

Lumped kinetics and acute toxicity of intermediates in the ozonation of phenol in saline media

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Abstract

This work investigates the feasibility of ozonation for destroying phenol and removing organic matter in saline media. The reaction lumped kinetics was followed using the GLKM (General Lumped Kinetic Model). The main intermediate compounds were: catechol, hydroquinone, 4,4'-dihydroxybiphenyl, and 4-bromophenol. It could be noted no significant differences in phenol degradation, mineralization rates, and toxicity removal up to 2 g L^{-1} of salt. So, ozonation appears to be a technology that can be used in low salinity media, which is characteristic of waters destined to reuse and recycling programs inside industries.

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1. Introduction

The search for cleaner technologies has placed oxidation technologies as an adequate solution whenever the destruction of organic pollutants in wastewaters is desired [1]. Ozonation has been proved to be a good choice as ozone is a powerful oxidant. It has also the unique feature of decomposing itself into a safe, environmentally harmless, and non-toxic product—oxygen.

Phenol is a well-known environmental pollutant. Phenols are used in many kinds of industries, such as pulp and paper mills, herbicides and fungicides production, etc. [2]. Phenols

and their degradation products in the environment are major aquatic pollutants because they are quite toxic. Also, as they are relatively stable and soluble in water, their degradation to reach safety levels in the range of $0.1\text{--}1.0 \text{ mg L}^{-1}$ is not an easy task.

Ozonation is very effective in treating wastewaters containing phenolic compounds [3–9]. Several research papers have addressed the ozonation of phenol in aqueous solutions using gas–liquid contactors [3,4,10–23]. However, none of them have investigated the efficiency of this technology in saline media. This knowledge becomes fundamental as the increasing demand of water is leading to its intensive reuse and recycle, which generate the build-up of salts, making it necessary to assess the performance of ozonation in saline environments.

Two works have already investigated the reaction of chloride with ozone [24,25]. Rate constants of $2 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ (0°C) and $3 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ (23°C) have been reported, respectively. Those small values for the rate

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Nomenclature

BSTFA	<i>N,O</i> -bis(trimethylsilyl)trifluoroacetamide
<i>C</i>	phenol or ozone concentration (mg L^{-1})
$C_{B,\text{max}}$	maximum concentration of intermediates formed (mg L^{-1})
$C_{\text{O}_3}^*$	dissolved ozone concentration in equilibrium with its partial pressure at the interface (mg L^{-1})
<i>D</i>	diffusivity ($\text{m}^2 \text{s}^{-1}$)
E_i	enhancement factor for an instantaneous reaction
GLKM	General Lumped Kinetic Model
<i>H</i>	Henry's constant (atm mole fraction)
<i>Ha</i>	Hatta number
k_2	second order kinetic constant for the reaction between phenol and ozone ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{ij}	second order kinetic constant for the transformation of lump <i>i</i> into lump <i>j</i> ($\text{L mg}^{-1} \text{min}^{-1}$)
k_L	mass transfer coefficient (m s^{-1})
LC_{50}	lethal concentration to 50% of the test-organisms (%)
<i>p</i>	absolute pressure (atm)
$p_{1/2}$	pressure at the middle height of the liquid column (atm)
p_{O_3}	ozone partial pressure (atm)
t_{max}	the elapsed time until $C_{B,\text{max}}$ is attained (min)
<i>T</i>	absolute temperature (K)
TOC	total organic carbon (mg L^{-1})
<i>X</i>	mole fraction
<i>z</i>	stoichiometric coefficient for phenol

Greek letters

λ	wavelength (nm)
θ	centigrade temperature ($^{\circ}\text{C}$)

constant show that the reaction between ozone and chloride is an extremely slow process, even in high saline waters. On the other hand, the rate constant for the reaction between bromide and ozone was determined to be $1.6 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ (23°C) [25], which is approximately 5.3×10^4 times greater than the one for chloride.

Therefore, this work investigates the feasibility of ozonation for destroying phenol and removing organic matter at two levels of salinity: 2 and 50 g L^{-1} of sodium chloride (representative of reuse and marine waters, respectively), without rendering the final effluent more toxic than the initial one.

2. Materials and methods

The study was carried out in a bubbling column 1.5 m high and 0.10 m external diameter. The diffuser, a 316L stainless steel disk with $10 \mu\text{m}$ pore diameter, generated bubbles of

approximately 3 mm in diameter. The column was operated in batch mode (discontinuous for the liquid phase).

Ozone was produced from pure oxygen using a PCI Ozone Generator Model G2, with a capacity of 40 g h^{-1} of ozone. Ozone was fed at 5.0 N L min^{-1} and 2.0% in weight. Under these conditions, ozone generation was $\pm 130 \text{ mg min}^{-1}$.

A 6.0 L solution of phenol (Merck P.A., bidistilled under vacuum) at 100 mg L^{-1} and pH 7.0 (natural pH of the phenol solution) was fed to the column. Three sodium chloride (Merck, P.A.) concentrations were tested: 0, 2, and 50 g L^{-1} . The oxidation process was stopped when phenol concentration decreased to less than 0.5 mg L^{-1} (according to phenol absorbance measures in the UV region of the spectrum, $\lambda = 269.5 \text{ nm}$, using a UV-160A Shimadzu spectrophotometer) and a mineralization of at least 60% was achieved (through total organic carbon (TOC) analyses, using a TOC-5000A Shimadzu Carbon Analyzer). As TOC analyses measure the content of organic carbon present in the samples, when this content decreases, it is an indication that organic carbon has been transformed into inorganic carbon (CO_2), i.e., part of the organic matter has been mineralized.

Chromatographic analyses were performed in order to determine phenol degradation and identify the intermediates produced. Prior to the chromatographic analyses, samples were extracted to dichloromethane (CH_2Cl_2) using an adapted methodology [26,27]. This methodology is depicted in Fig. 1.

For determining the remaining phenol concentration, a Shimadzu GC-17A gas chromatograph provided with a DB-5 ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) column and a FID detector was employed. The GC was temperature programmed: the injection and detector ports were held at 250 and 280°C , respectively, and the GC oven started at 75°C and was increased to 250°C at $10^{\circ}\text{C min}^{-1}$. The column head pressure was also programmed: it started at 40 kPa and was increased to 70 kPa at 1.7 kPa min^{-1} . The carrier gas (H_2) was then kept at a flow rate of 0.80 mL min^{-1} and a linear speed of 25 cm s^{-1} . One microlitre of the extract was injected in split mode (1:30).

The samples used for identifying the intermediate products formed in the course of ozonation were derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The analyses were performed in a 5890 Series II Hewlett Packard gas chromatograph coupled with a 5972 Hewlett Packard mass spectrometer in scan mode between 40 and 400 m/z . The same DB-5 column and temperature program described previously were used. The column head pressure was kept at 41 kPa. The carrier gas (He) flow rate and linear speed were 0.86 mL min^{-1} and 34 cm s^{-1} , respectively. Two microlitres of the derivatized extract were injected in splitless mode.

The CO_2 evolved during ozonation was calculated by subtracting the initial TOC from the remaining one.

Toxicity assays were carried out according to standards N-2588 and N-2594 [28,29], which are based on well-established methods [30]. The test-organism used was

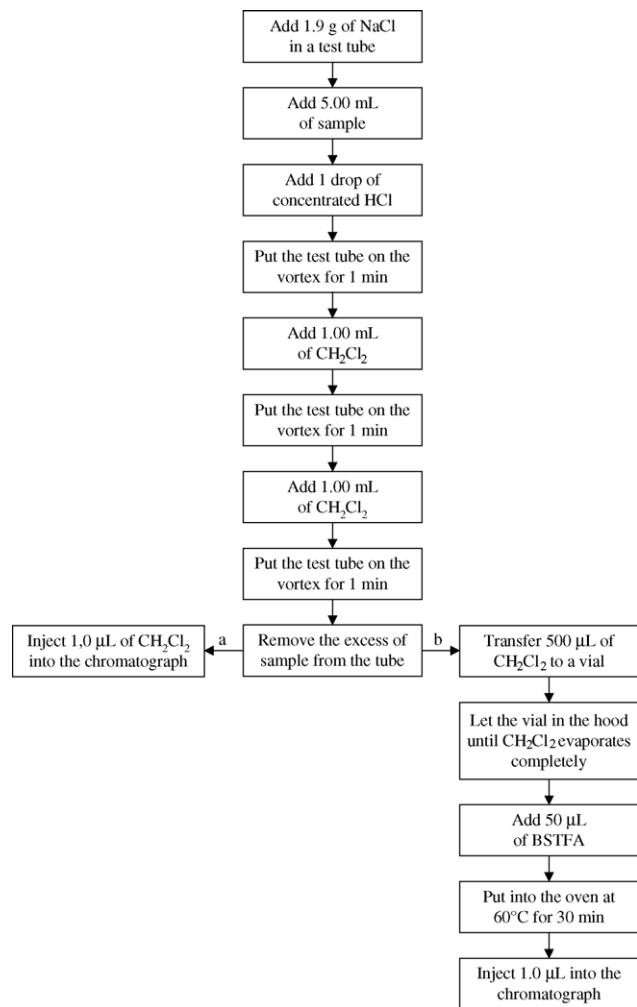


Fig. 1. Liquid-liquid extraction scheme: (a) phenol and (b) intermediates determination.

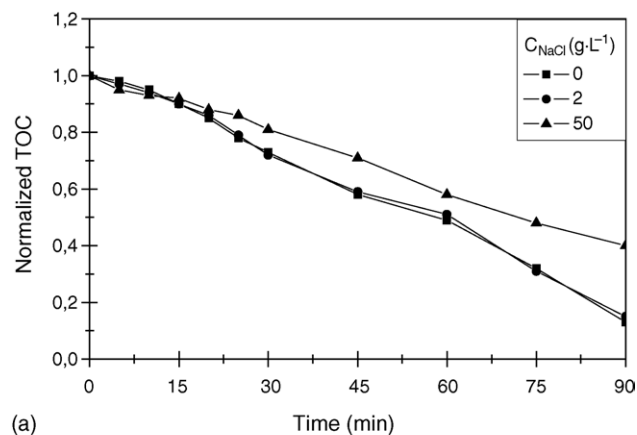
Artemia sp., which is a species that lives in the coastal areas of Brazil. It is an organism quite alike *Artemia salina* as they share the same gender. This gender is appropriate to test the toxicity of high saline environments [31]. Statistical analyses performed to determine LC_{50} were based on the adjusted Spearman–Kärber method [32].

Reaction rate equations were integrated by an explicit method for stiff problems (Runge–Kutta type) where the Jacobian matrix was provided. Kinetic and adsorption constants were estimated by a least squares regression quasi-Newton algorithm [33,34].

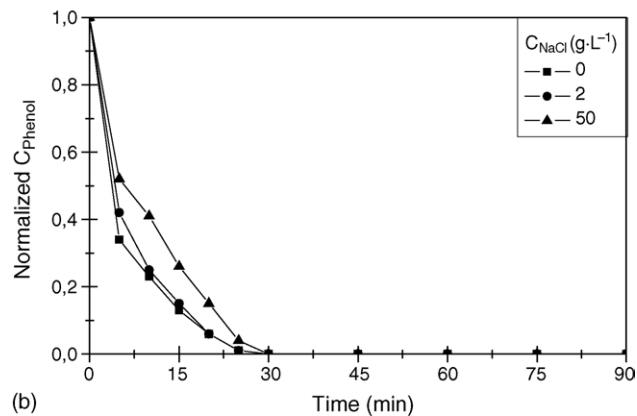
3. Results and discussion

3.1. Total organic carbon and Gas chromatography (GC)

Fig. 2a shows that the presence of salt inhibited mineralization, although the inhibition depends on the salt concentration. For the small concentration (2 g L^{-1}) no significant



(a)



(b)

Fig. 2. (a) Mineralization and (b) remaining phenol concentration vs. treatment time.

change was observed. However, when the salt concentration was increased to 50 g L^{-1} , mineralization dropped from 90% to 60%, approximately. On the other hand, Fig. 2b shows that phenol degradation was not significantly changed, although a slight delay in the high salinity medium (50 g L^{-1}) can be observed.

3.2. Ozone consumption

Apparently, by observing Fig. 3, ozone consumption was not significantly affected by the medium salinity. However, when ozone consumption is related to the amount of phenol or TOC removed (Table 1) it becomes clear that the amount of ozone consumed is proportional to the salt content. The behavior observed in Fig. 3 can be explained by a compensatory mechanism: while ozone consumption increases with salinity, ozone self-decomposition rate decreases proportionally to the salt concentration [1]. Therefore, those two

Table 1
Ozone consumption vs. phenol and TOC removal

C _{NaCl} (g L ⁻¹)	mg O ₃ /mg phenol removed	mg O ₃ /mg TOC removed
0	3.2	15.3
2	3.5	17.9
50	3.8	20.4

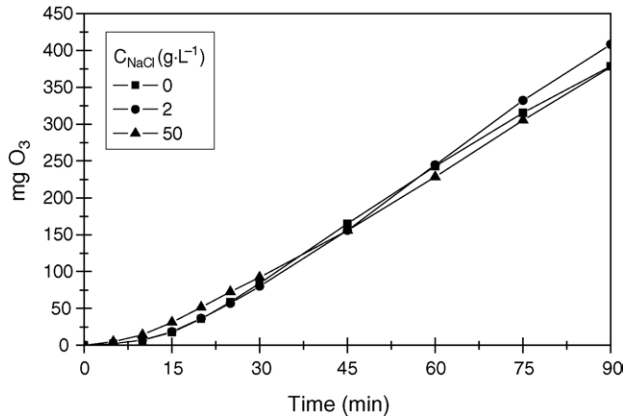


Fig. 3. Ozone consumption vs. treatment time.

opposite effects somewhat cancel each other and no significant changes are observed in the overall ozone uptake.

3.3. Ozone absorption kinetics

The ozone absorption kinetics is determined by the use of two parameters: the Hatta number (Ha) [35] and the Enhancement factor for an instantaneous reaction (E_i) [36].

The Hatta number is a dimensionless parameter defined by Eq. (1) (where D_{O_3} is the ozone diffusivity, k_2 the second order kinetic constant for the reaction between phenol and ozone, C_{P_0} the initial phenol concentration, and k_L is the mass transfer coefficient in the liquid phase) that indicates whether the reaction takes place in the bulk of the liquid ($Ha < 0.3$), in the liquid film around the bubble ($Ha > 3$), or in both ($0.3 < Ha < 3$). For calculating the Hatta number, the following data were used: $D_{O_3} = 1.74 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $k_L = 2 \times 10^{-4} \text{ m s}^{-1}$ [37], and $k_2 = 1.8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ [9].

$$Ha = \frac{\sqrt{D_{O_3} k_2 C_{P_0}}}{k_L} \quad (1)$$

The enhancement factor for an instantaneous reaction represents how many times the ozone absorption is increased due to the chemical reaction, taken as an instantaneous one. That factor is defined by Eq. (2) (where D_P is the phenol diffusivity, z the stoichiometric coefficient for phenol, and $C_{O_3}^*$ is the dissolved ozone concentration in equilibrium with its partial pressure at the interface). For calculating the factor, the following data were used: $D_P = 1.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [38] and $z = 1/3$ [39].

$$E_i = 1 + \frac{D_P}{z D_{O_3}} \frac{C_{P_0}}{C_{O_3}^*} \quad (2)$$

For obtaining $C_{O_3}^*$, the first step is to calculate the Henry's constant using Eq. (3), where T is the absolute temperature [40]. Eq. (3) can be used within the ranges: $3.5 < \theta < 60^\circ \text{C}$ and $0.65 < \text{pH} < 10.2$.

$$H = 3.84 \times 10^7 [\text{OH}^-]^{0.035} e^{-2.428/T} \quad (3)$$

Table 2

Calculated Henry's constants (H) and ozone equilibrium concentrations ($C_{O_3}^*$) in function of the medium salinity

C_{NaCl} (g L ⁻¹)	H (atm X)	$C_{O_3}^*$ (mg L ⁻¹)
0	6.322	8.8
2	6.385	8.7
50	8.219	6.5

For pH 7.0 and $\theta = 25^\circ \text{C}$, $H = 6.322 \text{ atm } X_{O_3}^{-1}$. Considering 1 L of solution, $C_{O_3}^*$ can be expressed in terms of X_{O_3} , according to Eq. (4).

$$C_{O_3}^* = \frac{48}{18} \times 10^6 X_{O_3} = 2.6 \times 10^6 X_{O_3} \quad (4)$$

The second step is to calculate pressure. The overall pressure was considered to be the absolute pressure plus the one at the middle height of the liquid column. The column height was 0.94 m. As 1.0 atm corresponds to 10.33 m of water column, $p_{1/2}$ can be calculated by Eq. (5).

$$p_{1/2} = \frac{1}{2} \frac{0.94 \text{ atm}}{10.33 \text{ m}_{\text{H}_2\text{O}} \text{ atm}^{-1}} = 0.046 \text{ atm} \quad (5)$$

Therefore, the overall pressure is: $p = 1.00 + p_{1/2} = 1.046 \text{ atm}$. As ozone concentration in the inlet is 2%, ozone partial pressure is given by Eq. (6).

$$p_{O_3} = 0.02 \times 1.046 = 0.021 \text{ atm} \quad (6)$$

The third and last step is to use Henry's law and the ozone partial pressure to calculate the ozone molar fraction, as shown in Eq. (7).

$$p_{O_3} = H X_{O_3} \Rightarrow X_{O_3} = \frac{0.021}{6.322} = 3.3 \times 10^{-6} \quad (7)$$

Finally, Eq. (4) is used to calculate $C_{O_3}^*$: $C_{O_3}^* = 2.6 \times 10^6 \times 3.3 \times 10^{-6} = 8.8 \text{ mg L}^{-1}$.

The same procedure was used to calculate $C_{O_3}^*$ for the saline media. The only detail is that the Henry's constant had to be corrected due to the differences in the ozone gas solubility when electrolytes are present. This was achieved by an empirical method proposed [36] which takes into account the ionic strength of the solution. Table 2 shows the Henry's constants and $C_{O_3}^*$ calculated in this way.

Table 3 shows the calculated Hatta numbers and the enhancement factors. It can be seen that, initially, the reaction absorption kinetics can be regarded as fast ($Ha > 3$), between the pseudo first order and the instantaneous one

Table 3

Calculated Hatta numbers (Ha) and enhancement factors for an instantaneous reaction (E_i), at the beginning of the ozonation, regarding the medium salinity

C_{NaCl} (g L ⁻¹)	Ha	E_i	$E_i/2$	Kinetic regime
0	9.51	13.7	6.84	Fast
2	10.2	16.0	7.98	
50	9.81	19.3	9.64	

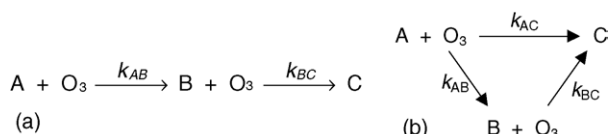


Fig. 4. Reaction lumped kinetics models: (a) in series and (b) General Lumped Kinetic Model (GLKM).

($E_i/2 < Ha < 10E_i$). Therefore, ozonation was controlled by the chemical kinetics and occurred in the film and not in the bulk of the liquid.

3.4. Kinetic constants estimation

The reaction lumped kinetics was followed using two models: the classic in series and one of the lumped oxidation schemes available [41], called General Lumped Kinetic Model (GLKM) [42], depicted in Fig. 4.

Eqs. (8)–(13) describe the in series model and the GLKM one, respectively. They were simultaneously integrated in time and the kinetic constants were estimated. Fig. 5 presents the experimental data obtained (symbols) and the integrated lumps distribution curves (lines).

$$\frac{dC_A}{dt} = -k_{AB}C_A C_{O_3}^* \quad (8)$$

$$\frac{dC_B}{dt} = (k_{AB}C_A - k_{BC}C_B)C_{O_3}^* \quad (9)$$

$$\frac{dC_C}{dt} = k_{BC}C_B C_{O_3}^* \quad (10)$$

$$\frac{dC_A}{dt} = -(k_{AB} + k_{AC})C_A C_{O_3}^* \quad (11)$$

$$\frac{dC_B}{dt} = (k_{AB}C_A - k_{BC}C_B)C_{O_3}^* \quad (12)$$

$$\frac{dC_C}{dt} = (k_{AC}C_A + k_{BC}C_B)C_{O_3}^* \quad (13)$$

From Fig. 5, it can be seen that in the absence of salt and for the high salinity medium (50 g L^{-1}), there is no visual difference between the two kinetic models, regarding the fit of the lines to the experimental data. However, the 3 parameters model (GLKM) does give a better representation of the low salinity data (2 g L^{-1}).

Tables 4 and 5 present the estimates obtained for the rate constants, along with the respective determination coefficients.

Table 4
Estimates for the reaction kinetic constants (in series model)

NaCl (g L^{-1})	Parameters			R^2
	k_{AB}	k_{BC}		
0	$(1.95 \pm 0.300) \times 10^{-2}$	$(1.76 \pm 0.295) \times 10^{-3}$		0.974
2	$(1.70 \pm 0.142) \times 10^{-2}$	$(1.65 \pm 0.398) \times 10^{-3}$		0.958
50	$(1.56 \pm 0.196) \times 10^{-2}$	$(1.71 \pm 0.116) \times 10^{-3}$		0.986

Note: $[k] = \text{L mg}^{-1} \text{ min}^{-1}$.

Table 5
Estimates for the reaction kinetic constants (GLKM model)

NaCl (g L^{-1})	Parameters			R^2
	k_{AB}	k_{BC}	k_{AC}	
0	$(2.03 \pm 0.340) \times 10^{-2}$	$(1.76 \pm 0.191) \times 10^{-3}$	*	0.974
2	$(1.39 \pm 0.109) \times 10^{-2}$	$(1.03 \pm 0.119) \times 10^{-3}$	$(3.16 \pm 0.584) \times 10^{-3}$	0.992
50	$(1.53 \pm 0.132) \times 10^{-2}$	$(1.66 \pm 0.230) \times 10^{-3}$	*	0.986

Note: $[k] = \text{L mg}^{-1} \text{ min}^{-1}$.

* Constants with no statistical significance.

The following considerations can be made based on the results:

- Regardless of the model used, k_{AB} is approximately 10 times greater than k_{BC} . This is a common feature of ozonation processes, in which the intermediates formed react with smaller rates than the parent compound (ozone is a very selective oxidant).
- In the absence of salt and in the high salinity medium, regardless of the model used, the estimates obtained for k_{AB} and k_{BC} are roughly the same. This is also true for the determination coefficients. Therefore, both models can represent equally well the experimental data, although k_{AC} constants in the 3 parameters model had no statistical significance. This means that k_{AC} can be neglected without decreasing the quality of data representation.
- Again, for the low salinity medium, the 3 parameters model gives a quite better representation of the data. This does not mean that there is a reaction that transforms phenol into carbon dioxide directly, but that intermediate compounds are formed which can be converted very quickly into CO_2 . In fact, the estimate for k_{AC} is three times greater than the one obtained for k_{BC} .

Table 6 presents two estimated kinetic parameters: $C_{B,\max}$, which is the maximum concentration of intermediates formed, and t_{\max} (the elapsed time until $C_{B,\max}$ is attained). It can be seen that t_{\max} increases with salinity, an indication that the presence of salt plays an inhibitory role during ozonation. On the other hand, $C_{B,\max}$ is practically not affected by the presence of salt. Taking into consideration that $C_{O_3}^*$ decreases with salinity and the rate constants are not significantly affected by it, this inhibition is probably caused by the depletion of ozone in the interface.

Table 6
 t_{\max} and $C_{B,\max}$ observed during ozonation

Kinetic parameters	$C_{\text{NaCl}} (\text{g L}^{-1})$		
	0	2	50
$t_{\max} (\text{min})$	15.2	20.1	25.0
$C_{B,\max} (\text{mgTOC L}^{-1})$	66.0	65.5	67.8

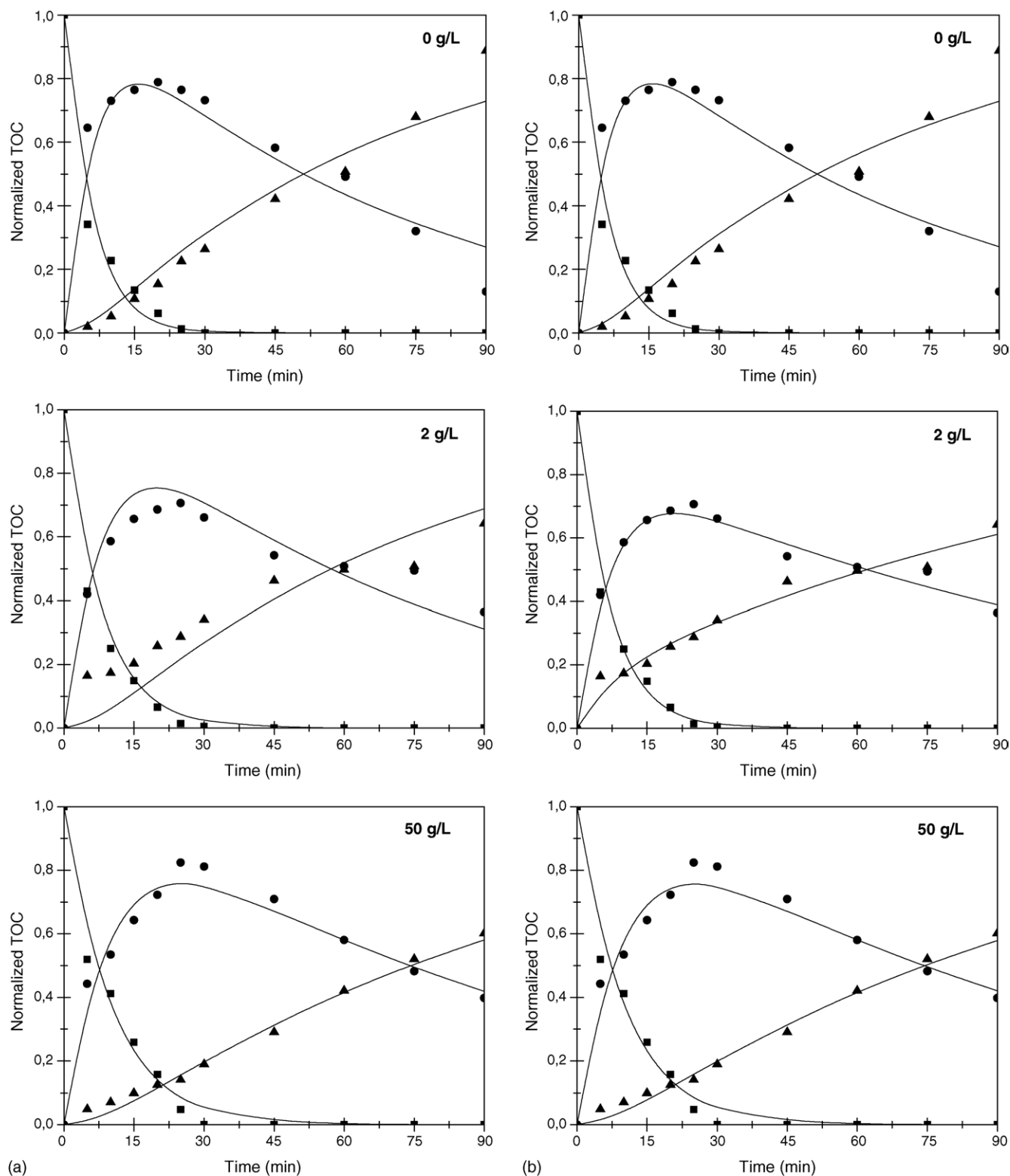


Fig. 5. Lumps concentration profiles related to NaCl content: (a) in series model and (b) GLKM.

3.5. Compounds identification by GC-MS

The intermediate compounds formed during ozonation were identified by gas chromatography coupled with

mass spectrometry, as shown in Table 7. Four compounds – catechol, hydroquinone, 4-bromophenol, and 4,4'-dihydroxybiphenyl – were produced in significant amounts during the course of the degradation. Those compounds have

Table 7
Identified compounds by GC–MS

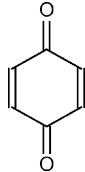
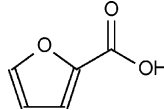
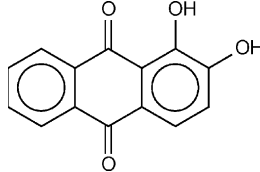
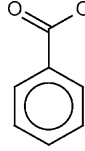
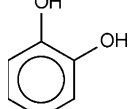
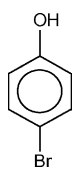
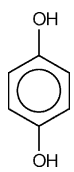
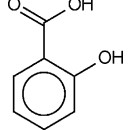
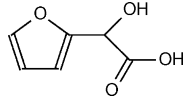
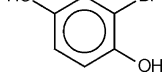
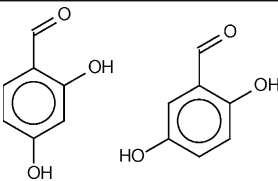
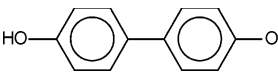
Compounds	Structural formula	C_{NaCl} (g L ⁻¹)		
		0	2	50
<i>p</i> -Benzoquinone		nd	✓	nd
2-Furancarboxylic acid		✓	✓	✓
1,2-Dihydroxy-antraquinone		✓	✓	✓
Benzoic acid		✓	✓	✓
Catechol		✓	✓	✓
4-Bromophenol		nd	✓	✓
Hydroquinone		✓	✓	✓
Salicylic acid		nd	nd	✓
α -Hydroxy-2-furan-acetic acid		✓	✓	✓
Bromohydroquinone		nd	nd	✓

Table 7 (Continued)

Compounds	Structural formula	C_{NaCl} (g L ⁻¹)		
		0	2	50
2,4-Dihydroxy-benzaldehyde or 2,5-dihydroxy-benzaldehyde		nd	nd	✓
4,4'-Dihydroxy-biphenyl		✓	✓	✓

nd, not detected.

already been reported [43–45], except the 4-bromophenol. The occurrence of brominated compounds is due to the bromide present as an impurity in the NaCl. Although the reaction between ozone and chloride is very slow, the one between ozone and bromide is fast [25]. This finding suggests that waters with bromide ions are not suited for being treated by ozonation, as brominated compounds will be formed. Fig. 6 shows that salinity inhibited the formation of catechol and promoted the formation of the other substances. The reason for this behavior is not clear.

3.6. Acute toxicity

It could be noted that ozonation was quite efficient in removing the toxicity in the non-saline and low salinity (2 g L⁻¹) media, as depicted in Fig. 7. However, in the high salinity one (50 g L⁻¹), after an initial toxicity removal, it began to increase again, a fact already reported in the literature [46,47]. This points out probably to the formation of highly toxic substances that were not identified due to their small concentration.

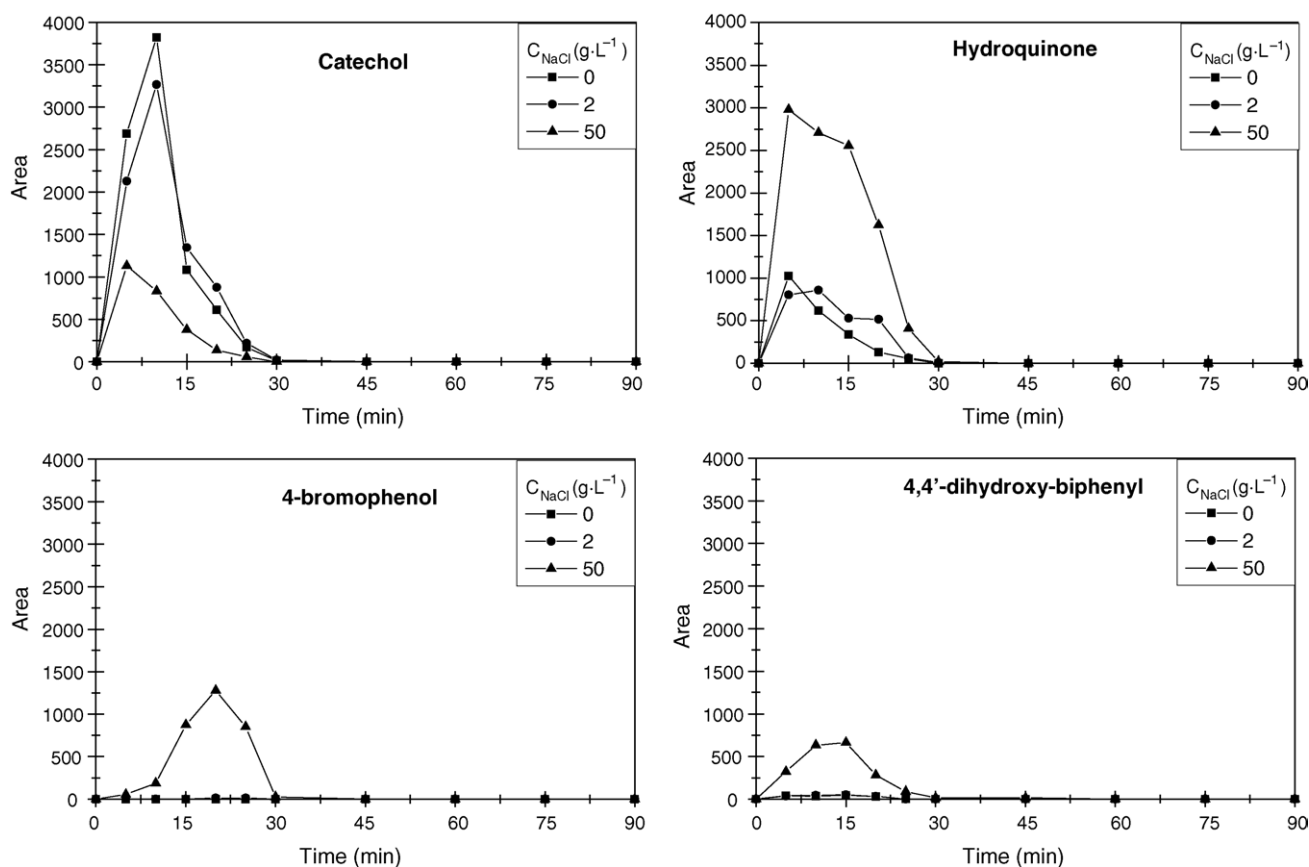


Fig. 6. Plots of peak area (concentration) vs. treatment time regarding salinity for the four main intermediates identified.

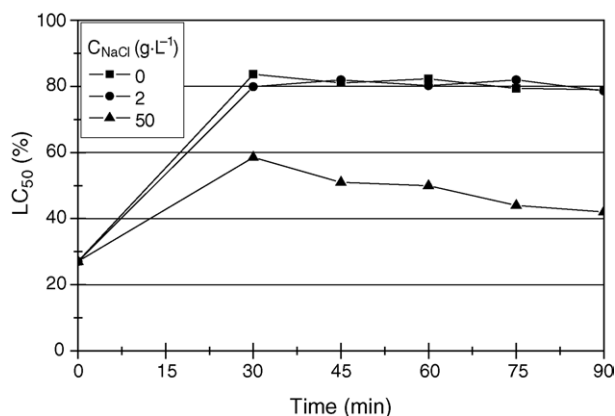


Fig. 7. LC₅₀ (%) vs. treatment time.

4. Conclusions

It was shown that for low concentrations of salt, ozonation is quite efficient in removing phenol from wastewaters, although this is not true regarding mineralization. Salinity inhibited reaction rates and catechol formation, while promoting hydroquinone and 4,4-dihydroxybiphenyl ones. Ozonation was also efficient in removing toxicity, but in the high salinity (50 g L⁻¹) medium, highly toxic compounds were produced.

So, it could be demonstrated that ozonation is a technology that can be used in saline media with similar efficiencies to the ones obtained in non-saline media. This is true up to a concentration of 2 g L⁻¹ of salt, which is characteristic of waters destined to reuse and recycling programs inside industries.

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