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Biocatalytic removal of mono-chlorobenzene vapor in trickling filters

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Abstract

Removal of mono-chlorobenzene (m-CB) vapors from air streams in a biotrickling filter unit was studied under various operating conditions concerning inlet m-CB concentration (C_{gi}), air residence time (τ), liquid recirculation rate (Q), pH, and frequency of medium replenishment. Removal of m-CB was high under all conditions especially when compared to the performance of conventional biofilters removing compounds similar to m-CB. The effect of pH was found to be much less than what is observed with suspended cultures of the same biomass. Concentration profiles of m-CB along the filter bed suggest either zero- or first-order rate law for the process, depending on the inlet m-CB concentration value. © 1998 Elsevier Science B.V.

1. Introduction

The presence of volatile organic compounds (VOCs) in the air creates a number of problems for human health and environmental quality as some of the VOCs are hazardous substances and many of them contribute to smog formation. Environmental regulations regarding VOC emissions have become increasingly stringent in recent years in most of the industrialized world. Due to these regulations, a number of existing technologies for VOC treatment are reexamined for improvement and new approaches to solving the VOC-control problem are being explored. Among the new technologies which have attracted a lot of attention in the recent years, is the one based on biological destruction of VOCs present in air streams.

Biological destruction of pollutants is not really a new technology. Relatively new, however, is the use of biologically based methods for treatment of air laden with VOC vapors without the use of a separate unit for the absorption of VOCs in a liquid stream. These technologies employ what could be called vapor-phase biological reactors which are commonly known as biofilters.

Conventional biofilters are packed-bed reactors employing porous particles of an organic base (e.g., compost, peat moss, bark, etc.). Microorganisms which are either indigenously present in the solid particles or separately grown and immobilized on the particles destroy the VOCs by using them as carbon and/or energy sources in their cellular economy. Conventional biofilters do not involve the use of a continuous liquid phase, and the moisture required for biological activity is provided by humidifying the contaminated air stream prior to its passage through the biofilter bed and periodic addition of water to the

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bed of solids. Removal of various VOCs in conventional biofilters has been reported by numerous researchers, and systematic studies of the process involving both experiments and mathematical modeling can be found in the literature [1–6].

Biotrickling filters constitute a modification of conventional biofilters and are being explored as a means of overcoming the shortcomings of the latter. Biotrickling filters employ non-porous particles of an inorganic base (e.g., plastics, ceramics, etc.) on which biofilms of properly selected microorganisms are formed. A liquid stream which is continuously recirculated through the bed of solids allows for pH-control of the unit and supply of nutrients other than carbon sources (e.g., nitrogen and phosphorous sources) to the microorganisms. The foregoing features of biotrickling filters are not present in conventional biofilters and allow the former to achieve higher removal rates per unit volume of the reactor and treat chlorinated compounds. Chlorinated compounds, when biologically degraded, release chloride ions which lead to substantial drop in pH with a concomitant reduction in biological activity and thus VOC treatment. Results from studies with biotrickling filters have been reported at various meetings but few are the detailed studies which have appeared as journal articles on the topic [7–10].

In the study reported here, an experimental biotrickling filter unit was designed and built, and experiments with air streams contaminated with mono-chlorobenzene (m-CB) vapor were performed. In the experiments a number of operating conditions were varied and their impact on process performance evaluated. The conditions which were investigated are the air residence time in the unit, liquid recirculation rate, pH, m-CB concentration in the contaminated air, and frequency of liquid medium replenishment.

Biological destruction of pollutants have many similarities with autocatalytic processes. Microorganisms (biomass) generate the real catalyst (enzymes) for the process, and biomass is one of the products of the biological destruction of organic compounds. It should be also mentioned that proper biomass selection for the process can lead to complete mineralization of pollutants, i.e., their transformation to carbon dioxide, water, inorganic constituents (e.g., chloride ions) and biomass.

2. Experimental

The unit built and used in the experiments reported here is shown schematically in Fig. 1. Its main part was a glass column (15.2 cm in diameter and 80 cm in height) packed with 3/4 in. Intalox ceramic saddles (Norton Chemical Process Product, Acron, OH) provided with sampling ports at its entrance, exit, and middle point. The bed of solids had a height of 74 cm and a void fraction of 0.64. On the surface of the saddles, biofilms of a microbial consortium (obtained from the microbiology laboratory of Professor R. Bartha of Rutgers University, NJ) known to be capable of completely mineralizing m-CB were formed during process start-up as follows.

Originally, the column contained no solid particles. 3 l of a mixture of two solutions A and B at a B:A ratio of 1:99 by volume were placed in the column. Solution A contained the following chemicals per liter of distilled water: 4.0 g $NaHPO_4$, 1.5 g KH_2PO_4, 1.0 g NH_4NO_3, and 0.2 g $MgSO_4{\cdot}7H_2O$. Solution B contained 0.5 g $FeNH_4$-citrate and 0.2 g $CaCl_2$ per liter of distilled water. All chemicals were obtained from Fisher Scientific (Springfield, NJ). The 1:99 mixture of solutions B and A is a buffer of pH 7.0 and is called the medium for the microbial culture. The medium in the column was inoculated with the microbial con-

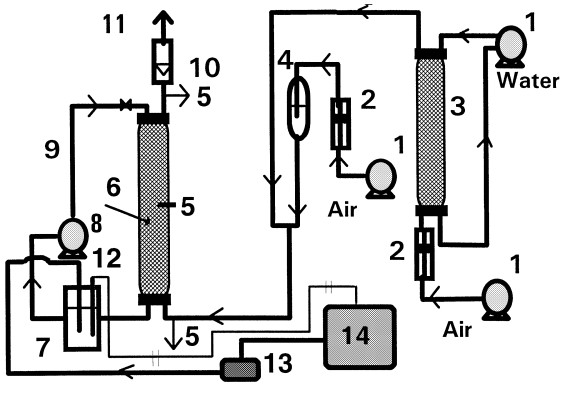

Fig. 1. Schematic representation of the experimental biotrickling filter unit: (1) pump; (2) rotameter assembly; (3) humidification tower; (4) m-CB tank; (5) sampling ports; (6) packing material; (7) medium tank; (8) peristaltic pump; (9) recircuting liquid; (10) air flowmeter; (11) exhaust; (12) pH-electrode; (13) NaOH tank; and (14) pH-controller.

sortium mentioned earlier and bubbled with air containing m-CB vapor at a concentration of 2 gm^{-3} for about two days. By then a noticeable change in optical density of the medium (indicating growth of the culture) had occurred. The column was then packed with ceramic saddles to a height of 74 cm and additional fresh medium was provided so that the solids were totally submerged. Air containing m-CB at about 2 gm^{-3} was bubbled through the bed. The column was drained every 2–3 days, aerated for about 1 h, and then filled with fresh medium before m-CB laden air was again bubbled through the bed of solids. The procedure was repeated for a total time of about one month and led to the development of biofilms on the surface of the saddles. At that point, the medium was drained off the column and the bed of solids started being operated in the trickling bed mode with m-CB laden air and liquid flowing counter-currently. The liquid consisted of the same medium used in the development of the biomass in the biofilter bed.

The m-CB laden air streams treated in the column were prepared by mixing two different air streams. The main one was pure air which was humidified in a tower (column) as shown in Fig. 1 before it was mixed with a low flow rate air stream which carried the m-CB vapor after it was bubbled through a vessel containing liquid m-CB. Proper adjustment of relative flow rates of the two air streams allowed for variation, as desired, of the m-CB concentration in the air stream supplied to the filter bed.

The biotrickling filter operated at a pressure of about 18 psig. Excess biomass was removed from the bed every 15 days through the passage of about 20 l of water over a period of about 15 min. Removal rates were observed to be the same before and after biomass removal.

The medium which flew through the bed was adjusted for its pH at the exit of the column through the use of NaOH and a pH-controller (Chemcadet model, Cole-Palmer Instrument, Niles, IL) before it was sent again to the top of the column. The medium was replenished with a fresh one on a daily basis except for experiments performed in order to determine the effect of the frequency of medium replenishment on the process.

The process was monitored by subjecting air samples obtained from various locations on the column to gas chromatographic (GC) analysis. The GC unit used was a Hewlett-Packard model 5890 Series II (Hewlett-Packard, Paramus, NJ) equipped with a 6 ft×1/8 in. stainless steel column packed with 80/100 Carbopack C/0.1% SP-1000 packing (Supelco, Bellefonte, PA), and a flame ionization detector (FID). Nitrogen, at 21 ml min^{-1} and 21 psig, was used as the carrier gas while hydrogen, at 26.3 ml min^{-1} and 14 psig, was used for the detector. The GC unit was operated under the following temperatures: injection-port 200°C; oven (column) 200°C; and detector 200°C. Under these conditions the retention time for m-CB was 3.83 min. The GC calibration was repeated once every week. The area of the peaks was automatically determined by an HP3396A integrator (Hewlett-Packard, Paramus, NJ) to which the GC unit was connected.

3. Results and discussion

The process has been found to depend on the m-CB vapor concentration (C_{gi}) in the air stream supplied to the filter bed, the residence time (τ) of the air stream in the reactor, the flow rate (Q) and the pH of the liquid stream recirculating through the bed, and the frequency of medium replenishment.

Independent experiments which are not reported here showed that the optimal pH for the culture is about 6.8. Using this value of pH and keeping the value of τ constant at 3.8±0.1 min (based on empty reactor), various series of experiments were performed. In each series, either the value of Q or the value of C_{gi} was keep constant. In Table 1 results from four series of experiments are reported. In each series, the value of Q was kept constant whereas C_{gi} was varied. As can be seen from the table, when Q is constant and the value of C_{gi} increases the percent removal decreases whereas the removal rate (calculated as the product of the inverse residence time and the difference between inlet and outlet m-CB concentration) increases. Both removal rate and percent removal values obtained are substantially high. This is especially true when the results of Table 1 are compared to the performance of conventional biofilters treating benzene and toluene [3,11], compounds which are structurally similar to m-CB. The differences between benzene and m-CB removal rates in conventional and trickling biofilters can reach two orders of magnitude. The differences between toluene

Table 1
Steady-state data on m-CB removal under constant Q values at pH=6.9±0.1, τ=3.8±0.1 min^{-1} and various C_{gi} values

Inlet concentration (gm^{-3})	Percent removal	Removal rate (gm^{-3}-reactor h^{-1})
Q=3.0 l h^{-1}		
1.5±0.1	88.9	21.0±2.0
2.0±0.1	88.9	28.1±2.2
2.8±0.1	84.2	37.2±2.4
3.8±0.1	69.6	41.8±2.2
4.5±0.1	68.6	48.7±2.5
Q=3.9 l h^{-1}		
1.4±0.1	91.1	20.1±2.1
1.9±0.1	91.5	27.5±0.7
2.3±0.1	88.7	32.2±2.3
2.7±0.1	85.6	36.5±2.3
3.3±0.1	79.3	41.3±2.4
3.7±0.1	73.0	42.6±2.4
4.4±0.1	71.9	50.0±2.5
6.9±0.1	57.7	62.9±2.6
Q=5.6 Lh^{-1}		
0.6±0.1	94.2	8.9±1.8
1.1±0.1	92.9	16.1±1.9
1.8±0.1	92.7	30.3±2.3
2.1±0.1	91.5	30.3±2.3
2.7±0.1	89.1	38.0±1.4
3.0±0.1	85.3	40.4±2.5
3.6±0.1	78.9	44.8±2.5
4.1±0.1	74.6	48.3±2.4
Q=18.0 l h^{-1}		
0.8±0.1	94.5	11.9±1.9
1.5±0.1	93.6	22.2±2.1
2.0±0.1	90.9	28.7±2.3
4.2±0.1	73.9	49.0±2.5
4.6±0.1	68.7	49.9±2.5

and m-CB removal rates are less pronounced (up to one order of magnitude) but even this is quite remarkable as toluene is very easily biodegraded as opposed to m-CB. The higher removal rates obtained with biotrickling filters are primarily the result of non-carbon containing nutrients supplied to the biomass. Such nutrients are not externally supplied to conventional biofilters. Due to fluctuations in the volumetric flow rate of the air and the inlet m-CB concentration, the τ and C_{gi} values reported in Table 1, as well as in the subsequent tables, represent average values over the course of an experimental run. Corresponding maximum and minimum values observed are shown with ± sign. The removal rates reported represent an average of two values, one based on the maximum C_{gi} and minimum τ observed and one based on the minimum C_{gi} and maximum τ observed. The maximum and minimum removal rates that could be calculated based on the observed values are shown with the ± amount around the average.

The data of Table 1 show that for m-CB concentration values in air of up to 2.0 gm^{-3} the percent removal well exceeds the 90% level which is a typical requirement of various environmental regulations. One set of the data shown in Table 1 is also shown graphically in Fig. 2 (curve (a)) in the typical biofilters form of removal rate versus load. The load is defined as C_{gi}/τ, i.e., the ratio of inlet VOC concentration to the residence time of the air in the biofilter (based on empty reactor). The removal rate is defined as $(C_{gi}-C_{ge})/\tau$, where C_{ge} is the VOC concentration in the air exiting the filter bed and the other symbols are as defined before. Curve (b) in Fig. 2 is for another set of data (Q=1.7 l h^{-1}) not reported in Table 1. The

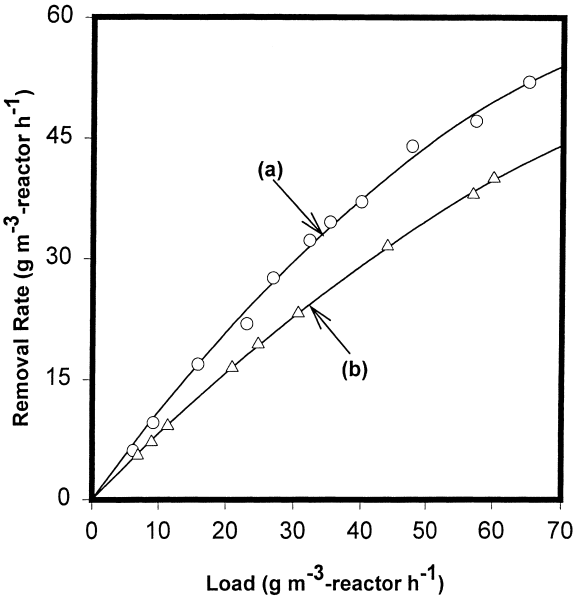

Fig. 2. m-CB removal rate versus load when τ=3.8±0.1 min, pH=6.9±0.1 and Q equal to: (a) 5.6 and (b) 1.7 l h^{-1}.

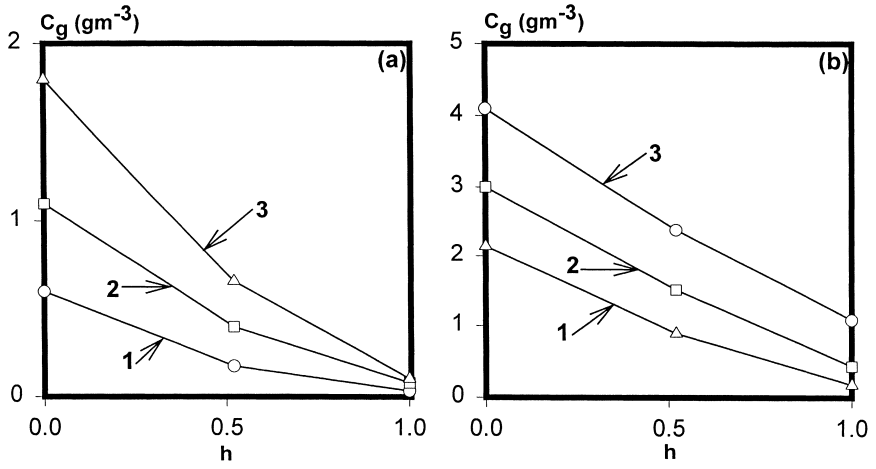

Fig. 3. m-CB concentration profiles in the air along the dimensionless height (h) of the filter bed for low (a) and high (b) inlet concentrations. In all cases, Q=5.6 l h^{-1}, τ=3.8±0.1 min, and pH=6.9±0.1. Curves 1, 2, 3 correspond to inlet concentrations of 0.6, 1.1, 1.8 gm^{-3} in (a) and 2.1, 3.0, 4.1 gm^{-3} in (b).

data for Q=3.0 and 3.9 l h^{-1} reported in Table 1 form curves which fall between curves (a) and (b) of Fig. 2, whereas the data for Q=18 l h^{-1} form a curve slightly above curve (a) of Fig. 2. The indication is that as the load increases the removal rate increases with a tendency to reach a maximum (saturation) value.

Since the m-CB concentration in the air streams was monitored not only at the entrance and exit of the filter bed but at the middle point of the unit as well, experimental concentration profiles have been constructed as shown in Fig. 3. Concentrations of m-CB (C_g) have been plotted against the dimensionless height (h) of the bed with h=0 and h=1 indicating the inlet and exit of the unit, respectively. As Fig. 3(a) indicates, and this is also true for other data sets, the amount of m-CB removed in the first half of the bed (h from 0 to 0.5) is higher than that removed in the second half (h from 0.5 to 1) when the m-CB inlet concentration is low. This implies that removal rates depend on the concentration of the pollutant. On the other hand, as shown in Fig. 3(b), at high m-CB concentrations the profiles appear to be linear suggesting no dependence of the process on the pollutant concentration. Although this has not been fully elucidated yet, the speculation is that at high m-CB concentrations the process is controlled (or limited) by the availability of oxygen in the biofilms. It should be mentioned that the biological process discussed here is aerobic and thus, oxygen can play a determining role on the filter performance.

The effect of the flow rate (Q) of the liquid stream on the process was studied in series of experiments where all parameters but Q were kept unchanged. Results from five such series are shown in Table 2. Initially, as Q increases the percent removal increases as well. This increase should be attributed to a larger wetted area of biofilm (i.e., more catalyst) rather than to overcoming mass transfer limitations. What is of interest is that at high Q values (e.g., 18 l h^{-1}) the percent removal decreases. This drop can be attributed to either channeling or sloughing off of biomass from the surface of the particles. Biomass detachment has been in fact experimentally observed. Although these results are only preliminary, they suggest that when all other conditions are set there is an optimal value for Q. The concentration profiles shown in Fig. 4 suggest that at low values of Q, and when Q increases, the whole profile, rather than the exit concentration alone, is shifted to lower values.

The effect of pH was studied in a large number of series of experiments. In Table 3 results from eight sets at various Q, C_{gi} and τ values are shown. It is clear that as the pH drops from the 6.8 value the m-CB removal decreases and the increase is more substantial at higher C_{gi} values. The deterioration of the process performance as pH decreases is observed throughout

Table 2
Steady-state data on m-CB removal under constant C_{gi}-values at pH=6.9±0.1, τ=3.8±0.1 min and various Q values

Q (l h^{-1})	Percent removal	Removal rate (gm^{-3}-reactor h^{-1})
C_{gi}=0.6±0.1 gm^{-3}		
1.7	80.5	7.4±1.7
5.6	94.2	8.9±1.8
C_{gi}=0.9±0.1 gm^{-3}		
2.2	84.4	11.9±1.7
3.9	91.8	13.1±1.8
C_{gi}=1.5±0.1 gm^{-3}		
1.7	81.1	19.2±1.8
5.6	92.5	21.9±2.1
C_{gi}=3.0±0.1 gm^{-3}		
1.7	74.4	35.3±2.2
2.7	80.8	38.2±2.4
5.6	85.3	40.4±2.5
C_{gi}=4.4±0.2 gm^{-3}		
3.0	68.9	47.7±3.5
3.9	71.9	50.0±3.6
5.6	74.6	54.7±3.8
18.0	73.9	51.3±3.8

the column as shown in the diagrams of Fig. 5. It is also observed at the first segment of the column (entrance of air but exit of liquid) where more chloride ions are expected to be present due to the washing effect from the liquid flowing through the column. The most interesting finding, however, is that for pH drops from 6.8 to even values of about 5.0, the decrease in m-CB vapor removal is not as substantial as in the case where the reaction takes place with suspended cultures (i.e., cells dispersed in liquid medium). In fact, experiments with suspended cultures and C_{gi} values comparable to those shown in Table 3 have indicated a decrease in m-CB removal by 50% when the pH drops from 6.8 to about 5.0. This suggests that mass transfer effects in the biofilms are very important. At low pH values (i.e., presence of high chloride ions) parts of the biofilms must be at high enough pH which allows a substantially good, albeit non-optimal, process performance.

Using the same liquid over long periods of time has clearly shown that process performance deteriorates. This is primarily due to exhaustion of nutrients from the liquid medium. In fact, the frequency of medium replenishment for keeping a constant process performance is inversely proportional to the C_{gi} value. For example, when Q=3.9 l h^{-1}, τ=2.5 min and pH=6.9, percent removal one day after medium replenishment was 79.3, 76.5, and 71.2 for C_{gi} values of m-CB of 2.4, 3.3, and 4.3 gm^{-3}, respectively. After a day, the

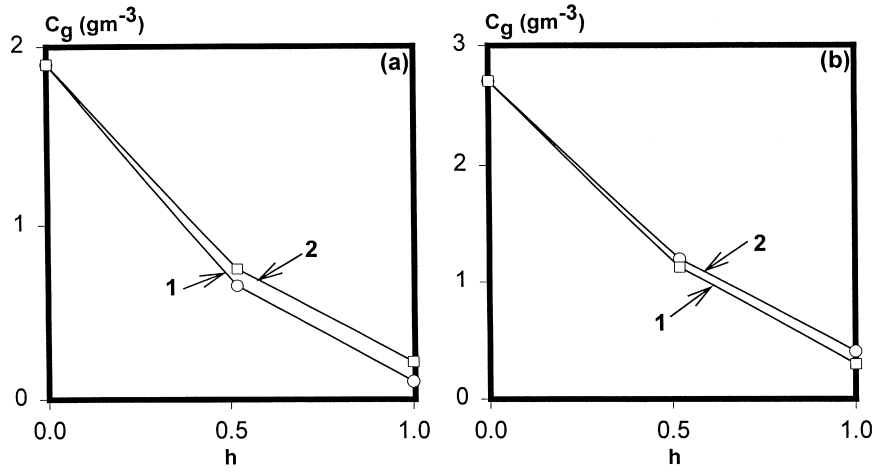

Fig. 4. m-CB concentration profiles at τ=3.8±0.1 min, and C_{gi} values of 1.9 gm^{-3} (a) and 2.7 gm^{-3} (b). The values of Q (l h^{-1}) for curves 1 and 2, respectively, are: (a) 5.6 and 3.0; and (b) 5.6 and 3.9.

Table 3
Steady-state data on m-CB removal as a function of pH at different Q and τ values, and constant C_{gi} values

Inlet concentration (gm^{-3})	Percent removal	Removal rate (gm^{-3}-reactor h^{-1})	pH
Q=0.7 l h^{-1}, τ=8.45±0.35 min			
1.9±0.1	90.1	12.2±1.1	6.5±0.2
1.9±0.1	84.3	11.4±1.1	5.2±0.1
1.9±0.1	81.9	11.0±1.1	4.8±0.1
Q=2.2 l h^{-1}, τ=5.25±0.15 min			
2.1±0.1	83.5	20.0±1.6	6.8±0.1
2.1±0.1	69.4	16.7±1.3	5.7±0.2
Q=2.7 l h^{-1}, τ=4.00±0.10 min			
1.3±0.1	82.8	16.1±1.7	6.4±0.1
1.3±0.1	72.4	14.1±1.5	5.7±0.1
1.3±0.1	66.9	13.0±1.4	5.4±0.1
1.6±0.1	80.6	19.3±1.8	6.1±0.1
1.6±0.1	70.6	16.9±1.7	5.2±0.1
3.8±0.1	71.5	40.8±2.1	6.6±0.2
3.8±0.1	60.1	34.3±1.8	5.3±0.2
4.2±0.1	69.9	44.1±2.4	6.8±0.3
4.2±0.1	56.7	35.7±1.8	5.1±0.1
Q=3.9 l h^{-1}, τ=3.80±0.20 min			
1.1±0.1	94.6	16.5±2.5	6.8±0.2
1.1±0.1	89.9	15.6±2.4	5.2±0.2
1.1±0.1	82.7	14.4±2.1	4.4±0.2
3.7±0.1	73.2	42.8±3.6	6.6±0.2
3.7±0.1	60.9	35.6±3.0	4.7±0.2
3.7±0.1	48.3	28.2±2.4	3.8±0.2

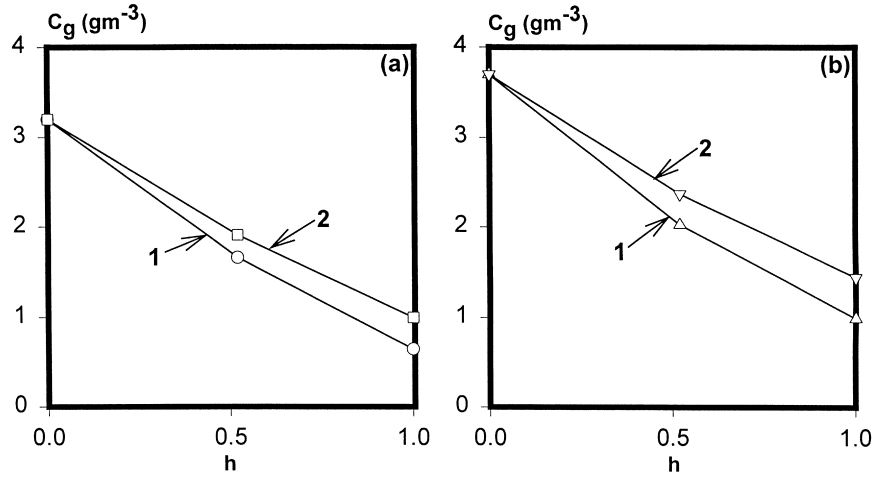

Fig. 5. m-CB concentration profiles at τ=4.0±0.1 min. Values of C_{gi} (gm^{-3}) and Q ($l\,h^{-1}$), respectively, are: (a) 3.2 and 2.7; and (b) 3.7 and 3.9. Curves 1 and 2 are, respectively, for pH values of: (a) 6.8 and 5.4; and (b) 6.6 and 4.7.

percent removal for the same C_{gi} values are, correspondingly, 76.9, 70.7, and 60.9.

In conclusion, this study has demonstrated that m-CB vapors can be successfully removed in biotrickling filters. The process depends on the concentration of m-CB in the polluted air stream, the size of the filter bed and the flow rate of the air stream (residence time), and the flow rate and composition (frequency of replenishment) of the liquid stream.

The removal rates obtained in this study are high when compared to conventional biofilters operating under similar conditions and treating structurally similar compounds. The better performance of biotrickling filters can be attributed mainly to the following three reasons: higher amounts of biomass presence, supply of additional nutrients, and better moisture control when compared to conventional biofilters. Biomass accumulation may be a serious problem for biotrickling filter operation, and strategies for biomass control have been discussed by some authors [10]. This was not a problem for the study presented here as some biomass was lost from the system with the daily replenishment of the nutrient medium and the periodic removal of excess biomass discussed earlier. The experimental results reported here are currently analyzed with a detailed mathematical model which is expected to be published soon.

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