Development of Foamed Emulsion Bioreactor for Air Pollution Control

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Abstract: A new type of bioreactor for air pollution control has been developed. The new process relies on an organic-phase emulsion and actively growing pollutant-degrading microorganisms, made into a foam with the air being treated. This new reactor is referred to as a foamed emulsion bioreactor (FEBR). As there is no packing in the reactor, the FEBR is not subject to clogging. Mathematical modeling of the process and proof of concept using a laboratory prototype revealed that the foamed emulsion bioreactor greatly surpasses the performance of existing gas-phase bioreactors. Experimental results showed a toluene elimination capacity as high as 285 $g_{toluene}\ m^{-3}{}_{reactor}\ h^{-1}$ with a removal efficiency of 95% at a gas residence time of 15 s and a toluene inlet concentration of 1–1.3 g m^{-3}. Oxygen limited the reactor performance at toluene concentration above about 0.7–1.0 g m^{-3}; consequently, performance was significantly improved when pure oxygen was added to the contaminated air. The elimination capacity increased from 204 to 408 g $m^{-3}\ h^{-1}$ with >77% toluene removal at toluene inlet concentrations of 2–2.2 g m^{-3}. Overall, the results show that the performance of the FEBR far exceeds that of currently used bioreactors for air pollution control. *Biotechnol Bioeng* **84**: 240–244, 2003.
Keywords: VOC control; biofilter; air pollution control; toluene; biologically activated foam; biodegradation

INTRODUCTION AND NEW BIOREACTOR CONCEPT

Biological treatment is an emerging technique for air pollution control. It often offers a cost-effective solution for the treatment of large volumetric air streams containing low levels of pollutants (Devinny et al., 1999; Leson and Winer, 1991). The most widely used bioreactors for air pollution control are biofilters and biotrickling filters (Cox and Deshusses, 1998), but both have significant limitations. Biofilter performance is usually limited to <100 g of pollutant removed per cubic meter bed per hour (g $m^{-3}\ h^{-1}$), most probably because the biodegradation process relies essentially on resting cells (Cherry and Thompson, 1997; Fürer and Deshusses, 2000). Biotrickling filters often exhibit higher performance than biofilters (Gabriel and Deshusses, 2003), but it has been frequently shown that accumulation of biomass in the bed correlates with pollutant elimination. Excess biomass clogs the reactor, which requires costly remedial or preventive actions (Cox and Deshusses, 1999; Laurenzis et al., 1998; Smith et al., 1996; Wübker et al., 1997).

A large body of research exists on biofilters and biotrickling filters (Devinny et al., 1999) and possible improvements of these techniques. This includes rotating biofilters (Sabo et al., 1995), the use of rotating biological contactors (Vaidila and Welch, 2000; Vinage et al., 2001), and the recent proposal of a modified type of a rotating biotrickling filter (Yang et al., 2002). Unfortunately, these new developments have only resulted in modest improvements of the performance over existing techniques. Only a few authors have made attempts to develop completely new gas-phase bioreactors that would overcome the limitations of biofilters and biotrickling filters. The most relevant attempts include the use of a second nonmiscible phase to improve mass transfer of hydrophobic compounds (Cesario et al., 1997; Collins and Daugulis, 1999; Malinowski, 2001) and biologically active foams to increase gas/liquid interfacial area (Lejeune et al., 1998; Phipps, 1998).

In the present paper, we present for the first time a combination of these two concepts into what we refer to as the foamed emulsion bioreactor (FEBR). The FEBR consists of an emulsion of highly active pollutant-degrading microorganisms and a water-immiscible organic phase, which is made into a foam with the air being treated (Fig. 1). After the desired treatment is achieved, the foam is collapsed continuously, and the emulsion cells are reused. Motivations for this approach lie on the increased gas/liquid interfacial area provided by fine foams and on the increase in driving force for mass transfer resulting from the presence of a water-immiscible organic phase. Further, the FEBR relies on a high-density culture of actively growing organisms in order to attain high volumetric pollutant removal rates. At the same time, bed clogging and associated pressure drop problems are avoided by using a moving foam rather than an immobilized culture growing on a support. Herein, the proof of concept of foamed emulsion bioreactors is presented and the effects of key operating parameters on the performance of a prototype bioreactor are examined.

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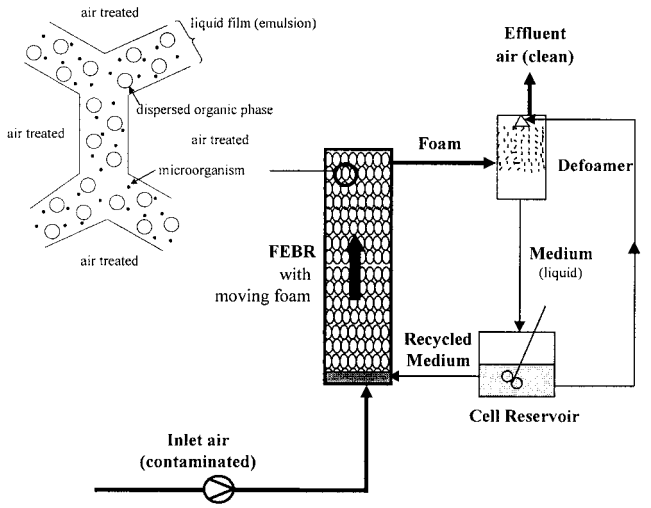

Figure 1. Schematic of the FEBR concept and experimental prototype.

MATERIALS AND METHODS

Reactor Setup and Operating Conditions

The prototype foamed emulsion bioreactor system consisted of the actual foam column, a cell reservoir, and a defoamer (Fig. 1). The foam column (4.04 cm ID, 40 cm high, volume 0.51 L) had a fine gas sparger at the bottom of the reactor. A metered stream of toluene-contaminated air was introduced through the gas sparger while an emulsion consisting of mineral medium containing 1 g L^{-1} KH_2PO_4, 1 g L^{-1} K_2HPO_4, 1 g L^{-1} KNO_3, 1 g L^{-1} NaCl, 0.2 g L^{-1} $MgSO_4$, 26 mg L^{-1} $CaCl_2 \cdot 2H_2O$, 5.2 mg L^{-1} EDTA $Na_4(H_2O)_2$, 1.5 mg L^{-1} $FeCl_2 \cdot 4H_2O$, 0.12 mg L^{-1} $CoCl_2 \cdot 6H_2O$, 0.1 mg L^{-1} $MnCl_2 \cdot 2H_2O$, 0.07 mg L^{-1} $ZnCl_2$, 0.06 mg L^{-1} H_3BO_3, 0.025 mg L^{-1} $NiCl_2 \cdot 6H_2O$, 0.025 mg L^{-1} $NaMoO_4 \cdot 2H_2O$, 0.015 mg L^{-1} $CuCl_2 \cdot 2H_2O$, the active culture (see below), the organic phase (oleyl alcohol, Sigma Chemical Co., St. Louis, MO), and the surfactant (DC-100 silicone, Sigma) were introduced at the bottom of the reactor. Proportions of each component are given below. After rising through the reactor, the foam leaving through a side port was defoamed in a defoamer consisting of a 1-L flask, by continuously spraying the foam with the emulsion from the cell reservoir. The liquid was returned to the cell reservoir (a 0.5-L flask) prior to being recycled to the foam-generation column. The total amount of liquid in the system was about 0.3 L, and the liquid hold-up volume in the FEBR column was about 10%. Note that the defoamer and cell reservoir volumes were not optimized at this stage of the research.

The toluene-degrading consortium used in the experiments was initially obtained from a biotrickling filter in our laboratory. The mixed culture was grown prior to each experiment by bubbling toluene-laden air (1–2 g m^{-3}) through mineral medium in a 10-L bubble column reactor and concentrated by centrifugation before each experiment.

Experiments

To determine the performance of the reactor, the effects of gas flow rate, oleyl alcohol concentration, and culture density were examined. All the experiments were carried out with continuously fed toluene-contaminated air, while the cell suspension/emulsion was recycled in a closed-loop through the EFBR–defoamer–cell reservoir (Fig. 1). Batch operation without wasting any biomass was warranted, as all experiments were relatively short (2–8 h). Some experiments were conducted at toluene inlet concentrations of 0.5–0.8 g m^{-3} and others, at 1.1–1.3 g m^{-3}. To investigate the effect of the gas velocity on the reactor performance, the reactor was operated with 0.3 L of culture containing 5% (v/v) oleyl alcohol, 0.2% (v/v) silicone surfactant, and 48 g_{dw} L^{-1} of the toluene-degrading consortium at air linear velocities ranging from 1.0 to 3.1 m min^{-1} (corresponding to empty bed residence times of 8–22 s). Similar conditions were used to determine the effect of varying the oleyl alcohol concentration from 0 to 3% (v/v) at a linear air velocity of 1.6 m min^{-1}. The effect of culture density (2–32 g_{dw} L^{-1}) was determined at 3% (v/v) oleyl alcohol and the conditions described above. A series of experiments was conducted in an attempt to increase the elimination capacity by increasing the toluene loading and increasing the dissolved oxygen concentration in the FEBR. For this, a high toluene inlet concentration (2–2.2 g m^{-3}) was selected and 0.5 mL min^{-1} of 3% hydrogen peroxide was continuously added to the reactor or a metered stream of pure oxygen was added to the contaminated air being treated.

Analytical Methods

Biomass was monitored either by measuring the optical density at 600 nm with a spectrophotometer (Shimazu, Kyoto, Japan) or by dry weight determination after overnight drying of aliquots at 70°C. The reactor setup included on-line monitoring of CO_2 (non-dispersive infrared) and dissolved oxygen (electrochemical sensor) both from Vernier Instruments (Beaverton, OR). Gaseous toluene concentrations were measured by gas chromatography (HP 5890) and a FID detector. Gas sampling ports were located before the FEBR (inlet) and after the defoamer (outlet). Simultaneous analysis of selected samples collected at the top of the FEBR column and after the defoamer confirmed that no pollutant biodegradation was occurring in the defoamer.

Definition

The performance of the FEBR was reported as the toluene elimination capacity defined in Eq. (1). Consistent with other research on gas-phase bioreactors (Devinny et al., 1999), the volume of the active bed, i.e., the volume of the rising foam, is used for the normalization of the performance, as this is where the main processes are occurring.

Elimination Capacity (EC) =

$$\frac{\text{Gas flow} \times (Cg_{in} - Cg_{out})}{\text{Volume FEBR}} (\text{g m}^{-3}\ \text{h}^{-1}) \quad (1)$$

RESULTS AND DISCUSSION

Oleyl alcohol was chosen as the organic phase in the FEBR due to its biocompatibility and high partition coefficient for toluene (Collins and Daugulis, 1999), while the silicone surfactant was selected for its biocompatibility and excellent foaming ability (Hill, 1999). Even so, biocompatibility tests consisting of *Escherichia coli* growth kinetic determinations (not shown) were performed. A pure culture rather than a toluene-degrading consortium was used to avoid possible flaws resulting from the different effects of the surfactant or organic phase on the various members of the consortium. The biocompatibility tests revealed little or no negative effects on *E. coli* growth by oleyl alcohol concentrations up to 30% and silicone surfactant concentrations up to 1%. Experiments proceeded with the proof of concept of the FEBR.

The key parameters expected to influence the performance of the FEBR are gas velocity, toluene concentration, organic-phase fraction, and culture density. The oleyl alcohol concentration influences the mass transfer of the treated pollutant and possibly local biokinetics, whereas culture density and toluene concentration affect the biodegradation rate. Therefore, the effects of those key parameters were investigated. First, the oleyl alcohol fraction was varied from 0 to 3% (v/v); a high-density culture (48 $g_{dw}\ L^{-1}$) was used to avoid kinetic limitations.

Results reported in Fig. 2 show that the toluene removal efficiency and the elimination capacity increased up to a concentration of 2% of oleyl alcohol but appeared to level off at about 3% oleyl alcohol. The maximum performance reached was a toluene elimination capacity (EC) of 240 g $m^{-3}\ h^{-1}$ at 91% removal. This performance is very high compared to other studies on toluene removal in gas-phase bioreactors. Usual reported maximum ECs for toluene in biofilters and biotrickling filters range from about 30 to 80 g $m^{-3}\ h^{-1}$, which is usually achieved at partial removal of 30–60% (Cox and Deshusses, 1999; Kirchner et al., 1989; Pedersen and Arvin, 1995, 1977; Smith et al., 1996; Sorial et al., 1994; Weber and Hartmans, 1996). One exception is the high performance (up to about 270 g $m^{-3}\ h^{-1}$) achieved by fungal biofilters (Garcia-Pena, 2001; Woertz et al., 2001). However, fungal-based systems are sometimes subject to process instabilities, especially if dimorphic fungi are used (Woertz et al., 2001), and fungal-based biofilters may not apply to as many pollutants as bacterial-based systems. Examination of Fig. 2 further reveals that an improvement of about 45% is achieved at 3% oleyl alcohol compared to a foam reactor operated without oleyl alcohol, proving the substantial benefit of adding a second phase into the foam reactor.

Next, the effect of varying the cell density (from 2 to 32 $g_{dw}\ L^{-1}$) was investigated. As shown in Fig. 3, there was roughly a doubling of the performance when the cell density was increased from 2 to 4 $g_{dw}\ L^{-1}$, indicating that the FEBR was kinetically limited at lower cell density. Above 16 $g_{dw}\ L^{-1}$, there was no significant enhancement of the reactor performance. Under these conditions a removal efficiency of 95% and an EC of 285 g $m^{-3}\ h^{-1}$ were obtained. The process was limited both by oxygen (see low DO on Fig. 3) and by the supply of the toluene substrate (i.e., nearly all toluene was removed). Determination of the carbon-CO_2 recovery showed most (75–100%) of the toluene degraded was mineralized to CO_2 by the process culture.

The effect of the gas velocity on the reactor performance is reported in Fig. 4. In this experiment, a high-density culture (48 $g_{dw}\ L^{-1}$) was used again so that the biological reaction would not be limiting. The FEBR exhibited toluene removal efficiencies exceeding 90% and an elimination capacity of 67–130 g $m^{-3}\ h^{-1}$ at gas velocities below 1.6 m min^{-1}, i.e., empty bed residence time above 15 s. As the

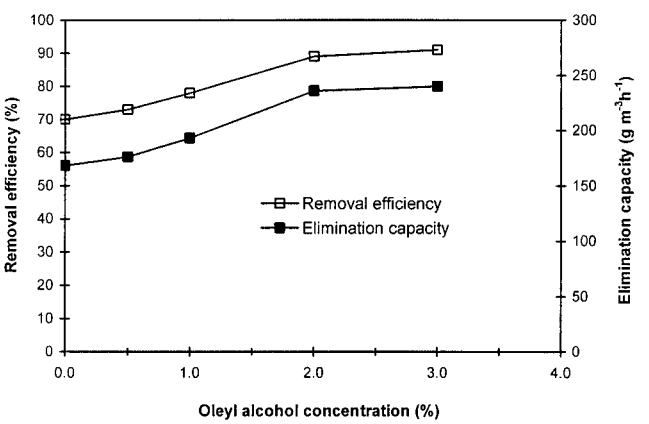

Figure 2. Effect of oleyl alcohol concentration on toluene removal and elimination capacity. Conditions: toluene inlet concentration, 1.0–1.1 g m^{-3}; empty bed residence time, 15 s; culture density, 48 g_{dw}/L; silicone surfactant concentration, 0.2% (v/v).

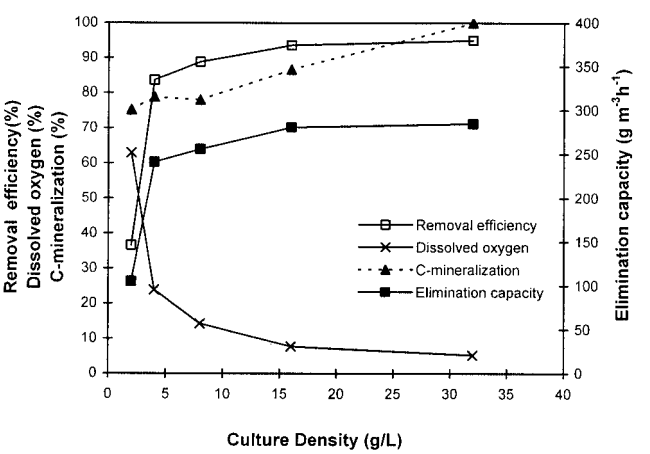

Figure 3. Effect of culture density on toluene removal and elimination capacity. Carbon mineralization is calculated as C-CO_2 produced/C-toluene degraded. Conditions: toluene inlet concentration, 1.2–1.25 g m^{-3}; empty bed residence time, 15 s; oleyl alcohol concentration, 3%; silicone surfactant concentration, 0.2% (v/v).

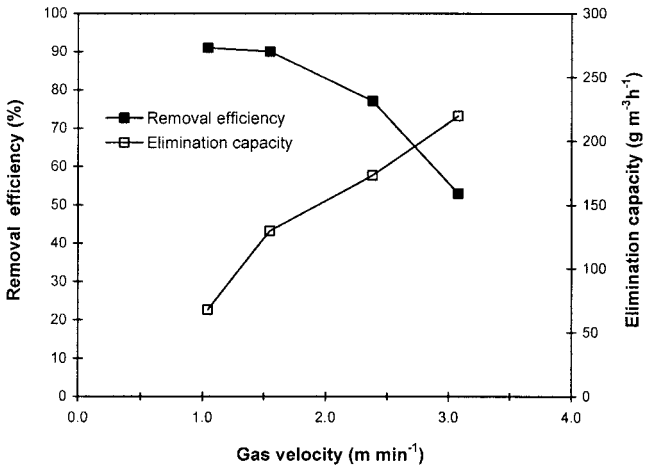

Figure 4. Effect of gas velocity (corresponding air residence time is 8–23 s.) on toluene removal and elimination capacity. Conditions: toluene inlet concentration, 0.46–0.87 g m^{-3}; oleyl alcohol concentration, 3%; silicone surfactant concentration, 0.2% (v/v); culture density, 48 g_{dw} L^{-1}.

flow rate increased and the empty bed residence time decreased, toluene loadings increased and the removal efficiencies dropped to 50% while the elimination capacity reached values of about 220 g m^{-3} h^{-1}. At high velocities, the performance of the FEBR was visibly affected by foam stability and air short-circuiting. Still, as discussed above, the observed performance was well above commonly reported values for toluene elimination in biofilters and biotrickling filters.

Further experiments at higher toluene loadings were warranted to demonstrate that the limits of the FEBR had not yet been reached. The toluene loading could be increased either by decreasing the gas contact time or by increasing the toluene inlet concentration. As mentioned, it was difficult to reduce the gas residence time in the FEBR prototype to less than 8 s because of foam instability at high air linear velocity. Instead, the loading was increased by increasing the toluene inlet concentration. However, on the basis of the stoichiometry of complete biodegradation, oxygen diffusion is expected to become limiting at toluene concentrations above about 0.7 g m^{-3} (see also Fig. 3), making it necessary to supplement oxygen in the process culture. Possible means to provide oxygen include adding hydrogen peroxide to the culture as an oxygen source and adding pure oxygen to the air treated (Lifke and Onken, 1992; Zappi et al., 2000). Both approaches were investigated in the FEBR at a high inlet toluene concentration (2–2.2 g m^{-3}), although it should be stressed that adding oxygen to the air undergoing treatment has no practical application, as it would be cost prohibitive. It was used here solely to demonstrate high performance by lessening the oxygen limitation.

There was no improvement of the toluene elimination in the FEBR when feeding continuously 0.5 mL min^{-1} of 3% hydrogen peroxide, i.e., the exact amount required to oxidize the toluene load (data not shown). This may have been due to the effect of oxygen scavengers in the culture or due to a toxic effect of peroxide to the cells, although the exact reasons have not been further investigated. When pure oxygen was added to the contaminated air treated, there was a very significant improvement of the toluene EC, from 204 to 408 g m^{-3} h^{-1} (Fig. 5), with corresponding increases in CO_2 production (80–86%, of toluene degraded recovered as CO_2). Still, during the experiment, the dissolved oxygen concentration in the FEBR was found to be only 0.6–0.7 ppm, indicating that the process culture was still subject to significant oxygen limitations. Thus the performance of the FEBR could be further increased if more oxygen could be supplied to the culture to prevent oxygen limitation.

CONCLUSIONS

A new gas-phase bioreactor for air pollution control, referred to as a foamed emulsion bioreactor (FEBR), was developed, and the proof of concept was shown. Experiments with a laboratory-scale prototype demonstrated that rapid mass transfer of toluene between the air undergoing treatment and pollutant-degrading organisms was achieved in the foamed emulsion, and that using a high-density cell culture resulted in rapid and complete mineralization of toluene, the model pollutant. Adding a second nonmiscible phase to the culture to form an emulsion improved the performance of the bioreactor by 45%. The effect of various parameters (gas flow, organic phase concentration, cell density) on the reactor performance was investigated in order to better understand the performance and limits of the new bioreactor. Under selected conditions, performances as high as 95% removal at toluene elimination capacities of 285 g m^{-3} h^{-1} were achieved. Under these conditions, both oxygen and pollutant-substrate limitations occurred. At higher toluene inlet concentrations (2.2 g m^{-3}) and loadings, the EC improved significantly, from 204 to 408 g m^{-3} h^{-1}, when pure oxygen was added to the contaminated air being treated to lessen oxygen limitation in the culture. Such high

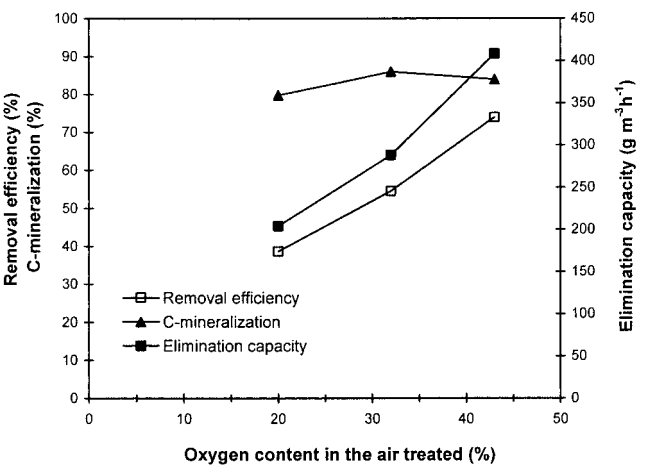

Figure 5. Effect of adding pure oxygen to the air treated on the reactor performance. Conditions: empty bed residence time, 15 s; toluene inlet concentration, 2.2 g m^{-3}; oleyl alcohol concentration, 3%; silicone surfactant concentration, 0.2% (v/v); culture density, 32 g_{dw} L^{-1}.

toluene-elimination performance is far superior to any previously reported for conventional or novel bioreactors for air pollution control. Clearly, however, the next challenges will be to solve foam stability issues at high air velocity and to find means to supply enough oxygen to the culture, especially in the case of the treatment of hydrophilic compounds. The full potential of the FEBR has not yet been explored. For example, the FEBR could prove to be a very effective setup for treating air toxics such as trichloroethylene (TCE) that require cometabolism, as the FEBR system allows for a clear separation of the cell production and the biodegradation steps.

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References

Cesario MT, Wit HL, Tramper J, Beeftink HH. 1997. Dispersed organic solvent to enhance the overall gas/water mass transfer coefficient of apolar compounds in the biological waste-gas treatment. Modeling and evaluation. Biotechnol Prog 13:399–407.

Cherry RS, Thompson DN. 1997. The shift from growth to nutrient-limited maintenance kinetics during acclimation of a biofilter. Biotechnol Bioeng 56:330–339.

Collins LD, Daugulis AJ. 1999. Benzene/toluene/*p*-xylene degradation. Part I. Solvent selection and toluene degradation in a two-phase partitioning bioreactor. Appl Microbiol Biotechnol 52:359–365.

Cox HH J, Deshusses MA. 1998. Biological waste air treatment in biotrickling filters. Curr Opin Biotechnol 9:256–262.

Cox HH J, Deshusses MA. 1999. Biomass control in waste air biotrickling filters by protozoan predation. Biotechnol Bioeng 62:216–224.

Devinny JS, Deshusses MA, Webster TS. 1999. Biofiltration for air pollution control. New York: CRC Lewis Publishers. p 10–15.

Fürer C, Deshusses MA, 2000. Biodegradation in biofilters: did the microbe inhale the VOC? Paper 799. In: Proceedings of the 93rd Annual Meeting and Exhibition of the Air & Waste Management Association. Pittsburgh, PA: Air & Waste Management Association. 13 pp.

Gabriel D, Deshusses MA. 2003. Retrofitting existing chemical scrubbers to biotrickling filters for H_2S emission control. Proc Natl Acad Sci U.S.A. 100(11):6308–6312.

Garcia-Pena EI, Hernandez S, Favela-Torres E, Auria R, Revah S. 2001. Toluene biofiltration by the fungus *Scedosporium apiospermum* TB1. Biotechnol Bioeng 76:61–69.

Hill RM. 1999. Siloxane surfactant. In: Hill RM, editor. Silicone surfactants. New York: Marcel Dekker Inc. p 13–28.

Kirchner K, Schlachter U, Rehm HJ. 1989. Biological purification of exhaust air using fixed bacterial monocultures. Appl Microbiol Biotechnol 31:629–632.

Laurenzis A, Heits H , Wübker SM, Heinze U, Friedrich C, Werner U. 1998. Continuous biological waste gas treatment in stirred trickle-bed reactor with discontinuous removal of biomass. Biotechnol Bioeng 57:497–503.

Lejeune KE, Wild JR, Russell AJ. 1998. Nerve agents degraded by enzymatic foams. Nature 395:27–28.

Leson G, Winer AM. 1991. Biofiltration—an innovative air pollution control technology for VOC emissions. J Air Waste Manage Assoc 41: 1045–1054.

Liefke E, Onken U. 1992. Influence of total and oxygen partial pressure on growth and metabolism of *Methylomonas clara.* Biotechnol Bioeng 40:719–724.

Malinowski JJ. 2001. Two-phase partitioning bioreactors in fermentation technology. Biotechnol Adv 19:525–538.

Pedersen AR, Arvin E. 1995. Removal of toluene in waste gases using a biological trickling filter. Biodegradation 6:109–118.

Pedersen AR, Arvin E. 1997. Toluene removal in a biofilm reactor for waste gas treatment. Water Sci Technol 36:69–76.

Phipps DW. 1998. Biodegradation of volatile organic contaminants from air using biologically activated foam. US Patent No. 5,714,379.

Sabo F, Schneider T, Fischer K. 1995. Improvement and application of high-efficiency biofilters. In: Hodge DS, Reynolds FE Jr, editors. Proceedings of the 1995 USC–TRG conference on biofiltration. Tustin, CA: The Reynolds Group. p 217–224.

Smith FL, Sorial GA, Suidan MT, Breen AW, Biswas P, Brenner RC. 1996. Development of two biomass control strategies for extended, stable operation of highly efficient biofilters with high toluene loadings. Environ Sci Technol 30:1744–1751.

Sorial GA, Smith FL, Smith PJ, Suidan MT, Biswas P, Brenner RC. 1994. Biofilters treat contaminated air. Water Environ Technol 6:50–54.

Vaidila AK, Welch C. 2000. BIOSCRUB—an innovative process for VOC and odor control. Paper 0587. In: Proceedings of the 93rd Annual Meeting and Exhibition of the Air & Waste Management Association. Pittsburgh, PA: Air & Waste Management Association. 9 pp.

Vinage I, Wegmann A, Rudolf van Rohr P. 2001. Novel reactor for waste gas purification: modified rotating biological contactor. Paper 0195. In: Proceedings of the 94th Annual Meeting and Exhibition of the Air & Waste Management Association. Pittsburgh, PA: Air & Waste Management Association. 6 pp.

Yang C, Suidan MT, Zhu X, Kim BJ. 2002. Comparison of structures and performances of two types of rotating biofilters for VOC removal. In: Hodge DS, Reynolds FE Jr, editors. Proceedings of the 2002 USC–TRG conference on biofiltration. Tustin, CA: The Reynolds Group. p 231–240.

Woertz JR, Kinney KA, McIntosh NDP, Szaniszlo PJ. 2001. Removal of toluene in a vapor-phase bioreactor containing a strain of the dimorphic black yeast *Exophiala lecanii-corni.* Biotechnol Bioeng 75: 550–558.

Weber FJ, Hartmans S. 1996. Prevention of clogging in a biological trickle-bed reactor removing toluene from contaminated air. Biotechnol Bioeng 50:91–97.

Wübker SM, Laurenzis A, Werner U, 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.

Zappi M, White K, Hwang H, Bajpai R, Qasim M. 2000. The fate of hydrogen peroxide as an oxygen source for bioremediation activities within saturated aquifer system. J Air Waste Manage Assoc 7: 1818–1830.