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COD/DOC balanced models for the oxidation process of organic compounds

Edgardo Martín Contreras¹

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Abstract

Nowadays, several advanced oxidation and enzymatic processes are available for the removal of organic compounds. Mathematical models are crucial to optimize the operating conditions and to reduce the costs associated with the studied oxidation process. The present work deals with a procedure to develop COD/DOC balanced models to represent the oxidation process of organic compounds. The procedure is of general nature since no hypothesis is made regarding the identity of the organic compounds or the oxidant employed. Using the developed procedure, proposed oxidation pathways always fulfill elemental and electron balances. Several examples of oxidation pathways were studied to demonstrate the usefulness of the procedure. From the analysis of a particular pathway, several restrictions regarding the range of possible values of the model coefficients can be found. These restrictions can be used to enhance the robustness of the fitting procedure of the model by using different types of data, such as COD, DOC and/or the actual concentration of some relevant species. This work will help researchers in areas related to the removal of organic compounds using any oxidation process.

Keywords Dissolved organic carbon · Chemical oxygen demand · Advanced oxidation process · Oxidation pathway · Enzymatic oxidation

Introduction

Nowadays, several advanced oxidation processes (AOP), such as the Fenton and Fenton-like reactions, photo or electro-Fenton, ozonation, and others are available for the oxidation of organic compounds (Babuponnusami and Muthukumar 2014; Doumic et al. 2015; Inchaurredo et al. 2016; Zhou et al. 2016). If the complete mineralization of the target compound is not necessary, enzymatic processes can also be employed (Cabrera et al. 2017; Morales Urrea et al. 2018a, b). As a general rule, during a given oxidation process, several oxidants such as hydrogen peroxide (H_2O_2) and/or ozone (O_3) can be used. In addition to a desirable high degradation efficiency, a key factor concerning the selection of a given oxidation process for treating a particular wastewater is the cost associated with the reagents

employed (Babuponnusami and Muthukumar 2014). In this sense, mathematical models are crucial to optimize the operating conditions and to reduce the costs associated with the studied oxidation process.

Environmental regulations in most countries consider global parameters such as dissolved organic carbon (DOC) or chemical oxygen demand (COD) to evaluate the effluent quality. For practical purposes, it is neither possible nor necessary to develop a detailed model of all the reactions between species that may occur during the oxidation of a given wastewater. In fact, several works in this field report lumped kinetic expressions which are very useful for process design and optimization purposes. In most studies in this topic, authors follow several variables of the process as a function of time, such as COD, DOC, oxidant concentration, pH, and some pertinent organic species (Zazo et al. 2009; Doumic et al. 2013; Babuponnusami and Muthukumar 2014; Inchaurredo et al. 2014). However, the kinetic analysis usually considers just a few of them and frequently there is no attempt to conciliate all the available data applying the restrictions imposed by material and charge balances, even when they indeed exist. In this sense, COD/DOC balanced models overcome this deficiency, helping researchers to state correctly the mathematical

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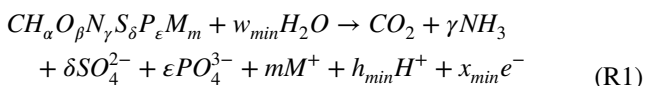
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treatment of the collected data and understand which data are strictly needed.

By definition, a COD/DOC balanced model is a lumped model that fulfills carbon (e.g., DOC) and electron (e.g., COD) balances. These balances can be used to impose restrictions on the model coefficients or to enhance the model robustness by using different types of data, such as COD, DOC and/or the actual concentration of some relevant species. In this sense, the objective of this work is to propose a method to develop COD/DOC balanced models to represent the oxidation process of organic compounds that allow a better analysis of the available data.

Definitions

By definition, the theoretical oxygen demand (ThOD) is the calculated amount of oxygen necessary to oxidize a compound to a given set of oxidation products. If these products are equal to the products obtained during the COD assay, then the ThOD and COD values are equivalent. During the measurement of the COD of a given sample, the carbon from organic compounds is oxidized to CO_2 , sulfur to sulfate, and phosphorous to phosphate (Orhon and Artan 1994). Thus, CO_2 , sulfate, and phosphate are usually assumed as the final products during the calculation of the ThOD. However, the final product obtained in the COD assay from nitrogen-containing compounds depends on the stability of the nitrogenous moiety. Under the typical conditions employed during the COD test, nitrogen from proteins and amino acids (e.g., nitrogen from bacteria) is released as NH_3 , while nitrogen from azo-dyes, for example, is usually oxidized to nitrate. Thus, ThOD depends on the nitrogenous oxidation product assumed in the calculations. For example, the oxidation of one C-mol of a given compound with a general elemental formula $CH_\alpha O_\beta N_\gamma S_\delta P_\epsilon M_m$ considering ammonia as the oxidation product is shown in reaction R1:



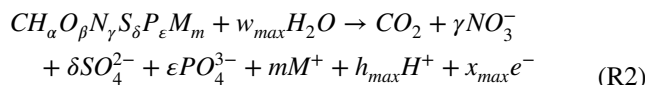
In reaction R1, the product mM^+ represents the sum of charges over all the inert cations of the compound (Stumm and Morgan 1996). Solving the charge balance, and mass balances for hydrogen and oxygen, the following expressions can be obtained:

$$w_{min} = 2 - \beta + 4\delta + 4\epsilon \quad (1)$$

$$h_{min} = 4 + \alpha - 2\beta - 3\gamma + 8\delta + 8\epsilon \quad (2)$$

$$x_{min} = 4 + \alpha - 2\beta - 3\gamma + 6\delta + 5\epsilon + m \quad (3)$$

In the case of some nitrogen-containing compounds (e.g., azo-dyes), nitrogen may be further oxidized to nitrate



where

$$w_{max} = 2 - \beta + 3\gamma + 4\delta + 4\epsilon \quad (4)$$

$$h_{max} = 4 + \alpha - 2\beta + 6\gamma + 8\delta + 8\epsilon \quad (5)$$

$$x_{max} = 4 + \alpha - 2\beta + 5\gamma + 6\delta + 5\epsilon + m \quad (6)$$

The electrons released from R1 and R2 are accepted by the oxidant employed. In the case of molecular oxygen



Combining reactions R1 to R3, the amount of oxygen corresponding to the complete oxidation of one C-mol (z , $gO_2/C\text{-mol}$) of a given organic compound with formula $CH_\alpha O_\beta N_\gamma S_\delta P_\epsilon M_m$ ranges between the following values:

$$z_{min} = \frac{32}{4} x_{min} = \frac{32}{4} (4 + \alpha - 2\beta - 3\gamma + 6\delta + 5\epsilon + m) \quad (7)$$

$$z_{max} = \frac{32}{4} x_{max} = \frac{32}{4} (4 + \alpha - 2\beta + 5\gamma + 6\delta + 5\epsilon + m) \quad (8)$$

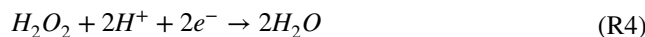
The difference between z_{max} and z_{min} arises from the oxidation of the nitrogen to nitrate. For this reason, compounds devoid of nitrogen ($\gamma=0$) have a unique value of z .

In most cases, the elemental composition of the target compound (or the wastewater) is not known. However, if DOC (in C-mol/L) and COD (in gO_2/L) data are available, z can be obtained from Eq. (9):

$$z = \frac{COD}{DOC} \quad (9)$$

During the treatment of a wastewater with a given oxidation process, several intermediates may appear, yielding in most cases a mixture of compounds with unknown composition. In these cases, the ratio COD/DOC changes as a function of time and it represents an indication of the average oxidation degree of the carbon atoms in the mixture (Doumic et al. 2013).

Instead of oxygen, other oxidants (Ox), such as hydrogen peroxide, or ozone can be used. Even Cr(VI), the true oxidant in the COD assay, can also accept the electrons released from R1 or R2:



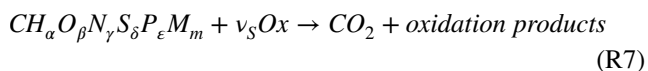
Expressing reactions R3 to R6 per mol of electrons, the following expression can be obtained:

$$1e^- \equiv \frac{1}{4}O_2 \equiv \frac{1}{2}H_2O_2 \equiv \frac{1}{6}O_3 \equiv \frac{1}{3}Cr(VI) \quad (10)$$

Equation (10) can be used to obtain the conversion factor (f_{Ox} , gO₂/molOx) between oxygen units (e.g., from COD values) and other oxidants that are usually employed in different oxidation processes. For example, according to Eq. (10), one mol of electrons that are released from the oxidation of a given compound can reduce 1/4 mol of molecular oxygen to water, or 1/2 mol of hydrogen peroxide to water. Thus, the reduction of one mol of hydrogen peroxide is equivalent to one-half mol of molecular oxygen. Considering the molecular weight of molecular oxygen, the conversion factor for hydrogen peroxide units (mol) to oxygen units (g) is $f_{H_2O_2} = 16 \text{ gO}_2/\text{molH}_2\text{O}_2$. Using a similar procedure, conversion factors corresponding to ozone and Cr(VI) can be obtained: $f_{O_3} = 48 \text{ gO}_2/\text{molO}_3$, $f_{Cr(VI)} = 24 \text{ gO}_2/\text{molCr(VI)}$. These conversion factors are useful for calculating the stoichiometric amount of oxidant required to completely oxidize one mol of C from a given organic compound (ν_S , molOx/C-mol) according to Eq. (11):

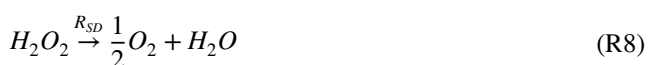
$$\nu_S = \frac{z}{f_{Ox}} \quad (11)$$

where f_{Ox} represents the conversion factor corresponding to the oxidant used (Ox). According to this definition, the complete oxidation of one C-mol of an organic compound with formula $CH_\alpha O_\beta N_\gamma S_\delta P_\epsilon M_m$ by a given oxidant (Ox) can be represented by reaction R7



where the value of ν_S depends on the oxidation products (R1, R2) and on the oxidant used (R3 to R6).

It must be noted that the stoichiometric coefficient ν_S in reaction R7 represents the lower limit for the consumption of oxidant due to the complete oxidation of one C-mol of the target compound. In most cases, the actual consumption of oxidant often increases due to the self-decomposition reactions. For example, overall self-decomposition reactions for hydrogen peroxide and ozone can be represented by reaction R8 as follows (Beltrán 2004; Babuponnusami and Muthukumar 2014):



where R_{SD} represents the self-decomposition rate of the oxidant. It must be noted that if the rate of these decomposition

reactions is much lower than the oxidation rate (R7), the actual stoichiometric coefficient (ν_A) will be close to the stoichiometric one (ν_S).

As a general rule, when a given process is used to oxidize a single compound, a mixture of compounds, or a wastewater, molecular oxygen reactivity toward the organic compounds is usually negligible under the conditions employed. In fact, high oxygen partial pressures (0.5–1.25 MPa) and temperatures (373–413 K) are necessary to use molecular oxygen as the oxidant (Zapico et al. 2015). For this reason, in most cases the molecular oxygen generated by reactions R8 or R9 can be considered as an inert product. Even though the oxygen released from self-decomposition reactions of the oxidant could oxidize the organic matter, from the stoichiometric point the net effect is the consumption of the oxidant used to oxidize the organic compound. In these cases, oxygen plays the role of an intermediate oxidant during the oxidation process.

Reaction R7 represents the stoichiometric relationship between reagents and products during a given oxidation process. This overall reaction could proceed in different ways, such as consecutive or parallel reactions, in both cases with the formation of many intermediates, for example. Because of the great diversity of oxidation pathways, it is not possible to develop a generalization. For this reason, in the following sections, some particular cases are discussed.

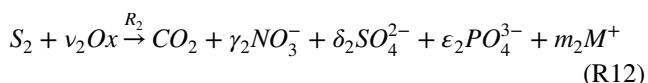
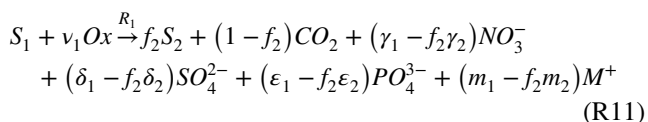
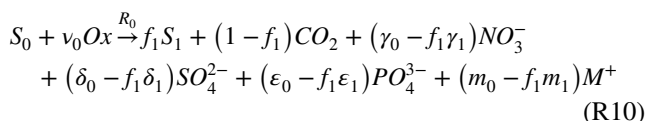
Examples of COD/DOC balanced oxidation pathways

Consecutive degradation pathway with complete oxidation

In this case, it is assumed that the oxidation pathway of an organic compound (or a mixture of compounds) with formula $CH_{\alpha 0} O_{\beta 0} N_{\gamma 0} S_{\delta 0} P_{\epsilon 0} M_{m 0}$ (S_0) with a given oxidant (Ox) proceeds in three sequential steps. In the first steps, two intermediates $CH_{\alpha 1} O_{\beta 1} N_{\gamma 1} S_{\delta 1} P_{\epsilon 1} M_{m 1}$ (S_1) and $CH_{\alpha 2} O_{\beta 2} N_{\gamma 2} S_{\delta 2} P_{\epsilon 2} M_{m 2}$ (S_2) are produced. Finally, during the third step, S_2 is mineralized to carbon dioxide, nitrate, sulfate and phosphate. It must be pointed out that model intermediates S_1 or S_2 could be actual compounds, or a mixture of compounds that, from a practical standpoint, can be represented as a single compound. This approach is widely used by several authors. For example, available kinetic models for the classic Fenton process vary in complexity. The simplest models use empirical kinetic expressions to represent the experimental data (Khan et al. 2009; Ramírez et al. 2009; Bach et al. 2010; Emami et al. 2010; Inchaurredo et al. 2012). Several researchers suggested simplified

reaction mechanisms and proposed lumped models in which organic compounds are grouped according to their susceptibility to oxidation (Guo and Al-Dahhan 2003; Zazo et al. 2009). Finally, although detailed models that describe actual elementary reactions are also available (Kang et al. 2002; Villota et al. 2007; Pontes et al. 2010), these models are usually excessively complex to be useful in actual wastewater treatment facilities.

Each proposed oxidation step can be represented by reactions R10 to R12 as follows:



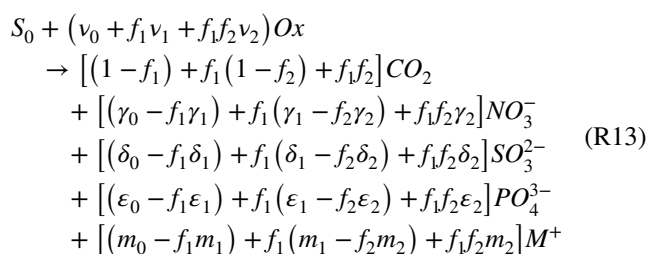
where R_i represents the oxidation rate of S_i .

For each oxidation step (R10, R11, R12), stoichiometric coefficients arise from the elementary mass balance. The stoichiometric coefficient f_i represents the fraction of the organic carbon of the compound S_{i-1} that appears in the oxidation product S_i ; according to this definition, $f_i \leq 1$. Moreover, because all reactions are based on one C-mol, the amount of released CO_2 during each step is $(1 - f_i)$. For this reason, if during a given oxidation step no CO_2 is released then $f_i = 1$. Another important constraint arises from the fact that each stoichiometric coefficient must be positive or zero. For example, in the case of nitrate:

$$(\gamma_i - f_{i+1} \gamma_{i+1}) \geq 0 \quad (12)$$

If during a given oxidation step no nitrate is released, then $\gamma_i - f_{i+1} \gamma_{i+1} = 0$. Taking into account that $f_i \leq 1$, it can be concluded that $\gamma_i \leq \gamma_{i+1}$. Conversely, if a given partial oxidation product S_i is devoid of nitrogen then $\gamma_i = 0$. Also, it is important to note that, if γ_i and γ_{i+1} are known, then Eq. (12) imposes that $f_{i+1} \leq \frac{\gamma_i}{\gamma_{i+1}}$. Moreover, once nitrogen is released from the original compound, further oxidation products are also devoid of nitrogen ($\gamma_{i+1} = \gamma_{i+2} = \dots = 0$). Similar considerations are valid for the other stoichiometric coefficients (δ , ε , m).

The overall oxidation reaction (R13) can be obtained by combining R10 to R12:



It must be noted that reaction R13 fulfill all the elemental mass balances. For example, considering that S_0 stands for $CH_{\alpha_0} O_{\beta_0} N_{\gamma_0} S_{\delta_0} P_{\varepsilon_0} M_{m_0}$, mass balance corresponding to P is:

$$\varepsilon_0 = (\varepsilon_0 - f_1 \varepsilon_1) + f_1(\varepsilon_1 - f_2 \varepsilon_2) + f_1 f_2 \varepsilon_2 \quad (13)$$

Equation (13) demonstrates that the proposed reactions R10 to R12 satisfy the mass balance for P for any value of ε_i and f_i . Similar considerations are also valid for C, N, S, and M. Moreover, from the comparison between R7 and R13, the following equation was obtained:

$$\nu_S = \nu_0 + f_1 \nu_1 + f_1 f_2 \nu_2 \quad (14)$$

Equation (14) is a very important result because it poses a restriction involving the coefficients that represent the degree of mineralization (f_i) and the consumption of oxidant (ν_i) during each step (i) of the proposed oxidation pathway. This equation can be used to reduce one fitting variable during the fitting of the proposed model to the available experimental data, improving the results obtained in of the fitting procedure.

From the environmental standpoint, DOC and COD values are usually more important than the actual concentration of single compounds. In this sense, COD/DOC balanced models can help to calculate these parameters as follows. According to the proposed reactions (R10 to R12), if $[S_i]$ is the concentration (expressed in C-mol/L) of compound i, the DOC of the reaction mixture is

$$DOC = \sum_{i=0}^{i=2} [S_i] \quad (15)$$

where the summation is performed over the 3 compounds of the proposed pathway. In a similar manner, the COD value corresponding to all the organic compounds in the mixture is:

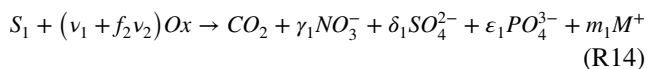
$$COD = \sum_{i=0}^{i=2} z_i [S_i] \quad (16)$$

Although a priori z_i values are not known, in a COD/DOC balanced model the coefficients z_i (gO₂/C-mol) of Eq. (16) can be related to the corresponding ν_i (molOx/C-mol) as follows. According to reaction R12, ν_2 mol of oxidant are

consumed for the complete oxidation of one C-mol of S_2 . Thus, considering Eq. (11):

$$z_2 = f_{Ox}v_2 \tag{17}$$

In contrast with R12, in R11 the partial oxidation of S_1 produces f_2 C-mol of S_2 . The complete oxidation of S_1 can be obtained from the combination of R11 and R12:



According to reaction R14

$$z_1 = f_{Ox}(v_1 + f_2v_2) = f_{Ox}v_1 + f_2z_2 \tag{18}$$

Equation (18) indicates that the complete oxidation of S_1 is the result of its partial oxidation to S_2 (represented by the term $f_{Ox}v_1$), followed by the complete oxidation of f_2 C-mol of S_2 (f_2z_2). Using a similar procedure, z_0 can be obtained:

$$z_0 = f_{Ox}v_0 + f_1z_1 \tag{19}$$

Besides, considering the global reaction R7 and Eq. (11), z_0 can also be obtained using Eq. (20):

$$z_0 = f_{Ox}v_S \tag{20}$$

By the combination of Eqs. (17) to (20)

$$f_{Ox}v_S = f_{Ox}v_0 + f_1(f_{Ox}v_1 + f_2f_{Ox}v_2) \tag{21}$$

It must be noted that Eq. (14) can also be obtained by simplification of Eq. (21), demonstrating the reliability of the developed procedure. Finally, it must be remembered that v_S represents the stoichiometric amount of oxidant for the complete oxidation of S_0 . As a general rule, due to the presence of self-decomposition reactions, the actual oxidant consumption (v_A) is higher than the stoichiometric one (v_S). If this is the case, self-decomposition reactions (SD) must be taken into account to calculate v_A . Besides, from the difference between v_A and v_S , the contribution of the self-decomposition reactions on the consumption of oxidant can be evaluated from the experimental data.

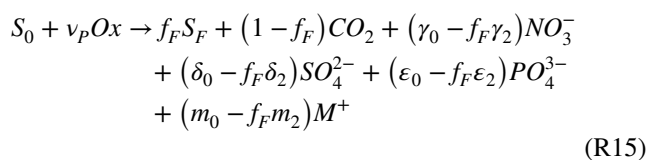
Table 1 shows the stoichiometric matrix corresponding to the analyzed degradation pathway. Because this is a COD/DOC balanced model, DOC and COD values can be computed using Eqs. (15) and (16). Conversely, COD and DOC

data contain information concerning the evolution of the proposed compounds S_i . Moreover, nitrate, sulfate, phosphate, and CO_2 measurements can also be used to obtain a better estimation of all the stoichiometric and kinetic coefficients corresponding to the analyzed oxidation pathway. At this point, it is worth mentioning that from a stoichiometric perspective, the actual expressions corresponding to the reaction rates are not relevant. For this reason, this issue is out of the scope of the present work.

Consecutive degradation pathway with partial oxidation

In some cases, the complete mineralization of the tested compound (or a mixture of compounds) requires huge amounts of oxidant and/or long reaction times which are not technically feasible. Keeping in mind that the main objective of a wastewater treatment process is the local law compliance, for most purposes, it is neither necessary nor practical to achieve complete oxidation. For example, in a recent work, Hinojosa Guerra et al. (2019) studied the oxidation of amoxicillin and paracetamol by a photo-Fenton solar process. These authors reported that DOC removals ranged from 6 to 26% due to the accumulation of hydroxylated intermediates under the tested conditions. To improve the DOC conversion, high amounts of H_2O_2 , as well as longer reaction times, would be necessary.

According to the example depicted in the previous section, the partial oxidation of S_0 with an oxidant (Ox) proceeded up to the formation of S_2 . In the present example, it is assumed that S_2 is a non-oxidizable compound under the experimental conditions. Table 2 shows the stoichiometric matrix corresponding to the example analyzed in the present section. Considering only the initial and final states, the oxidation of S_0 to a given $S_F = S_2$ can be represented by reaction R15



where v_p represents the stoichiometric amount of oxidant necessary to partially oxidize S_0 to S_F , and f_F is the fraction

Table 1 Stoichiometric matrix corresponding to the complete oxidation of an organic compound (or a mixture of compounds) with formula $CH_{\alpha_0}O_{\beta_0}N_{\gamma_0}S_{\delta_0}P_{\epsilon_0}M_{m_0}$ (S_0) using a given oxidant (Ox)

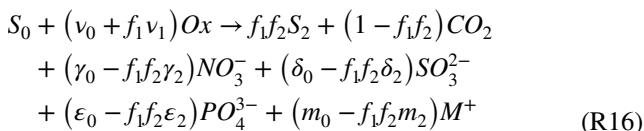
Step	S_0	S_1	S_2	Ox	CO_2	NO_3^-	SO_4^{2-}	PO_4^{3-}	M^+	Rate
1	-1	f_1		$-v_0$	$1 - f_1$	$\gamma_0 - f_1\gamma_1$	$\delta_0 - f_1\delta_1$	$\epsilon_0 - f_1\epsilon_1$	$m_0 - f_1m_1$	R_0
2		-1	f_2	$-v_1$	$1 - f_2$	$\gamma_1 - f_2\gamma_2$	$\delta_1 - f_2\delta_2$	$\epsilon_1 - f_2\epsilon_2$	$m_1 - f_2m_2$	R_1
3			-1	$-v_2$	1	γ_2	δ_2	ϵ_2	m_2	R_2

Table 2 Stoichiometric matrix corresponding to the partial oxidation of S_0 to S_2 using a given oxidant (Ox)

Step	S_0	S_1	S_2	Ox	CO_2	NO_3^-	SO_4^{2-}	PO_4^{3-}	M^+	Rate
1	-1	f_1		$-\nu_0$	$1-f_1$	$\gamma_0-f_1\gamma_1$	$\delta_0-f_1\delta_1$	$\epsilon_0-f_1\epsilon_1$	$m_0-f_1m_1$	R_0
2		-1	f_2	$-\nu_1$	$1-f_2$	$\gamma_1-f_2\gamma_2$	$\delta_1-f_2\delta_2$	$\epsilon_1-f_2\epsilon_2$	$m_1-f_2m_2$	R_1

of the initial organic carbon of S_0 that remains in solution due to the presence of S_2 . It must be noted that, according to the analyzed oxidation pathway, in this case, S_F corresponds to S_2 .

On the other hand, combining reactions R10 and R11, the partial oxidation of S_0 to S_2 can be obtained as follows:



From the comparison between R15 and R16, the following relationships can be obtained:

$$\nu_P = \nu_0 + f_1\nu_1 \quad (22)$$

$$f_F = f_1f_2 \quad (23)$$

By definition, the complete oxidation of S_0 is the result of its partial oxidation to produce f_F C-mol of S_2 ($f_{Ox}\nu_P$), followed by the complete oxidation of S_2 (f_Fz_2):

$$z_0 = f_{Ox}\nu_P + f_Fz_2 \quad (24)$$

For example, knowing the initial and final values corresponding to COD and DOC, the following stoichiometric coefficients can be obtained:

$$z_0 = \frac{COD_0}{DOC_0} \quad (25)$$

$$z_2 = z_F = \frac{COD_F}{DOC_F} \quad (26)$$

$$f_F = \frac{DOC_F}{DOC_0} \quad (27)$$

Then, combining Eqs. (24) to (27)

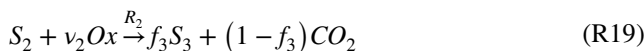
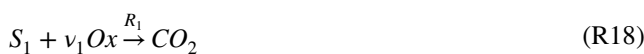
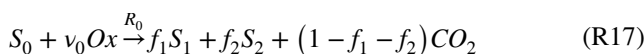
$$COD_0 = TOC_0f_{Ox}\nu_P + COD_F \quad (28)$$

In other words, the difference between initial and final COD values represents the stoichiometric amount of oxidant (expressed in oxygen units) necessary to oxidize the sample from the initial oxidation state to a given final one. Thus, even when initial and final species are not known, the oxidant employed exclusively to partially oxidize the sample (ν_P) can be obtained from experimental data (Eq. 28). Moreover,

if data corresponding to the actual oxidant consumption (ν_A) are available, from the difference between ν_A and ν_P the contribution of the self-decomposition reactions to the overall consumption of oxidant can be evaluated. Finally, it must be pointed out that Eq. (28) is of general nature, since it is based on experimental data, without making a hypothesis regarding the identity of the organic compounds that are present in the reaction mixture.

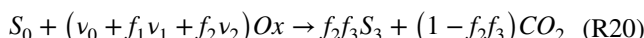
Parallel pathways with partial oxidation

This case is the most frequent one when studying the oxidation of xenobiotics. Examples of this type of oxidation pathway can be found in Feng et al. (2017), Gan et al. (2018), and Lim et al. (2019). Those works report that the oxidation of the target compound (S_0) by the tested oxidant (Ox) proceeds via two intermediates S_1 and S_2 . However, the subsequent reactions depend on the case analyzed. In the present pathway, it was assumed that S_1 is oxidized to CO_2 but the oxidation of S_2 releases a non-oxidizable (e.g., inert) product S_3 . To abbreviate the analysis, we will focus attention on the carbon balance only. The complete stoichiometric matrix corresponding to this case can be found in “Appendix”. The proposed reactions are

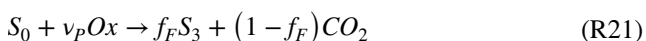


According to these reactions, six stoichiometric coefficients are necessary to completely define the oxidation pathway: ν_0 , ν_1 , ν_2 , f_1 , f_2 , and f_3 . Besides, four more coefficients are required to calculate the COD of the reaction mixture: z_0 , z_1 , z_2 , and z_3 . However, it must be noted that the final product of the analyzed oxidation pathway is S_3 ; thus, in this case $S_F=S_3$. Hence, among the ten coefficients, z_0 and $z_F = z_3$ can be evaluated from the initial and final values of COD and DOC via Eqs. (25) and (26).

Combining reactions R17 to R19, the overall oxidation reaction is:



Besides, according to the analyzed pathway, the overall reaction is



Thus, from the comparison between reactions R20 and R21, and considering Eqs. (27) and (28):

$$\nu_P = \frac{COD_0 - COD_f}{DOC_0 f_{Ox}} = \nu_0 + f_1 \nu_1 + f_2 \nu_2 \quad (29)$$

$$f_F = f_2 f_3 = \frac{DOC_f}{DOC_0} \quad (30)$$

Equation (29) imposes a restriction regarding the combination of possible values of the coefficients. Moreover, taking into account that all stoichiometric coefficients are non-negative values, coefficients $\nu_1, \nu_2, f_1,$ and f_2 can only adopt values that satisfy the following expression:

$$f_1 \nu_1 + f_2 \nu_2 \leq \nu_P \quad (31)$$

Because reaction R18 represents the complete oxidation of S_1, z_1 is simply

$$z_1 = f_{Ox} \nu_1 \quad (32)$$

According to reaction R19, the complete oxidation of S_2 is the result of its oxidation to S_3 , followed by the complete oxidation of S_3 , thus

$$z_2 = f_{Ox} \nu_2 + f_3 z_3 \quad (33)$$

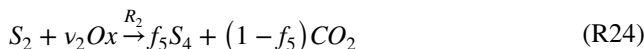
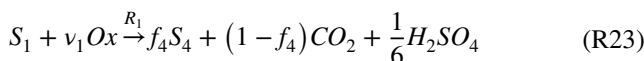
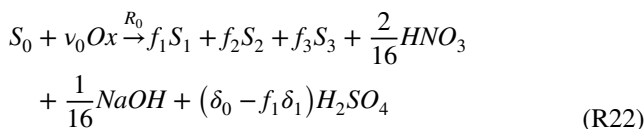
In a similar manner, considering reaction R17

$$z_0 = f_{Ox} \nu_0 + f_1 z_1 + f_2 z_2 \quad (34)$$

Although the analyzed pathway contains ten stoichiometric coefficients ($\nu_0, \nu_1, \nu_2, f_1, f_2, f_3, z_0, z_1, z_2, z_3$), seven relationships between them were derived from the above analysis (Eqs. 25, 26, 29, 30, 32, 33, 34). Therefore, if data concerning the evolution of COD and DOC of the reaction mixture as a function of time are available, only three coefficients must be fitted to completely define the stoichiometry of the pathway analyzed. According to this result, the convenience of developing a COD/DOC balanced model is evident.

Application of a COD/DOC balanced model to a real case

This example is included to demonstrate the usefulness of a COD/DOC balanced model applied to a real case. Chahbane et al. (2007) studied the oxidation of Orange II by H_2O_2 (Ox) catalyzed by iron(III) complexed to tetra amido macrocyclic ligands (Fe-TAML) in aqueous solutions. According to these authors, the first step (R22) is the oxidation of Orange II (S_0) to give 4-hydroxybenzenesulfonic acid (S_1), phthalic acid (S_2), and other unidentified organic compounds (S_3). While under the excess of H_2O_2 the unidentified products (S_3) are stable, 4-hydroxybenzenesulfonic acid (S_1) and phthalic acid (S_2) are further oxidized to give a mixture (S_4) of oxalate, glycolate, formate, and CO_2 (Table 3). The main findings reported by Chahbane et al. (2007) can be represented by the following scheme



In reaction R22, it was assumed that the unidentified products (S_3) are devoid of nitrogen and sulfur and that the nitrogen from Orange II is oxidized to nitrate. Also, it is important to note that the term $(\delta_0 - f_1 \delta_1)$ must be introduced in reaction R22 to close the sulfur balance. The stoichiometric coefficients $\delta_0 = \frac{1}{16}$, and $\delta_1 = \frac{1}{6}$ represent the sulfur content per C-mol of Orange II and 4-hydroxybenzenesulfonic acid, respectively (Table 3). Because the term $(\delta_0 - f_1 \delta_1)$ must be a positive value, it can be concluded that $f_1 \leq \frac{\gamma_0}{\gamma_1} = 0.375$.

According to reaction R22, one C-mol of Orange II is converted to $S_1, S_2,$ and S_3 . Thus, from the carbon balance of reaction R2, Eq. (35) can be obtained

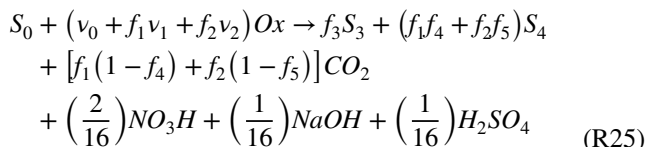
Table 3 Species employed in the COD/DOC balanced model to represent the oxidation of Orange II (S_0) by H_2O_2 (Ox) catalyzed by iron(III) complexed with tetra amido macrocyclic ligands (Fe-TAML) in aqueous solutions (Chahbane et al. 2007)

Species	Compound	C-mol based formula	z_i (gO ₂ /C-mol)
S_0	Orange II	$CH_{\left(\frac{11}{16}\right)} O_{\left(\frac{4}{16}\right)} N_{\left(\frac{2}{16}\right)} S_{\left(\frac{1}{16}\right)} Na_{\left(\frac{1}{16}\right)}$	$z_0 = 42$
S_1	4-hydroxybenzenesulfonic acid	$CHO_{\left(\frac{4}{6}\right)} S_{\left(\frac{1}{6}\right)}$	$z_1 = 37.3$
S_2	Phthalic acid	$CH_{\left(\frac{6}{8}\right)} O_{\left(\frac{4}{8}\right)}$	$z_2 = 30$
S_3	Unknown products	–	–
S_4	A mixture composed by oxalate, glycolate and formate	–	$z_4 = 8-24$

$$1 = f_1 + f_2 + f_3 \tag{35}$$

With regard to reaction R23, because S₄ represents a mixture composed of oxalate, glycolate and formate, the oxidation of 4-hydroxybenzenesulfonic acid must release all the sulfur of S₁ ($\delta_1 = \frac{1}{6}$).

The overall oxidation of Orange II to the final products (S₃, S₄) proposed by Chahbane et al. (2007) is as follows:



The stoichiometric amount of hydrogen peroxide (v_p) necessary to oxidize one C-mol of Orange II to the proposed final products is given by Eq. (36)

$$v_p = \frac{COD_0 - COD_f}{DOC_0 f_{Ox}} = v_0 + f_1v_1 + f_2v_2 \tag{36}$$

where $f_{Ox} = 16 \text{ gO}_2/\text{molH}_2\text{O}_2$.

According to this example, DOC and COD values corresponding to the reaction mixture can be obtained from the concentrations of the model species:

$$DOC = [S_0] + [S_1] + [S_2] + [S_3] + [S_4] \tag{37}$$

$$COD = z_0[S_0] + z_1[S_1] + z_2[S_2] + z_3[S_3] + z_4[S_4] \tag{38}$$

Assuming that at the beginning of the experiment the reaction mixture only contains Orange II, initial DOC (DOC_i) and COD (COD_i) values are:

$$DOC_i = [S_0]_i \tag{39}$$

$$COD_i = z_0[S_0]_i \tag{40}$$

where $[S_0]_i$ represents the initial concentration of Orange II.

Although DOC and COD change as the oxidation proceeds, their final values can be calculated as follows. Reaction R25 indicates that under the excess of oxidant, for each C-mol of S₀ oxidized, f_3 C-mol of S₃ and $(f_1f_4 + f_2f_5)$ C-mol of S₄ are obtained. Accordingly, the reaction mixture DOC and COD final values are:

$$DOC_f = (f_3 + f_1f_4 + f_2f_5)[S_0]_i \tag{41}$$

$$COD_f = [z_3f_3 + z_4(f_1f_4 + f_2f_5)][S_0]_i \tag{42}$$

Then, from the combination of Eqs. (39) to (42) the following is obtained:

$$\frac{DOC_f}{DOC_i} = f_3 + f_1f_4 + f_2f_5 \tag{43}$$

$$\frac{COD_f}{DOC_i} = z_3f_3 + z_4(f_1f_4 + f_2f_5) \tag{44}$$

Considering reactions R22 to R24, the following oxidation degree balances can be derived:

$$z_0 = v_0f_{Ox} + f_1z_1 + f_2z_2 + f_3z_3 \tag{45}$$

$$z_1 = v_1f_{Ox} + f_4z_4 \tag{46}$$

$$z_2 = v_2f_{Ox} + f_5z_4 \tag{47}$$

It must be noted that Eq. (36) can also be obtained from the combination of Eqs. (39), (40), (42), and (45) to (47), demonstrating the reliability of the procedure.

In summary, the proposed oxidation pathway of Orange II by hydrogen peroxide catalyzed by iron(III) complexed by tetra amido macrocyclic ligands (Fe-TAML) is composed of three coefficients related to the consumption of the oxidant during each oxidation step (v_0, v_1, v_2), five coefficients that represent the carbon flow from Orange II to intermediates and final species (f_1, f_2, f_3, f_4, f_5), and five coefficients that are necessary to calculate the COD of the reaction mixture (z_0, z_1, z_2, z_3, z_4). Among these 13 coefficients, z_0, z_1 , and z_2 can be obtained from the ThOD corresponding to S₀ (Orange II), S₁ (4-hydroxybenzenesulfonic acid), and S₂ (phthalic acid), respectively. Moreover, taking into account that S₄ represents a mixture composed of oxalate, glycolate and formate, z_4 must range from 8 gO₂/C-mol in the case of oxalate, to 24 gO₂/C-mol if the product is glycolate only (Table 3). From the analysis of the oxidation pathway, four equations (Eqs. 35, 45, 46, 47) that relate several coefficients were obtained. Additionally, if initial and final DOC and COD values under the excess of oxidant are known, Eqs. (36), (43), and (44) can be used to further reduce the degrees of freedom of the model.

A simulation exercise corresponding to the reaction studied by Chahbane et al. (2007) was performed to demonstrate the convenience of developing a COD/DOC balanced model. Table 4 shows the stoichiometric matrix and the assumed kinetic expressions; the corresponding coefficients are shown in Table 5. It must be remarked that those kinetic expressions were adopted for simulation purposes only. Figure 1 shows the simulated concentration profiles of the model species as a function of time. While the concentration of Orange II (S₀, Fig. 1a) is easy to follow by absorbance measurements at 485 nm, intermediates and final species absorb in the UV-region (Morales Urrea et al. 2018a, b). Chahbane et al. (2007) showed that absorbance at 350 nm first increases and then

decreases due to the formation and degradation of an intermediate. This behavior can be represented by the model according to the concentration profiles corresponding to the intermediates S1 and S2 (Fig. 1b). In addition to the individual species (Fig. 1a, b), nitrate, sulfate (Fig. 1c), hydrogen peroxide, COD, and DOC are also depicted (Fig. 1d). COD, DOC, and hydrogen peroxide are routine parameters used to follow oxidation reactions. Thus, these data can be employed to obtain the coefficients of the developed COD/DOC balanced oxidation pathway. Moreover, nowadays nitrate and sulfate sensors are available to monitor this reaction on a real-time basis. The use of these data during the fitting procedure could enhance the reliability of the obtained coefficients.

$$R_0 = \frac{K_I K_{II} [Fe - TAML][Ox][S_0]}{K_I [Ox] + K_{II} [S_0]}$$

$$R_1 = k_1 [S_1][Ox]$$

$$R_2 = k_2 [S_2][Ox]$$

Conclusions

The present work deals with a procedure to develop COD/DOC balanced models to represent the oxidation process of organic compounds. Because no hypothesis is made regarding the identity of the organic compounds or the employed oxidant, using the procedure proposed in this work, the developed oxidation pathways always fulfill elemental and electron balances. From the analysis of a particular pathway, several restrictions regarding the possible values that the model coefficients can adopt can be found. Moreover, these restrictions can be used to enhance the robustness of the fitting procedure of the model by using different types of data, such as COD, DOC and/or the actual concentration of some relevant species, for example. This work will help researchers in areas related to the oxidation of organic compounds.

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Table 5 Stoichiometric and kinetic coefficients corresponding to the oxidation of Orange II (S₀) by H₂O₂ (Ox) catalyzed by iron(III) complexed by tetra amido macrocyclic ligands (Fe-TAML) in aqueous solutions

Stoichiometric coefficients		Kinetic coefficients	
f ₁ (C-mol/C-mol)	0.3*	K _I (mM ⁻¹ min ⁻¹)	84**
f ₂ (C-mol/C-mol)	0.5*	K _{II} (C-mM ⁻¹ min ⁻¹)	112**
f ₃ (C-mol/C-mol)	0.2 (Eq. 35)	k ₁ (mM ⁻¹ min ⁻¹)	0.05*
f ₄ (C-mol/C-mol)	0.1*	k ₂ (mM ⁻¹ min ⁻¹)	0.20*
f ₅ (C-mol/C-mol)	0.1*		
v ₀ (molOx/C-mol)	0.88 (Eq. 45)		
v ₁ (molOx/C-mol)	2.28 (Eq. 46)		
v ₂ (molOx/C-mol)	1.45 (Eq. 47)		
z ₃ (gO ₂ /C-mol)	24*		
z ₄ (gO ₂ /C-mol)	8*		

*Assumed values for simulation purposes only

**Adapted from Chahbane et al. (2007)

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Appendix: COD/DOC balanced models to represent the oxidation of organic compounds

Parallel pathways with partial oxidation

In this example, the oxidation of S₀ by an oxidant (Ox) produces two intermediates S₁ and S₂. While S₁ is further oxidized to CO₂, the oxidation of S₂ release a non-oxidizable product S₃. Considering that the elemental composition of a given compound S_i is CH_{α_i}O_{β_i}N_{γ_i}S_{δ_i}P_{ε_i}M_{mi}, the reaction scheme to represent this case is the following:

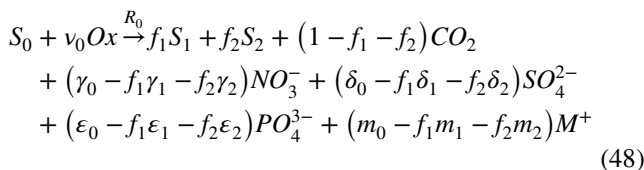


Table 4 Stoichiometric matrix corresponding to the oxidation of Orange II (S₀) by H₂O₂ (Ox) catalyzed by iron(III) complexed by tetra amido macrocyclic ligands (Fe-TAML) in aqueous solutions

Process ↓	Species								Rate (mM/min)
	S ₀	S ₁	S ₂	S ₃	S ₄	Ox	NO	SO	
R22	-1	f ₁	f ₂	f ₃		-v ₀	2/16	δ ₀ - f ₁ δ ₁	R ₀ *
R23		-1			f ₄	-v ₁		1/6	R ₁ **
R24			-1		f ₅	-v ₂			R ₂ **

*Adapted from Chahbane et al. (2007)

**Assumed expressions for simulation purposes only

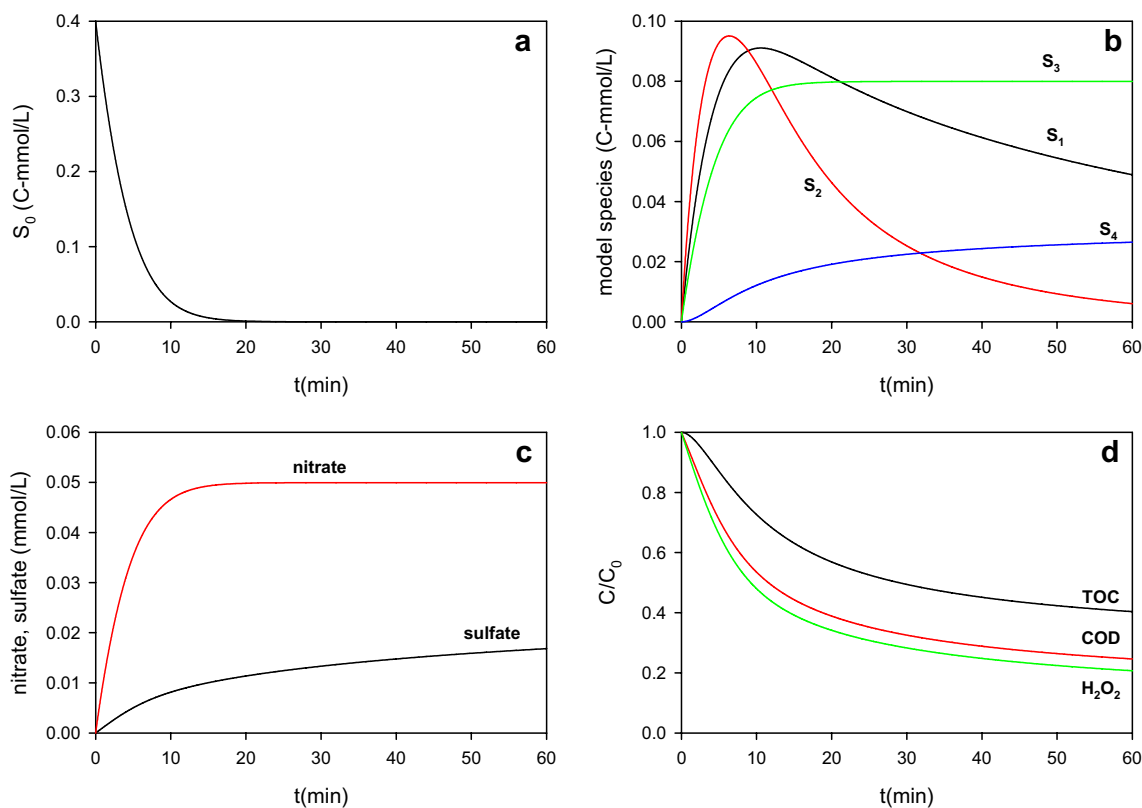
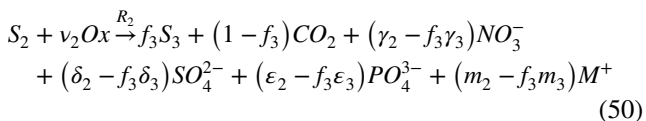
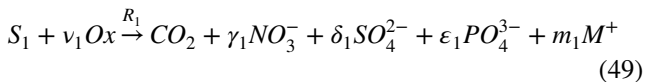


Fig. 1 Simulated concentration profiles of **a** S_0 ; **b** S_1 , S_2 , S_3 , S_4 ; **c** nitrate, sulfate, and **d** DOC, COD, and H_2O_2 , corresponding to the oxidation of Orange II (S_0) by H_2O_2 catalyzed by iron(III) complexed to tetra amido macrocyclic ligands (Fe-TAML) in

aqueous solutions. Stoichiometric and kinetic coefficients are depicted in Tables 4 and 5. Initial concentrations are the following: $[H_2O_2] = 1 \text{ mmol/L}$, $[Fe - TAML] = 0.003 \text{ mmol/L}$, $[S_0] = 0.4 \text{ mmol/L}$

Table 6 Stoichiometric matrix corresponding to the analyzed pathway

Step	S_0	S_1	S_2	S_3	Ox	CO_2	NO_3^-	SO_4^{2-}	PO_4^{3-}	M^+	Rate
1	-1	f_1	f_2		$-v_0$	$1 - f_1 - f_2$	$\gamma_0 - f_1\gamma_1 - f_2\gamma_2$	$\delta_0 - f_1\delta_1 - f_2\delta_2$	$\epsilon_0 - f_1\epsilon_1 - f_2\epsilon_2$	$m_0 - f_1m_1 - f_2m_2$	R_0
2		-1			$-v_1$	1	γ_1	δ_1	ϵ_1	m_1	R_1
3			-1	f_3	$-v_2$	$1 - f_3$	$\gamma_2 - f_3\gamma_3$	$\delta_2 - f_3\delta_3$	$\epsilon_2 - f_3\epsilon_3$	$m_2 - f_3m_3$	R_2



See Table 6.

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