S and NH₃ are toxic and can cause malodorous nuisances, while toluene is a suspected carcinogen. The lowest value of smell level for H₂S is 0.00047 ppmv. According to the toxicity report, H₂S can break down the central nervous system at the concentration level of 100 ppmv. Even more seriously, H₂S is eventually deadly toxic at the concentration above 100 ppmv. The threshold value of smell level for NH₃ is 50 ppmv in the open air. NH₃ is known to irritate eyes and throat. In Korea, the current regulation levels are 2-10 ppmv for H₂S and 50-100 ppmv for NH₃ depending on the regions and sources of the pollutants. Toluene is not yet exclusively controlled, nevertheless, toluene is controlled as a part of total VOCs or benzene derivatives, and their legally allowed level is 30 ppmv in the open air. The toluene is a Title III toxic compound of the 1990 Clean Air Act Amendment proposed by US EPA.

Recently, numbers of research works have been focused on the removal of malodorous gases. However, up to now, most of researches on the biofiltration are limited to single or binary contaminants, 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. Cox et al. investigated on the treatment of the binary toluene-H₂S containing waste air using bio-trickling beds. The H₂S 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 NH₃ and H₂S, the removal efficiency widely varied depending on the experimental conditions and the supporting media. The removal efficiency ranged from 80% to 100% for NH₃ and from 90 to 100% for H₂S. Malhautier et al. observed that elemental sulfur and sulfate were the products of H₂S oxidation and subsequently reduced the void fraction of the biotrickling bed. Kim et al. reported that microbial activity decreased due to accumulation of sulfur on the surface of packing materials during a long-term operation of packed-bed biofilter system. Chung et al. also reported that the substrates (i.e., NH₃ and H₂S) have inhibitory effect on the removal efficiency when the concentrations of the H₂S and/or NH₃ are relatively high. Liu et al. also reported on the inhibitory effect of a biofilter system treating binary gases of toluene and ethylacetate.

In this study, the simultaneous removal of ternary gases of NH₃-H₂S-toluene in a packed-bed biofilter was investigated using a new inorganic/polymeric composite carrier as a packing material. The removal efficiency and elimination capacity were carefully examined at various inlet loadings and gas concentrations during unsteady and steady state operations.

2. Materials and Methods

2.1. Microbial Fixing Carrier

A commercial inorganic/polymeric composite carrier (BioM™) was provided by Envichem Co., Ltd, Ulsan, Korea. This carrier has been used as a fluidizing carrier in an aerobic bioreactor for wastewater treatment system mainly because it has an extremely large void space (bed porosity = 0.80-0.86) compared to other conventional carriers. The composite packing material showed no pressure-drop due to the large void volume, while it kept the same levels of removal activities observed from the conventional packing materials during a long-term operation of biofiltration systems. Fig. 1 shows a photograph of the microbial fixing carrier. The physicochemical properties of the HDPE chips are summarized in Table 1. The carrier is black in color and has tubular shape with lattices. The major component of the carrier is high-density polyethylene (HDPE). Several inorganic powders (e.g., activated carbon, zeolite, clay and slag) were embedded into the HDPE in order to provide a sufficient adsorptive property toward the treating gases and habitats to microorganisms. The density of fresh carriers was adjusted to 0.97-0.98 g/cm³ by adding density-controlling materials.

![Fig. 1. A photograph of BioM™ carrier.](image)

Table 1. Physicochemical properties of the composite carrier

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Unit</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter, (d_p)</td>
<td>1.0×10⁻²</td>
<td>m</td>
<td>Controlled</td>
</tr>
<tr>
<td>Length, (L_p)</td>
<td>1.0×10⁻²</td>
<td>m</td>
<td>Controlled</td>
</tr>
<tr>
<td>Thickness, (t_p)</td>
<td>3.0×10⁻⁴</td>
<td>m</td>
<td>Controlled</td>
</tr>
<tr>
<td>Surface area, (Sₐ)</td>
<td>4.47×10⁻³</td>
<td>m²/g</td>
<td>Measured</td>
</tr>
<tr>
<td>Bed porosity, (ε_{bed})</td>
<td>0.80-0.86</td>
<td>m³/m³</td>
<td>Measured</td>
</tr>
<tr>
<td>Specific surface, (A_s)</td>
<td>1,000</td>
<td>m²/m³</td>
<td>6(1-(ε_{bed}))/(d_p)</td>
</tr>
<tr>
<td>Particle density, (ρ_p)</td>
<td>9.70×10⁻⁵</td>
<td>g/m³</td>
<td>Measured</td>
</tr>
<tr>
<td>Packing density, (ρ_{pp})</td>
<td>1.0×10⁵</td>
<td>g/m³</td>
<td>Measured</td>
</tr>
</tbody>
</table>

2.2. Biofiltration System

A schematic of the lab-scale biofiltration system used for the simultaneous removal of ternary NH₃-H₂S-toluene mixtures in the air stream was depicted in Fig. 2. The biofilter column was made of a 4-cm-id and 110-cm-long transparent Pyrex glass. The column was packed with a commercial inorganic/polymeric
Simultaneous Biofiltration of H₂S, NH₃ and Toluene using an Inorganic/Polymeric Composite Carrier

2.3. Operation of the Biofiltration System

The biofiltration system was continuously operated for 185 days at room temperature and atmospheric pressure. No pressure-drop was observed during the operation of the biofiltration system. Total volumetric air flow rate was maintained at 0.030 and 0.060 m³/hr that corresponds to 60 and 120 sec of empty bed residence time (EBRT). The feed concentration was about 0.0325 - 0.0651 g/m³ for NH₃, 0.0636 - 0.141 g/m³ for H₂S and 0.0918 - 0.383 g/m³ for toluene, respectively. The inlet loading (IL) was 1.060 - 2.970 g/m³/hr for NH₃, 1.909 - 6.364 g/m³/hr for H₂S and 3.444 - 18.828 g/m³/hr for toluene, respectively. The initial pH was adjusted to 7.0 by using NaOH and HNO₃.

2.4. Measuring of Performance on the Biofiltration System

Conventionally, the performance of the biofiltration system can be characterized by several measuring factors. They are (i) the inlet loading of the pollutant gas component (IL, g/m³/hr), (ii) the elimination capacity (EC, g/m³/hr), (iii) the empty bed residence time (EBRT, seconds) and (iv) the removal efficiency (X, %). Among the factors, IL, 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. The 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. The 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:

\[ EBRT = \frac{V_B}{q_0} \]  
\[ IL_i = \frac{C_{IN_i}^G}{EBRT} \]  
\[ EC_i = \frac{(C_{IN_i}^G - C_{OUT_i}^G)}{EBRT} \]  
\[ X_i = \frac{(C_{IN_i}^G - C_{OUT_i}^G)}{C_{IN_i}^G} = \frac{EC_i}{IL_i} \]

where \( C \) (g/m³) is the concentration in the gas phase, \( q_0 \) is the inlet volumetric gas flow rate (m³/hr) and \( V_B \) is the packed-bed volume (m³). Superscript \( G \) represents the physical properties observed in the gas phase, subscript \( i \) is the gas component (i.e., NH₃, H₂S and toluene) and subscripts \( IN \) and \( OUT \) indicate the

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>MW (g/mol)</th>
<th>Henry’ law constant, ( H_i^* ) (dimensionless)</th>
<th>Solubility (g/m³)</th>
<th>Overall mass transfer coefficient (( k_{L,a, hr^{-1}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>17.03</td>
<td>1,387</td>
<td>953,680</td>
<td>623-7,344</td>
</tr>
<tr>
<td>H₂S</td>
<td>34.08</td>
<td>2.43</td>
<td>3,340</td>
<td>15-24</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>3.96</td>
<td>14,740</td>
<td>54-72</td>
</tr>
</tbody>
</table>

Note: \(^*H_i = C_{Liquid}/C_{gas}\) and \(^*Data obtained from references 34, 41-43.\)
inlet and outlet conditions, respectively.

2.5. Analytical Methods

Both the inlet and outlet concentrations of NH₃, H₂S 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 NH₃, 1-120 ppmv for H₂S, and 1-100 ppmv for toluene. The lowest detection limit was 0.5 ppmv for NH₃, 0.2 ppmv for H₂S, and 0.5 ppmv for toluene. The residuals, pale yellow colored cakes, formed on the carrier surface and in the drain water were characterized using 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 carrier was measured by a mercury porosimeter (Microstructure Lab., Carlo Erba Strumentazione). The BET surface area was measured by nitrogen adsorption using a surface area analyzer (Micromeritics, Model ASAP 2021C).

2.6. Microorganisms

Three different types of microorganisms were independently cultivated in aqueous mineral 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 POSTECH, Pohang, Korea. The nitrifying bacteria were grown in a mineral nutrient medium prepared by dissolving 0.2357 g of Na₂HPO₄, 1.8 g of KH₂PO₄, 0.1 g of MgSO₄, 23645), was obtained from the Korean Collection for Type Cultures (KCTC). The organism was cultivated in a mineral solution containing 3.0 g of beef extract and 5.0 g of peptone. The Microorganisms (KCTC). The organism was cultivated in a mineral solution containing 3.0 g of beef extract and 5.0 g of peptone in 1.0 L of double-distilled water. A H₂S 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 Na₂HPO₄, 1.8 g of KH₂PO₄, 0.1 g of MgSO₄·7H₂O, 0.1 g of (NH₄)₂SO₄, 0.03 g of CaCl₂, 0.02 g of FeCl₃, 0.02 g of MnSO₄, and 10.0 g of Na₂S₂O₃ 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 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 5 containing 3.0 g of beef extract and 5.0 g of peptone in 1.0 L of double- distilled water at pH 6.8. The Pseudomonas putida (ATCC 23973) was cultivated in ATCC medium 1271 containing a benzoate nutrient medium containing 3.0 g of (NH₄)₂PO₄, 1.20 g of KH₂PO₄, 5.0 g of NaCl, 0.20 g of MgSO₄·7H₂O, 0.50 g of yeast extract, 3.0 g of sodium benzoate (filter- sterilized) in 1.0 L of double-distilled water. All culture media were autoclaved at 121°C for 15 min prior to use.

After cultivation, the microorganisms were mixed together immediately before inoculation. The mixed microorganisms were sprayed over the carriers in an open vessel with aeration for several hours. The inoculated carriers were then packed into the biofiltration column and acclimated for the next two weeks. The inlet loadings (IL) of NH₃, H₂S and toluene, were kept at a quarter of those used for normal operating conditions.

2.7. Microbiological Analysis

In order to count the microbial populations of Nitrosomonas, Nitrobacter, Thiobacillus thioparus and Pseudomonas putida, the colony-forming unit (CFU) was measured at the 105th day of operation by employing the conventional most probable number method (MPN) 36,37. A portion of three different biofilm-deposited on carrier samples were collected from the upper, middle and lower sampling port attached on the biofilter column. The microorganisms attached on the carrier samples were separated by vortexing for 2 min in a centrifuge tube containing a basal salt medium. The salt medium was prepared by dissolving 2.5 g of (NH₄)₂SO₄, 0.5 g of KH₂PO₄, 50 mg of MgSO₄·7H₂O, 4 mg of CaCl₂·2H₂O, and 0.1 mg of Fe-EDTA in 1.0 liter double-distilled water with pH 8.0-8.2 and autoclaving at 121°C for 15 minutes. The microorganisms were collected by centrifugation at 10,000 rpm for 20 min and then suspended in 10 mL of the salt medium. 0.5 mL aliquots of the homogenized suspension were diluted 10 times in serial test tubes containing 4.5 mL of the salt medium and shaken. The final dilutions were spread onto petri plates containing each medium with nutrient agar described previously. Subsequently the samples were incubated for 21 days at 30°C in an incubator (Jeio Tech, SI-900R). After 21 days of incubation, the agar plates were scored. The values for the microbial populations were finally obtained by referring to the MPN table.

3. Results and Discussion

3.1. Removal Efficiencies

Fig. 3 shows the results of a long-term operation of the biofiltration system for the simultaneous removal of NH₃, H₂S and toluene. The inlet air flow rate was maintained at 0.030 m³/hr from the 0th day to the 102nd day and then increased to 0.060 m³/hr from the 103rd day to the 180th day, and the corresponding EBRT was 120 sec and 60 sec, respectively. As summarized in the Table 1, the bed porosity was > 0.80 and the feed concentration of NH₃, H₂S and toluene was 0.033 - 0.065, 0.064 - 0.141, 0.092 - 0.383 g/m³, respectively. The corresponding IL for NH₃, H₂S and toluene were 1.060 - 2.970 g/m³/hr, 1.909 - 6.364 g/m³/hr and 3.444 - 18.83 g/m³/hr, respectively.

As shown in Fig. 4, in the early stage of the long-term experiments (i.e. from the start to the 5th day), all gases showed high removal efficiencies. 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. However, the adsorptive effect of the carrier was lower than those of other conventional carriers. 9,10 After the 5th day, the adsorption capacity of the biofilter column was under thermodynamic equilibrium with the pollutant gases. Since the micro-
organisms were not fully acclimated yet, biodegradation was not active and thus the removal efficiencies of all gases decreased until the 20th day.

The removal efficiency was gradually increased from the 20th day to the 40th day for H$_2$S removal. This was one of the typical characteristics of the composite carrier. Presumably, the gradual increase in the removal efficiency during this period was closely related to the increase in wetting surface area of the carrier. Physically, hydrophilic porous inorganic particles were included in the hydrophobic HDPE-based polymer surface of the carrier. Therefore, due to this physical configuration of the carrier surface, a certain period of surface wetting was required. Optical microscopic investigation revealed that during the early stage of biofilter operation, microorganism seed spots were formed near the inorganic particles that exist on the outermost surface of the carriers (Figure not shown). Once the spots were formed, the spots became enlarged and eventually formed uniform biofilm over the entire surface of the carrier. After this wetting period, the overall system response became stable for changes of the inlet conditions.

A plot of elimination capacity ($EC$) vs. inlet loading ($IL$) was shown in Fig. 5. Among the gases, H$_2$S showed a complete elimination almost over the entire range of the experimental conditions; i.e., data points lied on the diagonal line that represents 100% removal. Exceptionally, several points positioned below the diagonal line. This was because these data were measured during the early stage of and time for carrier surface wetting was not enough. In Fig. 4, the surface wetting time for H$_2$S was
about 40 days.

The removal efficiency of NH₃ increased gradually from 10% to 70% from the 20th day to 80th day, and then became stable (Fig. 4). The removal efficiency of NH₃ was kept at nearly constant value, i.e., > 70%, until the inlet air flow rate increased on the 103rd day. Hereafter, the removal efficiency was almost constant value of over 90%. The elimination capacity of NH₃ increased as inlet loading of NH₃ increased. The elimination capacity at near the inlet loading of 1.5 g/m³/hr was again the elimination capacity measured during the wetting period of time. In Fig. 4, the removal efficiency of toluene gradually increased from 10% to 40% from the 20th day to the 80th day, and became constant. About 80 days of wetting time was observed for toluene.

The surface wetting time for the carrier surface to be fully covered by biofilm was 80 days for NH₃ and toluene which was longer than that for H₂S (40 days). In order to understand the difference in the surface wetting time for the carrier, both the residuals of drain water from the bottom reservoir and the deposited pale yellow colored cake on the carrier surface were collected on the 30th day and 131th day and analyzed by XRD and the elemental analyzer. The results revealed that the deposited pale yellow cake on the carrier surface was mainly elemental sulfur, while the residual in the drain water was ammonium sulfate (data not shown). Both the elemental sulfur and the ammonium sulfate ((NH₄)₂SO₄) were known as the byproducts of H₂S oxidation. According to these results, it appeared that the carrier surface was quickly deteriorated by the elemental sulfur even at the very early stage of operation. As shown in the Fig. 5, microorganisms for the H₂S removal were more active showing higher elimination capacity than the others and thus metabolized H₂S rapidly producing hydrophobic elemental sulfur. Wetting of the carrier surface for biofilm formation was hindered by the elemental sulfur deposition, influencing the removal efficiencies of NH₃ and toluene. However, the elemental sulfur deposition on the carrier surface did not affect H₂S removal. According to Oyarzun et al., elemental sulfur is an intermediate of H₂S metabolism and is one of substrates being further oxidized by Thiobacillus thioparus, that was used for H₂S removal in this study. Generally, Thiobacilli species can withstand and survive when exposed to elemental sulfur and/or sulfur-containing environments. This was the main reason why the surface wetting time for H₂S removal was shorter than those for NH₃ and toluene removals. As shown in Fig. 4, once the carrier surface was fully covered by biofilm, the H₂S removal efficiency was highly stable.

On the 102nd day, the total inlet air flow rate increased from 0.03 m³/hr to 0.06 m³/hr. Upon this change, the removal efficiency of NH₃ increased but the removal efficiency of toluene decreased, while the removal efficiency of H₂S was nearly 100%. Comparison of Fig. 4 and Fig. 5 shows that the inlet loading for the NH₃ removal reached to the maximum, that for H₂S removal was still far below the maximum, while that for the toluene removal was already far beyond the maximum. Besides, toluene removal efficiency was the lowest among the three gases. In part, this is attributed to the influence of elemental sulfur and ammonium sulfate deposition on the carrier surface. Liu et al. observed that, at a certain concentration level, the removal of toluene was inhibited by presence of ethylacetate. Chung et al. reported that a competitive inhibition exists between the NH₃ and H₂S when the substrate concentrations are relatively high. They used the Andrews-Haldane biokinetic model account for the inhibition effect of binary substrates in the biofiltration system. In this work, we intended to treat a mixture of three substrates (NH₃, H₂S and toluene) using a mixture of microorganisms cultured in one single column: Thiobasillus thioparus, an autotroph, for the oxidation of H₂S; Nitrosomonas and Nitrobacter, autotrophs, for the degradation of NH₃; and Pseudomonas putida, a heterotroph for the oxidation of toluene. Then, competitive inhibition among the three substrates may exist in this system. Therefore, we performed a biokinetic study using the Andrews-Haldane biokinetic model. The inhibition effect between the ternary substrates was analyzed by the Andrews-Haldane biokinetic model. The model is given as:

$$r_i = \frac{\mu_{m,i} C_i}{K_{S,i} + C_i + \frac{C_j}{K_{I,i}}}$$

where $r_i$ (g/m³/hr) = the apparent removal rate of pollutant component, $i$, $\mu_{m,i}$ (g/m³/hr) = the maximum removal rate of a pollutant component, $i$, $C_i$ (g/m³) = the concentration of component, $i$, $K_{S,i}$ (g/m³) = the half saturation coefficient for removal of component, $i$, and $K_{I,i}$ (g/m³) = the inhibition coefficient for component, $i$.

Through the kinetic study, however, we were not able to find any evidence on the competitive inhibition effect on toluene removal. 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. The Andrews-Haldane biokinetic model equation can be reduced to the pseudo-first-order reaction in the low substrate concentration region (i.e., $K_{S,i} \gg C_i$). 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. The trends of the ECs (Fig. 5) indicate that neither reaction nor inhibition is limiting in the biofiltration system within the tested conditions. In addition, our results are consistent with those of others regarding the H₂S removal kinetic study that uses the Andrews-Haldane biokinetic model. According to their observations, 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 study (H₂S concentration = 0.06 g/m³ up to 0.14 g/m³). The EC value increased asymptotically as the inlet H₂S concentration increased.

On the 105th day, the microbial populations were measured by the conventional MPN method. The microbial populations in the bottom layer were two to three orders of magnitude lower than those in the upper layer.
higher than those in the middle and upper layers. This is simply because more substrates are available in the bottom layer of the biofilter.

3.2. Effects of Inlet Feed Condition on the Elimination Capacity

The elimination capacity of the biofilter as a function of the inlet loading for NH3, H2S and toluene was shown in Fig. 5 and the results were summarized in the Table 4. Relatively lower elimination capacities were observed when the inlet loadings were low. This was because the data were obtained during the 40th-80th days and thus surface wetting of the carrier was not enough. The elimination capacity of NH3 was almost linearly proportional to the inlet NH3 loading in the range of 1 g/m³/hr - 3 g/m³/hr. The maximum value of the elimination capacity for the NH3 removal was 2.7 g/m³/hr within the experimental conditions. For the NH3 removal, 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). Only except the data obtained at earlier surface wetting period, all the data points for the H2S elimination capacity were positioned on the diagonal line (Fig. 5(b)). This confirms that the removal efficiency is nearly 100% within the entire experimental conditions regardless of the amount of H2S gas introduced into the biofilter. Therefore, the inlet loading of the H2S removal was still far below the maximum elimination capacity (>6.4 g/m³/hr). For toluene removal, microbial activity was relatively poor, and most of the data for the elimination capacities were positioned below the diagonal line. The maximum value of the elimination capacity for the toluene was about 5.0 g/m³/hr at the loading of >10 g/m³/hr. The relatively poor microbial activity for the toluene removal is explained by (i) the inlet loading was too high for the biofiltration system that already accumulations of biofilm and/or the packing materials are broken down. If the biofilter column packed with this inorganic/polymeric composite carrier, the recovery process or replacement procedure is not necessary. This was the major advantage of using this commercial microbial fixing carrier. This work demonstrated that the inorganic/polymeric composite carrier was feasible for the simultaneous removal of multiple gases in a biofilter. The new composite carrier with a very large void volume may overcome the inherent problems of the conventional packing materials showing gradual pressure drop during

### Table 3. Microbial populations in the biofilm fixed on the carrier

<table>
<thead>
<tr>
<th>Logarithmic counts for microbial populations, log (CFU/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Section</td>
</tr>
<tr>
<td>Upper</td>
</tr>
<tr>
<td>Middle</td>
</tr>
<tr>
<td>Lower</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Component</th>
<th>C100 (g/m³)</th>
<th>IL (g/m³/hr)</th>
<th>X (%)</th>
<th>EC (g/m³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>0.0325-0.0651</td>
<td>1.060-2.970</td>
<td>2-98</td>
<td>0.064-2.715</td>
</tr>
<tr>
<td>H2S</td>
<td>0.0636-0.141</td>
<td>1.909-6.364</td>
<td>2-100</td>
<td>0.297-6.364</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0918-0.383</td>
<td>3.444-18.83</td>
<td>2-80</td>
<td>0.115-6.888</td>
</tr>
</tbody>
</table>
the long-term operations. Only a minor problem of this new composite carrier is that it requires relatively a long period of time for wetting of the carrier surface.

4. Conclusions

In the evaluation of feasibility of a new inorganic/polymeric composite carrier for the simultaneous removal of NH$_3$, H$_2$S and toluene, no significant pressure-drop was observed; meanwhile a relatively long time for surface wetting was required. Pressure-drop and gradual compaction by gravity or air stream were prevented by the inherent physical nature of the new inorganic/polymeric composite carrier during the long-term operation of the biofiltration system. Interruptions in a biofilter operation often caused by the pressure-drop can be improved by introducing the composite carrier. Once the surface of the carrier was fully wetted, the system showed the same level of removal activity as the other conventional carriers. In addition, there was no competitive inhibition among the different microorganisms. Therefore, the new inorganic/polymeric composite carrier is feasible in the development of the single-stage biofiltration system for the simultaneous removal on the trace amount of ternary NH$_3$, H$_2$S and toluene. In design and stability aspects, this system can be operated up to inlet loading of 2.7 g/m$^3$/hr for NH$_3$, 6.4 g/m$^3$/hr or even higher for H$_2$S and 5.0 g/m$^3$/hr for toluene, respectively. The removal efficiencies of above 98% for NH$_3$ and nearly 100% for H$_2$S were achieved, however, the toluene removal efficiency was relatively low (about 40%), because the tested inlet concentration was too high.

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References

Simultaneous Biofiltration of H₂S, NH₃ and Toluene using an Inorganic/Polymeric Composite Carrier


