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Calibration of a kinetic model for wet air oxidation (WAO) of substituted phenols: Influence of experimental data on model prediction and practical identifiability

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ABSTRACT

Calibration of kinetic models of wet air oxidation (WAO) is usually performed through minimisation algorithms with respect to total organic carbon (TOC) experimental data. However, the reliability of the estimated value of the kinetic parameters is frequently not reported. Moreover, the influence of data quantity/quality in the kinetic parameters identifiability is not properly assessed. The objective of this study is to compare the calibration goodness of a proposed kinetic model when using one set of data (total effluent TOC [TOC_{eff}]) or two sets of independent experimental measurements (total effluent TOC [TOC_{eff}] and residual TOC of target pollutant [$TOC_{[A]}$]). The systematic comparison was made using identifiability analysis with contour plots of both objective functions and the confidence intervals were calculated through the Fisher information matrix (FIM). The experimental data used in this study comes from a previous one, where WAO was investigated as a suitable precursor for the biological treatment of industrial wastewater containing high concentrations of *o*-cresol or 2-chlorophenol [M.E. Suárez-Ojeda, J. Carrera, I.S. Metcalfe, J. Font, Wet air oxidation (WAO) as a precursor to biological treatment of substituted phenols: refractory nature of the WAO intermediates, Chem. Eng. J. 144 (2008) 205–212.]. The results show that the model correctly fitted the experimental [TOC_{eff}] in all cases with less than 6% as averaged relative deviation, either using one set of data ([TOC_{eff}]) or two sets of independent experimental measures ([TOC_{eff}] and [$TOC_{[A]}$]) in the objective function. However, when using only [TOC_{eff}], the model was not capable of fitting the proportion between [$TOC_{[A]}$] and intermediates TOC. The obtained E_{ACT} for the calibration made with [TOC_{eff}] and [$TOC_{[A]}$] were 71 ± 20 kJ mol^{-1} ($R^2 = 0.92$) and 47 ± 9 kJ mol^{-1} ($R^2 = 0.96$) for *o*-cresol and 2-chlorophenol, respectively. However, when using just [TOC_{eff}], the obtained E_{ACT} values were not in the range of the values reported in the literature and had smaller regression coefficients. Moreover, the calibration with just [TOC_{eff}] presented a high correlation between the obtained rate constants, whereas the calibration with [TOC_{eff}] and [$TOC_{[A]}$] was statistically more reliable. As example, the D-criterion values are three to six times larger for the calibration made with ([TOC_{eff}] and [$TOC_{[A]}$] than for the calibration made only with [TOC_{eff}], in the framework of OED/PE criteria, this is related to minimisation of the geometric mean of the identification errors.

1. Introduction

A review of past literature reveals that a large number of kinetic studies of the WAO process employed a single organic compound to simulate the wastewater. Whereas, the disappearance rate of the pure compound is useful for understanding reaction mechanisms, what is needed, for design purposes, is to predict the behaviour of all organic species present in a wastewater, regardless of whether they are originally present or formed as intermediate products. Therefore, the rate law has to be expressed by means of a lumped parameter such as total organic carbon (TOC), or chemical oxygen demand (COD). Li et al. [2] proposed a lumped generalised kinetic model (GKM) which is based on a simplified reaction scheme with acetic acid as the rate-limiting reactant, all reactions being first-order. This model paved the way for the kinetic model in WAO for different industrial wastewaters and is perhaps one of the most extensively used with reasonably good fits [3]. Also it has been the starting point for more complex models accounting for other refractory reaction intermediates different from acetic acid [4].

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However, for a reliable utilisation of the lumped kinetic model, the assessment of the confidence interval of the kinetic parameters should be as important as the estimation of the parameter values itself. Much research has been conducted in assessing the precision of the parameters of very different mathematical models estimated from experimental data [5–8]. Confidence interval assessment is not a straightforward task, since many different factors are involved such as the experimental data, the inherent structure of the model or the minimisation approach used [9–12].

In general, when employing mathematical models aiming to fit experimental data, the problem of structural and practical identifiability arises. As explained by Dochain and Vanrolleghem [6], the structural identifiability is related to the possibility of giving a unique value to each parameter of a mathematical model, whereas the practical identifiability is related to the quality of the experimental data and their content. Therefore, two questions may occur: given a model structure and perfect data (i.e. data fits perfectly to the model) of model variables, are all the parameters of the model identifiable or, are the available data informative enough for identifying the model parameters and, more specifically, for giving accurate values? For instance, in the model $y = ax_1 + bx_2$ the parameters “a” and “b” are structurally identifiable, but they will not be practically identifiable, if the experimental conditions are such that the independent variables x_1 and x_2 are always proportional ($x_1 = \alpha x_2$), the combination $a\alpha + b$ is the only one practically identifiable. The problem of practical identifiability comes up when a limited set of experimental and/or noise corrupted data is used for parameter estimation. Under these conditions, the uniqueness of parameter estimates predicted by the structural analysis may not be guaranteed, because a change in one parameter can be compensated almost completely by a proportional shift in another.

In this sense, very few studies pay attention to the identifiability of the GKM parameters obtained with calibrations based only on total effluent TOC concentrations [$\mathrm{TOC_{eff}}$]. This fact could be problematical if these parameters are used for the prediction of intermediates and target pollutant concentrations instead of predicting only the total effluent TOC concentration.

Therefore, the objective of this study is to compare the calibration goodness, i.e. prediction of lumped intermediates concentration and accuracy/uniqueness of kinetic parameters of the proposed kinetic model, when using different sets of data for calibration. Two different set of data [1], containing different information, are used: the first one corresponds to [$\mathrm{TOC_{eff}}$] as the sole experimental measure for calibration, whereas the second one corresponds to two independent experimental measurements, namely [$\mathrm{TOC_{eff}}$] and residual TOC of target pollutant [$\mathrm{TOC_{[A]}}$]. This comparison has been performed by applying a detailed statistical analysis

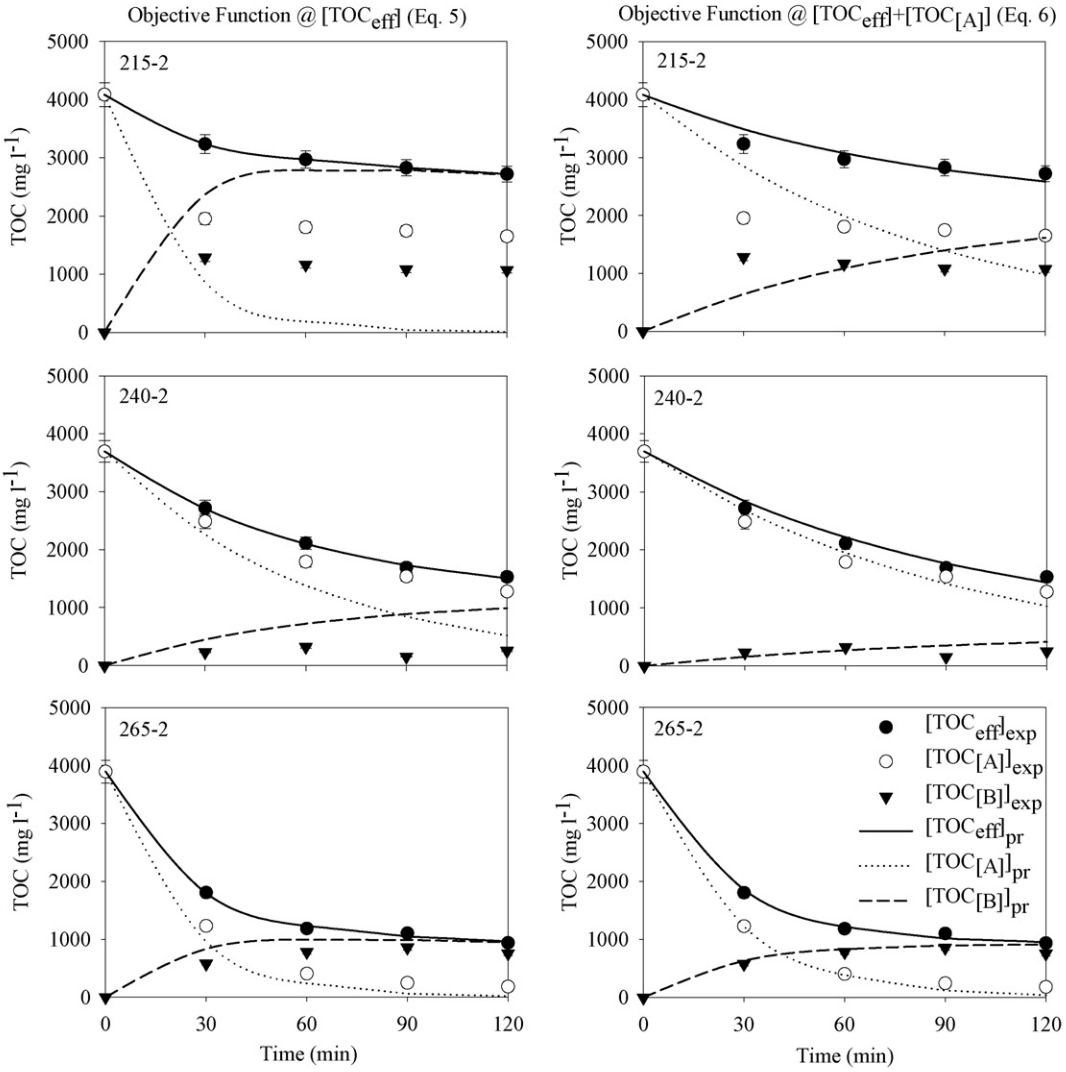


Fig. 1. Experimental data [1] and model prediction of WAO of a high-strength *o*-cresol wastewater.

with data-model plots, confidence intervals and contour plots of the two objective functions used in this work.

2. Methodology

2.1. Kinetic modelling and calibration procedure

The WAO experimental data used in this study for calibration purposes were reported in a previous work [1]. A GKM type was established following that suggested by Li et al. [2]. For engineering purposes, it is sufficient to quantify the global reaction rate by identifying the major WAO pathways [2] and as a result, key intermediates, which were considered to be rate controlling, were selected in this study. The model equations were solved by a program written in Matlab® R2006a. The rate constants (k_i) estimation was carried out using the Matlab function *fminsearch*, which uses the classical simplex Nelder and Mead minimisation algorithm [13] using as the objective function the norm of the square difference between the experimental data and the predicted by the kinetic model.

Several assumptions were used in the kinetic modelling: first-order dependence was assumed for the organic concentration term [2], due to the large amount of water present in the system, the water concentration was excluded from the model, in addition, since an excess oxygen was maintained at a constant partial pressure in the reactor, oxygen concentration in the aqueous phase was considered unchanged throughout the experiments [14]. Finally, all concentration terms are expressed by means of the theoretical TOC concentration, calculated stoichiometrically by total oxidation of each target pollutant.

GKM is based on a simplified reaction scheme involving the formation and destruction of rate controlling intermediates. These models are usually based on the existence of two types of compounds/intermediates present in solution: (a) compounds and intermediates that undergo relatively fast oxidation to carbon dioxide and water, and (b) compounds and intermediates that are difficult to oxidise (mostly acetic acid). Most researchers refer to these types of compounds as type “A” or “B”, respectively. GKMs for various complex solutions have been developed by several researchers [2,15] using the aforementioned types of compounds.

Therefore, we considered three groups in the reaction pathway of our proposed GKM. Group A comprises the target pollutants (*o*-cresol or 2-chlorophenol). Group B is represented by oxidation intermediates such as glyoxylic, oxalic, formic, propionic and acetic acids, as these type of low molecular weight carboxylic acids are well known refractory intermediates for WAO, being acetic acid the most refractory one [2,16–19]. Group C includes end products such

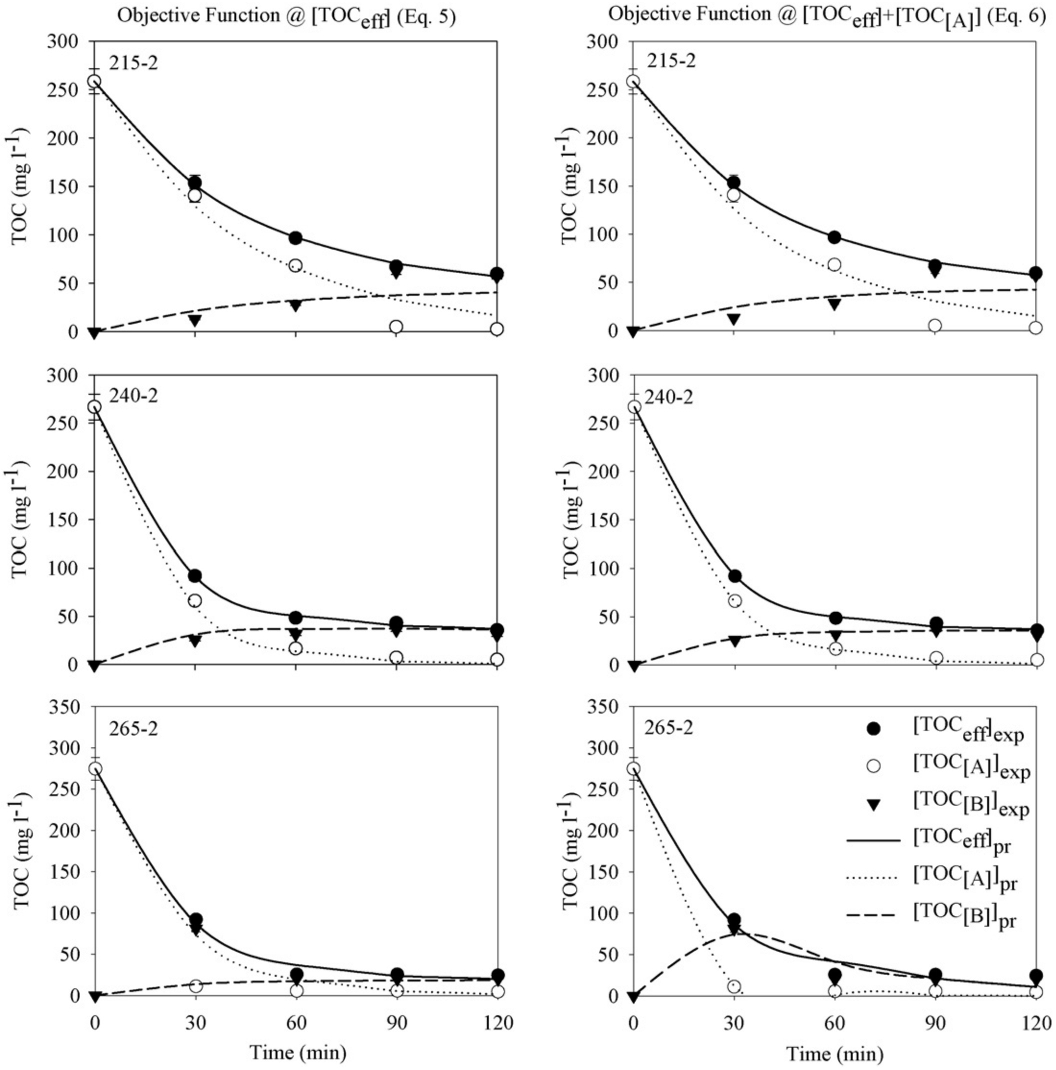
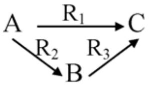


Fig. 2. Experimental data [1] and model prediction of WAO of a high-strength 2-chlorophenol wastewater.

as carbon dioxide and water. Thus, the reaction routes of this model can be shown as



(1)

The final equations used in our model are expressed as

$$[\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{pr}} = [\mathrm{TOC}_{[\mathrm{A}]}]_{t=0} \cdot e^{-(k_1+k_2)t} \tag{2}$$

$$\begin{aligned}[\mathrm{TOC}_{[\mathrm{B}]}]_{\mathrm{pr}} = {} & [\mathrm{TOC}_{[\mathrm{B}]}]_{t=0} \cdot e^{-k_3 \cdot t} + (k_2[\mathrm{TOC}_{[\mathrm{A}]}]_{t=0}/(k_1+k_2-k_3)) \\ & \cdot [e^{-k_3 t} - e^{-(k_1+k_2)t}]\end{aligned} \tag{3}$$

$$[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{pr}} = [\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{pr}} + [\mathrm{TOC}_{[\mathrm{B}]}]_{\mathrm{pr}} \tag{4}$$

In which $[\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{pr}}$ and $[\mathrm{TOC}_{[\mathrm{B}]}]_{\mathrm{pr}}$ are the predicted TOC concentrations at time t of residual target pollutant and intermediates, respectively. $[\mathrm{TOC}_{[\mathrm{A}]}]_{t=0}$ and $[\mathrm{TOC}_{[\mathrm{B}]}]_{t=0}$ are the TOC concentrations at initial time of residual target pollutants and intermediates, respectively. $[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{pr}}$ is the predicted total effluent TOC concentration. Finally, k_1, k_2 and k_3 are the rate constants of reactions R_1, R_2 and R_3, respectively.

Two objective functions ($F^i(k)$) were used for calibration. The first one uses only the experimental values of total effluent TOC ($[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp}}$), whereas the second one uses both $[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp}}$ and concentration of residual target pollutant (*o*-cresol or 2-chlorophenol) measured by HPLC and expressed as TOC concentration ($[\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{exp}}$):

$$F^1(k) = \sqrt{\left(\sum_{j=1}^{n}([\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp},j} - [\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j})^2\right)} \tag{5}$$

$$F^2(k) = \sqrt{\left(\sum_{j=1}^{n}([\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp},j} - [\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j})^2 + \sum_{j=1}^{n}([\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{exp},j} - [\mathrm{TOC}_{[\mathrm{A}]}(k)]_{\mathrm{pr},j})^2\right)} \tag{6}$$

In which $[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp}}$, $[\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr}}$, $[\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{exp}}$ and $[\mathrm{TOC}_{[\mathrm{A}]}(k)]_{\mathrm{pr}}$ are vectors of n measured values and model predictions at times t_j (j from 1 to n) and k is the vector of the rate constants of the model.

The objective of this study is to compare the goodness of the model calibration when using just one set of data $[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp}}$ or two sets of independent experimental measurements $[\mathrm{TOC}_{\mathrm{eff}}]_{\mathrm{exp}}$ and $[\mathrm{TOC}_{[\mathrm{A}]}]_{\mathrm{exp}}$.

2.2. Theoretical framework for optimal experimental design for parameter estimation (OED/PE)

The OED/PE can be used to compare the practical identifiability of the parameters obtained with different calibration procedures. It is based on the Fisher Information Matrix (FIM) [6,9,10,20,21], which summarises the information content of the experimental data. The inverse of the FIM is the parameter estimation covariance matrix and the diagonal elements of this matrix can be used to calculate the confidence interval of each estimated rate constant. In the present study, the FIM can be estimated using Eq. (7) or Eq. (8), depending on the objective function selected for calibration:

$$\mathrm{FIM}^{[\mathrm{TOC}]_{\mathrm{eff}}} = \sum_{j=1}^{n}\left(\frac{\partial[\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j}}{\partial k}\right)^{\mathrm{T}} Q_j^{[\mathrm{TOC}]_{\mathrm{eff}}}\left(\frac{\partial[\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j}}{\partial k}\right) \tag{7}$$

$$\begin{aligned}\mathrm{FIM}^{[\mathrm{TOC}_{\mathrm{eff}}]+[\mathrm{TOC}_{[\mathrm{A}]}]} &= \sum_{j=1}^{n}\left[\frac{\partial[\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j}}{\partial k}\;\frac{\partial[\mathrm{TOC}_{[\mathrm{A}]}(k)]_{\mathrm{pr},j}}{\partial k}\right]^{\mathrm{T}}\begin{bmatrix} Q_j^{[\mathrm{TOC}_{\mathrm{eff}}]} & 0 \\ 0 & Q_j^{[\mathrm{TOC}_{[\mathrm{A}]}]}\end{bmatrix} \\ &\quad \times \left[\frac{\partial[\mathrm{TOC}_{\mathrm{eff}}(k)]_{\mathrm{pr},j}}{\partial k}\;\frac{\partial[\mathrm{TOC}_{[\mathrm{A}]}(k)]_{\mathrm{pr},j}}{\partial k}\right]\end{aligned} \tag{8}$$

where $[\mathrm{TOC}_{\mathrm{eff}}(k)]$ and $[\mathrm{TOC}_{[\mathrm{A}]}(k)]$ are vectors of n values calculated at times t_j (j from 1 to n), k is the vector of the rate constants and Q is a measurement error covariance matrix (Q is a 1×1 matrix for Eq. (7) and a 2×2 for Eq. (8)), In this case, the measurement error is constant for all measurements; therefore the value for Q can be estimated as

$$Q = (s^2)^{-1} \tag{9}$$

where s is the measurement error in the total effluent TOC analysis ($Q^{[\mathrm{TOC}_{[\mathrm{eff}]}]}$) or in the residual pollutant concentration analysis ($Q^{[\mathrm{TOC}_{[\mathrm{A}]}]}$).

Different OED/PE criteria can be obtained using scalar measures of the FIM and its inverse [6,21]:

$$\text{A-optimal design criterion}: \quad \min[\mathrm{tr}(\mathrm{FIM}^{-1})] \tag{10}$$

$$\text{Modified A-optimal design criterion}: \quad \max[\mathrm{tr}(\mathrm{FIM})] \tag{11}$$

$$\text{D-optimal design criterion}: \quad \max[\det(\mathrm{FIM})] \tag{12}$$

$$\text{E-optimal design criterion}: \quad \max[\lambda_{\min}(\mathrm{FIM})] \tag{13}$$

$$\text{Modified E-optimal design criterion}: \quad \min\left[\frac{\lambda_{\max}(\mathrm{FIM})}{\lambda_{\min}(\mathrm{FIM})}\right] \tag{14}$$

where tr is the trace of the matrix, det is the determinant and $\lambda_{\min}$ and $\lambda_{\max}$ are the smallest and largest eigenvalues of the matrix. The numerical method based on the FIM was also programmed in Matlab® R2006a.

3. Results and discussion

The results and discussion are divided into two sections. In the first one, the calibration and model prediction is discussed. In the second section, the practical identifiability analysis is presented. During the discussion, the WAO conditions will use the following

Table 1
Rate constants estimation with objective function with only $[\mathrm{TOC}_{\mathrm{eff}}]$ (Eq. (5)) and 95% of confidence interval.

Parameter/target pollutant	*o*-cresol	2-chlorophenol
215-2		
k_1 (10^2 min^{-1})	1.3 ± 0.2	1.9 ± 0.2
k_2 (10^2 min^{-1})	3.9 ± 0.2	0.4 ± 0.2
k_3 (10^2 min^{-1})	0.1 ± 0.2	0
240-2		
k_1 (10^2 min^{-1})	1.1 ± 0.7	4.2 ± 0.4
k_2 (10^2 min^{-1})	0.5 ± 0.2	0.8 ± 0.4
k_3 (10^2 min^{-1})	0	0.1 ± 0.5
265-2		
k_1 (10^2 min^{-1})	3.3 ± 0.7	4.1 ± 0.5
k_2 (10^2 min^{-1})	1.3 ± 0.7	0.30 ± 0.1
k_3 (10^2 min^{-1})	0.2 ± 0.2	0

nomenclature: 215-2 will refer to 215 °C and 2 bar of P_{O_2}, 245-2 equals to 245 °C and 2 bar of P_{O_2} and so on.

3.1. Calibration and model prediction

Figs. 1 and 2 depict the evolution of $[TOC_{eff}]$, $[TOC_{[A]}]$ and $[TOC_{[B]}]$ both experimental [1] and model predicted for WAO of *o*-cresol and 2-chlorophenol, respectively. The intermediates concentration were obtained by difference between $[TOC_{eff}]$ and $[TOC_{[A]}]$. Table 1 shows the rate constants, for the two target pollutants in WAO experiments, estimated by fitting the model to the proposed reaction network using Eq. (5), whereas Table 2 shows the rate constants estimation, but using Eq. (6) as objective function.

As Figs. 1 and 2 show, the model correctly fitted (less than 6% as averaged relative deviation) the experimental $[TOC_{eff}]$ in all cases,

Table 2
Rate constants estimation with objective function $[TOC_{eff}]$ and $[TOC_{[A]}]$ (Eq. (6)) and 95% of confidence interval.

Parameter/target pollutant	*o*-Cresol	2-Chlorophenol
215-2		
k_1 (10^2 min^{-1})	0.58 ± 0.09	1.9 ± 0.3
k_2 (10^2 min^{-1})	0.62 ± 0.09	0.4 ± 0.3
k_3 (10^2 min^{-1})	0	0.07 ± 1
240-2		
k_1 (10^2 min^{-1})	0.90 ± 0.06	4.1 ± 0.2
k_2 (10^2 min^{-1})	0.16 ± 0.06	0.6 ± 0.2
k_3 (10^2 min^{-1})	0	0.01 ± 0.5
265-2		
k_1 (10^2 min^{-1})	2.94 ± 0.08	6 ± 2
k_2 (10^2 min^{-1})	0.92 ± 0.08	5 ± 2
k_3 (10^2 min^{-1})	0	2.3 ± 1.1

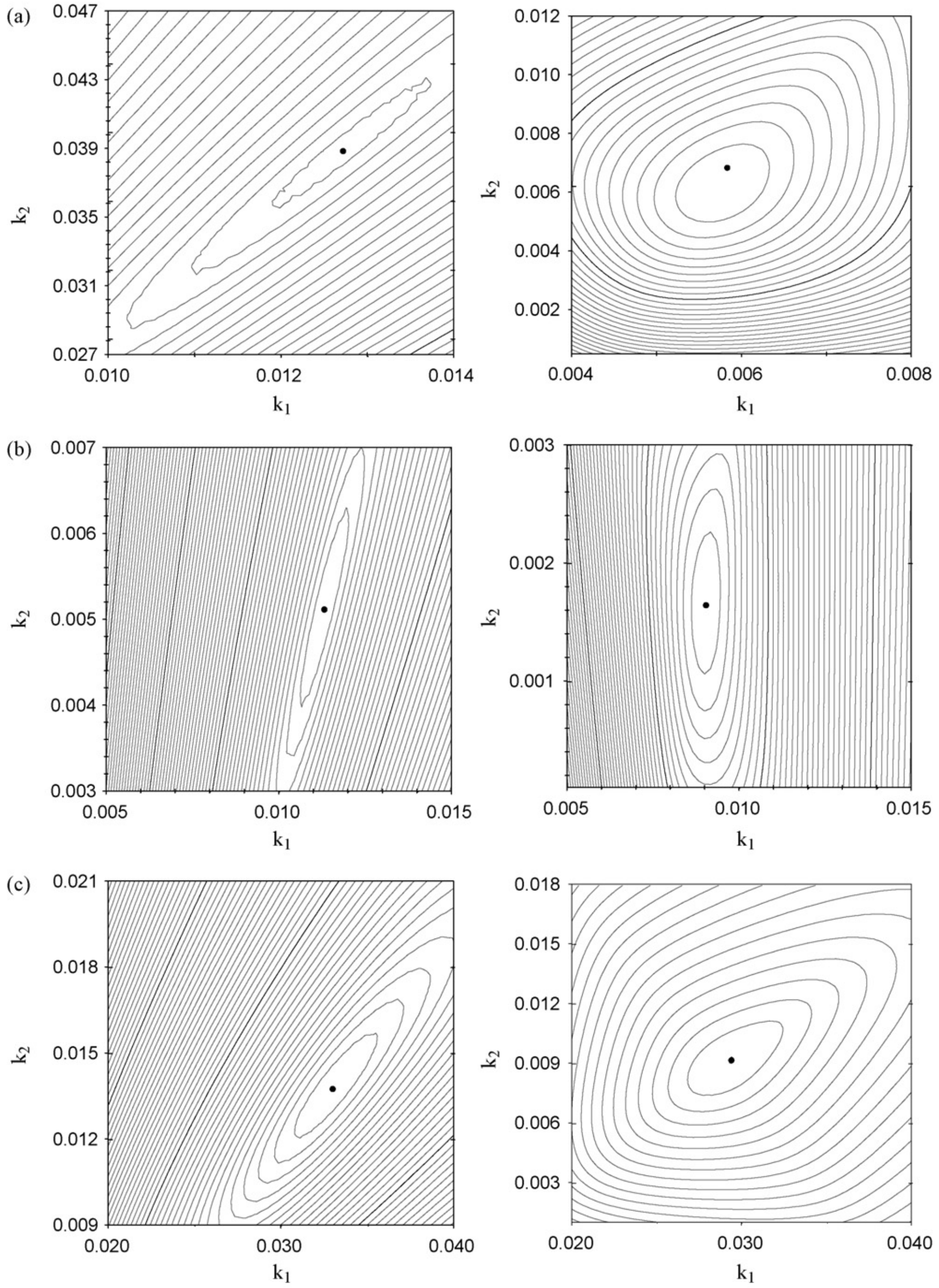


Fig. 3. Contour plots of the objective function (left: $[TOC_{eff}]$, right: $[TOC_{eff}]$ and $[TOC_{[A]}]$) for pairs of parameters: k_1–k_2 in WAO of *o*-cresol at (a) 215-2, (b) 240-2 and (c) 265-2.

either using Eq. (5) or Eq. (6) as objective function. However, when using Eq. (5) as objective function, the model was not capable of fitting the proportion between [$TOC_{[A]}$] and [$TOC_{[B]}$].

From Figs. 1 and 2, two different behaviours in the oxidation of target compounds can be outlined at the tested conditions: low oxidation progression (*o*-cresol) and high oxidation progression (2-chlorophenol).

For *o*-cresol the total TOC removal ranges from only 33 to 80% (Fig. 1), with intermediates production around 40–80% of the total remaining TOC (at 120 min). Nevertheless, when using Eq. (5) as the objective function, the model predicted that intermediates production should be between 65 and 100% (at 120 min). On the contrary, when using Eq. (6) as objective function, the intermediates production predictions were between 30 and 95% (at 120 min) which is closer to the experimental values. As can be seen in Table 2, both calibrations predicted comparable values for k_1 and k_2, and therefore, the predicted velocities of R_1 and R_2 were similar. In spite of this, when using Eq. (6) as objective function, the kinetic constants diminished, for example at 215-2, k_2 passed from 3.9 ± 0.2 (10^2 min^{-1}) (Table 1) to 0.62 ± 0.09 (10^2 min^{-1}) (Table 2), thus, the model calibrated with Eq. (6) as objective function predicted similar velocities for R_1 and R_2, but both slower than those predicted using Eq. (5). In addition, at 215-2 the model calibrated with Eq. (5) predicted no further improvement of the oxidation progress beyond 60 min, whereas the model calibrated with Eq. (6) predicted an extra improvement in the oxidation progress is beyond 120 min. In the case of k_3, both calibrations (with Eq. (5) or (6)) predicted negligible or null velocity for R_3.

In the case of 2-chlorophenol, the oxidation progress was the highest one, being the total TOC removal from 62 to 81% (Fig. 3) and the intermediates proportion around 80–95% of the total remaining TOC (120 min). It should be noted that the total TOC removal

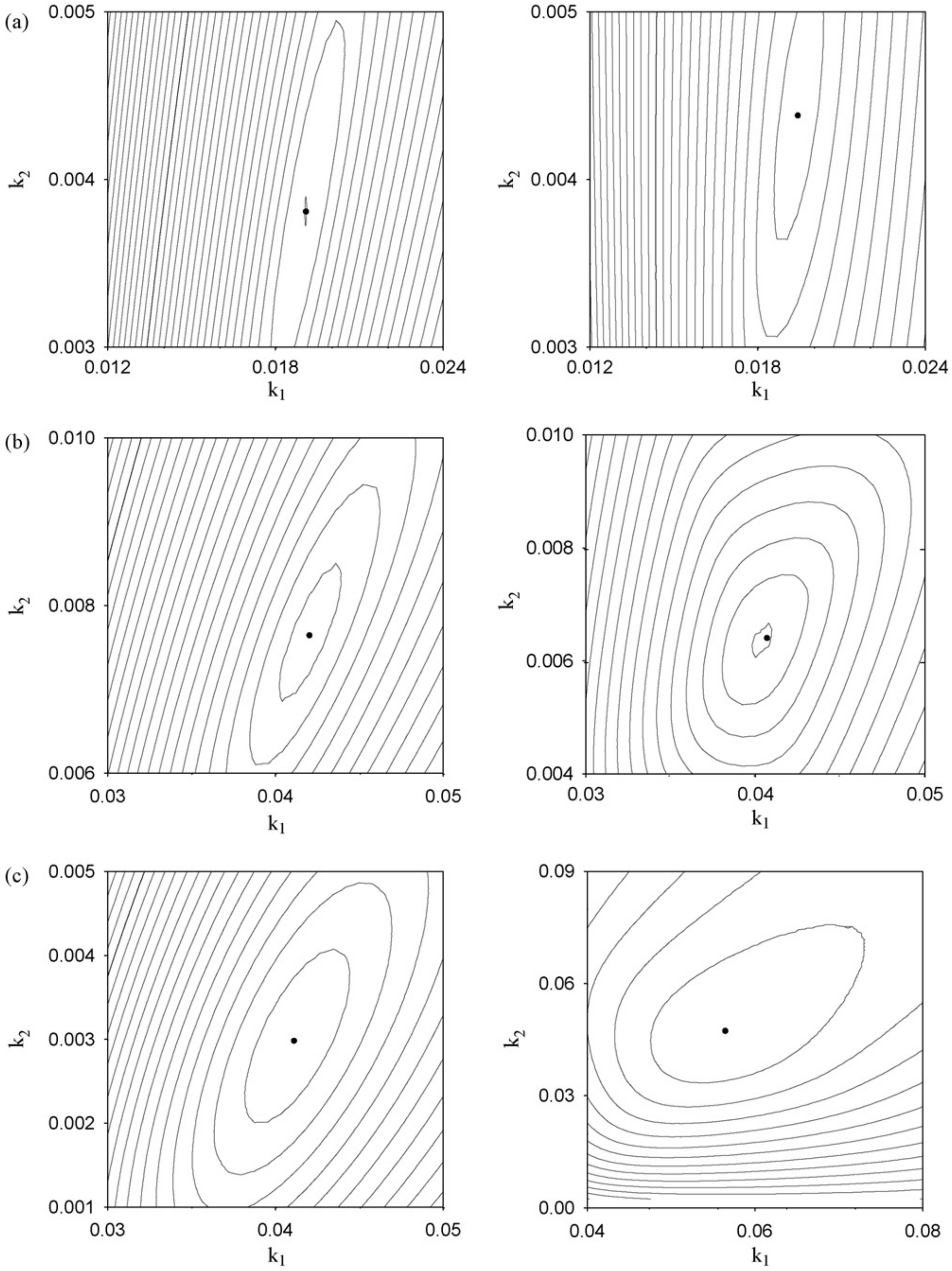


Fig. 4. Contour plots of the objective function (left: TOC_{eff}], right: [TOC_{eff}] and [$TOC_{[A]}$]) for pairs of parameters: k_1–k_2 in WAO of 2-chlorophenol at: (a) 215-2, (b) 240-2 and (c) 265-2.

at 90 min was almost the same that at 120 min, therefore, those points did not have good quality for calibration purposes. This was reflected in the kinetic parameter estimation; as can be seen in Tables 1 and 2, at 215-2 and 240-2 the kinetic constants remained almost unchanged. However, at 265-2, the intermediates production followed a different trend than the rest of experiments of 2-chlorophenol, being the highest one at 30 min. In this case the model calibrated with Eq. (6) was the only one able to predict this trend, as reflected by the kinetic constants obtained which are all of the same order of magnitude.

Also, from Table 2, it is easily noticeable that temperature has a clear influence on the process kinetics, since increasing the temperature from 215 to 265 °C increased the k_1 around 5 times for *o*-cresol and around 3 times for 2-chlorophenol. According to Joglekar et al. [22], the activation energies (E_{ACT}) values range from 34.7 to 144.8 kJ mol^{-1} for *o*-cresol and from 50.5 to 95.7 kJ mol^{-1} for 2-chlorophenol. When using Eq. (6) as objective function and with 95% of confidence interval, the obtained E_{ACT} for the first reaction were 71 ± 20 kJ mol^{-1} ($R^2 = 0.92$) and 47 ± 9 kJ mol^{-1} ($R^2 = 0.96$) for *o*-cresol and 2-chlorophenol, respectively. However, when using Eq. (5), the E_{ACT} were 41 ± 31 kJ mol^{-1} ($R^2 = 0.63$) and 34 ± 19 kJ mol^{-1} ($R^2 = 0.75$) for *o*-cresol and 2-chlorophenol, respectively. As can be seen, the obtained E_{ACT} values for *o*-cresol lie in the range reported by Joglekar et al. regardless the equation used as objective function; for 2-chlorophenol the E_{ACT} obtained with Eq. (6) is closer to the values reported by Joglekar et al. than that obtained with Eq. (5). But, in both cases when using Eq. (5), it is clear from Table 1 that k_1 values do not follow an increasing trend as it should be expected. Therefore, the E_{ACT} values obtained with Eq. (5) as objective function has larger errors than the ones obtained with Eq. (6). This fact is also supported by the regression coefficients (R^2), which are as low as 0.63 for *o*-cresol and 0.75 for 2-chlorophenol.

It is generally accepted that due to the complex composition of the wastewater (remaining target pollutant plus reaction intermediates), a lumped parameter, such as total effluent TOC, is usually applied in order to describe the evolution of overall concentration of organic compounds during the WAO reaction [23–28]. There is no doubt of the usefulness of lumped kinetics, however the description of the evolution of the total effluent TOC is not enough when the intermediates distribution from the WAO process is needed, as in the case of designing an integrated process of WAO followed by a biological degradation. In this sense, it is clear that the use of a more complete set of data in the objective function should lead to not only to a good fit to the total effluent TOC, but also to a better prediction of the intermediates distribution. This fact is also supported by the works of Santos et al. [29] and Eftaxias et al. [30].

As stated previously [1,31], the differences in the intermediates distribution helped to explain the differences in biodegradability enhancement between several WAO effluents obtained at different operating conditions. Therefore, the kinetic model calibrated with Eq. (6) as objective function will be more reliable for design purposes, because it could be used as a first approximation to set the proportion between residual target pollutant and oxidation intermediates concentrations of the WAO process.

3.2. Practical identifiability analysis

A practical identifiability analysis for the model was performed by obtaining the contour plots for the objective function with respect to different pairs of parameters (k_1–k_2, k_1–k_3 and k_2–k_3). Each parameter was modified around the optimum value of the objective functions expressed by Eqs. (5) and (6). The presence of a clear minimum in the plots indicates that the explored parameters are identifiable. On the contrary, a valley in a contour plots indicates a high correlation between parameters [6].

Table 3
Comparison of both calibration procedures for WAO of *o*-cresol using OED/PE criteria.

OED/PE criteria	[TOC$_{eff}$]	[TOC$_{eff}$] and [TOC$_{[A]}$]
215-2		
Minimum A tr(FIM^{-1})	4.26×10^{-7}	1.12×10^{-10}
Maximum modified A tr(FIM)	7.05×10^{10}	1.67×10^{12}
Maximum D det(FIM)	2.02×10^{26}	8.20×10^{32}
Maximum E λ_{min}(FIM)	2.35×10^{6}	1.12×10^{10}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	2.95×10^{4}	1.45×10^{2}
240-2		
Minimum A tr(FIM^{-1})	3.24×10^{-8}	1.20×110^{-10}
Maximum modified A tr(FIM)	7.05×10^{10}	1.67×10^{12}
Maximum D det(FIM)	9.85×10^{26}	8.20×10^{32}
Maximum E λ_{min}(FIM)	3.17×10^{7}	1.03×10^{10}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	7.70×10^{2}	1.59×10^{2}
265-2		
Minimum A tr(FIM^{-1})	3.48×10^{-8}	2.17×10^{-9}
Maximum modified A tr(FIM)	1.22×10^{10}	9.17×10^{10}
Maximum D det(FIM)	2.29×10^{26}	8.41×10^{29}
Maximum E λ_{min}(FIM)	3.01×10^{7}	4.71×10^{8}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	3.83×10^{4}	1.33×10^{2}

Figs. 3 and 4 illustrate the typical shape of the contour lines observed during the estimation of the pair k_1–k_2. In the case of *o*-cresol (Fig. 3), there was a clear improvement in the minimum estimation when using [TOC$_{eff}$] and [TOC$_{[A]}$] (Eq. (6)) to calibrate the model instead of only [TOC$_{eff}$] (Eq. (5)). The contour lines obtained with the parameters of the second calibration (Eq. (6)) were well-centred around the most probable point whereas the contour lines obtained with the parameters of the first calibration (Eq. (5)) showed valley-like shape. These results indicate that there is a high correlation between the pair k_1–k_2 obtained for WAO of *o*-cresol at any temperature with the first calibration. In other words, although there is a true minimum for the objective function at these values, there exist many other combinations of k_1 and k_2 which give almost the same value of the objective function [20]. However, for the second calibration, there is a unique value for the pair k_1–k_2 that corresponds to the minimum of the objective function. In the case of 2-chlorophenol (Fig. 4), the contour lines obtained with both calibrations were, in general, well-centred around the most probable point and consequently, the pair k_1–k_2 were identifiable in both calibration procedures.

Table 4
Comparison of both calibration procedures for WAO of 2-chlorophenol using OED/PE criteria.

OED/PE criteria	[TOC$_{eff}$]	[TOC$_{eff}$] and [TOC$_{[A]}$]
215-2		
Minimum A tr(FIM^{-1})	2.03×10^{-5}	1.91×10^{-6}
Maximum modified A tr(FIM)	8.84×10^{7}	1.24×10^{9}
Maximum D det(FIM)	2.53×10^{19}	1.88×10^{22}
Maximum E λ_{min}(FIM)	4.98×10^{4}	5.34×10^{5}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	2.27×10^{3}	1.65×10^{3}
240-2		
Minimum A tr(FIM^{-1})	6.79×10^{-6}	1.88×10^{-6}
Maximum modified A tr(FIM)	3.70×10^{7}	1.64×10^{8}
Maximum D det(FIM)	1.06×10^{19}	1.11×10^{21}
Maximum E λ_{min}(FIM)	1.60×10^{5}	5.57×10^{5}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	2.70×10^{2}	2.18×10^{2}
265-2		
Minimum A tr(FIM^{-1})	1.54×10^{-5}	2.10×10^{-6}
Maximum modified A tr(FIM)	5.96×10^{6}	4.73×10^{7}
Maximum D det(FIM)	5.33×10^{17}	5.69×10^{19}
Maximum E λ_{min}(FIM)	6.80×10^{4}	6.32×10^{5}
Minimum modified E[λ_{max}(FIM)/λ_{min}(FIM)]	7.06×10^{1}	5.69×10^{1}

Regarding to the other pairs of rate constants (k_1–k_3 and k_2–k_3), both present a high correlation in both calibrations. This lack of identifiability is due to the low value of k_3 obtained in both calibration procedures. Figs. 1 and 2 show that the progression of R_3 (Eq. (1)) is very low because the [TOC$_{[B]}$] concentration achieved a maximum value and then remained constant for any WAO experiment. Consequently, the data of [TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$] of these experiments have low quality for describing the evolution of R_3 and any change in k_3 can be compensated almost completely by a proportional shift in the pair k_1–k_2, still producing a satisfying fit between experimental data and model prediction. In fact, if k_3 has a value different from zero, the confidence interval of k_3 has almost the same magnitude of k_3.

The values of the scalar measures of the FIM and its inverse obtained for each calibration are summarised in Tables 3 and 4. These results confirm that the calibration with [TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$] measurements is the best for any target pollutant considering any of the OED/PE criteria. As explained by Dochain and Vanrolleghem [6], the A- and D-optimal designs minimise the arithmetic and geometric mean of the identification errors respectively, while the E-criterion-based experimental designs aim at minimising the largest error. The modified E-criterion should be interpreted in the frame of the objective functional shape, i.e. smallest values indicate closer Eigenvalues of the FIM matrix and, therefore a more round shape.

Another theoretical calibration procedure was evaluated in order to test if the difference between calibration with only [TOC$_{\mathrm{eff}}$] and the calibration with [TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$] was due to the larger amount of experimental data in the second one (10 TOC determinations instead of the 5 measurements in the first one) or due to the different experimental design of the calibration. This theoretical procedure consisted in a calibration performed only with [TOC$_{\mathrm{eff}}$] data but with 10 measurements. All the OED/PE criteria indicate (data not shown) that the results obtained with this procedure were better than those achieved with the first calibration (only [TOC$_{\mathrm{eff}}$] data and 5 measurements) but worse than those achieved with the second calibration ([TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$] data) and the same number of measurements.

4. Conclusions

Two different sets of data were employed to obtain two different objective functions to calibrate a GKM model. Both calibrations showed excellent agreement with experimental total effluent TOC data ([TOC$_{\mathrm{eff}}$]) data leading to a very small mean error of no more than 6%. However, the model calibrated with two independent experimental measurements, namely total effluent TOC and residual TOC of target pollutant ([TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$]) was the only one able to satisfactorily predict the proportion between the remaining target pollutant and the reaction intermediates in the effluent. In this sense, it was clear that the use of a more complete set of data for kinetic model calibration leads to a better prediction of the intermediates distribution, key factor for the designing of an integrated process of WAO followed by a biological degradation.

The practical identifiability analysis showed that the calibration performed with only [TOC$_{\mathrm{eff}}$] data provides highly correlated values for the rate constants and consequently the parameters obtained with this procedure are not unique. Whereas the calibration with [TOC$_{\mathrm{eff}}$] and [TOC$_{[A]}$] data provides poorly correlated parameters and consequently, better estimation of the rate constants.

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