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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 [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 [TOC_{eff}] as the sole experimental measure for calibration, whereas the second one corresponds to two independent experimental measurements, namely [TOC_{eff}] and residual TOC of target pollutant [$TOC_{[A]}$]. This comparison has been performed by applying a detailed statistical analysis

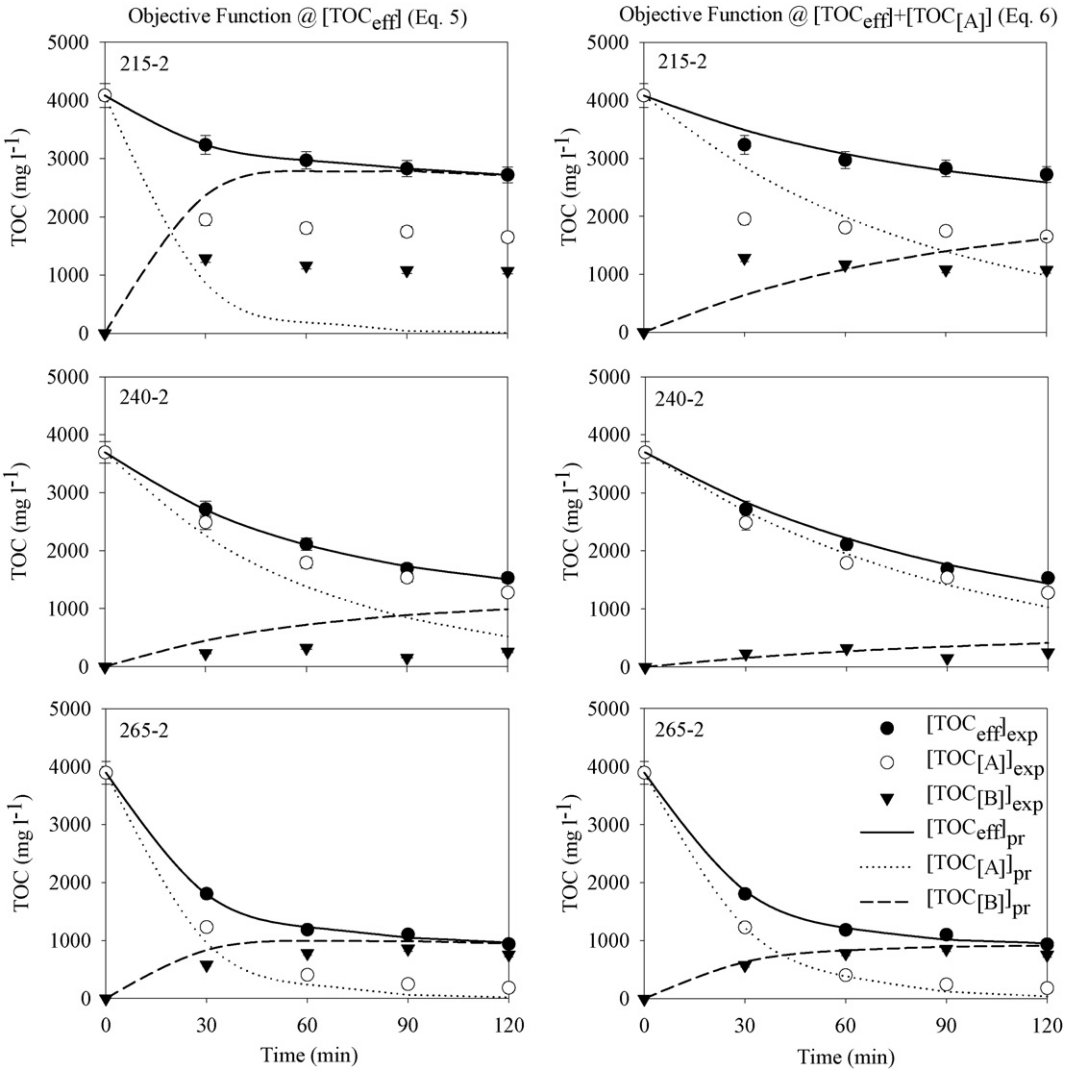

Fig. 1. Experimental data [1] and model prediction of WAO of a high-strength *o*-cresol wastewater.