

Mathematical Modeling for Volatile Organic Compounds Removal in a Biofilter: Model Validation and Sensitivity Analysis

S. Ranjbar, A. Ghaemi*

School of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran

Abstract

In this work, a dynamic model has been developed for prediction of biofilters performance. The model includes most of the phenomena occurring in a biofilter. For biodegradation of pollutants in the biofilm, the Michaelis-Menten kinetic has been considered. The model equations including gas phase and biofilm partial differential equations were solved simultaneously using finite difference and method of lines. The model parameters were evaluated by sensitivity analysis to determine their respective effects on the model performance. The model predictions were validated by experimental data for mixture of methyl propyl ketone, toluene, p-Xylene and n-Butyl acetate. The simulation results of empty bed residence times 30, 60, 90 seconds were compared with experimental data. The comparison of results showed the model predictions had a good agreement with experimental data. The sensitivity analysis of the model parameters showed that Henry's constant and specific area of biofilter had the strongest influence on biofilter performance.

Keywords: *Biofilter, VOCs biodegradation, Mathematical modeling, Sensitivity analysis*

1. Introduction

In recent years, biofiltration has emerged as an efficient and reliable biological process for treatment of pollutants from contaminated air emissions. This technology has been successfully used to remove a wide range of pollutants such as volatile organic compounds (VOCs), ammonia and sulphurous compounds, etc. [1-2]. It could cost-effectively remove VOCs and odours from waste gas stream [3-5]. Biofiltration involves the passage of a polluted air stream through a packed bed containing

microorganisms immobilized within a biofilm attached to the bed-packing material. Contaminants are transferred to the interface between the gas and the biofilm and are subsequently absorbed into the biofilm [6]. Effective simulation of the complex process is helpful to better understand the mechanisms occurring in the biofilters, and consequently to better designing and operation of biofilters. Many mathematical models were proposed for biofiltration processes including the basis of the adsorption-biodegradation model [7] and the

* Corresponding author: aghaemi@iust.ac.ir

absorption-biodegradation theory [8]. Both steady-state and dynamic mathematical models have been developed to evaluate performance of biofilters. No single model has become a generally accepted standard; each research group has developed its own approach, often specific to the experiments being performed [9].

Modeling of biofilters for the biotreatment of volatile organic compounds in air began in the 1980s with the work of Ottengraf et al. by considering diffusion and biodegradation of pollutants in biofilms [8]. The kinetics of biodegradation of the single pollutants by the microorganisms on the biofilm was described by a Monod-type expression, assuming first or zero-order kinetics. While several models with increased degree of complexity were reported thereafter [10-12], the original model often has been used to represent biofiltration data [13].

Mathematical modeling of biofiltration systems is faced with the complexity of the physicochemical and microbiological phenomena involved in multiphase systems. Majority of the published models include parameters that were not measured independently by experimentation but were obtained by fitting experimental data, thus masking their real influence as they are generally lumped in the equations. These parameters often include the superficial transfer area, the biofilm thickness, the partition coefficient, the effective diffusivity and majority of the bio-kinetic parameters [14].

The aim of this work is to present a dynamic model to predict performance of biofilters. The equations for the mass transport and bioreactions within the biofilm phase and gas

phase and the accumulation of biofilms in this model were solved using finite difference and method of lines. The model predictions were validated by experimental data for mixture of MPK, Toluene, p-Xylene and n-Butyl acetate that were obtained from the literature [15]. The kinetic parameters of the model were determined using experimental data [15]. Also, sensitivity analysis of the model parameters was done to determine the biofilter significant parameters.

2. Model development

The model was built considering the most relevant phenomena occurring during the biofiltration process including convection, absorption, diffusion and biodegradation. The degradation of pollutants in the biofilter was described by a dynamic model based on mass balances. A schematic representation of the model is shown in Fig.1.

The following major assumptions are made in developing a mathematical model:

1. The flow pattern of the air stream through the filter bed is plug flow-type and the flow velocity remains constant.
2. Gas-biofilm interface equilibrium is described by Henry's law.
3. Diffusion in the biofilm is described by Fick's law.
4. Planar geometry and perpendicular diffusion in biofilm are used to derive model equations considering that the solid support size is significantly higher than the biofilm thickness.
5. Biomass properties (thickness, specific surface area and kinetic coefficients) are uniform along the bed. This assumption was experimentally verified

by monitoring a practically constant pressure drop and reactor weight in the whole studied operation period as shown in Maestre et al. [16].

6. Adsorption of pollutant onto the support is neglected due to the low pollutants concentrations.

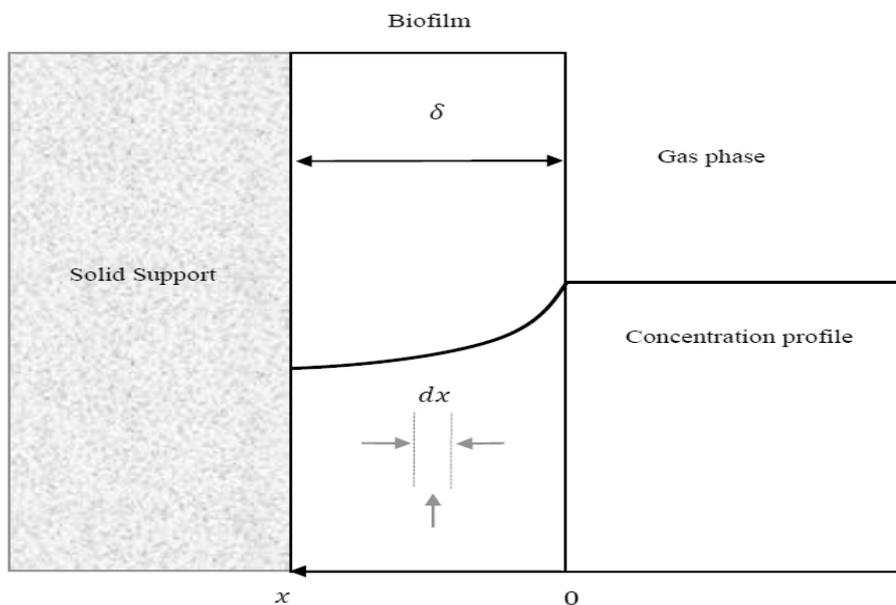


Figure 1. Schematic diagram of biodegradation of pollutants in biofilm.

3. Mass balance of pollutant in the gas phase

Volatile organic compounds concentration in the gas phase can be assumed to be uniform in the column cross section. Model equation for the bulk gas phase in the dynamic state is shown in equation 1[24].

$$\frac{\partial C_g}{\partial t} = D_g \frac{\partial^2 C_g}{\partial Z^2} - v_z \frac{\partial C_g}{\partial Z} - \frac{A_s}{\epsilon} N \quad (1)$$

N is the specific mass flux from gas phase to the biofilm phase for pollutant and it is given by Fick's law:

$$N = -D_b \left(\frac{\partial C_b}{\partial x} \right)_{x=0} \quad (2)$$

The interstitial gas velocity was calculated by considering the porosity of the reactor bed:

$$v_z = \frac{Q}{A \epsilon} \quad (3)$$

Where C_g is Concentration of pollutant in gas phase (g/m^3), D_g is diffusion coefficient of pollutant in gas phase (m^2/s), Z is axial direction (m), Q is flow of gas phase (m^3/s), A is cross section area (m^2), ϵ is the bioreactor bed porosity, A_s is the specific surface area (surface area per unit volume of bed reactor) (m^2/m^3), D_b is the diffusion coefficient of pollutant in biomass (m^2/s), C_b

is the concentration of pollutant in biomass (g/m^3), x is the position in the biofilm from the surface (m) and v_z is the interstitial gas velocity (m/s). Initial and boundary condition for gas phase equation (eq. 1) are:

$$\text{at } t = 0, C_g = 0 \quad (4)$$

$$\text{at } Z = 0, C_g = C_{in} \quad (5)$$

$$\text{at } Z = H, \frac{\partial C_g}{\partial Z} = 0 \quad (6)$$

Where $C_{g,in}$ is the concentration of pollutant in influent (g/m^3) and H is the height of biofilter (m).

Average Absolute Relative Error (AARE) was used to determination the accuracy of the model:

$$AARE \% = \frac{100}{N} \sum_{t=1}^N \left| \frac{A_t - P_t}{A_t} \right| \quad (7)$$

Where, A_t is experimental data P_t is predicted data and N is the number of data.

4. Mass balance of pollutant in the biofilm phase

Model equation for the biofilm under dynamic conditions contains diffusion term and biodegradation term [24]:

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} - r \quad (8)$$

Initial and boundary condition for biomass phase equation:

$$\text{at } t = 0, C_b = 0 \quad (9)$$

$$\text{at } x = 0, C_{g,interface} = h(C_b)_{x=0} \quad (10)$$

$$\text{at } x = \delta, \frac{\partial C_b}{\partial Z} = 0 \quad (11)$$

The last boundary condition states that the concentration gradient at the biofilm/media interface is zero. It implies there is no mass transfer to the media and it, therefore, follows that the media is inert. Where $C_{g,interface}$ is interface concentration of pollutant, h is the gas-liquid distribution coefficient given by Henry's law and δ is biomass thickness (m).

5. Biodegradation kinetic expression

Several kinetic expressions have been used in *VOCs* degradation by biofiltration such as zero or first-order kinetics depending on the pollutant concentration in the bio filter [8]. Haldane type kinetics has been also used for modeling interaction between pollutants during the biological degradation in the biofilm [17]. Currently, in the most works, the specific consumption rate for *VOC* degradation is described by a Michaelis-Menten kinetic expression as it is used here:

$$r = \frac{r_{max} \times C_b}{K_s + C_b} \quad (12)$$

Maximum rate of reaction (r_{max}) and half saturation constant (K_s) for each component, were obtained using experimental data [15]. Michaelis-Menten equation was used for calculation of r_{max} and K_s [18-20]:

$$\frac{(C_{in} - C_{out})}{\ln(C_{in}/C_{out})} = r_{max} \left(\frac{\theta}{\ln(C_{in}/C_{out})} \right) - K_s \quad (13)$$

Where C_{in} is the concentration of pollutant in inlet and C_{out} is effluent concentration and θ is empty bed residence time (EBRT) (s). A plot of $(C_{in} - C_{out})/\ln(C_{in}/C_{out})$ versus $(\theta/\ln(C_{in}/C_{out}))$ should correspond to a

straight line, and K_s and r_{max} can be determined. In Fig. 2, for instance, the plot for toluene was presented. For the other Compounds, the results were presented in Table 1.

The model parameters and biofilter characteristics were presented in Table 2 and 3 respectively.

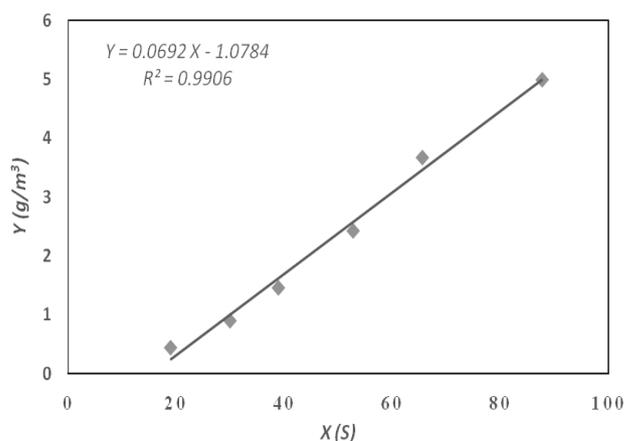


Figure 2. Plot of $(C_{in} - C_{out})/\ln(C_{in}/C_{out})$ vs. $(\theta/\ln(C_{in}/C_{out}))$ for toluene.

Table 1. Biodegradation kinetics parameters for n-Butyl Acetate, p-Xylene, MPK, Toluene.

Compound	Equation	Ks (g/m3)	rmax (g/m3.s)	R2
n-Butyl Acetate	Y=0.12X-0.593	0.593	0.120	0.97
p-Xylene	Y=0.055X-0.678	0.678	0.055	0.96
MPK	Y=0.091X - 0.512	0.512	0.091	0.97
Toluene	Y=0.069X-1.07	1.070	0.069	0.99

Table 2. Model parameters value for simulating [15, 21].

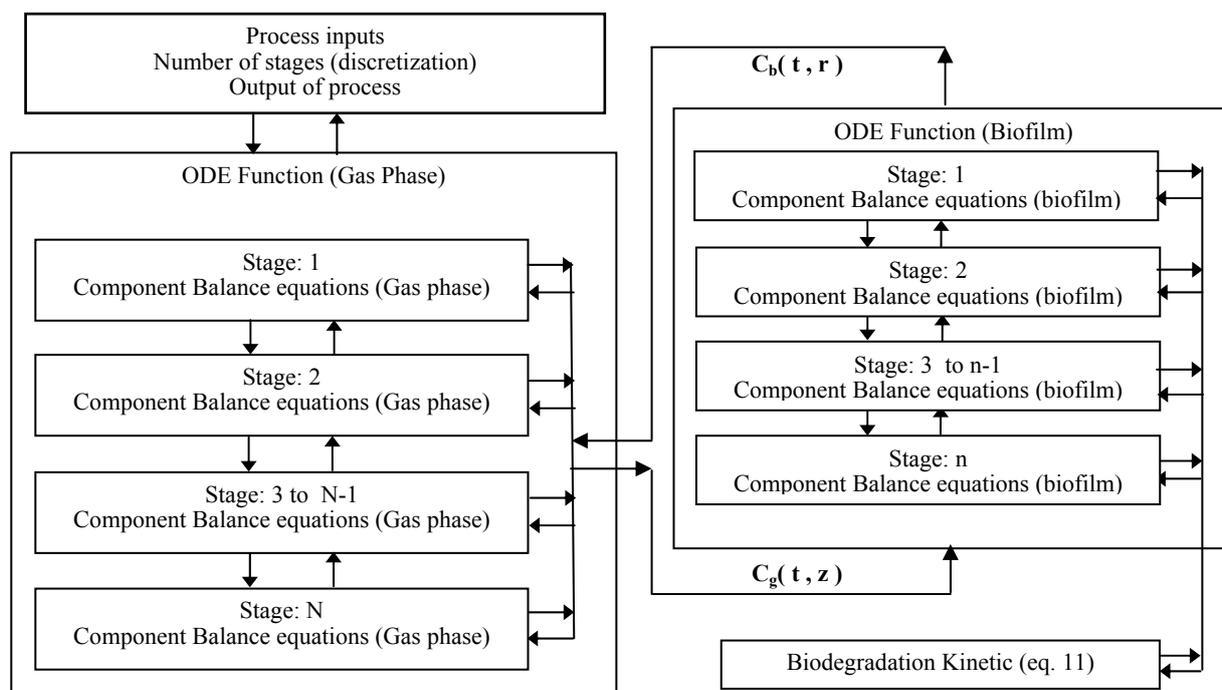
Component	D_g (m²/sec)	D_b (m²/sec)	h (atm/mol. m³)	C_{in} (g/m³)
n-Butyl acetate	7.3×10^{-6}	8×10^{-10}	2.57×10^{-4}	0.1
Toluene	8.7×10^{-6}	8.5×10^{-10}	6.35×10^{-3}	0.081
p-Xylene	7.7×10^{-6}	8.4×10^{-10}	5.15×10^{-3}	0.084
Methyl propyl ketone	9.25×10^{-6}	8.2×10^{-10}	7.29×10^{-5}	0.417

Table 3. Physical characteristics of biofilter [15].

Parameter	value
$A_s(m^2/m^3)$	340
$\theta(s)$	30, 60, 90
$V(m^3)$	0.014
$A(m^3)$	0.031
$\delta(m)$	13e-5
$Q(lit/min)$	13.2, 19.8, 29.7
ε	0.65
$H(m)$	1

6. Numerical solution

The model equations including a set of partial differential equations of gas phase and biofilm were discretized in space along the bed height and biofilm thickness, respectively. The resulting sets of ordinary differential equations were solved using MATLAB in a home-made modeling environment using finite difference and method of lines. The algorithm of equations solution was presented in Fig. 3.

**Figure 3.** the algorithm of gas phase and biofilm equations solution.

7. Model validating

The simulation results were compared with experimental data for each of the VOCs [15]. In Figs 4 to 6, the predicted profiles of pollutants concentrations for 3 EBRTs of 90, 60, and 30 seconds were presented. Also, in order to better understand what happened in biofilter, in Figs. 7 and 8, toluene and p-xylene concentration at EBRT 60 sec was presented along the biofilter height and during time. The results showed that the model had good agreement with experimental data for MPK and n-butyl acetate whereas for p-xylene and toluene the model results deviated slightly from experimental data in shorter contact times of pollutants and bed. The figures showed that the model has better prediction of concentration profile for the longest EBRTs. Although for n-Butyl acetate, the results showed that for all of the EBRTs, the experimental data agreed with the model prediction completely.

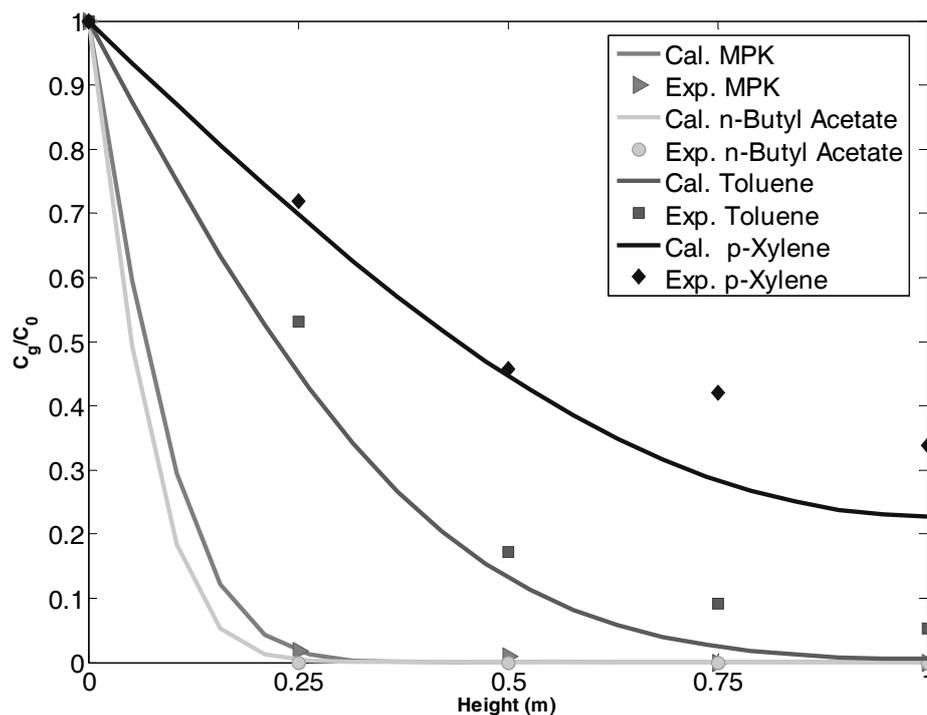


Figure 4. pollutants concentrations profiles along the biofilter height for EBRT 90 s.

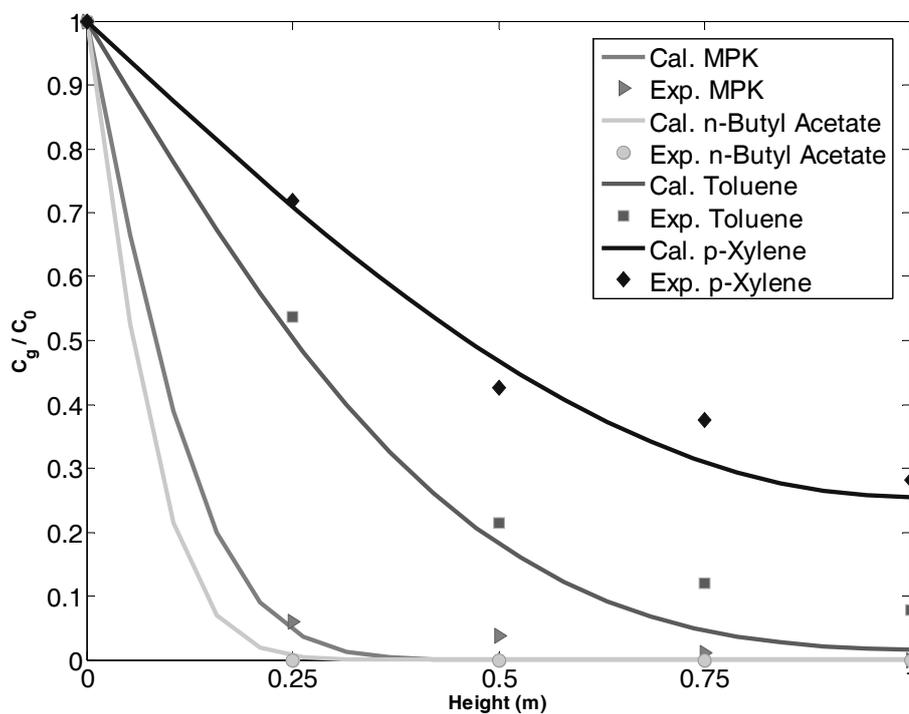


Figure 5. pollutants concentrations profiles along the biofilter height for EBRT 60 s.

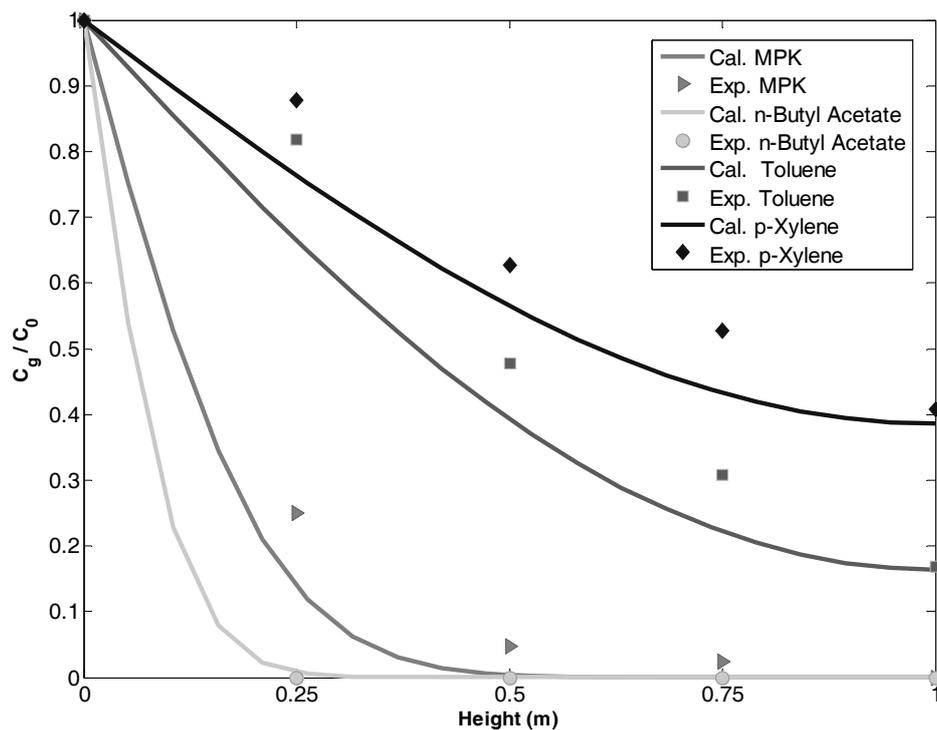


Figure 6. pollutants concentrations profiles along the biofilter height for EBRT 30 s.

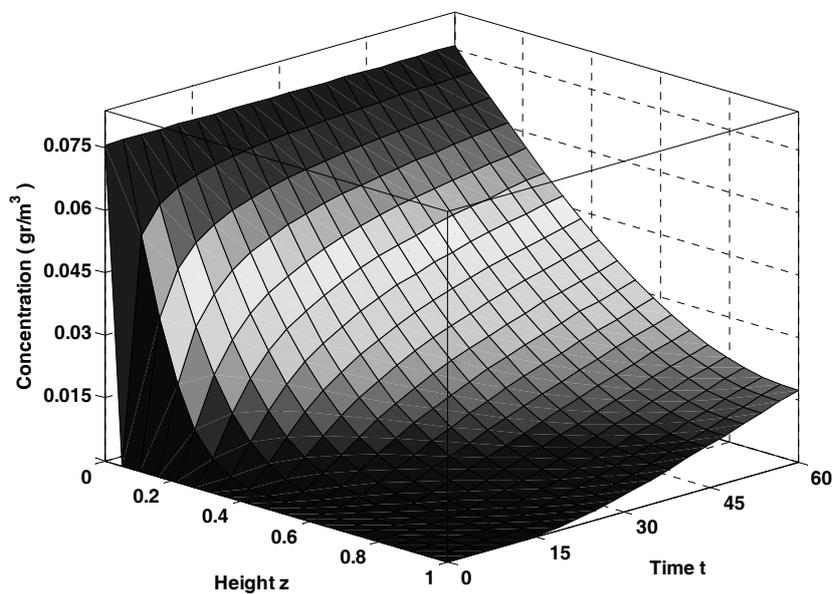


Figure 7. Toluene concentrations along the biofilter height and time.

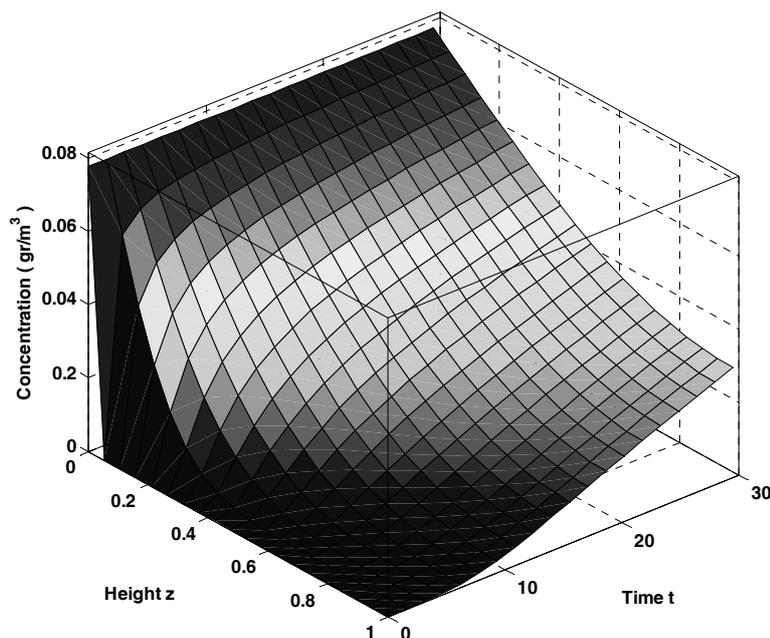


Figure 8. P-xylene concentrations along the biofilter height and time.

8. Sensitivity analysis of model parameters

A sensitivity analysis of the model parameters was performed in order to determine their influence on the model predictions (Table 4). Sensitivity was assessed by increasing and decreasing 10% the values of the parameters in Tables 2 and 3 (the default parameters), and comparing the relative change of the state variables to a relative change of the value of the parameter according to the following expression:

$$\text{Sensitivity} = \frac{\Delta\omega / \omega_d}{|\Delta P / P_d|} \quad (14)$$

Where $\Delta\omega$ is the difference between the simulated variable under the new conditions

and the value of the variable in the default conditions (ω_d). Similarly ΔP means the difference between the value of the parameter at the $\pm 10\%$ change and the value of the default parameter (P_d) [22]. Table 4 shows that the model predictions are strongly dependent on specific surface area and Henry's constant. Table 4 also shows that r_{max} has a relatively effective role on model prediction. Similar results have also been obtained by the other researchers [22-23].

The model result was compared with the results of previous models. The comparison result was presented in Table 5. It shows that the presented model has good predictivity to compare with previous models.

Table 4. Sensitivity analysis for the main parameters of the model.

Parameter	Default Value	$\Delta\%$	Changed Value	C_{out}	Sensitivity of C_{out}
A_s	340	+10	347	0.0124	-1.65
		-10	306	0.0156	+2.16
ε	0.65	+10	0.715	0.0129	0.0
		-10	0.585	0.0129	0.0
δ	130	+10	143	0.0136	+0.52
		-10	117	0.0123	-0.42
K_s	1.07	+10	1.177	0.0130	0.10
		-10	0.963	0.0127	-0.11
r_{max}	0.069	+10	0.0759	0.0119	-0.70
		-10	0.0621	0.0139	+0.78
h	6.35×10^{-3}	+10	6.98×10^{-3}	0.0147	1.40
		-10	5.72×10^{-3}	0.0110	-1.48

Table 5. Comparison of present work with other works.

Authors	Steady/ Unsteady Model	Degradation Kinetic	Model Sensitive Parameters	Pollutant	AARE%
Spigno et. al.[25]	Steady	Monod	r_{max}, h	Phenol	18
Liao et. al.[27]	Steady	Haladene-type	A_s	Toluene	16
Dorado et. al.[26]	Unsteady	Monod	A_s, h	Toluene	23
Alvarez et. al.[9]	Unsteady	Haladene-type	ε, Y	Ethyl acetate	10
				Toluene	21
Lu et. al.[23]	Steady	Monod	$A_s, Y, EBRT$	Butyl acetate	14
Baquerizo et. al.[22]	Unsteady	Haladene-type	A_s, δ, Y	Ammonia	20
Present work	Unsteady	Monod	A_s, h, r_{max}	Xylene	11
				Toluene	12
				MPK	4
				nBA	2

9. Conclusions

In this work, a dynamic model was developed for prediction of biofilter performance. The model simulation has been proven suitable in describing the gas concentration profiles within the bed for the biofiltration of methyl propyl ketone, toluene, p-xylene and n-butyl acetate as a mixture over different EBRTs conditions. The main differences between the

experimental data and the model predictions occurred when short contact times were applied, indicating the necessity of including the representation of the distribution of the active biomass density in the biofiltration modeling. The important parameters were evaluated by sensitivity analysis to determine their respective effects on model performance. It was found that Henry's constant and specific surface area had more

influence on the performance of biofilter versus other parameters. The complete degradation of MPK and n-butyl acetate in lower height of biofilter occurred because of having more solubility in water. This result also was obtained in sensitivity test, in which henry's constant has strong influence on degradation.

Nomenclature

A_s	$[m^2/m^3]$	Specific surface area
ε	[—]	Bed porosity
δ	$[m]$	Biofilm thickness
K_s	$[g/m^3]$	Half-saturation constant
r_{max}	$[g/m^3S]$	Maximum rate of degradation
h	$[atm/mol.m^3]$	Henry's constant
H	$[m]$	Bio filter height
Q	$[m^3/s]$	Flow of gas phase
A	$[m^2]$	Cross section area of bio filter
V	$[m^3]$	Volume of bio filter
θ	$[s]$	Empty bed residence time (EBRT)
D_g	$[m^2/s]$	Diffusion coefficient of pollutant in gas phase
D_b	$[m^2/s]$	Diffusion coefficient of pollutant in biomass
C_{in}	$[g/m^3]$	Concentration of pollutant in input
C_{out}	$[g/m^3]$	Concentration of pollutant in effluent
C_b	$[g/m^3]$	Concentration of pollutant in biomass
C_g	$[g/m^3]$	Concentration of pollutant in bio filter
N	$[g/m^3S]$	Specific mass flux
x	$[m]$	Position in the biofilm
Z	$[m]$	Axial direction
v_z	$[m/S]$	Interstitial gas velocity
Y	$[g/g\ biomass]$	Microbial yield coefficient

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