ELSEVIER

Chemical Engineering Journal 140 (2008) 52–61

Chemical Engineering Journal

www.elsevier.com/locate/cej

# Modeling of a bacterial and fungal biofilter applied to toluene abatement: Kinetic parameters estimation and model validation

Antoni David Dorado [a], Guillermo Baquerizo [a], Juan Pedro Maestre [b], Xavier Gamisans [a,*], David Gabriel [b], Javier Lafuente [b]

[a] *Department of Mining Engineering and Natural Resources, Universitat Politècnica de Catalunya, Bases de Manresa 61-73, 08240 Manresa, Spain*
[b] *Department of Chemical Engineering, Universitat Autònoma de Barcelona, ETSE, 08193 Bellaterra, Barcelona, Spain*

Received 15 March 2007; received in revised form 4 September 2007; accepted 5 September 2007

**Abstract**

Biofiltration has been established as a promising alternative to conventional air pollution control technologies. However, gas biofilters modeling has been less developed than experimental research due to the complexity of describing the fundamental processes and the lack of globally accepted physical, chemical and biological parameters. In addition, biofiltration modeling based on degradation activity of fungi has been rarely considered. For this reason, in this work, a dynamic model describing toluene abatement by a bacterial and fungal biofilter is developed, calibrated and validated. The mathematical model is based on detailed mass balances which include the main processes involved in the system: convection, absorption, diffusion and biodegradation. The model was calibrated and validated using experimental data obtained from two equal lab-scale biofilters packed with coconut fiber and pine leaves, respectively. Both reactors were operated under similar conditions during 100 days at an empty bed residence time of 60 s and an average inlet load of 77 g toluene $m^{-3}$ $h^{-1}$. Biofilters were initially inoculated with a bacterial consortium, even though reactors were mostly colonized by fungi after 60 days of operation according to microscopic observation and reactors pH. Removal efficiency increased notably from 20% for the bacterial period to 80% for the fully developed fungal biofilters. Since kinetic parameters are strongly dependent on the biological population, semi-saturation constants for toluene and maximum growth rates were determined for bacterial and fungal operation periods. Kinetic parameters were fitted by means of an optimization routine using either outlet concentrations or removal efficiency data from the coconut fiber biofilter. A novel procedure in gas biofilters modeling was considered for checking the model calibration, by the assessment of the parameters confidence interval based on the Fisher Information Matrix (FIM). Kinetic parameters estimated in the coconut fiber reactor were validated in the pine leaves biofilter for bacterial and fungal operation. Adequate model fitting to the experimental outlet gas concentration for both bacterial and fungal operation periods was verified by using a standard statistical test.


*Keywords:* Kinetic parameters estimation; Modeling; Toluene abatement; Fungal biofilters; Confidence interval; Fisher information matrix

## 1. Introduction

Traditionally physical and chemical processes have been applied to treat polluted air emissions. However, the high costs of operation and energy consumption associated to conventional treatments have lead to increase the attention on biological processes. During the last years biofiltration has emerged as an efficient and reliable biological process to treat 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, amongst others [1–4].

In general, a biofilter consists in a reactor packed with a carrier material (organic or inorganic) serving as a support for biofilm growth. The contaminated air stream to be treated is passed through the fixed-bed and the pollutant is transferred from the gas to the biofilm by absorption. In the biofilm, diffusion and biodegradation take place simultaneously. Thus, biofiltration employs the metabolic activity of microorganisms to degrade pollutants which are the energy source for microbial growth. Bacteria and fungi are definitely the two dominant microorganisms in biofilters but depending on the biofilter operation microorganisms may develop according to their capacities to adapt to the biofilters ecosystem [5]. Bacteria normally present a

* Corresponding author.
*E-mail address:* xavierg@emrn.upc.edu (X. Gamisans).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.09.004

rapid substrate uptake and growth. Under favourable conditions bacteria will be the dominant consortia, even though fungi may be also present. On the other hand, fungi generally grow slower than bacteria, but they are capable of degrading a broad variety of pollutant and can withstand with more adverse conditions [6,7].

High moisture content in the biofilter must be kept in order to maintain biodegradation activity. Usually, the moisture content in the biofilter is achieved by humidifying the air stream before entering the reactor and/or sprinkling water from the top of the biofilter periodically. Additionally, watering is employed to remove the excess of biomass and to avoid clogging episodes and toxics accumulation within the reactor [8,9]. Generally, micronutrients are supplied during watering periods to support microbial activity.

Toluene abatement by biofiltration has been widely investigated using biofilters inoculated with bacterial consortia [10,11]. Several packing materials and operating conditions have been employed to study toluene removal performance. Recently, biofiltration based on the degradation activity of fungi has been satisfactorily applied to treat both slight and considerable hydrophobic compounds such as toluene, hexane and α-pinene [5,12–15].

In the case of toluene, results have demonstrated that fungal biofilters are capable of obtaining higher elimination capacities than biofilters based on bacterial activity. Weber and Hartmans [16] reported a larger elimination capacity (EC) in a biofilter inoculated with fungi ($45\,g\,m^{-3}\,h^{-1}$) instead of one inoculated with bacteria ($28\,g\,m^{-3}\,h^{-1}$). Likewise Maestre et al. [12] studied the performance of four organic packing materials in biofilters inoculated with activated sludge from an urban wastewater treatment plant. An enhancement of removal efficiencies (RE > 80%) and EC up to $95\,g\,m^{-3}\,h^{-1}$ were obtained when biofilters evolved from neutral to acidic pH (i.e. when the consortium in the packed bed switched to fungi). In their experiments, García-Peña et al. [5] and Woertz et al. [17] obtained removal efficiencies up to 95% with maximum toluene elimination capacities in the range of 258–270 $g\,m^{-3}\,h^{-1}$ which is 2–7 times greater than the elimination capacities typically reported for bacterial-based biofilters.

Several hypotheses have been provided to explain the superior performance of fungal biofilters in comparison to biofilters based on bacterial activity. It has been reported that bacterial biofilter stability is often hindered by the poor absorption of pollutants on the biofilm besides acidification and drying out of the filter bed [7]. Fungal population presents several advantages due to their ability to tolerate acidic and dryer conditions than bacteria [18–20]. Additionally, it has been hypothesized that aerial mycelia of fungi can take up pollutants faster than flat, aqueous biofilm surfaces in the case of hydrophobic compounds [7,15,21]. Also, it has been recently suggested that a greater affinity of hydrophobic pollutants (i.e. air/biofilm partition coefficient) is encountered in fungal biomass rather than bacterial biofilms [21,22]. As a drawback, releasing of spores to the environment may occur in cases of severe drying.

Some of the main purposes of modeling are to organize experimental data, to understand simple relationships between parameters and pollutant removal, to design equipments according to a specific operation, to predict the performance under given conditions and to perform processes optimization [4]. In any case, biofiltration modeling has received less attention in comparison to experimental approaches. Numerous studies dealing with mathematical models of toluene removal by biofiltration can be found in literature. Simple and complex models have been employed to emulate toluene biofiltration under both steady-state and dynamic operating conditions [23–29]. In all modeling works reported in the literature toluene removal in biofilters is based on bacterial degradation activity without taking into account fungal operation.

In addition, kinetic parameters (i.e. yield coefficient or biomass concentration) are frequently taken from the literature in which experimental conditions may be considerably different and the results may vary significantly. Although direct experimental determination of kinetic parameter is not a trivial task due to the difficulty to reproduce an experimental system, it must be stressed the necessity to calibrate each model for each specific experimental conditions instead of using values of parameters reported in previous works. Only a reduced number of studies have dealt with direct calculation of kinetic parameters from experimental data by using complex determination routines [30,31], even though the results obtained were close to those obtained by curve fitting experimental data using classical optimization routines. On the other hand, in biofiltration, unlike water treatment, the interval of confidence in the model parameters estimation has not been commonly assessed, even though it should be as important as the estimation of the parameter values themselves [32].

The aim of this work was to contribute to the general understanding on how switching populations from bacteria to fungi can be modelled in a biofilter. Taking this into consideration, in this work, a general dynamic biofiltration model applied to toluene removal is developed, calibrated and validated. Mathematical equations are based on discretized mass balances taking into account the main chemical and physical phenomena involved in the system. Previous experimental results obtained by Maestre et al. [12] in which a toluene degrading biofilter inoculated with microbial populations evolved to a fungal biofilter were used herein as input data to calibrate and validate a biofiltration model. In addition a statistical procedure is applied to check the confidence intervals of the parameters obtained during the model calibration procedure. Finally a rigorous statistical test is used in order to assess the accuracy of model predictions.

## 2. Materials and methods

Experiments were carried out using a lab-scale plant consisting of two PVC columns with an inner diameter of 8.6 cm and a height of 90 cm (Fig. 1). Reactor 1 and Reactor 2 ($R_1$ and $R_2$) were packed with coconut fiber and pine leaves, respectively, to a height of 50 cm meaning a total bed volume of 2.9 L each one. Water content was kept around 80% in $R_1$ and 70% in $R_2$, while the organic matter content prior to biofilters startup was 80% in the former and 90% in the latter.

As shown in Fig. 1, a primary air stream passed through two water columns in series in order to increase the inlet air rela-

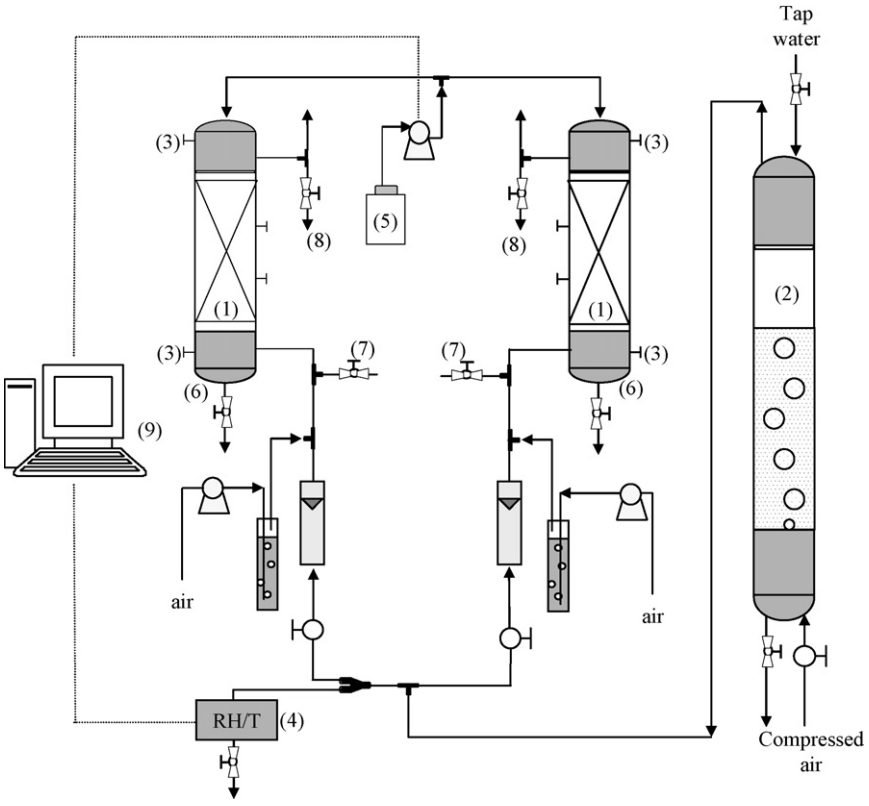


Fig. 1. Experimental setup of the lab-scale biofiltration system; (1) reactors; (2) humidification column; (3) differential pressure meter; (4) relative humidity and temperature sensor; (5) nutrient reservoir; (6) leachate collection port; (7) inlet gas sampling port; (8) outlet gas sampling port; (9) PC-PLC.

tive humidity up to 90%. A secondary air stream was pumped by a peristaltic pump (Masterflex L/S) into a glass bubbler unit of 200 ml of volume containing pure liquid toluene (Panreac 99.5%). Both gaseous flowrates were mixed in a mixing chamber and the resulting gas mixture was fed from the base of the reactor. Throughout this study, the gaseous stream was supplied in up-flow mode to obtain homogeneous humidity conditions and avoid a long residence time of secondary products in the bed [4]. The outlet gas stream was passed through an activated carbon vessel to retain any remaining pollutant. Pressure drop across the fixed-bed reactor was measured in the gas phase by means of a water-filled U-tube manometer. Also the reactors weight was periodically measured during the experimental period.

In order to keep a suitable moisture content, provide the necessary nutrients for the microorganisms and wash out dead cells and end-products of toluene degradation, tap water or a nutrient solution was automatically sprinkled daily over the biofilter beds at a flowrate of 200 mL $day^{-1}$ by means of a diaphragm dosing pump (Alldoss, Primus 221). The nutrient solution was composed by $KH_2PO_4$ (1 g $L^{-1}$), $K_2HPO_4$ (1 g $L^{-1}$), $NH_4Cl$ (1 g $L^{-1}$), NaCl (1 g $L^{-1}$), $MgSO_4$ (0.2 g $L^{-1}$), $CaCl_2$ (0.02 g $L^{-1}$) and trace elements (1 mL $L^{-1}$). Periodically the excess of solution (leachate) was manually collected at the bottom section to report measurement of the medium pH.

A structured control system with a PLC (Siemens, S7-314C-2DP) and a commercial SCADA software (Siemens, WinCC v.5.2) were used to automate the pilot-plant. The system was used for regulating the water addition and to monitor the inlet gas temperature and relative humidity (Testo, Hygrotest 600 PHT).

Gas samples were collected from sampling ports at the inlet and outlet of each reactor by means of Tedlar® bags. Toluene concentration was measured in triplicate in each port using a gas chromatograph (series 6890N GC, Agilent Technologies) equipped with a capillary column (HP-5, Agilent technologies) and a flame ionization detector (FID).

## 3. Model development

The model was built considering the most relevant phenomena occurring during the biofiltration process like convection, absorption, diffusion and biodegradation. The theoretical model describing the elimination of toluene in a biofilter bed is based on the mass balance in the gas phase and within the biofilm. Important assumptions underlying the model are based on consolidate models reported [25,27,28]:

(1) Gas phase circulation regime is modelled as plug flow pattern. Thus, axial dispersion is not considered.
(2) Gas-biofilm interface equilibrium is described by Henry's law.
(3) 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. Diffusion in the biofilm is described by Fick's law.
(4) Biofilm is formed on the external surface of the packing material. Thus, biomass does not grow in the pores of the packing material and reactions only take place in the biofilm phase.
(5) Physical properties of the species in the biofilm are assumed to be the same as in water since this is the main component.
(6) There is no accumulation of biomass in the filter bed in each period and 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. [12].
(7) Adsorption of pollutant onto the support is neglected due to the low pollutant concentration and the low adsorption capacity of the packing material. Moreover, under steady-state conditions, the adsorption process is in equilibrium [28].

### 3.1. Mass balance in the bulk gas phase

Model equation for the bulk gas phase in the dynamic state is shown in Eq. (1).

$$\frac{\partial C_g}{\partial t} = -v_z \frac{\partial C_g}{\partial z} - \frac{N_{g-b} \cdot a}{\varepsilon} \quad (1)$$

with boundary conditions:

$$\text{at } z = 0, \quad C_g = C_{gi}$$

where $C_g$ is the concentration of toluene in the gas phase in g m$^{-3}$; $v_z$ the interstitial gas velocity in m h$^{-1}$; $C_{gi}$ the inlet gas concentration in g m$^{-3}$; $z$ the position along the biofilter height in m; $N_{g-b}$ the specific mass flux from the gas to the biofilm phase for toluene in g m$^{-2}$ h$^{-1}$; $a$ the specific surface area (surface area per unit volume of bed reactor) in m$^2$ m$^{-3}$; $\varepsilon$ is the bioreactor bed porosity. Interstitial gas velocity is calculated considering the porosity of the reactor bed (Eq. (2)) and the mass flux given by Fick's law (Eq. (3)).

$$v_z = \frac{Q_g}{A \cdot \varepsilon} \quad (2)$$

$$N_{g-b} = -D \left( \frac{\partial C_b}{\partial x} \right) \Bigg|_{x=0} \quad (3)$$

where $Q_g$ is the volumetric air flow in m$^3$ h$^{-1}$; $A$ the cross-section area of the bioreactor in m$^2$; $D$ the diffusion coefficient in m$^2$ h$^{-1}$, $C_b$ the pollutant concentration in the biofilm phase in g m$^{-3}$; $x$ is the position in the biofilm from the surface in m.

### 3.2. Mass balance in the biofilm phase

Model equation for the biofilm under dynamic conditions is shown in Eq. (4).

$$\frac{\partial C_b}{\partial t} = D \frac{\partial^2 C_b}{\partial x^2} + r \quad (4)$$

with boundary conditions:

$$\begin{aligned} &\text{at } x = 0, \quad C_b = \frac{C_g}{H} \\ &\text{at } x = \delta, \quad \frac{\partial C_b}{\partial x} = 0 \end{aligned},$$

where $r$ is the substrate consumption rate in g m$^{-3}$ h$^{-1}$; $\delta$ the biofilm thickness in m; $H$ is the gas–liquid distribution coefficient given by Henry's law.

### 3.3. 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 biofilter [27,33]. Haldane-type kinetics have been also used for modeling interaction between pollutants during the biological degradation in the biofilm [34]. Currently, in most of works, the specific consumption rate for toluene degradation is described by a Monod-type kinetic expression as this work considers (Eq. (5)).

$$r = \upsilon_{max} \frac{C_b}{K_S + C_b} \quad (5)$$

where $K_S$ is the semi-saturation or affinity constant in g m$^{-3}$ and $\upsilon_{max}$ is the volumetric maximum growth rate in g m$^{-3}$ h$^{-1}$ as described in Eq. (6):

$$\upsilon_{max} = \mu_{max} \frac{X}{Y_P} \quad (6)$$

where $\mu_{max}$ is the specific growth rate in h$^{-1}$, $X$ the biomass density in g m$^{-3}$ and $Y_P$ is the biomass to substrate yield coefficient. The volumetric kinetic expression is generally used in biofilter modeling due to the difficulty to determinate the biomass density in the system with a non-destructive technique and without modifying experimental conditions. Moreover, $\mu_{max}$ and the active fraction of the degrading biomass separately are not identifiable. Consequently, there is not a unique parameter set able to describe the behaviour of the system and lumped parameters have to be estimated together [35].

In this case, oxygen limitation was not included in the kinetic expression because of the low pollutant concentration, the low biofilm thickness and the hydrophobic character of toluene. Previous simulations (results not shown) were performed to confirm that oxygen consumption was not a limiting process in the degradation of toluene. Oxygen concentration in the biofilm was superior to 5.5 g m$^{-3}$ under the maximum oxygen consumption rate. Thus, oxygen was not depleted in the whole biofilm thickness and oxygen concentration was high enough to have no influence on the toluene consumption rate. Otherwise, a

Monod term including oxygen concentration should be added in a multisubstrate type kinetics.

Moreover, it must be stressed that other phenomena that affect the degradation rate such as nutrient limitation might be present in the kinetic of the model. In the present work, the effect of nutrient concentration was lumped into the volumetric maximum growth rate in the kinetic expression. Either provided by the packing material or externally fed through the watering system, nutrient concentration was considered to be constant along the height of the reactor during biofilters operation.

### 3.4. Mathematical solution

The set of partial differential equations was discretized in space along the bed height and biofilm thickness. The conversion of the tubular reactor into serial stirred reactors was checked. An optimal discretization of the biofilter was found resulting in eight nodes along the bed height and eight nodes along the biofilm thickness.

The resulting set of ordinary differential equations was solved using MATLAB in a home-made modeling environment. A variable order method was used for solving stiff differential equations based on the numerical differentiation formulas (NDFs), which are generally more efficient than the closely related family of backward differentiation formulas (BDFs), also known as Gear's methods. The time step used in the numerical solution routine was established in 1 h, which was significantly lower than the time interval of the experimental data (i.e. normally higher than 24 h). Since the inlet toluene concentration and inlet gas flow changed along biofilters operation, a linear interpolation was considered for the time interval comprised between two consecutive inlet data.

### 3.5. Model calibration and validation

In the model calibration step, the volumetric maximum growth rate and the saturation constant were the set of parameters to estimate. To start with the procedure, initial guesses were assigned to kinetic parameters according to the literature. Predicted outlet concentrations by the model were compared with the experimentally measured data and the deviations between both were used to obtain updates for kinetic parameters. The values of parameters were sought to minimize the objective function (OF) given in Eq. (7) for each period simulated.

$$\mathrm{OF} = \sqrt{\sum_{i=1}^{N} [C_{\mathrm{g,out}}(p_1, p_2) - C^*_{\mathrm{g,out}}]^2} \tag{7}$$

where $C_{\mathrm{g,out}}$ is the outlet concentration of toluene in gas phase predicted by the model in $\mathrm{g\,m^{-3}}$, $p_1$ and $p_2$ the unknown parameters to fit, $C^*_{\mathrm{g,out}}$ the outlet concentration of toluene experimentally measured in gas phase in $\mathrm{g\,m^{-3}}$, and $N$ is the total number of data sets.

The parameter estimation was performed using a MATLAB algorithm based on a multidimensional unconstrained nonlinear minimization (Nelder–Mead). This is a direct search method that does not use numerical or analytical gradients.

Regarding confidence intervals of estimated parameters, these were assessed through a numerical method based on the Fisher Information Matrix (FIM) [36,37]. The FIM matrix is related to the quantity and quality of information obtained from experiments and considers the sensitivity of optimized parameters and the measurement errors of the experimental data. Assuming white measurement noise and no model mismatch, the inverse of the FIM provides the lower bound of the parameter estimation covariance matrix, which can be used for assessing the estimation uncertainty of the parameters. Moreover, since output sensitivities of parameters are calculated using a model, the FIM also depends on the structure of the model. This property has widely been used to study the practical identifiability of the models under the available experimental data in the field of wastewater treatment [37] but previous works have not been found in gaseous pollutant modeling. Model validation of the present work was checked by performing a statistic analysis based on a paired *t*-Student's test at 5% level of significance.

## 4. Results and discussion

### 4.1. Experimental conditions

The calibration and validation of the developed dynamic model was carried out using part of the experimental data of the previous work of Maestre et al. [12], in which performance of four organic packed biofilters was studied under different operation conditions in a period of 240 days. The suitability of the different packing materials was compared for the treatment of toluene. In the work presented herein, the first 100 days of operation of two out of the four biofilters were chosen for modeling purposes. In this period, reactors were operated at an average inlet load of 77 g toluene $\mathrm{m^{-3}\,h^{-1}}$ and at an EBRT of 60 s.

Reactors were initially inoculated with activated sludge from a municipal wastewater treatment plant and operated during the first 50 days as bacterial biofilters. After 50 days of operation the pH dropped at values as low as 3 and fungal activity was detected proving that both biofilters evolved from bacteria to fungal reactors [13]. It is hypothesized that the pH decrease is related to the production of acidic by-products such as benzoic acid, which arise from toluene degradation [38]. Simultaneously, a notable increment of removal efficiency (RE) from around 20% to 80% was observed along the operation time in both biofilters (Fig. 2), which was related to an increment on the amount of nutrients provided after day 44.

Three different operation periods were identified and used for modeling purposes. In each selected period a pseudo steady-state operation was experimentally verified. Thus, pseudo steady-state conditions were assumed for biomass accumulation in each period to perform parameter determination and further model validation. In the first period (from day 22 to 38), namely *Period A*, a watering rate of 200 mL $\mathrm{day^{-1}}$ of tap water was supplied. Thus, watering was only used in order to keep suitable moisture in the system. During *Period A*, the pH in the collected leachate was near the neutrality for both reactors. No fungal colonies were

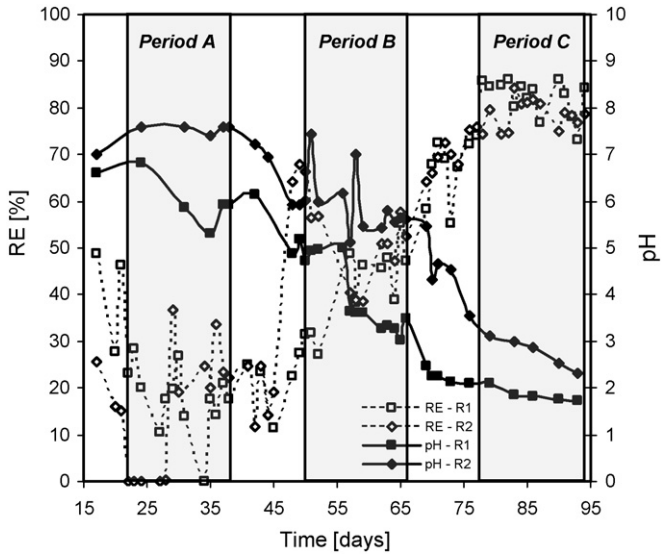


Fig. 2. pH and removal efficiency profiles for coconut fiber ($R_1$) and pine leaves ($R_2$) biofilters.

observed during *Period A*. In the second period (from day 50 to 66), namely *Period B*, 200 mL $day^{-1}$ of a nutrient solution were supplied in excess due to the low removal efficiency achieved in *Period A*. A transition from bacterial to fungal reactor was identified in both reactors by microscopic observation, which correlated well with the decrease in the pH observed in both reactors (Fig. 2). A third and last period (from day 78 to 94), namely *Period C*, was mainly carried out by fungal consortia according to microscopic observations. In a previous work, two fungal genus were isolated and recognised as *Aureobasidium* sp. and *Clonostachys* sp. [12]. The pH measured in the leachate was below 3 in *Period C*, which hindered the presence of other kind of microorganisms in the medium. The watering rate and nutrient supply was kept for both reactors with the purpose of ensuring an excess of nutrients.

### 4.2. Kinetic parameter determination

Since both reactors were operated under identical loading and EBRT conditions, kinetic parameters may be determined using experimental data from either reactor $R_1$ or $R_2$. Thus, kinetic parameters were calculated using experimental data from reactor $R_1$ (coconut fiber) for each periods A, B and C. Therefore, a set of volumetric maximum growth rate ($\upsilon_{max}$) and half-saturation constant ($K_S$) was assessed for each period (Table 1). For bacterial operation (*Period A*), a $\upsilon_{max}$ of $815 \pm 290$ g toluene $m^{-3}$ $h^{-1}$ was obtained and a value of $5.01 \pm 2.95$ g $m^{-3}$ was determined for $K_S$. Results were in accordance with values found in the literature [28,29].

Table 1
Kinetic parameters for each operation period

| Parameter | *Period A* | *Period B* | *Period C* |
|---|---|---|---|
| $\upsilon_{max}$ | 815 ± 290 | 810 ± 38 | 5000 ± 230 |
| $K_S$ | 5.01 ± 2.95 | 0.16 ± 0.09 | 0.21 ± 0.04 |

For fungal operation (*Period C*), a $\upsilon_{max}$ of $5000 \pm 230$ g toluene $m^{-3}$ $h^{-1}$ was found, indicating that fungal operation presents a significant better capacity to biodegrade toluene than bacteria. Thus, a higher $\upsilon_{max}$ is in part due to the increment on nutrients concentration that caused an increase in the biomass concentration, parameter that is lumped into the $\upsilon_{max}$. In the same way, low values of $K_S$, $0.21 \pm 0.04$ g $m^{-3}$ were calculated for *Period C*, demonstrating a higher affinity between the studied pollutant and fungi than between the pollutant and bacteria. Previous works comparing kinetic parameters between fungi and bacteria have not been found in the literature.

In the period of transition (*Period B*), the first sign of change in the behaviour of the system was observed. The volumetric maximum growth rate obtained by optimization was similar to that of *Period A* but the saturation constant decreased until $0.16 \pm 0.09$ g $m^{-3}$. Though there was not a dominant population in the biofilter, a higher presence of fungi was detected in the bioreactor. Thus, estimation of kinetic parameters in *Period B* let to follow the evolution from bacterial to fungal operation by means of an increase in the affinity between toluene and the microbial population. In comparison to this period of transition, a better degradation capacity was obtained in *Period C*, according to the $\upsilon_{max}$ estimated.

Outlet toluene concentration was accurately fit to experimental data (Fig. 3) through the evaluation of the objective function (Eq. (7)). *Period C* needed a superior number of iterations (data not shown) to search the minimum of the function due to a higher number of experimental data.

It should be emphasized that the effects of potential changes in some parameters are lumped in the estimated kinetic parameters. Owing to the system restrictions (only gas phase is measured), the separate determination of additional parameter in both bacterial and fungal operating periods could not be conducted. In order to include the potential variation of the specific area, determination of this parameter in reactor 2 was performed in the stage B where the evolution from bacteria to fungi was confirmed.

A sensitivity analysis of model parameters was performed in order to determine their influence on model predictions (Table 2). This analysis revealed that the specific surface area and the Henry coefficient are the most sensible parameters in the model. Comparison of physicochemical parameters in bacterial and fungal consortia applied to biofiltration has been only conducted for the partition coefficient [22]. They found that the partition coefficient (i.e. gas/biofilm) for a fungal biofilm was about 50 times lower than that for a bacterial biofilm for an extremely hydrophobic compound. Although potential variations in physicochemical parameters may lead to improve the removal capacity of the reactors, an additional simulation was performed for the fungal period (*Period C*) to demonstrate that enhancement of the removal capacity is mainly due to the modification of the microorganisms consortia in the reactors (Fig. 4). Simulation results show that model predictions could not match experimental data by using the same kinetic parameters found for the bacterial period and different, lower values of the partition coefficient. *H* values ranging from 1 to 100 were used for

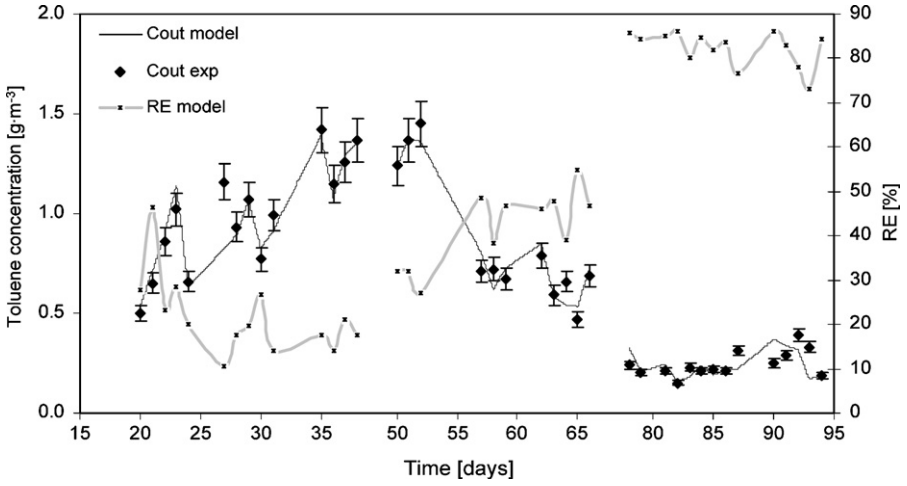


Fig. 3. Experimental data and model calibration for Reactor 1.

Table 2
Sensitivity analysis for the main parameters of the model

| Parameter | Value | $\Delta$ | Value | $C_{out}$ | Sensitivity of $C_{out}$ |
|---|---|---|---|---|---|
| $H$ | 0.263 | 10% | 0.2893 | 0.2290 | 1.45 |
| | | −10% | 0.2367 | 0.1697 | 1.51 |
| $\upsilon_{max}$ | 5000 | 10% | 5500 | 0.1846 | −0.77 |
| | | −10% | 4500 | 0.2181 | −0.91 |
| $K_S$ | 0.21 | 10% | 0.2310 | 0.2043 | 0.22 |
| | | −10% | 0.1890 | 0.1953 | 0.23 |
| $\varepsilon$ | 0.85 | 10% | 0.935 | 0.1999 | 0.00 |
| | | −10% | 0.765 | 0.1999 | 0.00 |
| $\delta$ | 130 | 10% | 143.0 | 0.2085 | 0.43 |
| | | −10% | 117.0 | 0.1914 | 0.43 |
| $a$ | 360 | 10% | 396.0 | 0.1621 | −1.89 |
| | | −10% | 324.0 | 0.2462 | −2.31 |

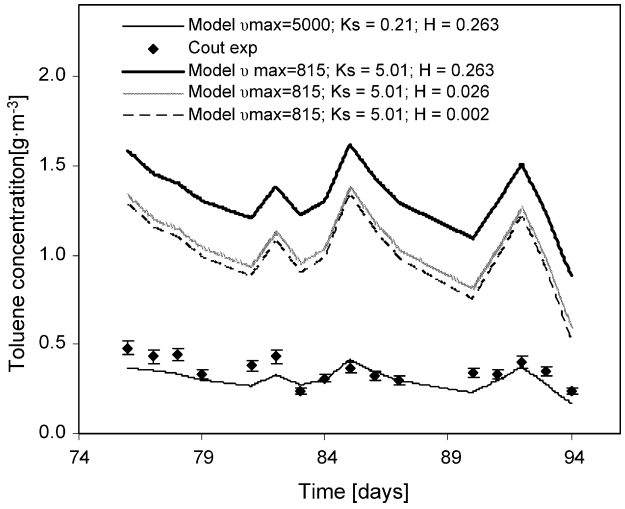


Fig. 4. Influence of coefficient Henry in the calibration of the model for fungal period.

the gas/water and gas/biofilm ratios. Results demonstrated that the enhancement of the degradation capacity of the biofilters is mainly related to the colonization of the filter bed by a fungal consortium.

The large confidence intervals assessed through the FIM method in all periods were in great part due to the low quantity of experimental data measured in the whole operation time. In *Period C*, the relative errors associated to the optimized parameters were estimated around 5% for $\upsilon_{max}$ and 21% for $K_S$, according to the FIM method. In *Period A*, the estimated confidence intervals reached values up to 36% and 59% for $\upsilon_{max}$ and $K_S$, respectively. This is related to a lower sensitivity of the kinetic parameters in model predictions according to the low biological degradation achieved during the bacterial period (around 20%). Thus, the low identifiability of kinetic parameters in *Period A* clearly demonstrated that the physical behaviour of the reactor is correctly described by mass transfer equations, according to predicted concentrations in comparison to experimental data (Fig. 3). For the same reason, a similar variability of the inlet load in the whole operation period produces higher output fluctuations in *Period A* than in *Period C* (Fig. 3).

### 4.3. Model validation

Once the kinetic parameters were calibrated for $R_1$ (coconut fiber), model validation was performed by comparing the simulation results to experimental data in $R_2$ (pine leaves) for *Period A* and *Period C*, in other words, for bacterial and fungal operation. According to Baquerizo et al. [3], results predicted by the model are strongly dependent on the specific surface area available into the biofilter, which does not correspond to that of the virgin packing material once biomass has grown over its surface. In consequence, the specific surface area is the only physicochemical parameter that needs to be separately determined for both reactors. Thus, prior to the validation step, a specific surface area of 420 $m^2\ m^{-3}$ was optimized by simulation from experimental data in *Period B* for the pine leaves reactor, and further used for model validation in the rest of periods (Fig. 5).

In case of $R_1$, the specific surface area for coconut fiber for a colonized biofilter was chosen in concordance to that reported by Baquerizo et al. [3] for an almost identical biofilter. Other

Table 3
Physicochemical model parameters for $R_1$ and $R_2$

| Parameter | Symbol | Value | Units | Reference |
|---|---|---|---|---|
| Diffusion coefficient for toluene | $D$ | $3.11 \times 10^{-6}$ | $m^2\ h^{-1}$ | [24] |
| Henry coefficient for toluene | $H$ | 0.263 | – | [24] |
| Specific surface area ($R_1$/$R_2$) | $a$ | 360/420 | $m^2\ m^{-3}$ | Adapted from [3] and adjusted by simulation |
| Bed reactor porosity ($R_1$/$R_2$) | $\varepsilon$ | 0.85/0.75 | – | Experimental determination |
| Biofilm thickness | $\delta$ | 130 | μm | Adapted from [24] |

physicochemical model parameters used in the present work are shown in Table 3. Bed porosity was determined experimentally by standard methods [39].

Model predictions for *Period A* are shown in Fig. 6a illustrating a good agreement with experimental data for the bacterial period. Moreover, the almost constant removal efficiency shows the steady-state achieved in each period. In Fig. 6b, simulated results for *Period C* in the pine leaves reactor show that experimental data is properly predicted by the model, even if the model predicts lower outlet toluene concentration values in first days than those obtained experimentally. This is probably explained by the biomass transition from bacteria to fungi because some bacteria might be still present in the reactor during the first days of *Period C*. Results are more satisfactory at the end of the period indicating a pseudo biomass steady-state operation in terms of biomass populations.

A statistic analysis based on a paired *t*-Student's test was evaluated in the validation process in order to quantify the agreement between results predicted by the model with the optimized kinetic parameters and experimental data. The *t*-test executed on the outlet toluene concentration yielded an absolute value of 0.93 for the validation in $R_2$. A *t*-value of 2.04 at 5% level of significance for 30 degrees of freedom [40] indicates that the difference between outlet toluene concentration measured experimentally and outlet toluene concentration predicted by the model are not statistically significant in the whole operation. Thus, it could be certainty affirmed that periods were satisfactorily described by the model under both bacteria and fungal operation.

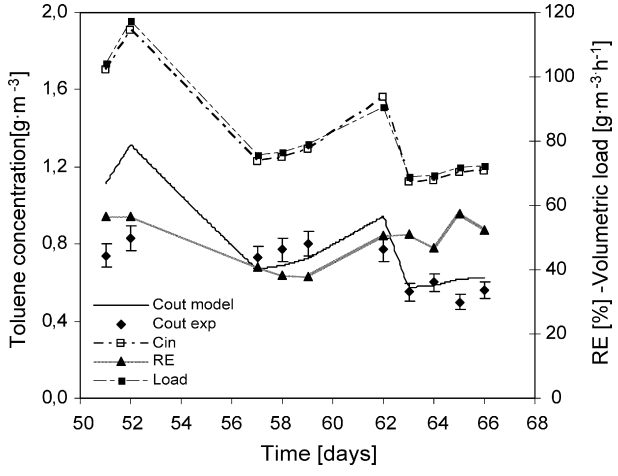


Fig. 5. Model predictions and experimental data for the specific surface area estimation in the pine leaves reactor.

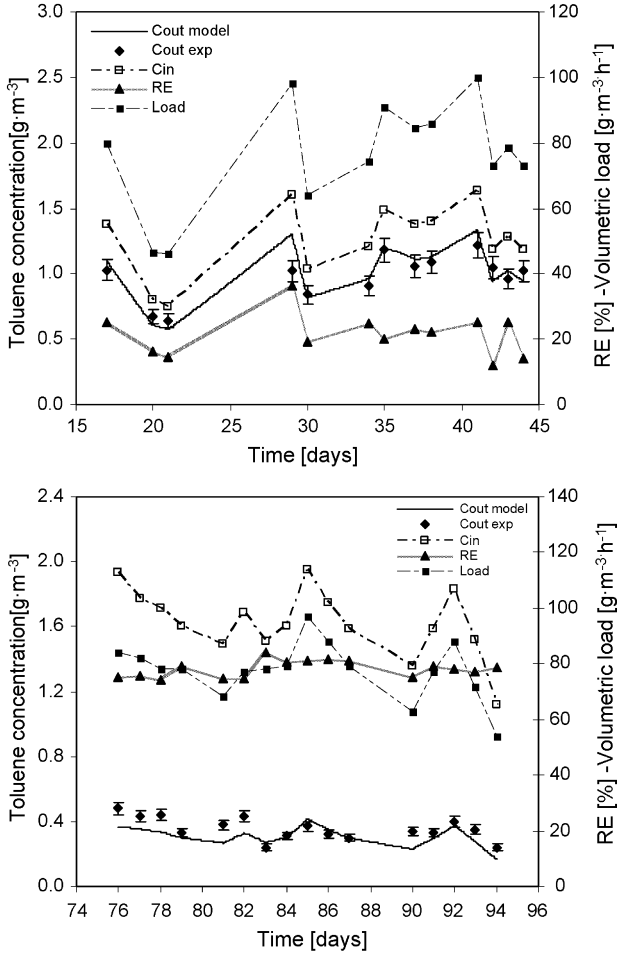


Fig. 6. Experimental data and model predictions for (a) *Period A* and (b) *Period C*.

## 5. Conclusions

A dynamic model to simulate toluene abatement by bacterial and fungal biofilters has been developed, calibrated and validated through a set of different experimental conditions for biofilters with switching populations from bacteria to fungi. The model was able to predict satisfactorily different operation periods, including bacteria, transition from bacteria to fungi, and fungi based operation be means of a small number of parameters. Results clearly demonstrate that a higher complex model is not necessary to describe properly the performance of the biofilter. However, a correct procedure in biofilter modeling force to determinate model parameters for each situation instead of taking them from literature. Moreover, the

physico-chemical model was checked by model predictions in the operation where biological degradation was not the predominant process. Otherwise, estimation of kinetic parameters corroborated the biomass evolved from bacteria to fungi in both biofilters in concordance to pH changes reported along the entire experiment and microscopic observation. Kinetic parameters confirmed that fungi provide a better capacity to degrade toluene from gas phase. Moreover, a higher affinity was observed between fungi and the pollutant in comparison to pollutant and bacteria consortium. Thus, determination of volumetric maximum growth rate and semi-saturation constant for both biofilters with their corresponding confidence interval pointed out that biofilters colonized by fungi showed a better performance than those colonized by bacteria. The model calibration was checked by a novel procedure in gas biofilters modeling based on the Fisher Information Matrix and the model validation was verified using a rigorous statistical test. Deviations on model predictions are explained by biomass modification in the bioreactors obtaining better results at the end of each period due to the pseudo biomass steady-state achieved.

## Acknowledgments

This work was supported by the Spanish CICYT project PPQ2003 - 02482. A.D. Dorado received a predoctoral fellowship from the M.E.C. (Ministerio de Educación y Ciencia, Spain). The discussion with Dr. Juan Antonio Baeza Labat from the Department of Chemical Engineering at UAB and Dr. Josep M. Rossell Garriga from the Department of Applied Mathematics at UPC are gratefully acknowledged.

## References

[1] J.W. van Groenestijn, N.J.R. Kraakman, Recent developments in biological waste gas purification in Europe, Chem. Eng. J. 113 (2–3) (2005) 85–91.
[2] M.C. Delhomenie, M. Heitz, Biofiltration of air: a review, Crit. Rev. Biotechnol. 25 (1–2) (2005) 53–72.
[3] G. Baquerizo, J.P. Maestre, T. Sakuma, M.A. Deshusses, X. Gamisans, D. Gabriel, J. Lafuente, A detailed model of a biofilter for ammonia removal: model parameters analysis and model validation, Chem. Eng. J. 113 (2–3) (2005) 205–214.
[4] J.S. Devinny, M.A. Deshusses, T.S. Webster, Biofiltration for Air Pollution Control, vol. 1, Lewis Publishers, New York, 1999, pp. 299.
[5] E.I. García-Peña, S. Hernández, E. Favela-Torres, R. Auria, S. Revah, Toluene biofiltration by the fungus Scedosporium apiospermum TB1, Biotechnol. Bioeng. 76 (1) (2001) 61–69.
[6] H.H.J. Cox, R.E. Moerman, S. vanBaalen, W.N.M. vanHeiningen, H.J. Doddema, W. Harder, Performance of a styrene-degrading biofilter containing the yeast Exophiala jeanselmei, Biotechnol. Bioeng. 53 (3) (1997) 259–266.
[7] J.W. van Groenestijn, W.N.M. van Heiningen, N.J.R. Kraakman, Biofilters based on the action of fungi, Water Sci. Technol. 44 (9) (2001) 227–232.
[8] J. Nikiema, L. Bibeau, J. Lavoie, R. Brzezinski, J. Vigneux, M. Heitz, Biofiltration of methane: an experimental study, Chem. Eng. J. 113 (2–3) (2005) 111–117.
[9] M.C. Delhomenie, L. Bibeau, J. Gendron, R. Brzezinski, M. Heitz, A study of clogging in a biofilter treating toluene vapors, Chem. Eng. J. 94 (3) (2003) 211–222.
[10] M.E. Acuña, F. Pérez, R. Auria, S. Revah, Microbiological and kinetic aspects of a biofilter for the removal of toluene from waste gases, Biotechnol. Bioeng. 63 (2) (1999) 175–184.
[11] Y. Matteau, B. Ramsay, Active compost biofiltration of toluene, Biodegradation 8 (3) (1997) 135–141.
[12] J.P. Maestre, X. Gamisans, D. Gabriel, J. Lafuente, Fungal biofilters for toluene biofiltration: evaluation of the performance with four packing materials under different operating conditions, Chemosphere 67 (2007) 684–692.
[13] A. Aizpuru, B. Dunat, P. Christen, R. Auria, I. García-Peña, S. Revah, Fungal biofiltration of toluene on ceramic rings, J. Environ. Eng. 131 (3) (2005) 396–402.
[14] G. Spigno, C. Pagella, M.D. Fumi, R. Molteni, D.M. De Faveri, VOCs removal from waste gases: gas-phase bioreactor for the abatement of hexane by Aspergillus niger, Chem. Eng. Sci. 58 (3–6) (2003) 739–746.
[15] J.W. van Groenestijn, J.X. Liu, Removal of alpha-pinene from gases using biofilters containing fungi, Atmos. Environ. 36 (35) (2002) 5501–5508.
[16] F.J. Weber, S. Hartmans, Prevention of clogging in a biological trickle-bed reactor removing toluene from contaminated air, Biotechnol. Bioeng. 50 (1) (1996) 91–97.
[17] J.R. Woertz, K.A. Kinney, N.D.P. McIntosh, P.J. Szaniszlo, Removal of toluene in a vapor-phase bioreactor containing a strain of the dimorphic black yeast Exophiala lecanii-corni, Biotechnol. Bioeng. 75 (5) (2001) 550–558.
[18] N. Nikolova, V. Nenov, BTEX degradation by fungi, Water Sci. Technol. 51 (11) (2005) 87–93.
[19] E. Estevez, M.C. Veiga, C. Kennes, Biofiltration of waste gases with the fungi Exophiala oligosperma and Paecilomyces variotii, Appl. Microbiol. Biotechnol. 67 (4) (2005) 563–568.
[20] W.M. Moe, B. Qi, Performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading, Water Res. 38 (9) (2004) 2259–2268.
[21] A. Vergara-Fernandez, B. Van Haaren, S. Revah, Phase partition of gaseous hexane and surface hydrophobicity of Fusarium solani when grown in liquid and solid media with hexanol and hexane, Biotechnol. Lett. 28 (24) (2006) 2011–2017.
[22] S. Arriaga, S. Revah, Removal of *n*-hexane by Fusarium solani with a gas-phase biofilter, J. Ind. Microbiol. 32 (11–12) (2005) 548–553.
[23] R.J. Abumaizar, E.H. Smith, W. Kocher, Analytical model of dual-media biofilter for removal of organic air pollutants, J. Environ. Eng. 123 (6) (1997) 606–614.
[24] M. Amanullah, S. Farooq, S. Viswanathan, Modeling and simulation of a biofilter, Ind. Eng. Chem. Res. 38 (7) (1999) 2765–2774.
[25] M.A. Deshusses, G. Hamer, I.J. Dunn, Behaviour of biofilters for waste air biotreatment. 1. Dynamic model development, Environ. Sci. Technol. 29 (4) (1995) 1048.
[26] A. Metris, A.M. Gerrard, R.H. Cumming, P. Weigner, J. Paca, Modelling shock loadings and starvation in the biofiltration of toluene and xylene, J. Chem. Technol. Biotechnol. 76 (6) (2001) 565–572.
[27] S. Ottengraf, H.C. Van der Oever, Kinetics of organic compunds removal from waste gases with a biological filter, Biotechnol. Bioeng. 25 (1983) 3089–3102.
[28] Z. Shareefdeen, B.C. Baltzis, Biofiltration of toluene vapor under steady-state and transient conditions: theory and experimental results, Chem. Eng. Sci. 49 (24A) (1994) 4347–4360.
[29] S.M. Zarook, A.A. Shaikh, Z. Ansar, Development, experimental validation and dynamic analysis of a general transient biofilter model, Chem. Eng. Sci. 52 (5) (1997) 759–773.
[30] C. Alonso, X. Zhu, M.T. Suidan, B.R. Kim, B.J. Kim, Parameter estimation in biofilter systems, Environ. Sci. Technol. 34 (11) (2000) 2318–2323.
[31] T.R. Bhat, D. Venkataramani, V. Ravi, C.V.S. Murty, An improved differential evolution method for efficient parameter estimation in biofilter modeling, Biochem. Eng. J. 28 (2) (2006) 167–176.
[32] A. Guisasola, J.A. Baeza, J. Carrera, G. Sin, P.A. Vanrolleghem, J. Lafuente, The influence of experimental data quality and quantity on parameter estimation accuracy, Educ. Chem. Eng. 1 (1) (2006) 139–145.
[33] D.S. Hodge, J.S. Devinny, Modeling removal of air contaminants by biofiltration, J. Environ. Eng. 121 (1) (1995) 21–32.
[34] M. Morales, S. Hernandez, T. Cornabe, S. Revah, R. Auria, Effect of drying on biofilter performance: modeling and experimental approach, Environ. Sci. Technol. 37 (5) (2003) 985–992.

[35] M. Mohseni, D.G. Allen, Biofiltration of mixtures of hydrophilic and hydrophobic volatile organic compounds, Chem. Eng. Sci. 55 (9) (2000) 1545–1558.

[36] R.K. Mehra, Optimal input signals for parameter estimation in dynamic systems, survey and new results, IEEE Trans. Autom. Control 19 (6) (1974) 753–768.

[37] D. Dochain, P.A. Vanrolleghem, Dynamical Modeling and Estimation in Wastewater Treatment Processes, vol. 1, IWA Publishing, London, UK, 2001, p. 342.

[38] F.X. Prenafeta-Boldu, D.M.A.M. Luykx, J. Vervoort, J.A.M. Bont, Fungal metabolism of toluene: monitoring of fluorinated analogs by F-19 nuclear magnetic resonance spectroscopy, Appl. Environ. Microbiol. 67 (3) (2001) 1030–1034.

[39] P.B. Leege, W.H. Thompson, Test Methods for the Examination of Composting and Compost, vol. 1, US Composting Council, Bethesda, 1995, p. 350.

[40] W. Mendenhall, T. Sincich, Probabilidad y Estadística para Ingeniería y Ciencias, vol. 1, Prentice Hall, México, 1997, p. 739.