



## Lumped kinetic models for single ozonation of phenolic effluents

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### ABSTRACT

In this work, the mineralization of a phenolic wastewater was investigated by several lumped kinetic models to predict the total organic carbon depletion during single ozonation of a mixture of six phenolic compounds present in olive oil mill wastewater. Firstly, the kinetic equations were developed in terms of lumped compounds representing the parent pollutants and reaction intermediates according different models: First-Order Kinetic (FOKM, with one oxidation step), Two Step First Order Kinetic (TSFOKM, including also and intermediate path), Modified First-Order Kinetic (MFOKM, adding initial non-oxidizable pollutants to the FOKM), Lumped Kinetic (LKM, accounting for non-oxidizable species production), Generalized Kinetic Model (GKM, where, besides the direct mineralization step, formation and degradation of intermediates provide a three step alternative model) and Modified Generalized Kinetic Models (MGKM, a five step proposal with the addition of two paths accounting for non-oxidizable species possible to be produced from the oxidation of raw or intermediate compounds). Secondly, the behavior of these various models was studied at different operational conditions. The FOKM failed to describe the process while TSFOKM incorporates the drawback of requiring the choice of a transition point between the two types of oxidation behaviors. MFOKM, assuming the presence of refractory compounds in the initial wastewater, was rejected since all the parent phenolic compounds were totally removed from the effluent along the treatment. LKM gave good agreement with the experimental results at low ozone inlet concentrations, due to the high recalcitrant character of the organic intermediates that were formed. Nevertheless, for higher ozone inlet concentration some by-products degradation occurs, which is not predicted by this model. Finally, the GKM fitted satisfactorily the laboratorial data with errors in the range of  $\pm 10\%$  and, even with the shortcoming of involving a large number of parameters, MGKM was the most reliable model to describe this complex process.

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### 1. Introduction

Environment protection is one of the key challenges to be faced by mankind this century. In countries whose economy is based upon agro-industries such as Portugal and Mediterranean countries, Olive Mills Wastewaters (OMWs) pose serious environmental problems. Traditional solutions are not suitable because of the bio-recalcitrant character of these effluents mainly caused by their high phenolic content (TPh) which implies the development of chemical methodologies to remediate them. Ozonation is a feasible technology to eliminate TPh due to the high reactivity of molecular ozone with activated aromatic rings and it is industrially interesting since occurs at room conditions of pressure and temperature reducing, hence, the operational costs associated to the treatment.

A crucial issue for the design of industrial units is the kinetic model that is able to describe the reaction process. In real wastew-

aters, normally characterized by a complex mixture of chemical species, it is impossible to follow single compounds abatement, being, therefore, of major importance to develop kinetic equations for lumped compounds representing groups of pollutants. In the non-catalytic ozonation domain, the kinetic models proposed in the literature are related with the abatement of different model compounds, such as phenolic acids [1–3] and low molecular weight acids [4–6]. Considering lumped parameters, some studies have been done in this ambit such as those from Beltran-Heredia et al. [7], which developed a first order model with respect to the Chemical Oxygen Demand (COD) and to the Aromaticity (A) during the ozonation treatment of black-olive wastewater. Shang et al. [8] used a first order kinetic model to describe Total Organic Carbon (TOC) concentration during the ozonation of aqueous solutions of mono-chlorophenols. Azevedo et al. [9] compared a Lumped Kinetic Model in series and the Generalized Kinetic Model (GKM) to describe TOC removal during the catalytic ozonation of phenol at different medium salinities. GKM gave a better representation of the experimental data.

In this context, the present work addresses a comparing study involving the applicability of five lumped kinetic models to predict

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**Table 1**  
Lumped kinetic models.

Model	Mechanism
First Order Kinetic Model (FOKM)	$A + O_3 \xrightarrow{k_1'} C$
Two Step First Order Kinetic Model (TSFOKM)	$A + O_3 \xrightarrow{k_1' \text{ 1st step}} B$ $B + O_3 \xrightarrow{k_2' \text{ 2nd step}} C$
Modified First Order Kinetic Model (MFOKM)	$A + O_3 \xrightarrow{k_1'} C$ $D$
Lumped Kinetic Model (LKM)	$A + O_3 \xrightarrow{k_1'} C$ $k_2' \downarrow$ $D$
Generalized Kinetic Model (GKM)	$A + O_3 \xrightarrow{k_1'} C$ $k_2' \searrow$ $B + O_3 \xrightarrow{k_3'} C$
Modified Generalized Kinetic Model (MGKM)	$A + O_3 \xrightarrow{k_1'} C$ $k_2' \searrow$ $B + O_3 \xrightarrow{k_3'} C$ $k_4' \downarrow$ $D \xrightarrow{k_5'} C$

TOC during single ozonation of a mixture of six phenolic compounds present in OMW.

## 2. Development of lumped models

This section discusses the models used in our work: First-Order Kinetic Model, Two Step First Order Kinetic Model, Modified First Order Kinetic Model, Lumped Kinetic Model, Generalized Kinetic Model and Modified Generalized Kinetic Model, whose mechanisms are presented in Table 1. As alternative to the impossible task to account for all the numerous compounds in solution, either formed along the treatment process or initially present in real wastewaters, the chemical pollutants are generally lumped into four groups as described by Silva et al. [10] in the ambit of the catalytic wet oxidation process also used for wastewaters treatment. Unstable species easily oxidized are named as *A*, pollutants that are difficult to oxidize are designed as *B*, refractory compounds no further oxidized are represented as *D* and the desired final products ( $CO_2$  and  $H_2O$ ) are commonly referred as *C*.

The apparent kinetic constants ( $k'$ ) will be considered as function of the gas inlet concentration of ozone, as well as first-order reactions with respect to the pollutants.

### 2.1. First Order Kinetic Model

The use of a First-Order Kinetic Model, hereafter designed as FOKM, to describe TOC depletion during single ozonation was used by Shang et al. [8]. In this model, all the pollutants are lumped in one group *A*, which represents then both unstable and refractory species, and the reaction mechanism assumes only one step, where the pollutants (*A*) react to the final desired products (*C*). Considering that the reaction follows a first-order with respect to *A*, the following kinetic equation can be deduced:

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = k_1' C_{TOC_A} \quad (1)$$

where  $k_1'$  is the apparent kinetic constant. Therefore, the total TOC concentration is given by Eq. (2):

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_A}}{C_{TOC_0}} = e^{-k_1' t} \quad (2)$$

Hence,  $-\ln(C_{TOC}/C_{TOC_0})$  should give a straight line with slope  $k_1'$  when plotted versus time if this model is adequate.

### 2.2. Two Step First Order Model

The Two Step First Order Kinetic Model (TSFOKM) admits oxidation on two first order sequential steps (Table 1) which are obtained by:

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = k_1' \text{ 1st step } C_{TOC_A} \quad (3)$$

$$-r_{TOC_B} = -\frac{dC_{TOC_B}}{dt} = k_2' \text{ 2nd step } C_{TOC_B} \quad (4)$$

The kinetic expressions for each step are attained from the integration of these equations:

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_A}}{C_{TOC_{A0}}} = e^{-k_1' \text{ 1st step } t} \quad (5)$$

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_B}}{C_{TOC_{B0}}} = e^{-k_2' \text{ 2nd step } t} \quad (6)$$

These expressions should adjust to the experimental data represented by  $-\ln(C_{TOC}/C_{TOC_{A0}})$  and  $-\ln(C_{TOC}/C_{TOC_{B0}})$  for the first and second step, respectively, giving a linear behavior with time in case the model fits the kinetic results.

### 2.3. Modified First Order Kinetic Model

The Modified First-Order Kinetic Model (MFOKM) was firstly proposed by Hu et al. [11] to represent TOC degradation during the Wet Oxidation (WO) of printing and dyeing wastewater. This model takes into account the presence of both oxidizable (*A*) and non-oxidizable matter (*D*) in the initial mixture, as seen in Table 1. The oxidizable compounds will contribute with a fraction  $\beta$  for the global TOC concentration, being the remaining TOC due to the presence of the refractory pollutants. Considering a first order kinetics for the oxidation of the *A* species:

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = k_1' C_{TOC_A} \quad (7)$$

Integrating Eq. (7) one reaches Eq. (8) which represents the oxidation of *A*:

$$C_{TOC_A} = C_{TOC_{A0}} e^{-k_1' t} \quad (8)$$

The overall TOC along reaction also accounts for the contribution of *D* compounds and will be then given by Eq. (9):

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_D}}{C_{TOC_0}} + \frac{C_{TOC_A}}{C_{TOC_0}} = a + b \times e^{-ct} \quad (9)$$

where  $a = 1 - \beta$  represents the fraction of non-oxidizable matter (*D*),  $b = \beta$  the fraction of oxidizable pollutants (*A*) and  $c = k_1'$  is the apparent kinetic constant of the oxidation step considered in this mechanism.

### 2.4. Lumped Kinetic Model

The Lumped Kinetic Model (LKM) was developed by Zhang and Chuang [12] for WO and considers two oxidation steps as described in Table 1. The oxidation of *A* into the desired products *C* and a second step accounting for the possible degradation of *A* leading to non-oxidizable species *D*. Therefore, the kinetic expressions involve the TOC contribution of these compounds *A* (Eq. (10))

and  $D$  (Eq. (11)):

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = (k'_1 + k'_2)C_{TOC_A} \quad (10)$$

$$-r_{TOC_D} = -\frac{dC_{TOC_D}}{dt} = -k'_2 C_{TOC_A} \quad (11)$$

Integrating the two equations above, TOC evolution along the time will be given by Eq. (12) which can be simplified to Eq. (13) considering that  $D$  is not present in the initial effluent ( $C_{TOC_{D0}} = 0$ ).

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_A} + C_{TOC_D}}{C_{TOC_{A0}} + C_{TOC_{D0}}} = \frac{C_{TOC_{D0}}}{C_{TOC_0}} + \frac{C_{TOC_{A0}}}{C_{TOC_0}} \left( \frac{k'_2}{k'_1 + k'_2} + \frac{k'_1}{k'_1 + k'_2} e^{-(k'_1 + k'_2)t} \right) \quad (12)$$

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_A} + C_{TOC_D}}{C_{TOC_{A0}}} = \frac{k'_2}{k'_1 + k'_2} + \frac{k'_1}{k'_1 + k'_2} e^{-(k'_1 + k'_2)t} = a + b \times e^{-ct} \quad (13)$$

with  $a = (k'_2/(k'_1 + k'_2))$  the fraction that reacts into no further oxidizable products  $D$ ,  $b = (k'_1/(k'_1 + k'_2))$  the fraction of the initial pollutants that are oxidized into desired products  $C$  and  $c = k'_1 + k'_2$  the global apparent kinetic constant of the process. Both LKM (Eq. (13)) and MFOKM (Eq. (9)) are equally described in mathematical terms even if differing on the methodology supporting their development.

### 2.5. Generalized Kinetic Model

The Generalized Kinetic Model (GKM) was firstly developed by Li et al. [13] for the Wet Oxidation of organic compounds and in the ozonation field was used by Azevedo et al. [9] to describe TOC degradation in phenol oxidation. This model consists of a three-step mechanism (Table 1) with the compounds lumped into three groups: easier degraded pollutants ( $A$ ), intermediates with difficult degradation ( $B$ ) and the desired products ( $C$ ). The reaction rates are given by Eqs. (14) and (15):

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = (k'_1 + k'_2)C_{TOC_A} \quad (14)$$

$$-r_{TOC_B} = -\frac{dC_{TOC_B}}{dt} = k'_3 C_{TOC_B} - k'_2 C_{TOC_A} \quad (15)$$

Integrating these equations (Eq. (16)) and considering as simplification that the initial concentration of  $B$  is equal to zero, the normalized TOC is given by Eq. (17):

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_A} + C_{TOC_B}}{C_{TOC_{A0}} + C_{TOC_{B0}}} = \frac{C_{TOC_{A0}}}{C_{TOC_0}} \left( \frac{k'_2}{k'_1 + k'_2 - k'_3} e^{-k'_3 t} + \frac{k'_1 - k'_3}{k'_1 + k'_2 - k'_3} e^{-(k'_1 + k'_2)t} \right) + \frac{C_{TOC_{B0}}}{C_{TOC_0}} e^{-k'_3 t} \quad (16)$$

$$\frac{C_{TOC}}{C_{TOC_0}} = \frac{k'_2}{k'_1 + k'_2 - k'_3} e^{-k'_3 t} + \frac{k'_1 - k'_3}{k'_1 + k'_2 - k'_3} e^{-(k'_1 + k'_2)t} \quad (17)$$

### 2.6. Modified Generalized Kinetic Model

Despite the good agreement between the experimental results and the GKM for early reaction times Silva et al. [10] verified the formation of refractory compounds during the Catalytic Wet Oxidation (CWO) of a formaldehyde solution which was not predicted by the model. To overcome this drawback the authors [10] proposed the Modified Generalized Kinetic Model (MGKM), which is also schematized in Table 1. This model encompasses the formation of non-oxidizable matter ( $D$ ) either from the oxidation of the

initial compounds ( $A$ ) or from the decomposition of intermediate organic pollutants ( $B$ ) enabling then to take into account the various groups of lumped compounds, namely the easily oxidizable ( $A$ ), the intermediates ( $B$ ) and those resistant to oxidation ( $D$ ). Assuming first order, the reaction rates for this pathway are given by Eqs. (18)–(20). The mathematical integration of these equations enables the calculation of the TOC content of the liquid mixture (Eq. (21)):

$$-r_{TOC_A} = -\frac{dC_{TOC_A}}{dt} = (k'_1 + k'_2 + k'_4)C_{TOC_A} \quad (18)$$

$$-r_{TOC_B} = -\frac{dC_{TOC_B}}{dt} = (k'_3 + k'_5)C_{TOC_B} - k'_2 C_{TOC_A} \quad (19)$$

$$-r_{TOC_D} = -\frac{dC_{TOC_D}}{dt} = -k'_4 C_{TOC_A} - k'_5 C_{TOC_B} \quad (20)$$

$$\begin{aligned} \frac{C_{TOC}}{C_{TOC_0}} = \frac{C_{TOC_{A0}}}{C_{TOC_0}} & \left( \frac{k'_1(k'_1 + k'_2 + k'_4 - k'_3 - k'_5) - k'_3 k'_2}{(k'_1 + k'_2 + k'_4)(k'_1 + k'_2 + k'_4 - k'_3 - k'_5)} e^{-(k'_1 + k'_2 + k'_4)t} \right. \\ & + \frac{k'_3 k'_2}{(k'_2 + k'_5)(k'_1 + k'_2 + k'_4 - k'_3 - k'_5)} e^{-(k'_3 + k'_5)t} \\ & \left. + \frac{k'_4(k'_3 + k'_5) + k'_5 k'_2}{(k'_1 + k'_2 + k'_4)(k'_3 + k'_5)} \right) \\ & + \frac{C_{TOC_{B0}}}{C_{TOC_0}} \left( \frac{k'_3}{k'_3 + k'_5} e^{-(k'_3 + k'_5)t} + \frac{k'_5}{k'_3 + k'_5} \right) + \frac{C_{TOC_{D0}}}{C_{TOC_0}} \quad (21) \end{aligned}$$

The MGKM is a more flexible model but has the shortcoming of dealing with many parameters (Eq. (21)). For this system, the following simplifications can be, however, done to the global model: since that by HPLC none of the parent compounds was detected in solution after 75 min of reaction [15] no non-oxidizable compounds are present at the beginning of the experiments being eventually formed along the reaction and therefore,  $C_{TOC_{D0}} = 0$ . Moreover it will be also considered that no by-products ( $B$ ) are in the effluent at the initial time ( $C_{TOC_{B0}} = 0$ ). These simplifications to the model lead to Eq. (22):

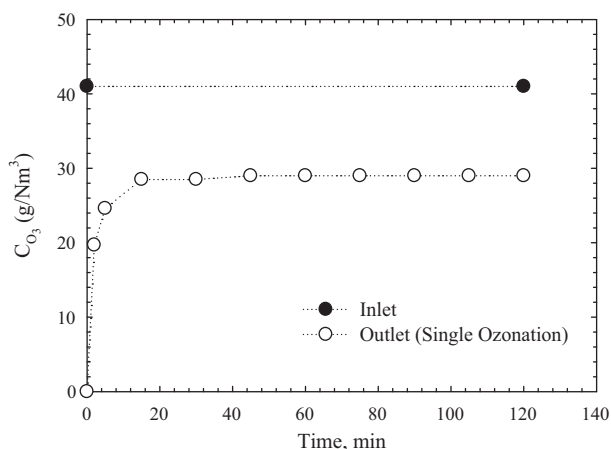
$$\begin{aligned} \frac{C_{TOC}}{C_{TOC_0}} = \frac{k'_1(k'_1 + k'_2 + k'_4 - k'_3 - k'_5) - k'_3 k'_2}{(k'_1 + k'_2 + k'_4)(k'_1 + k'_2 + k'_4 - k'_3 - k'_5)} & e^{-(k'_1 + k'_2 + k'_4)t} \\ & + \frac{k'_3 k'_2}{(k'_2 + k'_5)(k'_1 + k'_2 + k'_4 - k'_3 - k'_5)} e^{-(k'_3 + k'_5)t} \\ & + \frac{k'_4(k'_3 + k'_5) + k'_5 k'_2}{(k'_1 + k'_2 + k'_4)(k'_3 + k'_5)} \quad (22) \end{aligned}$$

Resuming, the philosophy behind these models can be looked within two main branches, either extended to full oxidation ending in  $CO_2$  and  $H_2O$  ( $C$ ) or partially leading to non-oxidizable species ( $D$ ) also possible to be initially present for MGKM. Inside total conversion to end-products, two methodologies are proposed; one admitting only direct oxidation of all the pollutants ( $A \rightarrow C$ ) as for FOKM, MFOKM and LKM and a second one opening the possibility to consider as well another group of initial compounds firstly reactive into intermediates prior to the formation of final species ( $A \rightarrow C$ ;  $A \rightarrow B \rightarrow C$ ) as for TSOFM, GKM and MGKM.

## 3. Experimental

The simulated wastewater was prepared using 100 ppm of each one of the following phenolic acids (Sigma–Aldrich): Protocatechuic, Syringic, Veratric, Vanillic, 4-Hydroxybenzoic and 3,4,5-Trimethoxybenzoic.

Ozonation was carried out in a magnetically stirred glass reactor [14], provided with two gas diffusers and immersed in a thermostatic bath to control the reaction temperature. The process was



**Fig. 1.** Inlet and off-gas ozone concentration along ozonation process (ozone inlet concentration  $40 \text{ gO}_3/\text{Nm}^3$ ,  $T = 296 \text{ K}$ ).

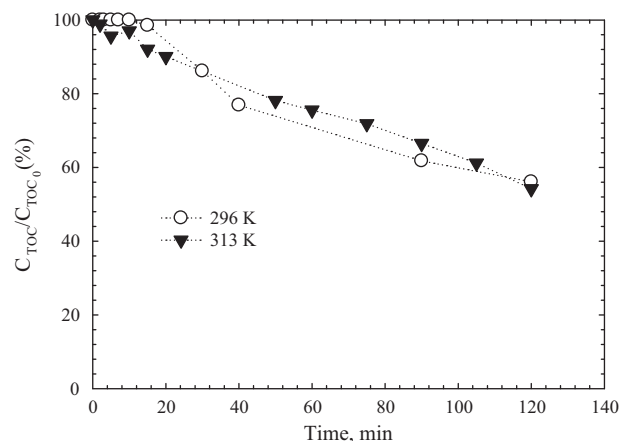
developed in a semi-batch mode, being the gas ( $500 \text{ mL/min}$ ) continuously fed to the reactor. Ozone was generated from a pure oxygen stream (Praxair, Portugal) in an ozone generator (802N, BMT, Berlin, Germany) and the gas ozone concentration was measured using a BMT 963vent ozone analyzer (BMT, Berlin, Germany). The oxidations proceeded as follows:  $500 \text{ mL}$  of the synthetic effluent were added to the reactor, brought to the desired temperature and the experiment started when the ozonated oxygen started to run. The ozone gas leaving the reactor quickly reached a stable value (as it can be confirmed in Fig. 1 for the case where  $40 \text{ gO}_3/\text{Nm}^3$  were used) being possible to assume, thus, that the aqueous solution was saturated in ozone during the process. pH was measured using a Crison micropH 2002 and it was maintained at its initial value of 3.4 by adding NaOH whenever necessary. Samples were periodically withdrawn and the process efficiency was obtained by measuring the Total Organic Carbon (TOC) of the wastewater along time in a TOC-5000 analyzer (Shimadzu). In a previous work [15] several gas flow rates and stirring speeds values were tested until the degradation results become independent upon those operating conditions. In this context, using  $500 \text{ mL/min}$  and  $750 \text{ rpm}$  chemical regime was ensured. Moreover, since the ozone outlet gas concentration quickly reached a constant value (Fig. 1) one can conclude that the reaction system rapidly becomes saturated in ozone and that the process is not gas–liquid mass-transfer dependent.

## 4. Results and discussion

In the following sections, the effect of temperature and ozone concentration will be firstly analyzed and the Lumped Kinetic Models described above will be further discussed for single ozonation of the phenolic effluent. The model parameters were calculated through a commercially available software (Mathworks, Matlab v7.0.4.287) based on the minimum square method using the algorithm of Levenberg–Marquardt.

### 4.1. Effect of temperature

In our system, little effect of temperature was observed (Fig. 2) in the phenolic mixture mineralization when temperature rose from 296 to 313 K. Only a slight difference is seen in the early 10 min of reaction, where no TOC removal is detected when the process developed at 296 K. In contrast, at a temperature of 313 K a mineralization degree of 3% is reached for that experimental time. The slight effect of temperature over the ozonation process can be related with the fact that this parameter involves two opposite contributions: on one side as temperature increases, Henry's constant

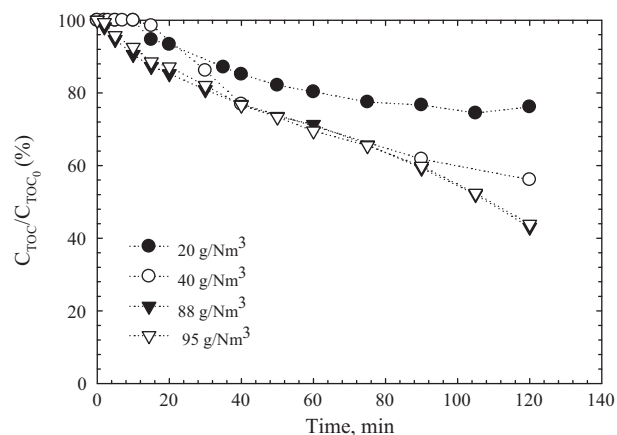


**Fig. 2.** Normalized TOC evolution along single ozonation for different temperatures (ozone gas inlet concentration:  $40 \text{ gO}_3/\text{Nm}^3$ ).

decreases leading to lower ozone solubility, but, by another hand, the Arrhenius equation predicts a raise in the ozonation rate with temperature. Indeed, one of the main advantages of the ozonation process is the fact that it occurs at normal conditions of temperature and pressure which is economically preferably since no investment is required to heat up the reactor. Therefore, hereafter only data taken at 296 K will be analyzed.

### 4.2. Effect of ozone gas concentration

One of the main drawbacks in the industrial implementation of the ozonation process for the treatment of wastewaters is the cost of ozone production. Since ozone is a very unstable compound, it has to be formed *in situ*, requiring the acquisition of a generator whose electricity consumption increases with the ozone content in the gas feeding the reactor [6]. The effect of ozone inlet concentration was then studied in the range of  $20\text{--}95 \text{ g/Nm}^3$ . As can be observed in Fig. 3, which represents TOC degradation along time, for the lowest ozone inlet concentration ( $20 \text{ g/Nm}^3$ ), an induction period is developed for the first 15 min of reaction where no mineralization occurs. Molecular ozone is highly reactive with compounds comprising high electronic density sites (such as benzenic rings). Phenolic acids are, thus, quickly destroyed by this oxidant. Nevertheless, partially oxidized organic intermediates, without significant mineralization, are formed which explains the low TOC removal attained for the first minutes of reaction. Afterwards, those more refractory compounds are slowly degraded



**Fig. 3.** Normalized TOC evolution along single ozonation for different ozone gas inlet concentrations (temperature: 296 K).

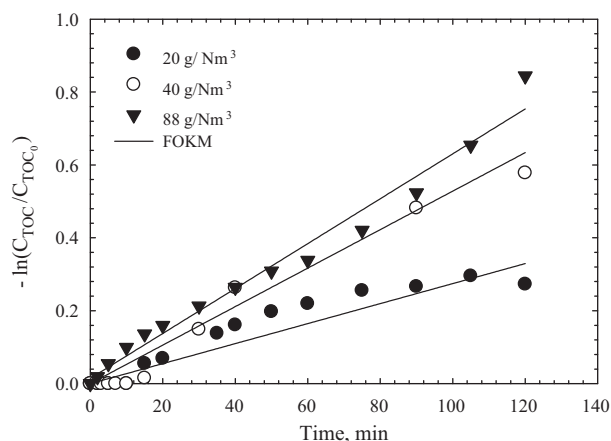


Fig. 4. First-Order Kinetic Model plot for TOC removal during single ozonation (temperature: 296 K).

revealing some total mineralization. The increase of ozone from 20 to 40 g/Nm<sup>3</sup> has no significant effect for the first times of reaction, and an induction period is still observed for the early 15 min. Nevertheless, further different oxidation levels are achieved with the final TOC removal increasing from 24 to 44%. The additional aggressive oxidant conditions attained with the augment in ozone concentration improve the intermediates decomposition leading to higher depuration levels. The process improvement when the oxidant concentration augmented to 88 g/Nm<sup>3</sup> is initially more evident without no induction period and almost 13% of decomposition after 15 min of reaction, while the final TOC degradation reaches 57%. No advantages are assessed with the raise of the ozone from 88 to 95 g/Nm<sup>3</sup> since the reaction becomes independent of ozone concentrations for these experimental conditions.

### 4.3. Kinetic studies

#### 4.3.1. First Order Kinetic Model

The main objective of this work is to achieve a kinetic model suitable to describe the mineralization of a phenolic mixture by ozone. In the ozonation field, the First-Order Kinetic Model (FOKM) is used to describe either compounds degradation [1,2] or TOC removal [8]. Therefore, this model was tested to fit our mineralization data achieved at 296 K in the ozone feed range 20–88 g/Nm<sup>3</sup>. According to Eq. (2),  $-\ln(C_{TOC}/C_{TOC_0})$  should give a straight line with slope  $k'_1$  when plotted versus time but Fig. 4 shows that the respective FOKM fitting FOKM does not provide good agreement with the experimental results (the apparent kinetic constants are given in Table 2) where the correlation factor ( $R^2$ ) and the sum of the squares due to error (SSE) are also presented.

Table 2  
Kinetic parameters for FOKM.

$C_{O_3}^g$ (gO <sub>3</sub> /Nm <sup>3</sup> )	$k'_1$ (min <sup>-1</sup> )	$R^2$	SSE
20	0.0025	0.89	89.54
40	0.0053	0.97	47.97
88	0.0062	0.97	65.31

Table 3  
Kinetic parameters for TSFOKM.

$C_{O_3}^g$ (gO <sub>3</sub> /Nm <sup>3</sup> )	$k'_{1st\ step}$ (min <sup>-1</sup> )	$R^2$	SSE	$k'_{2nd\ step}$ (min <sup>-1</sup> )	$R^2$	SSE
20	0	1	0	0.0025	0.88	89.54
40	0	1	0	0.0053	0.96	47.97
88	0.0065	0.94	49.3	0.0059	0.94	5.57

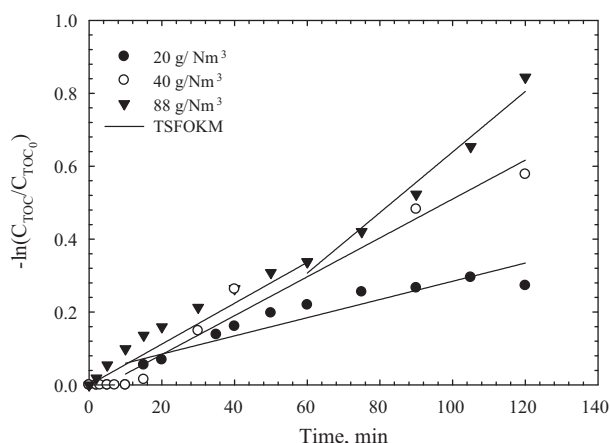


Fig. 5. Two Step First Order Kinetic Model plot for TOC removal during single ozonation (temperature: 296 K).

In fact, this model assumes that the entire reaction pathway occurs in one step (Table 1), making no distinction between unstable and refractory compounds. Even though the ozone has the ability to react with high electronic density compounds, as is the case of phenolic acids, their degradation generally leads to the formation of small carboxylic acids no further oxidizable. Therefore, the accumulation of these organic intermediates minimizes the mineralization by single ozonation, which is not predicted by this model

#### 4.3.2. Two Step First Order Kinetic Model

The TSFOKM admits the occurrence of two sequential oxidation steps where, on a first stage, the parent pollutants are converted to intermediates which will react on a second phase into final products (Table 1). Fig. 5 shows that also this model does not agree satisfactorily with the experimental data since, as verified for the FOKM a linear behavior is not observed between  $-\ln(C_{TOC}/C_{TOC_0})$  versus time. Moreover, this kinetic strategy requires the knowledge of the time transition point between the two steps which occasionally is not clear. In fact, while for low ozone inlet concentrations (20 and 40 g/Nm<sup>3</sup>) an induction period with no TOC removal is obviously separated from a further mineralization period, this changeover is not so evident when 88 gO<sub>3</sub>/Nm<sup>3</sup> are used. Table 3 presents the apparent kinetic constants obtained for each step using different ozone inlet concentrations.

#### 4.3.3. Modified First Order Kinetic Model and Lumped Kinetic Model

Within the above mentioned results, models accounting with the possible existence of non-oxidized organic matter in the wastewater were then tested. Mathematically, both Modified First Order Kinetic Model (MFOKM) and Lumped Kinetic Model (LKM) give the same adjustment (Eqs. (9) and (13)). Nevertheless, while MFOKM predicts the existence of unstable (A) and refractory compounds (D) in the initial wastewater, the LKM only considers the presence of A in the initial effluent and its oxidation into end products (C) or non-oxidizable matter (D) (Table 1). Fig. 6 presents the experimental results of TOC depletion for several ozone inlet con-

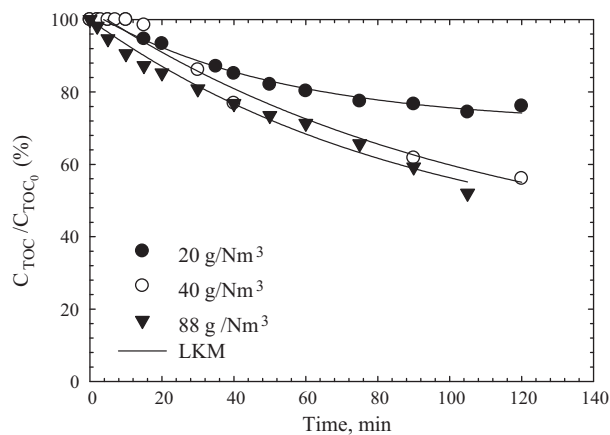


Fig. 6. Lumped Kinetic Model plot for TOC removal during single ozonation (temperature: 296 K).

centrations as well as the respective fitting by MFOKM/LKM. The initial phenolic compounds are extremely reactive with ozone and according to previous results [14,15] none of those six acids were found in the synthetic effluent after 120 min of ozonation. Therefore, it is clear that no refractory matter is present in the original wastewater, whereas accumulation of oxalic and malonic acids, two compounds known to be refractory to ozone oxidation, were actually detected, during the ozonation process. Hence, the kinetic model to be considered should be LKM rather than MFOKM.

A good fitting between the model and the experimental results for low inlet ozone concentrations (20 and 40 gO<sub>3</sub>/Nm<sup>3</sup>) is observed discounting the induction period, corresponding to a retardation of the beginning of reaction not accounted for the models. Nevertheless, for the higher ozone concentration (88 gO<sub>3</sub>/Nm<sup>3</sup>), LKM does not show good agreement with the experimental results, which is statically confirmed by the augment of the sum of square due to errors (SSE) given in Table 4, especially for the first 20 min of reaction where the model predicts lower mineralization. With the oxidant inlet concentration increase, the fraction of organic matter that reacts into non-oxidizable products (*D*) decreases as it can be observed by the *a* decrease (from 70% to 15% for 20 and 88 gO<sub>3</sub>/Nm<sup>3</sup>, respectively, in Table 4) with the consequent augment on oxidizable fraction *b* (from 30% to 85% for 20 and 88 gO<sub>3</sub>/Nm<sup>3</sup>, respectively) (see Eq. (13)). The higher ozone available reduces the formation of refractory organic intermediates with kinetics much slower (lower *k*<sub>2</sub> values) whereas low impact over *k*<sub>1</sub> is observed.

#### 4.3.4. Generalized Kinetic Model

A more versatile model involving the formation of intermediates more difficultly oxidizable (*B*) and, eventually, their subsequent degradation was used aiming to take into consideration more than one step in the oxidation process. Indeed, it is quite difficult that such a complex system, encompassing a vast diversity of possible reaction pathways can be represented by the simple one step schemes. Even still apart from reality, simplified lumped models should offer, at least, two different routes for reactivity of oxidizable compounds: a direct conversion to end-products (*k*<sub>1</sub>) and a final oxidation preceded by formation of intermediates (*k*<sub>2</sub>, *k*<sub>3</sub>). This way, more meaningful fittings can be assigned to experimental

Table 4  
Kinetic parameters for LKM.

C <sub>O<sub>3</sub></sub> <sup>g</sup> (gO <sub>3</sub> /Nm <sup>3</sup> )	<i>k</i> <sub>1</sub> (min <sup>-1</sup> )	<i>k</i> <sub>2</sub> (min <sup>-1</sup> )	<i>a</i>	<i>b</i>	R <sup>2</sup>	SSE
20	0.0059	0.013	0.70	0.30	0.98	33.37
40	0.0064	0.0026	0.30	0.70	0.98	46.18
88	0.0060	0.0013	0.15	0.85	0.97	56.25

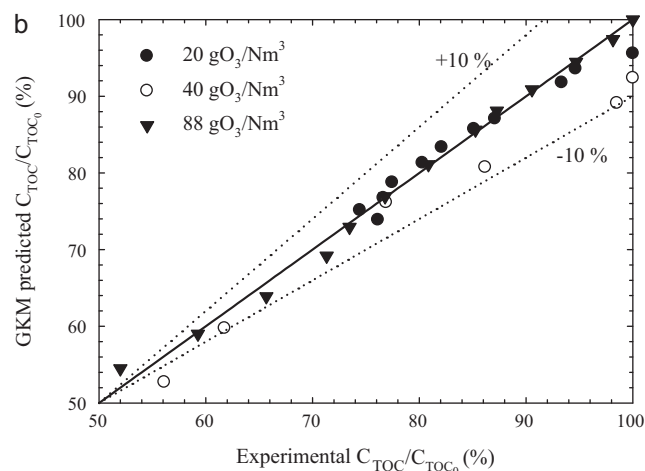
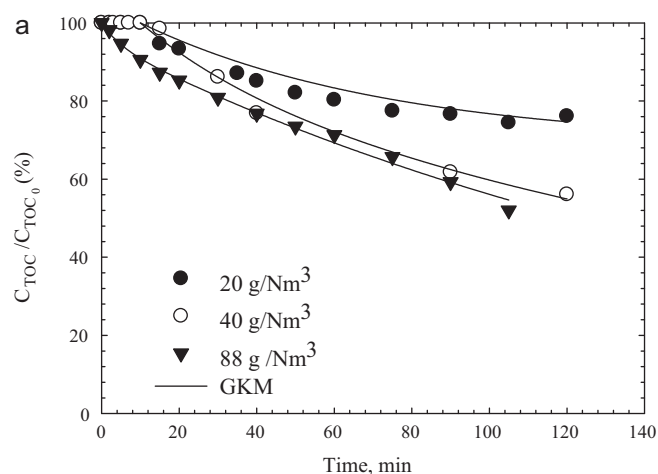


Fig. 7. (a) Generalized Kinetic Model plot for TOC removal during single ozonation. (b) Errors between GKM and the experimental results (temperature: 296 K).

data resulting from a highly complicated interaction among reaction rates competing within a huge map of possible slower and faster steps, either immediately converted into CO<sub>2</sub> and H<sub>2</sub>O, or firstly decomposed into intermediate chemicals only after totally oxidized.

In this context, the Generalized Kinetic Model (GKM) was tested (Table 1). This model shows a good agreement with the experimental points (Fig. 7a) for all the inlet ozone gas concentrations used and the predicted values are in the range of ±10% when compared with the experimental results (Fig. 7b). Once more, for low ozone inlet concentrations (20 and 40 g/Nm<sup>3</sup>) the induction period of 20 min should not be considered since no TOC removal occurs for that time interval.

Table 5 summarizes the values of the apparent reaction rate dependent on ozone [*k*' = *f*(C<sub>O<sub>3</sub></sub>)] for each one of the three reaction steps involved in the use of different ozone inlet gas concentrations. As expected, the increase of ozone inlet concentration leads to higher apparent kinetic constants and for each experimental condition *k*<sub>2</sub> > *k*<sub>1</sub> ≫ *k*<sub>3</sub>. This means that the direct mineralization

Table 5  
Kinetic model parameters for GKM.

C <sub>O<sub>3</sub></sub> <sup>g</sup> (gO <sub>3</sub> /Nm <sup>3</sup> )	<i>k</i> <sub>1</sub> (min <sup>-1</sup> )	<i>k</i> <sub>2</sub> (min <sup>-1</sup> )	<i>k</i> <sub>3</sub> (min <sup>-1</sup> )	R <sup>2</sup>	SSE
20	0.0048	0.011	1.47 × 10 <sup>-10</sup>	0.95	33.37
40	0.0080	0.022	0.0038	0.97	8.60
88	0.0143	0.180	0.0053	0.99	15.67

**Table 6**  
Kinetic model parameters for MGKM.

$C_{O_3}^g / \text{gO}_3 / \text{Nm}^3$	$k'_1 \text{ (min}^{-1}\text{)}$	$k'_2 \text{ (min}^{-1}\text{)}$	$k'_3 \text{ (min}^{-1}\text{)}$	$k'_4 \text{ (min}^{-1}\text{)}$	$k'_5 \text{ (min}^{-1}\text{)}$	$R^2$	SSE
20	0.0052	0	0	0.0162	0	0.98	33.37
40	0.0093	0.0019	0.0019	0.0080	0.0002	0.99	6.19
88	0.0151	0.0317	0.0317	0.1590	0.0005	0.99	15.89

( $k'_1$ ) of the phenolic compounds is not the primordial step of the reaction pathway. Instead, ozone seems to react with the parent molecules mainly leading to the formation of intermediate organic compounds ( $k'_2$ ) which showed to be refractory to further mineralization ( $k'_3$ ). For low ozone inlet concentrations ( $20 \text{ gO}_3 / \text{Nm}^3$ ) the mineralization step regarding the intermediate decomposition is almost negligible with very low apparent kinetic constants indicating that non-oxidizable matter will be present at the end of the process. This explains the previous good agreement with LKM, with the intermediates substances considered here as refractory to further oxidation accumulating in the reactor along the time. The accordance between the two models for those operational conditions is confirmed by the similarity of both apparent kinetic constants and SSE values (Tables 5 and 4). Nevertheless, for higher ozone inlet concentrations LKM fails as seen before, since total oxidation of intermediates is possible to occur due to the presence of higher oxidant quantities thus enhancing conversion of such difficult oxidizable organic products so that GKM predicts a large augment on  $k'_3$  when the inlet ozone concentration increases from 20 to  $40 \text{ gO}_3 / \text{Nm}^3$ . In fact, while for LKM SSE values increase with

the augment of the inlet ozone concentration the reverse occurs for GKM meaning that this last model is more significant for those operational conditions.

#### 4.3.5. Modified Generalized Kinetic Model

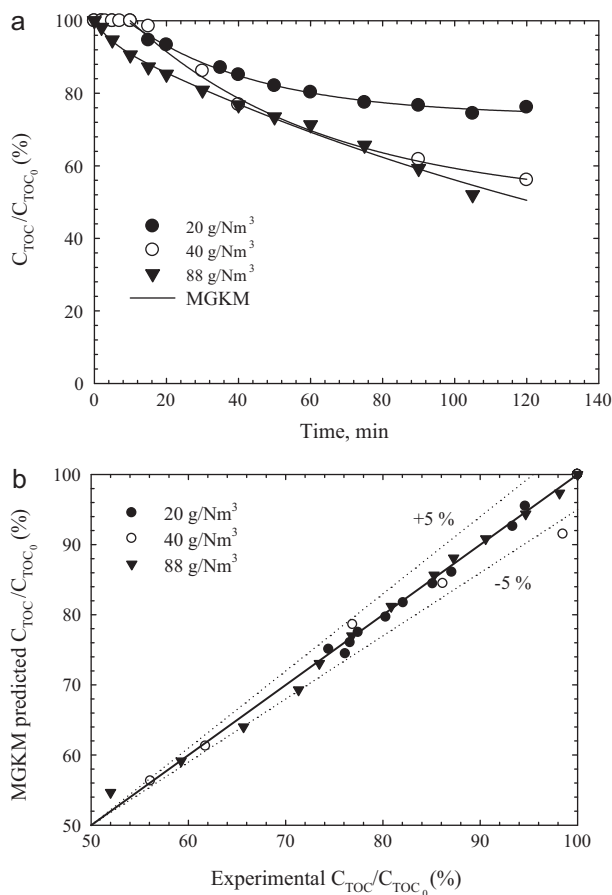
MGKM is a more complete model predicting, besides the formation of intermediates difficult to oxidize (*B*), the degradation of the organic compounds present in solution (*A* and *B*) into refractory by-products no further reactive (*D*) which will lead to a plateau in TOC decomposition (Table 1). In this context, the suitability of MGKM (Eq. (22)) predicting the experimental values for the phenolic mixture mineralization was checked. Fig. 8a shows that the model is very efficient adjusting to the experimental data with a square correlation factor ( $R^2$ ) of 0.99 for all the experiments (Table 6) and is slightly better than GKM due to its higher flexibility gathering up not only the formation of organic compounds difficult to oxidize (*B*) but also the possibility of producing totally refractory by-products (*D*). The errors associated with the MGKM predicted values when compared with the experimental ones are low, in the range  $\pm 5\%$ , as shown in Fig. 8b highlighting the good agreement between them.

Table 6, which shows the apparent kinetic constants for MGKM, depicts that for the lower inlet ozone concentration ( $20 \text{ gO}_3 / \text{Nm}^3$ )  $k'_2 = k'_3 = k'_5 = 0$  and  $k'_4 \gg k'_1$ . These results point out that for those conditions the reaction pathway is well described (as referred earlier) by LKM which comprises the total mineralization of the organic pollutants (*A*) in addition to the formation of intermediates with refractory characteristics (*D*) that will lead to a plateau in TOC removal. Once more, at those conditions the complex MGKM agrees with the LKM which is confirmed by the similarity between the apparent kinetic constants and SSE values attained by both models (Tables 6 and 4). With the augment of the oxidant available ( $40 \text{ gO}_3 / \text{Nm}^3$  and  $88 \text{ gO}_3 / \text{Nm}^3$ ) the formation of by-products more difficult to oxidize but not totally refractory (*B*) becomes doable. Nevertheless, the main reaction route is still towards *D* which is in accordance with the low  $k'_3$  attained with GKM in the previous section. In fact, the agreement between GKM and MGKM for those harsher operational conditions is verified by the similar SSE values attained by both models, Tables 6 and 5. Actually the kinetic results achieved confirm the selectivity of ozone molecule headed for high electronic density compounds forming low molecular weight saturated substances refractory to further oxidation.

As final conclusion it is worthy to strengthen that MGKM revealed to be quite a convenient model to describe complex reaction systems grasping the many kinds of possible behaviors along the degradation process. The foremost drawback of such a complete model is to involve the estimation of a large number of parameters which can complicate the fitting task. Even so, having in mind the know-how acquired about the specific reactions under study, some simplifications can be always thoroughly analyzed with the seek of obtaining kinetic expressions easier to handle still able to accurately describe the process.

## 5. Conclusions

In order to represent the experimental results obtained for TOC degradation during single ozonation, several kinetic models were



**Fig. 8.** (a) Modified Generalized Kinetic Model plot for TOC removal during single ozonation. (b) Errors between MGKM predicted values and experimental results (temperature: 296 K).

tested. The FOKM was not able to describe the TOC profiles since this model assumes TOC mineralization in just one step involving total removal of the parent compounds. TSFOKM failed on the experimental results adjustment and has as shortcoming the need of knowing the transition point between the two steps. Therefore, four models involving either the presence of initial refractory organic compounds in the mixture (Modified First Order Kinetic Model, MFOKM) or the formation of recalcitrant matter during the process (Lumped Kinetic Model, LKM) as well as the decomposition into intermediate species difficult to oxidize (Generalized Kinetic Model, GKM) or both (Modified Generalized Kinetic Model, MGKM) were further tested. MFOKM was rejected by the experimental evidences showing that the initial compounds were removed, excluding then the possibility of the presence of refractory compounds in the parent solution. LKM, GKM and MGKM provided the same trend for the results obtained at low ozone inlet concentration for TOC decrease by single ozonation since the mineralization of the intermediates was almost null. However while LKM failed in the prediction of the data for higher inlet values, GKM gave meaningful results with relative errors of  $\pm 10\%$ . Finally, MGKM gave reliable data for all the experiments (errors within the range  $\pm 5\%$ ) even if involving the drawback of handling a larger number of parameters. As a consequence, this study enables relevant modelling tools to follow design and analysis of continuous systems aiming proper application of ozonation in industry.

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