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

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Abstract : Biofiltration is a simple, effective, economically viable and the most widely used gas treatment
 technique for treating malodor 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
 (H₂S) and ammonia (NH₃) removal. The removal efficiency (RE, %) and the elimination capacity (EC,
g/m³·hr) profiles were monitored by subjecting the biofilters to different loading rates of H₂S (0.3 to 8
g/m³·hr) and NH₃ (0.3 to 4.5 g/m³·hr). The removal efficiencies were greater than 99% when inlet loading
 rate to the biofilters were up to 6 gH₂S/m³·hr and 4 gNH₃/m³·hr respectively. The performance of the
 biofilters were also ascertained by conducting shock loading studies at a loading rate of 10 gH₂S/m³·hr and
 6 gNH₃/m³·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 (H₂S) and ammonia (NH₃) 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 plants¹.² 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 H₂S and NH₃ 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 complexity³.⁴. Hence, biological treatment processes based on microbial oxidation process are often considered to be desirable and can serve as suitable alternatives to physico-chemical systems⁵.⁶. 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 biofilters⁶.⁷. Amarsanaa et al⁸ carried out a detailed investigation on the removal of toluene vapors in a novel synthetic packing material.
(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 ($V_m = 11.04 \text{ g toluene/kg dry material/day}$) and saturation constant ($K_s = 26.57 \text{ ppm}$) 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$_2$S and NH$_3$ to understand the removal dynamics under steady state conditions. The removal efficiency of H$_2$S, methyl mercaptan, dimethyl sulfide and dimethyl disulfide was compared in an immobilized biofilter using Thiobacillus novellus as the dominant microorganism and it was observed that H$_2$S (100% removal) could be removed better under all tested conditions.\(^{11}\)

The main objective of this research work was targeted to remove H$_2$S 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 sensitivity 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°C. The composition of the modified mineral salt media is shown in Table 1. The nutrient media used for continuous removal experiments in the immobilized biofilters had the following composition: MgCl$_2$$\cdot$6H$_2$O: 0.2 g/L, NaH$_2$PO$_4$: 0.78 g/L, Na$_2$HPO$_4$: 0.89 g/L, CaCl$_2$: 0.00074 g/L, FeSO$_4$$\cdot$7H$_2$O: 0.01 g/L, CuSO$_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°C, the cells

<table>
<thead>
<tr>
<th>Table 1. Composition of the mineral salt medium</th>
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<tr>
<td><strong>Thiosulfate oxidizer medium</strong></td>
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<tr>
<td>NH$_4$Cl</td>
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<tr>
<td>MgCl$_2$$\cdot$6H$_2$O</td>
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<td>NaH$_2$PO$_4$</td>
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<td>Na$_2$HPO$_4$</td>
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<td>Na$_2$SO$_4$$\cdot$5H$_2$O</td>
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<td>FeSO$_4$$\cdot$7H$_2$O</td>
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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 H₂S and NH₃. The inlet H₂S and NH₃ 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.

**Analytical Methods**

Gas phase concentrations of NH₃ were measured using gas detector tubes (GASTEC, Japan), while the concentration of H₂S was measured by IR Gas Detector (GA 94A1-Geotechnical Instruments, UK).

**RESULTS AND DISCUSSION**

**Effect of Inlet Loading Rate**

Biofiltration of H₂S and NH₃ 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 H₂S, and in 13 steps for the biofilter treating NH₃. 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 gH₂S/m²-hr and 0.3 to 4.5 gNH₃/m²-hr respectively over a period of 66 days. During the first 5 days, when the loading rates were less than 1 gH₂S/m²-hr for the biofilter treating H₂S, the RE increased gradually from 45 to nearly 100%, which indicated good activity of the immobilized cells to treat H₂S. However, the biofilter treating NH₃ showed steady and consistent removal even during the acclimatization step. The loading rate of H₂S was gradually increased to 1.7 g/m³-hr on the 6th day of continuous operation. The response was a sudden decline in the RE from 100% to
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$^3$/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$^3$/hr on the 14$^{th}$ 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 16$^{th}$ day where the RE was 98%. Hence, the loading rate was decreased to 1.7 gNH$_3$/m$^3$/hr and subsequently increased in small time steps to a maximum of 4.5 gNH$_3$/m$^3$/hr. The biofilter RE profiles displayed minor ameliorating fluctuations due to step increase in loading rate between 1 to 4.5 gNH$_3$/m$^3$/hr. At a loading rate of 4.5 gNH$_3$/m$^3$/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$_2$S and NH$_3$ with immobilized cells of Thiothrix thiooxidans, Nitrosomonas europaea, Arthrobacter oxidans and Pseudomonas putida and inhibition/synergistic effects have been reported$^{[2]}$. 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$^3$/hr for the biofilter handling H$_2$S. 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 Thiothrix thiooxidans immobilized with calcium.
alginate pellets and found an optimal S-loading of 25 g/m$^3$·hr. The RE was 52 % at an EBCT of 32 sec for the biofilter treating H$_2$S, while at a loading rate of 8 gNH$_3$/m$^3$·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$^3$·hr in a compost biofilter handling NH$_3$ and observed similar EC profiles at a loading rate of 2 gNH$_3$/m$^3$·hr. The results from this study further delineate that, at similar loading rates of H$_2$S and NH$_3$ (5 g/m$^3$·hr), H$_2$S 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$_2$S 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$_2$S/m$^3$·hr and 4.5 gNH$_3$/m$^3$·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$_2$S/m$^3$·hr and 6 gNH$_3$/m$^3$·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.

**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$_2$S and NH$_3$ respectively.

![Figure 5. Effect of shock loading on the performance of immobilized cell biofilters.](image)

With an increase in the inlet NH$_3$ load from 4.5 to 6 gNH$_3$/m$^3$·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$^3$·hr, where the RE remained constant at 100%. When the next shock load was done at 6 gNH$_3$/m$^3$·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$^3$·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$^3$·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$^3$·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.\(^7\) 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\(_2\)S at inlet loads corresponding to 0.1 to 10 gH\(_2\)S/m\(^3\)-hr. During the first shock load of 10 gH\(_2\)S/m\(^3\)-hr, the RE was 78%, however this value was 100% when the loading rate was reduced to 0.1 gH\(_2\)S/m\(^3\)-hr. While repeating experiments at a shock load of 10 gH\(_2\)S/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 gH\(_2\)S/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\(^8\).

CONCLUSIONS

The potential application of immobilized cell biofilters for H\(_2\)S 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 gNH\(_3\)/m\(^3\)-hr, while it was 65 to 100% at inlet loading rates of 0.1 to 10 gH\(_2\)S/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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