Biofiltrtion of VOCs in an Effluent Gas from Zeolite Rotor Concentrator

Ching-Yi Wu and Ming-Shean Chou

***Abstract*—In this study, a biotrickling filter (BF) packed with 32 to 64 liters of wood chips with average sizes 2.03cm×2.25cm, wet packing density 470 kg/m3, void fraction 0.57, and specific surface area 300 m2/m3 was tested for the removal of < 10 ppm THC (total hydrocarbon, expressed as methane equivalent) in gases vented from a field zeolite rotary concentrator for waste gas treatment in a TFT-LCD manufacturing plant. Results indicate that with operation parameters of EBRT (empty bed retention time) 2.0 s, pH 6.5-8.0, and daily nutrition milk 0.11 L/m3 chips (10 g milk powder/m3 chips), 50% THC in the influent gas could be removed. It was estimated that around 0.016 USD is required for treating 1000 m3 of the vented gas from concentrators with a gas flow of 2,000 Nm3/min.**

***Index Terms*—Biotrickling filter, volatile organic compounds, TFT-LCD.**

I. Introduction

Semiconductor and thin-film transistor-liquid crystal displayer (TFT-LCD) manufacturing industries have became promising in these years, especially in Asia. The industries use common raw materials such as developer, photoresist and organic solvents which may contain acetone, isopropyl alcohol (IPA), propylene glycol monomethyl ether (PGME) and propylene glycol monomethyl ethyl acetate (PGMEA) etc.[1] Vented gases from the industries should be treated to remove volatile organic compounds contained therein.

One of the most applied equipments for the VOC removal is honeycomb zeolite rotor concentrator (ZRC) in semiconductor and TFT-LCD industries. [1], [2] The ZRC system is suitable for removing VOCs in exhaust gas with characteristics of high flow rate and low VOC concentrations.[2] However, zeolite in rotors may get poisoned or degenerated with time and probably result in a poorly treated gas with VOCs not meeting the upper limit(s) of regulation. Therefore, a post treatment may be necessary for a further removal of the residual VOCs in the ZRC effluent gases. The post treatment may extend the service life of high-cost ZRC.

Biotrickling filtreation (BF) technology has been well developed in theses decades, and it is among the most economical methods for treating VOC-laden gases. A BF process consists of a bed of media for biofilm attachment and a recycling-flow liquid system for supplying water and the required nutrients to the attached biofilm. Fern chips, wood chips, or inorganic plastic packings etc. have been used for the media. VOCs in an influent gas to a BF transferred into the biofilms are then degraded by the organisms therein. Inoculation of suitable microorganisms may be helpful to the degradation of VOCs.

VOCs with properties of low toxicity and high water solubility are suitable for treatment by BFs or biofilters.[3]-[13] Chou and Li used a biofilter with a packing of fern chips to eliminate mixed VOCs gas composted of IPA, acetone, hexamethylene disilazane, PGME, and PGMEA. The biofiter could achieve over 90 % of efficacy with influent VOC concentration of 150-450 mg/m^3, media moisture content of 52-65 %, media pH 7-8 and an empty bed residence time (EBRT) of 45 s.[5] Chou *et al.* also indicated that instant milk addition as a nutrient was essential to keep a good and stable performance for a fern-chip-packed biofilter which could reach an overall PGMEA removal efficiency of approximately 94%.[4] Shareefden *et al.* applied a commercial biofilter to treat emission from a printed circuit board manufacturing facility, and the biofilter could obtain a 99 % removal efficiency of PGMEA with an EBRT of 17 s.[7]

Lafita et al.[8] used a full-scale BF system to treat two sources of waste gases containing mixed VOCs in a painting plant. VOCs of the first source composed of toluene, xylenes, i-butyl acetate, ethylbenzene and n-butyl acetate , and the second consisted of acetone, toluene, and n-butyl acetate. VOCs could be efficiently removed by the BF system to meet local legal emission limits with EBRTs of 20 s and 85 s, respectively, for the two gas streams when passing through the bed. Economic assessment was also evaluated, and the total operation cost was individually US$1.1 and US$ 4.7 per 1000 m^3 for the first and second sources. Sempere et al. [9] directed laboratory and pilot of BF tests to treat n-butyl acetate, toluene and m-xylene and the results indicated that fluctuating and oscillating VOC feeding had a negative effect on BF efficacy, and an installation of an activated carbon prefilter could buffer the inlet VOC loading. Lopez et al. [10] applied a one-stage BF to eliminate mixtures of methanol, α-pinene, and hydrogen sulfide and maximum removal efficacies of 100, 67, and >99%, respectively, with EBRT of 38 or 26s could be reached. The study revealed that BF with specific microbial inoculation could effectively overcame space constraints in industrial facilities.

As above mentioned, BFs have shown potential in field VOC elimination. This study aimed to develop a BF technology which was expected to apply to the removal of low concentrations (< 10 ppm expressed as methane equivalent) of VOCs in effluent gases from ZRCs for TFT-LCD industry. Low-cost and readily-available wood chips for virgin pulp production were used as BF media. Effects of EBRT and nutrient addition on VOC removal efficacy were investigated, and operation parameters for the BF were suggested from the experimental results.

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II. Procedure

A. Experimental Setup

This study was performed in a TFT-LCD manufacturing plant of a photo-electronic company. An effluent gas obtained from a ZRC of the plant was used as a test one. The influent gas contains methanol, acetone and PGMEA etc. Due to the low concentration (<1 ppm) of each individual VOC in the test gas, an unit of total hydrocarbon compound (THC) concentration was used to express the total VOC concentration in the gases influent to and from the test BF. A schematic diagram of the experimental system is shown in Fig. 1. The system consists of an acrylic tank (0.4 mW×0.8 mL×0.6 mH) for holding packing media, a tank (140L) for holding circulation liquid and nutrient addition, a water diaphragm membrane pump for nutrient water recirculation, and a blower for introducing the test gas. As shown in Table 1, the wood-chip packing volume was regulated as the EBRT changed.

The filter media was a blend of wood chips for pulp making and was obtained from a papermaking factory located in southern Taiwan. Characteristics of the wood chips are shown in Table 2. A dry packing density of around 300 kg/m^3 was obtained by measuring the mass of 1 L chips packed in a 2-L beaker. The 1 L chips were then saturated with water by soaking them with water overnight. A wet packing density of 470 kg/m^3 and water-holding capability of 57% (170 kg water in 300 kg dry chips) for the water-saturated chips could be obtained. Besides, a void fraction (ε) of the wet bed was estimated to be 0.57 by water displacement method. The chips had length (L) of 2.03±0.69 cm and width (W) of 2.25±0.37 cm, which were obtained by using a common straight rule. In addition, the specific surface area (a) was calculated by dividing the total surface area of the ten chips by their packing volume obtained by dividing the total wet mass by the estimated wet packing density of 470 kg/m^3.

Before packing, approximately 64 L of the wood chips were soaked in water for a week to ensure the wood chips were totally saturated.

TABLE I: Wood Chips Packing Volumes with Different EBRT

Operating Day	Experimental Phase	Influent gas flow rate, Q (m^3/min)	Packing volume of woodchips (L)	EBRT (s)
0-96th	A	1.50	64	2.56
97th -218^{h}	B	1.84	64	2.08
219th -258th	C	2.19	32	0.88
259th -300th	D	2.37	45	1.14

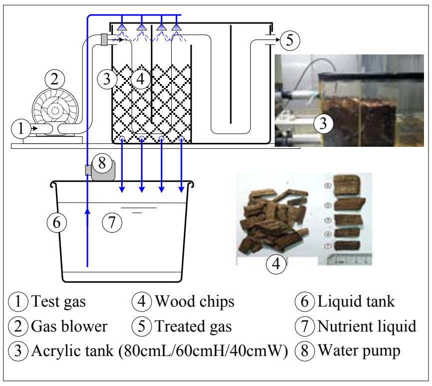


Fig. 1. Schematic diagram of the experimental BF system

TABLE II: Characteristics of the Wood Chips

Item	Value
pH	6.82
Bed bulk density *	300 kg/m^3
Bed bulk density **	470 kg/m^3
Bed void fraction**(ε)	0.57
Bed specific surface area **	300 m^2/m^3
Chip size (cmL×cmW)	(2.03±0.69)×(2.25±0.37)
Chip material	Brown to red wood

*Chips with 20 % moisture content; **Chips with 56 % moisture content

B. Operation

The water-saturated wood chips were put in the acrylic tank to the desired volume, and the BF system started to operate without any seeding. To investigate effects of EBRT and nutrients on the THC elimination efficacy, the operational sequence was divided into five phases based on EBRT and nutrition rates as shown in Tables 1 and 3. In 69th to 96th days (Phase A-2), 200 mL milk, urea, and KH_2PO_4 were added to the nutrient liquid once per week to evaluate the THC removal efficiency. With the THC removal had become stable (after 97th days), urea and KH_2PO_4 were stopped and only 200 mL milk was supplemented once for a month.

The recycled liquid system was supplied with tap water to a volume of around a half, and the water with nutrients was sprayed onto the media surface every 15 minutes in 30 minutes and drained back to the liquid tank. The recycled liquid was replaced once at the 69th day in the whole test time of 300 days. pH of the liquid was in 6.5 to 8.0 without any adjustment.

TABLE III: Operating Condition and Nutrients Addition

Operating Day	Phase	Daily milk (L/m^3 chips)	Daily urea (g/m^3 chips)	Daily KH_2PO_4 (g/m^3 chips)
0-68th	A-1	0.45	0	0
69th -97th	A-2	0.45	169	70.4
97th -218th	B	0.11	0	0
219th -258th	C	0.22	0	0
259th -300th	D	0.16	0	0

C. Analysis

THC concentrations in gases were sampled in Tedlar bags and analyzed by a gas chromatography (GC-14B, Shimazhu Co, Japan) with a capillary column (50 mL×0.53 mm i.d., Alltech Co.) and a flame-ionization detector (FID). pH values were measured using a pH meter (portable pH 3110, WTW, Germany) with a combined pH probe (Sentix 21, WTW, Germany). Biofilms on wood chip surface were examined using an environmental scanning electron microscope (ESEM), model FEI Quanta 2000, before and after field experiments. A small piece of wood chip was picked up from the BF and dried at 50-60 ^oC for 8 hours before being scanned.

III. Results and Discussion

A. EBRT Effects

Fig. 2 illustrates time variations of EBRT, influent THC concentration, and VOC removal efficiency. In Phase A with a duration of 96 days, which included a primary domestication with influent THC of 3.15±1.99 ppm, effluent THC of 1.70±1.99 ppm were obtained. The average removal efficiency was 44.6±15.9 % with an EBRT of 2.56 s in the Phase.

It seemed that the removal efficacy became stable at the end of Phase A, the EBRT was shifted to 2.1 s in Phase B which had an influent and effluent THC concentrations of 4.42±2.13 and 2.45±1.86 ppm, respectively. The influent concentrations were slightly increased, however, the average removal efficiency was 48.5±24.1 %. Because the influent gas of the ZRC was obtained from the exhaust gas from the manufacturing process of the factory, THC in the influent gas to the ZRC might vary with the operation strength of the process, both the removal efficiencies of the ZRC and the BF might also affected by the influent concentrations.

To investigate the feasible EBRT for the BF, a half volume of the packed wood chips was removed and the influent gas flow rate increased in Phase C, an EBRT of 0.88 s was obtained. In the Phase which lasted 39 days, the THC removal efficiency was lower than 20 %. For improving the performance, some used wood chips were refilled to the BF to a packing volume of 45 L. The average removal efficiency was 50.1±10.7 % with an EBRT of 1.14 s with influent THC of 5.49±1.73 ppm and effluent THC of 2.63±0.32 ppm in the last Phase D.

In general, it requires a relatively longer EBRT for the influent to a biofilter or BF to get a reasonable VOC removal efficiency as compared with chemical or physical treatment ones. However, because of the influent VOC concentrations were relatively lower than those cited in the literature, an EBRT of 1.14 s in the present study was much shorter than those of others as shown in Table IV. The plant managers satisfied with the average removal efficacy of 50.1±10.7 % because the odor intensity and the VOC concentration in the effluent gas would meet the regulations by using the BF with limited packing space and installing cost.

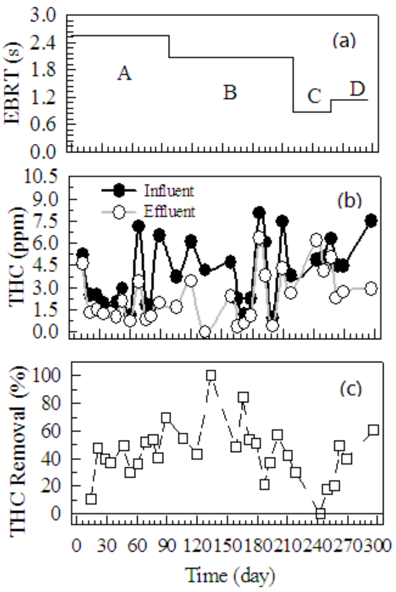


Fig. 2. Time variations of (a) EBRT (b) THC concentrations, and (c) THC removal efficiency.

B. Elimination Capacity

Fig. 3 shows volumetric THC elimination capacity (K) *vs.* volumetric THC loading (L) for EBRT = 2.08s (Phase B) and EBRT = 2.56s (Phase A). The data indicate that performances with an EBRT of 2.56 s were a little better than those with 2.08 s. The former had an THC removal (K/L) of around 52%, and the later around 43%.

C. Nutrition Effects

In Phase A-1, milk was the sole nutrient for the BF in the initial 68 days, the average THC removal was 36.0±12.8% with influent THC of 2.60±1.29 ppm and effluent THC of 1.77±1.32 ppm.

To evaluate effects of nutrient addition on the THC removal, urea and KH_2PO_4 were supplied in Phase A-2. The average removal efficiency raised to 54.2±11.9 %, with influent THC of 4.31±2.91 ppm and effluent THC of 1.81±1.16 ppm.

Take a consideration of nutrient costs, urea and KH_2PO_4 were stopped and daily milk addition decreased from 0.45 L to 0.11 L per m^3 wood chips in Phase B. The THC removal sustained at 41.9±13.1% with influent THC of 4.24±2.96 ppm and effluent THC of 2.73±2.22ppm. The efficacy did not fall obviously with the nutrient reduction, however, significant THC removal dropped down as the EBRT shifted down to 0.88 s in Phase C. The milk addition was increased to those shown in Table III.

It was observed that the nutrient addition slightly increased the removal efficiency and that should be taken into consideration for obtaining an acceptable operation cost.

TABLE IV: COMPARISON WITH OTHER STUDY

Packing media	VOCs	EBRT (s)	Loading (g/m³.hr)	THC Removal Efficacy (%)	Ref.
Wood chips	Acetone, PGMEA, Methanol etc.	1.14	9.20-15.4	50±11	This study
Fern chips	PGMEA	16.2-24	<170	94	[4]
Fern chips	PGMEA, IPA, Acetone , and etc.	45	11-34	90	[5]
Plexiglass chips	Acetone	114	30	About 99	[12]
Coconut fibre	Acetone	114	30	About 95	[12]
Wood-based Biomix	PGMEA	17	<40	76	[7]

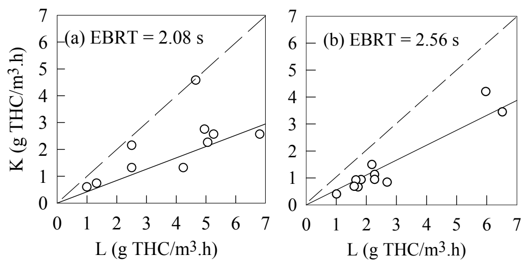


Fig. 3. Volumetric THC elimination capacity (K) vs. volumetric THC loading (L) (a) EBRT = 2.08s (Phase B) and (b) EBRT = 2.56s (Phase A-2)

D. Operation Cost

Table IV gives a simple cost analysis based on the results of the present study for the additional removal of VOCs by the developed BF from the vented gas of zeolite rotor concentrators with an air flow of 2000 Nm^3/min. The analysis was based on a BF with an EBRT of 2.1 s, milk as the sole nutrient, and 50% removal of influent THC of lower than 10 ppm as methane.

As shown in Table IV, it was estimated that around 0.016 USD is required for treating 1000 m^3 of the vented gas from zeolite rotor concentrators with a gas flow of 2,000 Nm^3/min.

TABLE IV: ECONOMICAL ANALYSIS BASED ON THIS STUDY

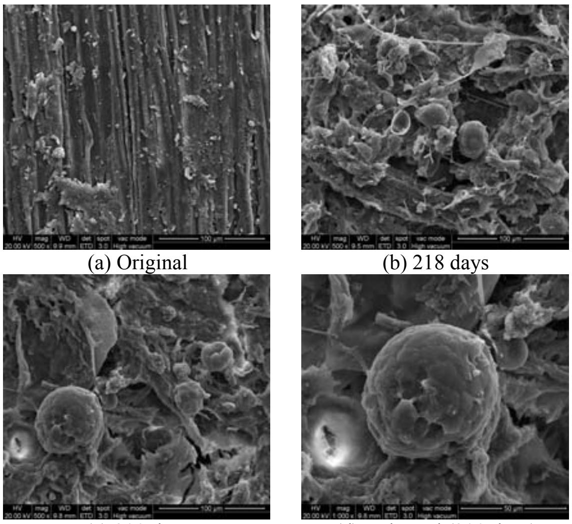
Item	Quantity	Life (year)	Cost (USD/ year)
Required equipment area	50 m^2		
Wood chips*	70 m^3	5	4,670
Equipment *	1 set	15	6,670
Nutrient (milk)**	2.81 m^3	1	5,620
Total			16,960

*Wood chips cost USD 100/m^3, equipment cost USD 100,000/set, milk cost USD 2/ L

** Daily milk addition 0.11 L/m^3 chips

E. ESEM Observation

Samples of the filter media were withdrawn from the BF and observed by the ESEM. Fig 4(a) shows that there was no apparent microorganism on the surface of an examined wood chip. Fig 4(b) shows microorganisms adhered on the surface of a chip packed at the inlet gas end after an operation time of 218 days without any innoculation at the start of the experiment. Fig 4(c) shows the biofilm after 300 days of operation which is similar to that of 218 days. Fig 4(d) shows a closer observation of Fig 4(c) and presents more clear appearance of the attached microorganisms. Further experiments should be done to examine the species of the microorganisms responsible for the PGMEA degradation.



(a) Original (b) 218 days

(c) 300 days (d) Enlarged (300 days)

Fig. 4. ESEM images of the wood chips (a)original (b) 218 days (c) 300 days (4) closer observation of 300 days

IV. CONCLUSIONS

The following conclusions were drawn from the present study:

1) The tested BF packed with wood chips with sizes (2.03±0.69)cm×(2.25±0.37)cm, wet packing density 470 kg/m^3, void fraction 0.57, and specific surface area 300 m^2/m^3 could be used to treat gases with THC of less than 10 ppm (as methane) vented from zeolite rotor concentrators.
2) Suggested operation parameters for the BF of are EBRT 2.0 s, pH 6.5-8.0, and daily nutrition milk 0.11 L/m^3 chips (10 g milk powder/m^3 chips). By the parameters, it is expected that 50% THC in the influent gas could be removed. In addition, it can be estimated that around 0.016 USD is required for treating 1000 m^3 of the vented gas from concentrators with a gas flow of 2,000 Nm^3/min.

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