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## CHEMICAL REMOVAL OF BIOMASS FROM WASTE AIR BIOTRICKLING FILTERS: SCREENING OF CHEMICALS OF POTENTIAL INTEREST

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**Abstract**—A protocol was developed to rapidly assess the efficiency of chemical washing for the removal of excess biomass from biotrickling filters for waste air treatment. Although the experiment was performed on a small scale, conditions were chosen to simulate application in full-scale biotrickling filters. From 18 treatments with different combinations and concentrations of chemicals, only washing with 0.4% (w/v) NaOH, 0.26 and 1.31% (w/v) NaClO and 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> resulted in a biomass removal significantly higher than treatment with pure water with wet biomass removal efficiencies of 50.2, 49.2, 77.0 and 69.0%, respectively. Biomass removal by H<sub>2</sub>O<sub>2</sub> and NaClO was accompanied by complete loss of activity of unremoved biomass, whereas after treatment with NaOH low residual biological activity was observed. However, treatment with NaOH resulted in generation of relatively large amounts of suspended solids (22.3% of dry biomass removed) and dissolved carbon (65.3% of C-biomass removed). NaClO was found to be the most promising reagent for biomass control in biotrickling filters because of its ability to remove large amounts of biomass and its low cost. © 1999 Elsevier Science Ltd. All rights reserved

**Key words**—biotrickling filters, waste air treatment, biomass control, chemical removal

### INTRODUCTION

Biological waste gas treatment in biotrickling filters relies on the transfer of pollutants from the gas phase into a biofilm immobilized on a packed bed and subsequent biodegradation. High pollutant degradation rates are obtained by continuous recirculation of a liquid phase over the immobilized mixed culture, which allows for pH control, addition of nutrients and removal of inhibitory compounds.

Clogging of high-performance biotrickling filters caused by excessive biomass growth is one of the main obstacles to the industrial deployment of waste air biotrickling filters (Sorial *et al.*, 1995; Weber and Hartmans, 1996; Cox and Deshusses, 1997). To extend the life-time of biotrickling filters, several strategies have been proposed to either prevent clogging or to remove excess biomass. Reduction of the microbial growth rate in biotrickling filters may be obtained either by nutrient limitation (Holubar *et al.*, 1995; Schönduvel *et al.*, 1996; Weber and Hartmans, 1996) or by maintaining high concentrations of sodium chloride in the recycle water (Diks *et al.*, 1994; Schönduvel *et al.*, 1996). However, reducing the process culture growth rate

usually results in a decrease of the pollutant degradation rate; larger reactor volumes are required, which increases the investment costs. Farmer *et al.* (1995) proposed to increase the life-time of biotrickling filters by periods of starvation, i.e. intermittent treatment of waste gases. Although starvation may result in a decrease of biomass concentration in the starved reactor, for practical applications this may not be economically feasible since at least two reactors would be required to ensure continuous treatment (Cox and Deshusses, 1999). We investigated the use of protozoa that prey upon bacteria for controlling biomass accumulation in toluene-degrading biotrickling filters. Inoculation with protozoa resulted in a lower biomass accumulation rate and an increased carbon mineralization (Cox and Deshusses, 1997). However, further optimization of protozoan predation is required to obtain a zero-balance of biomass growth in these biotrickling filters.

Techniques of mechanical removal of excess biomass in biotrickling filters include backwashing of the reactor and periodic stirring of the packed bed. A stable toluene-degrading biotrickling filter was obtained by frequent backwashing of the reactor with water (Sorial *et al.*, 1995; Smith *et al.*, 1996). Although this technique proved effective, biomass removal required high liquid flow rates to obtain full medium fluidization. Backwashing appears to

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be limited to those biotrickling filters containing support materials that are easily fluidized and a 40% larger reactor volume is required to allow for bed expansion during fluidization (Sorial *et al.*, 1997). A proposed alternative to backwashing is to periodically stir the packed bed to shear off excess biomass (Wübker *et al.*, 1997). It is unclear how the latter proposal can be implemented at an industrial scale.

Chemical removal of biomass is an attractive alternative for biomass control in biotrickling filters but it remains a relatively unexplored area. So far, biomass removal from biotrickling filters by chemical washing has only been reported by Weber and Hartmans (1996), who used a sodium hydroxide solution. In the present contribution, we discuss results on the screening of various chemicals (oxidants, surfactants, bactericidal and hydrolyzing agents) to remove biomass from samples taken from a toluene-degrading biotrickling filter. Experimental conditions were chosen in order to simulate future industrial treatment in biotrickling filters. As an inhibitory action on bacteria by the selected chemicals was expected, the biological activity of unremoved biomass was also measured.

#### MATERIALS AND METHODS

##### Biomass samples

Biomass was grown on the surface of 2.5 cm polypropylene Pall rings (Flexirings<sup>®</sup>, Koch Engineering, Wichita, KS) in a source biotrickling filter (1.3 m in height, 0.152 m in diameter) degrading toluene. The inoculum was a bacterial species isolated from sludge using toluene as the sole carbon and energy source. Compressed air with a metered amount of toluene resulting in an average inlet concentration of  $1.03 \text{ g m}^{-3}$  was passed through the reactor from top to bottom at a volumetric load of  $64 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ , resulting in a toluene load of  $65.9 \text{ g m}^{-3} \text{ h}^{-1}$ . Liquid was recirculated concurrently with the air flow at a superficial velocity of  $7.9 \text{ m h}^{-1}$  and a mineral medium (Cox and

Deshusses, 1997) was continuously fed at a flow rate of  $0.24 \text{ l h}^{-1}$ . Pall rings with biomass were randomly taken from the upper part of the source biotrickling filter after 79 to 147 days of operation for the experiments described below.

##### Experimental set-up

Removal of biomass was investigated in a small test biotrickling filter (0.3 m in height, diameter 0.152 m) stacked with clean Pall rings. A schematic of the experimental set-up is shown in Fig. 1 and a picture of biomass attached on the Pall rings is shown in Fig. 2. For each treatment, five rings with biomass were taken from the source biotrickling filter, weighed after 10 min of drying in air (wet biomass weight plus ring before treatment) and placed at regular intervals along the longitudinal axis of the test biotrickling filter. In most experiments, 0.75 l of liquid containing the tested chemical was recirculated for 3 h over the packed bed at a superficial liquid velocity of  $7.9 \text{ m h}^{-1}$  using a centrifugal pump (model 1P677A from Dayton Electric Mfg. Co., Chicago, IL) and a needle valve and flowmeter combination. At the top of the test biotrickling filter, a liquid distribution system made of a container with equally spaced holes ensured homogenous distribution of the recycle liquid over the packed bed. All treatments lasted for 3 h (except for a treatment with hot water which lasted 30 min) and was ended by stopping the liquid recirculation. The liquid was then allowed to drain from the test biotrickling filter for 10 min and collected for analysis of suspended solids and total dissolved carbon. The rings with unremoved biomass were carefully removed from the test biotrickling filter, air-dried for 10 min and weighed (wet biomass weight plus ring after treatment). Unremoved biomass was separated from the Pall rings and immediately analyzed for biological activity in oxygen uptake rate (OUR) experiments. The Pall rings were cleaned, dried and weighed in order to calculate the amount of wet biomass before and after treatment. The efficiency of biomass removal was calculated as the percentage removal of wet biomass.

In total, 18 different treatments were investigated. The principal action mechanism of each chemical is listed in Table 1. The general procedure as outlined above was followed for the treatment with demineralized water (control experiment,  $\text{H}_2\text{O}$ ), 0.04 and 0.4% (w/v) sodium hydroxide (NaOH), 0.1 and 0.5% (w/v) sodium dodecylsulfate (SDS), 0.01% (w/v) NaOH with 0.1% (w/v) SDS, 0.05

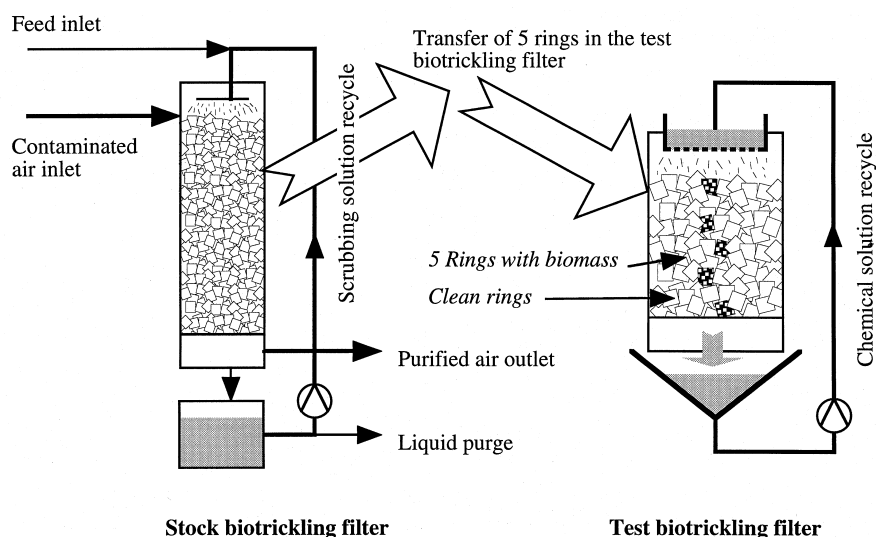


Fig. 1. Schematic of the experimental set-up.



Fig. 2. Picture of a clean Pall ring (left) and one covered with biomass (right) before cleaning. Since the biomass content was very high, a large portion of the inner volume of the ring was filled with biomass.

and 0.2% (w/v) sodium azide ( $\text{NaN}_3$ ), 0.011, 0.26 and 1.31% (w/v) sodium hypochlorite ( $\text{NaClO}$ ), 1.1 and 11.3% (w/v) hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), saturated iodine in 4% (v/v) ethanol [0.02% (w/v)  $\text{I}_2$  as determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$ ], 0.9% (w/v) ammonia ( $\text{NH}_3$ ) and 0.9% (w/v)  $\text{NH}_3$  in combination with 0.22% (w/v) formaldehyde ( $\text{HCO}$ ). For the treatment with demineralized water at elevated temperature ( $\text{H}_2\text{O}$ ,  $T = 63^\circ\text{C}$ ), a heating plate was used to maintain 1.2 l of recycle liquid at  $65^\circ\text{C}$ . This treatment lasted for only 30 min and the average temperature inside the column was  $63^\circ\text{C}$ . For the treatment with ozone, demineralized water was circulated over the column for 3 h while ozone-containing air was passed counter-currently at a flow rate of  $1.9 \text{ l min}^{-1}$ . Ozone was prepared with an ozone generator model 100-O2 from California Acrylic Industries (Pomona, CA). The ozone concentration in the gas phase was  $0.5 \text{ g m}^{-3}$  as determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$  after trapping of ozone in 2% KI (APHA *et al.*, 1985).

#### Analytical procedures

The dry matter content of the biomass was determined in quadruplicate by drying, at  $95^\circ\text{C}$  overnight, known amounts of wet biomass, taken from the source biotrickling filter after 162 days of operation. Analyses of the dried biomass for C, H and N content were done by Desert Analytics Laboratory (Tucson, AZ). Suspended solids in the liquid after treatment were determined by

centrifugation at  $17,000g$  for 10 min and by drying the pellet at  $95^\circ\text{C}$  overnight. Total dissolved carbon in the liquid after treatment was determined in triplicate by analyzing the supernatant using a model TOC-5050 total carbon analyzer (Shimadzu, Kyoto, Japan). The activity of the biomass remaining on the rings after the treatment was determined in OUR experiments. Each of the 5 rings was placed into 100 ml of mineral medium and shaken vigorously to separate the biomass from the ring. OURs with and without 0.19 mM toluene were determined in single experiments at room temperature in a custom made 57 ml glass vial and by using an oxygen electrode and meter (Orion model 860, Boston, MA). OURs were related to the amount of unremoved, wet biomass and toluene-induced OURs were corrected for endogenous respiration.

## RESULTS

#### Characterization of biomass samples

Biomass sampling from the source biotrickling filter started after 79 days of toluene supply, at which time the reactor contained 14.065 kg wet biomass (approximately 60% of the reactor volume). The average amount of wet biomass on the Pall rings was 11.2 g (average of 90 rings, a range of 7.1 to 16.5 g with a standard deviation of 1.9 g). Since the biomass content of the bioreactor was high, biomass was present both inside and on the outer surface of the rings. Assuming a biofilm density of  $1 \text{ kg l}^{-1}$  and that Pall rings can be represented by empty cylinders, the maximum amount of wet biomass needed to fill the ring would be 12.3 g. The average amount of biomass on the rings (11.2 g) indicates that the amount of biomass on the outer surface was small compared to the amount of bio-

Table 1. Principal action mechanisms of the chemicals tested to remove excess biomass in biotrickling filters

Compound	Mechanism
$\text{H}_2\text{O}$	none, control
$\text{NaOH}$	hydrolysis
$\text{NaClO}$ , $\text{H}_2\text{O}_2$ , $\text{O}_3$ , $\text{I}_2$	oxidation
SDS	surfactant
$\text{NaN}_3$	toxic/reduction
Water ( $63^\circ\text{C}$ ), $\text{NH}_3$ , $\text{NH}_3 + \text{HCO}$	other

Table 2. Wet biomass removal efficiency from Pall rings during 3 h treatment in a test biotrickling filter

Treatment No.	Treatment	Wet biomass removal efficiency (%) <sup>a</sup>	pH liquid	
			start	end
1	H <sub>2</sub> O	12.9 (11.0)	ND <sup>c</sup>	7.6
2	H <sub>2</sub> O, <i>T</i> = 63°C <sup>b</sup>	14.6 (11.5)	ND	8.0
3	0.4% (w/v) NaOH	50.2 (22.4)	12.8	12.4
4	0.04% (w/v) NaOH	10.3 (9.8)	12.0	9.5
5	0.5% (w/v) SDS	10.9 (7.0)	6.7	8.0
6	0.1% (w/v) SDS	10.4 (12.0)	6.2	7.4
7	0.04% (w/v) NaOH + 0.1% (w/v) SDS	9.6 (5.1)	11.8	9.2
8	0.2% (w/v) NaN <sub>3</sub>	20.4 (8.0)	7.8	7.9
9	0.05% (w/v) NaN <sub>3</sub>	2.8 (6.7)	7.4	8.3
10	1.31% (w/v) NaClO	77.0 (16.1)	12.1	9.1
11	0.26% (w/v) NaClO	49.2 (13.2)	11.4	9.0
12	0.011% (w/v) NaClO	14.3 (5.6)	ND	8.0
13	11.3% (w/v) H <sub>2</sub> O <sub>2</sub>	69.0 (19.4)	4.3	6.5
14	1.1% (w/v) H <sub>2</sub> O <sub>2</sub>	28.2 (16.0)	5.1	7.3
15	0.02% (w/v) I <sub>2</sub>	10.8 (3.7)	5.4	7.4
16	0.5 g O <sub>3</sub> m <sup>-3</sup> air	5.9 (3.2)	ND	ND
17	0.9% (w/v) NH <sub>3</sub>	6.5 (6.4)	11.5	9.3
18	0.9% (w/w) NH <sub>3</sub> + 0.22% (w/v) HCO	9.9 (11.8)	11.2	10.2

<sup>a</sup>Average of five determinations, standard deviation ( $\sigma_{n-1}$ ) in parentheses. <sup>b</sup>30 min treatment. <sup>c</sup>Not determined.

mass inside the ring. This was confirmed by visual observation (Fig. 2). The average dry matter content of the biomass was 4.86%. Elemental analysis of the dried biomass showed a C:H:N ratio of 43.4:6.2:7.8% on a dry weight basis.

#### Chemical removal of biomass

The control experiment with recirculation of demineralized water resulted in an average loss of wet biomass of 12.9%. Visual observation indicated that mainly biomass from the outer surface of the rings was removed, whereas biomass inside the rings was still present. Since no chemical reaction between water and biomass is expected, selective removal of biomass from the outer surface of the rings in this case was due to shear stresses caused by trickling of liquid on the rings in the column and/or to losses during handling of the rings.

Table 2 summarizes the wet biomass removal efficiencies of the treatments investigated as well as pH measurements of the liquid before and after treatment. Most treatments had about the same removal efficiency as the control treatment with water. Only treatments with 0.4% (w/v) NaOH, 0.26 and 1.31% (w/v) NaClO and 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> resulted in statistically significant higher removal efficiencies (Student *t*-test, *p* > 0.95). Biomass in the treatments using 0.26 and 1.31% (w/v) NaClO and 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> turned from an initial brown color to yellowish-white at the end of the treatment. This was not observed in treatments with 0.011% (w/v) NaClO nor with 1.1% (w/v) H<sub>2</sub>O<sub>2</sub>. In treatments using NaOH, only the 0.4% (w/v) NaOH application resulted in the remaining biomass becoming a highly viscous liquid. All treatments with SDS resulted in significant foaming. Comparison of the pH during treatment and removal efficiencies at

0.04 and 0.4% NaOH (w/v) (Table 2) indicates that biomass removal induced by an alkaline environment may be expected at a pH of about 12.4 and higher.

#### Analysis of the liquid after treatment

Biomass reduction may either be due to biofilm detachment (cells and flocs), to solubilization of biomass by chemical reaction or to oxidation of biomass to volatile compounds. In order to quantify these processes, the amounts of suspended solids and total dissolved carbon in the liquid after treatment were determined. It should be noted that larger flocs tended to be captured on clean Pall rings below the test rings in the test biotrickling filter and thus determination of suspended solids in the liquid is an underestimation of biofilm detachment. The liquid after treatment contained small amounts of suspended solids and dissolved carbon in cases of treatments with low biomass removal efficiencies, whereas the highest amounts were found in treatments with high biomass removal efficiencies (Table 3).

Since the total amounts of wet biomass on five rings before and after treatment were known and biomass dry matter and carbon content were determined, mass balances were calculated for the treatments with high removal efficiencies. As reported in Table 4, treatment with 0.4% (w/v) NaOH resulted in a slightly higher recovery of removed biomass as suspended solids, which may indicate that detachment of cells and biofilm flocs was a more important process in this treatment as compared to the treatments with NaClO and H<sub>2</sub>O<sub>2</sub>. Marked differences were found in the recovery of removed C-biomass as dissolved carbon, with values ranging from 18.5% for the treatment with 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> to

Table 3. Removal of biomass from Pall rings as suspended solids and total dissolved carbon

Treatment	Suspended solids (SS)		Dissolved carbon (C)	
	total (mg)	biomass recovered as SS (%) <sup>a</sup>	total (mg)	biomass recovered as dissolved C (%) <sup>b</sup>
H <sub>2</sub> O	45	2.3	10	1.2
H <sub>2</sub> O, T = 63°C	128	6.2	40	4.5
0.4% (w/v) NaOH	194	11.2	247	32.8
0.04% (w/v) NaOH	81	3.3	110	10.5
0.5% (w/v) SDS	54	2.5	132 <sup>d</sup>	14.3
0.1% (w/v) SDS	70	3.3	0 <sup>d</sup>	0
0.04% (w/v) NaOH + 0.1% (w/v) SDS	31	1.5	110 <sup>d</sup>	12.0
0.2% (w/v) NaN <sub>3</sub>	51	1.9	15	1.3
0.05% (w/v) NaN <sub>3</sub>	28	1.6	11	1.4
1.31% (w/v) NaClO	245	11.2	353	37.3
0.26% (w/v) NaClO	155	6.8	224	22.6
0.011% (w/v) NaClO	82	3.9	37	4.11
1.3% (w/v) H <sub>2</sub> O <sub>2</sub>	187	9.9	105	12.8
1.1% (w/v) H <sub>2</sub> O <sub>2</sub>	172	7.7	39	4.0
0.02% (w/v) I <sub>2</sub>	77	4.1	ND	ND
0.5 g O <sub>3</sub> m <sup>-3</sup> air	ND <sup>c</sup>	ND	ND	ND
0.9% (w/v) NH <sub>3</sub>	39	1.5	125	11.1
0.9% (w/v) NH <sub>3</sub> + 0.22% (w/v) HCO	54	2.1	21 <sup>d</sup>	1.9

<sup>a</sup>Dry suspended solids in the liquid after treatment, as percentage of the total amount of dry biomass present on five Pall rings before treatment (dry biomass = 0.0486 × wet biomass). <sup>b</sup>Total dissolved carbon in the liquid after treatment, as percentage of the total amount of C-biomass present on five Pall rings before treatment (C-biomass = 0.4339 × dry biomass). <sup>c</sup>Not determined. <sup>d</sup>Values corrected for the presence of carbon containing reagents, assuming that the reagent concentration at the end of the treatment was the same as initially present.

65.3% for the treatment with 0.4% (w/v) NaOH. No attempts were made to close dry matter and carbon balances, which would have required analysis of the liquid for dissolved solids and analysis of the gas phase for production of CO<sub>2</sub> and volatile organic compounds. However, assuming that the carbon content in suspended solids was the same as that in the biomass before treatment, the ratio of C-liquid produced to C-biomass removed in the treatments with 0.4% (w/v) NaOH, 0.26 and 1.31% (w/v) NaClO and 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> was 88, 60, 63 and 33%, respectively (Table 4). These results may indicate that oxidation of biomass to gaseous or

volatile compounds was significant in the treatments using oxidants, such as NaClO and especially H<sub>2</sub>O<sub>2</sub>.

#### Biological activity of unremoved biomass

Endogenous and toluene-induced OURs of fresh biomass analyzed before chemical treatment were on average 1.31 and 1.46 μg O<sub>2</sub> g<sup>-1</sup> wet biomass · min<sup>-1</sup>, respectively. In the control experiment with water, unremoved biomass had approximately the same activity (Table 5). This indicates that 3 h of trickling of a liquid on the test rings in the test biotrickling filter is in itself not a cause for loss of biological activity. The data reported in Table 5 shows

Table 4. Mass balances for four treatments with the highest biomass removal efficiency

Parameter	Treatment			
	0.4% (w/v) NaOH	0.26% (w/v) NaClO	1.31% (w/v) NaClO	11.3% (w/v) H <sub>2</sub> O <sub>2</sub>
<i>Dry biomass</i>				
Biomass before treatment (g)	1.733	2.282	2.182	1.892
Biomass removed <sup>a</sup> (g)	0.870	1.123	1.680	1.306
Recovered as suspended solids (g)	0.194	0.155	0.245	0.187
Recovery of removed biomass as suspended solids (%)	22.3	13.8	14.6	14.3
<i>Carbon</i>				
C-biomass before treatment (g)	0.752	0.990	0.947	0.821
C-biomass removed <sup>b</sup> (g)	0.378	0.487	0.729	0.567
Recovered as dissolved C (g)	0.247	0.224	0.353	0.105
Recovery of removed C-biomass as dissolved C (%)	65.3	46.0	48.4	18.5
Total carbon recovery <sup>c</sup> (%)	88	60	63	33

<sup>a</sup>Assuming that the dry matter content in biomass before and after treatment is the same (0.0486 g dry biomass g<sup>-1</sup> wet biomass). <sup>b</sup>Assuming that the carbon content of dry biomass before and after treatment is the same (0.4339 g C g<sup>-1</sup> dry biomass). <sup>c</sup>(Suspended solids × 0.4339 + dissolved carbon)/C-biomass removed.

Table 5. Biological activity of unremoved biomass measured as the oxygen uptake rate ( $\mu\text{g O}_2 \text{g}^{-1} \text{wet biomass min}^{-1}$ ; average of five determinations with standard deviation ( $\sigma_{n-1}$ ) in parentheses)

Treatment	Endogenous	Toluene-induced
H <sub>2</sub> O	1.21 (0.27)	1.92 (0.54)
H <sub>2</sub> O, T = 63°C	0	0
0.4% (w/v) NaOH	0.76 (0.52)	0.12 (0.26)
0.04% (w/v) NaOH	1.27 (0.22)	0.06 (0.11)
0.5% (w/v) SDS	1.54 (0.51)	0.59 (0.37)
0.1% (w/v) SDS	2.54 (0.59)	0.59 (0.70)
0.04% (w/v) NaOH + 0.1% (w/v) SDS	1.69 (0.78)	0.15 (0.18)
0.2% (w/v) NaN <sub>3</sub>	0.55 (0.11)	0.27 (0.21)
0.05% (w/v) NaN <sub>3</sub>	1.45 (0.39)	1.13 (0.70)
1.31% (w/v) NaClO	0	0
0.26% (w/v) NaClO	0	0
0.011% (w/v) NaClO	0.93 (0.15)	0.78 (0.43)
11.3% (w/v) H <sub>2</sub> O <sub>2</sub>	0	0
1.1% (w/v) H <sub>2</sub> O <sub>2</sub>	0.24 (0.21)	0.09 (0.15)
0.02% (w/v) I <sub>2</sub>	1.63 (0.41)	0.64 (0.32)
0.5 g O <sub>3</sub> m <sup>-3</sup> air	1.21 (0.58)	0.82 (0.38)
0.9% (w/v) NH <sub>3</sub>	0.67 (0.33)	0.05 (0.09)
0.9% (w/w) NH <sub>3</sub> + 0.22% (w/v) HCO	0	0

that chemical treatments caused various levels of inhibition of biological activity of the remaining biomass, depending on the chemical used. Interestingly, toluene oxidation generally appeared to be more inhibited than endogenous respiration, but this was not further investigated. From the four treatments with high biomass removal efficiencies, only unremoved biomass in the treatment with 0.4% (w/v) NaOH showed some level of biological

activity. In fact, toluene oxidation activity was found in only one sample out of the five examined. Treatments with 0.26 and 1.31% (w/v) NaClO and 11.3% (w/v) H<sub>2</sub>O<sub>2</sub> resulted in a complete loss of respiration activity of the unremoved biomass. In these cases it was found that residual H<sub>2</sub>O<sub>2</sub> and NaClO concentrations in suspensions for OUR experiments (i.e. after ten-fold dilution of unremoved biomass in mineral medium and assuming that the biomass was saturated with the reagent in a concentration as initially present at the start of the treatment) were sufficiently high to cause complete inhibition of respiration activity of fresh and untreated biomass.

#### DISCUSSION

The efficiency of biomass removal of biomass from Pall rings was investigated in a laboratory test biotrickling filter at a superficial liquid velocity commonly used in biotrickling filter operation. Experimental conditions were chosen to simulate chemical removal of biomass in full-scale biotrickling filters, with the exception being that the Pall rings with biomass in the test biotrickling filter were surrounded by clean Pall rings. The high ratio of reagent to biomass may have facilitated reaction in the test biotrickling filter and, consequently, removal efficiencies as reported in Table 2 may be higher than with actual treatment in biotrickling filters under otherwise identical conditions. As indi-

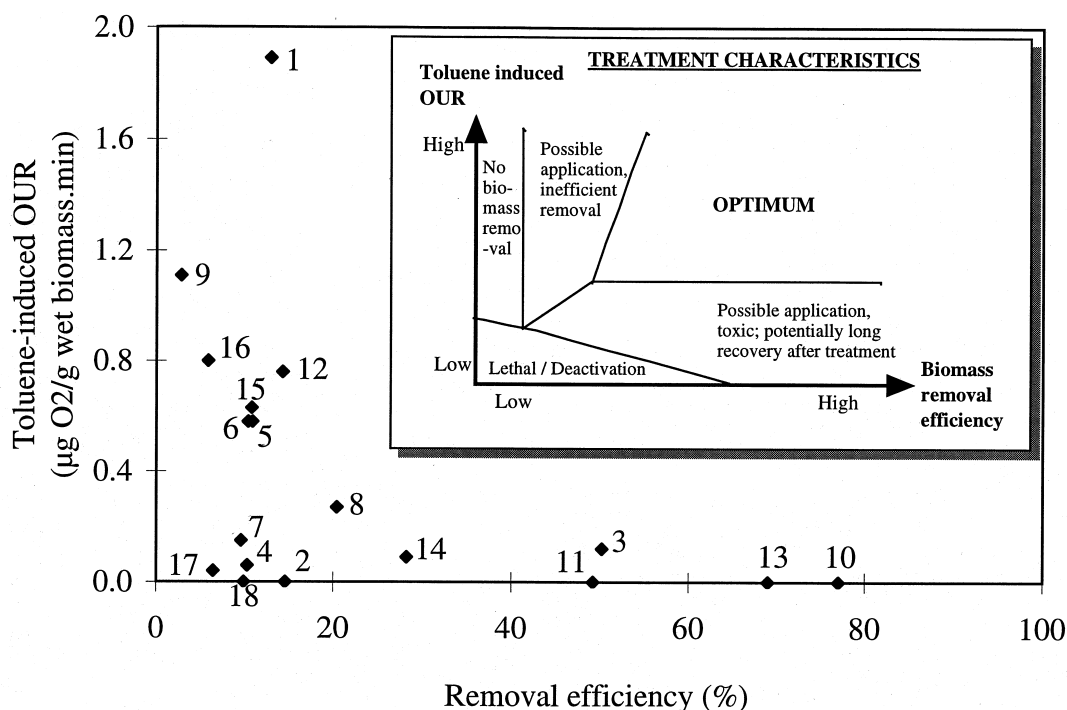


Fig. 3. Correlation between toluene-induced oxygen uptake rate in the biomass remaining after treatment and wet biomass removal efficiency of the various treatments (see Table 2 for identification of each treatment). The inset shows target characteristics for various treatments.

cated by the high standard deviation, removal efficiencies per treatment sometimes varied considerably (Table 2). Since the distribution of biomass on the ring was different for each sample, access of liquid to the biomass may have differed as well. This may also have resulted in different ratios of inactive to active biomass in samples within each treatment, causing large fluctuations in the biological activity of unremoved biomass as observed in OUR experiments (Table 5).

Chemical treatment of clogged biotrickling filters should result in a high efficiency of biomass removal to reduce the frequency of cleaning. Ideally, chemical treatment should also have minimum adverse effects on the activity of biomass remaining on the rings in order to reduce the time of recovery of the biotrickling filter after treatment (Fig. 3, Inset). In Fig. 3, the toluene oxidation activity of the unremoved biomass after the treatment is plotted vs biomass removal efficiencies. Many treatments resulted in partial or complete inactivation of the biomass without significant removal of biomass. These include the treatments with SDS (a surfactant commonly used with NaOH in an alkali lysis procedure to disrupt cell membranes; Sambrook *et al.*, 1989),  $I_2$  (an alternative for NaClO/Cl<sub>2</sub> in wastewater disinfection; White, 1972), NaN<sub>3</sub> (an inhibitor of the respiratory chain at concentrations of 0.0065–0.065%; Heinen, 1971) or water at 63°C. Biomass removal efficiencies could have been better for these treatments if higher reagent concentrations were tested. OUR experiments however show that these treatments should probably not be considered because of their toxicity at low concentration. The low biomass removal efficiency in these and other treatments is most probably due to the fact that cells in a biofilm are embedded in a polymer matrix. This may have served as a means to increase cell detention but did not offer much protection against the diffusion of aggressive chemicals. It further suggests that successful development of biomass washing strategies should consider chemicals that have a proven effect on the components of the polymer matrix.

Treatment with ozone did not result in biomass removal, although ozone is a stronger oxidant than NaClO ( $E^0 = 1.24$  and  $0.90$  mV, respectively; Lide, 1996). Apparently the ozone concentration in the gas phase ( $0.5 \text{ g m}^{-3}$ ) and the corresponding concentration in the liquid phase ( $0.1 \text{ mg l}^{-1}$ , dimensionless Henry coefficient of 0.2; White, 1972) were too low to effectively oxidize or remove biomass. This is further supported by Siddiqui *et al.* (1997) who observed that removal of biodegradable dissolved organic carbon (BDOC) from drinking water sources was optimal at an applied ozone to DOC ratio of 2:1 ( $\text{g g}^{-1}$ ). Although ozone treatment of BDOC and immobilized biomass may not be directly comparable, the results of Siddiqui *et al.* (1997) indicate that the ozone to carbon ratio

applied in our experiment was too low ( $0.25 \text{ g g}^{-1}$ ). The economical and ecological impacts of using a 2:1 ratio to remove excess biomass in biotrickling filters is not yet known.

No treatment was found that can combine a high biomass removal efficiency and high toluene oxidation activity of the biomass remaining after treatment (Fig. 3). OUR experiments did not allow for distinction between loss of activity due to cell death during chemical treatment and permanent or temporary inhibition of still viable cells. Also, since unremoved biomass was not washed after treatment (to simulate industrial operation), residual reagents may have affected OUR experiments. In control experiments with H<sub>2</sub>O<sub>2</sub> and NaClO, calculated residual reagent concentrations were sufficiently high to completely inhibit respiration of fresh biomass, even after a ten-fold dilution to suspend the biomass for OUR experiments. H<sub>2</sub>O<sub>2</sub> and NaClO are well-known disinfectants and concentrations used in this study were several orders of magnitude higher than that required for disinfection (White, 1972). The present results indicate that rapid recovery of biotrickling filters after treatment with NaClO or H<sub>2</sub>O<sub>2</sub> may be hindered by both cell death during treatment as well as the presence of residual reagent in unremoved biomass after treatment. This suggests that post treatments using a reducing agent in the case of a chemical wash with an oxidant or using an acid or pH buffer after an alkali treatment might be beneficial. Such a post treatment would neutralize the active chemical and eliminate the effect of any residual chemicals. This could potentially speed up the recovery of the process culture filter after chemical treatment. From the four treatments with significantly higher biomass removal efficiencies, only biomass after treatment with 0.4% (w/v) NaOH showed some biological activity in OUR experiments. This speaks in favor of the use of NaOH to control biomass accumulation in biotrickling filters. Weber and Hartmans (1996) indeed observed that the toluene elimination capacity of a biotrickling filter was fully restored within one day after treatment with 0.4% (w/v) NaOH. They also found that the NaOH washes resulted in an average removal of 230 g dry biomass from a 71 l reactor, i.e.  $3.2 \text{ kg dry biomass m}^{-3}$ . The percentage biomass removal in the case of Weber and Hartmans (1996) could not be calculated and compared to the results of the present research, because the amount of biomass in their reactor was not determined. However, a removal of  $3.2 \text{ kg dry biomass m}^{-3}$  reactor volume is insufficient for controlling biomass in high performance biotrickling filters that are subject to rapid clogging. Our source-biotrickling filter gained approximately  $0.37 \text{ kg dry biomass m}^{-3} \text{ reactor-day}^{-1}$ , which would require treatment with 0.4% (w/v) NaOH once every 8.7 days to maintain a constant biomass concentration in the reactor. A more effective reagent may be desired to obtain a higher

biomass removal efficiency and to reduce the frequency of treatment. Furthermore, our experiments showed that treatment with NaOH resulted in a liquid with relatively high concentrations of suspended solids and dissolved carbon in the recycle water (Table 4). This may cause a problem for the disposal of the wastewater in an industrial application. Hence, the most promising chemical for application in full-scale biotrickling filters appears to be sodium hypochlorite. It is effective at low concentrations, inexpensive and does not require complex instrumentation or major process changes to be made to current biotrickling filter systems. Subsequent experiments (results not shown) where clogged biotrickling filters were treated with hypochlorite confirmed the effectiveness of NaClO in removing large amounts of biomass. While initially, inactivation of pollutant degrading organisms was a concern because of the results presented in Table 5, these subsequent experiments indicated that the down time following treatment could be shortened to less than two or three days. At this time, even if issues related to the formation of volatile chlorinated compounds during treatment with hypochlorite require additional investigations, the historical acceptance of using chlorination for large-scale water disinfection may facilitate the implementation of chlorination for the control of biomass accumulation in biotrickling filters.

#### CONCLUSIONS

1. A protocol was developed which allowed a rapid evaluation of the ability of various chemicals to remove excess biomass in biotrickling filters for air pollution control. While simulating real operating conditions, the protocol is very simple and allows for significant time and cost savings.
2. Of the seventeen combinations tested, only treatment with 0.4% NaOH (wet biomass removal efficiency 50.2%), 0.26% NaClO (49.2% removal efficiency), 1.31% NaClO (77.0% removal efficiency) and 11.3% H<sub>2</sub>O<sub>2</sub> (69.0% removal efficiency) showed a significantly higher removal of biomass than the control treatment with pure water.
3. In most cases, efficient biomass removal resulted in a complete loss of biological activity as measured in OUR experiments. Both cell death during treatment and inhibition by residual reagent concentrations are likely to influence the acclimation period of biotrickling filters after treatment with chemicals such as with NaOH, NaClO and H<sub>2</sub>O<sub>2</sub>.
4. Some treatments resulted in complete cell death or complete inhibition of microbial activity, but were relatively ineffective in removing biomass. This may indicate that the development of suc-

cessful strategies to chemically remove excess biomass should focus on the destruction of the biofilm polymer matrix, rather than on the bacterial cells.

5. NaClO was found to be one of the most promising reagents for further evaluation because biomass removal efficiency was high at a relatively low NaClO concentration. Furthermore, experience from large-scale use of NaClO/Cl<sub>2</sub> in water disinfection may help rapid implementation of the use of NaClO to control biomass in industrial biotrickling filters for waste air treatment.

#### REFERENCES

- APHA, AWWA and WPCF (1985) *Standard Methods for the Examination of Water and Wastewater Treatment*, 16th edn. Washington, DC.
- Cox H. H. J. and Deshusses M. A. (1997) The use of protozoa to control biomass growth in biological trickling filters for waste air treatment. In *Proc. Air and Waste Manage. Assoc. 90th Annual Meeting and Exhibition*, June 9–13, 1997, Nashville, TN, 10 pp. Paper 97-RA71C.05.
- Cox H. H. J. and Deshusses M. A. (1999) Biomass control in waste air biotrickling filters by protozoan predation. *Biotechnol. Bioeng.*, in press.
- Cox H. H. J., Nguyen T. T. and Deshusses, M. A. (1998) Elimination of toluene vapors in biotrickling filters: performance and carbon balances. In *Proc. Air and Waste Manage. Assoc. 91st Annual Meeting and Exhibition*, June 14–18, 1998, San Diego, CA, 15 pp. Paper 98-WAA.04P.
- Diks R. M. M., Ottengraf S. P. P. and Van den Oever A. H. C. (1994) The influence of NaCl on the degradation rate of dichloromethane by *Hyphomicrobium* sp.. *Biodegradation* **5**, 129–141.
- Farmer R. W., Chen J.-S., Kopchynski D. M. and Maier W. J. (1995) Reactor switching: proposed biomass control strategy for the biofiltration process. In *Biological Unit Processes for Hazardous Waste Treatment*, eds. R. E. Hincee, S. D. Sayles and R. S. Skeen, pp. 243–248. Battelle Press, Columbus, OH.
- Heinen W. (1971) Inhibitors of electron transport and oxidative phosphorylation. In *Methods in Microbiology*, eds. J. R. Norris and D. W. Ribbons, Vol. 6A, pp. 383–393. Academic Press, London, U.K.
- Holubar P., Andorfer C. and Braun R. (1995) Prevention of clogging in trickling filters for purification of hydrocarbon-contaminated air. In *Proc. 1995 Conference on Biofiltration*, 5–6 Oct., pp. 115–122. University of Southern California, Los Angeles, CA.
- Lide D. R. (1996) *Handbook of Chemistry and Physics*, 77th edn. CRC Press, Boca Raton, FL.
- Sambrook J., Fritsch E. F. and Maniatis T. (1989) *Molecular Cloning: A Laboratory Manual*, 2nd edn. Cold Spring Harbor Laboratory Press, New York, NY.
- Schönduvel P., Sára M. and Friedle A. (1996) Influence of physiologically relevant parameters on biomass formation in a trickle bed bioreactor used for waste gas cleaning. *Appl. Microbiol. Biotechnol.* **45**, 286–292.
- Siddiqui M. S., Amy G. L. and Murphy B. D. (1997) Ozone enhanced removal of natural organic matter from drinking water sources. *Waste Air Treat. Res.* **31**, 3098–3106.
- Smith F. L., Sorial G. A., Suidan M. T., Breen A. W., Biswas P. and Brenner R. C. (1996) Development of two biomass control strategies for extended, stable oper-



- ation of highly efficient biofilters with high toluene loadings. *Environ. Sci. Technol.* **30**, 1744–1751.
- Sorial G. A., Smith F. L., Suidan M. T. and Biswas P. (1995) Evaluation of trickle bed biofilter media for toluene removal. *J. Air Waste Manage. Assoc.* **45**, 801–810.
- Sorial G. A., Smith F. L., Suidan M. T., Pandit A., Biswas P. and Brenner R. C. (1997) Evaluation of trickle bed air biofilter performance for BTEX removal. *J. Environ. Eng.* **123**, 530–537.
- Weber F. J. and Hartmans S. (1996) Prevention of clogging in a biological trickle-bed reactor removing toluene from contaminated air. *Biotechnol. Bioeng.* **50**, 91–97.
- White G. C. (1972) *Handbook of Chlorination*. Van Nostrand Reinhold Company, New York, NY.
- Wübker S.-M., Laurenzis A., Werner U. and Friedrich C. (1997) Controlled biomass formation and kinetics of toluene degradation in a bioscrubber and in a reactor with a periodically moved trickle-bed. *Biotechnol. Bioeng.* **55**, 686–692.