

# Degradation of mixtures of phenols using boron doped diamond electrodes for wastewater treatment

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## Abstract

A model is proposed for describing the electrochemical oxidation of multicomponent mixtures of organic compounds, when significant mineralization (i.e., combustion to CO<sub>2</sub>) of the compounds occurs. This is known to be the case of the degradation of many organic compounds on boron doped diamond (BDD) and other new electrocatalytic materials used as anodes. The proposed model predicts the variation of concentrations of each component present in the mixture, chemical oxygen demand (COD) and current efficiency as a function of time, under different rate control regimes (diffusive, kinetic and mixed) at constant current. Mass transfer coefficients of each component of the mixture, needed for the application of the model, were obtained from single solute experiments. Tests were conducted in a conventional three-electrode cell, using a commercial BDD electrode as anode. Good agreement between predicted and experimental results was generally obtained, though some deviations had been observed when the highest concentrations of the solutes were used, with concentrations decreasing faster than predicted. These deviations were found for both single- and multi-component systems, and can be explained by the occurrence of side reactions or the accumulation of intermediate compounds of the combustion mechanism.

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## 1. Introduction

In recent years, many papers have been published focusing the application of electrochemical methods for wastewater treatment. References [1,2] review the subject in general. Of particular interest is the study of the oxidation of organic compounds on electrocatalytic materials like PbO<sub>2</sub>, SnO<sub>2</sub>, Ti/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>5</sub> [3,4] and more recently on boron doped diamond (BDD) electrodes, where the overpotential for oxygen evolution is particularly high [5–7]. For this kind of electrodes, very high current efficiencies may be obtained, and complete mineralization of the organic compounds can be achieved. Phenols are probably the most extensively studied compounds in the field of wastewater treatment, as they are persistent pollutants with high toxicity that are released in the wastewaters of a considerable number of industries. References [5,8] are examples of studies on degradation of

phenol using BDD anodes. Degradation of benzoic acid [9], 2-naphtol [10] and 4-chlorophenoxyacetic acid [11] was also studied on BDD electrodes.

A model for the determination of current efficiencies in the electrochemical oxidation of organic compounds was presented by Comninellis and Plattner [12]. In this model, the instantaneous current efficiency ( $\eta$ ) is calculated from experimentally obtained oxygen flow rate.  $\eta$  can also be calculated by determination of the rate of chemical oxygen demand (COD) removal, during an electrolytic process, using the following relationship [9,11,13–15]:

$$\eta = \frac{(\text{COD})_t - (\text{COD})_{t+\Delta t}}{8I \Delta t} FV \quad (1)$$

It is important to note that this equation makes no assumptions about the nature or number of components in the system, since the observed COD differences along the time are exclusively related to the degree of oxidation of the organic matter as a whole. Thus we may expect that the differential dCOD/dt in a multicomponent system will reflect the current efficiency of the electrolytic process.

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This theory was extended to achieve the prediction of the rate of COD removal (thus  $\eta$ ) in a system where combustion of an organic compound occurs [8,10,16]. These authors proposed a model in which the current efficiency is given by  $\eta = j_L/j$ , if the applied current density is higher than the limiting current density, otherwise  $\eta = 1$ . This hypothesis is equivalent to consider that while there are organic species to be degraded at the electrode's surface, no oxygen evolution occurs. If a single organic compound is completely oxidized (to  $\text{CO}_2$ ) in an electrochemical process, and  $n$  is the total number of electrons transferred to the anode by each molecule of that compound, then its rate of consumption is given by:

$$v_i = \text{rate (mol s}^{-1}) = -V \frac{dc}{dt} = \frac{jA}{nF} \eta \quad (2)$$

The limiting current density,  $j_L$ , is defined, as usual, by

$$j_L = nFk_d c \quad (3)$$

Integrating Eq. (2) using  $\eta = j_L/j$  or  $\eta = 1$  gives

$$\eta = j_L/j \Rightarrow c = c_0 e^{-k_d A t / V} \quad (4)$$

$$\eta = 1 \Rightarrow c = c_0 - \frac{jAt}{nFV} \quad (5)$$

Thus, depending on the type of control regime, a linear or exponential decay of the concentration of the organic compound versus time can be expected. The corresponding expressions for the variation of COD with time are readily obtained by substituting  $c$  by  $\text{COD}/8n$ , noting that, for any given  $\text{C}_x\text{H}_y\text{O}_z$  that is completely oxidized to  $\text{CO}_2$ , that equality is verified [8]:

$$\eta = j_L/j \Rightarrow \text{COD} = \text{COD}_0 e^{-k_d A t / V} \quad (6)$$

$$\eta = 1 \Rightarrow \text{COD} = \text{COD}_0 - \frac{8jAt}{FV} \quad (7)$$

and also,

$$j_L = \frac{Fk_d \text{COD}}{8} \quad (8)$$

These expressions will be used to analyze data obtained in single-component systems, namely to obtain mass transfer coefficients and recognize the type of rate control regime.

The authors of this model also presented expressions to be applied in a batch process when there is a change from kinetic to diffusive control (due to the consumption of the organic pollutant). These expressions can also be used for plug-flow reactors [8], and in this latter reference, expressions for continuous stirred tank reactors, are also presented.

This kind of models can be viewed as very important tools for optimization purposes in the field of the application of diamond electrodes (or other electrocatalytic materials) to wastewater treatment. In order to apply this type of model to real effluents, the existing theory must be developed and further applied to multicomponent systems.

## 2. Development of the model

We present here a first attempt on modeling the oxidation of a multicomponent system of organic compounds. The model is based on three fundamental assumptions: (a) All the components in the mixture are degraded at the same time. (b) The combustion of the compounds to  $\text{CO}_2$  is very fast (i.e., no intermediates are considered to be present in significant concentrations). (c) There will be no oxygen formation until all the organic species are removed from the region near electrode's surface.

The first assumption can be justified by the fact that in this type of electrodes the oxidation of the organic compounds is an indirect process, carried out by hydroxyl radicals [3,15,17–19]. Thus we expect that, in a multicomponent mixture, any ordinary organic molecule that comes close to the electrode is immediately attacked by the hydroxyl radicals present in that region. Second and third assumptions are not new, and were also used to derive the model for single-component systems.

The fundamental set of equations that describes the individual rates of consumption of the organic compounds will be, for each component:

$$v_i (\text{mol s}^{-1}) = -V \frac{dC_i}{dt} = \frac{j_i A}{n_i F} \quad (9)$$

where  $j_i$  is a partial current density, defined as the portion of the total current density that is used for the oxidation of the organic species  $i$ , in the mixture. If a new, more general, definition of current efficiency is also introduced

$$\eta = \frac{\sum_j j_i}{j} \quad (10)$$

then, the partial current density can be related to a fraction of net current,  $\phi_i$ , defined as

$$j_i = \phi_i j \eta \quad (11)$$

Substituting Eq. (11) into Eq. (10) gives:

$$\sum \phi_i = 1 \quad (12)$$

To complete the setup of the model, the partial current densities must be calculated. Different expressions for  $j_i$  calculation, depending on the type of rate control regime, are derived in Appendix A. These proposed expressions are summarized in Table 1. Calculations were carried out for a system of  $N$  components, using a set of  $N$  equations in the form of Eq. (9), that was numerically solved. Mass transfer coefficients were calculated from experimental data obtained in single-component tests.

## 3. Experimental details

Phenolic compounds tested were phenol, phenyl-methanol, 1-phenyl-ethanol and *m*-cresol. All the reagents used were of analytic grade. Experiments were carried out in

Table 1

Expressions for calculation of partial current density ( $j_i$ ) and current efficiency ( $\eta$ ) for electro-oxidation of multicomponent mixtures of organic compounds, to be used depending on the available data

Type of regime	Knowing $C_i$ , $k_{d,i}$ and $n_i$	Knowing $COD_i$ and $k_{d,i}$
Diffusive control	$j_i = n_i F k_{d,i} C_i$ $\eta = \sum j_{L,i} / j$	$j_i = (1/8) F k_{d,i} COD_i$ $\eta = \sum j_{L,i} / j$
Mixed control	$j_q = n_q F k_{d,q} C_q$ , with $C_{s,q} = 0$ $j_k = \phi'_k (j - B)$ , with $C_{s,k} > 0$ $B = \sum_q j_{L,q}$ $\phi'_k = n_k C_k / \sum_k n_k C_k$ $\eta = 1$	$j_q = (1/8) F k_{d,q} C Q O_q$ , with $COD_{s,q} = 0$ $j_k = \phi'_k (j - B)$ , with $COD_{s,k} > 0$ $B = \sum_q j_{L,q}$ $\phi'_k = COD_k / \sum_k COD_k$ $\eta = 1$
Kinetic control	$j_i = (n_i C_i / \sum n_i C_i) j$ $\eta = 1$	$j_i = (COD_i / \sum COD_i) j$ $\eta = 1$

a three-electrode stirred cell, using a *Diachem*<sup>®</sup> boron doped diamond electrode, with an immersed area of  $1.014 \times 10^{-3} \text{ m}^2$ , as anode. A copper foil, with large area, was used as cathode. Supporting electrolyte was  $\text{Na}_2\text{CO}_3$  0.1 M, neutralized to pH 7.0 using  $\text{H}_2\text{SO}_4$  5%

(v/v). Current was controlled with a *Tacussel* PJT 35-2 potentiostat-galvanostat. The anode potentials were measured *versus* a saturated calomel electrode and monitored along the time of experiment. The processed volumes were  $2.50 \times 10^{-4} \text{ m}^3$  in each run. Initial concentrations of the organic compounds are specified in Table 2.

Concentrations of the various components in mixtures were determined by HPLC in a *Spectra-Physics* system equipped with a gradient pump, a reversed phase column *Spheri-10 RP-18*, with a stationary phase particle size of  $10 \mu\text{m}$ , from *Brownlee Laboratories*. A mobile phase of 10% acetonitrile–90% water (v/v) was used for  $1 \text{ ml min}^{-1}$  of flow rate. Detection was carried out at 210 and 254 nm simultaneously. For COD determinations, the standard colorimetric (titrimetric) method, with closed reflux [20] was used.

## 4. Results and discussion

### 4.1. Single-component systems

Results of tests performed under diffusive and kinetic control conditions are presented in Figs. 1–2. In these tests, the

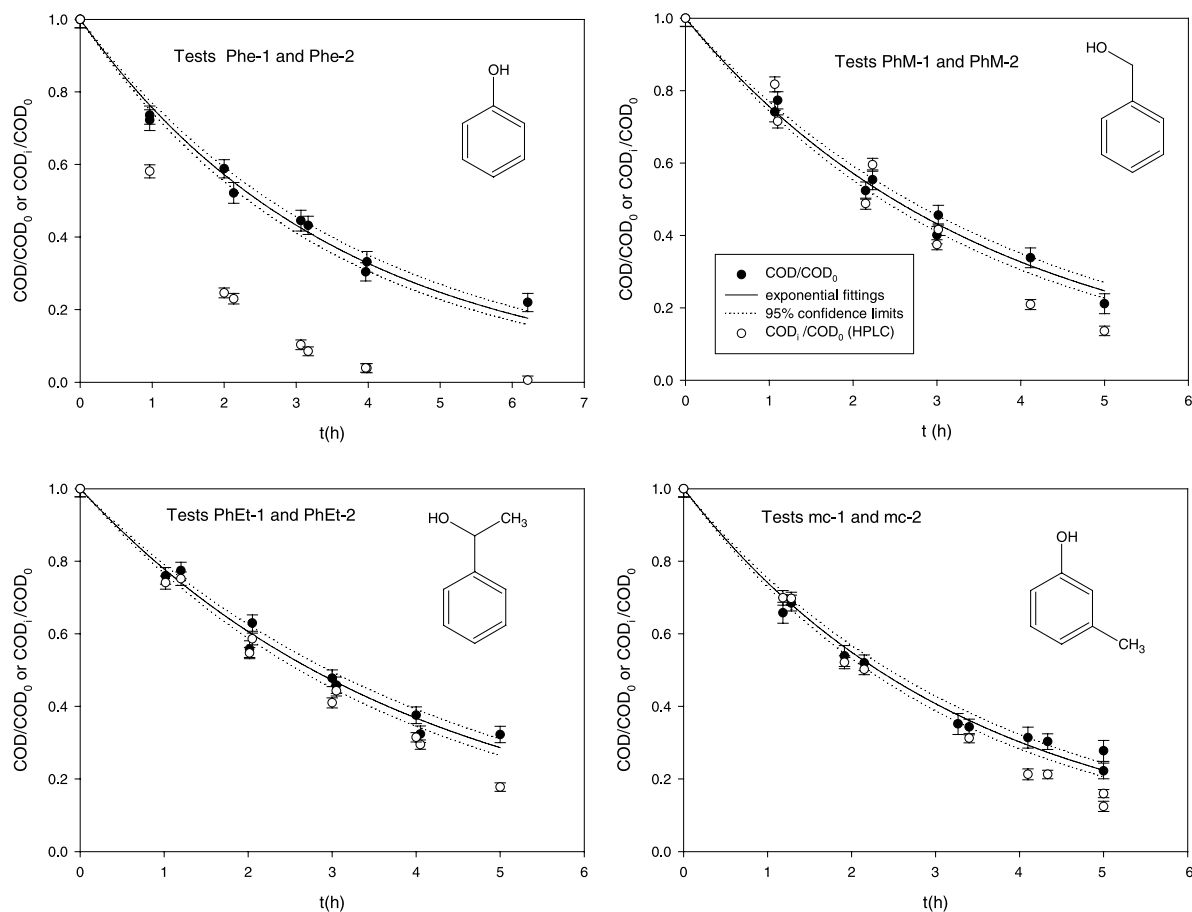


Fig. 1. Degradation of phenols in single-component solutions at low concentrations (tests *Phe-1*, *Phe-2*, *PhM-1*, *PhM-2*, *PhEt-1*, *PhEt-2*, *mc-1* and *mc-2*). Determination of mass transfer coefficients by fittings of COD vs. time. Comparison of COD with  $COD_i$  values determined by HPLC. Volume:  $2.50 \times 10^{-4} \text{ m}^3$ ; applied current:  $300 \text{ A m}^{-2}$ ; temperature:  $25^\circ\text{C}$ ; anode: BDD; cathode: copper.

Table 2  
Essays run and the corresponding concentrations of organic components (g l<sup>-1</sup>)

	Phenol	Phenyl-methanol	1-Phenyl-ethanol	<i>m</i> -Cresol
<i>Phe-1</i>	0.202	–	–	–
<i>Phe-2</i>	0.222	–	–	–
<i>Phe-3</i>	2.189	–	–	–
<i>PhM-1</i>	–	0.199	–	–
<i>PhM-2</i>	–	0.229	–	–
<i>PhM-3</i>	–	1.230	–	–
<i>PhEt-1</i>	–	–	0.232	–
<i>PhEt-2</i>	–	–	0.227	–
<i>PhEt-3</i>	–	–	1.214	–
<i>mc-1</i>	–	–	–	0.183
<i>mc-2</i>	–	–	–	0.244
<i>mc-3</i>	–	–	–	1.243
<i>mix-1</i>	–	0.159	0.368	–
<i>mix-2</i>	–	0.583	0.329	–
<i>mix-3</i>	–	1.201	0.355	–
<i>mix-4</i>	–	0.556	0.329	–
<i>mix-5</i>	–	0.155	0.353	–
<i>mix-6</i>	–	0.323	0.599	1.216
<i>mix-7</i>	–	0.730	1.200	0.339
<i>mix-8</i>	–	1.230	0.332	0.616

degradation of the compounds was followed by COD measurements and by HPLC.

As it can be seen in Fig. 1, for low concentrations of the compounds (tests *Phe-1*, *Phe-2*, *PhM-1*, *PhM-2*, *PhEt-1*, *PhEt-2*, *mc-1* and *mc-2*) mass transfer coefficients of the individual compounds can be estimated by exponential fitting of COD/COD<sub>0</sub> values against time, using Eq. (6). With the obtained  $k_d$  for each product, the critical COD for which the rate control regime changes from diffusive to kinetic, COD\*, can be also estimated using Eq. (8) as shown in Table 3.

On the other hand, for much higher concentrations of the compounds (tests *Phe-3*, *PhM-3*, *PhEt-3* and *mc-3*) kinetic control conditions are attained, as it can be seen by the linear decrease of concentration for all the compounds tested (Fig. 2); this is in agreement with Eq. (7). Thus, we may conclude that current efficiencies near 100% are in fact obtained with these electrodes, as it was suggested in the setup of the model, provided that concentrations of the solutes being above the critical values.

Concentrations of individual compounds in single-component systems were also followed by HPLC, and the

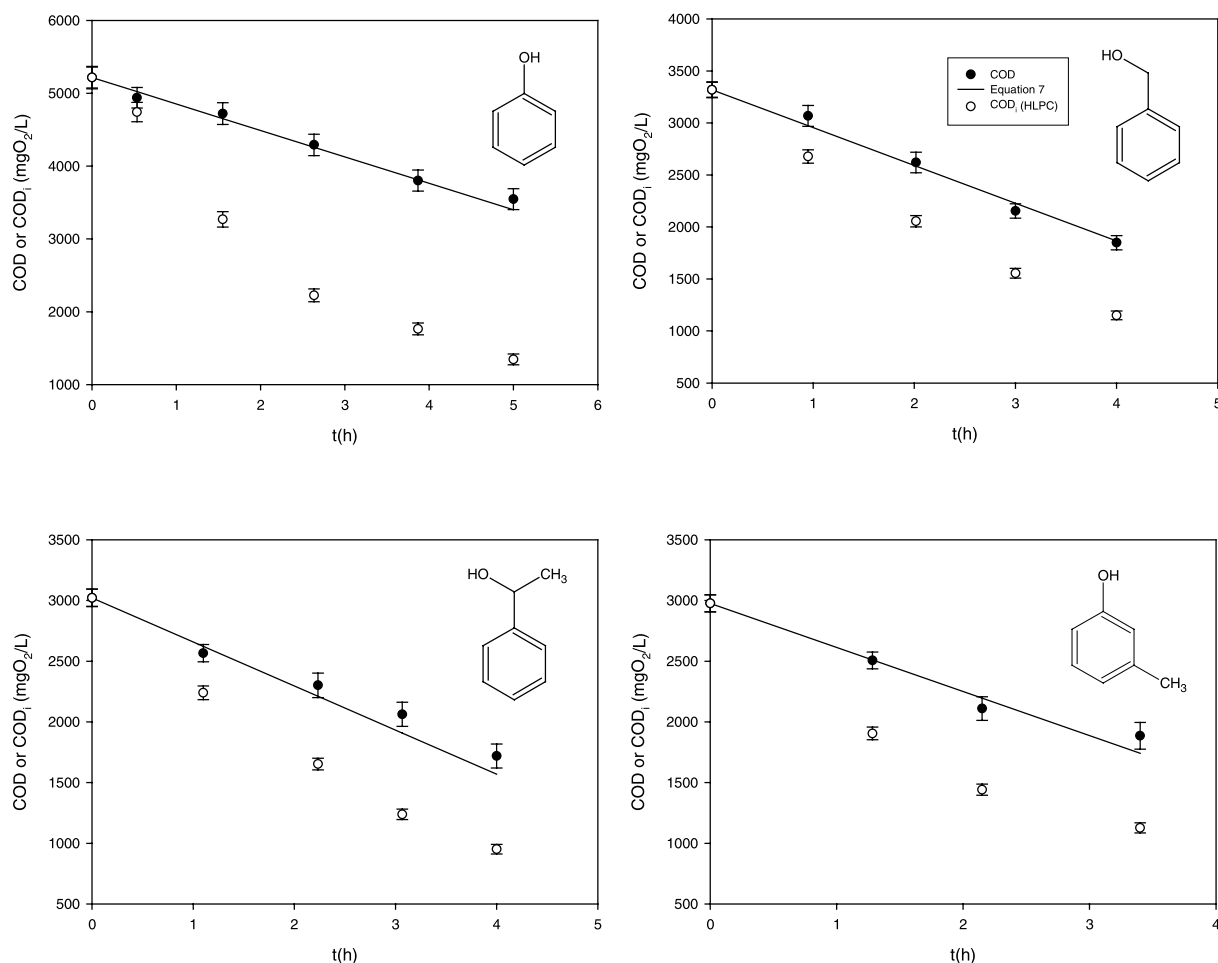


Fig. 2. Degradation of phenols in single-component solutions at high concentrations (tests *Phe-3*, *PhM-3*, *PhEt-3* and *mc-3*). The filled line is the theoretical prediction of COD vs. time for single-component systems (using Eq. (7)), assuming  $\eta = 1$  (i.e., assuming full kinetic control). Comparison of COD with COD<sub>i</sub> values determined by HPLC. Volume:  $2.50 \times 10^{-4}$  m<sup>3</sup>; applied current: 300 A m<sup>-2</sup>; temperature: 25 °C; anode: BDD; cathode: copper.

results were compared with those obtained from COD measurements. This comparison is made in terms of  $COD_i$  (see also Figs. 1–2), that were calculated from the concentrations determined by HPLC, multiplied by the theoretical values of specific COD (sCOD, expressed as  $mgO_2 g^{-1}$  of compound; Table 3). The results are quite unexpected, as the HPLC analysis clearly shows that, at higher concentrations, compounds are consumed faster than predicted. In addition, it is important to note that the chromatograms

Table 3

Mass transfer coefficients ( $k_d$ ), theoretical specific COD (sCOD), critical concentrations ( $c^*$ ) and critical  $COD^*$  (at  $30 mA cm^{-2}$ ) for each organic compound

Compound	$k_d$ ( $10^{-5} m s^{-1}$ )	sCOD ( $mgO_2 g^{-1}$ )	$c^*$ ( $g l^{-1}$ )	$COD^*$ ( $mgO_2 l^{-1}$ )
Phenol	$1.9 \pm 0.1$	2383	0.55	1300
Phenyl-methanol	$1.9 \pm 0.1$	2519	0.52	1300
1-Phenyl-ethanol	$1.7 \pm 0.1$	2623	0.56	1500
<i>m</i> -Cresol	$2.1 \pm 0.1$	2519	0.47	1200

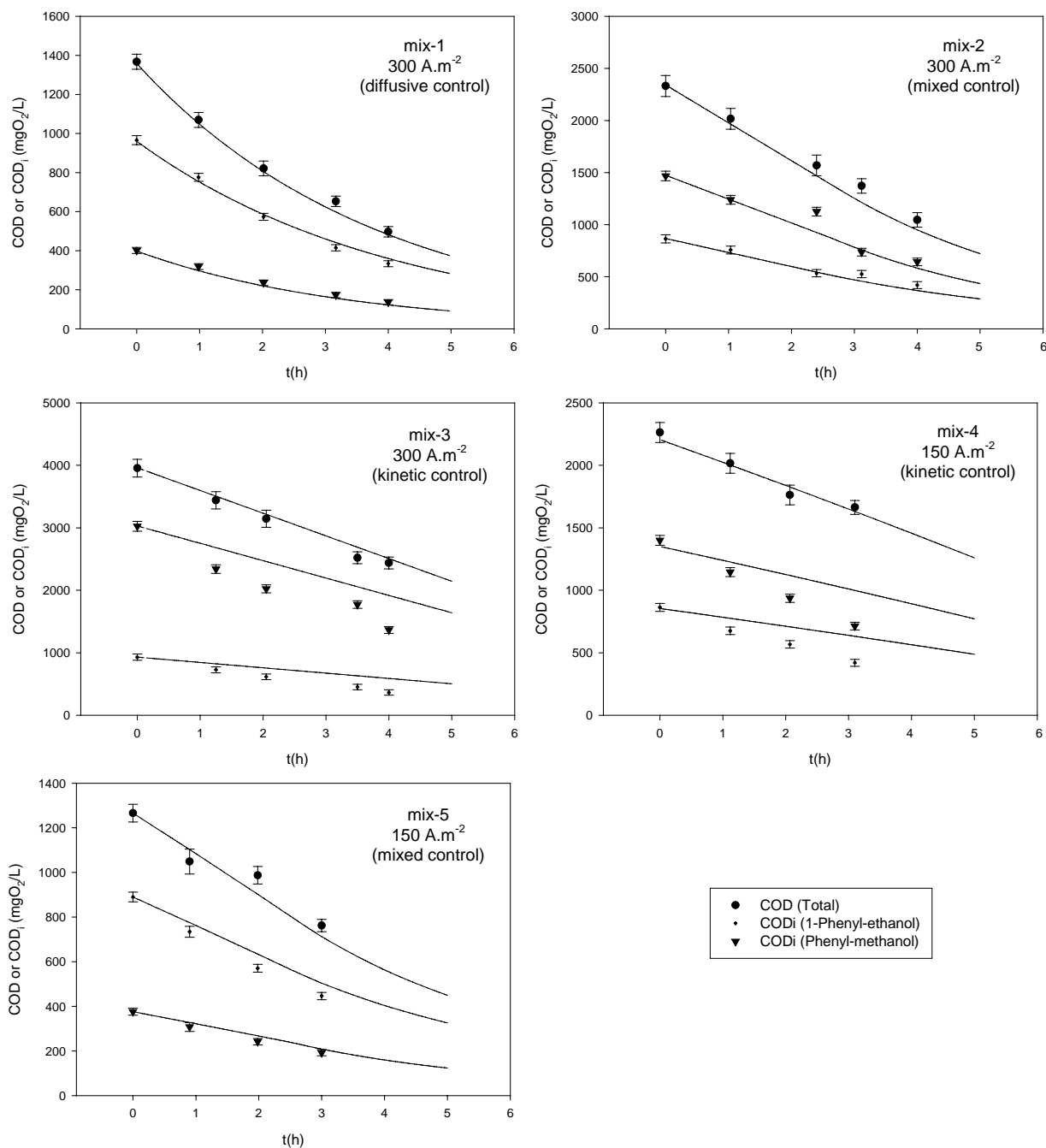


Fig. 3. Degradation of phenols in binary systems (*mix-1–5*). The filled lines are the theoretical predictions of COD and  $COD_i$  vs. time under different control regimes (see the corresponding equations in Table 1). Volume:  $2.50 \times 10^{-4} m^3$ ; applied current: as shown; temperature:  $25^\circ C$ ; anode: BDD; cathode: copper.

also show the appearance of new bands (at low retention times) that are not initially present, and also that solutions become brownish colored along the time of electrolysis. These results may be interpreted, at least, in two different ways: one is that phenyl compounds apart from being oxidized to  $\text{CO}_2$  can possibly be involved in side reactions leading to an increase of their rate of consumption; another possibility is that the compounds can be converted into more stable intermediates, i.e., having lower rates of combustion (in that case the initial products would be consumed faster than predicted and the intermediates would be accumulated). The formation and accumulation of intermediates during the oxidation of phenol in 0.1 M  $\text{HClO}_4$  on BDD has been previously reported by Iniesta et al. [21].

Results obtained with phenyl-methanol, phenyl-ethanol and *m*-cresol clearly show less significant deviations between COD and  $\text{COD}_i$ , than those found for phenol, particularly at lower concentrations. For this reason, experiments with multicomponent mixtures proceeded with these three compounds, but phenol was discarded. High concentrations of the components in the mixtures were also avoided, if possible.

#### 4.2. Binary systems

Results obtained for binary mixtures of phenyl-methanol and phenyl-ethanol, at  $300 \text{ A m}^{-2}$ , are presented in Fig. 3. These results are compared with those predicted by the model for multicomponent mixtures, using as input the initial values of  $\text{COD}_i$ , the operating conditions, and the mass transfer coefficients previously determined. In these tests, the concentration of phenyl-ethanol was kept approximately constant, and that of phenyl-methanol was varied to obtain diffusive, mixed and kinetic control regimes (respectively tests *mix-1*, *mix-2*, *mix-3*). As it can be seen, a good agreement is found between the predicted and obtained results, both in terms of COD and  $\text{COD}_i$  as a function of time, for diffusive and mixed control. For kinetic control, good agreement is also found for COD versus time, but in this case  $\text{COD}_i$  values significantly deviates from the predicted trends. This means that under these conditions other products are formed, apart from  $\text{CO}_2$ , and these products will contribute to a significant fraction of the total COD.

In test *mix-4*, applying a lower current density,  $150 \text{ A m}^{-2}$ , and using approximately the same concentrations of test *mix-2*, kinetic control was also obtained (Fig. 3) and similar

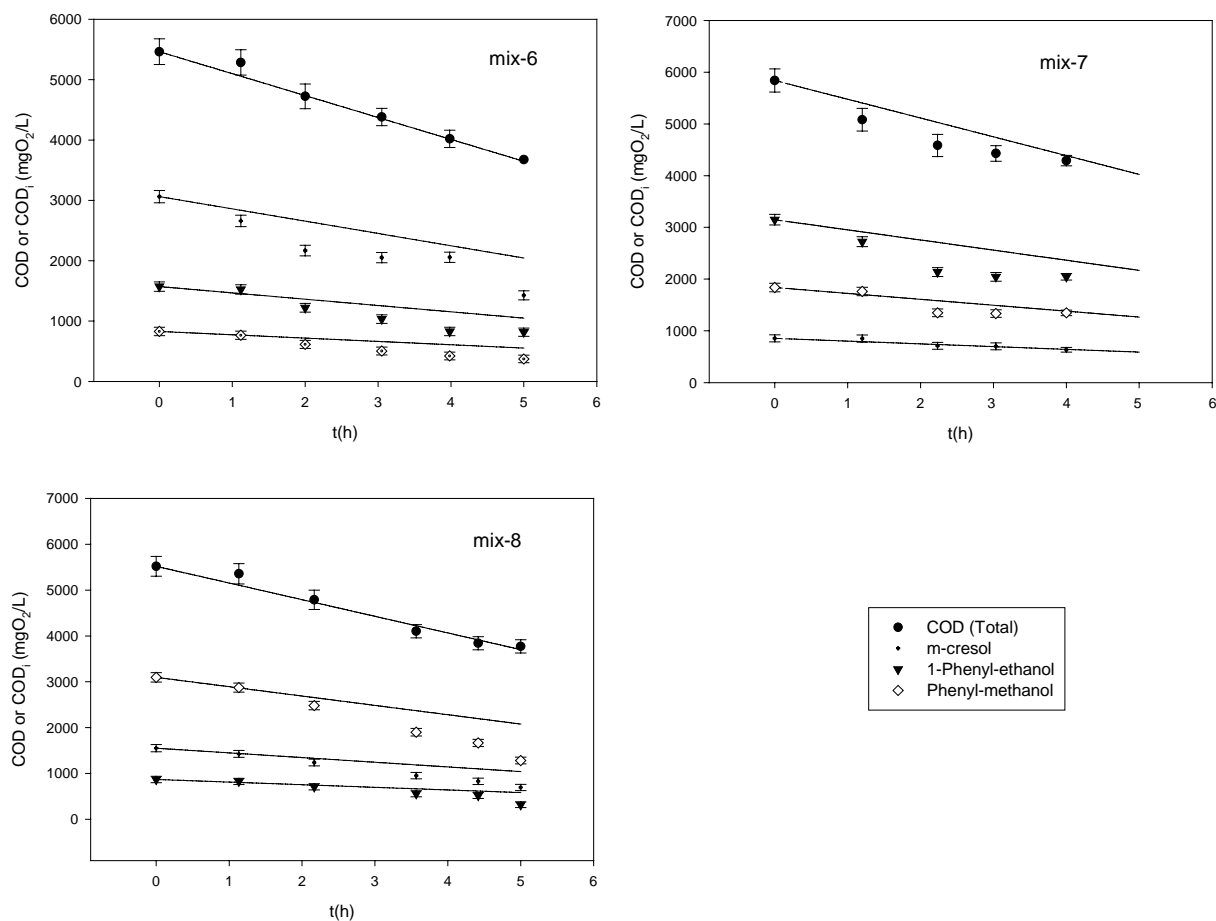


Fig. 4. Degradation of phenols in ternary systems (*mix-6–8*). The filled lines are the theoretical predictions of COD and  $\text{COD}_i$  vs. time under kinetic control (see the corresponding equations in Table 1). Volume:  $2.50 \times 10^{-4} \text{ m}^3$ ; applied current:  $300 \text{ A m}^{-2}$ ; temperature:  $25^\circ\text{C}$ ; anode: BDD; cathode: copper.



Table 4  
Average degradation rates of individual components under kinetic control conditions for binary and ternary mixtures ( $\text{mol s}^{-1}$ )

Test	Phenyl-methanol	1-Phenyl-ethanol	<i>m</i> -Cresol
Binary mixtures			
<i>mix-3</i>	$3.4 \times 10^{-7}$	$1.1 \times 10^{-7}$	–
<i>mix-4</i>	$1.8 \times 10^{-7}$	$0.96 \times 10^{-7}$	–
Ternary mixtures			
<i>mix-6</i>	$0.90 \times 10^{-7}$	$1.4 \times 10^{-7}$	$2.7 \times 10^{-7}$
<i>mix-7</i>	$1.3 \times 10^{-7}$	$2.3 \times 10^{-7}$	$0.55 \times 10^{-7}$
<i>mix-8</i>	$3.3 \times 10^{-7}$	$0.81 \times 10^{-7}$	$1.6 \times 10^{-7}$

results to those of test *mix-3* were found (i.e., good agreement between theoretical and experimental values of COD versus time, but deviations in  $\text{COD}_i$  versus time).

In test *mix-5*, the concentration of phenyl-methanol was lowered to obtain mixed control at  $150 \text{ A m}^{-2}$ . A good prediction of COD was obtained, and deviations in  $\text{COD}_i$  were again found to be negligible.

From these results, we may conclude that the proposed model is very accurate in the prediction of COD versus time, under diffusive, mixed and kinetic control regimes. The model also describes well the variations of concentrations of the individual components of the mixture, under diffusive and mixed control regimes. The results obtained for diffusive control are in agreement with the idea that the sum of the limiting current densities gives the net fraction of current that is used to degrade the organic compounds, and so the proposed expression for the calculation of the current efficiency is also confirmed.

Under kinetic control, deviations between the predicted and obtained values of  $\text{COD}_i$  may be explained by the same arguments used in the case of the deviations found in single-component systems, because for both compounds the degradation rates are higher than predicted. It is also important to note that, apart from these quantitative deviations, the results are qualitatively in accordance with the proposed model in that of components being degraded simultaneously and in that higher degradation rates are found for the more concentrated compound (Table 4). In ternary systems, the same behavior was also found.

#### 4.3. Ternary systems

Test were carried out using different concentrations of the compounds, under the same operating conditions, to confirm the simultaneous degradation of the components, and also to investigate if the order of the degradation rates is the same of the initial concentrations, as suggested by the model.

As it can be seen in Fig. 4, for ternary mixtures of phenyl-methanol, phenyl-ethanol and *m*-cresol, apart from the deviations, the results confirm the model, as the higher degradation rates are always found for the most concentrated compounds, irrespectively of the compound itself (see also Table 4).

## 5. Conclusions

Apart from some deviations found for higher concentrations of the organic compounds, the results are clearly in accordance with the proposed model. Firstly, it is a fact that simultaneous degradation of all the components of the mixture takes place, as it was assumed. Thus, there is infact a partial current density that can be ascribed to each organic component of the mixture. This is also in accordance with the hypothesis that an indirect oxidation process occurs (probably carried out by hydroxyl radicals, as pointed out by a number of authors previously cited). Secondly, under kinetic control conditions, the higher degradation rates were always found for the more concentrated compounds (irrespective of the compound itself), confirming that the partial current, or current fraction of each compound can be given by an expression similar to that what was proposed. Thirdly, under diffusive control conditions, the deviations between predicted and obtained results are very small, confirming that the addition of limit current densities gives the net fraction of current used to degrade the organic compounds, and so, the expression for the calculation of the current efficiency is also confirmed.

The highest deviations from the model were found for the more concentrated solutions, resembling what is found in single component systems under kinetic control. It is important to note that these deviations occur in the individual  $\text{COD}_i$  predictions, but for the global COD the predictions were found to be always very accurate, even for the more concentrated solutions.

Due to the good agreement between the predicted and obtained results, this model can be viewed as a starting point for further theoretical developments, and can also be used in practical applications of multicomponent systems, in those cases where the determination of individual mass transfer coefficients of the components is a feasible task.

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## List of symbols

<i>A</i>	area ( $\text{m}^2$ )
<i>B</i>	constant
<i>c</i>	concentration ( $\text{g l}^{-1}$ )
<i>C</i>	concentration ( $\text{mol m}^{-3}$ )
COD	chemical oxygen demand—oxygen needed for total oxidation to $\text{CO}_2$ ( $\text{mgO}_2 \text{ l}^{-1}$ )

COD <sub><i>i</i></sub>	COD values calculated by multiplying the sCOD values by HPLC concentrations
<i>F</i>	Faraday constant (96,485 C mol <sup>-1</sup> )
<i>I</i>	current intensity (A)
<i>j</i>	current density (A m <sup>-2</sup> )
<i>j<sub>L</sub></i>	limit current density defined by Eq. (3) (A m <sup>-2</sup> )
<i>j<sub>i</sub></i>	partial current density defined by Eq. (9) (A m <sup>-2</sup> )
<i>k<sub>d</sub></i>	mass transfer coefficient (m s <sup>-1</sup> )
<i>n</i>	number of electrons transferred to the electrode by a compound
sCOD	oxygen needed to achieve the complete conversion of the organic compound to CO <sub>2</sub> , per gram of compound.
<i>t</i>	time (s)
<i>V</i>	volume (m <sup>3</sup> )
<i>v</i>	rate of degradation (mol s <sup>-1</sup> )

#### Subscripts and superscripts

<i>i</i>	that of individual compound
<i>k</i>	that of individual compound for which $C_s > 0$
0	initial (i.e., for $t = 0$ )
<i>q</i>	that of individual compound for which $C_s = 0$
<i>s</i>	at the surface of the electrode
*	critical, i.e., for when $j = j_L$

#### Other symbols

$\phi$	fraction of net current defined by Eq. (11)
$\phi'$	fraction of current, under mixed control, for compounds with $C_s > 0$
®	registered trade mark

## Appendix A

For deriving the equations that describe the multicomponent process of oxidation, three different situations are considered: diffusive control, mixed control and kinetic control.

### A.1. Diffusive control

In this situation, all compounds have their rate of degradation controlled by the rate of mass transfer from the bulk of the solution to the electrode's surface, where all the concentrations are zero. Thus, assuming that all the compounds are degraded simultaneously, for each component the partial current density will be given by

$$j_i = n_i F k_{d,i} C_i \quad (\text{A.1})$$

If the molar concentration of each compound is substituted by (COD<sub>*i*</sub>/8*n<sub>i</sub>*), for a C<sub>*x*</sub>H<sub>*y*</sub>O<sub>*z*</sub> compound that is completely oxidized to CO<sub>2</sub>, then

$$j_i = \frac{1}{8} F k_{d,i} \text{COD}_i \quad (\text{A.2})$$

### A.2. Full kinetic control

It is assumed that full kinetic control only occurs when for all the components  $C_s > 0$ , i.e., all the components of the mixture have a concentration at the electrode's surface different from zero. Under these circumstances, it is assumed that the current efficiency is unitary, like in the single-component models referred in the introduction, and Eq. (11) becomes

$$j_i = \phi_i j \quad (\text{A.3})$$

Then by Eqs. (9) and (10) assuming  $\eta = 1$

$$\phi_i = \frac{n_i F v_i}{A j} \Rightarrow \phi_i = \frac{n_i v_i}{\sum n_i v_i} \quad (\text{A.4})$$

At this point, two more assumptions are made. Firstly that, like in single-component systems, the rate of degradation of each compound is kept always constant during time, as long as kinetic control is maintained. Secondly, that the rate of consumption of each product depends on the probability of a molecule of a certain species reach the electrode among other molecules of different species; this probability corresponds approximately to the mole fraction of that component. Thus,

$$\phi_i = \frac{n_i K_i C_i / \sum C_i}{\sum n_i K_i C_i / \sum C_i} \Rightarrow \phi_i = \frac{n_i K_i C_i}{\sum n_i K_i C_i} \quad (\text{A.5})$$

where the  $K_i$  are constants for a given set of operating conditions. Finally, for simplifying, it may be assumed that, if the species are sufficiently alike (in terms of structure, reactivity, stability, etc.) then all the  $K_i$  values will be probably similar, and so

$$\phi_i = \frac{n_i C_i}{\sum n_i C_i} \quad (\text{A.6})$$

### A.3. Mixed control

This situation occurs when there are species with  $C_s > 0$  and others with  $C_s = 0$ . The former will be denoted by the subscript *k* and the latter by the subscript *q*. Under these circumstances is also assumed that the current efficiency is 1. Thus, according to Eq. (A.1):

$$j_q = j_{L,q} \Rightarrow j_q = n_q F k_{d,q} C_q \quad (\text{A.7})$$

and

$$j_k = \phi'_k (j - B) \quad (\text{A.8})$$

where

$$\phi'_k = \frac{n_k C_k}{\sum_k n_k C_k} \quad (\text{A.9})$$

and

$$B = \sum_q j_{L,q} \quad (\text{A.10})$$

Note that if  $\eta = 1$ , as it is assumed, then by Eqs. (10), (A.8) and (A.10):



$$\begin{aligned} \sum_i j_i &= \sum_k \phi'_k (j - \sum_q j_{L,q}) + \sum_q j_{L,q} \\ &= (j - \sum_q j_{L,q}) \sum_k \phi'_k + \sum_q j_{L,q} \end{aligned} \quad (\text{A.10})$$

thus,

$$\sum_k \phi'_k = 1 \quad (\text{A.11})$$

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