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Performance of a Biofilter in MTBE Removal

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ABSTRACT

The objectives of this study were to determine the effectiveness of a laboratory-scale biofilter in the removal of MTBE (methyl tertiary butyl ether) and to investigate the effects of operating parameters on biofilter performance. The experimental results show that MTBE removals exceeded 80% during operation throughout the 42-day biofilter acclimation period. The maximum elimination capacity (EC) of the biofilter was about 18 g MTBE • m^{-3} • h^{-1}. Furthermore, MTBE removal efficiency increased from 72% to 86% as the liquid feeding rate (LFR) increased from 10 to 40 ml/min. However, the removal efficiency dropped to 78% as the LFR increased to 60 ml/min. It is believed that high moisture contents in the biofilter caused the reduction of the mass transfer rate, leading to the decrease in removal efficiencies. More than 99% removal efficiencies were achieved for inlet MTBE concentration at 50 ppm with the highest empty-bed residence time (EBRT). Hence, MTBE removal efficiency increases while EBRT increases.

***Key Words*: biofilter, elimination capacity, empty-bed residence time, MTBE, organic loading**

以生物濾床處理含 MTBE 廢氣之效率評估

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摘　要

本研究之主要目的乃以改良式生物濾床系統，進行含 MTBE（methyl tertiary butyl ether）廢氣之處理效率評估，同時探討生物濾床之操作條件對 MTBE 去除效率之影響。研究結果顯示，本生物濾床於 42 天之馴化啓動階段其去除效率皆可維持在 80% 以上，而最大分解能力則可達 18 g MTBE • m^{-3} • h^{-1}，約爲其他處理 MTBE 生物濾床的 2-3 倍。當循環水流量由 10 ml/min 增加至 40 ml/min 時，MTBE 之去除效率由 72% 提升至約 86%，顯示足夠含水量有助於提升生物濾床之去除效率，但再提高循環水流量至 50、60 ml/min 時，則去除效率分別下降至 83% 與 78%，由此顯示過高含水率易造成濾床內部產生阻塞（clogging）或管流（channeling）現象，因而導致去除效率之下降。當濾床之停留時間爲 188 秒及於進流濃度爲 50 ppm 時，系統之去除效率可達 99% 以上，因此較長之接觸時間將使得微生物具有充足的時間以分解 MTBE。

關鍵詞：生物濾床，分解能力，空塔停留時間，甲基第三丁基醚，有機負荷

I. INTRODUCTION

Methyl tertiary butyl ether (MTBE) is a synthetic chemical which widely used as fuel oxygenates to improve gasoline combustion reduce the resulting concentrations of carbon monoxide and unburned hydrocarbons. Since 1979, the production of MTBE was significant. The massive production of MTBE, combined with its mobility, persistence, and toxicity, poses adverse effects on the quality of groundwater. A nationwide US Geological Survey conducted by National Water Quality Assessment program found that MTBE was the second most frequently detected compound in groundwater [11]. According to studies that have shown that MTBE to be a carcinogen in animals, the USEPA (United States Environmental Protection Agency) has tentatively classified MTBE as a possible human carcinogen [13]. In addition, MTBE is also listed as the fourth category of toxic chemical by Environmental Protection Administration of Taiwan.

Biofiltration is one possible VOC (volatile organic compounds) treatment method that has advantages of low operating costs and minimum generation of by-product in waste streams [4]. Biofiltration has been successfully applied to control odors, and organic and inorganic air pollutants from wastewater treatment plants, industrial sources, and remediation operations [1, 5, 9]. Of these, biofilter has been received widespread attention as a reliable and economical alternative air pollution control technology in soil vapor extraction operations [6]. In the case of soil or groundwater contaminated with MTBE and biofilters may be used to treat gases containing MTBE extracted during soil vapor extraction operations for soil remediation, or to treat emissions resulting from air stripping unit in groundwater remediation. Most reports have been published addressing aerobic biodegradation of MTBE in batch systems under controlled laboratory conditions [7, 12]. However, little research has been done on addressing biodegradation in engineered processes. In studies by Eweis et al. [2], a compost biofilter was used to treat air streams containing MTBE. However, the removal rate of MTBE was only 6 to 8 $g \cdot m^{-3} \cdot h^{-1}$. Fortin and Deshusses [3] used moisture-rich laboratory-scale biotrickling filters for the removal of MTBE. Following a 6-month acclimation period, the removal of MTBE in the unit reached a maximum of 50 $g \cdot m^{-3} \cdot h^{-1}$. The results of these studies suggest that optimal moisture content in the filter media might be a key factor in obtaining and maintaining active MTBE-degrading populations in bioreactors. However, there are several operational problems that biofilters were encountered. Some of these problems include clogging, channeling, and dryness of the filter bed [8].

In this study, a laboratory-scale biofilter with filter media of wood chips (tree fern) and with higher water content was introduced because tree fern provides several advantages, such as greater moisture retention and porosity. Additionally, the ways to overcome the drying out problem of the bed are to increase the moisture content, to use a liquid recycle unit, and to supply liquid water intermittently. The objectives of this research were to assess the application of biofiltration to remove MTBE in gas streams, and to estimate the spatial distributions of MTBE across the depth in the biofilter. Furthermore, the research was to observe the biofilter response to change in operating parameters such as start-up microbial acclimation, MTBE loading, liquid flow rate, and empty bed residence time (EBRT).

II. MATERIALS AND METHODS

1. Experimental Set-Up

The laboratory-scale biofiltration unit was constructed and the experimental set-up is shown in Figure 1. Table 1 gives the specifications of the biofilter unit. The biofilter consisted of a transparent cylindrical plastic acrylic glass column 10 cm in diameter and 1 m in length. The column was constructed in six sections joined by flanges. The center three sections were each 20 cm long and packed with media providing a total bed depth of 60 cm and a total packed bed volume of approximately 4.7 L. A perforated stainless steel plate located at the bottom of each section served to support the packing media. In the upper two sections, a 30 cm head space was designed for the gas inlet and for the housing of a sprinkler nozzle controlled by a solenoid valve, while a 10 cm bottom space was used as the outlet zones. Leachate was collected at a flask installed in a temperature-controlled water bath at the bottom of the biofilter. During the operation, the pH was maintained at around 6.8. Four gas sampling ports were located above each section, at the inlet and outlet to determine the concentration gradient along the biofilter. Wood chips of tree fern were selected as the primary packing media in this study. Tree fern is naturally and commercially available in Taiwan, and it is generally marked for horticultural purposes because of its character of sorbability to retain water and manure for plants. The main characteristics of filtering media included volumetric weight 0.103 $g \cdot m^{-3}$, void ratio of 0.93, and moisture content of 3.7% (dry mass basis) and 67.2% (wet mass basis). The filter bed was initially inoculated with an enriched aerobic microbial culture taken from an activated sludge system in a petroleum refinery plant using MTBE as one of the carbon sources.

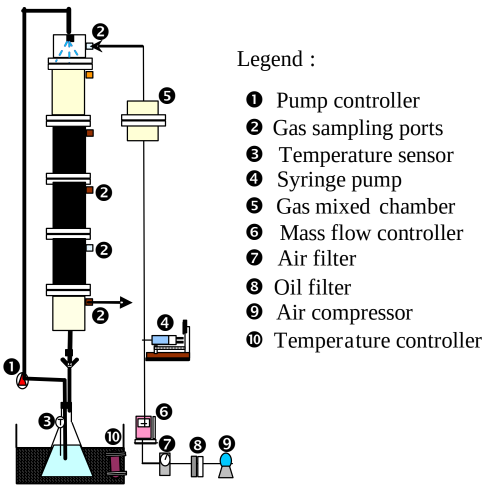


Fig. 1. Schematic diagram of experimental apparatus

Table 1. Summary of biofilter system specifications

Characteristic	Specification
Material	Acrylic
Total height (cm)	100
Inner diameter (cm)	10
Packing material	Tree fern
Packing height (cm)	60
Temperature control (circulating water) (℃)	28-30
pH control (circulating water)	6.8

Compressed air was passed through oil and air filters to remove oil, particulate matter, and microbes. After purification, the air to biofilter is mass flow controlled. MTBE was continuously injected by a syringe pump (Kd Scientific, model 100) into the influent air stream where it vaporized and entered the gas mixed chamber for further mixing. The flow rates of both gas and solvent streams are controlled using previously calibrated flow-meters to obtain the desired gas flow rate and concentration of the contaminant at the biofilter entrance. In order to avoid dryness of the packing material in the filter bed, moisture was provided to the media using a sprinkler nozzle controlled by a solenoid valve. The liquid nutrient feed contained all necessary macronutrients, micronutrients, and buffers. The biofilter system was operated in a co-current manner with the air and liquid flows directed downward.

2. Analytical Methods

In order to examine the performance of the biofilter, inlet and outlet concentrations of MTBE were measured. Air samples were withdrawn from the biofilter column in 5 ml gastight syringe equipped with Luer-lok valves, and directed to a gas chromatograph equipped (GC) with a flame ionization detector (FID) (Shimadzu 14B) for MTBE concentration measurements. MTBE inlet mass loading, L ($g \cdot m^{-3} \cdot h^{-1}$), biofilter elimination capacity, EC($g \cdot m^{-3} \cdot h^{-1}$), and the biofilter removal efficiency, RE (%) were determined using the relationships between the influent and effluent gas phase concentrations, gas flow rate, and the volume of the biofilter material as follows:

$$L = \frac{C_{g.in} \times Q_g}{V} \tag{1}$$

$$EC = \frac{\left(C_{g.in} - C_{g.out}\right) \times Q_g}{V} \tag{2}$$

$$RE = \frac{\left(C_{g.in} - C_{g.out}\right) \times 100}{C_{g.in}} \tag{3}$$

Where, $C_{g,\,in}$ and $C_{g,\,out}$ ($g \cdot m^{-3}$) represent the respective inlet and exit MTBE concentration in the gas phase, Q_g ($m^3 \cdot h^{-1}$) the volumetric airflow rate, and V (m^3) the volume of the filter bed.

3. Experimental Plan

The experimental plan included abiotic MTBE sorption test, start-up acclimation test (Phase I), and continuous tests (Phases II-IV). Abiotic MTBE sorption test was aimed to determine the time required to reach the state of saturated sorption by the filter media and moisture. In the start-up acclimation test, the system was operated for 42 days by increasing the MTBE concentration gradually from 16-50 ppmv, and maintaining the liquid flow rate and empty bed residence time (EBRT) of 50 ml/min and 140 seconds to establish steady state conditions as indicated by MTBE removals remaining constant with time. Continuous tests (Phases II-IV) were conducted by varying the inlet MTBE concentrations from 100 ppmv to 500 ppmv, liquid flow rates from 10 to 60 ml/min, and EBRTs of 83 to 188 seconds. Each run was operated approximately two weeks to achieve the pseudo-steady-state conditions.

III. RESULTS AND DISCUSSION

1. Effect of Abiotic Sorption

Abiotic sorption of MTBE to biofilter did not contribute appreciably to the overall removal of the MTBE during the start-up experiments. Figure 2 shows that the necessary time to saturate all the sorption sites on the uninoculated column was approximately 35 minutes under inlet MTBE concentrations of 50 and 100 ppmv. This result confirms that biofilter packed with tree fern has the better capability for retaining the moisture and for adsorping targeted compounds.

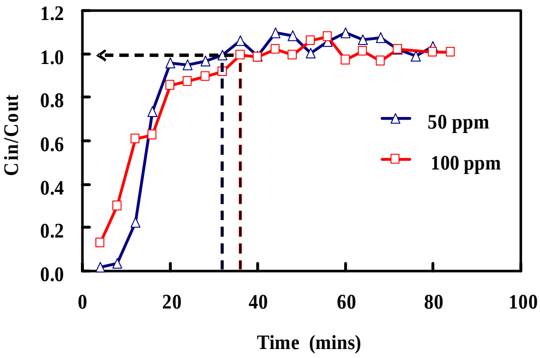


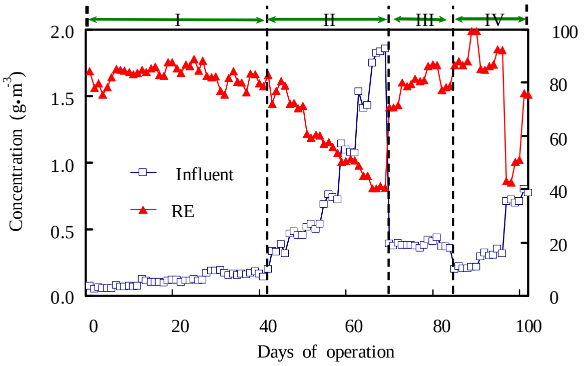
Fig. 2. Abiotic sorption test conducted on moist packed column before the biofilter was inoculated

2. Overall Biofilter Performance

The effectiveness of biofilter system on control of the target compounds was evaluated based upon the removal efficiency of MTBE calculated its inlet and outlet concentrations during each sampling event. The changes in the inlet MTBE concentration, and removal efficiencies during 102-day operation are shown in Figure 3. Four tests including the start-up acclimation test (Phase I) and three continuous tests (Phases II-IV) were conducted. The system was initially acclimated by increasing the MTBE concentration gradually ranging between 16 and 50 ppmv. Throughout the acclimation program, MTBE removals consistently exceeded 80% during 42-day operation. In Phase II study (Days 43-69), MTBE removals decreased from 90% to 40% by increasing MTBE inlet concentrations from 100 to 500 ppmv. In Phase III study (Days 70-84), the removal efficiencies varied between 70.6% and 86.8% for liquid flow rates ranging from 10 ml/min to 60 ml/min. In Phase IV study (Days 85-102), the removal efficiencies varied between 42.7% and 99.4% for EBRTs ranging from 83 seconds to 188 seconds.

3. Effect of Organic Loading on Removal

Figure 4 shows the variation of EC and RE with MTBE loading. As can be seen in the figure, EC increased with influent loading. The maximum elimination capacity (EC) was defined as the value when the removal capacity leveled off. Note that the maximum EC was about 18 g MTBE $\cdot$ m^{-3} $\cdot$ h^{-1} for this supporting media. This elimination capacity was not very remarkable, compared to the high maximum EC (42-50 g $\cdot$ m^{-3} $\cdot$ h^{-1}) for MTBE in a moisture-abundant biotrickling filter [3]. However, the maximum EC in this biofilter was 2-3 times higher than that in a compost biofilter for treating MTBE [2]. We believe that is attributed to the higher moisture content applied in this biofilter, and the ability of biofilter for MTBE removal makes it valuable for treating high solubility contaminants such as MTBE.



I: Acclimation test: Inlet loadings (16-50 ppmv) with LFR of 50 mL/min and EBRT of 140 sec.

II: Continuous test: Inlet loadings (100-500 ppmv) with LFR of 50 mL/min and EBRT of 140 sec.

III: Continuous test: LFRs (10-60 mL/min) with inlet loading of 100 ppmv and EBRT of 140 sec.

IV: Continuous test: LFR (50 mL/min) with inlet loadings (50-200 ppmv) and EBRTs (83-188 sec).

Fig. 3. Performance of a biofilter for 102 days

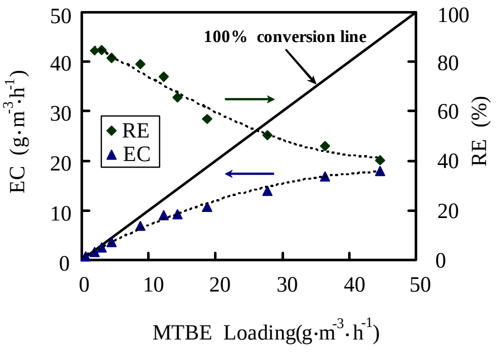


Fig. 4. Elimination capacity & removal efficiency vs MTBE loading

As can be seen from Figure 4, RE decreased with increased influent loading. In the initial three days of the operation, the RE was maintained approximately at 80-85% under inlet MTBE loadings below 9 g $\cdot$ m^{-3} $\cdot$ h^{-1}. Then, when the inlet MTBE concentration was raised from 100 to 300 ppm (L=28 g $\cdot$ m^{-3} $\cdot$ h^{-1}), the RE was declined to 50%. Subsequently, the RE was further declined to 40%. These decreases are believed to be due primarily to the quick increase in the inlet MTBE concentrations from 300 to 500 ppm (L=45 g $\cdot$ m^{-3} $\cdot$ h^{-1}).

4. Effect of EBRT on Removal Efficiency

As indicated in Table 2, biofilter removed MTBE up to 99% at the highest retention times (EBRT=188 seconds), with the lower retention time (EBRT=83 seconds) and achieved 86% removal at 50 ppmv inlet concentration. Because the

Table 2. REs under different EBRTs

Conc. (ppmv)	EBRT (sec)	RE (%)
50	83	86.7
	100	87.3
	140	88.1
	188	99.3
100	83	85.2
	100	86.6
	140	90.6
	188	92.5
200	83	42.9
	100	50.7
	140	63.2
	188	75.9

microorganisms can have sufficient time to degrade more MTBE if gas transporting time does not limited in a biofilter, greater degree of removal are achieved with the higher EBRT. However, the removal efficiency declined to 75% at the highest EBRT and 42% at the lowest EBRT under 200 ppmv conditions. Thus, the biofilter appears to be very effective for MTBE removal under low loading and high EBRT conditions.

5. Effect of Liquid Fowrate on Removal Efficiency

Figure 5 shows the relationship between removal efficiency and liquid recirculation rate. It was found that MTBE removal improved with the increase of liquid phase flow rates from 10 to 40 ml/min. However, the removal efficiency decreased to 78% when keep increasing the liquid flow rate to 60 ml/min. It is believed that the better moisture retainability for the filter media of tree fern may bring about biomass growing, thereby leading to the increasing of the removal efficiencies. It should be noted that too high of the moisture content (64%) in the bed may result in the high mass transfer resistance in the biofilm, which is another possible explanation for this low removal efficiency. These results indicate that the use of tree fern as a medium and better control of the liquid flow rates are an effective way to maintain moisture in a biofilter, particularly in the field of applications where drying problems often occur.

6. MTBE Concentration Gradient along the Biofilter

Figure 6 displays the variation in MTBE loading across the depth of the biofilter. As can be seen from the figure, MTBE concentration was the highest in the first section (i.e. 0-20 cm) and gradually declined in the following two sections (i.e. 20-60 cm). Therefore, the biofilter was effective on removal of MTBE in the first section but performed poorly in the subsequent sections. The average removal percentage in the first section of the biofilter to overall removal was 72%, demonstrating that most biological reactions occurred in the first section of the biofilter. These removal variations against the incremental biofilter length are believed to be due primarily to sufficient organic loading, moisture content, and nutrient in the earlier sections of the biofilter [10]. However, the lower removals in the lower section of biofilter may have been partially attributed to the low carbon source, moisture content, and nutrient, which hampered a rapid biofilm build-up on the filter media.

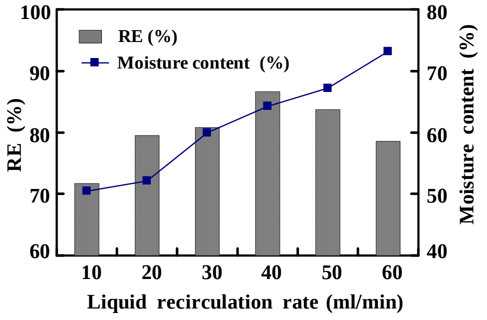


Fig. 5. Removal efficiency & moisture content vs liquid flow rate

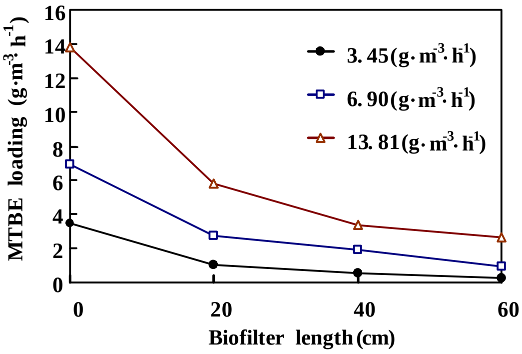


Fig. 6. MTBE loading profiles across the depth of the biofilter

IV. CONCLUSIONS

Based on these results, the following conclusions can be drawn:

- More than 80% removal efficiencies were observed under inlet MTBE loadings below 9 g • m^{-3} • h^{-1}. This indicates that the biofilter is effective on removal of MTBE-contaminated gas.
- Biofilter showed MTBE removal up to 99% at the highest retention times (188 seconds), with the lower retention time achieving an 86% removal at 50 ppmv inlet concentration.
- MTBE removal at the bottom section of the biofilter were

consistently lower than for the top section, which was likely due to the insufficient growing of microorganisms with the low organic loading, moisture content, and nutrient at the bottom section.

- Biofilter operation was strongly affected by the moisture content, and with an optimal removal efficiency of 87% at LFR of 40 ml/min and 64% of moisture content.

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