ELSEVIER

Chemosphere 55 (2004) 751–756

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

# Biofiltration of trimethylamine-containing waste gas by entrapped mixed microbial cells

Chang-Tang Chang [a,*], Bor-Yann Chen [b], I-Shing Shiu [c], Fu-Teng Jeng [c]

[a] *Department of Environmental Engineering, National I-Lan University, I-Lan, Taiwan*
[b] *Department of Chemical Engineering, National I-Lan University, I-Lan, Taiwan*
[c] *Graduate Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan*

Received 16 October 2002; received in revised form 25 March 2003; accepted 4 November 2003

**Abstract**

The study provides novel attempt to use an aerobic biofiltration system containing *e*ntrapped *m*ixed *m*icrobial *c*ells (EMMC) for removal of $(CH_3)_3N$-dominant waste gases. In the study, heterotrophic microflora-immobilized cellulose was packed into an EMMC reactor to degrade $(CH_3)_3N$. Effects of $(CH_3)_3N$ inlet concentrations in continuous mode of operation at various flow rates are indicated. The result indicated that the $(CH_3)_3N$ removal efficiency is higher than 90% at inlet loading below 27.2 mg N $h^{-1}$ and retention time 5.3 min. In addition, the maximal mass loading to reach approximately 99% efficiency was 95.5 mg N $h^{-1}$ for trimethylamine treatment. This EMMC biofiltration system also showed higher tolerance to endure fluctuations in concentrations and flow rates and still maintained in stable performance for removal. Adaptability test in response to gradual shift up and down of inlet TMA loading indicated that lack of steady-state multiplicity and hysteresis guarantees the microbial communities more precisely adapted to continuous treatment for maintaining stability.


*Keywords:* Biofiltration; Entrapped mixing microbial cell (EMMC); Trimethylamine (TMA); Maximum loading

## 1. Introduction

Biofiltration units are microbial ecosystems for the treatment of low-concentration and biodegradable waste gases. Trimethylamine (TMA) is potentially toxic and likely carcinogenic as a threat to public health, causing odor and visibility problems. Representative discharges of TMA are often from wastewater treatment, disposal waste landfill, livestock farming, and hog manure (Shieh and Keenan, 1986; Leson and Winer, 1991; Cao and Du, 1997). Characteristic concentrations of TMA emitted in such discharges ranged in 5–100 ppm (Shieh and Keenan, 1986; Hodge and Devinny, 1994). Therefore, levels of TMA must be reduced for emission under environmental regulation not only to avoid safety and health hazards, but to eliminate environmental impacts as well (e.g. greenhouse effect, acid rain, and eutrophication; Furusawa et al., 1983; Sly et al., 1993). In particular, oxidation of TMA to $HNO_3$ depletes dissolved oxygen of the receiving water body, and evolution of acid products corrodes the structure of the pipe (Wade et al., 1986; Tangji et al., 1989; Ziminski and Tang, 1994). According to Taiwan Environmental Protection Agency (TEPA), standard levels of ambient TMA for air quality regulation are 1.0 ppm.

In the past decade, attentions on treatment of TMA have been paid on the bioremediation perspective, as this method is more economically feasible and environmentally friendly compared to other conventional means (e.g., adsorption, absorption, and incineration). In addition, contaminants can be completely destructed at a lower cost and faster rate, and with no lingering

* Corresponding author. Fax: +886-39359674.
*E-mail address:* ctchang@ilantech.edu.tw (C.-T. Chang).

0045-6535/$ - see front matter 
doi:10.1016/j.chemosphere.2003.11.037

liability. Although literature (Yang et al., 1994; Zita and Hermansson, 1994; Warren et al., 1997) mentioned that bioreactors packed with *Nitrosomonas* sp. have been only used to remove TMA in wastewater, application of a biofilter reactor for TMA treatment in waste gas is still remained open for discussion. Recently, attempts of cell-immobilization techniques have been applied to waste gas treatment (e.g. ammonia gas, Chung et al., 2001; Hartikainen et al., 2001); however, biochemical reaction characteristics for cell immobilization and treatment in TMA still need to be addressed to present the operation feasibility and system optimization. As Yang et al. (1997) mentioned, the inhibition of nitrification increased with TMA concentrations. Studies (Zilli and Lodi, 1993; Edwards and Nirmalakhandan, 1996; Chung et al., 2001) also indicated that the activated sludge, composing of *Arthrobacter oxydans* and *Pseudomonas putida* from swan wastewater treatment systems is very effective in removing $NH_3$. Here, we also used the activated sludge for swan wastewater treatment as seeding cultures to conduct this treatability study for TMA treatment.

According to results of the entrapped mixing microbial cell (EMMC) bioreactor fed with TMA in various substrate concentrations, the removal efficiency and capacity for TMA as well as the property of compost odors were evaluated over time. As input parameters (i.e. shock loading, input concentrations of TMA) are of great significance to operation performance, the aim of the study is also to determine conditions of maximal mass loading and optimal operation conditions (e.g. pH, flow rate, retention time) for treatment. This novel attempt is to apply an EMMC approach to TMA-containing waste-gas treatment, resulting in high removal efficiency of more than 90%.

## 2. Materials and methods

### 2.1. Conditioning of immobilized cells

The activated sludge (originally obtained from the swan wastewater treatment system in Hsinchu, Taiwan) was used as virgin (unconditioned) seeding cultures for EMMC. To maintain microbial activity and biological synchrony of EMMC cultures, acclimation of sludges was conditioned through total recycle of various fresh nutrient solutions, replenished each month and designed to acclimation in the specific pollutant. The component of inflow media contained $K_2HPO_4$ 1.5 $g\,l^{-1}$, $KH_2PO_4$ 1.8 $g\,l^{-1}$, $CaCl_2$ 0.74 $mg\,l^{-1}$, glucose 2.5 $g\,l^{-1}$ (Chung et al., 2001). Nutrient-containing aqueous solutions were sprayed downward at a rate of 200 $ml\,min^{-1}$ with a peristaltic pump (Masterflex, Model 7518) from the top of column for a week. $CO_2$ evolution was continuously monitored to guarantee an ecologically stable activity of steady-state mixed consortia to be established. Cellulose triacetate was selected as a polymeric-material matrix for cells immobilization. The EMMC, including cellulose triacetate carrier and microbial cells, were obtained instantaneously via polymerization on 1-cm-diameter co-immobilized beads as Yang and See (1993) described. The prepared EMMC beads were packed into a fixed-bed column bioreactor for study. Harvested cells (precipitated through high-speed centrifuge, CEPA Laboratory Centrifuge type LE, 7500 *g*, 10 min) were immobilized and entrapped onto the matrix. After the cell immobilization step, EMMC beads were placed into a 35.0-l (20 cm $\varphi \times 110$ cm H) vertical column reactor with a working volume of 28.3 l (20 cm $\varphi \times 90$ cm H, 80% of total column) at 25 °C for operation. Experimental schematic of the bioreactor set-up is shown in Fig. 1. Glass column was packed with 90 cm height EMMC, and a perforated sieve plate was fitted at the bottom of the column to ensure the uniform distribution and mass transfer of the inlet gas.

### 2.2. Experimental equipment and procedure

After conditioning, $(CH_3)_3N$ containing waste-gases were pumped upward to increase mass transfer efficiency (Chung et al., 2001) through EMMC columns (retention times—RT ranged from 1.4 to 21.7 min) for continuous treatment. Chung et al. (2001) mentioned that countercurrent flow in column provided the maximal mass transfer of gaseous pollutants. The new cells in the column were replenished each time for running every test. To ensure the removal efficiency, influent and effluent $(CH_3)_3N$ concentrations were analyzed by on-line GC/PID. In the continuous flow experiment, the TMA-containing waste gas was introduced into the reactor. Initially, the pH was controlled approximately at 4.0–10.0 to grasp the optimum pH for TMA removal. The

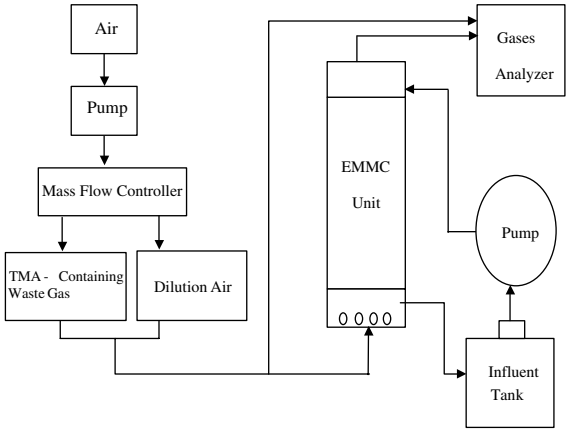


Fig. 1. The experimental set-up of the EMMC bioreactor.

TMA concentrations (75–221 ppm in vol/vol) were supplied at various flow rates (1.3–20.2 $l\,min^{-1}$) at pH $7.0 \pm 0.5$. The removal efficiency and degraded product ($CO_2$) of the biosystem were determined as indicator measures. The more organic carbon utilized, the higher energy used and the more $CO_2$ evolved during TMA removal. To evaluate the adaptability characteristics in response to shock-loading conditions (SLC), 75 ppm TMA was introduced at 1.3 (pre-SLC) and 10.6 $l\,min^{-1}$ (post-SLC).

To reveal whether the treatment performance is due to pure sorption (i.e. absorption and adsorption) capability of packing matrices or biodegradation of EMMC, breakthrough curve experiments with blank filter were carried out at 75 ppm TMA (1.3–20.2 $l\,min^{-1}$; Fig. 2) in various flow rates.

### 2.3. Analytical methods

The TMA concentrations were measured continuously by GC-PID (HNU GC-311 with Porapak Q column, 2 m × 0.32 cm ID). To guarantee reproducibility nature of results with statistical accuracy, the variation in inlet TMA concentration at steady-state within 3% was maintained for QA/QC of data sampling. In addition, TMA outlet concentrations were determined by average of at least 10 sampled data points.

### 2.4. Net maximum mass loading

According to material balance upon the pollutant, Eq. (1) can be obtained as indicated in Zarook and Shaikh (1997). In addition, the rate of TMA degradation can be expressed in first order reaction kinetics (i.e. Eq. (1)), since the inlet concentration was low and substrate concentration was much less than half saturation constant, $K_C$, in Monod's kinetic model, i.e.

$$q_p = \frac{q_{max} C_e}{K_C + C_e} \cong \frac{q_{max}}{K_C} C_e = kC_e$$

$$\frac{Q}{V}(C_0 - C_e) - kC_e = \frac{dC_e}{dt}, \quad (1)$$

where $k$, $Q$, $C_0$, $C_e$ and $V$ represents decay rate (kinetic) constant, gaseous flow rate, inlet concentration, outlet concentration and working volume, respectively. The parameters $q_p$ and $q_{max}$ are the specific TMA degradation rate and maximal degradation rate, respectively.

At steady-state (i.e. $\frac{dC_e}{dt} = 0$), Eq. (1) can be written as Eq. (2).

$$k = \frac{QC_0 - QC_e}{VC} \quad (2)$$

When the decay rate constant approaches maximum, the net maximum mass loading (MML) can be predicted as an asymptote

$$MML = (QC_0 - QC_e)_{max} = \lim_{k \to \infty} (QC_0 - QC_e). \quad (3)$$

The significance of the asymptote shows that net maximum mass loading is obtained when the reaction constant approaches zero, which indicates the inlet TMA to be eliminated completely.

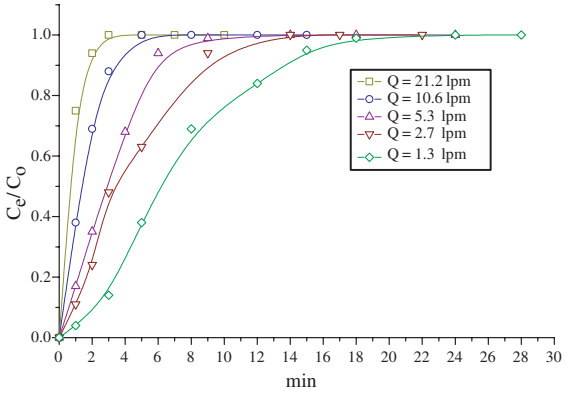


Fig. 2. Breakthrough curves of TMA removal with blank biofilter (pH = 7.0) $C_e$ and $C_0$ denote outlet concentration and inlet concentration, respectively.

## 3. Results and discussion

### 3.1. Blank experiments

As shown in breakthrough curves (Fig. 2), sorption saturation of blank filters was reached rapidly within 30 min (≪ effective operation time of EMMC (>5 days)). The breakthrough time decreases with an increase in flow rate. It indicates that TMA sorption only occurs in short-term and much less significant to TMA biodegradation.

### 3.2. Shock-loading effect

As Fig. 3 indicated, the removal performance could be recovered to 90% removal efficiency in 2 days to respond the loading shift up from 3.3 $mg\,N\,h^{-1}$ (1.3 $l\,min^{-1}$) to 27.2 $mg\,N\,h^{-1}$ (10.6 $l\,min^{-1}$) at fixed inlet TMA concentration (75 ppm in vol/vol). However, poor removal efficiency (<65%) was obtained as the loading changed to 51.9 $mg\,N\,h^{-1}$ (i.e. flow rate 20.2 $l\,min^{-1}$, concentration 75 ppm; Fig. 4). As the loading exceeds 27.2 $mg\,N\,h^{-1}$, induced degradation capacity cannot provide an efficient mechanism for removal due to relatively shorter retention time (RT; 2.7 min, Fig. 4). Without sufficient RT, TMA cannot be effectively

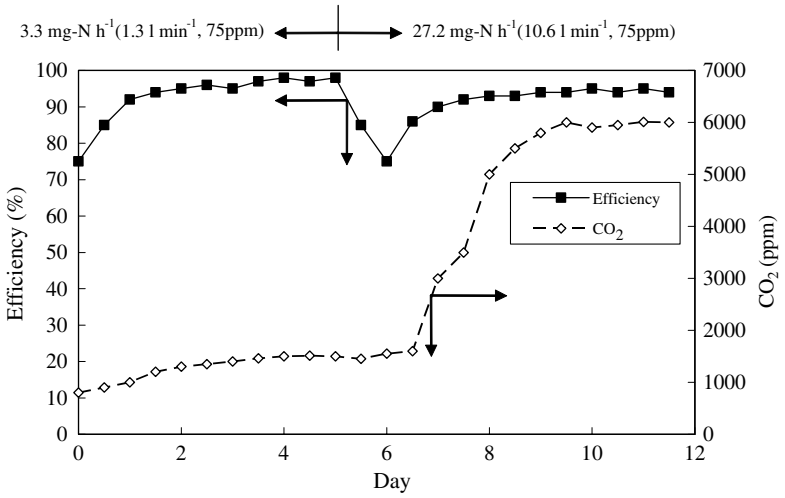


Fig. 3. The removal efficiency of TMA with EMMC biofiltration.

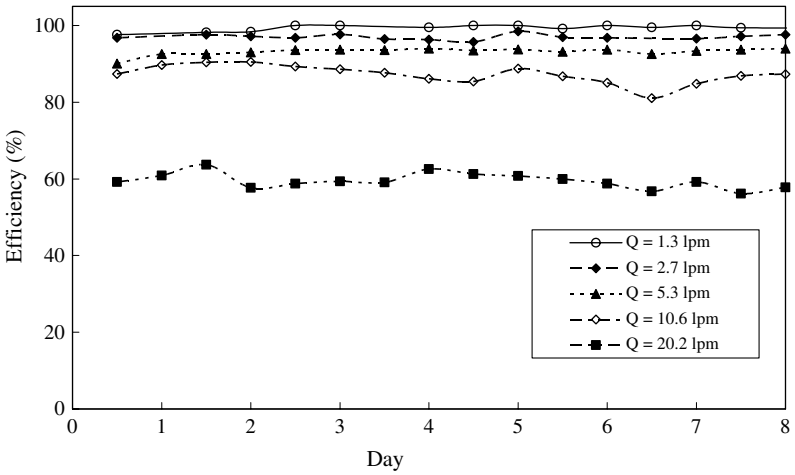


Fig. 4. The removal efficiency of TMA under different flow rate.

attached onto consortia existing on EMMC for degradation. In addition, there was a time delay for producing appropriate biodegradation activities in adapting to imposed environmental changes. This time-delay phenomenon is termed cell cycle or cell age related (Alberghina and Mariani, 1980). Once appropriate metabolic activity of microorganisms was induced, a new steady-state efficiency (94%) could be achieved. With the incorporation of flow rate shift up, damped transient of TMA (from ≈97% to 85%) was observed due to fast responses of biodegradation activity and a complete solubility of TMA. Adaptability tests in response to gradual shift up and down of inlet TMA loading indicated that lack of steady-state multiplicity and hysteresis guarantees the microbial communities more precisely adapted to continuous treatment for maintaining stability (Bailey and Ollis, 1997).

### 3.3. pH effects

The steady-state pHs at various flow rates were approximately fixed in the range 7.0–8.0, indicating no significant acidification during the entire operation. The reasons for making such stable pHs are straightforward. Since TMA (acid ionization constant, $K_b = 6.45 \times 10^{-5}$; AWMA, 2001) yields hydroxide ion ($OH^-$) in aqueous solution, hydrogen ions formed by $CO_2$ production, $CO_2 + H_2O \rightarrow H_2CO_3$, $H_2CO_3 \rightarrow H^+ + HCO_3^-$, can neu-

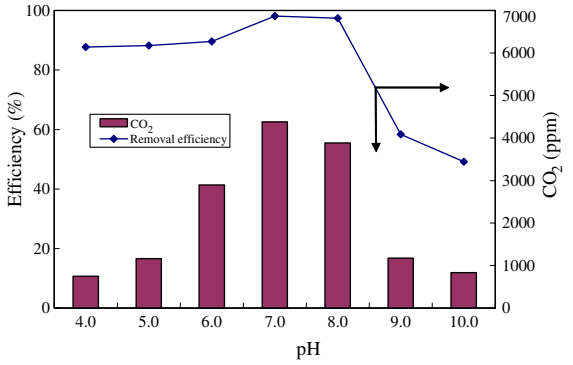


Fig. 5. pH effects on the removal efficiency of TMA at 10.6 lpm and 75 ppm.

tralize hydroxide ions to maintain such stable pHs as shown in Fig. 5. Therefore, the system seems to possess natural pH buffers and keeps the pH from changing drastically.

The $CO_2$ concentration was influenced intensely by pH of nutrient solution, and was lowered at $pH < 6.0$ and $> 8.0$ (Fig. 5). In contrast, the efficiency was only changed slightly when pH was smaller than 6.0, since the reaction $TMA \rightarrow \cdots \rightarrow NH_4OH$ in aqueous solution caused neutralization. At low pH, TMA biodegradation is inefficient due to neutralization predominated and low $CO_2$ production. Therefore, optimal pH for TMA treatment should be ranged from 6.0 to 8.0. Moreover, it is suspected that a neutral pH is an optimal pH of maximal enzyme activities for TMA degradation. This point may exclude the predominance of certain microbes which are tolerant to alkaline or slightly acidic habitats (e.g. cyanobacteria) in EMMC.

### 3.4. Flow rate effect

Since the inlet loading of the system depends on inlet concentration and flow rate, effects of both factors must be investigated. Moreover, to determine design criteria for maintaining stable removal efficiency of EMMC, the effective loading capacity should be established. Here, we defined the loading leading to an efficiency more than 90% as a "critical loading state (CLS)". When input loading exceeds CLS, lower degradation efficiency is obviously resulted as the microbial consortium in EMMC cannot degrade TMA in such short retention time or high tolerant concentration. According to Fig. 4, the efficiency is still higher than 90% when the inlet loading is below 27.2 mg N $h^{-1}$ (i.e. inlet flow rate <5.3 l $min^{-1}$, inlet concentration 75 ppm). In addition, $CO_2$ concentrations increased with increased inlet loading.

### 3.5. Inlet concentration effect

To assess the loading effect on EMMC performance, inlet concentration effects were investigated. As the inlet concentration in practical operation is time-fluctuated, it is essential to demonstrate the adaptability of the system in response to dramatic change in inlet loading. A field operation was simulated by gradually increasing the inlet TMA concentration and then gradually returned to the normal operation concentration (75 ppm). This is so-termed stability test for "steady-state multiplicity and hysteresis" (Bailey and Ollis, 1997). Treatment experiments of shift up and down in concentrations of TMA (75–221 ppm) showed reversible hysteresis and did not display steady-state multiplicity in continuous operations (Fig. 6). Thus, this system has higher tolerance to

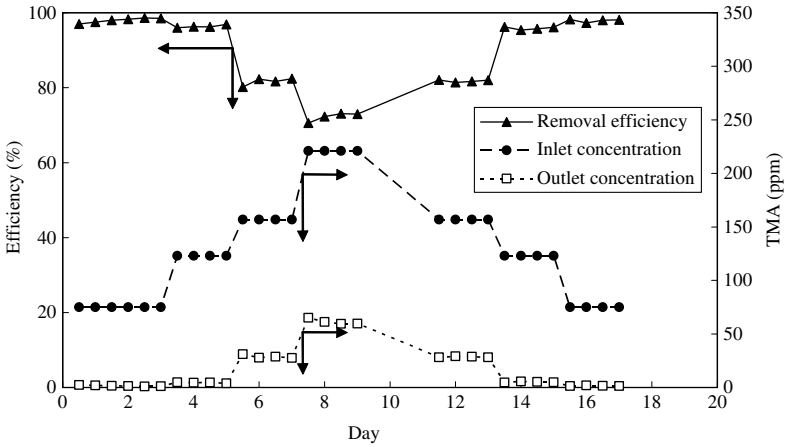


Fig. 6. The adaptability to dramatic change in inlet loading of TMA treatment at 2.7 lpm. Adaptation responses to gradual shift up and down of inlet TMA loading indicated that lack of steady-state multiplicity and hysteresis guarantees the microbial communities more precisely adapted to continuous treatment for maintaining stability.

endure fluctuations in concentrations and still maintained in stable performance for removal.

CLS of TMA was 27.2 mg N $h^{-1}$ at inlet concentration smaller than 75 ppm and flow rate 5.3 l $min^{-1}$. The predicted CLS of TMA based on inlet concentration effect was close to what was estimated from assessment of flow rate effect. According to Eq. (3), MML of TMA was obtained as 95.5 mg N $h^{-1}$. Therefore, the technically feasible range for TMA is approximately 27.2–95.5 mg N $h^{-1}$ and much higher than the researched results (Chung et al., 2001) for $NH_3$, only 0.02–0.24 mg N $h^{-1}$. It means that the EMMC has good performance since $NH_3$ is easier to be treated than TMA.

## 4. Conclusions

This study provides a first attempt to apply an EMMC biofiltration approach for TMA-containing waste-gas treatment, resulting in high removal efficiency of more than 90%. The maximal mass loading of EMMC to remove TMA is 95.5 mg N $h^{-1}$. In addition, the optimum pH of TMA is 7.0–8.0. Relatively shorter time (<2 days) to reach steady-state conditions for TMA removal by the EMMC bioreactor was required. Acidification is negligible in TMA removal, since dissolved TMA is slightly alkali. Satisfactory removal efficiencies (90% or higher) of TMA were reached at loading below 27.2 mg N $h^{-1}$. Further evidence in molecular level (e.g. bacterial identification, scanning electron microscopy) will be conducted for understanding species evolution in the microbial consortium.

## References


Air and Waste Management Association, 2001. Air Pollution Engineering Manual. Van Nostrand Reinhold, New York.

Alberghina, L., Mariani, L., 1980. Analysis of cell cycle model for *Escherichia coli*. J. Math. Biol. 9 (3), 389–398.

Bailey, J.E., Ollis, D.F., 1997. Design and Analysis of Biological Reactors, second ed. Chemical Engineering Series, McGraw-Hill, New York. pp. 533–657.

Cao, N.J., Du, J.X., 1997. Production of fumaric acid by immobilized *Rhizopus* using rotary biofilm contactor. Appl. Biochem. Biotechnol. 63 (3), 387–394.

Chung, Y.C., Huang, C.P., Liu, C.H., Bai, H.L., 2001. Biotreatment of hydrogen sulfide- and ammonia-containing waste gases by fluidized bed bioreactor. J. Air Waste Manage. Assoc. 51 (9), 163–172.

Edwards, F.G., Nirmalakhandan, N., 1996. Biological treatment of airstreams contaminated with VOCs: an overview. Water Sci. Technol. 34 (3), 565–571.

Furusawa, N., Togashi, I., Hirai, M., Shoda, M., Kubota, H., 1983. Removal of hydrogen sulfide by a biofilter with fibrous peat. J. Ferment. Technol. 62 (3), 589–601.

Hartikainen, T., Ruuskanen, J., Martikainen, P., 2001. Carbon disulfide and hydrogen sulfide removal with a peat biofilter. J. Air Waste Manage. Assoc. 51 (9), 387–392.

Hodge, D.S., Devinny, J.S., 1994. Biofilter treatment of ethanol vapors. Environ. Prog. 13 (5), 167–173.

Leson, G., Winer, A.M., 1991. Biofiltration—an innovative air pollution control technology for VOC emission. J. Air Waste Manage. Assoc. 41 (11), 1045–1054.

Shieh, W.K., Keenan, D.J., 1986. Fluidized bed biofilm reactor for wastewater treatment. Biochem. Eng. 33 (5), 132–168.

Sly, L.I., Bryant, L.J., Cox, J.M., Anderson, J.M., 1993. Development of a biofilter for the removal of methane from goal mine ventilation atmospheres. Appl. Microbiol. Biotechnol. 39 (3), 400–404.

Tangji, Y., Kanagawa, T., Mikami, E., 1989. Removal of dimethyl sulfide, methyl mercaptan, and hydrogen sulfide by immobilized *Thiobacillus thiopares* TK-M. J. Ferment. Bioeng. 67 (2), 280–293.

Wade, A., Shoda, M., Kubota, H., Kobayashi, T., Yoko, K.F., Kuraishi, H., 1986. Characteristics of $H_2S$ oxidizing bacteria inhabiting a peat biofilter. J. Ferment. Bioeng. 64 (1), 161–176.

Warren, J.S., Raymond, C.L., Fellow, A., 1997. Biofiltration fundamentals, design and operations principles, and applications. J. Environ. Eng. 32 (3), 538–546.

Yang, P.Y., Ma, T., See, T.S., Nitisoravut, N., 1994. Applying entrapped mixed microbial cell techniques for biological wastewater treatment. Water Sci. Technol. 29 (2), 487–495.

Yang, P.Y., See, T.S., 1993. Entrapment of mixed microbial cells for water and wastewater treatment. Water Sci. Technol. 28 (1), 165–170.

Yang, P.Y., Zhang, Z.Q., Jeong, B.G., 1997. Simultaneous removal of carbon and nitrogen using an entrapped-mixed-microbial-cell process. Water Res. 31 (12), 2617–2625.

Zarook, S.M., Shaikh, A.A., 1997. Analysis and comparison of biofilter models. Chem. Eng. J. 65 (1), 55–61.

Zilli, M.A., Lodi, A., 1993. Phenol removal from waste gases with a biological filter by *Pseudomonas putida*. Biotechnol. Bioeng. 41 (3), 693–699.

Ziminski, R.W., Tang Y., 1994. Control of hazardous air pollutants using a commercial biofilter. In: Proceedings of the 87th Annual Meeting and Exhibition, Air and Waste Management Association, Cincinnati, Ohio.

Zita, A., Hermansson, M., 1994. Effects of ionic strength bacterial adhesion and stability of floc in a wastewater actived sludge system. Appl. Environ. Microbiol. 60 (12), 3041–3048.