

QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS FOR VOC BIODEGRADATION IN BIOFILTERS

Camdon T. Johnson and *Marc A. Deshusses*

(University of California, Riverside, CA; Marc_Deshusses@qmail.ucr.edu)

ABSTRACT: VOC biodegradation in waste air biofilters is discussed, and a general model for the description of either the maximum elimination capacity or the load at which 95% pollutant removal occurs is presented and evaluated. The model used Henry's law coefficient, log of octanol-water partition, a molecular connectivity index and group contributions. Model parameters were calibrated using removal data for 17 compounds and excellent description of experimental data was achieved. Future efforts will focus on demonstrating the predictability of the model to improve its applicability for reactor design purposes.

INTRODUCTION

During the past decades, numerous research studies in biofiltration have focused on specific kinetic aspects of pollutant elimination, on the microbiology of the process culture, and mathematical modeling. Mathematical models were mainly developed to correlate a particular set of experimental data, to explain the influence of selected parameters on the efficiency of the process, and sometimes to seek a better fundamental understanding of the phenomena occurring in a biofilter (Ottengraf, 1986; Shareefdeen et al. 1993; Deshusses et al. 1995; Hodge and Devinny, 1996). More recently, promising quantitative structure activity relationships for biofiltration were presented (Choi et al. 1996). Unfortunately, none of these efforts has resulted in either a "universal theory" of biofiltration or in some sort of a predictive model, allowing *a priori* estimation of detailed pollutant elimination in biofilters to be achieved. As a matter of fact, the applicability of such models for reactor design is relatively low, and will probably remain so until a better fundamental understanding of the complex phenomena involved during the biofiltration process will be incorporated into the models. Under such circumstances, design of full-scale biofilters still relies, either on previous experience with a similar waste air stream, or on time consuming and expensive bench-scale or pilot-scale testing. Clearly, there is a need for a more comprehensive discussion of the parameters influencing the elimination of pollutants in biofilters. In addition, efforts should be directed towards the development of simple and predictive models. In the future, the combined knowledge could lead to better reactor design or optimized process control. In some instances, it could even speed-up the reactor design procedure by excluding lengthy bench or pilot-scale tests.

In the present paper, we discuss elimination capacity data of selected VOCs with respect to their physico-chemical properties, and present an attempt to correlate these elimination capacities in a multilinear regression using structure and physico-chemical descriptors.

DEFINITIONS

In a biofilter, performance is measured by the elimination capacity as defined in eq. 1; loading is defined in eq. 2. The maximum amount of a VOC that can be removed in a biofilter is called the maximum elimination capacity, or EC_{max} , whereas the ratio of the elimination capacity with the load is the removal percentage.

$$EC = \frac{(\text{concentration in out}) \text{ air flow rate}}{\text{biofilter bed volume}} \quad \left(\text{g m}^{-3} \text{ h}^{-1} \right) \quad (1)$$

$$\text{Load} = \frac{\text{concentration in} \cdot \text{air flow rate}}{\text{biofilter bed volume}} \quad \left(\text{g m}^{-3} \text{ h}^{-1} \right) \quad (2)$$

The database of VOC elimination capacities used in the present study is reported in Table 1 (see further, column of experimental values). All data were obtained using a protocol described before (Johnson and Deshusses, 1996). In summary, selected VOCs were injected in a compost-wood chips biofilter over a 48 hour period, and steady-state axial concentration profiles at two different pollutant inlet concentrations were used to generate an elimination capacity vs. load curve. Comparison of data obtained by others and data obtained with this protocol demonstrated the validity of the approach (Johnson and Deshusses, 1996).

APPROACH

Analysis of the factors likely to influence the rate of pollutant elimination in a biofilter should consider the fate of the pollutant undergoing treatment. For a simplistic approach, one can assume that gas/liquid transfer of the pollutant occurs and that it is followed by diffusion and biodegradation in the biofilm. Therefore, all factors affecting either transfer or biodegradation rate may influence the performance of the process. Our objective here, is to identify those factors, and combine them in a general equation in order to correlate elimination capacities of pollutants in biofilters.

One of the most appropriate descriptors for the elimination of a pollutant in a biofilter is probably Henry's law coefficient, because it links gas phase and biofilm concentrations. Here, it is worth noticing that the Henry coefficients for pollutants commonly treated in biofilters vary as much as 5 orders of magnitude, whereas gas concentrations generally fall within one or two orders of magnitude. This will have a significant impact on the concentrations perceived by the microorganisms. The diffusion coefficient of the pollutant undergoing treatment is probably not a good descriptor. The reason is that D values for commonly treated VOCs all fall within one order of magnitude, and therefore variations of diffusion coefficient are not expected to induce changes in pollutant removal. For this reason D was not considered here.

Recently, it was suggested that $\log P_{o/w}$ -the log of the octanol water partition coefficient- could be a good descriptor for the toxicity of organic

compounds (Rajagopal, 1996). The reason is that hydrophobic organics are more likely to damage cell membranes. Since substrate toxicity, herein described by $\log P_{o/w}$, and substrate biodegradation rate are not necessarily linked, other descriptors are needed to quantify biodegradation rates. Unfortunately, there is no one constant or listed chemical property that solely describes biodegradation rates, hence a more complex formulation will be necessary. Previous work in the field of wastewater treatment considered either group contributions (Govind et al. 1991; Boethling et al. 1994) or quantitative structure-activity relationships (QSAR) (Okey and Stensel, 1996) to correlate and to predict pollutant biodegradation rate. In the present case, a combined approach was chosen, using both a group contribution and the first order connectivity index, X_1 . Hence, a general formulation of a pollutant elimination in a biofilter can be written including the Henry and $\log P$ contribution:

$$\text{Log}(EC_{\max}) = \alpha \cdot H + \beta \cdot \log P_{o/w} + \gamma \cdot X_1 + \sum n \cdot \delta_{\text{group}} \quad (-) \quad (3)$$

Where EC_{\max} is expressed in $\text{g m}^{-3} \text{h}^{-1}$, and α , β , γ and the different δ are model parameters to be calibrated using experimental data. X_1 is a molecular connectivity index and can be calculated from the structure of the molecule (Kier and Hall, 1986). Here, only the first order connectivity index is used because for low molecular weight volatiles usually treated in biofilters, the second order connectivity index is often zero. The δ in eq. 3 represent the contribution of entities such as $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{OH}$, etc. out of which the molecule is made, and n , the number of time the group appears in the molecule.

A similar equation is used to describe the loading at which 95% of the inlet pollutant is removed:

$$\text{Log}(\text{Load}_{95\% \text{removal}}) = \alpha \cdot H + \beta \cdot \log P_{o/w} + \gamma \cdot X_1 + \sum n \cdot \delta_{\text{group}} \quad (-) \quad (4)$$

Where α , β , γ and δ in eq. 4 will take different values than those in eq. 3.

A major challenge in the determination of model parameters is that a statistical approach has to be performed with a fairly small database. Theoretically with 11 parameters (α , β , γ and 8 groups) and 17 compounds in the database, a solution could exist. In reality, elimination data for as much as 150-200 compounds would be required to converge to a satisfactory solution. However, we estimate that only about 40-70 compounds have been tested in biofilters so far, and reliable elimination data, i.e., complete elimination capacity vs. load curve, is probably only available for less than 30 compounds. Thus, with our database of 17 compounds, the problem is to find appropriate solutions to eqs. 3 and 4, keeping in mind that large discrepancies may exist for the fitting of one or another compound.

RESULTS AND DISCUSSION

The search for a correlation between dependent variable and supposed descriptors goes through the search for regularities in three (or more) dimensional space. Here, due the small number of data available, it was impossible to plot reliable 3D surfaces graphs, e.g., for maximum elimination capacity vs. Henry coefficient and $\log P$. Even so simple trends are shown on 2D graphs on Figure 1. Clearly, Figure 1 shows that pollutants with large Henry coefficient are more

difficult to treat in a biofilter. Also, even if the data is more scattered, there is some correlation between $\log P$ and the maximum elimination capacity or the loading at which 95% of the inlet VOC is removed. Similar graphs drawn for X_1 demonstrated ever more scattered data, suggesting that a linear combination for X_1 in eq. 3 and 4 might not be the best solution, and that non linear fitting could be considered in the future. However, this was not included here to limit the number of parameters.

Next, eqs. 3 and 4 were fitted to both the maximum elimination capacity and the load at which 95% removal occurred. The results are presented and compared to the experimental data in Table 1, and the value for the various model parameters are listed in Table 2. A very good agreement between the model and the experiment is observed in both cases. Experimental errors (not reported in Table 1), were generally greater than the difference between model and computed value. This demonstrates the validity of the approach described herein. It should be noted, that several solutions were found for the model parameters, depending on the initial values given for the parameters estimation. This is a usual problem in multi-variable model fitting. Two approaches are possible: first: the solution with the lowest residual is kept. Often, such an approach leads to a “mathematically” best solution, where most compounds are very well described and the residual is mainly due to one or two compounds with huge discrepancies between model and experimental value. Second: various solutions are considered and evaluated for their predictability

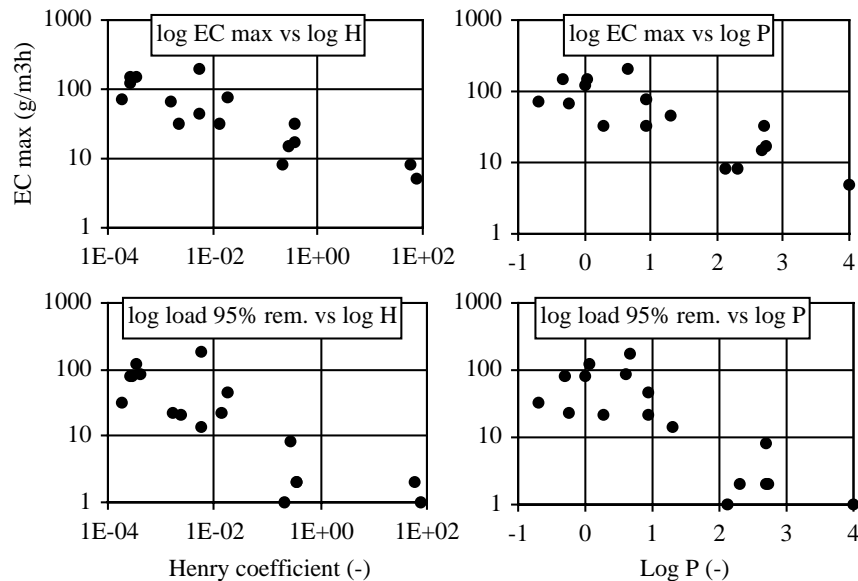


FIGURE 1. Maximum elimination capacities of VOCs listed in Table 1 in biofilters and load at which 95% removal occurs vs. dimensionless Henry coefficient and of log of octanol-water partition

for external data and parameter sensitivity is performed to verify the soundness of the various combinations of parameters. At this time, the second approach is

considered and further research is needed to validate the correlation presented herein. So far, prediction was only performed for 1-propanol and 2-butanol,

TABLE 1. Experimental results and model computations for the removal of selected VOCs in a compost/wood chips biofilter.

Compound	H (-)	log P _{o/w}	X ₁	EC _{max} (g m ⁻³ h ⁻¹)		Load at 95% removal (g m ⁻³ h ⁻¹)	
				experiment	model	experiment	model
1 Hexane	74.13	4	2.914	5	0.3	1	0
2 Isopentane	56.47	2.3	2.414	8	7	2	0
3 MEK	0.00235	0.28	1.765	32	57	21	14
4 MIBK	0.00571	1.31	2.043	45	25	14	23
5 Acetone	0.0016	-0.24	1.204	67	53	23	13
6 Ethyl acetate	0.00550	0.66	1.904	200	182	180	168
7 Butyl acetate	0.0135	0.94	2.904	32	63	30	45
8 Isobutyl acetate	0.0186	0.94 ^e	2.760	75	95	45	68
9 Methanol	0.000191	-0.7	0.447	70	118	32	73
10 Ethanol	0.000257	-0.31	1.023	150	111	80	66
11 2-propanol	0.000347	0.05	1.413	120 ^{ac} /25 ^d	86 ^b	80	55
12 1-propanol	0.000275	0.05 ^e	1.523	150	137	120	109
13 Toluene	0.275	2.69	2.411	15	21	8	0
14 Xylene	0.355	2.73	2.821	17	27	2	0
15 Ethyl benzene	0.355 ^e	2.7	2.971	32	12	2	0
16 Sec-butanol	0.000417	0.61	1.951	140 ^{ac} /20 ^d	148 ^b	85	120
17 Benzene	0.216	2.13	2.000	8	8	1	0

^avalue not included for model parameter determination; ^bmodel prediction; ^csignificant metabolite formation, value is for substrate disappearance; ^dvalue based on total carbon balance; ^eestimated value.

TABLE 2. Model coefficients for the fitting of VOC elimination in biofilters.

	coefficients for EC _{max} (Eq. 3)	coefficients for 95% removal load (Eq. 4)
α	-0.0928	-20.91
β	0.5458	0.5583
γ	0.8406	0.3010
$\delta_{\text{-CH}}$	-3.486	-0.7177
$\delta_{\text{-CH}_2}$	-0.7270	-0.4315
$\delta_{\text{-CH}_3}$	2.330	0.18530
$\delta_{\text{-CHO (keto)}}$	-3.817	0.5604
$\delta_{\text{-COOCH}_2\text{- (ester)}}$	-4.360	1.028
$\delta_{\text{-OH (alcohol)}}$	-0.2508	1.938
$\delta_{\text{-CH aromatic}}$	-0.3160	-0.2229
$\delta_{\text{-C aromatic}}$	-2.898	0.6978

because large amounts of metabolites were observed during their elimination in the biofilter, and no decision could be made as to which value to take for the model fitting. For these two compounds, comparison of model prediction and experimental value shows good agreement with the amount of alcohol removed from the gas phase.

It is difficult to comment on the values of the different model parameters, in particular for the differences between the parameters for the EC_{max} and those for the 95% removal correlation. As mentioned before, the parameters presented in Table 2 might be a “best mathematical fit”, whereas in the interest of the predictability of the model, a conceptually sound solution is desired. Fine tuning of the parameters is still needed. Future efforts will focus on the study of those parameters and will seek to demonstrate the predictability of the correlations presented herein.

CONCLUSIONS

For the first time, a model allowing to describe in a very broad manner the maximum performance and the range of optimum removal for VOCs in waste air biofilters was presented and discussed. The model only used parameters that do not require experimental determination, so that it might prove useful for design purpose. Excellent agreement between experimental data and model computations was achieved. So far, the predictability of the model was not fully verified, nor were model parametric sensitivities performed. Future efforts will focus on these fundamental aspects. Also, the fact that mixtures of pollutants sometimes exhibit mutual inhibition or that some pollutants produce significant amounts of metabolites when treated in a biofilter will be taken into consideration.

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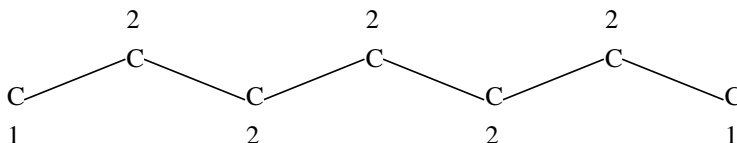
Additional information
HOW TO CALCULATE THE MOLECULAR DESCRIPTOR, ${}^1\chi^V$:

1. Assign a number to every non-hydrogen atom describing the number of carbons adjacent to that atom.
2. For atoms that are not carbon, count the number of valence electrons as well as the number of adjacent carbon atoms.
3. In the case where double bonds exist, treat each bond individually. Group numbers that are assigned to each carbon into adjacent carbon attachment pairs.
4. ${}^1\chi^V = \sum (\delta_i \delta_j)^{-0.5}$

Note: In the paper we used the notation X_1 , vX_1 , or ${}^1X^v$ for the molecular descriptor ${}^1X^v$. In fact ${}^1X^v$ and 1X are different: ${}^1X^v$ considers valance electrons, whereas 1X only considers carbon neighbors.

${}^1\chi^V$ example calculations

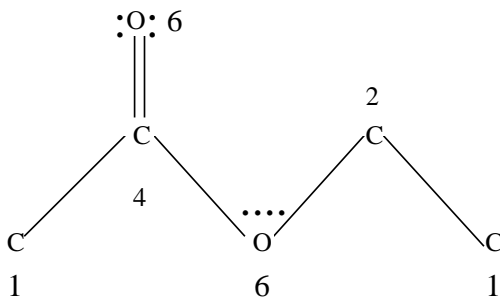
Heptane



Groups: (1,2), (2,2), (2,2),(2,2), (2,2), (1,2)

$${}^1\chi^V = (1*2)^{-0.5} + (2*2)^{-0.5} + (2*2)^{-0.5} + (2*2)^{-0.5} + (2*2)^{-0.5} + (1*2)^{-0.5} = 3.414$$

Ethyl Acetate



Groups: (1,4), (4,6), (4,6), (6,2), (2,1)

$${}^1\chi^V = (1*4)^{-0.5} + (4*6)^{-0.5} + (4*6)^{-0.5} + (6*2)^{-0.5} + (2*1)^{-0.5} = 1.904$$