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Biokinetics on simultaneous biofiltration of H_2S, NH_3 and toluene in waste air

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Abstract–In order to investigate inhibitory effects in the biofiltration system during simultaneous removal of ternary mixtures of NH_3-H_2S-toluene contaminants in air, a system modeling has been performed encompassing an inhibition biokinetic expression. Experimental data for removing the three contaminant gases were collected during a long term operation of two biofiltration systems that utilized mixtures of microorganisms fixed on zeocarbon and cork as microbial fixing carriers. Results of regression analyses of experimental data using suggested kinetic models reveal that there are no particular evidences or clues of interactions or inhibitions among microorganisms, and the three reactions are taken place independently within a finite area of biofilm that have been developed on the surface of packing materials.

Key words: Biofiltration, Deodorization, Biokinetics, Inhibition, Biofilm Process

INTRODUCTION

Biofiltration has been considered as the most suitable alternative process for high temperature incineration, i.e. thermal or catalytic, for treating low-level airborne pollutants. Typical application areas are deodorization and detoxification of the contaminated air. It has many fascinating advantages; avoiding emissions of secondary pollutants, low cost for maintenance or operation, and reduced running cost and so on. Nowadays, numbers of malodorous or volatile organic compounds (VOCs) that are emitted from various industrial or residential sources have been treated by means of the biofiltration system in commercial scale [Lim, 2005; Lim and Park, 2004; Acuna et al., 2002; Kim et al., 2000; Park et al., 1993; Wani et al., 1998; Zilli et al., 2003].

Generally, major sources of smell encountered in industrial or residential areas are H_2S and NH_3 [Acuna et al., 2002; Kim et al., 2000; Park et al., 1993; Wani et al., 1998; Zilli et al., 2003]. H_2S and NH_3 are colorless, corrosive, toxic, and malodorous nuisances meanwhile toluene has been classified as a carcinogen and explosive. It is also noted that toluene is the Title III toxic compound of the 1990 Clean Air Act Amendment proposed by US Environmental Protection Agency [Zilli et al., 2003]. The lowest value of smelt level for H_2S is 0.00047 ppmv [Oyarzun et al., 2003]. It is also well known that H_2S is highly dangerous chemicals for breakdown of the central nervous system near concentration level of 100 ppmv. It can be a deadly toxic over the 100 ppmv [Shojaosadati and Elyasi, 1999]. The threshold value of smelt level for NH_3 is 50 ppmv in the open air [Busca and Pistarino, 2003]. In addition, NH_3 irritates eyes and throat.

Traditionally, fundamental research works in these areas of biofiltration technologies have been dealt with the removal of single or binary gas, which seems impractical for real industrial applications since most of waste gases contain multiple contaminants including malodorous sulfur compounds, nitrogen compounds as well as VOCs, and rarely include single or binary contaminants [Delhomanie et al., 2003; Elias et al., 2002; Kim et al., 2002a; Shinabe et al., 2002; Yoon et al., 2002; Hirai et al., 2001; Cho et al., 2000]. In this point of view, it is obvious that there is a need of developing biofiltration systems on the removals for multiple pollutants in contaminated waste air, and of understanding interactions among the different gases or microorganisms involved in the biofiltration systems for practical purpose. Recently, Cox and Deshusses [2002] have reported results on the co-treatment of H_2S and toluene mixture using a biotrickling filter. According to him, there was neither competitive nor cross inhibitions. An inhibitory behavior has been observed by Chung et al. [2000, 2001] in biofiltration system for the H_2S and NH_3 removal in the range of relatively high gas concentrations. The biofiltration system for the binary H_2S and NH_3 removal has also been studied by Malhautier et al. [2003]. He assumes that there is a negative effect on activity of nitrifying bacteria when a high amount of H_2S involved in the system. Similar results for the H_2S and NH_3 removal have been reported by Kim et al. [2002b]. According to him, over H_2S concentration of 200 ppmv, the activity of nitrifying bacteria is hindered by the presence of H_2S. Inhibition between ethyl acetate and toluene has been studied by Liu et al. [2002]. They reported that the elimination activity of toluene is inhibited by the presence of ethyl acetate.

Expanding to the previous investigations on the removal of the binary gas systems, we have performed a mathematical modeling in order to describe the biofiltration system for the simultaneous removal on ternary NH_3-H_2S-toluene contaminants in waste air using an inhibition biokinetic expression. Apparent biokinetic parameters have been obtained on a packed bed biofiltration system utilizing various microbial fixing carriers with a mixture of microorganisms fixed on the carrier surface in order to understand interactions and/or influences among the different gas components and/or microorganisms, to provide a guideline for the system design, and to assess feasibility of removing the multiple contaminants.

MATERIALS AND METHODS

1. Modeling of the Biofiltration System Utilizing Inhibition Biokinetics

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The flow of bulk waste air inside the packed bed biofiltration column was assumed to be in the plug-flow regime. When the biofiltration system reached steady state, the system can be described by the following equations [Chung et al., 2001]:

$$\frac{dF_i^G}{dV^{BF}} = -R_i^{BF} \tag{1}$$

where, F_i^G (g/hr) is the mass flow rate of gas components in the waste air stream, V^{BF} (m^3) is the volume of biofilm and R_i^{BF} ($g/m^3/hr$) is the removal rate of the gas components in the biofilm. The superscripts G, BF indicate gas-phase, biofilm-phase, respectively. The subscript i mean NH_3, H_2S or toluene.

If the thickness of the biofilm is very thin, volume of the biofilm can be estimated by the following approximation:

$$V^{BF} \cong \eta(A_S \cdot \delta)(1-\varepsilon)(A_{CS} \cdot z) \tag{2}$$

where, A_S (m^2/m^3) is the wetted area of microbial fixing carriers, η (dimensionless) is the fraction of active biofilm, δ (m) is the thickness of the biofilm, ε (dimensionless) is the bed porosity of the biofilter column, A_{CS} (m^2) is the cross-sectional area of the biofilter column, z (m) is the length of the biofilter column. In this work, we were not able to measure effective thickness of the biofilm, and η is assumed to be unity. Some errors suppose to be involved due to this assumption.

Since it was not able to directly measure concentrations of the gas components in the biofilm-phase, we measured the concentrations in the gas-phase and estimated the concentrations in the biofilm-phase utilizing Henry's law [NIST, 2005] as follows:

$$H_i \equiv \frac{C_i^{BF}}{C_i^G} \tag{3}$$

where, C (g/m^3) and H (dimensionless) are the concentration of the gas components and Henry's law constant, respectively. Values of the Henry's law constants [NIST, 2005] are summarized in Table 1.

Through combining Eq. (1), Eq. (2) and Eq. (3), and subsequently setting $F_i^G = q \cdot C_i^G$, Eq. (1) can be transferred in Eq. (4):

$$\frac{dC_i^{BF}}{dz} = -(R_i^{BF})\frac{H_i \cdot (A_S \cdot \delta) \cdot (1-\varepsilon) \cdot A_{CS}}{q} \tag{4}$$

where q (m^3/hr) is the volumetric flow rate of waste air introduced into the biofilter column.

When the entire surface of the microbial fixing carrier is colonized by microorganisms after the column is being fully acclimated, presumably, in the macroscopic point of view, microorganism populations are linearly proportional to the surface area of the biofilm. Thus the biofilm area is nearly the same as that of overall wetted surface area of the microbial fixing carriers, and is assumed to be constant. It is also noted that, in the biofilter column, usually the effective thickness of biofilm is as difficult to measure as determine the depth of gas diffusion through the biofilm-phase. During the operation of the biofiltration system, the change of effective volume or effective area of the biofilm seems to be negligible. As a result, hereby, we are assuming that there is no significant change of the microorganism populations after the biofilm is being fully developed. Upon this assumption, biokinetic expressions, such as Monod for no inhibition case, or Andrews-Haldane for competitive inhibition case, can possibly be simplified [Chung et al., 2001; Edwards, 1970; Lallai and Mura, 1989; Hill and Robinson, 1975]. If the apparent removal rates for each component are inhibited, meanwhile are not influenced by the amount of oxygen, e.g. using a large excess of air, this system can be interpreted by using simplified Andrews-Haldane biokinetic expression as follows:

Table 1. Henry's law constant for gas components in pure water at 298.15 K and 1 atm

Component	Molecular weight	Henry' law constant, H_i (dimensionless)
NH_3	17.03	1,387
H_2S	34.08	2.43
toluene	92.14	3.96

$$R_i^{BF} = \frac{\mu_{M,i}^{BF} \cdot C_i^{BF}}{K_{S,i}^{BF} + C_i^{BF} + \dfrac{(C_i^{BF})^2}{K_{I,i}^{BF}}} \tag{5}$$

or

$$\frac{1}{R_i^{BF}} = \left[\frac{K_{S,i}^{BF}}{\mu_{M,i}^{BF}}\right]\left(\frac{1}{C_i^{BF}}\right) + \frac{1}{\mu_{M,i}^{BF}} + \left[\frac{1}{K_{I,i}^{BF} \cdot \mu_{M,i}^{BF}}\right](C_i^{BF}) \tag{6}$$

where $\mu_{M,i}^{BF}$ ($g/m^3/hr$) is the maximum removal rate of a pollutant component, i, $K_{S,i}^{BF}$ (g/m^3) is the half saturation coefficient for removal of i, and $K_{I,i}^{BF}$ (g/m^3) is the inhibition coefficient of i in the biofilm. When inhibition in the system is not significant, the third term in the denominator of Eq. (5) becomes zero. In such circumstance, Eq. (5) can be reduced into Michelis-Menten or Monod biokinetic equation [Chung et al., 2001; Edwards, 1970; Lallai and Mura, 1989; Hill and Robinson, 1975].

Adding Eq. (6) into Eq. (4) and integrating the resulting equation over the effective packing height, L (m), under the condition of $C_i^{BF} = C_{IN,i}^{BF}$ at z=0, and $C_i^{BF} = C_{OUT,i}^{BF}$ at z=L as Eq. (7), successively dividing all terms in the both sides of Eq. (7) by $C_{OUT,i}^G - C_{IN,i}^G$, finally Eq. (8) or more simplified Eq. (9) can be obtained:

$$\int_{C_{IN,i}^{BF}}^{C_{OUT,i}^{BF}} \left\{\left[\frac{K_{S,i}^{BF}}{\mu_{M,i}^{BF}}\right]\left(\frac{1}{C_i^{BF}}\right) + \frac{1}{\mu_{M,i}^{BF}} + \left[\frac{1}{K_{I,i}^{BF} \cdot \mu_{M,i}^{BF}}\right](C_i^{BF})\right\} dC_i^{BF} = -\int_0^L \left[\frac{H_i \cdot (A_S \cdot \delta) \cdot (1-\varepsilon) \cdot A_{CS}}{q}\right] dz \tag{7}$$

$$\left[\frac{K_{S,i}^{BF}}{H_i}\right]\left[\frac{1}{\mu_{M,i}^{BF}}\right]\left(\frac{1}{\langle C_{Ln,i}^G \rangle}\right) + \frac{1}{\mu_{M,i}^{BF}} + \left[\frac{1}{2}\right]\left[\frac{H_i}{K_{I,i}^{BF}}\right]\left[\frac{1}{\mu_{M,i}^{BF}}\right](C_{IN,i}^G + C_{OUT,i}^G) = \frac{(A_s \cdot \delta) \cdot (1-\varepsilon)}{(C_{IN,i}^G - C_{OUT,i}^G)}\left[\frac{V}{q}\right] \tag{8}$$

or

$$\frac{A_S \cdot (1-\varepsilon)}{EC_i^G} = \left[\frac{\overline{K}_{S,i}^{BF}}{\delta \cdot H_i}\right]\left[\frac{1}{\overline{\mu}_{M,i}^{BF}}\right]\left(\frac{1}{\langle C_{Ln,i}^G \rangle}\right) + \frac{1}{\overline{\mu}_{M,i}^{BF}} + \left[\frac{1}{2}\right]\left[\frac{\delta \cdot H_i}{\overline{K}_{I,i}^{BF}}\right]\left[\frac{1}{\overline{\mu}_{M,i}^{BF}}\right](C_{IN,i}^G + C_{OUT,i}^G) \tag{9}$$

with

$$\langle C_{Ln,i}^G \rangle \equiv \frac{(C_{OUT,i}^G - C_{IN,i}^G)}{\mathrm{Ln}(C_{OUT,i}^G / C_{IN,i}^G)} \tag{10}$$

$$EC_i^G \equiv \frac{q\cdot(C_{i,IN}^G - C_{i,OUT}^G)}{V} \tag{11}$$

$$\overline{\mu}_{M,i}^{BF} \equiv (\delta\cdot\mu_{M,i}^{BF}) \tag{12}$$

$$\overline{K}_{S,i}^{BF} \equiv (\delta\cdot K_{S,i}^{BF}) \tag{13}$$

$$\overline{K}_{I,i}^{BF} \equiv (\delta\cdot K_{I,i}^{BF}) \tag{14}$$

where EC_i^G is elimination capacity observed in the gas-phase. $\overline{\mu}_{M,i}^{BF}$ ($g/m^2/hr$), $\overline{K}_{S,i}^{BF}$ (g/m^2), $\overline{K}_{I,i}^{BF}$ (g/m^2) are the biofilm area based maximum apparent removal rate, the apparent half saturation coefficient, the apparent inhibition coefficient, correspondingly.

Chung et al. [2001] has pointed out if the inlet concentrations of the gas components in the waste air stream are relatively low in which the concentrations are near the half saturation coefficient and the system does not show inhibitory behavior, Eq. (9) becomes Eq. (15). This equation also can be directly derived using Michaelis-Menten or Monod biokinetic expression. In the case of the inlet concentration is relatively high and the inhibition level is not negligible, e.g. the removal rate stays constant or decreases upon the concentration increases, the Eq. (9) can be reduced into Eq. (16):

$$\frac{A_S\cdot(1-\varepsilon)}{EC_i^G} = \left[\frac{\overline{K}_{S,i}^{BF}}{\delta\cdot H_i}\right]\left[\frac{1}{\overline{\mu}_{M,i}^{BF}}\right]\left(\frac{1}{\langle C_{Ln,i}^G\rangle}\right) + \frac{1}{\overline{\mu}_{M,i}^{BF}} \tag{15}$$

$$\frac{A_S\cdot(1-\varepsilon)}{EC_i^G} = \left[\frac{1}{2}\right]\left[\frac{\delta\cdot H_i}{\overline{K}_{I,i}^{BF}}\right]\left[\frac{1}{\overline{\mu}_{M,i}^{BF}}\right](C_{IN,i}^G + C_{OUT,i}^G) + \frac{1}{\overline{\mu}_{M,i}^{BF}} \tag{16}$$

Where the range of the concentration is relatively high but the system does not show inhibitory behavior, the maximum apparent removal rate in the biofilm-phase can be estimated by the maximum elimination capacity, vice versa, as in the Eq. (17):

$$\frac{A_S\cdot(1-\varepsilon)}{EC_{M,i}^G} = \frac{1}{\overline{\mu}_{M,i}^{BF}} \tag{17}$$

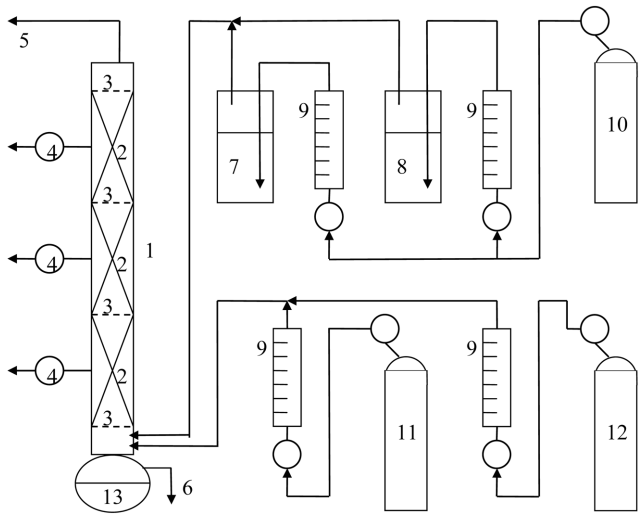

Fig. 1. A schematic represent of a biofiltration system.

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. Rota-meter
10. Air
11. H_2S gas
12. HN_3 gas
13. Water reservoir

2. Conditions for the Biofiltration Systems

Two identical bench-scale biofiltration systems were installed in order to measure the biokinetic parameters. Fig. 1 shows one of the experimental settings for the bench-scale biofiltration system used for the simultaneous removal of ternary NH_3-H_2S-toluene mixtures in air stream. The two biofilter columns were made of transparent Pyrex glass, and had an inside diameter of 0.04 m and a total length of 1.10 m each. One column was packed with a commercial zeocarbon granule (ZC-100, Zeobuilder Co., Republic of Korea), and another column was packed with cork chips as microbial fixing carriers. Particle size, d_p, specific wetted surface area, A_s and bed porosity, ε, of the zeocarbon granules are 1.18×10^{-3} m, 2,500 m^2/m^3 and 0.66 m^3/m^3, correspondingly, while for the cork chips 3.30×10^{-3} m, 900 m^2/m^3 and 0.53 m^3/m^3, correspondingly. The actual packing length of the microbial fixing carriers was 0.80 m each, and was evenly divided into three sections. Between sections inserted was a spacer (5 cm long) to prevent gradual compacting by gravity, to improve the distribution of air stream, and to support microbial fixing carrier. The spacer was made of a mesh screen of stainless steel. The total bed volume of the microbial fixing carrier packing was kept at 1.0 liter. A sampling port was installed at the middle point of the each section in order to allow sampling of the microbial supporting materials and measuring the concentrations of each pollutant gas. At the bottom of the biofilter column, retained was a 100 cc water reservoir. Any water collected and remaining excess was continuously drained out of the reservoir. Some portion of the feed air was passed through a water saturator containing double distilled water for moisturizing, and some portion through a toluene (J. T. Baker, 99.7%) saturator, and then the two streams were mixed together before being introduced into the bottom of the biofilter columns. The relative humidity was maintained over 95%. 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 biofiltration columns from the gas cylinders. The volumetric flow rates of all gas streams herein were controlled by means of pressure regulators and rotameters. Finally, the treated clean air was released from the top of the biofilter column.

The biofiltration systems were continuously operated for 215 days at room temperature and atmospheric pressure. During the course of the biofiltration experiments, the microbial fixing carriers were washed using a nutrient solution from time to time as soon as the column showed a pressure drop, which was caused by the accumulation of the elemental sulfur and/or ammonium sulphate across the biofilter column. Total volumetric airflow rates were fixed 0.030, 0.060 and 0.090 m^3/hr (corresponding empty bed residence time, *EBRT*, from 40, 60 and 120 sec). The ranges of the feed concentrations in the zeocarbon packed column for NH_3, H_2S and toluene gases were about 0.020-0.11 g/m^3, 0.050-0.23 g/m^3 and 0.15-0.21 g/m^3, correspondingly and the ranges of the feed concentrations in the cork packed column for NH_3, H_2S and toluene gases were about 0.035-0.13 g/m^3, 0.042-0.23 g/m^3 and 0.011-0.497 g/m^3, correspondingly. The pH was maintained 7.0 controlled by NaOH and HNO_3.

3. Characterizations

Both the inlet and outlet concentrations for NH_3, H_2S and tolu-

ene gases were measured by using gas detection tubes (Model 3La, 4L and 122L, respectively, Gastec Co., Japan). Thickness of the microbial fixing carriers was measured using an optical video microscope system (Model Camscope^{TM}: ICS-305B, Baestech Industrial Vision System Co., Republic of Korea). The residuals, these were pale yellow colored cakes, accumulated on the surface of the microbial fixing carriers and in the drain water were characterized using XRD (MAC Science Co., Model M18XHF, CuK_α) and elemental analysis (LECO Co., Model CHNS 932). The bed porosity of the microbial fixing carriers was measured by water. The BET surface area was measured by nitrogen adsorption using Micromeritics (model ASAP 2021C).

4. Microorganisms

Three different kinds of microorganisms were independently prepared using different mineral culture mediums. Following the cultivation, these were then mixed together just before performing the inoculation. The mixed microorganism consortiums were sprayed over the microbial fixing carriers in an open vessel with aeration for several hours. The inoculated microbial fixing carriers were then packed into the biofiltration columns. Subsequently, the biofilter columns were acclimated for the next two weeks by circulating the microorganism mixture. During the acclimation period of time, the amount of NH_3, H_2S and toluene introduced into the biofilter columns were kept at quarter of those used at the normal operating conditions.

Followings were the prescriptions for the cultivations of the different kinds of microorganisms. All of the microorganisms were cultured and enriched in solutions containing aqueous minerals at 30 °C using a shaking incubator (Jeio Tech, SI-900R) vibrating at 100 rpm. First, the nitrifying bacteria, presumably *Nitrosomonas* and *Nitrobactor*, were isolated from the activated sludge in a sewage water treatment facility located in the Pohang University of Science and Technology, Pohang, Republic of Korea. It was incubated in a mineral nutrient medium containing 0.2357 g $(NH_4)_2SO_4$, 0.080 g KH_2PO_4, 0.020 g $MgSO_4$ and 0.0085 g $Fe_2(SO_4)_2 \cdot H_2O$ dissolved in 1.0 liter double distilled water. Second, *Thiobacillus thioparus* (ATCC 23645, KCTC 2753), a H_2S oxidation bacterium, was obtained from the Korean Collection for Type Cultures (KCTC). It was cultivated in a mineral medium dissolved in 1.0 liter double distilled water: 1.2 g Na_2HPO_4, 1.8 g KH_2PO_4, 0.1 g $MgSO_4 \cdot 7H_2O$, 0.1 g $(NH_4)_2SO_4$, 0.03 g $CaCl_2$, 0.02 g $FeCl_3$, 0.02 g $MnSO_4$, 10.0 g $Na_2S_2O_3$. Finally, for the toluene elimination, *Psedomonas aeruginosa* (ATCC 15692, KCTC 1637), *Psedomonas putida* (ATCC 17484, KCTC 1641) and *Psedomonas putida* (ATCC 23973, KCTC 1643) were purchased from the Korean Collection for Type Cultures (KCTC). The *Psedomonas aeruginosa* was grown in KCTC 105, i.e., nutrient agar with 0.5% NaCl having composition of 3.0 g beef extract and 5.0 g peptone. The *Psedomonas putida* (ATCC 17484, KCTC 1641) was incubated in KCTC 1, i.e. nutrient agar at pH 6.8 having composition of 3.0 g beef extract, 5.0 g peptone and 15.0 g agar in 1.0 liter distilled water. The *Psedomonas putida* (ATCC 23973, KCTC 1643) was cultivated in KCTC 106, i.e. a benzoate nutrient medium having composition of 3.0 g $(NH_4)_2PO_4$, 1.20 g KH_2PO_4, 5.0 g NaCl, 0.20 g $MgSO_4 \cdot 7H_2O$, 0.50 g yeast extract, 3.0 g sodium benzoate (filter-sterilized) and 20 g agar noble (Difco 0142) in 1.0 liter double distilled water.

RESULTS AND DISCUSSION

In order to obtain system parameters and to understand interactions among the gas components or microorganisms, linear regressions were performed using experimentally measured values for the NH_3 and toluene gas components on both zeocarbon and cork microbial fixing carriers in gas-phase of the biofiltration system. In order to see the influence of H_2S on the other two gas components, the concentration for H_2S was maintained as high as possible if the systems show constant 100% removal efficiency for H_2S. For the other two components of ammonia and toluene, experimental data were plotted using Eq. (15) and (16). Using Eq. (15), measured val-

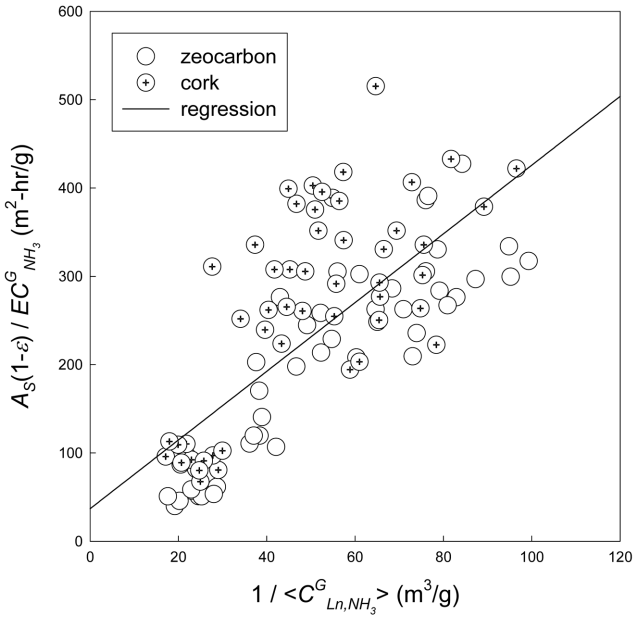

Fig. 2. A plot of $A_S(1-\varepsilon)/EC^G_{NH_3}$ against $1/\langle C^G_{Ln,NH_3}\rangle$ for the NH_3 removal in the biofiltration system using Eq. (15).

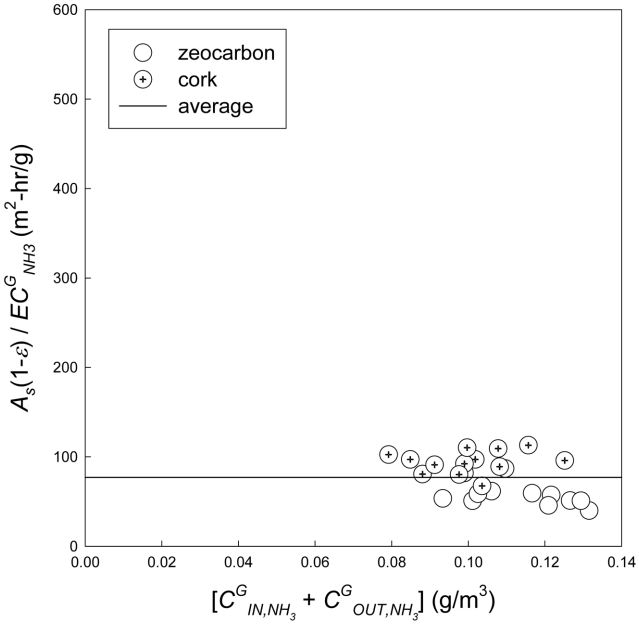

Fig. 3. A plot of $A_S(1-\varepsilon)/EC^G_{NH_3}$ against $[C^G_{IN,NH_3}+C^G_{OUT,NH_3}]$ for the NH_3 removal in the biofiltration system using Eq. (17).

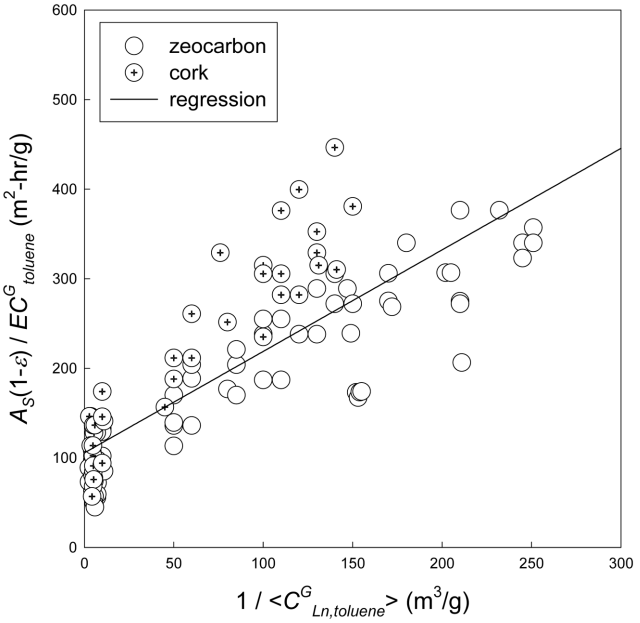

Fig. 4. A plot of $A_S(1-\varepsilon)/EC^G_{toluene}$ against $1/\langle C^G_{Ln,toluene}\rangle$ for the toluene removal in the biofiltration system using Eq. (15).

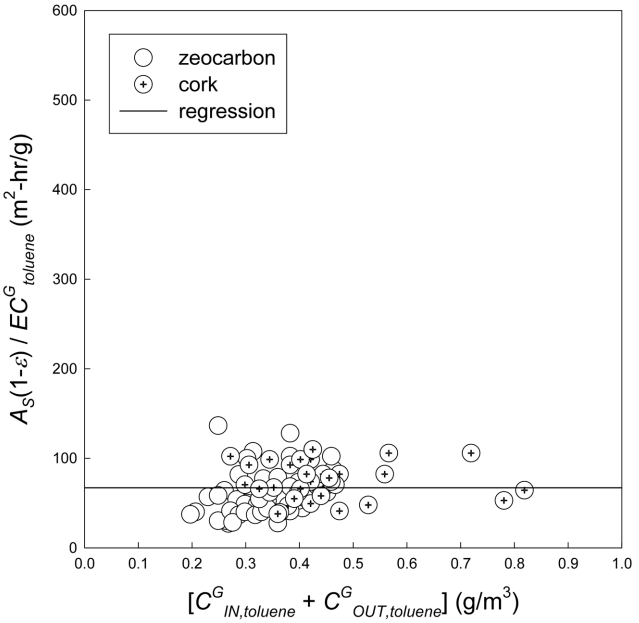

Fig. 5. A plot of $A_S(1-\varepsilon)/EC^G_{toluene}$ against $[C^G_{IN,toluene}+C^G_{OUT,toluene}]$ for the toluene removal in the biofiltration system using Eq. (17).

ues of the area divided by elimination capacity, $A_S(1-\varepsilon)/EC^G_{M,i}$ (m^2-hr/g), were plotted against reciprocal values of the logarithmic average concentrations, $1/\langle C^G_{Ln,i}\rangle$ (m^3/g), to obtain values for apparent half saturation coefficient, $\overline{K}^{BF}_{S,i}/\delta$, and the maximum apparent removal rate, $\overline{\mu}^{BF}_{M,i}$. In the range of conditions where inhibitory behavior assumes to be taken-place, the values of $A_S(1-\varepsilon)/EC^G_{M,i}$ were plotted against those of the sum of the inlet and the outlet concentrations, $[C^G_{IN,i}+C^G_{OUT,i}]$ (g/m^3) in Eq. (13). The measured values for the thickness of the biofilm were somewhere around 1×10^{-4} m. In Fig. 2, Fig. 3, Fig. 4 and Fig. 5, the circles indicate experimentally measured values on zeocarbon granules, while the x-hair circles indicate the values measured on cork chips as microbial fixing carriers. The solid lines represent the estimated values using the biokinetic regression parameters.

Experimental results on the NH_3 removal have been presented on Fig. 2 and Fig. 3 using Eq. (15), Eq. (16), respectively. It can be seen in Fig. 3 that, for the values of $[C^G_{IN,i}+C^G_{OUT,i}]$ higher than 0.08 g/m^3 (which corresponds to the reciprocal of the logarithmic average concentrations around 20 m^3/g in Fig. 2, the values of $A_S(1-\varepsilon)/EC^G_{M,i}$ remain more or less constant, which is presumably correspondent to the value of the maximum apparent removal rate. For the values of $[C^G_{IN,i}+C^G_{OUT,i}]$ below the 0.08 g/m^3 (where the systems were in the 1st order regime), the value of $A_S(1-\varepsilon)/EC^G_{M,i}$ was decreased with decreased value of $[C^G_{IN,i}+C^G_{OUT,i}]$ (data are not shown herein). Hence, it is concluded that there is no measurable level of inhibitory behavior between H_2S and NH_3 oxidation in the present range of experiment conditions even though the H_2S oxidation products, i.e. elemental sulfur and/or ammonium sulphate, have been accumulated on the surface of packing materials that were observed by means of XRD and elemental analysis. This result was obviously different from what observed by others [Chung et al., 2000, 2001; Kim et al., 2002a; Malhautier et al., 2003]. This difference was tentatively due by the different ranges of experimental conditions, system types, or even microorganism mixtures.

As summarized in Table 2, the obtained values of the regression parameters on the NH_3 removal using Eq. (15) for the apparent half saturation coefficient, $\overline{K}^{BF}_{S,NH_3}/\delta$, and the maximum apparent removal rate, $\overline{\mu}^{BF}_{M,NH_3}$ in the biofilm-phase were 146±13 g/m^3, 0.0271±0.0146 g/m^2/hr, respectively, and those calculated in the gas-phase utilizing

Table 2. Biokinetic parameters for simultaneous removals on ternary NH_3, H_2S and toluene gases in air using biofiltration systems

Components	by Eq. (15)					by Eq. (16) and/or Eq. (17)			
	$\overline{K}^{BF}_{S,i}/\delta$ (g/m^3)	$\overline{\mu}^{BF}_{M,i}$ (g/m^2/hr)	$K^G_{S,i}$ (g/m^3)	$EC^G_{M,i}$ (g/m^3/hr)		$\overline{K}^{BF}_{I,i}/\delta\overline{\mu}^{BF}_{M,i}{}^a$		$EC^G_{M,i}{}^a$ (g/m^3/hr)	
				ZC[b]	cork	(g/m^3)	(g/m^2/hr)	ZC[b]	cork
NH_3	146±13	0.0271±0.0146	0.105±0.0094	23±12	11±6	infinite	0.0130	11	5
H_2S	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
toluene	0.0425±0.0025	0.0095±0.0006	0.0107±0.0006	8±0.5	4±0.3	infinite	0.015	13	6

Note: Superscript 'a' indicates average value
Superscript 'b' indicates zeocarbon

Henry's law for the half saturation coefficient, K^G_{M,NH_3}, the maximum elimination capacities, EC^G_{M,NH_3} observed on the zeocarbon granules and EC^G_{M,NH_3} on the cork chips as microbial fixing carriers were 0.105±0.0094 g/m^3, 23±12 g/m^3/hr, 11±6 g/m^3/hr, correspondingly. Alternatively, using the Eq. (17) instead of Eq. (16) since there were no system inhibition, average values were taken into account for $\overline{\mu}^{BF}_{M,NH_3}$, EC^G_{M,NH_3} on zeocarbon and EC^G_{M,NH_3} on cork, and the values were 0.0130 g/m^2/hr, 11 g/m^2/hr, 5 g/m^2/hr, correspondingly. Differences between the values obtained using the Eq. (15) and the Eq. (17) were tentatively considered to be within uncertainty error ranges.

For the toluene removal, the linear regressions were also performed again using Eq. (15), Eq. (16) or Eq. (17). The results were summarized in Fig. 4 and Fig. 5 together with Table 2. The trends of the experimentally observed values for the toluene removal were as same as what we observed for the NH_3 removal. According to Table 2, the experimentally measured values for the apparent half saturation coefficient, $\overline{K}^{BF}_{S,toluene}/\delta$, and the maximum apparent removal rate, $\overline{\mu}^{BF}_{M,toluene}$, in the biofilm-phase were 0.0425±0.0025 g/m^3, 0.0095 ±0.0006 g/m^2/hr, respectively, and those in the gas-phase of observed $K^G_{S,toluene}$, $EC^G_{M,toluene}$ on zeocarbon and $EC^G_{M,toluene}$ on cork were 0.0107 ±0.0006 g/m^3, 8±0.5 g/m^3/hr, 4±0.3 g/m^3/hr, correspondingly. The average values using Eq. (17) for the $\overline{\mu}^{BF}_{M,toluene}$, $EC^G_{M,toluene}$ measured on zeocarbon and $EC^G_{M,toluene}$ on cork were 0.015 g/m^2/hr, 13 g/m^3/hr, 6 g/m^3/hr, correspondingly. The results are similar to those for the aforementioned NH_3 removal and to the results that were reported by Cox and Deshusses [2002] for the toluene removal in the presence of H_2S, letting us conclude that there is no influence of H_2S on the toluene removal.

Through the biokinetic studies using the well-known inhibition biokinetic expression, we were not able to observe interactions or inhibitions among the three different kinds of microorganisms, i.e. *Thiobasillus thioparus*, *Nitrosomonas* and *Nitrobactor* and *Pseudomonas putida*, or even between H_2S gas and other gases. It was a parallel process where many different reactions are simultaneously occurring in a finite area (at the same sites) of the microbial fixing carrier materials. Although there are a lot of chances for involving the competitive or cross-inhibitions among the three different kinds of microorganisms in terms of nutrients, byproducts for the metabolisms, etc., it was assumed that the simultaneous biodegradations for the ternary NH_3, H_2S and toluene substrates were indifferently taken place, in contrast with the results reported by others [Chung et al., 2000, 2001; Kim et al., 2002a; Malhautier et al., 2003] for the removal on the binary NH_3, H_2S. Furthermore, Cox and Deshusses [2002] have reported no interactions between two microorganisms during the simultaneous removal of the binary H_2S and toluene. In the range of experiments in this work, there was no clear evidence of the inhibition on toluene removal influenced by the presence of H_2S.

CONCLUSIONS

Through the biokinetic study associated with three different substrate gases, i.e. NH_3, H_2S and toluene, using an inhibition biokinetic expression occurring in a mixture of microorganisms fixed on zeocarbon granules or cork chips, it is confirmed that there is no particular evidence or clue of interaction or inhibition among three different kinds of microorganisms. In a view of system interruptions due to the inhibitory behavior, it is, therefore, feasible to establish the development of a single-stage biofiltration system for the simultaneous removal for low concentration levels of ternary NH_3, H_2S and toluene gas mixtures in waste air.

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