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Detoxification Kinetic Modeling for Nonbiodegradable Wastewaters: An Ecotoxicity Lumping Approach

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A lumped pseudokinetic model that is able to predict the toxicity change during the treatment of industrial wastewater as a function of the initial toxicity and temperature of the process is proposed. The original pollutant (or pollutant mixture), P, reacts to form a lumped intermediate species, I, which, in turn, reacts to form a nontoxic lumped species D. Therefore, only P and I in this serial scheme, P → I → D, are considered to contribute to the toxicity of the aqueous sample. The median effective nominal concentration of species I, $EC_{50}(I)$, is a fitting parameter in this lumping approach and gives an idea of the toxicity of the first organic intermediates generated, lumped as I. The model was successfully validated by analyzing the toxicity data obtained during the catalytic wet oxidation of phenolic solutions (with phenol, *o*-cresol, and *p*-cresol employed as pollutants) in a three-phase fixed-bed reactor. Moreover, the lumped kinetic model developed in a previous work for the mineralization of phenol was also validated by analyzing the total organic carbon (TOC) evolution data obtained with *o*-cresol and *p*-cresol as pollutants.

1. Introduction

Industrial wastewaters have become a problem of increased importance in recent decades.[1,2] One of the main differences between these streams and domestic wastewaters resides in the great diversity of compounds, concentration levels, and negative environmental effects of the pollutants contained in industrial wastewaters.[3,4] This is particularly true if toxic organic compounds, nonbiodegradable substances, and even biocides are present. As a result, global pollution parameters for organic matter commonly used to characterize the pollution of domestic wastewaters such as total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD) are not sufficient to assess the potential toxicity of an industrial aqueous effluent. Moreover, the introduction of the Integrated Pollution Prevention and Control (IPPC) regulations in the European Union (Council Directive 96/61/EC) requires monitoring of the toxicity of industrial liquid effluents. To take this property into account, a new parameter, called the toxicity unit (TU), has been introduced, and local environmental regulations specift maximum values for this parameter in industrial wastewater before its discharge and treatment in wastewater treatment plants (WWTPs).

One of the most standard procedures for determining TUs is the Microtox bioassay (AZUR Environmental, formerly Microbics Corporation, Carlsbad, CA). The Microtox experimental procedure was developed from the official standards of several countries (U.S., ASTM method D5660-1995; Germany, DIN 38412-1990; France, AFNOR T90-320-1991; and Spain, ISO 11348-3-1998).[5]

The standard Microtox test procedure (ISO 11348-3, 1998) is based on the decrease of light emission from *Photobacterium phosphoreum* resulting from its exposure to a toxicant, as measured using a Microtox M500 Analyzer (Azur Environmental). The inhibition of the light emitted by the bacteria is measured after 5 and 15 min of contact time. The median effective nominal concentration (EC_{50}) is defined as the concentration of toxicant (mg L^{-1}) that reduces the intensity of light emission by 50%. The median inhibitory concentration (IC_{50}) is defined as the percentage of the initial volume of the sample relative to the volume of sample yielding, after the required dilution, a 50% reduction of the light emitted by the microorganisms. The toxicity units of a wastewater sample are calculated as

$$TU = \frac{100}{IC_{50}} \quad (1)$$

If the aqueous sample contains only compound *i* at a concentration C_i, the toxicity units can be predicted by the relationship

$$TU = \frac{C_i}{EC_{50_i}} \quad (2)$$

The toxicity of an aqueous sample containing a mixture of compounds can be predicted based on the EC_{50} values corresponding to the individual components. Using the concept of concentration addition,[6,7] toxicity values, as TUs, can be predicted according to the expression

$$TU = \sum \frac{C_i}{EC_{50_i}} \quad (3)$$

where C_i is the concentration in the mixture, in mg$_C \cdot$L^{-1}, of the individual pollutant *i*.

In addition, it has been confirmed that, during the treatment of industrial wastewater with organic refractory pollutants by different techniques, the toxicity changes during the process. In some cases, even more toxic pollutants are produced in the first stages of the treatment process,[8–16] whereas the last oxidation compounds (CO_2 and short-chain organic acids) have no toxic effects.[17]

Therefore, the toxicity and its evolution are important additional factors to take into account in the design of a preliminary wastewater treatment, mainly if the process involves chemical reactions such as oxidation technologies (wet oxidation, catalytic or not, and advanced oxidation processes such as Fenton's reaction, ozonation, photocatalysis). Because decreasing of the COD and TOC cannot be directly correlated with the evolution of the toxicity, it must be considered by other approaches.

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At the moment, the evolution of the toxicity has been predicted only from the evolution of the composition during the process.[18] This requires the determination of a complex kinetic model that is able to predict changes in composition. This task could be quite hard, especially if the wastewater contains a mixture of pollutants, often not completely characterized.

The aim of this work is to propose a lumping approach to predict the toxicity evolution, in a manner similar to the lumping approaches used to predict the abatement of COD and TOC.[19-22] Herein, the theoretical development of the overall pseudokinetic model for detoxification is described, and the model is applied to experimental data obtained in the catalytic wet oxidation (CWO) of some phenolic aqueous solutions (containing phenol, o-cresol, and p-cresol as pollutants) using activated carbon (AC) as the catalyst.

In addition, the lumping approach developed elsewhere for the mineralization of phenol[23] is validated with data obtained from o-cresol and p-cresol TOC abatement.

Kinetic Lumping Approach. Detoxification Pseudokinetic Model. The following reaction scheme is considered

$$P \xrightarrow{R_1} I \xrightarrow{R_2} D \qquad (4)$$

where P is the original pollutant (or pollutant mixture) and I and D are the lumped species corresponding to the organic intermediates produced in serial steps in the oxidation process. The concentrations of the lumped compounds P, I, and D are expressed in terms of organic carbon content ($mg_C L^{-1}$). In addition, the first reaction, R_1, is assumed to have a rate of r_1, and the second reaction, R_2, has a rate of r_2.

Taking into account eq 3 and assuming that lumped species D (sum of CO_2 and biodegradable short-chain acids) has negligible toxic effects, the toxicity units of a sample at a certain stage of the treatment can be calculated as

$$TU = \frac{C_P}{EC_{50}(P)} + \frac{C_I}{EC_{50}(I)} \qquad (5)$$

where the $EC_{50}(P)$ and $EC_{50}(I)$ are the effective nominal concentrations (both in $mg_C L^{-1}$) of P and I, respectively, that reduce the intensity of light emission by 50%.

The $EC_{50}(P)$ value can be predicted if the initial composition of the mixture is known or experimentally determined. In this latter case, $EC_{50}(P)$ is calculated from the IC_{50} value obtained for an initial sample containing organic carbon content at a concentration of C_{P0} ($mg_C L^{-1}$). According to eqs 1 and 2, $EC_{50}(P)$ is defined as

$$EC_{50}(P) = C_{P0} \frac{IC_{50_0}}{100} \qquad (6)$$

On the other hand, the effective nominal concentration for lumped species I, $EC_{50}(I)$, is an unknown parameter that must be calculated from data fitting. The value of $EC_{50}(I)$ gives an idea of the toxicity of the intermediates generated during oxidation in relation to the toxicity of the original sample. If $EC_{50}(I)$ is lower than $EC_{50}(P)$ value, then compounds that are more toxic than those contained in the original wastewater are obtained as first intermediates, and this finding should be taken into account in determining the time required for the preliminary treatment applied to the wastewater.

From eq 5, the concentration of the lumped species I can be calculated as

$$C_I = EC_{50}(I) \left[TU - \frac{C_P}{EC_{50}(P)} \right] \qquad (7)$$

For the reaction scheme in eq 4, the mass balance for the compounds P and I in a batch or plug-flow reactor can be written as

$$\frac{-dC_P}{d\tau} = r_1 \qquad (8)$$

$$\frac{dC_I}{d\tau} = r_1 - r_2 \qquad (9)$$

where τ is a time variable defined specifically for the reactor employed.

From eqs 5, 8, and 9, the mass balance for the toxicity units can be expressed as

$$\frac{d(TU)}{d\tau} = \frac{-r_1}{EC_{50}(P)} + \frac{r_1}{EC_{50}(I)} - \frac{r_2}{EC_{50}(I)} \qquad (10)$$

The initial conditions are

$$\tau = 0: \quad C_P = C_{P0}, \; TU = TU_0 = \frac{C_{P0}}{EC_{50}(P)} \qquad (11)$$

If P and TU are chosen as key compounds, the prediction of the system evolution with τ can be done if the kinetic equations for reactions R_1 and R_2 are known.

The P and I profiles as functions of τ are obtained by integration the corresponding mass balances

$$C_P = C_{P0} - \int r_1 \, d\tau \qquad (12)$$

$$TU = TU_0 + \int \left[\frac{-r_1}{EC_{50}(P)} + \frac{r_1}{EC_{50}(I)} - \frac{r_2}{EC_{50}(I)} \right] d\tau \qquad (13)$$

If first-order pseudokinetic models are assumed for reactions R_1 and R_2, i.e.

$$r_1 = k_1 C_P \qquad (14)$$

$$r_2 = k_2 C_I \qquad (15)$$

then the following analytical solutions can be obtained by integration of eqs 9 and 12

$$C_P = C_{P0} \exp(-k_1 \tau) \qquad (16)$$

$$C_I = C_{P0} \frac{k_1}{k_2 - k_1} [\exp(-k_1 \tau) - \exp(-k_2 \tau)] \qquad (17)$$

Integration of eq 13 taking into account the relationship between C_I and TU given in eq 7 and using the initial Toxicity Units defined in eq 11 gives the following dimensionless expression for toxicity units

$$\frac{TU}{TU_0} = \exp(-k_1 \tau) + \frac{k_1}{k_2 - k_1} \frac{EC_{50}(P)}{EC_{50}(I)} [\exp(-k_1 \tau) - \exp(-k_2 \tau)] \qquad (18)$$

In the case of nonelementary kinetic equations for reactions R_1 and R_2, a fourth-order Runge–Kutta or Euler algorithm can be applied to obtain numerical solutions for eqs 12 and 13.

If the kinetic parameters are unknown, they can be determined by fitting the experimental data for P and TU to the corresponding mass balance equations. Moreover, in the case of first-order kinetic equations, it is possible to obtain the pseudokinetic parameters k_1 and k_2 and the $EC_{50}(I)$ value by only fitting the TU vs τ data, according to eq 18.

Mineralization Pseudokinetic Model. In a previous work,[23] the following scheme was determined to describe the mineralization of the total organic carbon to carbon dioxide and water

$$TOC = A + B \qquad (19)$$

$$A \xrightarrow{r_3} xB + (1-x)CO_2 \qquad (20)$$

This simplified pathway divides the TOC into two components, A and B, which correspond to the oxidizable and refractory fractions, respectively, of the organic matter. The original contribution of the earlier work[23] was to propose and validate the single reaction for the oxidation of A yielding B and CO_2 with fixed stoichiometric coefficients, x and $(1-x)$, corresponding to the fraction of the carbon content of A that reacts to B and to CO_2, respectively.

The mass balances for A and TOC species can be written as

$$-R_A = r_3 = \frac{-dC_A}{d\tau} \qquad (21)$$

$$-R_{TOC} = (1-x)r_3 = \frac{d(TOC)}{d\tau} = \frac{d(CO_2)}{d\tau} \qquad (22)$$

with the initial condition

$$C_{A0} = TOC_0 \qquad (23)$$

The relationship between TOC and A then gives

$$C_A = TOC_0 - \frac{TOC_0 - TOC}{(1-x)} \qquad (24)$$

The TOC profile as a function of τ can be obtained by integration the corresponding mass balance

$$TOC = TOC_0 - \int (1-x)r_3 \, d\tau \qquad (25)$$

If a first-order pseudokinetic model is assumed for r_3

$$r_3 = k_3 C_A \qquad (26)$$

and the relationship between C_A and TOC in eq 24 is taken into account, eq 25 can be integrated to give the following dimensionless expression

$$n=1: \quad \frac{TOC}{TOC_0} = 1 - (1-x)[1 - \exp(-k_3\tau)] \qquad (27)$$

The kinetic parameter k_3 can be calculated by fitting the experimental TOC vs τ data to eq 27. The stoichiometric coefficient x can be determined from the asymptotic TOC value as a function of τ or calculated as fitting parameter in eq 27.

The pseudokinetic parameters k_1, k_2, and k_3 can be calculated as functions of temperature by means of the Arrhenious expression

$$k_i = \exp\left(\ln k_{i0} - \frac{E_{a_i}}{RT}\right) \qquad (28)$$

2. Materials and Methods

2.1. Oxidation Runs. A commercial activated carbon (AC) catalyst, Industrial React FE01606A, kindly supplied by Chemviron Carbon, was used as the catalyst in the catalytic wet oxidation of 1000 mg L^{-1} phenolic solutions. Phenol, o-cresol, and p-cresol were used as the pollutants. Runs were carried out in an integral fixed-bed reactor (FBR) with cocurrent upflow of the gas and liquid phases at temperatures between 127 and 160 °C and an oxygen pressure of 16 bar. The FBR consisted of a stainless steel tube that was 0.75 cm in internal diameter and 25 cm in length. Details on the experimental setup and procedure are given elsewhere.[23] The ratio between the catalyst weight in the reactor and the liquid flow rate fed to the reactor

Table 1. Operating Conditions for Runs Performed in the Fixed-Bed Reactor at $P_{O_2} = 16$ bar

pollutant (P)	$C_{P0} = TOC_0$ (mg$_C$ L^{-1})	T (°C)	W/Q_L (g min L^{-1})
PhOH	760	127	1050–17500
PhOH	760	140	1050–17500
PhOH	760	160	500–17500
o-C	777	127	2100–8400
o-C	777	140	2100–16150
o-C	777	160	330–10500
p-C	777	127	2100–8400
p-C	777	140	2100–16150
p-C	777	160	150–3000

(W/Q_L) was changed from 150 to 17500 g min L^{-1}. The aqueous solution fed to the reactor contained 1000 mg L^{-1} of the phenol under investigation. The corresponding amounts in terms of carbon content for the oxidation runs performed are summarized in Table 1. Liquid samples were periodically withdrawn and analyzed when steady state at the reactor exit was reached.

2.2. Analytical Methods. Total organic carbon (TOC) values in the liquid phase were determined with a Shimadzu TOC-V CSH analyzer by oxidative combustion at 680 °C, using an infrared detector.

The toxicities of the liquid samples at the reactor outlet obtained at different oxidation conversions of the pollutants were determined by means of a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998), using a Microtox M500 Analyzer (Azur Environmental). Before toxicity measurements, the pH values of all os the samples were readjusted to between 6 and 7, in order to prevent pH effects.

All chemicals used were purchased from Sigma-Aldrich, and the microorganisms were Microtox Acute Reagent supplied by I.O. Analytical.

3. Results and Discussion

The operating conditions for runs carried out using the three pollutants (phenol, o-cresol, and p-cresol) are summarized in Table 1. Because a plug-flow fixed-bed reactor was used and because reaction rates r_1–r_3 are related to the catalyst weight, the time parameter τ was defined as the ratio

$$\tau = \frac{W}{Q_L} \qquad (29)$$

where W (g) is the catalyst mass in the reactor and Q_L (mL min^{-1}) is the liquid flow rate fed to the reactor, containing the P species.

The dimensionless remaining toxicity units (TU/TU$_0$) and total organic carbon fractions (TOC/TOC$_0$) determined in the reactor effluent at the three temperatures tested (127, 140, and 160 °C) are shown as functions of τ in Figures 1 (P = phenol), 2 (P = o-cresol), and 3 (P = p-cresol).

As can be seen in Figures 1a, 2a, and 3a, the toxicity of the reactor effluent for a given value of W/Q_L depends strongly on the temperature. This is particularly noticeable for the oxidations of phenol and o-cresol, whereas the influence of temperature on the TU evolution is not as important in the oxidation of p-cresol. Moreover, the oxidations of phenol and o-cresol yield more toxic intermediates at short oxidation times, as indicated by the maximum in the TU vs τ profile, and the TU/TU$_0$ ratio is higher than the unity in the initial stages. This maximum is obtained at small τ and quickly decreases as temperature is increased. On the contrary, the oxidation of p-cresol produces a decrease in TUs with values of TU/TU$_0$ that are always lower than the unity, indicating that the first oxidation intermediates are less toxic than the original pollutant.
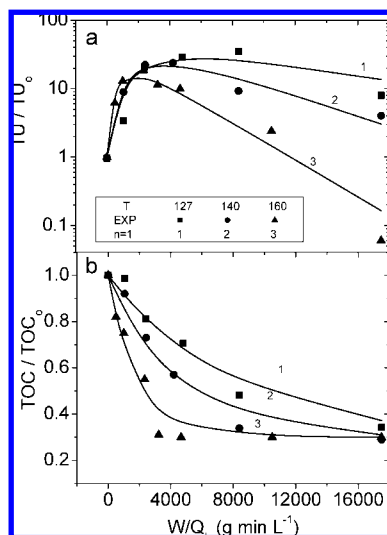
Figure 1. Experimental (symbols) and predicted (lines) values of TU/TU_0 and TOC/TOC_0 as functions of τ obtained in the CWO of phenol. Operating conditions: $T = 127-160$ °C, $P_{O_2} = 16$ bar, $C_{P0} = 760$ mg$_C$ L^{-1}.
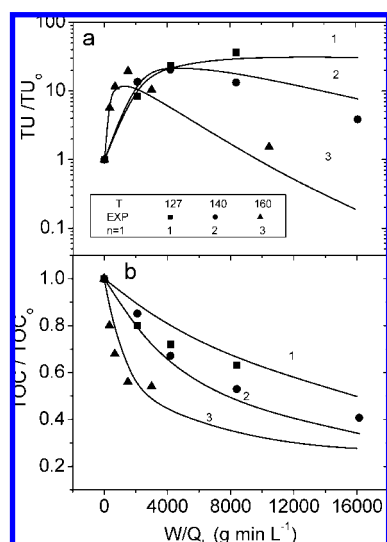

Figure 2. Experimental (symbols) and predicted (lines) values of TU/TU_0 and TOC/TOC_0 as functions of τ obtained in the CWO of o-cresol. Operating conditions: $T = 127-160$ °C, $P_{O_2} = 16$ bar, $C_{P0} = 777$ mg$_C$ L^{-1}.

The dimensionless remaining TOC vs τ results indicate that mineralization of the three phenols is not complete and that some refractory compounds remains in the media. It is also noticed that, for a given value of τ, the mineralized fraction increases as temperature increases. However, a similar asymptotic value for mineralization, not depending on the temperature, is reached.

The plots of the experimental dimensionless fractions TU/TU_0 and TOC/TOC_0 as functions of τ obtained for each pollutant were fitted to eqs 18 and 27, respectively. To consider the temperature as a variable, eq 28 was taken into account. Nonlinear regression using a Marquardt algorithm was applied in the fitting procedure. Values of the kinetic constants k_1-k_3 as functions of temperature were determined for each pollutant. The nominal effective concentration for the lumped species I, $EC_{50}(I)$, and the refractory fraction of the initial organic carbon, x, were also obtained by data fitting assuming that these parameters do not depend on temperature in the range studied here.

The value of the initial toxicity units in eq 27 was determined using eq 11. The effective nominal concentration in the initial
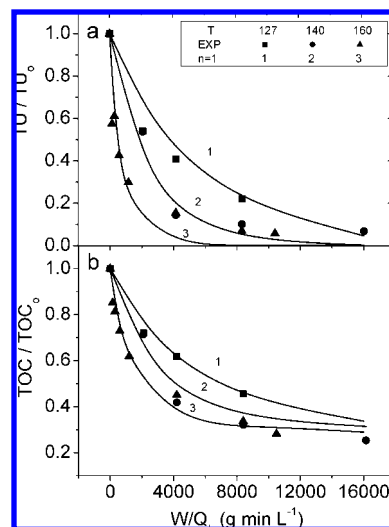

Figure 3. Experimental (symbols) and predicted (lines) values of TU/TU_0 and TOC/TOC_0 as functions of τ obtained in the CWO of p-cresol. Operating conditions: $T = 127-160$ °C, $P_{O_2} = 16$ bar, $C_{P0} = 777$ mg$_C$ L^{-1}.

Table 2. Experimental and Literature EC_{50} Values[24] of Phenol, o-Cresol, and p-Cresol and Toxicity Units of the Solution Fed to the Reactor

	$EC_{50}(P)$		
pollutant	this work/literature[24] (mg$_{compound}$ L^{-1})	this work (mg$_C$ L^{-1})	$TU_0 = C_{P0}/EC_{50}(P)$
PhOH	16/21.1−42	12	62.5
o-C	27/15.3−31.2	21	37
p-C	1.3/1.30−2.37	1	792

Table 3. EC_{50} of Lumped Species I (Toxic Intermediates) and Nonmineralized Fraction, x, Calculated by Fitting Data Obtained in the CWO of Phenol, o-Cresol, and p-Cresol Using Eqs 19 and 28, Respectively

pollutant	$EC_{50}(I)$ (mg$_C$ L^{-1})	x
PhOH	0.16	0.311
o-C	0.244	0.30
p-C	16.4	0.31

sample containing the pollutant P, $EC_{50}(P)$, that appears in eq 11 was experimentally determined from dilution of the initial sample containing a known amount of the pollutant to obtain the corresponding IC_{50} by means of the Microtox bioassay. The experimental results are summarized in Table 2, expressed as both compound concentrations (mg L^{-1}) and organic carbon concentrations (mg$_C$ L^{-1}), where the latter value is used in eq 18. The $EC_{50}(P)$ literature values found for the three phenols are also included in Table 2.[24] The toxicity units at $\tau = 0$, TU_0, were obtained from the $EC_{50}(P)$ and C_{P0} values using eq 11 as indicated in Table 2.

The $EC_{50}(I)$ and x values obtained by fitting of the experimental data are summarized in Table 3. The pseudokinetic equations obtained for r_1-r_3 are listed in Table 4. The values of the pseudokinetic parameters as functions of temperature were determined by data fitting. Residual sum of squares (SQR) for each pollutant were calculated for TU/TU_0 and TOC/TOC_0 by comparison of experimental data to the predictions of the corresponding pseudokinetic models. These SQR values are reported in Table 5. Predicted values for TU and TOC were calculated by substituting the parameters in Tables 3 and 4 into eqs 18 and 27 at the corresponding time values. These results are plotted as lines in Figures 1−3. As can be seen, a satisfactory fitting was obtained.

Table 4. Pseudo-Kinetic Constants (L g_{AC}^{-1} min^{-1}) Calculated by Fitting Data Obtained in the CWO of Phenol, o-Cresol, and p-Cresol Using Eqs 19 and 28

PhOH	o-C	p-C
$k_1 = \exp(-0.056 - 3470/T)$	$k_1 = \exp(7.95 - 6910/T)$	$k_1 = \exp(17.4 - 10374/T)$
$k_2 = \exp(14.8 - 9450/T)$	$k_2 = \exp(29.1 - 15400/T)$	$k_2 = \exp(107.1 - 13170/T)$
$k_3 = \exp(10.2 - 7667/T)$	$k_3 = \exp(15.2 - 9859/T)$	$k_3 = \exp(8.35 - 6740/T)$

Table 5. Weighted Residual Sum of Squares Corresponding to the Remaining Fractions of TU and TOC Predicted by Substituting the Kinetic Constants in Table 4 into Eqs 19 and 28, Respectively

pollutant	SQR_{TU/TU_0}	SQR_{TOC/TOC_0}
PhOH	249.34	0.041
o-C	204.53	0.063
p-C	0.16	0.037

From the results reported in Table 3, it can be seen that the asymptotic mineralizations achieved, $(1 - x)$, have similar values, about 70%, for the three phenolic pollutants tested. This means that 30% of the initial carbon content is refractory to oxidation under the conditions tested. The good fittings obtained for the TOC profiles (Figures 1b, 2b, and 3b) also validate the assumption of considering that the parameter x is independent of temperature, at least in the range studied here.

By comparison of the values in Tables 2 and 3, it can be seen that the effective nominal concentrations of the initial pollutants are much higher than those determined for the lumped intermediate oxidation species I in the CWO treatment of phenol and o-cresol solutions. This means that compounds that are much more toxic than the original are produced when phenol and o-cresol are fed to the reactor. This explains the marked increase in TUs of the reactor effluent noticed at short residence times (Figures 1a and 2a). Because species I is produced as an intermediate in a serial scheme, a maximum in the TU profile is observed. This corresponds to the maximum concentration achieved for this lumped species. High enough residence times or temperatures must be selected to ensure that the final toxicity of the effluent is under the required level.

In contrast, p-cresol has a lower effective nominal concentration value than its lumped intermediate I. Consequently, the toxicity of the reactor effluent always decreases as the residence time in the reactor increases for this pollutant (Figure 3a).

The adequate fittings obtained for the dimensionless remaining TU profiles (Figures 1a, 2a, and 3a) also validate the assumption of considering the parameter $EC_{50}(I)$ to be independent of temperature, at least in the range studied here.

As can be seen in Table 4, the activation energy for reaction R_2 (corresponding to the disappearance of I to form the nontoxic lumped species D) has higher values than those obtained for R_1 (reaction of P to produce I). These differences are particularly significant when phenol and o-cresol are fed as pollutants. Consequently, the yield of D species increases as the temperature increases, explaining the lower maxima in the TU profiles obtained in the CWO of phenol and o-cresol at higher temperatures (Figures 1a and 2a). Therefore, an increase in operating temperature would lead to a proper detoxification of the inlet.

4. Conclusions

The assessment of the toxicity of industrial wastewaters is required to determine the possibility for direct discharge of the effluents to a conventional WWTP. If a preliminary treatment involving chemical reactions is required before this discharge, the evolution of toxicity must be evaluated and predicted to establish adequate operating conditions because organic intermediates produced in the reaction can be more or less toxic than the initial pollutants. In practice, toxicity predictions requiring a complete estimation of the composition of the mixture with the time would be not viable. In this context, the proposal of lumping strategies yielding simplified pseudokinetic models that allow for the prediction of effluent toxicity units with time as a function of the toxicity of the initial sample and the temperature of the process are very attractive. In this work, an original lumping approach has been developed and tested successfully to predict the detoxification of wastewaters containing organic compounds by degradation technologies. Moreover, the mineralization of the initial sample, which is also a critical parameter defining treatment effectiveness, was also modeled by lumping species and validated by fitting the experimental data.

Notation

A = lumped species for oxidizable organic compounds in the liquid phase as organic carbon content (mg_C L^{-1})

AC = activated carbon

B = lumped species for refractory organic compounds in the liquid phase (mg_C L^{-1})

C_i = concentration of species i (A, P, B, I) expressed as carbon content (mg_C L^{-1})

D = lumped species (sum of CO_2 and biodegradable short-chain acids) (mg_C L^{-1})

E_a/R = activation energy /gas constant (K)

EC_{50} = effective nominal concentration, ($mg_{compound}$ L^{-1} or mg_C L^{-1})

I = lumped species corresponding to the toxic first organic intermediates (mg_C L^{-1})

IC_{50} = ratio of the initial volume of the sample to the volume of sample yielding a 50% reduction of the light emitted by the microorganisms

k = pseudokinetic constant for pollutant oxidation or mineralization (L g_{AC}^{-1} min^{-1})

P = lumped species for the pollutant or pollutant mixture in the initial aqueous sample (mg_C L^{-1})

P_{O_2} = oxygen pressure (bar)

Q_L = liquid flow rate (L min^{-1})

r = reaction rate (mg_C g_{AC}^{-1} min^{-1})

R_j = production rate of compound j (mg_C g_{AC}^{-1} min^{-1})

SQR = residual sum of squares of variable y, $\sum(y_{exp} - y_{calc})^2$, for $y = TU/TU_0$, TOC/TOC_0

T = temperature (°C, K)

TOC = total organic carbon concentration (mg_C L^{-1})

TU = toxicity unit

W = catalyst weight in the reactor (g)

x = overall fractional yield of organic carbon in the liquid phase relative to B

τ = time (batch) or W/Q_L ratio in the fixed-bed reactor

Subscripts

0 = related to the initial conditions or preexponential factor

1, 2, 3 = related to reactions 1−3, repectively

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