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Removal of toluene in waste gases using a biological trickling filter

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Abstract

The removal of toluene from waste gas was studied in a trickling biofilter. A high level of water recirculation (4.7 m h^{-1}) was maintained in order to keep the liquid phase concentration constant and to achieve a high degree of wetting. For loads in the range from 6 to 150 g m^{-3} h^{-1} the maximum volumetric removal rate (elimination capacity) was 35 ± 10 g m^{-3} h^{-1}, corresponding to a zero order removal rate of 0.11 ± 0.03 g m^{-2} h^{-1} per unit of nominal surface area. The surface removal was zero order above the liquid phase concentrations of approximately 1.0 g m^{-3}, corresponding to inlet gas concentrations above 0.7–0.8 g m^{-3}. Below this concentration the surface removal was roughly of first order. The magnitude of the first order surface removal rate constant, k_{1A}, was estimated to be 0.08–0.27 m h^{-1} ($k_{1A}a$ = 24–86 h^{-1}). Near-equilibrium conditions existed in the gas effluent, so mass transfer from gas to liquid was obviously relatively fast compared to the biological degradation. An analytical model based on a constant liquid phase concentration through the trickling filter column predicts the effluent gas concentration and the liquid phase concentration for a first and a zero order surface removal. The experimental results were in reasonable agreement with a very simple model valid for conditions with an overall removal governed by the biological degradation and independent of the gas/liquid mass transfer. The overall liquid mass transfer coefficient, K_La, was found to be a factor 6 higher in the system with biofilm compared to the system without. The difference may be explained by: 1. Difference in the wetting of the packing material, 2. Mass transfer occurring directly from the gas phase to the biofilm, and 3. Enlarged contact area between the gas phase and the biofilm due to a rough biofilm surface.

Introduction

Many volatile organic compounds are discharged to the atmosphere from human activities (industries, automobiles, etc.) and from natural processes. Stringent regulations have recently been enforced in several industrial countries. For example, according to Danish regulations the concentration in waste gases of compounds like dichloromethane, benzene, and toluene must not exceed 0.1–0.5 mg m^{-3}, 1–5 mg m^{-3} and 300 mg m^{-3}, respectively. Biofiltration is an attractive technique for elimination of volatile organics from waste gases both in terms of economic and environmental considerations since the technique only requires very little resources and, additionally, gives a total conversion of the pollutants to carbon dioxide and water. The technique is applicable for emissions of volatile organics in low concentrations which are biologically degradable and to some extent water-soluble. Removal of toluene in a mixture of ethylacetate, butylacetate and butanol was studied in order to investigate the application of a biological filter to lacqueries (Ottengraf & v.d. Oever 1983). The biological degradation of toluene followed zero order kinetics for inlet gas concentrations above 3 g m^{-3}. The removal capacity was 20 g m^{-3} h^{-1} at a constant load of 90 g m^{-3} h^{-1}. A high variability (± 10 g m^{-3} h^{-1}) was observed for the zero order removal. Severin et al. (1993) made a study of benzene, toluene, ethylbenzene and xylene removal in two different biofilter test systems. Toluene removal

was 60–80 g m^{-3} h^{-1} for loads ranging between 100–160 g m^{-3} h^{-1}, when toluene was added as sole component. A study by Kirchner and co-workers (1989) was on toluene elimination using a monoculture of a *Rhodococcus* sp. in a trickling filter. The elimination capacity followed a linear dependency of the load (constant gas flow with a residence time of one second), reaching a value of 42 g m^{-3} h^{-1} at a load of 220 g m^{-3} h^{-1}. Wolff (1992) investigated toluene removal in an intermittently wetted trickling filter. The removal capacity was 40–65 g m^{-3} h^{-1} at loads from 40 to 140 g m^{-3} h^{-1}. Using optimum conditions for the wetting, the half saturation constant, K_s was determined. The K_s-values ranged between 0.47–0.63 g m^{-3} compared to a value of 0.3 g m^{-3} for a suspended system. Schindler et al. also studied removal of toluene in a trickling filter (1994). The magnitude of the removal capacity was 11–40 g m^{-3} h^{-1} at loads ranging between 30–180 g m^{-3} h^{-1}. First order removal rate constants based on the filter volume were calculated and the values found varied from 5 to 250 h^{-1}. Only few mathematical models for the removal of volatile organics in different types of biological filters have been proposed in the literature until now. A detailed study done by Diks and Ottengraf (1991) evaluated a simplified model for the removal of dichloromethane in a trickling filter. The model, based on a zero order removal inside the biolayer, describes the concentration profiles of dichloromethane along the column and inside the biolayer. The model consists of a set of non-linear differential equations, which can be solved by a numerical procedure. In addition, Diks and Ottengraf (1991) developed an algebraic model assuming a uniform substrate concentration in the liquid phase. Ockeloen et al. (1992) developed an extension of the numerical model from Diks and Ottengraf, assuming Monod kinetics in a deep biofilm. They evaluated the uniform substrate concentration model from Diks and Ottengraf, concluding the model is only applicable for short columns (below 1 m), but no experimental verification was made. The purpose of this study was to:

- Determine the elimination capacity of a biological trickling filter treating toluene at different gas loads.
- Determine the rate of gas/liquid mass transfer versus the rate of biological degradation.
- Determine the concentration range and the associated kinetic parameters for various reaction orders (first to zero order).
- Evaluate a simple analytical model describing the effluent gas concentration as a function of the gas inlet concentration and the gas residence time in a biological trickling filter.

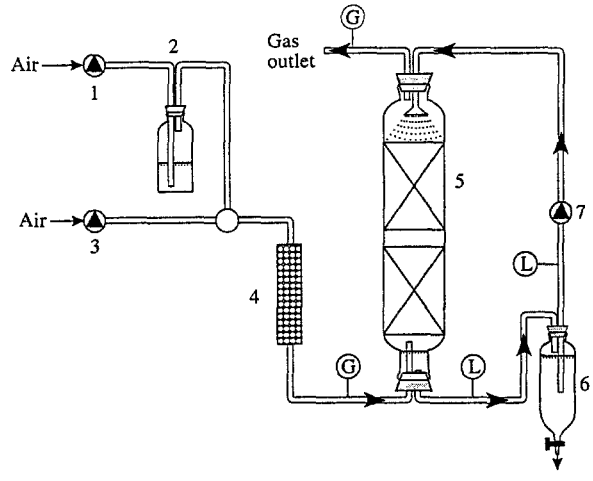

Fig. 1. Experimental set up: 1. Peristaltic pump; 2. Pure toluene flask; 3. Membrane pump for air supply; 4. Column for gas mixing; 5. Absorption column; 6. Liquid container; 7. Recirculation pump; G. Sampling point for gas; L. Sampling point for liquid.

Materials and methods

Experimental set up and culture conditions

The experimental system is illustrated in Fig. 1. The reactor consists of a cylindrical glass column with an inner diameter of 90 mm (cross sectional area 0.0064 m^2) and a height of 1.2 m. Two sections of packing material was used, each with a height of 0.35 m. The separation was made in order to secure an efficient water distribution. The total packing volume was 0.00445 m^3 and the total surface area, including the wall of the column, was 1.4 m^2. The packing material was steel Pall rings (diameter 15 mm, height 6 mm, thickness 0.3 mm) with a specific surface area of 317 m^2 m^{-3}. The toluene waste gas was produced by passing air through pure toluene. It was afterwards mixed with the major airflow before entering the column. The gas flow was supplied at the bottom of the column giving a counter current operation. The superficial gas velocity ranged from 16 to 78 m h^{-1}. The liquid phase was collected in a container at the outlet of the column, recirculated to the top of the column and distributed over the packing bed by a simple sprinkler head. A high level of water recirculation (super-

ficial velocity, u_L = 3.3–4.7 m h^{-1}) was maintained through the filter bed in order to obtain a constant liquid phase concentration. Nutrients were added at the following levels (g m^{-3}): 13.7 N (NH_4NO_3), 4.1 P ($Na_2HPO_4 \bullet 12H_2O$) and 2.7 Fe ($FeSO_4 \bullet 7H_2O$). The column was inoculated with a mixed culture from a creosote-polluted sandy aquifer (Fredensborg, Denmark). The mixed culture was adapted to toluene by cultivation in batch with toluene as sole carbon source (Jensen 1994). The inoculation was made by adding 20 ml of the culture suspension to the column filled with tap water (Lyngby, Denmark). After one day, the liquid was recirculated for two days in order to get the biomass attached to the packing material.

Analytical techniques

Analysis of toluene was performed with a Shimadzu gas chromatograph (GC-9A) equipped with a J. & W. Scientific column (DB1, 28 m, cat no. 125-1032, series 9416145). The detector was a flame ionisation detector connected with a computing integrator (Shimadzu C-R3A Chromatopac). The analysis was carried out isothermally at 40° C for the liquid samples and at 80° C for the gas samples. Liquid samples were collected in 10 ml volumetric flasks. Extraction of toluene was made by adding 500 μl of pentane containing heptane as an internal standard, and the solution was shaken for 2 minutes. 1 μl of the pentane phase was injected into the gas chromatograph, and the ratio of the response for toluene and heptane was compared with standards. The gas samples were taken with a gastight Hamilton syringe. Adsorption to the syringe glass wall was taken into account by letting equilibrium establish for each sample before injection directly into the GC. The response was compared with gas standards.

Experimental strategy

The study consisted of three 5^2 factorial experiments (2 factors at 5 different levels). The three experiments were named FAC 1, FAC 2 and FAC 3. The experiments were designed as reduced 5^2 factorial experiments using a central composite design with 13 treatments, including 4 centre points (4 repetitions of treatment with middle level of both factors) (Barker 1985). The factors studied were: 1. Inlet gas concentration of toluene and 2. Gas velocity. The factor levels for the inlet gas concentration were (g m^{-3}): 0.193, 0.4, 0.9, 1.4, and 1.607, and for the superficial gas velocity (m h^{-1}): 16, 25, 47, 69 and 78. The recirculation liquid was renewed for each experimental treatment, and no liquid loss was observed during any of the treatments. Each of the three experiments was performed within two days, and between each change of factor levels the system was stabilized for one hour, which has been shown to be sufficient. Each treatment was carried out in random order, FAC 1 was carried out as the first experiment at a temperature of 25° C, 8 days after inoculation of the biofilter, and FAC 2 and FAC 3 were carried out at 21° C, 21 and 29 days later, respectively. During the experiments the trickling filter seemed to be sufficiently humidified. The biofilm appeared smooth and thin covering the whole surface of the packing material, and no clogging was observed. Before inoculation of the column the overall liquid mass transfer coefficient, K_La was measured in order to evaluate the dependency of the gas and the liquid flows for the system without biomass (data not shown). The experimental set up consisted of the column, supplied with toluene gas and with the same packing as mentioned above but disinfected with chlorine. Tap water was added at the top of the column, giving a counter current mode. The gas and liquid concentrations were measured at steady state conditions. The K_La-value was determined using the logarithmic means of the driving forces at the inlet and outlet of the column. No relation between the gas flow and the K_La-volume was noticed. The following relationship between the superficial liquid velocity and the K_La-value was found: $K_La = 2.5 \bullet u_L^{0.86}$.

Model

The model described here is an analytical model predicting the effluent gas concentration from a trickling filter operated at different gas loads. The model implies a high recirculation of the liquid phase, so that a constant liquid concentration will be established under steady state conditions. The biological degradation is described as a surface removal following first or zero order depending on the liquid phase concentration. As a simplification of the model no transfer order is considered. The 'Uniform-Concentration-Model', UCM, from Diks and Ottengraf (1991) is based on a constant liquid concentration as well, but differs from our model by the assumption of only a zero order degradation inside the biofilm resulting in a zero or half order surface removal. Hence, the model does not take a first order removal into account. The model here is based on the following assumptions:

1. The gas and liquid phases move in plug flow.
2. The equilibrium between the gas/liquid interphase follows Henry's law.
3. Oxygen and nutrients are in excess, so that the biological degradation is limited by the toluene concentration only.
4. No biological degradation takes place in the liquid phase, but only in the biofilm attached to the packing material.
5. The whole biofilm surface is wetted by the liquid phase.
6. The surface removal rate of toluene is first order or zero order, depending on the toluene liquid phase concentration.
7. Under steady state conditions the removal of toluene from the gas phase equals the biological degradation inside the biofilm, and the liquid concentration is constant through the trickling filter.

A differential mass balance for the gas phase in a cross section of the column is as follows:

$$\frac{dS_g}{dh} = -K_L a\left(\frac{S_g}{H_c} - S_l\right)\frac{A}{U_g} \qquad (1)$$

Solving the differential equation for constant S_l gives:

$$S_{g,eff} = S_l H_c + (S_{g,in} - S_l H_c)exp\left(\frac{-T_h K_L a}{H_c}\right)$$
$$where\ T_h = \frac{hA}{U_G} \qquad (2)$$

As the removal from the gas phase equals the biological degradation, according to assumption 6, the effluent gas concentration is:

$$S_{g,eff} = S_{g,in} - r_A a\frac{V}{U_G} = S_{g,in} - B\frac{V}{U_G} \qquad (3)$$

Where the surface removal rate, r_A, is assumed to be either a first or a zero order:

$$r_A = k_{1A} S_l$$
$$r_A = k_{0A} \qquad (4)$$

Combining equations (2) and (3) gives an expression for the liquid concentration versus the gas inlet concentration and the gas residence time. In Table 1 expressions for the liquid concentration and the gas effluent concentration for a first and a zero order surface removal are shown. Also shown are expressions obtained for limiting cases with either very high or low values of T_h $K_L a/H_c$ where the exponential term reduces to zero or (1 - T_h $K_L a/H_c$), respectively. In the following we will focus on conditions with high values of T_h $K_L a/H_c$ (approximation (1) in Table 1), that is conditions with either a high $K_L a$-value (fast gas/liquid mass transfer) or a high residence time. Here equilibrium between the gas and the liquid phase will be established at the gas outlet of the column, so the effluent gas concentration is related to the liquid phase concentration by Henry's law. The expressions show that the effluent gas concentration and the liquid phase concentration are independent of the $K_L a$-value. This indicates that the overall process is governed by the biological removal. In case of first order removal, the effluent gas concentration is related to the load of toluene, $Ld_G = S_{g,in}/T_h$. If $k_{1A} a\ T_h/H_c >> 1$ the expression simply reduces to:

$$S_{g,eff} = Ld_G\frac{H_c}{k_{1A}a}\ where\ Ld_G = \frac{S_{g,in}}{T_h} \qquad (5)$$

In general, the elimination capacity, B, is given by a simple mass balance for the gas phase:

$$B = \frac{U_G}{V}(S_{g,in} - S_{g,eff}) = \frac{1}{T_h}(S_{g,in} - S_{g,eff}) \qquad (6)$$

Using the approximations for the effluent gas concentration (Table 1), the elimination capacity for a first order surface removal, equals the gas load for a high value of $k_{1A} a T_h$:

$$B = Ld_G\left(\frac{1}{H_c/k_{1A}aT_h + 1}\right) = Ld_G \qquad (7)$$

For a zero order surface removal of the elimination capacity equals the zero order removal:

$$B = k_{0A} a \qquad (8)$$

Results and discussion

A statistical analysis of the three different factorial experiments was performed in order to find out if the experiments should be treated separately with respect to kinetic parameters, or if the data might be pooled. During this analysis, using the SAS General Linear Model (SAS 1985), the effluent gas concentration, the elimination capacity, and the removal efficiency were the dependent variables, and the inlet gas concentration and the gas flow or alternatively the gas load were the independent variables. The analysis showed that there was a statistically significant difference between the experiments, but the difference was small. Therefore, the experimental data were pooled. The two first

Table 1. Expressions for the liquid phase concentration and the effluent gas concentration for a first order and a zero order surface removal.

General	$S_{g,eff} = S_{g,in} \exp\left(\frac{-T_h K_L a}{H_c}\right) + S_l H_c \left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)$	$S_{g,eff} = S_l H_c$ (1) $S_{g,eff} = S_{g,in}$ (2)
First order	$S_l = \frac{S_{g,in}\left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)}{k_{1A} a T_h + H_c \left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)}$	$S_l = S_{g,in}\left(\frac{1}{k_{1A} a T_h + H_c}\right)$ (1) $S_l = S_{g,in}\left(\frac{1}{H_c\left(1 + \frac{k_{1A} a}{K_L a}\right)}\right)$ (2)
	$S_{g,eff} = S_{g,in}\left(\exp\left(\frac{-T_h K_L a}{H_c}\right) + \frac{H_c\left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)^2}{k_{1A} a T_h + H_c\left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)}\right)$	$S_{g,eff} = S_{g,in}\left(\frac{1}{k_{1A} a T_h / H_c + 1}\right)$ (1) $S_{g,eff} = S_{g,in}\left(1 - \frac{k_{1A} a T_h}{H_c\left(1 + \frac{k_{1A} a}{K_L a}\right)}\right)$ (2)
Zero order	$S_l = \frac{S_{g,in}\left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right) - k_{0A} a T_h}{H_c\left(1 - \exp\left(\frac{-T_h K_L a}{H_c}\right)\right)}$	$S_l = \frac{S_{g,in} - k_{0A} a T_h}{H_c}$ (1) $S_l = \frac{S_{g,in}}{H_c} - \frac{k_{0A} a}{K_L a}$ (2)
	$S_{g,eff} = S_{g,in} - k_{0A} a T_h$	

(1) $\exp\left(\frac{-T_h K_L a}{H_c}\right) \rightarrow 0$ (2) $\exp\left(\frac{-T_h K_L a}{H_c}\right) \rightarrow \left(1 - \frac{T_h K_L a}{H_c}\right)$

treatments carried out in FAC 1 and FAC 2 and the first treatment in FAC 3 were lost due to operating problems.

Gas/liquid mass tranfer of toluene

The liquid phase concentration was determined at the outlet and inlet of the trickling filter. In Fig. 2 the concentrations at the top of the column are plotted against the concentrations at the bottom of the column. The straight line represents equality between the concentrations, showing that a nearly constant liquid phase concentration was established in the system.

In Fig. 3 the effluent gas concentrations are plotted versus the average of the inlet and outlet liquid phase concentrations for all the treatments. The relationship is approximately linear with a slope of 0.27 (linear regression with the line forced through the origin, R^2 = 0.89, std. err. of coef. = 0.01). The slope is very close to the Henry's law constant for toluene, suggesting that near-equilibrium is established at the gas outlet of the column: $S_{g,eff} = S_l H_c$. The Henry's law constants found in the literature are 0.23 at 20° C and 0.26–0.27 at

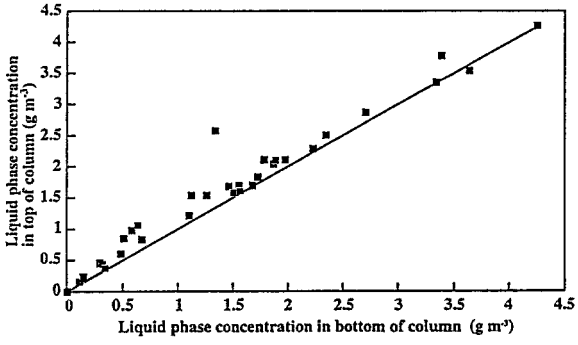

Fig. 2. Liquid phase concentration in top of column versus liquid phase concentration in bottom of column. Equality between the inlet and outlet liquid phase concentrations (—).

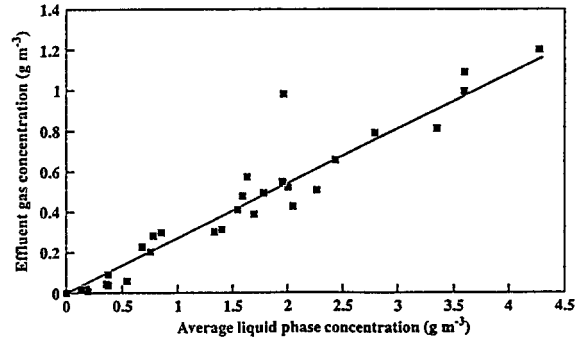

Fig. 3. Effluent gas concentration versus liquid phase concentration (average value of the inlet and the outlet liquid phase concentrations). Regression line: $S_{g,eff} = 0.27 \bullet S_l$ (—).

25° C (Mackay & Shiu, 1981; Ashworth et al., 1988). The fact that near-equilibrium conditions exist at the gas effluent means that the gas/liquid mass transfer is a relatively fast process compared to the biological degradation, indicating that the overall toluene removal is nearly independent of the gas/liquid mass transfer and governed by the biological degradation. This is in accordance to conditions with high values of T_h K_La/H_c (approximation (1) in Table 1).

Estimation of the mass transfer coefficient, K_La

Based on the gas residence time, T_h (0.04–0.009 h), and the Henry's law constant, H_c (0.23), the K_La-value can be estimated for the fully colonized reactor since the term $\exp(-T_h\ K_La/H_c)$ approaches zero. We assume that the term $\exp(-T_h\ K_La/H_c)$ is negligible to the extent that $\exp(-T_h\ K_La/H_c) < 0.1$. From this it follows that the K_La-value has to be minimum 60 h^{-1}.

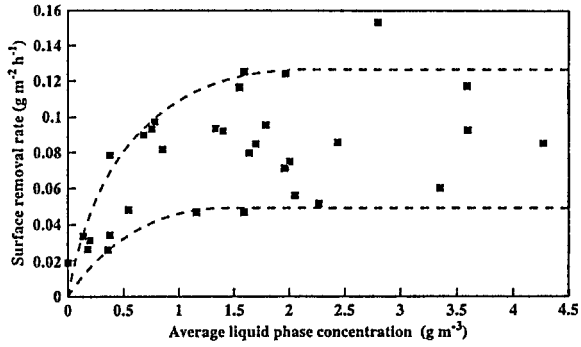

Fig. 4. Surface removal rate of toluene versus liquid phase concentration (average of inlet and outlet liquid phase concentration). Envelope (- - - -).

The K_La-value was determined for the same system before the inoculation and growing of the biofilm, and this value was approximately 10 h^{-1} at a superficial liquid velocity of 4.7 m h^{-1} (see *Experimental strategy*). The very large difference in gas/liquid mass transfer between the system with biofilm (K_La: 60 h^{-1}) and the system without biofilm (K_La: 10 h^{-1}) may result from a difference in the value of the specific surface area, a. This may be explained by three phenomena:

1. The a-value represents the wetted specific surface area of the system. Accordingly, when the surface is covered with a biofilm, the wetted area may be larger because of the hydrophilic properties of the biological material. This is in comparison to a system only with the fairly hydrophobic steel surface of the Pall rings.
2. Mass transfer may occur directly from the gas phase to the biofilm instead of from the gas phase to the liquid phase. The phenomenon may take place because the biofilm consists of approximately 98% water, and the gas phase in the column is saturated with water keeping the biofilm wet in the whole column. This means that the entire surface area of the biofilm will be active even if it is not wetted directly by the liquid flow. This phenomenon needs further investigations, especially concerning equilibrium conditions between biomass and gas phase and the effects of an insufficient replacement of water.
3. In addition to the phenomena mentioned above, the biofilm may have a rough surface (Characklis & Marshall 1990) leading to an enlarged contact area between the biomass and the gas phase.

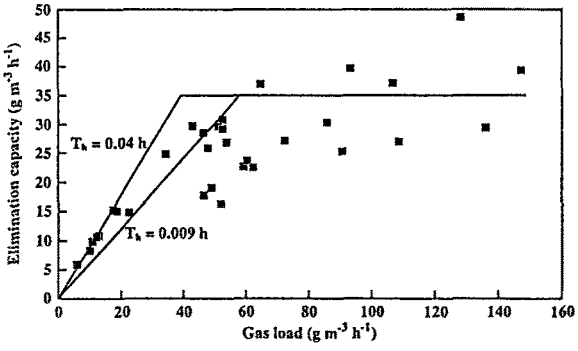

Fig. 5. Elimination capacity versus toluene load. Model curve (—). First order model curves are drawn for the minimum and the maximum gas residence time ($k_{0A}a = 35$ g m^{-3} h^{-1}, $k_1Aa = 40$ h^{-1}).

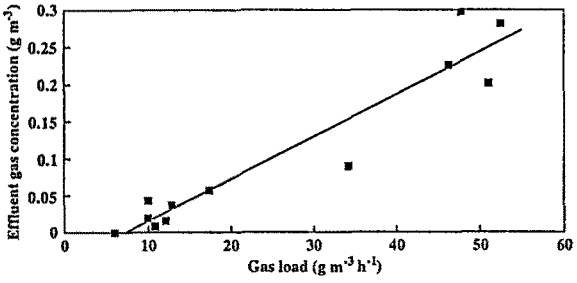

Fig. 6. Effluent gas concentration versus toluene load for treatments with low liquid phase concentration (below 1.0 g m^{-3}). Regression line: $S_{g,eff} = 0.0057$ Ld - 0.04 (—).

Biological degradation of toluene

The biological degradation depends on the liquid phase concentration according to assumptions 5 and 6. To illustrate the biological degradation of toluene, the surface removal rate, r_A, is plotted against the liquid phase concentration, S_1, in Fig. 4. In spite of the scattered data it appears that the removal is roughly first order for concentrations below 0.5–1.0 g m^{-3}, and zero order for concentrations above this, probably with a half order transfer region. As a simplification, only a first order or a zero order removal is assumed with a transition at a liquid concentration of approximately 1 g m^{-3}. An explanation to the high scattering of the surface removal seen in Fig. 4 may be that the biofilm surface is not totally wetted by the liquid phase and, according to the phenomenon mentioned above, degradation may take place even if the biofilm is not wetted directly by the liquid phase. Hence, the removal rate may depend not only on the liquid phase concentration but also on the gas phase concentration.

Estimation of the zero order rate constant, k_{0A}

A plot of the biological removal of toluene per volume of filter bed, B (elimination capacity), versus the gas load of toluene shows that maximum removal is established for high gas loads, Fig. 5. From the maximum elimination capacity, the removal rate constant, $k_{0A}a$, is estimated according to Equation (8). The average value of $k_{0A}a$ is determined to be 35 ± 10 g m^{-3} h^{-1} for loads of toluene above 60–70 g m^{-3} h^{-1}, corresponding to inlet gas concentrations of 0.7–0.8 g m^{-3}. Based on the nominal surface area in the filter bed, the maximum (zero order) biological removal rate constant, k_{0A}, is 0.11 ± 0.03 g m^{-2} h^{-1}. The removal rates found in this study seem to be of the same magnitude as elimination capacities found in the literature. A variability of 10 g m^{-3} h^{-1} on the maximum removal is also seen in the literature (Ottengraf & Oever 1983; Severin et al. 1993).

Estimation of the first order rate constant, k_{1A}

The first order surface removal rate constant, k_{1A}, is roughly estimated from Fig. 4. The magnitude of $k_{1A}a$, appears to be approximately 50 h^{-1} (24–86 h^{-1}). Based on the nominal surface area in the filter bed, the average removal rate constant is 0.16 m h^{-1} (0.08–0.27 m h^{-1}). The first order surface removal constant, k_{1A}, can also be estimated from a plot of the effluent gas concentration, $S_{g,eff}$ versus the gas load, $S_{g,in}/T_h$, according to Equation (5). Figure 6 shows the effluent gas concentration as a function of the gas load for treatments assumed to follow a first order removal i.e. liquid concentrations below 1.0 g m^{-3}. The relationship seems to be reasonably linear ($R^2 = 0.91$). The first order removal rate constant, $k_{1A}a$, is determined from the slope, $H_c/k_{1A}a$, giving a value of 40 h^{-1}. Based on the nominal surface area in the filter bed the rate constant, k_{1A}, is 0.13 m h^{-1}. This value is in same order of magnitude as the value estimated from Fig. 4. The magnitude of the removal rate constant, $k_{1A}a$, agrees with the values found by Schindler et al. (1994). Also in accordance with this study is a first order removal constant, k_{1A}, of 0.10 m h^{-1} found by Arcangeli & Arvin (1992), who investigated toluene degradation in a fixed film reactor.

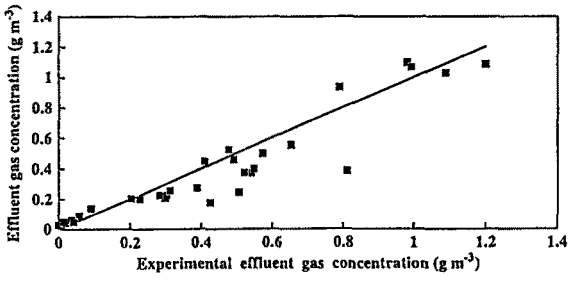

Fig. 7. Predicted effluent gas concentration versus experimental data. Model (■); Equality between predicted and experimental data (—).

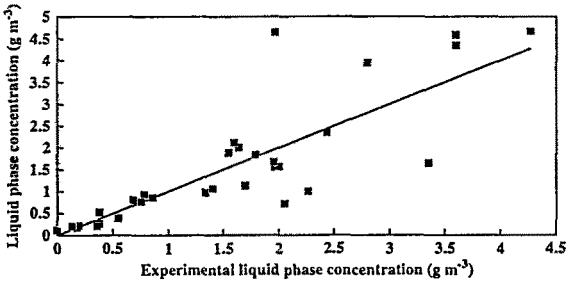

Fig. 8. Predicted liquid phase concentration versus experimental data. Model (■); Equality between predicted and experimental data (—).

Model

The constants estimated above are used to illustrate the predictive ability of the analytical model: $K_L a$ 60 h^{-1}, $k_{0A} a$ 35 g m^{-3} h^{-1} and H_c 0.23. The first order model is applied for liquid concentrations below 1.0 g m^{-3} and the zero order model for concentrations above. The modelled results are shown in Figs 7 and 8, where the predicted data for the gas effluent concentration and the average liquid concentration are plotted against the experimental values. The straight line with a slope of 1 represents equality between predicted and experimental data. Two model points corresponding to a zero order removal turned out with negative values of the liquid phase concentration and the gas effluent concentration (not shown). Common for the two points was a load of toluene less than the zero order removal rate, $k_{0A} a$, of 35 g m^{-3} h^{-1} used in the model calculation.

Effluent gas concentration

The model for the effluent gas concentration, Fig. 7, seems to predict the experimental data well. However, in the concentration range from 0.3 to 0.8 g m^{-3}, a minor discrepancy is seen. As the predicted effluent gas concentration is based on the liquid phase concentration, this discrepancy may be due to the scattering in the predicted liquid phase concentration seen in Fig. 8.

Liquid phase concentration

The modelled liquid phase concentration seems to predict the experimental data for the first order range (liquid concentrations below 1.0 g m^{-3}) very well, but some disagreement between the predicted and the experimental data for the zero order range are seen. One explanation may be that the order of the degradation was not of zero order, but a transition order between first and zero order. This could be due to diffusion limitation in the biofilm. A recalculation using the model for a half order surface removal was made for the intermediate concentrations. In spite of a slightly better agreement it was chosen to treat the results as a first and a zero order surface removal. The argument for this is to keep a very simple model description – in the light of the limitation of measured parameters. By introducing a half order surface removal, the model is less simple without giving a much better description of the experimental data. A counter current flow may cause a lower liquid concentration inside the column than at the inlet and outlet of the column (Diks & Ottengraf 1991). The surface removal may then be first order or a transition order instead of zero order in the whole column. Another phenomenon that has to be considered here is the possibility of mass transfer directly from the gas phase to the biofilm. If this is the case, the degradation in the biofilm depends on the gas phase concentration and not on the liquid phase concentration. The gas phase concentration varies through the column, leading to a change in the reaction order. Hence, the removal may depend on both the liquid phase concentration and the gas phase concentration. In spite of the disagreement for the zero order range, the first and zero order model seems to predict the experimental effluent gas concentration data reasonably. Under conditions with a fast gas/liquid mass transfer and a relatively high residence time of the gas in the column (overall process governed by the biological removal and independent of the gas/liquid mass transfer) the model becomes

very simple, and the application of the model is very convenient.

Conclusions

With loads of toluene above 60–70 g m^{-3} h^{-1} the average elimination capacity was 35 ± 10 g m^{-3} h^{-1}. This is in agreement with the data in the literature for removal of toluene from waste gases. The surface removal of toluene appears to be zero order for liquid phase concentrations above approximately 1.0 g m^{-3}, corresponding to inlet gas concentrations above 0.7–0.8 g m^{-3}. A zero order surface removal rate constant, k_{0A}, of 0.11 ± 0.03 g m^{-2} h^{-1} ($k_{0A}a = 35 \pm 10$ g m^{-3} h^{-1}) and a first order surface removal rate constant, k_{1A}, of approximately 0.13 m h^{-1} ($k_{1A}a = 40\ h^{-1}$) were determined. Near-equilibrium conditions between the gas phase and the liquid phase were observed at the gas effluent indicating that the mass transfer from gas to liquid was relatively fast compared to the biological degradation. This implies that the overall toluene removal was nearly independent of the gas/liquid mass transfer and governed by the biological degradation. The overall liquid mass transfer coefficient, K_La, was a factor 6 higher in the system with biomass compared to the system without. The deviation may be explained by:

1. Difference in wetting of the packing material,
2. Mass transfer occurring directly from the gas phase to the biofilm, and
3. An enlarged contact area between the gas phase and the biofilm due to a rough biofilm surface.

An analytical model based on a constant liquid phase concentration through the trickling filter column predicts the effluent gas concentration and the liquid phase concentration for a first and a zero order surface removal. The experimental results were in agreement with a very simple model valid for conditions with an overall removal governed by the biological degradation. The predicted effluent gas concentrations agreed well with the experimental data, but for the liquid phase concentrations some discrepancy between the predicted and the experimental data were observed in the zero order range. An obvious explanation may be that the degradation order was not a zero order, but a transition order between the first and zero order due to diffusion limitation in the biofilm. Another explanation may be that the biological removal depends not only on the liquid phase concentration, but also on the gas phase concentration in the column.

Nomenclature

A	m^2	Column cross sectional area
a	m^2 m^{-3}	Specific surface area
B	g m^{-3} h^{-1}	Biological removal (elimination capacity)
H_c	-	Henry's law constant
h	m	Height of column
k_{0A}	g m^{-2} h^{-1}	Zero order surface removal rate constant
k_{1A}	m h^{-1}	First order surface removal rate constant
k_La	h^{-1}	The overall liquid mass transfer coefficient
Ld_G	g m^{-3} h^{-1}	Load of gas
r_A	g m^{-2} h^{-1}	Surface removal rate
$S_{g,in}$	g m^{-3}	Inlet gas concentration
$S_{g,eff}$	g m^{-3}	Effluent gas concentration
S_l	g m^{-3}	Liquid phase concentration
T_h	h	Residence time of gas
U_G	m^3 h^{-1}	Volumetric gas flow
U_L	m^3 h^{-1}	Volumetric liquid flow
u_G	m h^{-1}	Superficial gas velocity
u_L	m h^{-1}	Superficial liquid velocity
V	m^3	Volume of filter bed

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