行政院國家科學委員會專題研究計畫　成果報告

畜舍揮發性有機臭氣之生物過濾研究(3/3)

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計畫主持人：廖中明

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行政院國家科學委員會專題研究計畫執行進度報告

Biofiltration of Livestock Generated Odor Causing VOCs (3/3)

計畫編號：NSC 91-2313-B002-295
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主 持 人：廖中明

摘要

第三年研究工作為進行一實驗室中微生物對畜舍產生氨氣之生物衰減實驗。氨氣為豬舍中主要氣態有害物之一，形成豬舍內甚大之污染問題並造成地下水硝化作用，對動物及人體亦具有相當之健康危害。本研究目的為，在無控溫下以低廉、結合多樣性微生物之無機及有機生物濾床形成之過濾器來減低豬舍惡臭。本研究使用泥煤及無機媒床為生物過濾材，將氣體灌入使通過此生物過濾管柱。結果顯示當室溫介於 27.5±4.5°C，氣流速率介於 0.03–0.06 m^3 h^{-1} 時，氨氣濃度 200 ppm 之生物移除效率明顯介於 99–100%間。此實驗過程下，氨氣於生物過濾小於 1 ppmv (0.707 mg m^{-3})時溢散，生物過濾性能於此廣大範圍溫度間，長期之生物過濾系統可以有效之低成本操作而達到去除效率。本研究中所獲得之最大氨氣移除效率之去除容量為 2.217 g m^{-3}。本生物過濾器具有高硝化效率並可於減壓情況下控制氨氣污染程度，由實驗起始操作至終結反應來看，本生物過濾氣之生物膜具有一優秀之穩定性。

關鍵字：氨氣、生物過濾、微生物衰減、移除效率

Abstract

We contacted a laboratory test for microbial degradation of livestock-generated ammonia in this year. Ammonia, one of the gases produced in greatest volume from swine waste, causes one of the biggest pollution problems in swine farming resulting in ground water nitrification and adverse effects on animal and human health. Our objective is to neutralize malodor by using biofilters packed with inexpensive inorganic and organic packing material combined with multicultural microbial load at uncontrolled temperatures. Peat and inorganic supporting materials were used as biofiltration matrix packed in a perfusion column through which gas was transfused. Results show the ammonia removal significantly fell in between 99-100 % when ammonia concentration of 200 ppmv was used at different gas flow rates ranged from 0.030 – 0.060 m^3 h^{-1} at a fluctuating room temperature of 27.5±4.5°C. Under these conditions, the emission concentration of ammonia that is liberated after biofiltration is less than 1 ppmv (0.707 mg m^{-3}) over the period of our study, suggesting the usage of low-cost biofiltration systems for long-term function is effective at wider ranges of temperature fluctuations. The maximum (100%) ammonia removal efficiency was obtained in this biofilter was having an elimination capacity of 2.217 g m^{-3} h^{-1}. This biofilter had high nitrification efficiencies and hence controlled ammonia levels with the reduced backpressure. The response of this biofilter to shut down and start up operation showed that the biofilm has a superior stability.

Keywords: Ammonia; Biofiltration; Microbial degradation; Removal efficiency

Introduction and Objectives

Ammonia, hydrogen sulfide and carbon dioxide are the three main pollutants released from swine house facilities.[1] Ammonia is one of the gases produced in greatest volume from swine waste causing one of the biggest pollution problems in swine farming. During summer and winter the ammonia emitted from swine house per animal per day is approximately 8.7 and 6.2 g, respectively.[2] Countries like Taiwan where land is scarce and hog farming is intensive face a major a malodor threat. Taiwan's swine production (19.07%) in 1999 was estimated to be nearly 61.5 billion NT dollars worth when compared to other livestock products (39.44%).[3]

A survey of about 8000 randomly selected farmers in some European countries demonstrated that hog farmers are at the highest risk (27.3%) among agricultural workers for the development of work related respiratory symptoms.[4] It was estimated that at least 60% of swine confinement workers have acute or sub-acute respiratory symptoms on exposure to the work environment; irritation of the nose, eye, throat and stuffy nose due to poor air quality.[5] The spacecraft maximum allowable concentrations (SMACs) values for ammonia for exposure periods of 1 and 24 hours are 30ppmv and 20ppmv, respectively. For an exposure period of 1 week to 6 months, the SMAC value is 10 ppmv.[6]

Due to some of the advantages of biofilters such as large removal efficacy, low installation cost, low process-maintenance cost and uniform consistency it is increasingly being acceptable in the European community. To a large extent it has been successfully used to control malodor and organic and inorganic pollutants that are toxic to human and animal life. Biofiltration of ammonia has been evaluated using heterotrophic bacteria *Arthrobacter oxydans* CH8, (isolated from hog waste water lagoon) and in comparison with *Nitrosomonas europaea* performed better in treating elevated concentrations of ammonia.[7,8] Huang[9] reported the usage of co-immobilized bacterial cells in removing hydrogen sulfide and ammonia together at appropriate proportions.

In Taiwan, the EPA has set an ambient air standard at 1 ppm for ammonia. In view of these stringent control measures, continuous improvement in selecting packing materials, microbial load and gaining control over the process parameters are considered highly necessary.

The objective of this investigation was to determine the performance and the removal efficiency of a low-cost continuously operated biofilter at a relatively high ammonia inlet concentration in a uncontrolled room temperature condition and the operation dynamic of the packed bed reactor system over long durations.

Materials and Methods

Organism and Culture Medium

To gain access to a wide range of chemoautotrophic bacteria particularly the ammonia oxidizing bacteria and the nitrite-oxidizing bacteria, soil harboring activated sludge from animal house facility was collected. Cells were harvested washed and transferred in LB Medium consisting of tryptone 1%; yeast extract 0.5%; NaCl 0.5%; aerated heavily under agitation in 200-rpm orbital shaker at 25°C for 48 hours. Since effective ammonia oxidation takes place at a pH above 7.5, we acclimated these microbes by maintaining their growth at a pH of 7.5 to increase their efficiency. Effect of nitrite on ammonia-oxidizing bacteria (AOB) suggests an ecological advantage for ammonia oxidizers to grow in consortia with nitrite-oxidizing bacteria (NOB). The growth and decay of AOB supplies nitrite and organic compounds that can serve as growth substrates for NOB and heterotrophic bacteria, respectively. Hence, ammonia oxidizers may be able to initiate biofilm formation in ammoniated distribution systems and provide conditions amenable to the development of a diverse microbial community aiding effective ammonia degradation.

Filter Materials

To support the growth of a wide range of chemoautotrophic bacteria, peat moss (91% organic) was selected. Perlite (inorganic) and vermiculite (inorganic) were incorporated to provide high aeration and water retention for long durations, respectively. This combination was preferred to eliminate the addition of water at frequent intervals, which is necessary to maintain adequate moisture content in the biofilter. Both supporting inert inorganic material serves to increase the bed porosity and to ensure more homogenous gas distribution across the perfusion column.

Keeping this in view, two types of packing material for the biofilter was meticulously designed. First reactor was designed to hold a mixture of peat moss, perlite (Number 3) and vermiculite (Number 2) at a ratio 3:1:1. The second reactor was designed to hold a mixture of peat moss and polystyrene beads of less than 3 mm size in the ratio 3:2. Chemoautotrophic bacteria obtained from activated sludge were harvested in buffered LB Medium (pH 7.5), mixed with filter material and packed in both the perfusion columns (reactors) simultaneously.

Experimental Set-Up

Aerobic up flow biofilter was used in our study. The perfusion column is made up of transparent polyacrylic tube with an internal diameter of 5 cm. The perfusion column was packed to height of 50 cm. The filter material was supported by a perforated plate at the bottom through which the gas was evenly distributed. One sampling port drilled on the perfusion column on the top was sealed by soft polyvinyl chloride septa mend for outlet gas analysis. Ammonia was passed through the packed bed at different flow rates and at different biofilter height. Concentrations of gas samples were analyzed from inlet and outlet ports at different time intervals. Although humidification of waste gas is considered most critical for effective treatment, here it was not considered necessary due to the inability of ammonia in stripping moisture from the supporting material. This bioprocess was investigated at fluctuating room temperatures of 23° - 32°C.

TABLE 1. Physical and chemical properties of the biofilter materials

Property	Range
Coarseness	< 20 mm particles
Density	178 kg m^{-3}
Moisture content	60 – 70%
pH	7.5
Carbon content	45%
Nitrate nitrogen	2.5%
Ammonium nitrogen	7.5%
Phosphorous	8%
Potassium	16%
Total sulfur	0.03%
Water capacity	74%
Volume of pores	95%
Water retention	9 g g^{-1}

Analytical Methods

Ammonia gas concentrations were analyzed using portable ammonia detector (GfG, Dortmund, Germany) at room temperature. The retention time of ammonia was less than a second.

Results and Discussion

The physical and chemical properties of the filter bed material are presented in Table1. The nutrients presented in the filter supported the growth of the microorganisms partially.

In order to support the growth of the microorganisms within the packed bed, filtered airflow at 60 L h^{-1}, was continuously provided for 48 hours through a compressor to both the reactors to achieve partial growth. In order to acclimatize the microbial population, ammonia at a concentration of 100 ppmv was transfused at 0.006 m^3 h^{-1} through the reactors for a period of 5 days. Distinctive performance of the two reactors show the attainment of stabilized state with high removal efficiency of ammonia, which manifests high microbiological activity in the filter (Fig. 1).

Since our aim was to imitate an ongoing natural emission process from livestock facilities, we neither heated nor cooled ammonia before treatment. Also considering the fact that animal responses at 100 to 200 ppm induces sneezing, salivation and loss of appetite followed by respiratory diseases, an inlet concentration of 200 ppmv of ammonia at a flow rate 500 cc per minute was considered

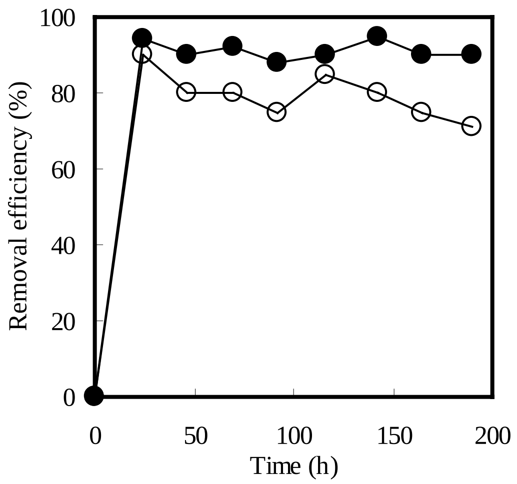

FIGURE 1. Steady state performance of the biofilters (first biofilter: peat, perlite and vermiculite; second biofilter: peat and polystyrene spheres) both having a filter bed height of 50cms in between 23°C – 32°C.

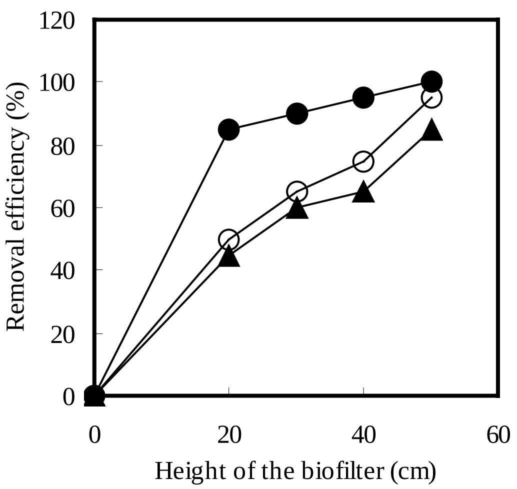

FIGURE 2. Removal efficiency of the first biofilter (peat, perlite and vermiculite) at different bed heights for 200 ppmv ammonia in between 23°C – 32°C.

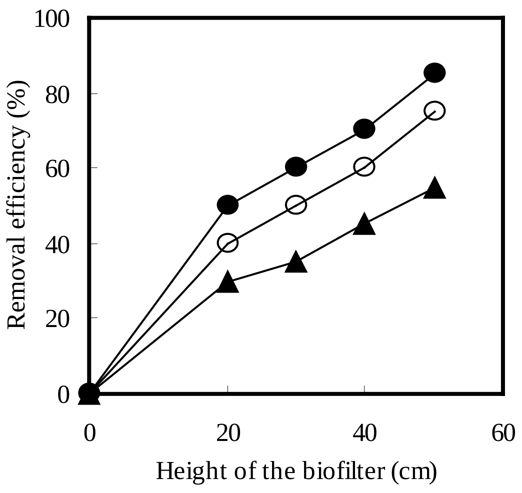

FIGURE 3. Removal efficiency of the second biofilter (peat and polystyrene spheres) at different bed heights for 200 ppmv ammonia in between 23°C – 32°C.

vital for our investigation. Based on earlier reports and comparing other VOC removal, we selected four different perfusion column (bed) heights for our investigations: 20, 30, 40, and 50 cm.

Effects of Filter Bed Type

Peat, Perlite and Vermiculite. The typical performance of the bed type of biofilter containing peat, perlite and vermiculite, where the removal efficiencies are plotted against the depth of the biofilter is shown in Fig. 2. The removal efficiency showed a distinct variation along the height of the filter. At high gas flow rates the residence time being inadequate; the removal efficiency did not remarkably decrease indicating biodegradation constraint of the biofilm. At a gas concentration of 200 ppmv with flow velocity of 0.030 m^3 h^{-1} when passed through a bed height of 50cm eliminated ammonia completely indicating a highly efficient consortium of microbial population mainly consisting of ammonia oxidizers and nitrite oxidizers were actively degrading ammonia sufficient to correspond the gas flow velocity.

Only 80% removal was achieved at a gas flow rate of 0.060 m^3 h^{-1} at the same bed height indicating the removal efficiency had decreased rapidly with an increase in the gas flow velocity. Hodge and Devinny[10] have confirmed the formation of organic acids in the biofilter.

Peat and Polystyrene Spheres. Deshusses *et al.*[11] used compost and polystyrene spheres as packing material in biofilters for the degradation of methylethyl ketone and methyl isobutyl ketone resulting in 98% removal efficiency. Keeping this in view, we selected 3 mm polystyrene spheres as packing and supporting material for our second reactor. The characteristic presentation of the second type of biofilter is shown in Fig. 3 where the removal efficiencies are plotted against the depth of the biofilter.

At a gas concentration of 200 ppmv with flow rate of 0.030 m^3 h^{-1} when passed through a bed height of 50 cm eliminated only 85 % of ammonia when compared to the first reactor indicating a reduction in biodegradation levels. Only 55 % removal was achieved at a gas flow rate of 0.060 m^3 h^{-1} at the same bed height indicating a 25% decrease in the removal efficiency when compared to the first type reactor.

Martens *et al.*[12] conducted similar studies by using packing materials designed by biochips coconut-peat, wood bark pellets and compost as packing and supporting materials for microbial anchorage. His reports indicate a reduction in microbial population in the biofilters over a period followed by a reduction in ammonia assimilation. Melvin *et al.*[13] studied gaseous ammonia removal in laboratory-scale biofilters (14-L reactor volume). These biofilters received 6 L min^{-1} of airflow with inlet ammonia concentrations of 20 or 50 ppmv, and removed more than 99.99% of the ammonia for 102 days.

Peat, Perlite and Vermiculite on Removal 400 ppmv Ammonia. Immediate irritation of eyes, nose and throat occurs at 400 to 700 ppm of ammonia causing edema, dyspnoea, bronchospasm, and chest pain, pink frothy sputum.[14] U.S. Navy Standards [U.S. Bureau of Ships 1962] Maximum allowable concentrations (MACs): Continuous exposure to ammonia for 60 days is 25 ppmv and 1hour is 400 ppmv.[15] Considering these facts, we choose to study the biodegradation effect of 400 ppmv of ammonia at different

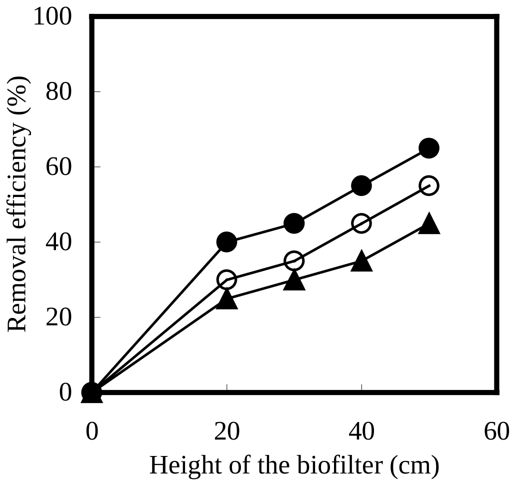

FIGURE 4. Removal efficiency of the first biofilter (peat, perlite and vermiculite) at different bed heights for 400 ppmv ammonia in between 23°C – 32°C.

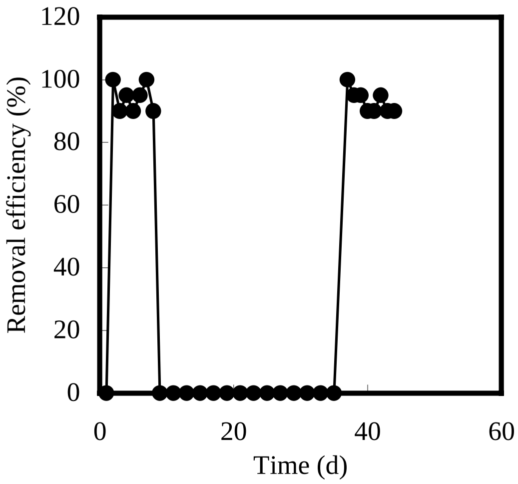

FIGURE 5. Response of the first biofilter (peat, perlite and vermiculite) to one month shut down and re-start-up operation ranging in between 23°C – 32°C.

flow rates in the first biofilter. A maximum of 65 % removal efficiency was achieved at a height of 50 cm of packed bed height at a flow rate of 0.030 m^3 h^{-1} with an elimination capacity of 1.414 g m^{-3} h^{-1} (Fig. 4) When the flow rate was increased to 0.060 m^3 h^{-1} the removal efficiency was only 25%.

A three-stage laboratory system, i.e., two biofilters in series followed by a liquid phase anaerobic reactor to treat leachate from the second biofilter, was designed to biodegrade acrylonitrile to ammonia, convert the ammonia to nitrate and then reduce the nitrate to nitrogen gas has recently been reported.[16] When considering dual reactors for treatments processes, our observation towards cost benefit evaluation is not appreciably high which affects the operation economics.

Stability of Biofilter Performance

A major problem associated with waste gas treatment operations is the variability in the flow and the concentrations in the effluent. To study the stability of the biofilm in the biofilter, the transient behavior of the shut down and re-start operation were investigated. With an initial ammonia concentration of 200 ppmv at a gas flow rates of 0.030, 0.045, and 0.060 m^3 h^{-1}, respectively, the biofilter was shut down for 30 days and re-started. Ammonia removal efficiency of the biofilter resumed immediately (Fig. 5) without any loss, neither in efficiency nor in their buffering capacity.

This confirms that the biofilm developed inside the biofilter was quite stable and the biodegradative activity of the chemolithotrophic microorganism in the biofilter is restored completely.

Removal Mechanisms

Ammonia in the gas phase through passive diffusion crosses the aqueous biofilm and then into the partially permeable membrane of those acclimated gram-negative chemo-lithotrophic microorganisms. These microbes obtain energy from oxidation-reduction reactions of ammonia using it as a nitrogen source or they degrade ammonia through non-specific enzymes regulated inside the mitochondria located in the protoplasm. These microbes oxidize ammonia to nitrite and then to nitrate.

As the biofilm is formed over the filter material, however, the removal mechanism shifts towards biodegradation. Similar observation is being observed by Dennis Mcnevin *et al.*[17] and Gilmore *et al*.[18]

After establishment of a biofilm, the feed ammonia and the gas flow rate were varied to study the performance of the biofilter for the removal of ammonia. Removal efficiency is the critical parameter, used to estimate the successful accomplishment of the biofilter.

The mechanism underlying for the degradation could be that when ammonia switches from gas phase to liquid phase and dissolves in the biofilm. In the presence of elemental copper, this reaction is catalyzed by *ammonia mono-oxygenase* located in the cell membrane. In the presence of iron *h*ydroxylamine is reduced to nitrite by *hydroxylamine reductase* and further reduced to nitrate by *nitrite reductase*, which is a iron-sulfur molybdenum flavoprotein.

Summary and Conclusions

Biodegradation in biofilter containing peat, perlite and vermiculite at the specified proportions as the main biomass support appears to be cost effective treatment method for ammonia. Concentrations as high as 200 ppmv could be completely degraded at a gas flow rate of 0.030 m^3 h^{-1} in a fluctuating room temperature condition.

At an influent ammonia concentration of 200 ppmv at a flow rate of 0.030 m^3 h^{-1}, when perfused through this biofilter with a bed height of 50 cm; a permissible limit of 1 ppmv of ammonia emission standards specified by Taiwan's Environmental Protection Agency (EPA) could easily be achieved. The maximum ammonia removal efficiency was obtained in the first biofilter (peat, perlite and vermiculite) which held an elimination capacity of 2.217 g m^{-3} h^{-1} which is comparable to the elimination capacities reported in the literature. At an influent ammonia concentration of 400 ppmv at a flow rate of 0.030 m^3 h^{-1} only 65% removal was achieved.

The removal efficiency of ammonia ranged from 98 to 100 %, which is equal or higher than the reported values in literature. Tests indicate that the lifetime of the filter media exceeded three months and predictably may well extend beyond nine months.

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