Appendix A

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BIOFILTRATION OF METHANOL AND TOLUENE FROM WASTE GAS

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Abstract: *Biofiltration technique for the purification of polluted air from volatile compounds was studied. The experimental approach was operated using two stainless steel biofilters, one for methanol and another one for toluene, consisting of palm shells and activated sludge as filter-bed material. There was no inoculation and only microorganisms indigenous to the bed medium were used throughout the whole process. Polluted air inlet concentration was varied from 0.3-4.7 g/m^3 with flow rates ranging from 0.06-0.45 m^3/h, equivalent to empty bed residence times of 9-71 s. Polluted air was successfully treated by biofiltration, 100% removal efficiencies can be obtained.*

Key Words: ***Biofilter/Biofiltration/VOCs/Methanol/ Toluene***

1. INTRODUCTION

Industrial plants and processes use and emit many types of volatile organic compounds (VOCs), which rapidly become atmospheric pollutants. Methanol is a hydrophilic VOC (with a water solubility of 1,000 g/l at 25°C) while toluene is a hydrophobic VOC (with a water solubility of 0.53 g/l at 25°C). They both are the hazardous air pollutants (HAPs) listed in Title III of the 1990 Clean Air Act Amendments (CAAA90) proposed by the US Environmental Protection Agency (EPA) [1].

The presence of VOCs in air emissions has been the subject of recent environmental regulations and the industry is required to apply an appropriate technology to reduce its emissions. The current control technologies for VOCs (e.g. thermal incineration, wet scrubbing, and adsorption onto activated carbon) are often cost intensive, especially in cases where there are low concentrations of the pollutants [2].

Biofiltration is relatively inexpensive compared with conventional techniques and very effective for treating large volumes of moist air streams with low concentrations of the biodegradable pollutants. In addition, the treatment is environmental friendly, treatment is performed at ambient temperatures, and it does not generate nitrogen oxides or secondary waste streams [3].

Generally, a biofilter is a column filled with a porous and humid packing material inoculated with microorganisms able to degrade pollutants. The air pollutants are transferred from the gas phase to the liquid phase and diffuse through the biofilm fixed on the surface of the packing material. The pollutants are subsequently biodegraded in the biofilm to water and CO_2 and used as the essential carbon source for the microbial growth [4].

Any porous material capable of adsorbing gaseous compounds and supporting biological growth can possibly be used as a packing material. The packing materials commonly used include natural materials such as peat, compost, soil, and sludge from sewage treatment plants and synthetic materials such as vermiculite, granular activated carbon, and extruded diatomaceous earth pellets [4, 5].

The degradation of VOCs by microorganisms is affected by various environmental factors such as moisture content, temperature, pH, VOC input rate, the kind of contaminant, and accessibility to the target substances [6]. The effectiveness of the biofilter largely depends upon the solubility of the compounds in the liquid layer of the biofilm [7]. The hydrophilic and hydrophobic characteristics of the pollutants discharged in air emissions may significantly influence their removal capacities in biofilters.

In this work, the feasibility of the biofilters consisted of palm shells and activated sludge as a filter bed medium to treat air polluted with methanol and air polluted with toluene was studied. The effects of operating conditions, such as VOC input concentration, empty bed residence time, height of the column, and pressure drop on the treatment were investigated.

2. MATERIALS AND METHODS

2.1 Volatile organic compounds

The VOCs used were methanol (99.8%) and toluene (99.5%) obtained from Merck, Germany.

2.2 Equipments

Two identical bench-scale biofilters were used to treat methanol and toluene from air streams. The biofilters were made of stainless steel and each consists of three equal segments connected in series (Fig.1). Each segment has a diameter of 5 cm and a height of 30 cm (being filled to a height of 20 cm with equal amounts of the prepared filter-bed material). In order to support the filter-bed and to ensure homogeneous radial distribution of the input gas, a stainless steel mesh was installed at the base of each section. These supports were reinforced with stainless steel rods in order to bear the weight of the wet filter material. Two ports were placed in each segment, one for gas sampling and another one for media sampling.

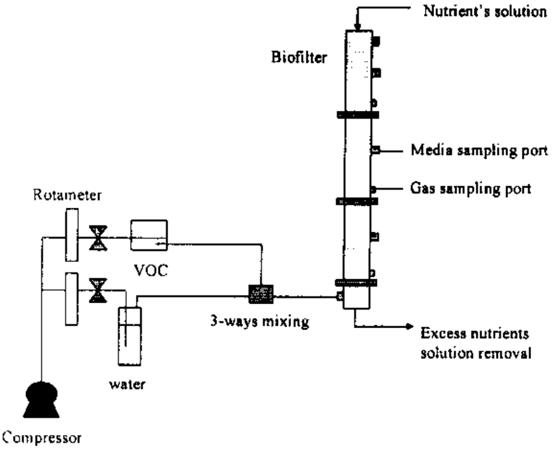

Fig. 1. *The experimental setup of the biofiltration system.*

The biofilter was fed by airflow provided by a continuous compressed air source. The major portion of the air was passed through a water column in order to become fully saturated. A secondary fraction of the main air was directed to a bubbler unit containing the liquid VOC reagent. The previous separate gas flows were then mixed together and the resultant polluted humid input gas mixture was carried to the base of the biofilter.

2.3 Nutrient solution

The nutrient solution was periodically distributed over the bed upper-surface to maintain an adequate level of bed filling moisture content and to provide those nutrients necessary for the growth of microorganisms present in the biofilter. The composition of nutrient solution used is shown in Table 1.

Table 1. *Composition of one liter of the nutrient solution.*

Composition	Amount
KH_2PO_4	0.91 g
$Na_2HPO_4.12H_2O$	2.39 g
KNO_3	2.96 g
$(NH_4)_2SO_4$	1.97 g
$NaHCO_3$	1.5 g
$FeSO_4.7H_2O$	0.2 mg
$MgSO_4.7H_2O$	2 mg
$MnSO_4.H_2O$	0.88 mg
$Na_2MoO_4.2H_2O$	1 mg
$CaCl_2$	3 mg

2.4 Filter material

The biofilter media were a mixture of palm shells (0.5-1cm) and activated sludge (Kingfisher Holdings Ltd.) in the proportion of 1:2 by volume. A pH buffer ($CaCO_3$) was added to the filter media when necessary. The media were kept for one night before packing in order to prevent the expansion of palm shells in the biofilter.

2.5 Analytical methods

Gas samples were taken by 100% polypropylene bags (0.5 liter) at the different outlets of the filters. VOC concentration was analyzed by a gas chromatograph unit (HP 6890, Hewlett Packard) equipped with a flame ionization detector (FID) using a 30-m capillary column (HP-1, crosslinked methyl siloxane). For methanol and toluene measurements, the temperatures of the injection port, the oven, and the detector were maintained at 180, 70, and 200°C, respectively. The flow rates of air and hydrogen for FID were 400 and 30 ml/min, respectively.

Gas pressure drop of the filter was measured by a U-tube manometer. Bed temperature and moisture content were monitored via AP-104 (Sila Research Co., Ltd., Thailand) while pH of the filter media was measured by a pH indicator paper (Merck, Germany).

2.6 Operating conditions

To describe the mechanisms of biofiltration clearly, general terminology pertinent to the field should be well defined. Studies were performed on the level of the VOC inlet load (IL) and empty bed residence time (EBRT) while the pollutant degradation performance of the biofilter can be expressed in terms of the pollutant removal efficiency (RE) and the elimination capacity (EC). The definitions for these four parameters are out below:

$$\mathrm{IL} = \frac{Q \times C_I}{V} \tag{1}$$

$$\mathrm{EBRT} = \frac{V}{Q} \tag{2}$$

$$\mathrm{RE} = \left(1 - \frac{C_0}{C_I}\right) \times 100 \tag{3}$$

$$\mathrm{EC} = \frac{Q \times (C_I - C_0)}{V} \tag{4}$$

with C_I = VOC concentration at inlet (g/m^3), C_0 = VOC concentration at outlet (g/m^3), Q = volumetric gas flow rate (m^3/h), V = filter bed volume (m^3). All of these parameters were studied in accordance with the operating conditions, as summarized in Table 2.

Table 2. *Biofilter operating conditions.*

Filter media	Palm shell + activated sludge
Pollutant	Methanol and toluene
Microorganisms	Indigenous to filter media
Diameter of palm shell	0.5 – 1 cm
Bed height	3×20 cm
Column diameter	5 cm
Inlet concentration	0.3-4.7 g/m^3
Air flow rate	0.06-0.45 m^3/h
EBRT	9-71 s

3. RESULTS AND DISCUSSION

3.1 Overall performance

The whole experimental period (113 days) was split into six successive stages, i.e. A, B, C, D, E, and F (Fig. 2). During stage A (air flow rate = 0.06 m^3/h), which was a start up period, the removal efficiency (RE) of the biofilter accounted for 100% on the first day of operation. The high value of 100% was due to the sorption of initial methanol on the wet filter material, regardless of the activity by microorganisms. Then the removal efficiency increased due to biodegradation and the steady state was reached 37 days after the start of the experiment (Fig. 2).

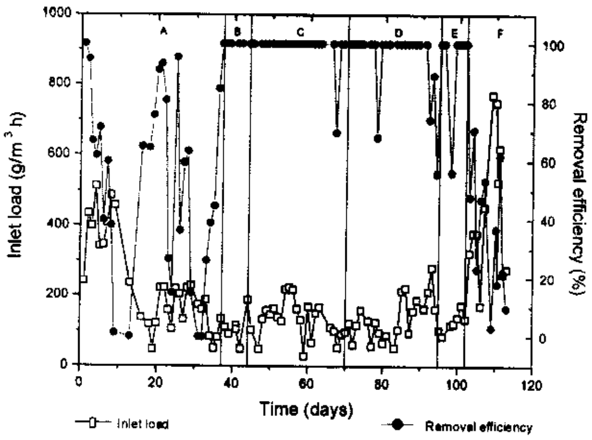

Fig. 2. *Inlet load concentration of methanol and removal efficiency as a function of time.*

For stages B, C, D, E, and F, the air flow rate was maintained at 0.06, 0.12, 0.18, 0.24, and 0.45 m^3/h, respectively. The experiment for removal of toluene was operated in the same way and the steady state was reached 18 days after the start of the experiment (Fig. 3).

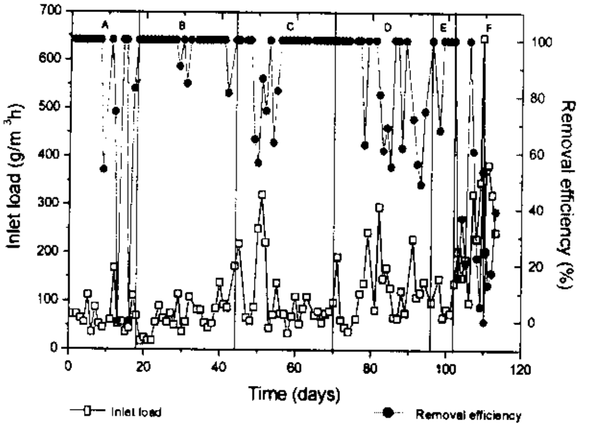

Fig. 3. *Inlet load concentration of toluene and removal efficiency as a function of time.*

Fig. 2, along with Table 3, shows that during stages B, C, and D the removal efficiencies of methanol were mostly maintained at 100%. The biofilter provided methanol removal as high as 250 g methanol/m^3 bed medium/h at the retention times as low as 18 s and in some instances up to 380 g/m^3h at retention time of 9 s.

For removal of toluene, the removal efficiencies were almost maintained at 100% during stages B and C. The biofilter provided toluene removal as high as 278 g/m^3h at the retention time as low as 24 s and in some instances up to 346 g/m^3h at the retention time of 9 s (Fig. 3 and Table 4).

The removal rates obtained in this study were comparable to (or higher than) the results obtained by other researchers as shown in Table 5. This suggests that a mixture of palm shells and activated sludge can be used as the filter bed media for an efficient biofilter. High elimination capacities in this work probably due to bed temperature, pH, and medium moisture content, which are the three most important parameters for an efficient biofilter [8], were maintained at the optimum conditions as can be seen in Fig. 4 and Fig. 5 (bed temperature ≈ 30°C, pH ≈ 7, and medium moisture content ≈ 97%).

Table 3. *Examples of the steady state results for the removal of methanol.*

Day	Inlet conc. (g/m^3)	Air flow rate (m^3/h)	EBRT (S)	Outlet conc. (g/m^3)	RE (%)	EC (g/m^3h)
37	2.7	0.06	71	0	100	136
44	1.8	0.12	35	0	100	188
70	0.6	0.18	24	0	100	96
95	0.5	0.24	18	0	100	101
102	0.3	0.45	9	0	100	134
111	1.6	0.45	9	0.6	62	380
113	0.7	0.45	9	0.6	14	38

Table 4. *Examples of the steady state results for the removal of toluene.*

Day	Inlet conc. (g/m^3)	Air flow rate (m^3/h)	EBRT (S)	Outlet conc. (g/m^3)	RE (%)	EC (g/m^3h)
18	1.4	0.06	71	0	100	70
44	1.7	0.12	35	0	100	172
70	0.6	0.18	24	0	100	98
95	0.5	0.24	18	0	100	98
102	0.4	0.45	9	0	100	137
109	1.7	0.45	9	0.8	53	346
113	0.6	0.45	9	0.4	39	96

Table 5. *Performance comparison between this work and other biofiltration studies.*

Study	Type of VOC	EC (g/m^3h)
Mohseni and Allen [2]	Methanol	200-250
Shareefdeen *et al.* [9]	Methanol	113
Lee *et al.* [10]	Methanol	20-40
Delhomenie *et al.* [11]	Toluene	42
Morales *et al.* [12]	Toluene	190
This study	Methanol	250-380
	Toluene	278-346

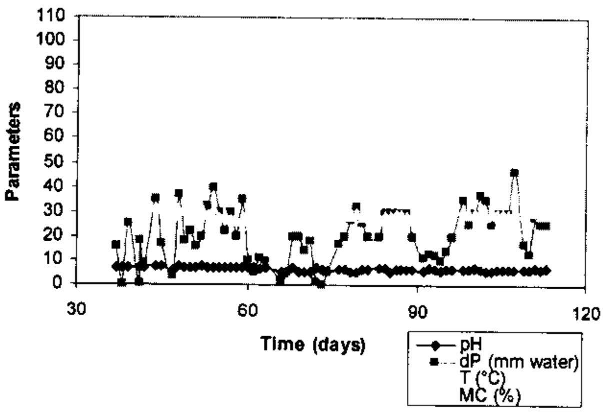

Fig. 4. *The measured values of pH, pressure drop (dP), temperature (T), and moisture content (MC) of the biofilter for removal of methanol.*

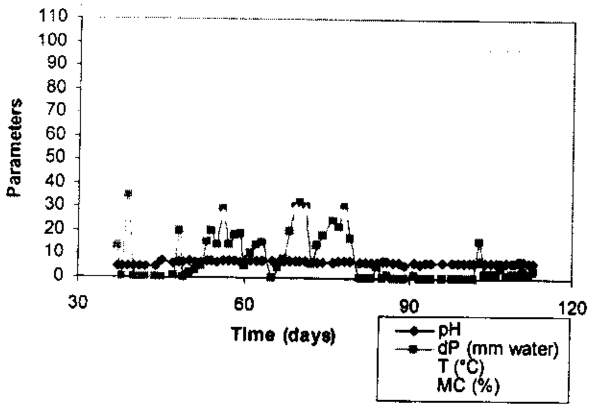

Fig. 5. *The measured values of pH, pressure drop (dP), temperature (T), and moisture content (MC) of the biofilter for removal of toluene.*

The medium bed pressure drops for methanol removal tends to be higher than the values for toluene removal; the maximum value was 47 mm H_2O on days 107 for methanol and 35 mm H_2O on days 39 for toluene. Delhomenie *et al.* stated that the medium bed pressure drop was related to the development of biomass accumulation in the biofilter column [10]. This is in agreement with our result that the accumulation of larger amounts of biofilm was visual observed in the case of methanol removal. To reduce the pressure drop and to protect the bed-clogging problem the biofilter bed was periodically washed with water. The application of bed washing had almost no effect on the microorganisms viability, satisfactory biofilter performance was soon reestablished (indeed by the next day). However, the bed clogging was still taking place resulting in pressure drop increases with time. Therefore, a reliable method for the prevention of the formation of excess biomass is required, especially in the case of methanol removal.

3.2 Influence of air flow rate

Fig. 6 shows the impact of EBRT on the average removal efficiency. It can be seen that the removal efficiency increased with EBRT, especially EBRT in the range of 9-18 s. For long EBRT (71 s) corresponding to air flow rate of 0.06 m^3/h, high removal efficiencies (100% for methanol and 98% for toluene) were observed. High values of EBRT were favorable for the VOC degradation because the contact time between the microorganisms and VOC is increased. On the other hand, for short EBRT (9 s), and thus for correspondingly higher flow rates of 0.45 m^3/h, the removal efficiencies fell to values of less than 42%. Even if VOC flow through the interface was favored by the higher flow rate, the contact time between the microorganisms and the VOC was too short and microorganisms had insufficient time to perform the required degradation on the available amount of VOC.

3.3 Influence of inlet concentration of VOC

Stage F (air flow rate = 0.45 m^3/h) was conducted to investigate the influence of inlet concentration of VOC on the removal efficiency. It was observed that removal efficiency was a decreasing function of the inlet concentration (Fig. 7). For VOC concentrations lower than 1.0 g/m^3, 60-100% of the VOC was eliminated. Over this concentration range, microorganisms were able to metabolize all of the available substrate. For higher concentrations, the level of microorganisms activity became the limiting factor for VOC elimination, the removal efficiency remained below 60% and 40% for methanol and toluene, respectively. However, it should be pointed out that decreasing of removal efficiency with inlet concentration was not observed at lower air flow rate (<0.45 m^3/h).

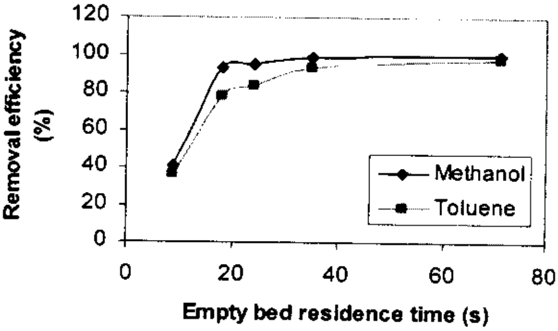

Fig. 6. *Influence of the airflow rate on the average removal efficiencies of the biofilter.*

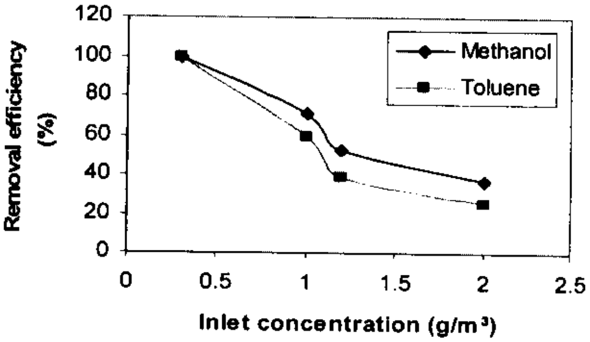

Fig. 7. *Influence of the inlet concentration of VOCs on the removal efficiency of the biofilter at constant air flow rate (0.45 m^3/h).*

3.4 Influence of column height

Removal of methanol increased with the column height as shown in Fig. 8. For removal of toluene, the similar results were observed. This suggests that the removal efficiency depends on the filter bed volume (V) as $V = \frac{\pi D^2 \times H}{4}$, with D = diameter of biofilter column and H = height of filter bed.

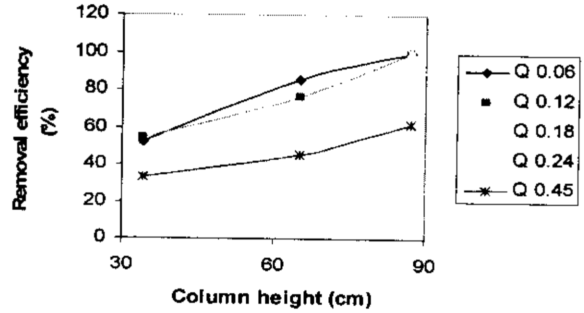

Fig. 8. *Influence of the column height on the removal efficiency of the biofilter for methanol removal, Q = volumetric gas flow rate (m^3/h).*

3.5 Design of biofilter

It is possible to design a biofilter system to treat air contaminated with methanol or toluene by using the elimination capacity obtained in this study. The minimal volume of filter bed can be calculated by $V_m = \frac{C_{Gi} \times Q}{EC_{max}}$, where V_m = minimal volume of filter bed, C_{Gi} = inlet concentration of VOC, and EC_{max} = maximum elimination capacity. If the calculated EBRT, $EBRT = \frac{V_m}{Q}$, is greater than or equal to the EBRT reported in this report, it may be appropriate for use. If not, the EBRT should be increased if a margin of safety is required.

4. CONCLUSIONS

Methanol, a hydrophilic compound, and toluene, a hydrophobic compound, were successfully treated in biofilter consisted of a mixture of palm shells and activated sludge as the filter bed media without inoculation. The bed temperature, pH, and medium moisture content should be maintained at the optimum conditions (bed temperature ≈ 30°C, pH ≈ 7, and medium moisture content ≈ 97%).

The biofilter removed as high as 250 g methanol/m^3 bed medium/h at the retention times as low as 18 s and 278 g toluene/m^3 bed medium/h at the retention time as low as 24 s. For the air flow rate lower than 0.45 m^3/h, the inlet concentration of VOC did not have significant effect on the removal efficiency of the biofilter. However, when the air flow rate was equal to 0.45 m^3/h, the inlet concentration of VOC should be less than 1.0 g/m^3 to obtain the removal efficiency not less than 60%. The removal efficiency is proportional to the filter bed volume. As the volume of media increases, the overall target compound removal efficiency also increases. Since the cost of a biofilter system is also proportional to the volume of media used, a balance between system cost and system performance must be established.

5. ACKNOWLEDGMENTS

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