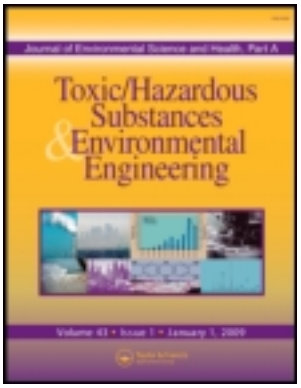

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FEASIBILITY OF FLUIDIZED-BED BIOREACTOR FOR REMEDIATING WASTE GAS CONTAINING H_2S OR NH_3

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FEASIBILITY OF FLUIDIZED-BED BIOREACTOR FOR REMEDIATING WASTE GAS CONTAINING H_2S OR NH_3

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ABSTRACT

Pseudomonas putida for H_2S and *Arthrobacter oxydans* for NH_3 were immobilized with Ca-alginate and packed inside glass columns to form fluidized-bed bioreactors. The feasibility of the lab-scale bioreactor for the treatment of H_2S or NH_3 was examined. Phosphate salt, being added to the nutrient solution as buffer solution, may chelate with Ca^{2+} in the Ca-alginate beads, resulting in the disintegration of gel structure. When the buffer capacity of the phosphate solution was over the critical point of 33.5 mM/pH, all calcium ions in the bead were released and beads were broken. Increasing liquid flowrate and inlet gas concentration favored to H_2S and NH_3 removal. Carbon source addition was essential and facilitated malodorous removal for this system. Removal capacity increased with inlet concentration. However, increasing pattern was dependent of H_2S or NH_3. The result clearly indicated that bioreactor was suitable to be applied for the industry of livestock farm for removing wastegas containing H_2S or NH_3.

Key Words: Hydrogen sulfide; Ammonia; Immobilized cell; Bioreactor.

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INTRODUCTION

Ammonia is colorless, but irritant and smelly, while H_2S is corrosive, extremely toxic, and also smelly. Both substances often exist in our surroundings. Considerable quantities of NH_3 and H_2S are produced and released from industrial sources such as petrochemical refining, metallurgy, food preparation, wastewater treatment, and treatment of fuels.[1–3] Excess amounts of NH_3 and H_2S have to be removed for the sake of safety and health[4–5] and also for the reduction of environmental impacts, such as greenhouse effect, acid rain, and eutrophication. The literature identifies many processes that involve chemical or physical principles for the treatment of air streams containing odor.[6–8] However, the recent focus has been shifted to the utility of biological process in this deodorizing process.[9] The economics, less secondary pollution and the perceived design simplicity make biological process an attractive treatment option to people unfamiliar with the technology.[10]

Immobilization technology was first used in enzyme immobilization. Recently, it has been applied in biofiltration for malodor removal, and achieving satisfactory result.[11–13] Using Ca-alginate bead for the packing material in the bioreactor has been proven to be effective with the following advantages:[14–15] (i) The high porosity between gels can result in a lower pressure drop. (ii) The Ca-alginate beads possess excellently mechanical strength and coating, which are capable of maintaining high operational stability, low cell losses, and low bioaerosol production. (iii) Beads included with appropriate bacteria can increase their removal efficiency, thus causing the decreases of both space of reactor and the cost of land.

Generally, the most often used method regarding immobilization technology is coating. And the most commonly used coating material are PVA-borax, agarose, carrageenan, acrylamide and alginate. However, alginate is the best packing material to be selected for fluidized-bed bioreactor after considering factors including compression strength, mass transfer efficiency, mechanical strength, toxicity and cost. The only drawback for the application of Ca-alginate is its tendency to proceed the chelating reaction with phosphate in the solution and further destroys the gel structure. In the bio-treatment system, the buffer solution was often used to maintain the optimal pH range for the cell growth. Based on the characteristics (for example: pKa) and cost of the buffer system, the phosphate salts were selected as buffer solution. Since the concentrated phosphate salts would destroy the gel structure, the adverse impact generated by the compound should be decreased if phosphate salts were used as buffer solution in the fluidized-bed system.

In this study, *Pseudomonas putida* for H_2S and *Arthrobacter oxydans* for NH_3 were immobilized with Ca-alginate and separately packed inside glass columns to form fluidized-bed bioreactors. The feasibility of the

lab-scale bioreactor for the treatment of H_2S or NH_3 was examined. A dynamic mathematical model was applied to predict the maximum inlet concentrations of H_2S and NH_3.

MATERIAL AND METHODS

Organism Cultivation and Medium Preparation

The original pure-culture strains of heterotrophic sulfur-oxidizing *Pseudomonas putida* and heterotrophic ammonia oxidizer, *Arthrobacter oxydans* were obtained from FIRDI in Taiwan. Stock cultures were both grown in plate count broth at 30°C. The plate count broth contained yeast extract 5 g/L, tryptone 10 g/L, and dextrose 2 g/L. In continuous experiments, the inflow medium (circulating liquid) was used and stored in the nutrient tank. The inflow medium contained NaH_2PO_4 2 g/l, Na_2HPO_4 2.6 g/l, $MgCl_2{\cdot}6H_2O$ 0.2 g/l, NH_4Cl 0.4 g/l, $FeSO_4{\cdot}7H_2O$ 0.01 g/l, and Glucose 0.5 g/l and the buffer capacity was control under 3.35 mM/pH.

Preparation of Immobilized Cells

P. putida and *A. oxydans* were each grown in 100 ml plate count broth, harvested by centrifugation (8,000×g, 10 min) and then were immobilized with Ca-alginate by the method described by Chung et al.[12] The initial biomass concentration in the beads for both organisms was 10^6 cells/g-bead. The immobilized beads with an average diameter of 4.0 mm were packed into the fluidized-bed bioreactor.

Preparation of Buffer Solution

A series of pH buffer solutions were prepared by mixing the various concentration ratio of phosphate salts (NaH_2PO_4/Na_2HPO_4). The values of buffer capacity were 0, 0.7, 3.5, 7, 33.5 and 70 mM/pH. For example, 70 mM/pH of buffer capacity was prepared by mixing 0.89 g of Na_2HPO_4 and 0.78 g of NaH_2PO_4 and then adding deionized water to one liter. Ten grams of beads were put in 200 ml bottle which contained 100 ml phosphate salts. The bottles were put in the shaker with 120 strokes/min. After the one-month operation, the appearance of Ca-alginate bead was observed and its concentration of calcium ion in the solution was also measured.

Characteristic of Physical Sorption for Odorous Removal

Effect of Liquid Flowrate

A conventional fluidized-bed reactor (60 mm-$\phi \times 40$ cm of working length) was used. The Ca-alginate beads without cells were packed into this reactor. The packing volume was about 0.6 liter. The inlet concentrations of H_2S and NH_3 were 60 ppmv. The gas flowrate and operating temperature were controlled at 36 *l*/hr and 30°C. The flow rates of circulating liquid were operated at 5–90 ml/min. The average removal efficiency was obtained from 3-day operation.

Effect of Gas Flowrate

The similar apparatus was used as above section mentioned. The inlet concentrations of H_2S and NH_3 were 60 ppmv. The liquid flowrate and operating temperature were controlled at 30 ml/min and 30°C. The flow rates of wastegas were operated at 36–150 *l*/hr. The average removal efficiency was obtained from 3-day operation.

Effect of Inlet Gas Concentration

The similar apparatus was used as above section mentioned. The liquid flowrate, gas flowrate and operating temperature were controlled at 30 ml/min, 36 *l*/hr and 30°C, respectively. The inlet concentrations of H_2S and NH_3 were introduced reactor ranging from 10 to 100 ppmv. The average removal efficiency was obtained from 3-day operation.

Apparatus and H_2S/NH_3 Removal in Continuous System

A fluidized-bed bioreactor (60 mm-$\phi \times 40$ cm of working length) was used (Figure 1). The packing volume and initial cell number in this column were 0.6 liter and 10^6 cells/g-bead, respectively. The column wall contained sampling ports for measuring H_2S or NH_3 concentrations during the experiments. The $H_2S_{(g)}$ or $NH_{3(g)}$, supplied from separate gas cylinders, was first diluted with compressed air and flowed upwards through the bottom of the biofilter. The concentration of H_2S or NH_3 ranging from 10 to 100 ppmv was introduced to the system. An inflow medium was recirculated by a peristaltic pump to supply nutrient to the immobilized cells at 30 ml/min. As the off-gas flowed upward through the packing material, medium flowed downward over the packing material. This countercurrent operation saturated the off-gas with water vapor.

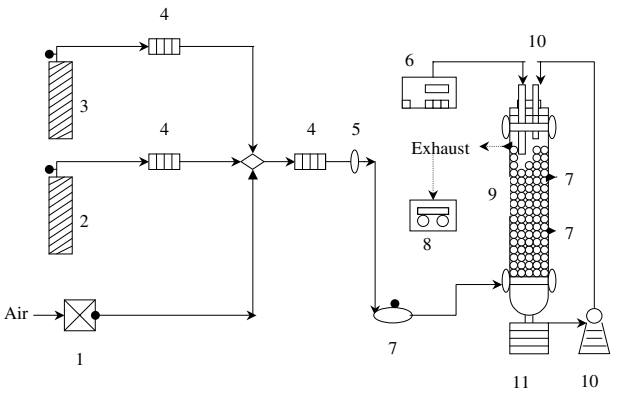

Figure 1. A schematic of the experimental set-up of the fluidized bed bioreactor. 1. air compressor; 2. H_2S gas cylinder; 3. NH_3 gas cylinder; 4. flow meter; 5. air filter; 6. pH meter; 7. sampling port; 8. single point monitor; 9. glass column; 10. pump; 11. nutrient tank.

The flow rates of wastegas were varied between 27 and 72 *l*/h (residence time: 36 to 96 sec) and the operating temperature was controlled at 30°C. The removal capacity experiments were processed after the 3-month operation.

Effect of Carbon Source for H_2S/NH_3 Removal

A similar bioreactor as indicated in Figure 1 was used. Inlet wastegas containing 15 ppmv of H_2S or NH_3 was supplied. The liquid flowrate, gas flowrate and operating temperature were controlled at 30 ml/min, 36 *l*/hr and 30°C, respectively. The pH values were ranged between 6.6–7.0. The circulating solutions with glucose or without glucose were conducted to evaluate the effect of carbon source to system's performance.

Design Criteria of Scale-up Biofilter

The emission limits of H_2S and NH_3 were targeted at 0.1 ppm or 1 ppm. The maximum inlet concentrations of H_2S and NH_3 to meet this effluent concentrations were determined at various retention time according to the following equation.[13]

$$\theta = \alpha \frac{(C_o - C_e)}{\frac{V_m \times C_{\ln}}{(K_s + C_{\ln})}} \tag{1}$$

where θ = retention time (min); C_o = inlet concentration (ppmv); C_e = outlet concentration (ppmv); K_s = apparent half-saturation constant (ppmv); V_m = maximum apparent removal rate (g-S or g-N/day/kg-bead); $C_{\ln}$ (ppm) = $(C_o - C_e)/\ln(C_o/C_e)$, logarithmic mean concentration of H_2S or

NH_3 at the inlet and outlet of the biofilter; and α = conversion coefficient (kg-bead ppm/g-S or g-N). Let C_e be 0.1 or 1 ppm in Eq (1), and the maximum C_o can be estimated at various retention times. The values of V_m and K_s could be obtained by modified Michaelis-Menten equation.[13]

Analytical Methods

$H_2S_{(g)}$ concentrations in the fluidized-bed bioreactor were measured either continuously by a Single Point Monitor (MDA Scientific, USA) ranging from 50 to 1500 ppb, or periodically by gas detector tubes (GASTEC, Japan) ranging from 1 to 100 ppm. $NH_{3(g)}$ concentrations in the fluidized-bed bioreactor were measured either continuously by a Single Point Monitor (MDA Scientific, USA) in the range of 0.01 to 10 ppm, or periodically by gas detector tubes (GASTEC, Japan) in the range of 5 to 100 ppm. Five grams (wet-weight) of beads were dissolved in 95 ml of 0.1 M sodium citrate solution and the calcium concentration of the solution was measured by AA (Hitachi_Z-8100).

RESULTS AND DISCUSSION

Effect of Buffer Capacity on Gel Structure

Since phosphate can chelate with calcium ion in the Ca-alginate bead and further destroy the structure of the gel, it is necessary to minimize the effect of phosphate salts in the fluidized-bed operation. Figure 2 indicates the effect of different buffer capacities of phosphate salts on gel structure. The ratio of Ca^{2+} release indicates the change of Ca^{2+} concentrations in the solution during the operation. Apparently, the Ca^{2+} release from the beads increased with the buffer capacity of the phosphate salts. As soon as the buffer capacity was over the critical point (i.e. 33.5 mM/pH), all calcium ions in the bead were released (release ratio = 1) and chelated by phosphate, and then gel structure was partially destroyed.

Table 1 indicates the average diameter of bead in different buffer capacity of phosphate solution after one-month shaking. Apparently, buffer capacity of less than 3.5 mM/pH had no significant effect on the size of the bead. However, higher buffer capacities caused beads to be swollen and evenly broken. During the procedure of immobilization, the net polymer (bead) is formed by crosslinking Ca^{2+} with alginate. In this reaction, the Ca^{2+} plays a role as gel-inducing agent. As bead contacts with phosphate salts, the calcium ion crosslinks with phosphate instead of alginate. The gel structure is destroyed slowly and the gel itself becomes swollen due to the Ca^{2+} release as well as the penetration of the water. If the concentration of the phosphate salts were further elevated to the critical point, the bead would be broken.

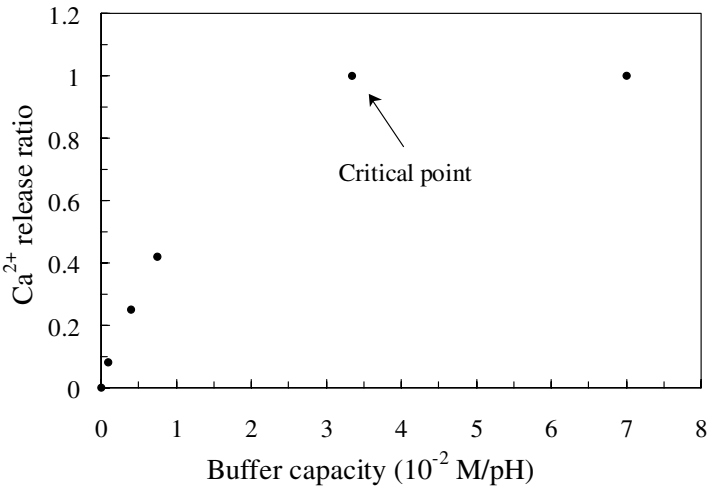

Figure 2. Effect of different buffer capacities of phosphate salts on gel structure and H_2S removal.

Table 1. Average Diameter of Ca-alginate Bead Stored in Different Phosphate Solution

Buffer Capacity (M/pH)	0	0.0007	0.0035	0.007	0.0335	0.07
Diameter (cm)	0.4	0.4	0.42	0.65	0	0

Characteristic of Physical Sorption for Odorous Removal

As shown in Figure 3a, gas removal efficiencies increase with the liquid flow rates whether H_2S or NH_3 gas is introduced. The maximal removal efficiency for H_2S and NH_3 were around 7% and 30%, respectively, in the operating liquid flowrates. The high NH_3's solubility than H_2S resulted in higher removal efficiency about four times. Similar gas removal efficiencies were found at liquid flow rates from 30 to 90 ml/min. To minimize the cost of energy and nutrition solution, the flow rate of liquid in the continuous experiment was set at optimal value of 30 ml/min. Figure 3b indicates that the effect of gas flowrate on gas removal by physical sorption (liquid absorption and bead adsorption). Apparently, removal efficiency decreased with increasing gas flowrate in the range of 36–150 *l*/h. Hence, the gas removal by physical sorption was limited by mass transfer. The sufficient residence time was necessary for gas removal by physical sorption. Figure 3c indicates that the effect of inlet concentration on gas removal in the range of 10–100 ppmv. Obviously, gas removal efficiencies increased with inlet gas concentrations. Dramatic effect on NH_3 removal was observed (efficiency from 15% upto 31%). Henry's law can explain the phenomenon. High gas concentrations result in high partial pressure and further increase the NH_3 concentration in the solution.

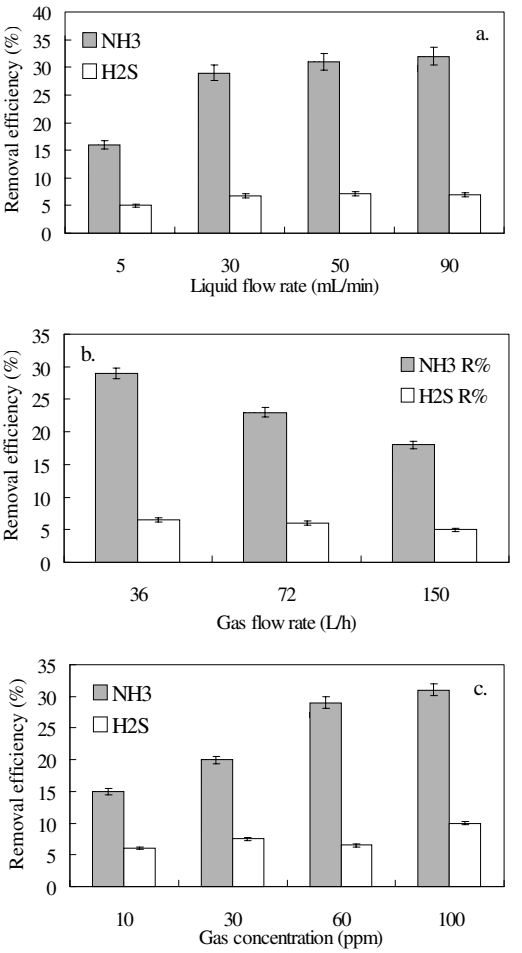

Figure 3. Characteristic of physical adsorption for H_2S or NH_3 removal. (a) effect of liquid flowrate. (b) effect of gas flowrate. (c) effect of inlet concentration.

Effect of Carbon Source for H_2S/NH_3 Removal

In the system the wastegas is removed by two ways. One is physical sorption by recirculated solution or alginate beads and the other is bioconversion by immobilized cells. Carbon sources are supplied to maintain the growth of heterotrophic bacteria, but H_2S and NH_3 oxidation by heterotrophic bacteria are supposed to be physiologically a detoxification process.[16] As shown in Figure 4, the breakthrough of H_2S concentration is appeared in the 9th day without glucose addition but NH_3's case delays to the 14th day. Apparently, higher solubility for NH_3 than H_2S resulted in the longer breakthrough time. In the case of glucose addition, the removal efficiency of NH_3 (97.4%) was higher than that of H_2S (95.2%). Hence, bioconversion other than sorption was mainly metabolized mechanism for

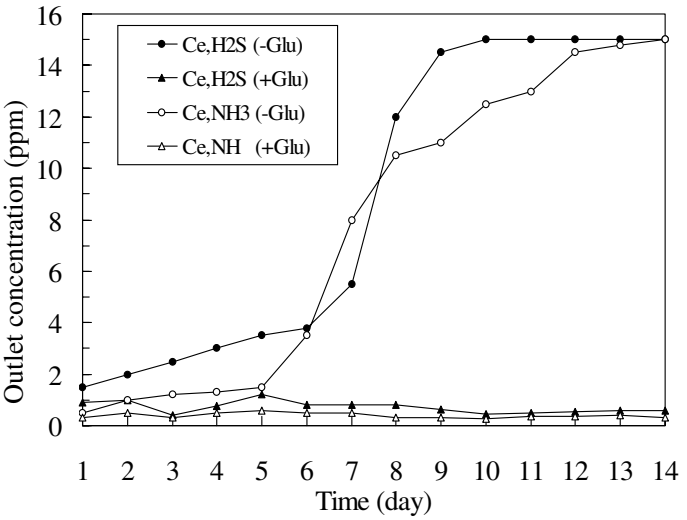

Figure 4. Effect of carbon source for H_2S/NH_3 removal in continuous system.

malodorous removal in this system. In a word, the addition of the carbon source facilitated to elevate the removal efficiency.

Relationship Between Inlet Concentration and Removal Capacity for H_2S and NH_3 Removal

Figure 5 indicates that relationships between inlet concentrations and removal capacities for H_2S and NH_3 removal at the various flow rates. As shown in Figure 5a, removal capacity increases with the inlet concentration. But, the different increasing tendencies were observed at the various flow rates (retention time). Removal capacities were proportional to inlet H_2S concentrations when the flow rate was controlled at 27 l/h. The removal curves raised up quickly and then leveled off when the flow rates were controlled at 54 or 72 l/h. In the cases, the average removal efficiency for H_2S about 65%. As shown in Figure 5b, removal capacity increases with the inlet concentration and flow rates are no significant effect on the increasing pattern. In the cases, the average removal efficiency for NH_3 was about 88%. Apparently, high NH_3 solubility favored the its removal and minimized mass-transfer limitation.

Design Criteria of Scale-up Biofilter

Estimations of the maximum inlet concentrations are important to apply the system in the field as well as satisfy current and prospective

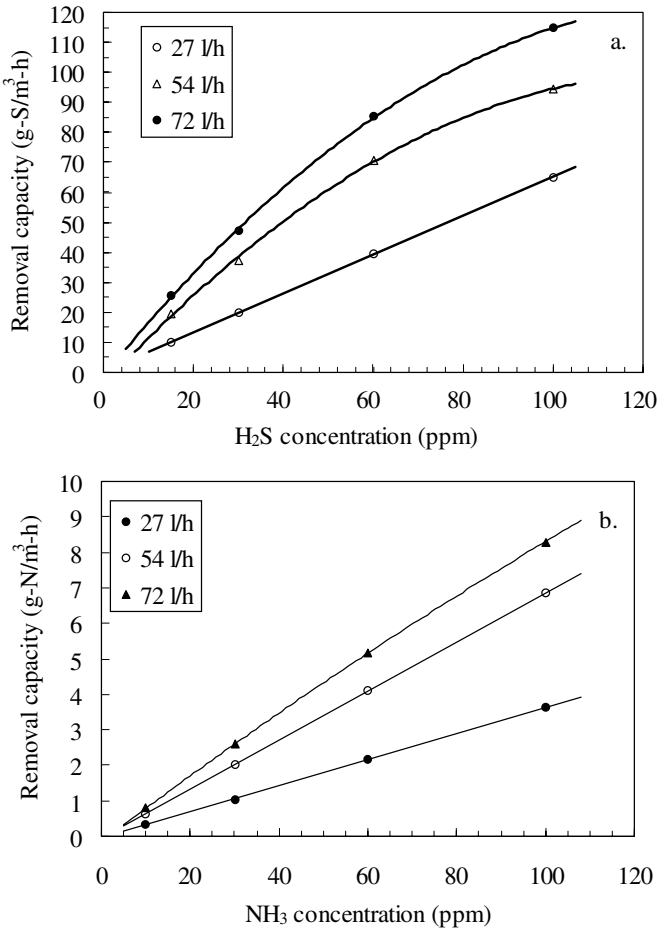

Figure 5. Relationship between inlet concentration and removal capacity. (a) H_2S removal (b) NH_3 removal.

emission limits. The currently ambient standards for H_2S and NH_3 in Taiwan are 0.1 and 1.0 ppm, respectively. Now, we suppose that the emission limits of the system for H_2S and NH_3 are just 0.1 and 1.0 ppm to estimate the maximum inlet concentrations. As shown in Figure 6, the allowable inlet concentration of NH_3 is about 45 ppm when the retention time maintains at 2 minutes. When the retention time extended for 2.25 minutes, the allowable inlet concentration increased upto 75 ppm (R% = 98.7%). For the case of H_2S, when the retention time was kept at 3 minutes, the maximum inlet concentration was 10 ppm. When the retention time extended for 4.5 minutes, the allowable inlet concentration was increased to 105 ppm. In this case, the theoretic removal efficiency was about 99.9%. Obviously, long retention time would minimize mass-transfer effect and favored H_2S and NH_3 removal. Because the concentrations of the waste gases containing H_2S and NH_3

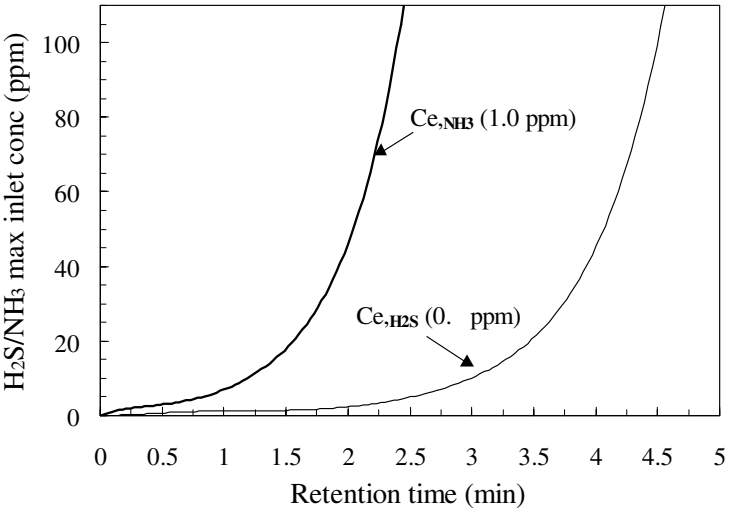

Figure 6. Design criteria of scale-up biofilter for H_2S or NH_3 removal.

released from the livestock farm in Taiwan were in the range of 10–60 ppm[3], the livestock farm is best treatment target.

CONCLUSION

The results of this experimental investigation have proved that the fluidized-bed bioreactor has a high potential to remove H_2S and NH_3, especially for livestock farm. Phosphate salts have succeeded to be applied in the system when the buffer capacity of the solution is controlled below 33.5 mM/pH. The high flowrate of the liquid and inlet gas concentration favor to gas removal. Additionally, the appropriate addition of the carbon source increases the bioconversion capacity and further elevates the removal efficiency. Removal capacity of the bioreactor increases with inlet gas concentration. The relationship between NH_3 removal and inlet concentration shows linear increase. However, the tendency of H_2S removal shows first raising and then flat. A dynamic mathematical model has developed and applied to predict the ideal inlet concentrations of H_2S and NH_3. The maximum inlet NH_3 and H_2S concentrations are determined at various retention times.

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