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# EFFECT OF INLET LOADING RATE ON THE ELIMINATION OF HYDROGEN SULFIDE AND AMMONIA IN IMMOBILIZED CELL BIOFILTERS

**Jung Hoon Kim[1], Eldon R. Rene[1], Seung Han Park[2] and Hung Suck Park[1,†]**

[1]Department of Civil and Environmental Engineering, University of Ulsan, P.O. Box 18 Ulsan 680-749, South Korea

[2]Safety Environmental Technology Team, SK Corporation Ltd, South Korea

**Abstract** : Biofiltration is a simple, effective, economically viable and the most widely used gas treatment technique for treating malodors at low concentrations and high flow rates. This paper reports the performance of two lab scale immobilized cell biofilters operated in continuous mode for hydrogen sulfide ($H_2S$) and ammonia ($NH_3$) removal. The removal efficiency (RE, %) and the elimination capacity (EC, $g/m^3 \cdot hr$) profiles were monitored by subjecting the biofilters to different loading rates of $H_2S$ (0.3 to 8 $g/m^3 \cdot hr$) and $NH_3$ (0.3 to 4.5 $g/m^3 \cdot hr$). The removal efficiencies were greater than 99% when inlet loading rate to the biofilters were upto 6 $gH_2S/m^3 \cdot hr$ and 4 $gNH_3/m^3 \cdot hr$ respectively. The performance of the biofilters were also ascertained by conducting shock loading studies at a loading rate of 10 $gH_2S/m^3 \cdot hr$ and 6 $gNH_3/m^3 \cdot hr$. The results from this study show high removal efficiency, good recuperating potential and stability of the immobilized microbial consortia to transient shock loads.

**Key Words** : Immobilized cell biofilter, Performance, Removal efficiency, Elimination capacity, Shock loading conditions

## INTRODUCTION

The malodors caused by emission of environmental pollutants like hydrogen sulphide ($H_2S$) and ammonia ($NH_3$) into the atmosphere has not only deteriorated air quality but has also affected normal societal activities. These malodors arise from the pulp and paper industry, food processing plants, common effluent treatment systems and night soil treatment plants[1,2]. The acute and chronic health effects of these compounds on human beings have been reported well in the literatures. The inhalation of low concentrations of $H_2S$ and $NH_3$ can cause headache, dizziness, nausea, cramps, staggering, excitability and drowsiness. Currently, the most commonly practiced end of pipe treatment systems like absorption, adsorption, photo-catalytic oxidation and thermal oxidation are energy intensive, use more chemicals and has operational complexity[3,4]. Hence, biological treatment processes based on microbial oxidation process are often considered to be desirable and can serve as suitable alternatives to physico-chemical systems[5,6]. Biofilters have proved to be a versatile treatment technique to treat these gases at low concentrations and high flow rates. The type of support matrix used in biofilters also affects the long term stability and performance of biofilters[6,7]. Amarsanaa et al[8] carried out a detailed investigation on the removal of toluene vapors in a novel synthetic packing material

† Corresponding author
E-Mail: parkhs@ulsan.ac.kr
Tel: +82-52-259-1050, Fax: +82-52-221-0152

(polyurethane foam, PUF + different adsorbents) for 60 days. The results from their study show that a combination of PUF and dolomite showed high removal rate ($V_m$ =11.04 g toluene/kg dry material/day) and saturation constant ($K_S$ = 26.57 ppm) when experiments were carried out at concentrations ranging from 10 to 160 ppm. Though many studies have reported the elimination of waste gases in biofilters having inert/natural support matrices, the use of synthetic and immobilized support media has gained popularity in recent years. Immobilization of microbes in support matrix such as alginate beads or suitable polymeric materials has been used extensively in wastewater treatment systems[9]. The main advantages of adopting immobilization techniques in biofiltration is to provide high cell concentrations, improve genetic stability, protection from shear damage and to enhance favorable microenvironment for microbes (nutrient gradients and pH).

The performance of biofilters in both laboratory and industrial scale are usually represented by their steady state removal efficiency and elimination capacities achieved with the target pollutant[10]. Therefore it is critical to evaluate the treating potential at different loading rates of $H_2S$ and $NH_3$ to understand the removal dynamics under steady state conditions. The removal efficiency of $H_2S$, methyl mercaptan, dimethyl sulfide and dimethyl disulfide was compared in an immobilized biofilter using *Thiobacillus novellas* as the dominant microorganism and it was observed that $H_2S$ (100% removal) could be removed better under all tested conditions[11].

The main objective of this research work was targeted to remove $H_2S$ and $NH_3$ as individual compounds in two simultaneously operated biofilter packed with a well acclimatized mixed culture immobilized in a suitable polymeric matrix. Moreover, one of the most frequent problems associated with long term operation in waste gas treatment technology is the sensitiveness and ability of the microorganisms to withstand shock loads. The investigations so far in immobilized cell biofilters have never addressed this discommoding problem. Hence the effect of shock loading on the performance of the two biofilters was also investigated at different loading rates.

## MATERIALS AND METHODS

### Microorganism and Media Composition

The mixed consortia was isolated from the sludge of a wastewater treatment plant (Ulsan, South Korea) and enriched suitably in batch reactors (Vol.-5 L) as ammonia and sulphate oxidizers. They were grown under well agitated conditions in a rotary shaker (150 rpm) at 30±2 ℃. The composition of the modified mineral salt media[12] is shown in Table 1. The nutrient media used for continuous removal experiments in the immobilized biofilters had the following composition: $MgCl_2 \cdot 6H_2O$: 0.2 g/L, $NaH_2PO_4$: 0.78 g/L, $Na_2HPO_4$: 0.89 g/L, $CaCl_2$: 0.00074 g/L, $FeSO_4 \cdot 7H_2O$: 0.01 g/L, $CuSO_4$: 0.00008 g/L and $NaHCO_3$: 1 g/L.

### Preparation of Immobilized Packing Media

After cultivation of the autotrophic ammonium oxidizers and sulfate oxidizers in separate batch systems at a pH of 7 and 30±2℃, the cells

Table 1. Composition of the mineral salt medium

| | Thiosulfate oxidizer medium | | Ammonia oxidizer medium | |
|---|---|---|---|---|
| Composition Unit : g/L *mg/L | $NH_4Cl$ | 0.02 | $(NH_4)_2SO_4$ | 0.47 |
| | $MgCl_2 \cdot 6H_2O$ | 0.01 | $MgSO_4$ | 0.25 |
| | $NaH_2PO_4$ | 0.06 | $NaH_2PO_4$ | 0.78 |
| | $Na_2HPO_4$ | 0.06 | $Na_2HPO_4$ | 0.89 |
| | $Na_2S_2O_3 \cdot 5H_2O$ | 0.40 | $CaCl_2$ | 0.74* |
| | $FeSO_4 \cdot 7H_2O$ | 0.01 | $FeSO_4 \cdot 7H_2O$ | 2.50* |
| | | | $CuSO_4$ | 0.08* |

were harvested by centrifugation (7500 g, 15 min) and then washed aseptically with distilled water. The resulting biomass contained ~3300 mg VSS/L of autotrophic ammonium and sulfate oxidizers respectively. The first step of media preparation involves mixing the purified cells with sterilized sodium alginate solution and then mixing them with 7.5 L of poly vinyl alcohol (PVA) solution. The resulting solution was injected in a mold tray, freeze gelled and by thawing, PVA beads (cubes) having a cell concentration of ~825 mg/L were obtained. The immobilized beads thus formed were packed in commercially available pall rings and then activated by flushing with distilled water.

### Experiment Setup

The schematic of an individual biofilter used in this study is shown in Figure 1. The biofilters were constructed with acrylic cylinders having an effective volume of 8.5 L. The pall rings containing the immobilized microbial cells were randomly packed into the biofilter to provide a packed bed volume of 6.5 L. The biofilter was operated in a down flow mode and provided with appropriate sampling points at the inlet and outlet of the filter bed. A mixing chamber fitted with baffles and flow regulators were provided at the inlet of the biofilter to enhance the mixing characteristics of $H_2S$ and $NH_3$. The inlet $H_2S$ and $NH_3$ concentrations were varied from 5 to 150 ppm, while the flow rates were varied to give an empty bed contact time (EBCT) of 51 and 32 sec respectively. The nutrient recycle system provided the essential nutrients necessary to sustain microbial activity. The nutrient solution was periodically sprayed through a nozzle from the top of the biofilter at the rate of 500 mL/min at intervals of 30 min each.

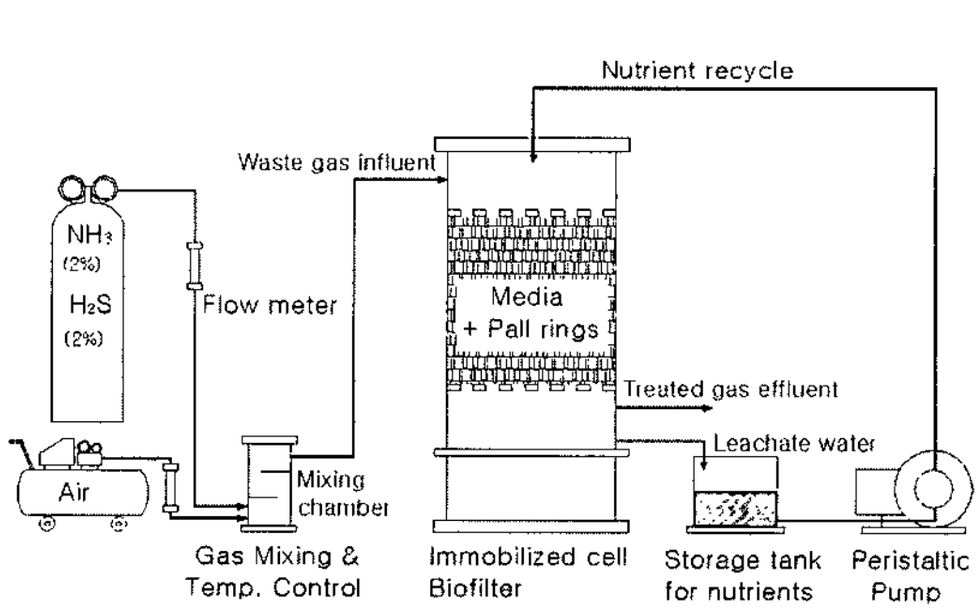


Figure 1. Schematic of the laboratory scale immobilized cell biofilter

### Analytical Methods

Gas phase concentrations of $NH_3$ were measured using gas detector tubes (GASTEC, Japan), while the concentration of $H_2S$ was measured by IR Gas Detector (GA 94A1-Geotechnical Instruments, UK).

## RESULTS AND DISCUSSION

### Effect of Inlet Loading Rate

Biofiltration of $H_2S$ and $NH_3$ were carried in two biofilters operated in parallel, over a period of 3 months to evaluate the performance of the immobilized cells to changes in inlet loading rates. The inlet loading rate was varied with time depending on the performance of the system, i.e, when the outlet concentration in the biofilters was below 1 ppm. During every step increase in the loading rates, it was observed that the biofilters took a few days to adapt to the new concentration and reached a new steady state value shortly. Thus the loading rates were varied in 8 steps for the biofilter treating $H_2S$, and in 13 steps for the biofilter treating $NH_3$. The results from this study are shown in Figure 2 and 3 respectively. The inlet loading rates to the two biofilters were varied between 0.3 to 8 $gH_2S/m^3 \cdot hr$ and 0.3 to 4.5 $gNH_3/m^3 \cdot hr$ respectively over a period of 66 days. During the first 5 days, when the loading rates were less than 1 $gH_2S/m^3 \cdot hr$ for the biofilter treating $H_2S$, the RE increased gradually from 45 to nearly 100%, which indicated good activity of the immobilized cells to treat $H_2S$. However, the biofilter treating $NH_3$ showed steady and consistent removal even during the acclimatization step. The loading rate of $H_2S$ was gradually increased to 1.7 $g/m^3 \cdot hr$ on the $6^{th}$ day of continuous operation. The response was a sudden decline in the RE from 100% to

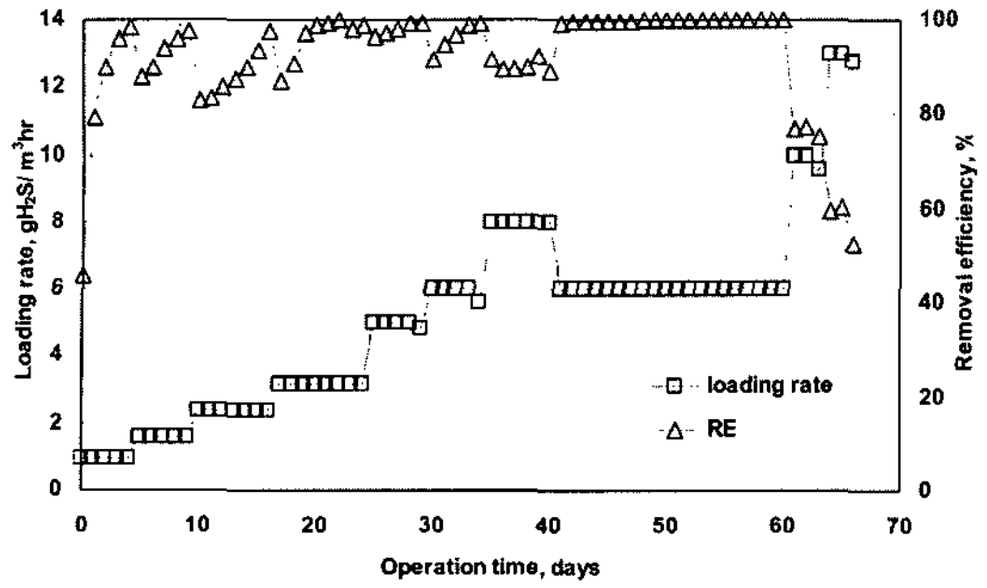


Figure 2. Influence of inlet loading rate on the removal efficiency of the biofilter treating $H_2S$.

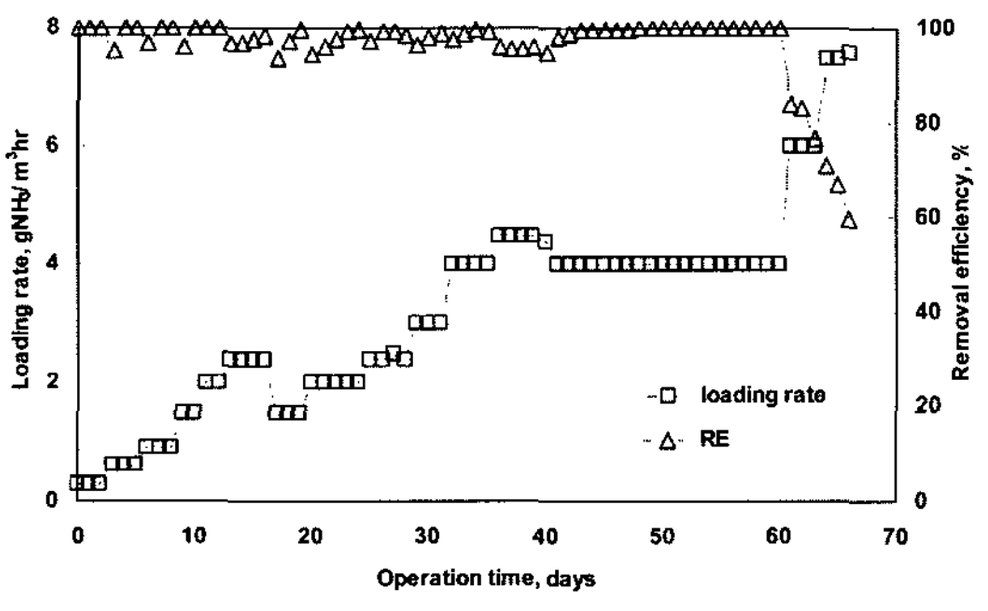


Figure 3. Influence of inlet loading rate on the removal efficiency of the biofilter treating $NH_3$.

85% followed by a new steady state at the end of the 10th day where the RE was 99%. However, when the loading rate was increased to 2.5 $g/m^3 \cdot hr$, the RE dropped again to nearly 80%. The response to the immobilized cells were rapid and evident from the decline of RE and the same performance (99%) was later reached within 5 days of continual operation at the given condition. The inputs were changed in 7 steps up to a loading rate of 8 $gH_2S/m^3 \cdot hr$, where the RE remained constant at 82%. In general $H_2S$ metabolism by heterotrophic sulfur oxidizing bacteria is a detoxification process and high inlet concentrations have often reported to decrease the $H_2S$ removal efficiency[13]. In a similar kind of study, a *Thiobacillus* sp. used in biofilter to remove $H_2S$ under autotrophic and mixotrophic environments showed nearly 99.5% removal[14]. On the 39th day, the loading rate was held constant at 6 $gH_2S/m^3 \cdot hr$, and the RE was 100%. During this step of operation, under the same loading rate, the concentration and flow rate (EBCT-51 and 32 sec) was varied intermittently and it was found that the RE remained unchanged irrespective of these variations.

In the case of the second biofilter handling $NH_3$, during the first 8 days, when the loading rates were less than 1 $gNH_3/m^3 \cdot hr$ the RE was nearly 100%. These removal profiles indicated that the immobilized cells possessed good activity with steady and consistent removal even during the beginning of the experiments. The loading rate of $NH_3$ was gradually increased to 2.5 $gNH_3/m^3 \cdot hr$ on the 14th day of continuous operation. The response was a sudden decline in the RE from 100% to 96% followed by a new steady state at the end of the 16th day where the RE was 98%. Hence, the loading rate was decreased to 1.7 $gNH_3/m^3 \cdot hr$ and subsequently increased in small time steps to a maximum of 4.5 $gNH_3/m^3 \cdot hr$. The biofilter RE profiles displayed minor ameliorating fluctuations due to step increase in loading rate between 1 to 4.5 $gNH_3/m^3 \cdot hr$. At a loading rate of 4.5 $gNH_3/m^3 \cdot hr$, the RE remained constant at 100%. During this step of operation, under the same loading rate, the concentration and flow rate (EBCT-51 and 32 sec) was varied intermittently and the biofilter was able to maintain steady state removal profiles. Immobilized biofilter systems have also been found very effective to treat mixtures of $H_2S$ and $NH_3$ with immobilized cells of *Thiobacillus thioparus, Nitrosomonas europaea, Arthrobacter oxydans and Pseudomonas putida* and inhibition/synergistic effects have been reported[12]. After 60 days of operation, the inlet loading rates to both the biofilters were increased significantly by varying both the concentration and flow rate to values as high as 13 $g/m^3 \cdot hr$ for the biofilter handling $H_2S$. It was found that there was a noticeable decrease in the RE values. Chung et al[13] evaluated the effects of operational factors such as retention time, temperature and inlet concentration on the performance of a biofilter packed with *Thiobacillus thioparus* immobilized with calcium

alginate pellets and found an optimal S-loading of 25 $g/m^3 \cdot hr$. The RE was 52 % at an EBCT of 32 sec for the biofilter treating $H_2S$, while at a loading rate of 8 $gNH_3/m^3 \cdot hr$ (EBCT-32 sec) the RE was nearly 60%. Pagans et al[15] reported removal efficiencies greater than 96% at loading rates between 0.8 to 6.7 $gNH_3/m^3 \cdot hr$ in a compost biofilter handling $NH_3$ and observed similar EC profiles at a loading rate of 2 $gNH_3/m^3 \cdot hr$. The results from this study further delineate that, at similar loading rates of $H_2S$ and $NH_3$ (5 $g/m^3 \cdot hr$), $H_2S$ was removed better (100%) than $NH_3$ (92%).

The elimination capacity, which reflects the capacity of the biofilter to remove the pollutants, is plotted as a function of the inlet $H_2S$ and $NH_3$ loading rate in Figure 4. It could be seen that, a near linear relation between the two variables was observed till an inlet load of 8 $gH_2S/m^3 \cdot hr$ and 4.5 $gNH_3/m^3 \cdot hr$. However, for higher initial concentration and higher flow rate used in the later steps, the elimination capacity of the filter bed increased at a slower rate, becoming nearly constant at inlet loads beyond 8 $gH_2S/m^3 \cdot hr$ and 6 $gNH_3/m^3 \cdot hr$. This can be attributed to the diffusion and reaction limitation steps mentioned by Ottengraf[16] and by the following mechanism; smaller pore sizes in the media could restrict the accessibility of nutrients on the pore surface by the microorganisms, while at large pore size the specific surface area could have been the limiting factor.

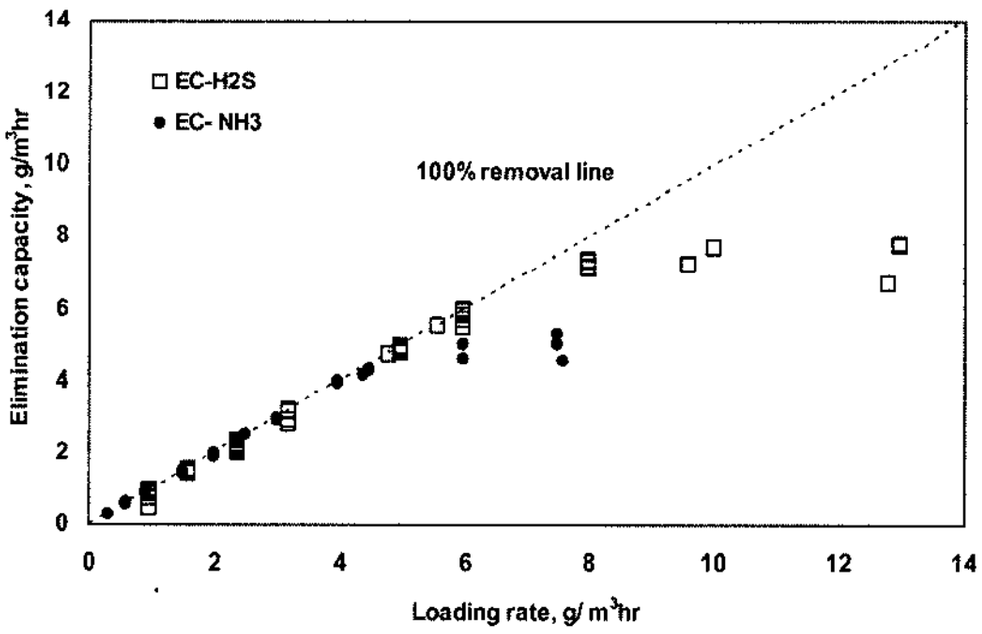


Figure 4. Influence of inlet loading rate on the elimination capacity of the biofilters treating $H_2S$ and $NH_3$.

## Effect of Shock Loading on the Performance of Biofilters

An active biofilter should be able to handle such adverse shock loading situations in order to provide maximum removal of the target contaminant[6]. However, in immobilized biofilter systems, the dynamics and response of the microorganisms to fluctuating pollutant loads has not been experimentally investigated. The transient behaviors of the two biofilters were monitored by subjecting fluctuating inlet loads. The results from this study are shown in Figure 5. for the biofilters treating $H_2S$ and $NH_3$ respectively.

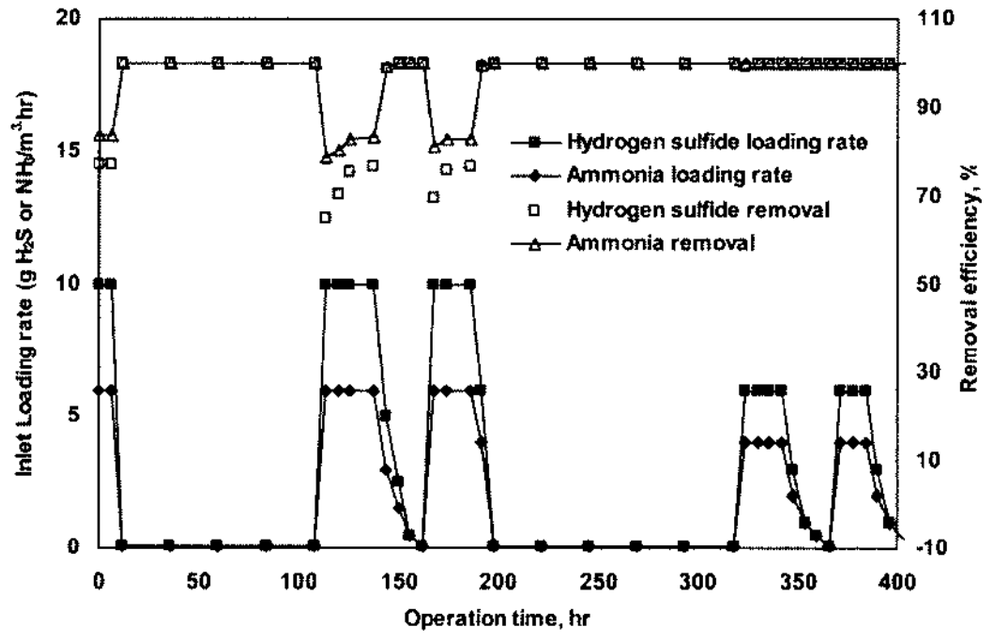


Figure 5. Effect of shock loading on the performance of immobilized cell biofilters.

With an increase in the inlet $NH_3$ load from 4.5 to 6 $gNH_3/m^3 \cdot hr$ the RE decreased significantly from >98% to 84%. For the next 5 days, both the concentration and flow rate were reduced to give an inlet load of 0.05 $gNH_3/m^3 \cdot hr$, where the RE remained constant at 100%. When the next shock load was done at 6 $gNH_3/m^3 \cdot hr$, the RE dropped to nearly 78%, and this value increased slowly to about 83%. The inlet load was now slowly decreased to 0.05 $g/m^3 \cdot hr$ over a period of 4 days and held constant for 6 days. The RE was 100% during this phase of operation. Subsequently during the next intermittent shock loads at 4 $gNH_3/m^3 \cdot hr$, the biofilter showed no irregular variations in the RE profile, thereby remaining constant at 100%. The EC values were between 0.05 to 5.5 $gNH_3/m^3 \cdot hr$, which is in close comparison with

the values observed during various previous steps of biofilter operation. These values are also comparable to the performance of biofilters packed with natural packing materials. Chen et al[17] *investigated the response of two biofilters* to variations of inlet loading rate, periods of non-use and inlet concentration pulse by packing them with mixtures of compost/perlite (5:1) and dry sludge/granular active carbon (5:1) to treat $NH_3$ gas. The biofilters were found to respond rapidly by attaining original removal rates (288 and 243 g $NH_3/m^3$·day) within 6-12 hr.

Similar studies were also carried out in the biofilter treating $H_2S$ at inlet loads corresponding to 0.1 to 10 g$H_2S/m^3$·hr. During the first shock load of 10 g$H_2S/m^3$·hr, the RE was 78%, however this value was 100% when the loading rate was reduced to 0.1 g$H_2S/m^3$·hr. While repeating experiments at a shock load of 10 g$H_2S/m^3$·hr, the RE reduced to 64% and slowly increased to 76%. The response of the biofilter was fast as seen from the immediate decrease in RE at high loading rates. However during the later phase of operation, shock loading experiments were carried out at 0.1, 0.5, 3 and 6 g$H_2S/m^3$·hr where the RE was consistently greater than 99%. In both the biofilters, the restoration time at high shock loads did not exceed 12 to 24 hr. This supports the fact that immobilized cells in the biofilter was quite stable and restored removal efficiencies rapidly irrespective of the fluctuations. Corroborating this behavior is the presence of macro and micronutrients which maintains the activity of the cells. Additionally, mechanisms related to diffusion and micro reactions have been reported in the literature to primarily influence the increasing/decreasing RE profiles in biofilters during shock loading conditions[18].

## CONCLUSIONS

The potential application of immobilized cell biofilters for $H_2S$ and $NH_3$ removal was assessed in continuous mode at different loading rates and process conditions. The removal efficiencies for the two lab scale biofilters during different steps of operation varied between 40 to 100% and this depended on the flow rate and the inlet concentration. The recuperating ability of the immobilized cells in the biofilter to fluctuations in the process conditions indicates the stability, sensitiveness and activity of the immobilized cells. The removal efficiencies during shock loading experiments were 78 to 100% at inlet loading rates of 0.05 to 6 g$NH_3/m^3$·hr, while it was 65 to 100% at inlet loading rates of 0.1 to 10 g$H_2S/m^3$·hr. The results from this study can be extended further to optimize and design large scale immobilized cell biofilters for industrial applications.

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