Steady State Models for the Biofiltration of Styrene/Air Mixtures

A. M. Gerrard*, O. Misiaczek, D. Hajkova**, M. Halecky,** and J. Paca****
*University of Teesside, Middlesbrough, TS1 3BA, England
Tel: ++44 1642 342401, Fax: ++44 1642 342499, a.m.gerrard@tees.ac.uk
**Institute of Chemical Technology, 166 28 Prague, Czech Republic
Tel: ++420 22044 3785, Fax: ++42 22044 5051, pacaj@vscht.cz

Original scientific paper
Received: August 31, 2004
Accepted: March 1, 2005

This paper gives some simple mathematical models for the biofiltration of styrene. Two different biofilters were used, with diameters of 50 and 100 mm. Granular activated carbon was used as the packing material (Silcarbon type SC40, particle diameter of 4-6 mm). The styrene level was measured at the inlet, outlet, and intermediate points to give a mass concentration profile through the reactors. The investigated data were divided into the three sets of experimental conditions. The changing parameters were the inlet concentration of styrene and flow rate of air. (However, the mass flow-rate of styrene was held approximately constant).

The bio-reactions broadly followed first order kinetics. In addition, a modified Ottengraf's first order kinetic model was developed and applied to see if it was possible to get a better fit. We found that values of $k = 0.1295$ g m^{-3} and $P = -0.0211$ s^{-1} in following equation:

$$\left(\frac{\gamma_g + k}{\gamma_{gi} + k}\right) = \exp\left(\frac{P h}{u_g}\right)$$

gave a reasonable fit to all the experiments, but that better accuracy could be obtained by using three separate fits for each group of experiments.

Keywords:
Biofiltration, styrene removal, mathematical model

Introduction

Biofiltration is a useful and economic way to purify air streams contaminated with volatile organic compounds (VOC).[1] It is particularly applicable when high volumetric rates and low inlet concentrations are involved and the substance to be removed is biodegradable. Otherwise, condensation, incineration or absorption processes may be more appropriate. This system of removing pollutants has other advantages such as low cost, no generation of hazardous by-products, and no fuel requirement. The disadvantages are lower efficiencies and a relatively narrow operating range.

There is a porous support material within the biofilter on which the microbes grow. In this study, activated carbon was used. A contaminated air stream was passed through the filter and the contaminant (styrene) was transferred from the gas to aqueous phase, where the biodegradation takes place. In order to keep the biocatalyst at a high degradation activity, a diluted mineral medium was added once a week to supply the cells with water and basic mineral nutrients, (this also maintained the pH value of the bed). The microbes break down the pollutant and convert it to carbon dioxide and water.

The contaminants must be biodegradable and non-toxic to the microbes. The best biodegradability is observed with low molecular mass, highly soluble compounds with simple bond structures. Hence, a styrene contaminated air stream is a real challenge to the process designer!

The Ottengraf model[2,3] was chosen to model the experimental results, because it is a relatively simple, steady-state model with an analytical solution. It considers convection in the gas phase and diffusion with reaction in the liquid bio-film. The kinetics can be of first or zero order. (In the latter case, there may be reaction or diffusion limiting steps.) In order to be analytically solvable, quite a few assumptions have to be made, namely:

– plug-flow is assumed in the gas phase together with a constant diffusion coefficient in the liquid,

– no resistance to mass transfer in the gas phase, (hence Henry's law will directly give the interfacial liquid concentration),

*Corresponding author is A. M. Gerrard

– the biofilm thickness is small compared to the particle diameter, (so the film can be modelled as being flat).

The mathematical representation of the three models is as follows:

For first order kinetics:

$$\frac{\gamma_g}{\gamma_{gi}} = \exp\left[\frac{-h k_1}{m u_g}\right] \quad (1)$$

This clearly gives an exponential concentration profile with respect to filter bed height.

Hence, the logarithm of the concentration ratio is a linear function of bed height.

For zero order kinetics with reaction limitation, we have a direct linear relationship between concentration and height:

$$\frac{\gamma_g}{\gamma_{gi}} = 1 - \left[\frac{h k_0}{\gamma_{gi} u_g}\right] \quad (2)$$

However, for zero order kinetics, with diffusion limitation, we find:

$$\frac{\gamma_g}{\gamma_{gi}} = \left[1 - \frac{h}{u_{gi}}\sqrt{\frac{k_0 D \alpha}{2 m \gamma_{gi} \delta}}\right]^2 \quad (3)$$

Hence, a quadratic concentration profile is found with respect to filter bed height. So, the square root of the concentration ratio is linearly related to the bed height.

(The apparent reaction coefficients (k_0, k_1) can be calculated from the above mentioned formulae, using the gradients of the linearised plots of (γ_g / γ_{gi}) versus the bed height.)

In addition, we note that *elimination capacity* (EC) and *degradation efficiency* (DE) are used to describe the overall performance of the biofilter.

EC can be calculated using:

$$\mathrm{EC} = \left(\frac{\gamma_{gi} - \gamma_{go}}{V_f}\right) Q \quad (4)$$

and DE can be calculated from:

$$\mathrm{DE} = \left(\frac{\gamma_{gi} - \gamma_{go}}{\gamma_{gi}}\right) \quad (5)$$

Preliminary analysis

All four sections of the biofilter were inoculated with a (mixed) enrichment culture. A preparation of the biocatalyst and the microbial analysis from the four different bed heights has been described elsewhere.[4] The microbial analysis was carried out after 45 days of the inoculum immobilisation. The highest total cell number was found in first two sections of the reactor, due to the higher organic loading. (The highest number of styrene degraders was present in the first section.) *Pseudomonas* was present throughout the reactor. Indeed, in the third and fourth sections, almost all the styrene degraders were *Pseudomonas*. An identification of the individual strains isolated from the biocatalyst has not been carried out. (But a determination of the procaryots, eucaryots, primary styrene degraders and *Pseudomonas* was performed.)

The first part of the data set consisted of 37 experiments. The steady-state inlet, outlet and three intermediate concentrations of the styrene pollutant were measured in a 50 mm diameter biofilter, (the experiments were done within a 95 h period). In addition, the steady state degradation along the bed was measured for a larger (100 mm diameter) unit.

At first, the mass concentration ratio (γ_g/γ_{gi}) was calculated for all the experiments and was plotted against the bed height on linear axes. Trend lines were added and the R^2 values were recorded. As we have summarised previously, if a good fit was obtained, then the zero order kinetics with reaction limitation were appropriate. Then the square root of the dimensionless concentration was calculated for all the experiments and plotted against the bed height. In this case, high values of R^2 would suggest the zero order kinetics with diffusion limitation. The same procedure was carried out with logarithm of the mass concentration ratio, where high values would mean that first order kinetics would constitute a reasonable model.

The values of the coefficient of determination, R^2, for the linear (γ_g versus h) plots were low (usually in the range of 0.69 – 0.9), therefore it can be stated that none of the experiments followed the zero order, reaction limited kinetics. The values of R^2 for zero order kinetics with diffusional limitation were higher, in the range 0.79 – 0.99, (this was tested using the square root of the concentration ratio against height). The highest R^2 (0.88 – 0.999) values were found for the logarithm of the concentration ratio plotted against height, indicating first order kinetics.

These first order kinetics were observed in the early runs, where there was small airflow rate (around 0.5 L min^{-1}) and a high inlet mass concentration (around 3.90 g m^{-3}) of the pollutant (e.g. run 4, shown in appendix 1). First order kinetics were also observed in the runs where there was medium airflow rate (1.0 L min^{-1}) and inlet mass concentration (1.6 g m^{-3}) of styrene. Rather surprisingly, the

zero order kinetics with diffusional limitation model was observed in later runs to be *marginally* better than the first order model. (This occurred when high airflow rate (2.0 L min^{-1}) and the lowest inlet concentrations (0.720 g m^{-3}) were used.)

The apparent reaction rate coefficients were calculated from the gradient of the trend lines for each case and were found to be approximately constant. To check for steady operating conditions, the rate constants were also plotted as a function of time – where we would expect a horizontal line. (A slight decline of these constants over time was observed in the case of the zero order reaction, a small increase was observed for the first order kinetics and it was flat, as expected, for the diffusion limitation kinetics.)

The same procedure was carried out on data from degradation along the larger bed (diameter of 100 mm). Three experiments were carried out at a higher mass concentrations (around 4, 6, and 8 g m^{-3}). With inlet mass concentrations around 4 g m^{-3}, the most suitable model was either the first order, or zero order with diffusional limitation. With higher concentrations, the filter followed the zero order diffusion limitation kinetics. This corresponds with the results usually found in the literature.

Simple extension to Ottengraf's model

The mass balance in liquid bio-phase equates the diffusional rate to the reaction rate.

$$D\frac{\mathrm{d}^2\gamma}{\mathrm{d}X^2} = r \tag{6}$$

and if we assume the general Monod form of kinetics:

$$r = \frac{\mu_{\max}\gamma}{K_s + \gamma} = \left(\frac{A\gamma}{B+\gamma}\right) \tag{7}$$

then this equation must be solved numerically. But if we can make a linear approximation to this form (following Atkinson's suggestion[5] in a study on biofilms):

$$r \cong A_1 + A_2 \cdot \gamma \tag{8}$$

and combining these equations we get:

$$\frac{\mathrm{d}^2\gamma}{\mathrm{d}X^2} - \frac{A_2\cdot\gamma}{D} = \frac{A_1}{D} \tag{9}$$

using the D operator method, we can solve this to get the mass concentration, γ, as a function of depth, X, in the bio-film:

$$\gamma = A\exp\left(\sqrt{\frac{A_2}{D}}X\right) + B\exp\left(-\sqrt{\frac{A_2}{D}}X\right) + \left(-\frac{A_1}{A_2}\right) \tag{10}$$

We can find the constants A and B from the boundary conditions:

At $X = 0$; $\gamma = \gamma_{\mathrm{int}}$

Hence,

$$\gamma_{\mathrm{int}} = A + B + \left(-\frac{A_1}{A_2}\right) \tag{11}$$

and at $X = L$, $\dfrac{\mathrm{d}\gamma}{\mathrm{d}X} = 0$

Hence,

$$A = B\cdot\exp\left(-2\sqrt{\frac{A_2}{D}}\cdot L\right) \tag{12}$$

We can combine these equations to find the concentration profile equation:

$$\begin{aligned}\gamma = (a\gamma_{\mathrm{int}} + b)\cdot\exp\left(\sqrt{\frac{A_2}{D}}\cdot X\right) + \\ + (a'\gamma_{\mathrm{int}} + b')\cdot\exp\left(-\sqrt{\frac{A_2}{D}}\cdot X\right) + \left(-\frac{A_1}{A_2}\right)\end{aligned} \tag{13}$$

(where a, a' and b, b' are new constants).

We also need to be able to differentiate this to find the removal rate of styrene from the gas phase:

$$\begin{aligned}\frac{\mathrm{d}\gamma}{\mathrm{d}X} = (a\gamma_{\mathrm{int}} + b)\sqrt{\frac{A_2}{D}}\cdot\exp\left(\sqrt{\frac{A_2}{D}}\cdot X\right) + \\ + (a'\gamma_{\mathrm{int}} + b')\cdot\left(-\sqrt{\frac{A_2}{D}}\right)\cdot\exp\left(-\sqrt{\frac{A_2}{D}}\cdot X\right)\end{aligned} \tag{14}$$

At the interface, this equals:

$$\left.\frac{\mathrm{d}\gamma}{\mathrm{d}X}\right|_{X=0} = (a\gamma_{\mathrm{int}}+b)\cdot\sqrt{\frac{A_2}{D}} + (a'\gamma_{\mathrm{int}}+b')\cdot\left(-\sqrt{\frac{A_2}{D}}\right) \tag{15}$$

Hence

$$\left.\frac{\mathrm{d}\gamma}{\mathrm{d}X}\right|_{X=0} = a''\gamma_{\mathrm{int}} + b'' \tag{16}$$

(Again, a'', b'' are newly defined constants, representing groups of constant quantities.)

Putting this into the usual mass balance for the gas phase:

$$u_g\cdot\frac{\mathrm{d}\gamma_g}{\mathrm{d}h} = \alpha\cdot(1-\varepsilon)\cdot\left.\frac{\mathrm{d}\gamma}{\mathrm{d}X}\right|_{X=0} \tag{17}$$

gives

$$u_g \cdot \frac{d\gamma_g}{dh} = \alpha \cdot (1-\varepsilon) \cdot (a''\gamma_{int} + b'') \qquad (18)$$

Noting that $\gamma_{int} = \gamma_g / m$ and integrating we get:

$$\ln\left(\frac{\gamma_g + \frac{b''}{a''}}{\gamma_{gi} + \frac{b''}{a''}}\right) = \frac{\alpha \cdot (1-\varepsilon) \cdot h \cdot a''}{u_g} \qquad (19)$$

This can be conveniently rewritten as:

$$\left(\frac{\gamma_g + k}{\gamma_{gi} + k}\right) = \exp\left[\frac{P\,h}{u_g}\right] \qquad (20)$$

where k and P are constants. Clearly, when k equals zero, we have the usual first order form of equation, analogous to equation 1.

Using the new equation

As noted before, the first measurements were carried out on a biofilter operated at steady state (diameter: 50 mm, bed height: 4 sections each of 27 mm, the filling was activated carbon with a void volume ε = 0.1848). In order to clarify the approach, we now average to them to give just three sets of raw results, (see Table 1).

Table 1 – *Averaged values of concentration ratios recorded at each measuring point in the bed for the three sets of experiments in the 50 mm bed*

Set	Air flow / L min^{-1}	γ_{in} / g m^{-3}	$\gamma_{out1}/\gamma_{in}$	$\gamma_{out2}/\gamma_{in}$	$\gamma_{out3}/\gamma_{in}$	$\gamma_{out4}/\gamma_{in}$
1	0.5	3.767	0.2973	0.0527	0.0132	0.0068
2	1	1.831	0.3931	0.1011	0.0183	0.0112
3	2	0.878	0.6689	0.3420	0.1225	0.0676

The values of R^2 for the zero order, reaction limited model were disappointingly low in all cases, see column two of table 2. Therefore, as noted before, it can be concluded that none of the experiments followed those kinetics. The values of R^2 for zero order kinetics with diffusion limitation were all higher (column three) than those just mentioned. However, Ottengraf's first order model was the best for sets 1 and 2, and was just inferior to the zero order diffusion limited model in the third set of experiments.

When we used the modification of original theory, (equation 20), including the additional, positive constant (k) which is added to each recorded concentration value, then we obtained the best value of R^2 for the third set of data (see right hand column of table 2). Figure 1 shows how an optimal value of the constant was found which maximised the coefficient of determination, R^2. (The highest value of R^2 was achieved when k = 0.100 g m^{-3}.)

Table 2 – *Summary of R^2 values with original models and the modified version*

Set	Reaction kinetics			
	Zero order models		First order models	
	Reaction limited	Diffusion limited	Ottengraf form	Modified form
1	0.5480	0.8014	0.9804	–
2	0.6694	0.8817	0.9744	–
3	0.9289	0.9837	0.9732	0.9840

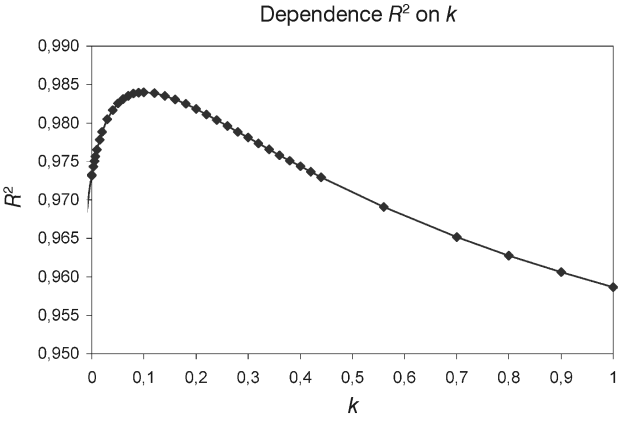


Fig. 1 – *Dependence of R^2 on k (for the third set of experiments)*

We then used a different criterion for goodness of fit, trying to minimise the sum of the square of the differences (SOS) between the measured and the predicted concentrations. This quantity was calculated using:

$$\text{Differences} = \sum_{i=1}^{4}\sum_{j=1}^{n} \frac{(\gamma_{i,j,out} - \gamma_{i,j,calc})^2}{n} \qquad (21)$$

where i is the position in the bed and j is experiment set number and n is the number of averaged experiments.

Applying the modified first-order kinetic model, we showed that values of k = 0.1295 g m^{-3} and P = –0.0211 s^{-1} gave a reasonable fit to all three of the averaged experiments. Better accuracy could, however, be obtained by using separate fits for each set

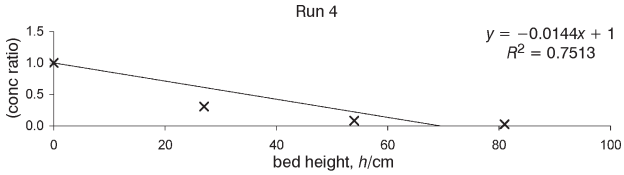
Table 3 – *Comparison of the original, first order model with the new proposal*

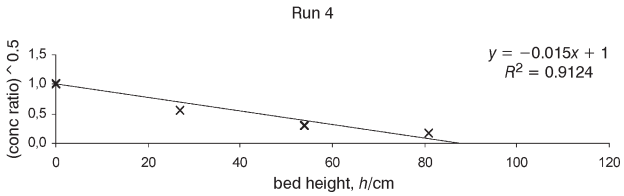
Set	SOS, using a first order model for each set	SOS, using new extended model for each set	$\frac{k}{\text{g m}^{-3}}$	$\frac{P}{\text{s}^{-1}}$	SOS, using new model on all thee sets	$\frac{k}{\text{g m}^{-3}}$	$\frac{P}{\text{s}^{-1}}$
1	43.620	26.280	0.0467	–0.01925	102.915		
2	36.229	13.210	0.0574	–0.02965	84.710		
3	34.780	18.740	0.1794	–0.02451	44.734		
Sum	114.629	58.229			232.359	0.1295	–0.02109

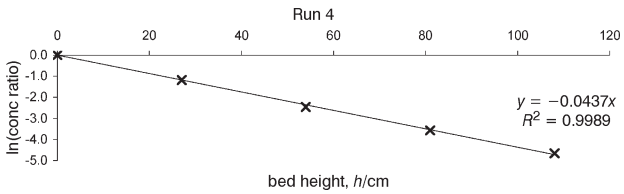
of experiments. (These optimal values of k and P for each set gave a better fit in comparison with the original Ottengraf first-order models (see Table 3)). The optimal values of k and P were calculated using the Solver tool included in the Excel spreadsheet.

Appendix 1 – example curve fits and performance data (for run 4)

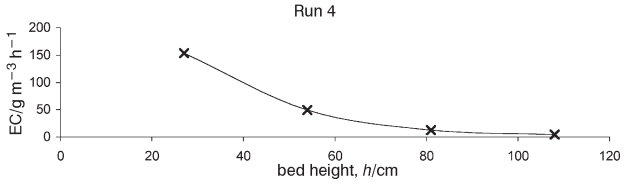
Showing linear, square root and logarithmic fits



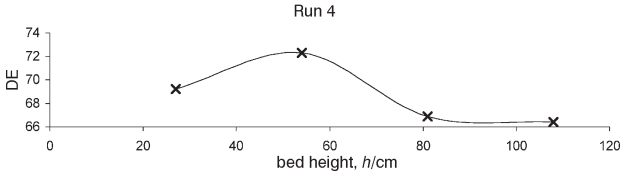




Elimination capacity (g m^{-3} h^{-1}) versus bed height



Degradation efficiency η_{DE} (%) versus bed height



Conclusions

Hence, we can conclude that the original, first order Ottengraf model, is appropriate to represent the styrene removal data, but the inclusion of the extra constant in equation 20 gives a worthwhile improvement in the goodness of fit of our experimental data.

The various experiments showed that biofilters could be used to remove styrene from air with degradation efficiencies around 60-70 % per bed (or well over 90 % for the four bed system). The elimination capacities ranged around 60 g m^{-3} h^{-1}, see appendix 1).

ACKNOWLEDGEMENT

The study was financially supported by the Czech Scientific Foundation, Project 104/05/0194.

Nomenclature

a, a', a'', A, A_1, A_2, b, b', b'', B – constants
D – liquid phase diffusion coefficient, m^2 s^{-1}
DE – degradation efficiency
ε – porosity of packing material
EC – elimination capacity, g m^{-3} h^{-1}
h – filter bed height, m
k – constant in equation 20, g m^{-3}
k_0 – zero order reaction coefficient, g m^{-3} s^{-1}
k_1 – first order reaction coefficient, s^{-1}
K_s – saturation constant in Monod equation, g m^{-3}
L – Biofilm thickness, m
m – gas liquid partition coefficient
P – constant in equation 20, s^{-1}
Q – air flow rate, m^3 s^{-1}
r – reaction rate g m^{-3} s^{-1}
u_g – superficial velocity, m s^{-1}
V_f – filter bed volume, m^3
X – depth in the liquid biofilm, m
α – ratio of surface area to volume, m^{-1}, m^2 m^{-3}
δ – biolayer thickness, m

γ – liquid mass concentration, g m^{-3}
γ_g – gas mass concentration, g m^{-3}
γ_{gi} – inlet gas mass concentration, g m^{-3}
γ_{int} – gas- liquid interface mass concentration in biofilm, g m^{-3}
γ_{go} – outlet gas mass concentration, g m^{-3}
μ_{max} – coefficient in Monod equation, s^{-1}

References

1. *Devinny, J. S., Deshusses, M. A., Webster, T.*, Biofiltration for Air Pollution Control, Lewis Publishers, Boca Raton, 1999.
2. *Ottengraf, S. P. P.,* Biofilters in Biotechnology, VCH Verlagsgeselltschaft, Weinheim, 1986, pp 436-446.
3. *Ottengraf, S. P. P.,* Trends Biotechnol. **5** (1987) 132.
4. *Paca, J., Koutsky, B.*, In proceedings of USC-TRG Conference of Biofiltration, The Reynolds Group, Tustin, California, October 19-20, 2000.
5. *Atkinson, B*., Chapter 5, "Biochemical Reaction Engineering" in Chemical Engineering, volume 3, edited by Richardson J. F. and Peacock D.G., Pergamon, Oxford, 1971.