This article was downloaded by: [National Chiao Tung University 國立交通大學]
On: 01 May 2014, At: 00:19
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of the Air & Waste Management Association
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uawm20

Biotreatment of Hydrogen Sulfide- and Ammonia-Containing Waste Gases by Fluidized Bed Bioreactor

Ying-Chien Chung [a] , Chihpin Huang [a] , Chia Ho Liu [a] & Hsunling Bai [a]
[a] Institute of Environmental Engineering, National Chiao Tung University , Hsinchu , Taiwan , Republic of China
Published online: 27 Dec 2011.

To cite this article: Ying-Chien Chung , Chihpin Huang , Chia Ho Liu & Hsunling Bai (2001) Biotreatment of Hydrogen Sulfide- and Ammonia-Containing Waste Gases by Fluidized Bed Bioreactor, Journal of the Air & Waste Management Association, 51:2, 163-172, DOI: 10.1080/10473289.2001.10464265

To link to this article: http://dx.doi.org/10.1080/10473289.2001.10464265

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **51**:163-172
Copyright 2001 Air & Waste Management Association

Biotreatment of Hydrogen Sulfide- and Ammonia-Containing Waste Gases by Fluidized Bed Bioreactor

Ying-Chien Chung, Chihpin Huang, Chia Ho Liu, and Hsunling Bai

Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan, Republic of China

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

ABSTRACT

Gas mixtures of H_2S and NH_3 are the focus of this study of research concerning gases generated from animal husbandry and treatments of anaerobic wastewater lagoons. A heterotrophic microflora (a mixture of *Pseudomonas putida* for H_2S and *Arthrobacter oxydans* for NH_3) was immobilized with Ca-alginate and packed into a fluidized bed reactor to simultaneously decompose H_2S and NH_3. This bioreactor was continuously supplied with H_2S and NH_3 separately or together at various ratios. The removal efficiency, removal rate, and metabolic product of the bioreactor were studied.

The results showed that the efficiency remained above 95% when the inlet H_2S concentration was below 30 ppm at 36 L/hr. Furthermore, the apparent maximum removal and the apparent half-saturation constant were 7.0×10^{-8} g-S/cell/day and 76.2 ppm, respectively, in this study. The element sulfur as a main product prevented acidification of the biofilter, which maintained the stability of the operation. As for NH_3, the greater than 90% removal rate was achieved as long as the inlet concentration was controlled below 100 ppm at a flow rate of 27 L/hr. In the NH_3 inlet, the apparent maximum removal and the apparent half-saturation constant were 1.88×10^{-6} g-N/cell/day and 30.5 ppm, respectively. Kinetic analysis showed that 60 ppm of NH_3 significantly suppressed the H_2S removal by *Pseudomonas putida*, but H_2S in the range of 5–60 ppm did not affect NH_3 removal by *Arthrobacter oxydans*. Results from bioaerosol analysis in the bioreactor suggest that the co-immobilized cell technique applied for gas removal creates less environmental impact.

IMPLICATIONS

A fluidized bed bioreactor was applied for H_2S- and NH_3-containing waste gases. The evidence indicated that the system has the potential to be an effective means of simultaneously removing H_2S and NH_3 at low concentrations. Optimal operation criteria were established for widespread use.

INTRODUCTION

H_2S is highly toxic and could cause a safety hazard, while NH_3 can produce odor and create visibility problems. The Taiwan Environmental Protection Agency has set the ambient air quality standards of NH_3 and H_2S at 1 and 0.1 ppm, respectively. NH_3 and H_2S in a wide range of concentrations are released from industrial processes, such as wastewater treatment, landfills for waste disposal, livestock farming, and hog manure.[1-3] Typical concentrations of NH_3 and H_2S emitted from these industries range from 5 to 60 and from 5 to 100 ppm, respectively.[2,4,5] The excess amounts of NH_3 and H_2S must be removed not only to avoid safety and health hazards,[6,7] but also to eliminate environmental impacts, such as greenhouse effect, acid rain, and eutrophication. H_2S is usually emitted from the crude oil refining process and often produces environmental problems. The process of oxidation of H_2S to H_2SO_4 can deplete the oxygen of the receiving water, and the acid products can damage the structure of the pipe.[8-10]

Biotreatments for NH_3 and H_2S removal have drawn great attention, because they are more economical than the conventional methods of comparable removal efficiency.[11] Application of a fluidized bed reactor in waste gas treatment is very rare. Some researchers have tried to use the fluidized bed reactor packed with *Nitrosomonas* sp. to remove NH_3 from wastewater.[12,13] Recently, some immobilized-cell technologies have been successfully applied in waste gas treatment. Although Chung et al. demonstrated the high removal efficiency and high operational stability of the immobilized-cell technology in the packed reactor,[14,15] the advantage of the fluidized-bed system over the traditional packed system for the removal of H_2S and NH_3 has not yet been demonstrated from the operational standpoint. Generally, the fluidized bed can provide better mass transfer and less loss of packing material with lower pressure drop.[16]

Until now, few studies have presented the chemical or biochemical relationship between NH_3 and H_2S. It was discovered that excess sulfide reduced nitrification by 50–100%, which led to the reduction in NH_3 removal.[17] However, Sato

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

et al. found that the inhibition of nitrification increased with NH_3 concentrations.[18] Hence, in treating waste gas containing more than one component, the inlet gas ratio must be appropriately controlled. In previous studies, we found that *Arthrobacter oxydans* is very effective in removing NH_3 and *Pseudomonas putida* is effective in eliminating H_2S.[14,19] These two species were, therefore, chosen in our fluidized bed system. In this study, the fluidized bed reactor was fed with NH_3/H_2S gas mixtures at various ratios, and the detailed removal characteristics and inhibitory phenomena between the co-exit gases are discussed.

MATERIALS AND METHODS

Microorganisms and Cultivation

Pseudomonas putida and *Arthrobacter oxydans* were obtained from FIDRI in Taiwan. Stock cultures were grown in plate count broth at 26 °C with 120 strokes/min. The broth contained 5 g/L yeast extract, 10 g/L tryptone, and 2 g/L dextrose. In all consecutive experiments, inflow media (cycling solutions) were used. The compositions of various inflow media are listed in Table 1. The final pH of the medium was adjusted to neutral with 2 N NaOH or HCl.

Preparation of Immobilized Cells

Pseudomonas putida and *Arthrobacter oxydans* were grown in 100-mL plate count broth separately, harvested by centrifugation (7500 × g, 10 min), and then washed 5 times with sterile distilled water. The cultures were mixed together in sterile 4% (w/w) Na-alginate solution. The Na-alginate solution, containing the mixture of cells, was dropped into a 4% $CaCl_2$ solution from a syringe. The droplets immediately formed 4-mm-diameter co-immobilized beads. Flushing with sterile buffer solution for 5 hr activated these beads. The immobilized beads were packed into the fluidized bed bioreactor.

Table 1. The composition of various inflow media.

	M1 Medium for *Pseudomonas putida*	M2 Medium for *Arthrobacter oxydans*	M3 Medium for Mix Culture
KH_2PO_4	0.035	0.035	0.035
K_2HPO_4	0.06	0.06	0.06
NH_4Cl	0.1	–	–
$MgCl_2·6H_2O$	0.2	0.2	0.2
$MgSO_4$	–	0.25	–
$FeSO_4·7H_2O$	–	0.0025	–
$FeCl_2$	0.01	0.01	0.01
$CuSO_4$	–	0.00008	–
$CaCl_2$	0.00074	0.00074	0.00074
H_2O	1000 mL	1000 mL	1000 mL
Glucose	0.5	0.5	0.5

Note: Units are g/1000 mL H_2O except where noted.

Apparatus and Hydrogen Sulfide/Ammonia Removal for Continuous Operation

A schematic set-up of the fluidized bed bioreactor is shown in Figure 1. Glass columns (60 mm ϕ × 60 cm of working height) were packed with cell-laden Ca-alginate beads, and a perforated sieve plate was fitted at the bottom of the column to ensure the uniform distribution of the inlet gas. The volumes of bead and inflow medium in the glass column were 600 and 520 mL, respectively. The initial number of cells in the column was determined to be 10^6 CFU/g-bead. $H_2S_{(g)}$ or $NH_{3(g)}$, supplied from separate gas cylinders, was diluted with compressed air passed through an air filter and flowed upward from the bottom of the biofilter. The gas flow rate was controlled to make the beads in the glass fluidized. The beads carrying the microorganisms were suspended in the solution, which the air was bubbled through. An inflow medium (composition shown in Table 1) was recirculated by a peristaltic pump at a flow rate of 25 mL/min to supply nutrient to the co-immobilized cells and modify the pH value.

In the continuous flow experiment, the H_2S- or NH_3-containing waste gas was introduced into the fluidized bed reactor. Gas concentrations in the range of 10–100 ppm were supplied at various flow rates (18, 27, 36, 54, and 72 L/hr). The empty bed detention times were 3.73, 2.49, 1.87, 1.24, and 0.92 min, respectively. The removal efficiency and the metabolic products of the biosystem were determined. In the co-immobilized system, the simulated H_2S- and NH_3-containing waste gases were prepared at ratios of 1:1 (30:30), 1:2 (30:60), 2:1 (60:30), and 2:2 (60:60), respectively, by concentration (ppm/ppm). These mixtures were supplied to the bioreactor at 36 L/hr, and the operating temperature was controlled at 28 °C. To evaluate the adaptability of the fluidized bed reactor to upset conditions, H_2S was sequentially fed into the reactor from low to high concentration (20, 40, 60, 80, and 110 ppm), and then the opposite method was used.

Bioaerosol Analysis

Microorganisms liberated from the bioreactor were collected by liquid impingement. The air escaped from the top of the bioreactor was forced through a 250-mL flask containing 100 mL of aseptically distilled water at 150 L/hr. One mL of the collected solution was inoculated to the medium, and the cell counts were determined by the serial dilution method. PDA, NA, thiosulfate, and modified Waksman media were used for fungi, heterotrophic bacteria, non-acidophilic *Thiobacilli*, and acidophilic *Thiobacilli*, respectively.[20] The counts were reported as colony forming units in air (CFU/m^3).

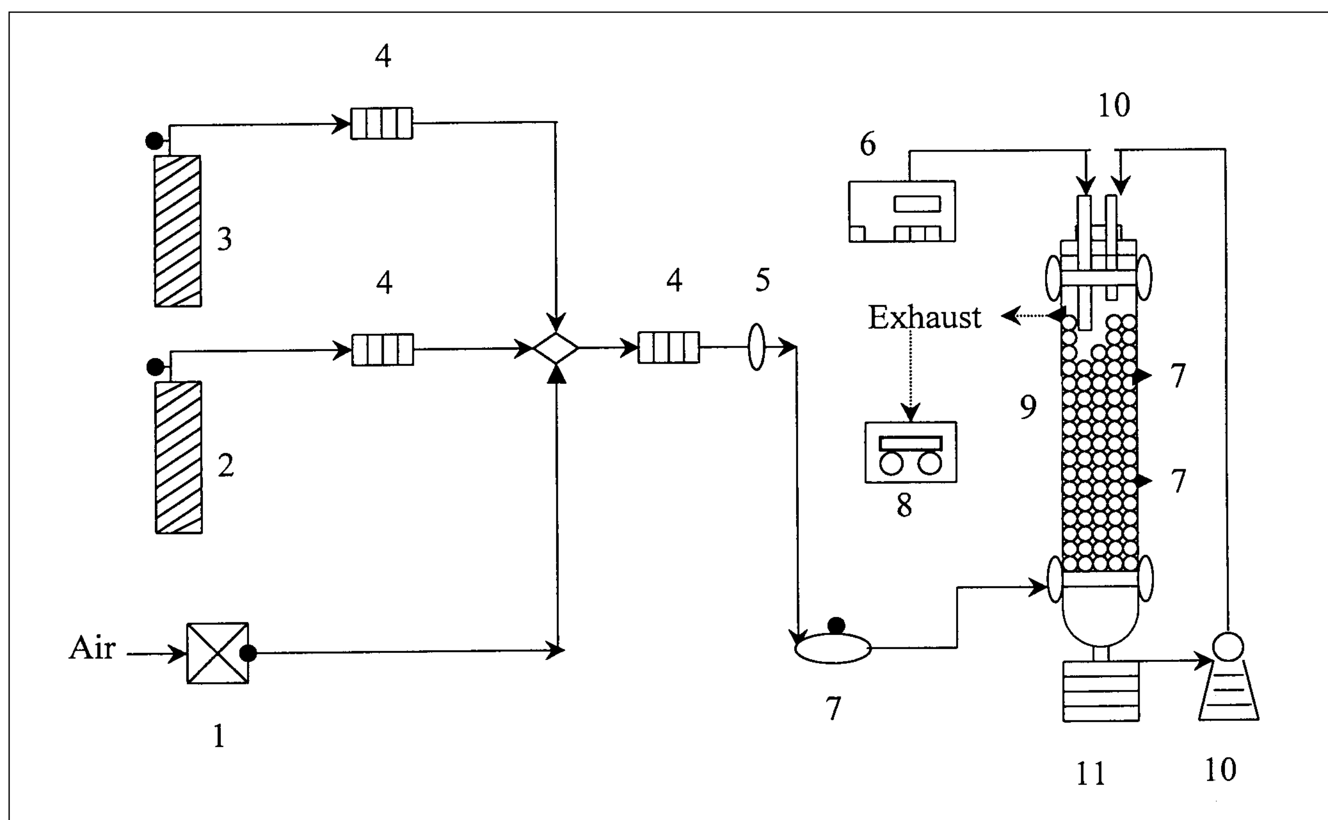


Figure 1. The experimental set-up of the fluidized bed bioreactor. (1) Air compressor; (2) H_2S gas cylinder; (3) NH_3 gas cylinder; (4) flow meter; (5) air filter; (6) pH meter; (7) sampling port; (8) single point monitor; (9) glass column; (10) pump; and (11) nutrient tank.

Analytical Methods

Concentrations of inlet and outlet H_2S/NH_3 gases of the reactor were measured either continuously by a single point monitor (MDA Scientific) ranging from 50 to 1500 ppb or periodically by gas detector tubes (GASTEC) ranging from 0.5 to 120 ppm. In all consecutive experiments, the variation in H_2S/NH_3 concentration at steady state was within ±5%. Therefore, the 12 values obtained at steady states were averaged as the H_2S/NH_3 outlet concentrations. The chemical composition in the cycling solution was also determined. SO_4^{2-}, NO_3^-, and NO_2^- concentrations in the solution were measured by ion chromatography (Dionex 4500i). Sulfide and NH_4^+ were determined using an ion-specific electrode. Sulfite was determined by the titration using a standard potassium iodide-iodate titrant and a starch indicator.[21] Elemental sulfur was determined by reacting with cyanide to produce thiocyanate, which was then quantified as $Fe(SCN)_6^{3-}$.[22] Organic nitrogen was determined by the Kjeldahl method.

RESULTS AND DISCUSSIONS

Hydrogen Sulfide Removal

A fluidized bed bioreactor packed with immobilized *Pseudomonas putida* bead was used to remove H_2S. This experiment was scheduled to continuously process for one month at 36 L/hr, while the inlet H_2S concentration was varied from 15 to 100 ppm. The removal efficiencies for various inlet concentrations at different periods are shown in Figure 2. When the inlet H_2S concentration was below 60 ppm, this system achieved greater than 92% removal efficiency. The average removal efficiency was greater than 95% for 15 ppm of inlet H_2S concentration. On the 15th day, a fresh nutrient solution was introduced into this system to start a new cycle. It was found that high removal efficiency was still maintained. As shown in Figure 2, the system achieved steady state in a short period of time. Therefore, the time to reach its optimum operation condition for H_2S removal was very short. It was also noted that the variation in pH was 6.3–7.5, showing very little acidification during the entire operation period.

In order to establish design criteria for the scale-up of the fluidized bed bioreactor, the correlation between inlet load and outlet load (removal capacity) needs to be studied. As shown in Figure 3, the dotted line represents the removal capacity at 100% removal efficiency, while the solid line represents 90% removal efficiency. When the inlet load was below 70 g-S/m^3-hr, the inlet load equaled the removal capacity. This point is called the critical loading state, since beyond this point, the system can no longer reach 100% removal. As inlet load exceeds the critical loading, the corresponding line curves downward to the right and deviates from the 100% coequal line. In addition, this system has a maximum inlet load of ~83

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

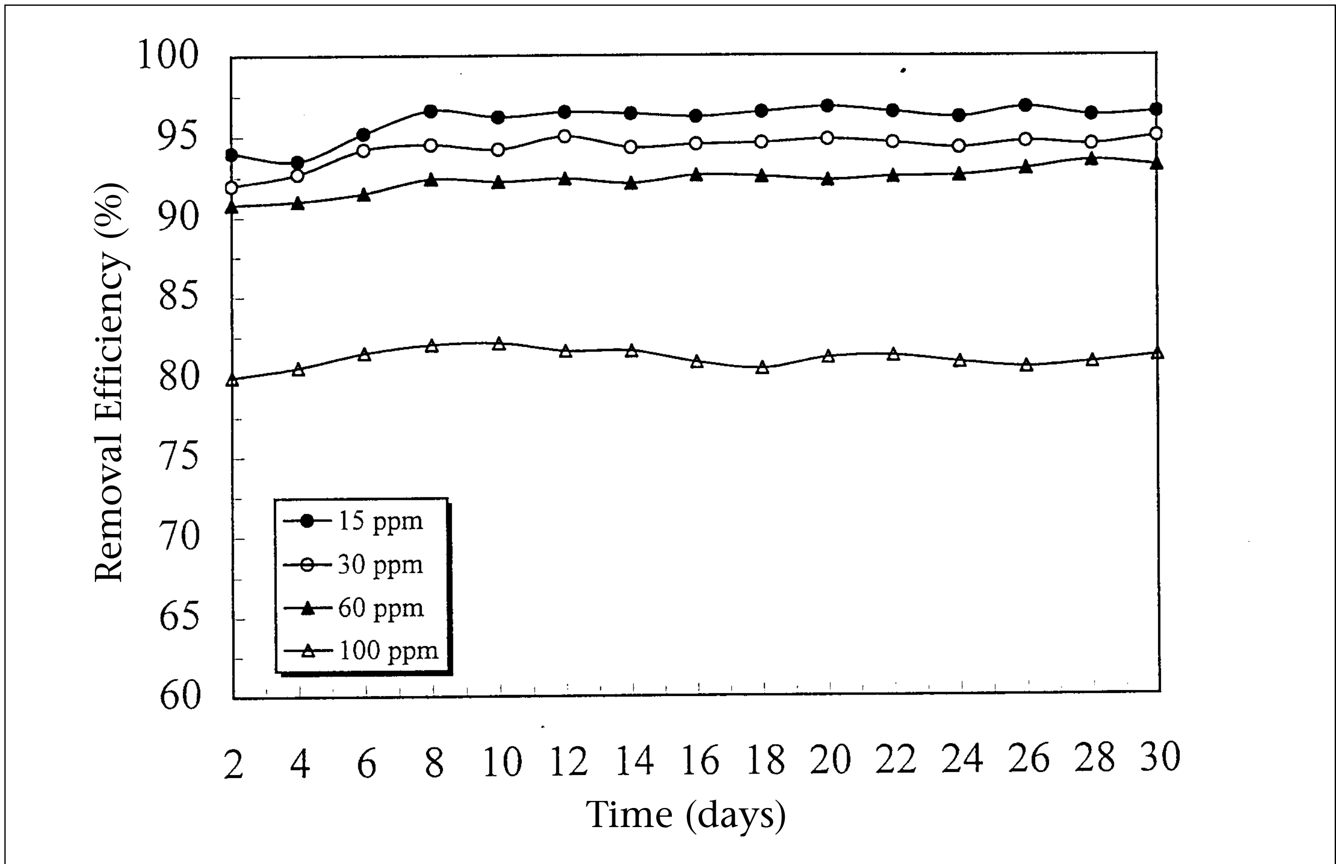


Figure 2. H_2S removal efficiency of a fluidized bed bioreactor at 36 L/hr in continuous operation.

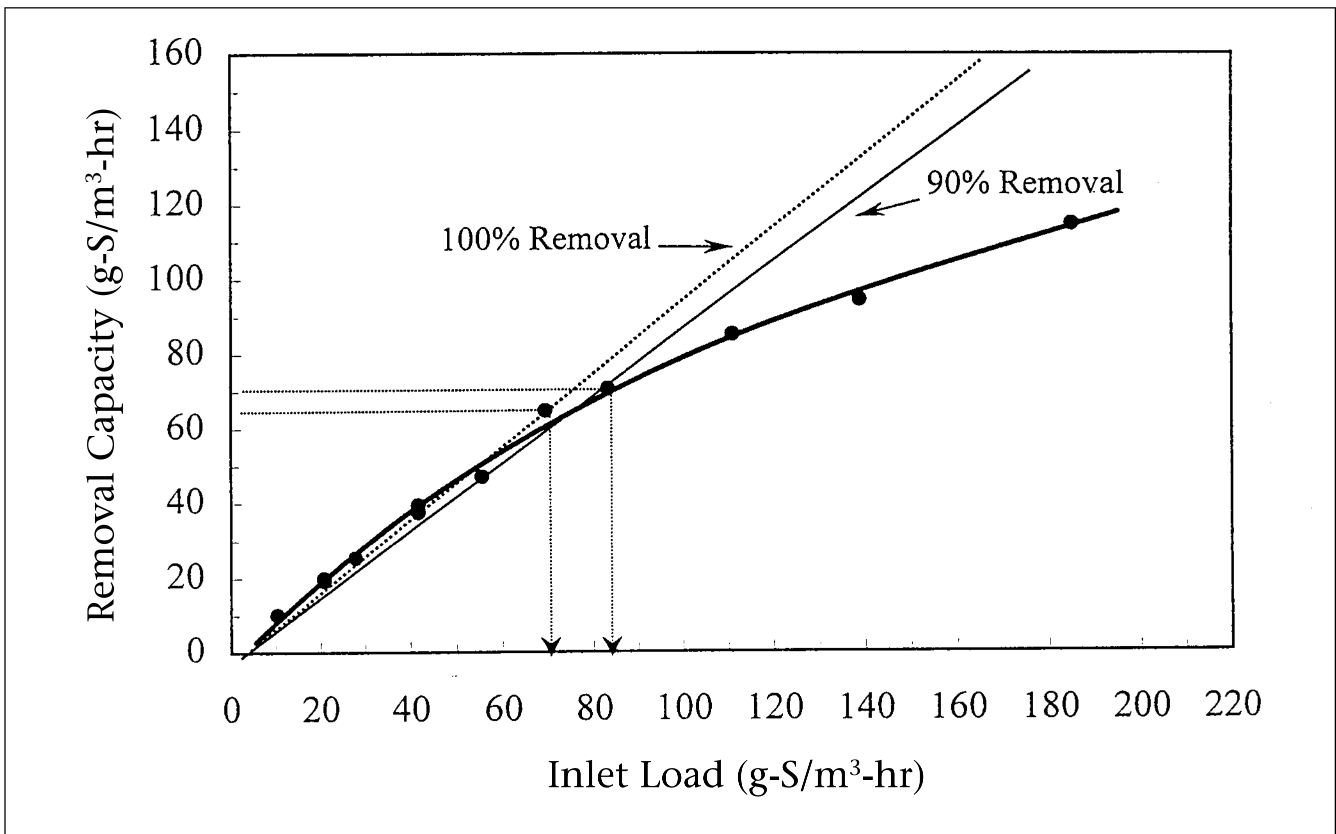


Figure 3. The relationship between the inlet load and the outlet load for H_2S.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

g-S/m^3-hr when the removal efficiency of the system is required to be 90% or more. Based on this graph, an operation model for H_2S removal can be established. If 100% H_2S removal is required, then the inlet load has to be controlled within 70 g-S/m^3-hr. Similarly, if 90% H_2S removal is needed, then an inlet load within 83 g-S/m^3-hr should be maintained. Since the inlet load of the system depends on inlet concentration and flow rate, any specific removal efficiency (e.g., 100% removal) can be achieved by adjusting the flow rate or the inlet concentration in compliance with emission limits.

Since the inlet concentration in the field operation is not constant, dramatic fluctuation can happen during the course of treatment. Therefore, it is necessary to demonstrate the adaptability of the system to dramatic change in inlet loading. A field operation was simulated by gradually increasing the inlet H_2S concentration from 20 to 110 ppm and then returning to the normal operation concentration (40 ppm). The correlation of inlet loading and outlet concentration in conjunction with the removal efficiency are shown in Figure 4. Greater than 96% removal efficiency was maintained in the first 32 hr of operation, as the inlet loading was below 75 g-S/m^3-hr. However, when the inlet concentration was suddenly raised to 110 ppm at the 32nd hour, the outlet concentration increased to 13 ppm, a 7% drop in the removal efficiency. The system resumed its original removal efficiency (96%) when the H_2S concentration was returned to lower concentration after the 40th hour. This result indicates that our bioreactor system is able to cope with the fluctuation of inlet concentration during field operation. On the whole, this bioreactor system can achieve a good removal efficiency (>96%) if the inlet loading is controlled within 75 g-S/m^3-hr.

Ammonia Removal

A fluidized bed bioreactor packed with immobilized *Arthrobacter oxydans* bead was used to remove NH_3 ranging from 10 to 100 ppm under various flow rates (18, 27, 54, and 72 L/hr). The effect of the flow rate on removal efficiency at different inlet concentrations is shown in Figure 5. The removal efficiency decreased with the increasing inlet concentration and flow rate. Meanwhile, it was discovered that the impact of flow rate on removal efficiency within the concentration range of 10–100 ppm was the same, as shown by the same slopes. For a typical NH_3 concentration (60 ppm) emitted from various types of industries in Taiwan, this system can accomplish greater than 93% removal efficiency when the flow rate is kept at less than 54 L/hr, which confirmed the applicability of this system in reducing the NH_3 emission.

To establish the operation criteria in removing NH_3, we studied the correlation between inlet load and outlet

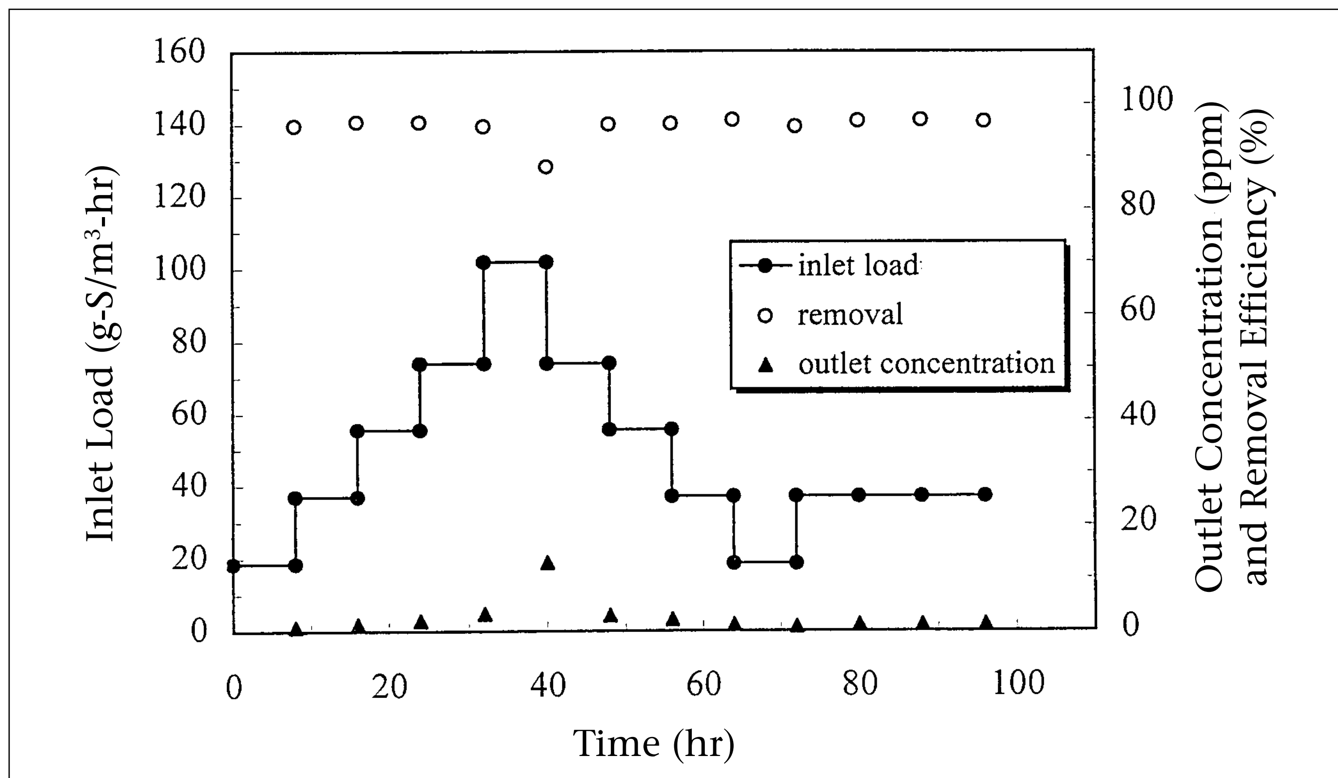


Figure 4. The correlation of inlet loading and outlet concentration in conjunction with the removal efficiency by an abrupted condition.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

load (removal capacity). As shown in Figure 6, the critical loading was determined to be 3.7 g-N/m^3-hr. To reach 90% removal efficiency, its maximum inlet load was ~7.5 g-N/m^3-hr. The extrapolated correlation line suggested a maximum removal capacity of 9.0 g-N/m^3-hr. There, acceptable NH_3 removal can be accomplished through adjusting the flow rate and the inlet concentration based on the correlation presented in Figure 6.

Simultaneous Removal of Hydrogen Sulfide/Ammonia

A fluidized bed bioreactor packed with co-immobilized *Pseudomonas putida* and *Arthrobacter oxydans* was used to simultaneously remove H_2S and NH_3. The removal efficiencies and pH variations for various ratios of H_2S/NH_3 gas mixtures (e.g., 1:1, 1:2, 2:2, and 2:1) at different periods are illustrated in Figure 7. During the initial 8 days (stage 1), an H_2S/NH_3 gas ratio of 1:1 (e.g., 30:30 ppm) was prepared as the inlet gas mixture. A gas ratio of 1:2 was operated from the 9th to the 16th day (stage 2). A gas ratio of 2:2 was run from the 17th to the 24th day (stage 3). During the final 8 days (stage 4), a gas mixture of 2:1 was used.

At stage 1, removal efficiencies of H_2S and NH_3 increased with time and reached the maximum values for the entire experiment, which are 97 and 95.5%, respectively. During the second period, the removal efficiency for H_2S in the gas mixture dropped from 97 to 93.5%, while the removal of NH_3 was about the same. Therefore, it was suggested that higher NH_3 concentration might affect the H_2S removal. Furthermore, the removal efficiency for H_2S dropped significantly (to 84%) in stage 3 at the inlet gas mixture of 2:2, a more significant drop than the 1:2 gas ratio. On the other hand, NH_3 was maintained at ~93%. The system can be used for at least 3 months, provided the cycling solution is routinely refreshed.

According to the results of this experiment, higher H_2S and NH_3 concentrations in the gas mixture can affect H_2S removal, especially the gas component of H_2S. However, the NH_3 removal is not affected by the concentration of the gas component in the mixture. Because the pH value of the system dropped to ~5, the decrease in H_2S removal could be attributed to the more acidic environment caused by the release of the H^+ when H_2S and NH_3 were partially oxidized to SO_4^{2-} and NO_2^-. During stages 3 and 4, the removal efficiency of H_2S was maintained at roughly 83% for an inlet gas mixture ratio of 2:1, and the removal efficiency of NH_3 was increased slightly. At the end of the experiment, the immobilized cells were sliced and observed under a scanning electronic microscope (SEM) to study the composition of these cluster cells. The SEM photograph (not shown) revealed that the spherical *Arthrobacter oxydans* outnumbered the rod-like *Pseudomonas putida*.

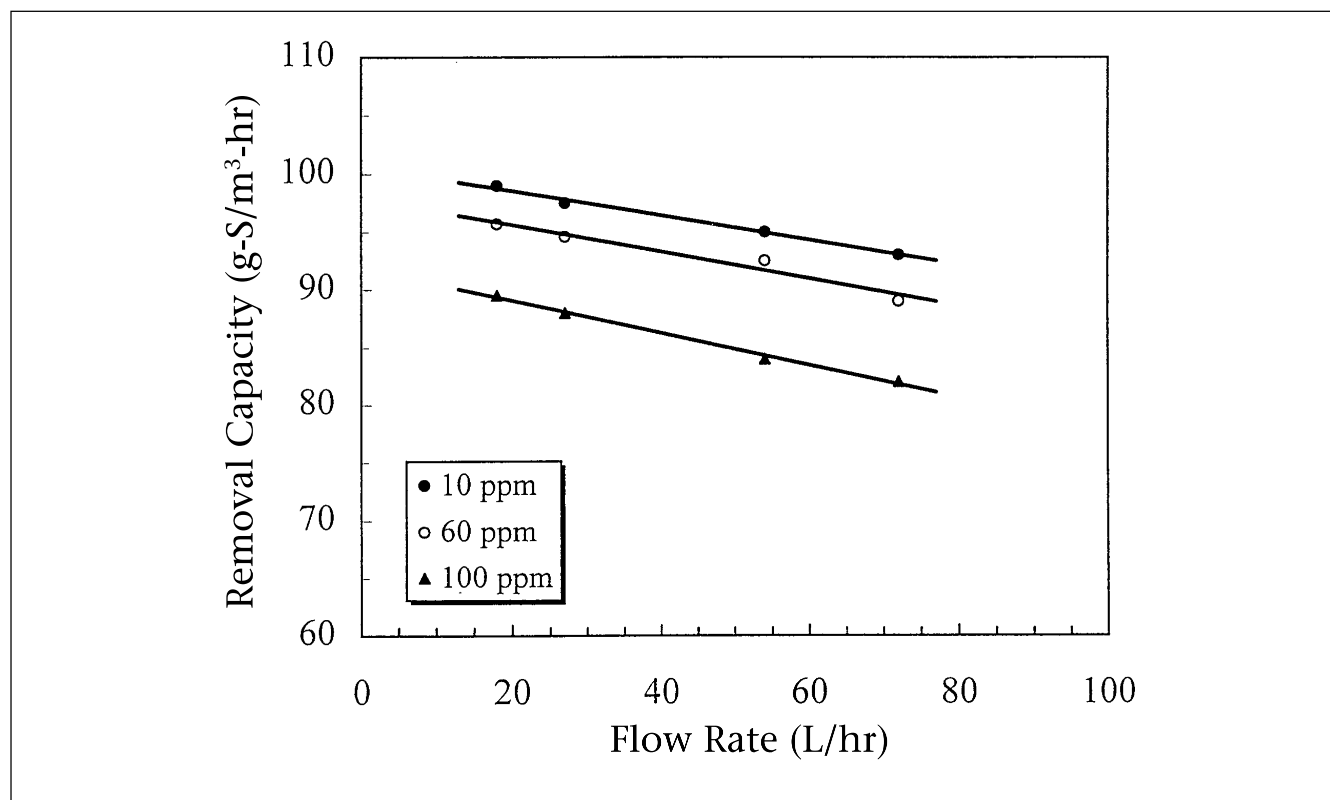


Figure 5. Effect of flow rate on NH_3 removal efficiency by the fluidized bed bioreactor.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

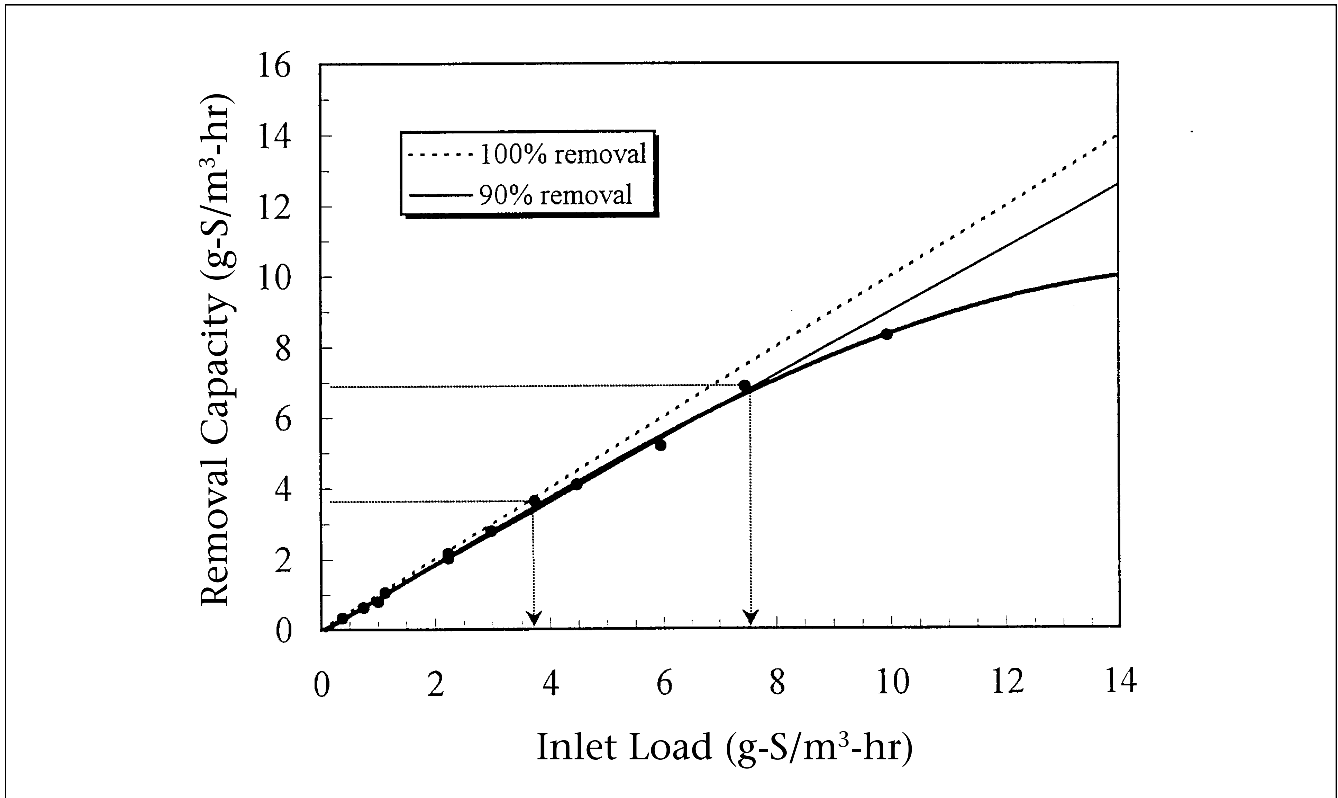


Figure 6. The relationship between the inlet load and the outlet load for NH_3.

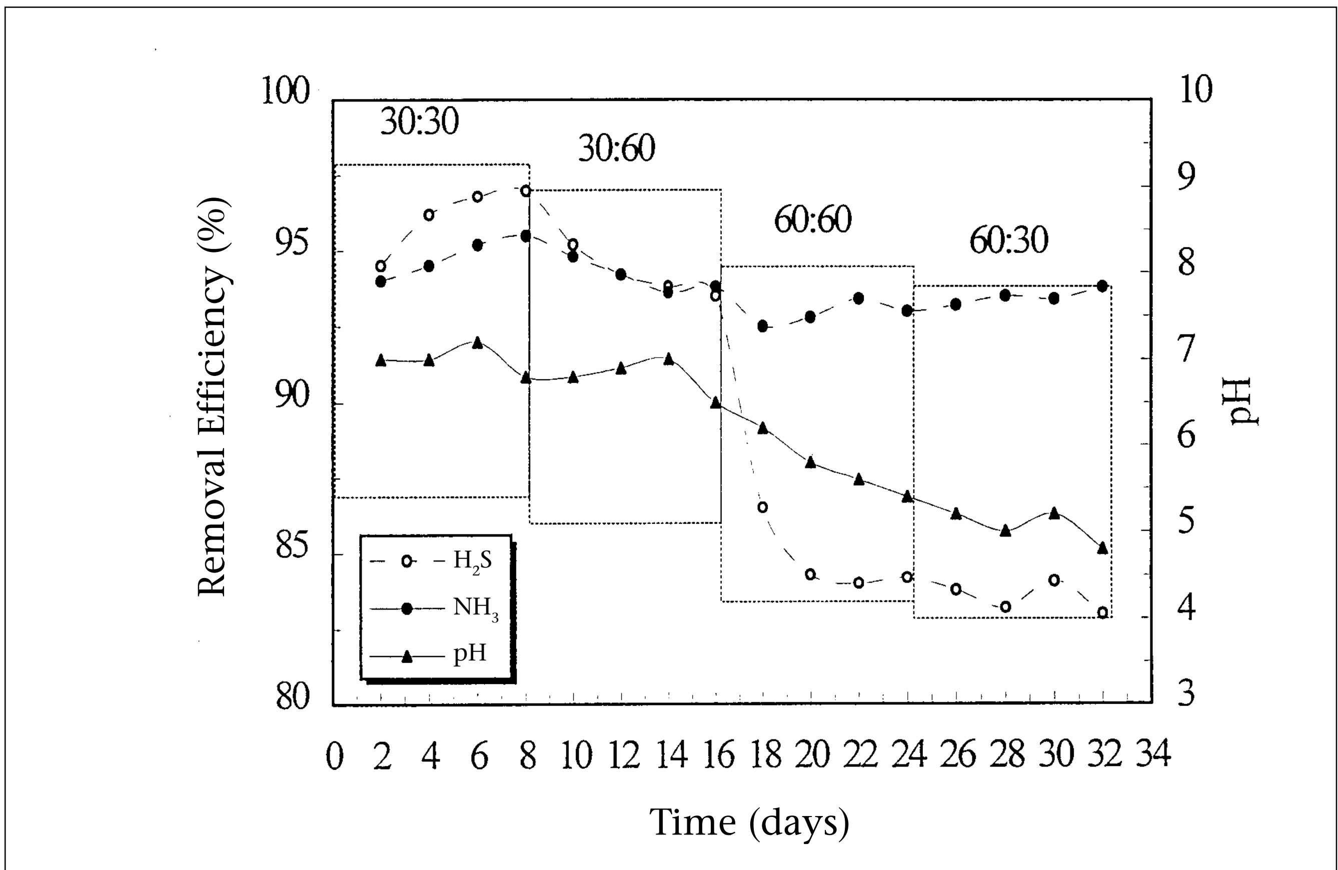


Figure 7. Relationships between the removal efficiency and operating time at different ratios (30:30, 30:60, 60:60, and 60:30) of H_2S/NH_3 gas mixtures.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

The head loss was an important parameter for the operational cost. In this experiment, the gas velocity was raised gradually from 18 to 72 L/hr. When the operation reached the steady state, gas velocity was changed for the test. The averaged 64-cm H_2O of head loss in the system (data not shown) was higher than a traditional biofilter (~10 cm). This might be a major disadvantage with respect to the conventional biofilter.

Kinetics Analysis

During the process of removing H_2S/NH_3, high concentrations of these compounds may inhibit the enzyme activity of *Pseudomonas putida* and *Arthrobacter oxydans* (mentioned in the section of simultaneous removal of H_2S/NH_3). Hence, inhibition in the system caused by high H_2S and NH_3 concentration should be presented by analyzing the apparent kinetic parameters, which have successfully applied for the system.[14,19] In the kinetics analysis, the gas flow rate was controlled to less than 36 L/hr to minimize the effect of mass-transfer limitation. The apparent kinetic parameters of the removal of single- and mixed-gas under various operating conditions are presented in Table 2. Generally speaking, the smaller the saturation constant (K_s), the higher the affinity of the substrate onto the bacteria cells and the better the effect of removal. In a co-immobilized system, the K_s of NH_3 removal was 31 ppm when the inlet H_2S/NH_3 concentrations were between 5 and 60 ppm, which was very close to the K_s generated from the system of single gas removal (5–30 ppm of inlet NH_3), namely 30.5. It is evident that the co-existence of H_2S and NH_3 did not affect the enzyme activity of *Arthrobacter oxydans*. When the inlet H_2S/NH_3 concentrations were between 5 and 30 ppm, the K_s of H_2S was 75.8 ppm, which is close to the K_s of 76.2 ppm obtained from the single-gas system. This indicates that "low" NH_3 concentration has no effect on H_2S removal. When the inlet NH_3 concentration in the gas mixture was increased to 60 ppm, the apparent kinetic parameter (K_s) for H_2S was 106.5 ppm, which is higher than the K_s (76.2 ppm) obtained from a single H_2S system. This indicates that the enzyme activity of *Pseudomonas putida* is inhibited by 60 ppm NH_3. When the inlet H_2S concentration was increased to 60 ppm along with the addition of 5–30 ppm NH_3, a saturation constant K_s of 186.3 ppm for H_2S was obtained, which was much higher than the K_s of 106.5 ppm obtained from a gas mixture with a high NH_3 concentration (60 ppm). Figure 7 also shows that the impact of high H_2S concentration was more significant on H_2S removal than a high NH_3 concentration was. Therefore, if the inlet H_2S/NH_3 concentrations can be controlled to within 60 ppm, this system can be applied to remove the H_2S- and NH_3-containing waste gases effectively and simultaneously.

Product Analysis

To understand the mechanism of NH_3/H_2S removal, various concentrations of the gases were introduced into a bioreactor at 36 L/hr for 7 consecutive days. Then the recycling solution was collected for product analysis. Tables 3 and 4 present the results of this analysis. Since the concentrations of metabolic products in the immobilized bed are far less than those in the recycling solution (data not shown), only the data regarding the recycling solution are given here.

As seen in Table 3, the amounts of S, SO_3^{2-}, SO_4^{2-}, and S^{2-} are 162.12, 5.88, 33.76, and 0.02 (mg-S), respectively, at an inlet H_2S concentration of 30 ppm. Among these metabolic products, elemental sulfur attained the highest percentage (80.3%), whereas the sulfide ions attained the least, only 0.1%. When the inlet H_2S concentration was changed to 60 ppm, the neutral sulfur remained the major metabolic product, at 84.5%. Obviously, these neutral sulfur products will not bring acidity to the system, and sulfur with economical value can be recycled. However, the higher concentration of sulfide indicated that part of the H_2S was not metabolized by sulfur-oxidizing bacteria. Fortunately, these sulfide ions made up a very low ratio, with an average of 0.15%. This suggested that most H_2S was converted into metabolic products and stored in the recycling solution. Hence, the

Table 2. Apparent kinetic analysis for H_2S and NH_3 removal by a fluidized bed bioreactor.

	Single Inlet		Mixture Inlet			
	NH_3 = 0 ppm H_2S = 5–30 ppm	NH_3 = 5–30 ppm H_2S = 0 ppm	NH_3 = 5–30 ppm H_2S = 5–30 ppm	NH_3 = 60 ppm H_2S = 5–30 ppm	NH_3 = 5–30 ppm H_2S = 60 ppm	NH_3 = 5–60 ppm H_2S = 5–60 ppm
H_2S	K_s = 76.2[a] V_m = 7.0 × 10^{-8}[b]	—	K_s = 75.8 V_m = 7.2 × 10^{-8}	K_s = 106.5 V_m = 9.3 × 10^{-8}	K_s = 186.3 V_m = 3.1 × 10^{-8}	K_s = 80.3 V_m = 6.4 × 10^{-8}
NH_3	—	K_s = 30.5 V_m = 1.88 × 10^{-6}[c]	K_s = 30.8 V_m = 1.61 × 10^{-6}	K_s = 31.2 V_m = 1.67 × 10^{-6}	K_s = 30.6 V_m = 1.82 × 10^{-6}	K_s = 31.0 V_m = 1.55 × 10^{-6}

[a]ppm; [b]g-S/cell/day; [c]g-N/cell/day.

Table 3. Metabolic products of H_2S by a fluidized bed bioreactor.

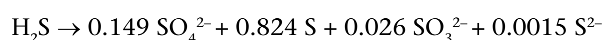
Inlet H_2S Concentration (ppm)	S^0 Produced (mg-S)	SO_3^{2-} Produced (mg-S)	SO_4^{2-} Produced (mg-S)	HS^-/S^{2-} Produced (mg-S)
30	162.12 (80.3%)	5.88 (2.9%)	33.76 (16.7%)	0.02 (0.1%)
60	376.12 (84.5%)	10.4 (2.3%)	57.91 (13.0%)	0.38 (0.2%)

Table 4. Metabolic products of NH_3 by a fluidized bed bioreactor.

Inlet NH_3 Concentration (ppm)	NH_4^+-N Produced (mg-N)	NO_2^--N Produced (mg-N)	NO_3^--N Produced (mg-N)	Organic N Produced (mg-N)
10	4.5 (6.6%)	52.2 (76.2%)	2.7 (3.9%)	9.1 (13.3%)
30	14.6 (7.2%)	159.5 (78.5%)	ND	29.2 (14.3%)
60	32.5 (7.8%)	314.5 (75.8%)	ND	67.9 (16.4%)

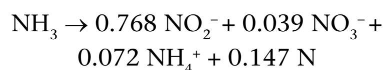
Note: ND indicates experimental data above MDL. The MDL of NO_3^--N is 0.0137 mg-N.

sulfur balance (average value) in Table 3 can be described as follows:



$$H_2S \rightarrow 0.149\ SO_4^{2-} + 0.824\ S + 0.026\ SO_3^{2-} + 0.0015\ S^{2-}$$

As shown in Table 4, the compositions of metabolic products are very similar regardless of the inlet NH_3 concentration. Among these metabolic products, NO^{2-}-N is the main product, taking up an average of 76.8%, followed by organic nitrogen, at 14.7% (as an average). Literature also shows that the main metabolic products from NH_3 through *Arthrobacter oxydans* are NO^{2-} and organic nitrogen.[19] Therefore, the presence of NH_3 indicates that some of it was not oxidized. At the same time, NH_3 in the recycling solution accumulates significantly as the inlet concentration increases. NO_3^- was not produced by *Arthrobacter oxydans*. It is likely that NO_2^- was chemically oxidized to NO_3^- after the sample was removed. The nitrogen balance (average value) in Table 4 can be described as follows:



$$NH_3 \rightarrow 0.768\ NO_2^- + 0.039\ NO_3^- + 0.072\ NH_4^+ + 0.147\ N$$

Table 5. Bioaerosol concentrations in the exhaust of a fluidized bed bioreactor.

Mixture Ratio	Nutrient Agar		Medium Types			
(H_2S/NH_3)	*A. oxydans*	*P. putida*	PDA	Thiosulfate	Nitrifying	Modified Waksman
1:1[a]	115	115	ND	ND	ND	ND
1:2	173	173	57	ND	ND	ND
2:1	173	115	ND	ND	ND	ND

Note: ND < 57 CFU/m^3; [a]1:1 = 30:30 (ppm/ppm).

Bioaerosol Detection

Biotreatment systems have recently become a major interest in removing malodor. However, as large quantities of gases are treated, the liberation of microbes from the bioreactor has to be considered. Because a large number of microbes are contained in the system, they can have a severe impact on the environment if released accidentally. In this experiment, aseptically distilled water was used to absorb the exhaust air, and the numbers of bioaerosols contained are counted as listed in Table 5. The results indicate that only very few heterotrophic *Arthrobacter oxydans* (115–173 CFU/m^3), *Pseudomonas putida* (115–173 CFU/m^3), and fungi (57 CFU/m^3) were present in the exhaust air, because the microbes were immobilized in the beads of Ca-alginate. The amount contained in these bioaerosols was far less than that released from some conventional biofilters.[23] The bioaerosol analysis assures the safety of our system to the environment.

CONCLUSIONS

The fluidized bed bioreactor, when used to remove H_2S, needs only a short time to reach its steady state. The metabolic products of the systems will not acidify the reactor because the main product is neutral sulfur. Since the sulfur element can be reclaimed, this makes the bioreactor system even more competitive. Under appropriate operating conditions, the removal efficiency can reach a satisfactory high (95% or higher) when H_2S or NH_3 is processed individually. In a co-immobilized system, relatively high H_2S/NH_3 concentrations have no inhibitory effect on the enzyme activity of *Arthrobacter oxydans*. On the other hand, both H_2S and NH_3 at high concentrations inhibit the enzyme activity of *Pseudomonas putida*. The influence of H_2S on enzyme activity is far greater than that of NH_3. The bioaerosols released from the reactor were discovered to be quite low, due to the use of an immobilized cell, which ensures its safety concerning environmental impact. It is concluded that this system may be operated near areas with high population density.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014

ACKNOWLEDGMENTS

This work was supported by the National Science Council, Republic of China. The authors would like to thank Dr. J.R. Pan for her editing.

REFERENCES

1. Yang, Y.; Allen, E.R. *J. Air & Waste Manage. Assoc.* **1994**, *44,* 863-868.
2. Langenhove, H.V.; Wuyts, E.; Schamp, N. *Water Res.* **1986**, *20,* 1471-1476.
3. Eikum, A.S.; Storhang, R. In *Odour Prevention and Control of Organic Sludge and Livestock Farming*; Neilsen, V.C., Voorburg, J.H., Hermite, P.L., Eds.; Elsevier Applied Science Publishers: London, 1986; pp 12-18.
4. Chung, Y.C.; Huang, C.; Tseng, C.P. *J. Environ. Sci. Health* **1996**, *A31,* 139-155.
5. Cho, K.S.; Hirai, M.; Shoda, M. *J. Ferment. Bioeng.* **1992**, *73,* 46-50.
6. Prosser, J.I. *Adv. Microb. Physiol.* **1989**, *30,* 125-181.
7. Buchnan, R.E.; Gibbons, N.E. *Bergey's Manual of Determinative Bacteriology*; Williams and Wilkins Co.: Baltimore, MD, 1974; pp 52-54.
8. Kobayaski, H.A.; Stenatrom, M.; Mah, R.A. *Water Res.* **1983**, *17,* 579-587.
9. Elmaleh, S.; Delgado, S.; Alvarez, M.; Rodriguez-Gomez, L.E.; Aguiar, E. *Water Sci. Tech.* **1998**, *38,* 241-248.
10. Delgado, S.; Alvarez, M.; Rodriguez-Gomez, L.E.; Aguiar, E. *Water Res.* **1999**, *33,* 539-547.
11. Leson, G.; Winer, A.M. *J. Air & Waste Manage. Assoc.* **1991**, *41,* 1045-1054.
12. Horan, N.J.; Gohar, H.; Hill, B. *Water. Sci. Tech.* **1997**, *36,* 369-375.
13. Cheng, S.S.; Chen, W.C. *Water Sci. Tech.* **1994**, *30,* 131-142.
14. Chung, Y.C.; Huang, C.; Tseng, C.P. *Biotechnol. Prog.* **1996**, *12,* 773-778.
15. Chung, Y.C.; Huang, C.; Tseng, C.P. *J. Biotechnol.* **1996**, *52,* 31-38.
16. Fan, L.S. *Gas-Liquid-Solid Fluidization Engineering*; Butterworth Publishers: 1989; pp 45-78.
17. Joye, S.B.; Holibaugh, J.T. *Science* **1995**, *270,* 623-625.
18. Sato, C.; Leung, S.W.; Schnoor, J.L. *Water Res.* **1998**, *22,* 1117-1127.
19. Chung, Y.C.; Huang, C.; Tseng, C.P. *Biotechnol. Prog.* **1997**, *13,* 794-798.
20. Cho, K.S.; Zhang, L.; Hirai, M.; Shoda, M. *J. Ferment. Bioeng.* **1991**, *71,* 44-49.
21. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; Greenberg, A.E., Clesceri, L.S., Eaton, A.D., Eds.; American Public Health Association: Washington, DC, 1992.
22. Schedel, M.; Truper, H.G. *Arch. Microbiol.* **1980**, *2-3,* 205-210.
23. Hartikainen, T.; Martikainen, P.J. *Environ. Technol.* **1996**, *17,* 45-53.

About the Authors

Dr. Huang (corresponding author) is chair of the Institute of Environmental Engineering at National Chiao Tung University in Taiwan, Republic of China. Dr. Bai is his colleague. Dr. Chung currently is a research associate at the Science and Technology Information Center, National Science Council, Taiwan. Both Dr. Chung and Mr. Liu were graduate students of Dr. Huang. Dr. Huang can be reached at fax: 886-3-5725958, phone: 886-3-5726463, or e-mail: cphuang@green.ev.nctu.edu.tw.

Downloaded by [National Chiao Tung University] at 00:19 01 May 2014