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A Study on the Reduction Process of VOCs Emission from Paint Booth – A Hybrid Process of Biotrickling Filter and Activated Sludge Reactor

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Abstract

A novel hybrid system composed of a biotrickling filter and an activated sludge reactor was investigated under the conditions of four different SRTs (sludge retention times). The performance of the hybrid reactor was found to be directly comparable among the four different sludge ages. Discernible differences in the removal performance were observed among four different SRTs of 2, 4, 6, and 8 days.

High removal efficiency was achieved by continuous circulation of activated sludge over the immobilized mixture culture, which allowed on pH control, addition of nutrients, and removal of paint VOCs (volatile organic compounds). The results also showed that the removal efficiency for a given pollutant depends on the activity of microorganisms based on the SRT. As the SRT increased gradually from 2 to 8 days, the average removal performance decreased. The highest removal rate was achieved at the SRT of 2 days at which the highest OUR (oxygen uptake rate), 6.1 mg-O_2/liter-min was measured. Biological activity in the recycle microbes decreased to a much lower level, 3.6 mg-O_2/liter-min at a SRT of 8 days. It is thus believed that young microorganisms were more active and more efficient for the VOCs removal of low concentrations and high flow rates. The apparent correlation of $R^2 = 0.996$ between the average removal efficiency and the average OUR at each SRTs suggests that VOCs degradation by young cells significantly affected the overall removal efficiency for the tested SRTs.

Key words : Biotrickling filter, Sludge retention time, VOCs, Oxygen uptake rate, Activated sludge

1. INTRODUCTION

In Korea, total amount of chemicals emitted to the environment was estimated to be 180.5 thousand tons per year in an year of 2002 (Korea MOE, 2004). The emissions from surface coating industry amounted to 57.2 thousand tons (31.7%) per year. Major chemicals were found to consist of toluene (18.4%), xylenes (18.0%), ethylene (9.6%), acetylene (8.5%), ethylacetic acid (5.5%), and others (40.0%). Major sources of toluene, xylenes, and ethylene are the surface coating and automobile industries. These industries have been forced by increasingly stringent environmental regulations (Korea MOE, 2004; Boundries *et al.*, 1997).

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Among treatment technologies of the paint VOC emissions under development, the biological treatment has been emerging in these days (Kinney *et al.*, 2002; Webster *et al.*, 2002). There are two typical types of biological system used to treat odors, VOCs, and HAPs in waste air, which are the biotrickling filter and the conventional biofilter. The main differences between a conventional biofilter and a biotrickling filter (or trickling biofilter) lie in the packing materials and aqueous phases. An aqueous phase in the biotrickling filter is trickling over the filter bed, usually in a continuous mode, while this is not the case in conventional biofilters (Kennes and Veiga, 2001; Cox *et al.*, 2000; Deshusses and Webster, 1997). One assumption commonly made for the process development of biotrickling filters is that biodegradation takes places only in the biofilm, i.e., biodegradation by suspended cells in the recycle liquid is ignored. But it has been recently known that suspended biomass such as activated sludges in the recycle liquid significantly contributes to the overall biodegradation (Deshusses and Johnson, 2000; Cox *et al.*, 1999). In addition, most of the studies (Seignez *et al.*, 2004; Cox *et al.*, 2000; Cox *et al.*, 1999; Bertoni *et al.*, 1996) on these treatment technologies deal with the relatively high concentration. A typical curve for the elimination capacity (EC) of the biofilter shown in Fig. 1 shows that low concentration leads to poor elimination capacity (Deshusses and Johnson, 2000). It should be true that low concentration of pollutant with high Henry's law coefficient and first-order kinetics results in a reduction of the maximum elimination capacity (Deshusses, 1997). Alonso *et al.* (1997) also addresses that not only the amount of microorganisms is important but also its accessibility for pollutant removal of low concentrations and high flow rates. Accumulation of dead and inactive biomass as well as the development of secondary population are likely to occur. Results (Pedersen *et al.*, 1997) obtained with a toluene degrading biotrickling filter indicate that cell death is already significant during the start-up of the filter. Based on the results from these previous studies, it is essential to relate biomass activity of biotrickling filter to the performance enhancement especially for the high flow rate containing the low concentrations of VOCs such as the paint booth emissions.

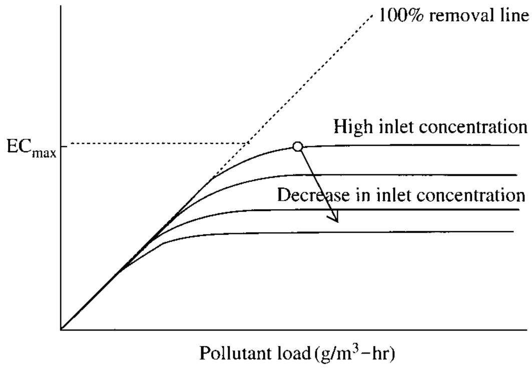

Fig. 1. A typical elimination capacity (EC, g/m^3-hr) vs. pollutant load curve for a biotrickling filter.

The purpose of this study was therefore focused on the dependency of the removal efficiency of the biotrickling filter on the age of microorganisms. It has been demonstrated in this paper that the removal efficiency for a given pollutant would depend on the activity of microorganisms based on the sludge retention time using a new hybrid process of a biotrickling filter and an activated sludge reactor.

2. EXPERIMENT

2. 1 Apparatus and materials

A bench-scale hybrid process of a biotrickling filter and an activated sludge was set up as shown in Fig. 2. In summary, the biotrickling filter consisted of an acrylic column tower 0.15 m (6 inch) in diameter and a length of 1.54 m (60 inch) filled with 0.025 m (1 inch) Pall rings as packing materials. The activated sludge reactor was also constructed of the acrylic material. The reactor consisted of two compartments for internal recycle, which were the aeration chamber with 3 liters of volume and the settling basin with 1.2 liters, separated by an adjustable baffle. Two air bubble diffusers were

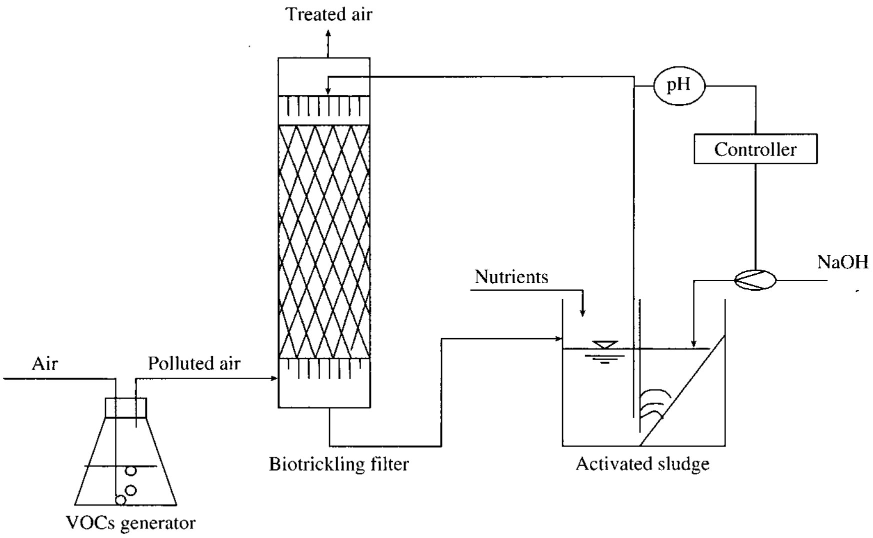

Fig. 2. Schematic of the experimental set-up of the hybride process of biotrickling filter and activated sludge.

used to supply air and provide adequate mixing of the reactor contents.

The aqueous phase carrying activated sludge is trickled over the packing material to maintain a certain level of the MLSS (mixed liquid suspended sludge) concentrations inside of the biotrickling filter. The aqueous phase fed to the biotrickling filter was also a medium containing nutrients, trace minerals, as well as a buffer solution for pH control, as summarized in Table 1. The aqueous phase is initially inoculated with microorganisms, thus a biofilm layer forms on the packing shortly after start-up. Contaminants are transferred to and degraded by microorganisms present within both the recirculating liquid and the biofilm layer.

Table 1. The composition of synthetic feed supplied to activated sludge.

Constituents	Amount
Ethylene glycol	1.13 mL
Ethyl alcohol	1.13 mL
Acetic acid	1.13 mL
Glucose	1.13 gr
Glutamic acid	1.13 gr
Salts: $(NH_4)_2SO_4$, $MgSO_4$, K_2HPO_4, $MnSO_4$, $CaCl_2$, $FeCl_3$	3.444 gr
Total volume of solution	20 L

2. 2 Experimental methods

Activated sludges were introduced into the biotrickling filter from the separated activated sludge system under control of the sludge retention time and the microorganism population in the reactor. The removal performance of the hybrid system was investigated at four different levels of the SRTs of 2, 4, 6, and 8 days with continuous supply of activated sludge from the sludge reactor. Four different air flow rates of 1.33, 2.65, 3.98, and 5.30 m^3/hr were applied, which corresponding to the EBCTs (empty bed contact times) of 72, 36, 27, and 18 seconds and also corresponding to specific volumetric air loads, 50, 100, 150 and 200 m^3/hr-m^3-media, respectively. The operation conditions of the hybrid system are summarized as shown in Table 2 and 3. The contaminated air was upwardly passed through the biotrickling filter and was constantly supplied to the system. Control of the air flow rate and the MLSS circulation rate were accomplished through manual adjustment of valves and an air supply compressor (HP2-LT24, Italy). The MLSS circulation rates controlled by a sludge pump (Milton Roy, model mm1-b-96r) were 24 and 48 liters/day. The temperature of the entire system was controlled by a room air conditioning system and maintained at the room temperature of about 22°C. The pH of the circulating MLSS was monitored using an in-line pH probe (Nema 4× 2530, REMCO, usa) and controlled using feedback to a caustic addition pump (Milton Roy, model mm1-b-96r). The synthetic feed solution containing nutrients was also added to the activated sludge reactor continuously using metering pumps (Milton Roy, model mm1-b-96r). Microorganisms were inoculated as circulating the MLSS for a certain period of time. The growth rates is defined as following equation derived from material balance;

$$\mu = \frac{F_W X_r + (F - F_W) X_e}{VX} \tag{1}$$

and from the above equation, the sludge waste rate can be derived as follows.

$$F_W = \frac{\mu_n VX - FX_e}{X_r - X_e} \tag{2}$$

where F_W=sludge waste rate, μ_n=observed specific growth rate, V=volume of reactor, F=influent flow rate, X_e=effluent suspended solids, X_r= waste solid concentration, and X=solid concentration in aeration tank. The units in the equation should be consistent.

The activated sludge system produced young microorganisms which had high activity. Activated sludge concentration was maintained at about 1,000 mg/L 100 in the reactor. The ages of microorganisms had been usually controlled by the sludge retention time based on the Equations (1) and (2). The activated sludge reactor was operated at four different growth rates (μ_n) of 0.125, 0.167, 0.250 and 0.50 (day^{-1}) as shown in Table 3. Dissolved oxygen concentration was maintained at level of 85 to 95 percent of the saturation value.

The biotrickling filter was operated for 5 days per week, 8 hours per day in a daily continuous mode. In the meantime, the activated sludge system was operated continuously for 24 hours during the given period of this experiment. The biotrickling filter performance was investigated under the operating conditions of biotrickling filter and activated sludge.

Table 2. The operating conditions of biotrickling filter.

Parameters	Operating conditions
SRT (days)	2, 4, 6, 8
pH	6.8～7.2
Air flow rate (m^3/m^3-hr)	50, 100, 150, 200
Empty bed contact time (sec)	18, 27, 36, 72
Toluene concentration (g/m^3)	0.02
Xylenes concentration (g/m^3)	0.02
Ethylene concentration (g/m^3)	0.02
Sludge flow rate (L/hr)	1
MLSS (mg/L)	1,000

Table 3. The operation conditions of activated sludge reactor.

SRT (day)	V (L)	F (L/day)	μ_n (day^{-1})	F_w (L/day)	HRT (hrs)
2	3	9	0.500	1.50	8
4	3	9	0.250	0.75	8
6	3	9	0.167	0.50	8
8	3	9	0.125	0.375	8

A hybrid system composed of a biotrickling filter and an activated sludge reactor was investigated under conditions of four different sludge retention times, and thus the performances of the hybrid reactor were considered to be directly comparable for the four different sludge ages. The VOCs degradation in the synthetic waste air was assessed by taking air samples and analyzing them using a gas chromatograph and also followed by immediate analysis of oxygen uptake rates (OUR) of activated sludge in the circulating liquid at the four different sludge ages. As a measure of the biological activity of the activated sludge during recycling of the culture liquid, the OUR was measured and depicted in Fig. 9. Activated sludge was circulated from an activated sludge reactor over the filter bed at a flow rate of 1.0 L/hr. The synthetic feed containing fresh mineral medium and phosphate buffer were continuously supplied to the activated sludge reactor at a rate of 273 mL/hr according to the SRTs as shown in Table 3. The feed rate of synthetic substrate was chosen from the results

Table 4. The removals of toluene, xylenes, and ethylene with SRTs and flow rates.

VOCs removals	Air flow rates (m^3/hr−m^3 media) 50 SRT (days)				100 SRT (days)				150 SRT (days)				200 SRT (days)			
	2	4	6	8	2	4	6	8	2	4	6	8	2	4	6	8
Xylenes (%)	96	90	87	86	94	87	84	83	92	85	82	81	90	83	80	78
Toluene (%)	94	87	83	81	91	84	81	79	90	82	78	77	88	78	74	72
Ethylene (%)	90	84	80	78	87	81	78	76	85	77	73	72	84	73	70	68
Average (%)	93	88	84	81	91	84	81	79	89	81	78	77	87	78	75	73

of the previous studies (Lim, 1998; Lim, 1986). Paint VOCs were supplied to air stream at a concentration of 0.02 g/m^3 by a metering valve. The paint VOCs included with toluene (99.8%, Fisher scientific), xylenes (98.5%, Fisher scientific), and ethylene (99.95%, Donghwa Energy Co. Ltd.) as shown in Table 2.

2. 3 Analysis

The inlet and outlet air sample analyses were performed using gas chromatographs (Shimatzu GC-14B, FID and TCD). A 30 m length with 0.53 mm ID capillary column was used for VOC separation. Nitrogen (99.99%, Donghwa Energy Co., Ltd.) was used as the carrier gas and the capillary column was set for an initial temperature of 60°C for one minute and ramped 10°C/min to 125°C. Methane gas (99.95%, Donghwa Energy Co. Ltd.) was used as a calibration standard and a commercially supplied standard gas mixture was used to quantify the individual target contaminants in the air samples. Inlet and outlet grab samples for analyses were obtained into 1 L Tedlar bags.

Water samples were periodically collected from both the biotrickling filter and the activated sludge reactor in order to assess the nutrient requirements of the microbes in the reactor. Oxygen up-take rates were measured for the activity of microbes using an oxygen probe (Armfield-W10). A specific set of conditions was maintained until a steady state was obtained as judged from constant paint VOCs and CO_2 concentrations in the outlet gas. Paint VOCs degradation, CO_2 production. biomass accumulation, pressure drop and carbon discharge via the liquid purge were determined on a daily basis over a steady state period of several days and average values were calculated. Analyses of the gas phase and the liquid purge and determination of the biomass accumulation rate allowed the calculation of carbon mass balances and the determination of the influence of biomass age on reactor performance. Each set of conditions was examined at least three times at different values of the sludge retention times in the activated sludge reactor.

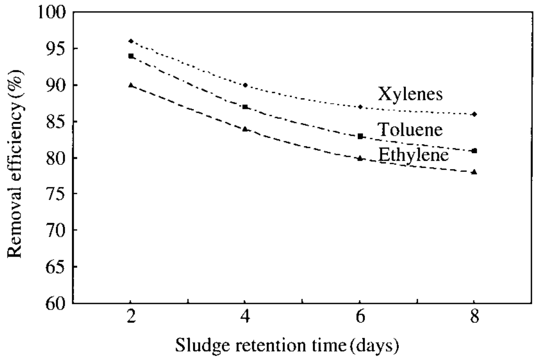

Fig. 3. The removal efficiency of toluene, xylenes, and ethylene with SRTs at air flow rate of 50 m^3/hr-m^3-media.

3. RESULTS AND DISCUSSIONS

The hybrid system was initially operated at a specific air flow rate of 50 m^3/hr−m^3−media, giving an EBCT of 72 seconds, as trickling activated sludges with four different SRTs of 2, 4, 6, and 8 days on the packing material. An effective biofilm was observed on the packing material by the naked eyes after about 5 days and the steady state operation was also established.

The removals of target VOCs at an air flow rate of 50 m^3/hr−m^3−media were in the range of 90% of ethylene to 96% of xylenes for the SRT of 2

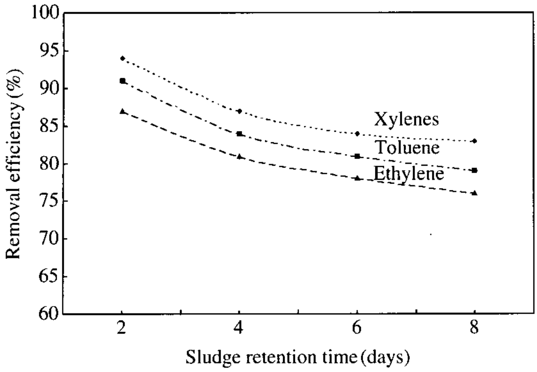

Fig. 4. The removal efficiency of toluene, xylenes, and ethylene with SRTs at air flow rate of 100 m³/hr-m³-media.

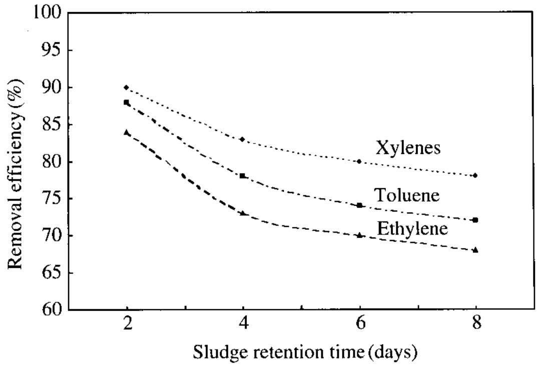

Fig. 6. The removal efficiency of toluene, xylenes, and ethylene with SRTs at air flow rate of 200 m³/hr-m³-media.

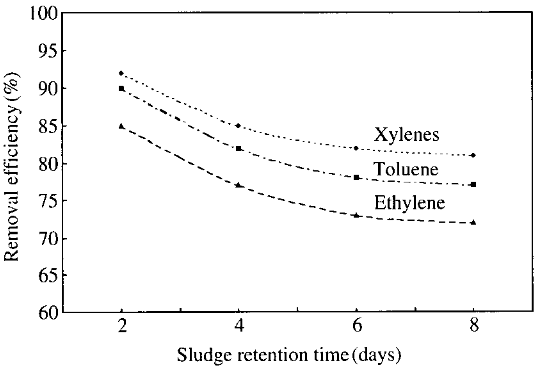

Fig. 5. The removal efficiency of toluene, xylenes, and ethylene with SRTs at air flow rate of 150 m³/hr-m³-media.

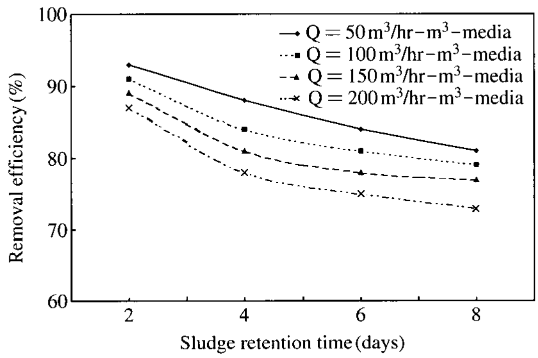

Fig. 7. The average removal efficiency of VOCs with SRTs and air flow rates.

days, 84% of ethylene to 90% of xylenes for the SRT of 4 days, 80% of ethylene to 87% of xylenes for the SRT of 6 days, and 78% of ethylene to 86% of xylenes for the SRT of 8 days as shown in Table 4 and Figure 3. The average removal efficiency was in the range between 81% and 93% for the air flow rate of 50 $m^3/hr-m^3$-media.

Discernible differences in the removal performance among four different SRTs were also observed from the results as shown in Figure 3. Thehighest removal efficiency was achieved on xylenes, whereas, the lowest removal efficiency on ethylene as expected based on the physical and chemical properties of the target pollutants.

For the second phase of the removal study with the same SRTs as ones applied in the previous step, the system was operated at the higher air flow rates of 100, 150, and 200 $m^3/hr-m^3$-media, giving the EBCTs of 36, 27, and 18 seconds, respectively. The VOCs removal rates were in the range of 68.0% of ethylene to 94.0% of xylenes as shown in Table 4 and Figures 4, 5, and 6, respectively.

As the SRT increased gradually from 2 to 8 days, the average removal performance decreased from 93% to 81% for a flow rate of 50 $m^3/hr-m^3$-media, from 91% to 79% for a flow rate of 100 $m^3/hr-m^3$-media, from 89% to 77% for 150 $m^3/hr-$

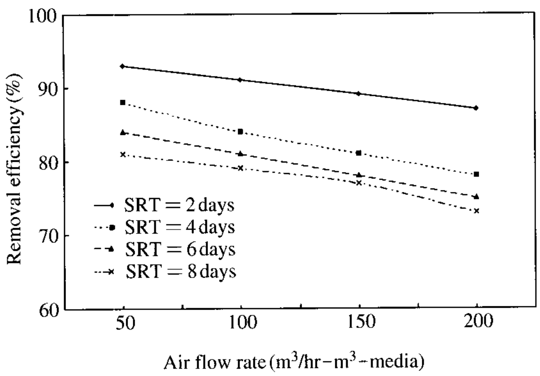

Fig. 8. The average removal efficiency of VOCs with air flow rates.

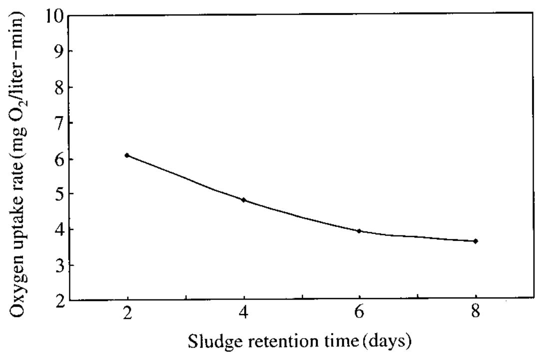

Fig. 9. Average oxygen uptake rate curve with sludge retention times at a specific air flow rate of 50 m^3/hr-m^3-media.

m^3-media, and from 87% to 73% for 200 m^3/hr-m^3-media as also shown in Table 4 and Figure 7. The highest removal rate achieved at the SRT of 2 days, at which the highest OUR, 6.1 mg-O_2/L-min was measured as shown in Figure 9. Biological activity in the recycle microbes decreased to a much lower level, 3.6 mg-O_2/L-min at a SRT of 8 days. It is thus believed that young microorganisms were more active and more efficient for the VOCs removal of low concentrations and high flow rates. From Figures 7 and 8, it is also obvious that the higher air flow rate affected adversary on the removal rates as expected. Therefore, in this hybrid process under study, the booming activity of the young microorganisms were taken advantage of and was not necessary to be avoided, although young microorganisms cause various up-set problems in clarifiers of activated sludge process so that the high portion of young cells in microorganisms should be avoided for the proper operation of clarifiers (Martins *et al.*, 2004; Kim *et al.*, 1998; Lim, 1998a, b, 1986). The filamentous bacteria were not observed so much enough to cause bulking sludge during the study period, but most of bacteria were observed to be pseudomonas sp. The apparent correlation of $R^2=0.996$ between the average removal efficiency and the average OUR at each SRTs suggests that VOCs degradation by young cells significantly affected to the overall removal efficiency for the tested SRTs.

4. CONCLUSIONS

1. A novel hybrid process of a biotrickling filter and an activated sludge reactor was particularly well suited for the treatment of large air streams with low concentrations of pollutants, which performed successfully the removal of paint VOCs containing xylenes, toluene, and ethylene at low SRTs.

2. The highest removal efficiency was achieved at the lowest SRT of 2 days, whereas the lowest removal efficiency at the highest SRT of 8 days.

3. As the SRT increased gradually from 2 to 8 days, the average removal performance decreased. The highest removal rate achieved at the SRT of 2 days, at which the highest OUR, 6.1 mg-O_2/L-min was measured. Biological activity in the recycle microbes decreased to a much lower level, 3.6 mg-O_2/L-min at a SRT of 8 days. It is thus believed that young microorganisms with low SRTs are more active and more efficient for the VOCs removal of low concentrations and high flow rates.

4. The higher air flow rate affected adversary on the removal rates as expected. This may indicates that the biodegradation was also under mass transfer limitation as well as biodegradation rate limitation

5. Although the experiment was performed on a lab-scale, conditions were chosen to simulate application in full-scale hybrid systems.

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