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Wet oxidation of 4-chlorophenol
Kinetic study

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Abstract

This study evaluates the application of wet oxidation for the treatment of solutions containing 4-chlorophenol and suggests a kinetic model in order to allow the prediction of the concentration of the compounds involved in the process throughout the reaction. 4-Chlorophenol is a compound of special interest due to its high toxicity and low biodegradability. The existence of an induction period previous to the oxidation was detected and a kinetic equation to describe the whole process was found out by adjusting the experimental data. The influence of some operating conditions such as temperature and partial pressure of oxygen were studied before carrying out the development of the reaction mechanism and the kinetic model. From the results, it can be concluded that an increase in the temperature in the range 433–463 K results in a faster degradation rate. On the other hand, an increase in the partial pressure of oxygen in the range from 5 to 10 bar involved a faster kinetic rate, however an increase from 10 to 15 bar does not show any improvement. It can be concluded that the degradation of 4-chlorophenol by wet oxidation follows pseudo first order kinetics, being hydroquinone and quinone the most relevant intermediates. It was observed as well that the chloride from the chlorophenol was released to the medium and no intermediates containing chloride were formed. A remarkable increase in the biodegradability was observed through the wet oxidation process.

Keywords: Wet oxidation; 4-Chlorophenol; Kinetics

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1. Introduction

The need to restore contaminated sites to avoid further risks to the environment has arisen in the last years the development of effective methods for chlorophenol (CP) removal. The main goal is to achieve complete mineralization to CO_2 and H_2O in addition to smaller amounts of some ions, e.g. chloride anions, or at least to produce less harmful intermediates. An ideal waste treatment process must completely mineralize the toxic species present in the waste streams without leaving behind any hazardous residues and it should be also cost-effective [1].

The conventional pollutant destructive technologies include biological, thermal and physico-chemical treatments [2]. Biological treatments usually require a long residence time for microorganisms to degrade the pollutant, because they are affected by CPs toxicity; thermal treatments present considerable emission of other hazardous compounds; and physico-chemical techniques, which include processes such as flocculation, precipitation, adsorption on granular activated carbon (GAC), air stripping or reverse osmosis (RO), require a post-treatment to remove the pollutant from the newly contaminated environment [3].

Alternative methods to these well-established techniques are the so-called *Advanced Oxidation Processes* (AOPs) [4,5] which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils providing almost total degradation [6]. AOPs are based on the initial formation of radicals, i.e. hydroxyl radicals ($OH^{\bullet}$) that later act as non-selective oxidation agents. Several technologies are included in the AOPs like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc. and the main difference between them is the way in which the radicals are formed. Even though these techniques can provide the conversion of contaminants to less harmful compounds, usually oxygenated organic

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Abbreviations: AOPs, advanced oxidation processes; 4-CP, 4-chlorophenol; CP(s), chlorophenol(s); Q, quinone; HQ, hydroquinone; TOC, total organic carbon; HPLC, high performance liquid chromatograph; BOD, biochemical oxygen demand; IC, ion chromatograph; t, reaction time; k_i, pseudo-kinetic constants; j, induction period

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products and low molecular acids are formed during the process [7,8]; in addition, they are limited to treatment of waters which contain low concentrations of organic or inorganic scavenging material [9]. Experiences with different oxidation technologies and substrates have shown that a partial oxidation of toxic water may increase its biodegradability up to high levels [10,11].

AOPs have shown promising results either for the complete mineralization of organic compounds or for their transformation into less complex structures, which are more biodegradable [12–14]. Among these technologies, supercritical water oxidation (SCWO), subcritical oxidation or wet oxidation (WO) and wet peroxide oxidation (WPO) are of special interest. These processes differ from the rest of the AOPs not only in terms of operating conditions but also in the higher concentration of the pollutants present in the wastewater. They are used mainly for concentrated wastewaters in order to allow autothermal operation, and thus a reduction in the operating costs [15]. A high concentration of the pollutant in the treated water can be achieved by some pre-treatment such as nanofiltration, where the obtained concentrate is already under the required pressure to WO. SCWO takes place above the critical point of water ($T \geq 648$ K and $P \geq 221$ bar) [16] and WO engages with oxidation at a temperature range of 398–673 K and pressures of 5–200 bar. The use of oxygen as the oxidizing agent is common to WO and SCWO processes.

Many kinetic models have been suggested in the literature in order to describe the wet oxidation of multi-compound solutions. One of first ones was the General Lumped Kinetic Model (GLKM) suggested by Li et al. [17]. Some other models have been found in the literature, such as the Lumped Kinetic Model (LKM) by *Zhang and Chuang* [18], the Multi-component Kinetic Model suggested by *Escalas* et al. [19], the Extended kinetic Model (ELKM) by *Belkacemi* et al. [20], the Lumped Kinetic Model for wastewater organic burden biodegradebility prediction by *Verenich and Kallas* [21], and the Lumped Kinetic Model for Oil Waters (LKM-OW) by *López Bernal* et al. [22].

As for the description of the kinetics of single-compound solutions, few data has been found about the WO kinetics of 4-chlorophenol (4-CP), however exists extensive literature regarding the wet oxidation of phenol. Many models have been suggested in order to describe the mechanistic pathway of phenol oxidation, some of them are based on the participation of free radicals [23] and some others include a complex network of reactions [24]. The data published in 1995 by *Mishira* et al. [25] appears to be of interest, especially chapter 2.2 (pages 9–11), which includes a description of wet oxidation of phenols and substituted phenols. Based on the literature collected until that moment, they affirmed that phenols and chlorophenols undergoing wet air oxidation exhibit an induction period, the length of which depends on the oxygen partial pressure and in the second place a fast reaction step. Thus, the reaction can be divided in two separate parts. In the first one, i.e. induction period, the radicals are formed and in the second part, the oxidation takes place. The orders of these reactions are assumed to be first order respect the organic [26] and zero respect the oxygen if excess of it is used. Consequently, the oxygen terms may be assumed as a constant [17]. According to this, the 4-CP degradation can be expressed as follows:

$$[4-\mathrm{CP}] = f(t, k_1) = [4-\mathrm{CP}]_{\mathrm{o}}\mathrm{e}^{[-k_1(t-j)]} \qquad (1)$$

where k_1 is the pseudo-first order reaction rate constant, in which the influence of the temperature can be expressed according to an equation of the Arrhenius type: $k_i = k_i^{\mathrm{o}}\,\mathrm{e}^{(-E_{\mathrm{a}i}/RT)}$ and "j" is the induction time. Regarding the induction period, some authors [27] have affirmed that it follows an equation of the Arrhenius type which contains a pressure term:

$$j = \frac{k_i'}{P}\,\mathrm{e}^{(E_{\mathrm{a}i}'/RT)} \qquad (2)$$

2. Materials and methods

Wet oxidation reactions were carried out in a high-pressure stainless steel (T316SS) Parr reactor (Parr Instrumental Co., USA) with a volume of 450 mL. This reactor permits experiments at neutral or close to acidic pH and is capable of performing batch experiments at pressures of up to 50 bar (1 bar = 1×10^5 Pa) and temperatures of up to 623 K. A drop band with one screw and a split ring pair with screws allow the use of the reactor under those conditions of pressure and temperature. The reactor is also equipped with a cooling and agitation system. The temperature was kept constant during the reaction by means of a temperature controller. Fig. 1 shows a scheme of the experimental equipment employed. The 4-CP, hydroquinone (HQ) and quinone (Q) used in this study were supplied by Sigma–Aldrich Chemicals (Germany).

Solutions containing 1000 and 500 ppm (mg L^{-1}) of 4-CP were used for this research. Once these solutions were ready, 300 mL were introduced in the reactor, which was then properly closed. The following step consisted on fixing the desired temperature on the controller and waiting until the temperature of the reactor reached the set value. Depending on the selected temperature, the preheating period lasted from 20 to 40 min. Once the temperature was reached, the oxygen partial pressure was adjusted to the designated value for the experiment. At this point, the reaction was assumed to start. Each reaction lasted 1.5 h and during this period several samples were withdrawn from the reactor and analyzed for total organic carbon (TOC), pH, high pressure liquid chromatograph (HPLC) and ion chromatograph (IC). Some of the samples were also analyzed for biochemical oxygen demand (BOD).

TOC was measured by means of a Shimadzu 5050 TOC analyzer. The concentration of 4-CP and intermediates was quantified by means of a HPLC system Hewlett-Packard, series 1100. The column used was a YMC-Pack Pro C18 supplied by YMC, Inc, c/o Waters (USA) with a length of 150 and 4.6 mm of inner diameter. The analysis was carried out under a wavelength of 254 nm and the mobile phase consisted of a 50% mixture of Millipore water and acetonitrile (Sigma–Aldrich Chemicals, Germany). To determine the free chloride ion concentration in each sample, a Dionex, DX-120 Ion Chromatograph from Dionex Corporation (USA) was employed. The solution used consisted of a 0.5 M of $\mathrm{HNaCO_3}$ and 0.5 M $\mathrm{Na_2CO_3}$. In addition 1 drop of acetonitrile was added into 1 L of the previous mixture

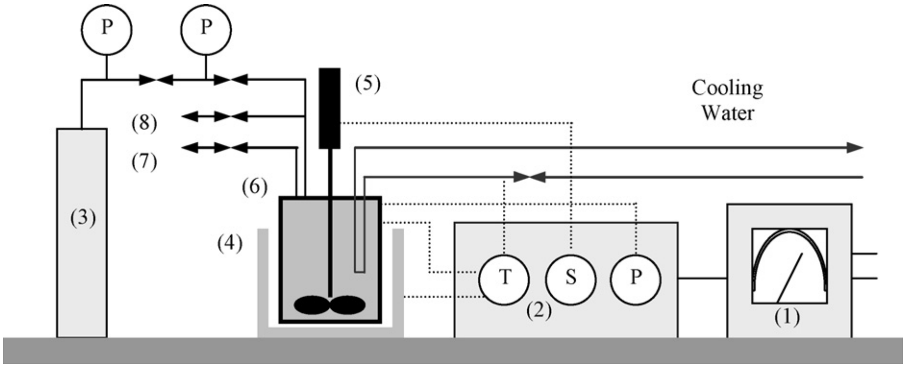

Fig. 1. Wet oxidation equipment: (1) power supply, (2) digital controller (temperature, pressure and stirring speed), (4) heater, (5) stirrer, (6) reactor, (7) samples extraction, (8) gas draining.

to avoid the growth of microorganisms inside the equipment. BOD_5 measurements started with the addition of a digestion set LCW917 (DR. LANGE, Germany) to the samples. Its task consisted of breaking long molecules in smaller pieces, so that they could be quickly digested by the bacteria. The bacteria used in this equipment were *Issatchenkia orientalis* and *Rhodococcus erythropolis* and they were placed in the interior of the BOD Sensor. The breakage of the organic chains took place in a reactor LT100 (DR. LANGE, Germany) maintained at 421 K during 1 h. Before introducing the samples into this reactor some HCl was added to the samples, and once the reaction was finished the assays were neutralized by adding NaOH, after this the samples were ready to be analyzed with the BOD sensor (DR. LANGE, Germany).

3. Results and discussion

3.1. *Influence of the operating conditions*

To study the influence of the temperature in the wet oxidation reaction of 4-CP solutions, reactions with an initial solution of 1000 and 500 ppm were carried out at four different temperatures (423, 433, 448 and 463 K). The other parameters (10 bar of partial pressure of oxygen and 750 rpm of stirring speed) were kept constant. From these results it can be concluded that an increase of the temperature results in a faster degradation rate of the target compound. The pH showed a faster decrease when working at higher temperatures, involving thus a faster formation of low molecular weight acids and consequently, a faster elimination of the 4-CP and intermediates. The same conclusion can be reached when observing the results of the TOC and the HPLC. In both cases the highest and fastest TOC and 4-CP removals were reached when carrying out the reaction at the highest temperature, i.e. 463 K (see Figs. 2 and 3a). In Table 1, the TOC and 4-CP removals achieved after 90 min of wet oxidation at the temperatures studied of solutions containing 500 and 1000 ppm of 4-CP are shown.

By means of the IC, the concentration of free chloride ion was measured throughout the reactions. These values showed that a higher release of the chloride was achieved when increasing the temperature, involving thus, a faster degradation of the chlorophenol since it is the only source of chlorine to the medium. In addition to this, the measured chloride was compared to the calculated values of the chloride related to the chlorophenol decomposed. These results proved that all the chloride present in the solution belonged to the degraded chlorophenol and consequently no intermediates containing chloride were formed during the reaction. The chloride related to the 4-CP destroyed was calculated as follows:

$$\mathrm{Cl^-(ppm)} = (4-\mathrm{CP}_{t=0} - 4 - \mathrm{CP}_t)(\mathrm{ppm}) \times \frac{1\,\mathrm{mmol}\,4-\mathrm{CP}}{\mathrm{molecular\ weight}\,4-\mathrm{CP}} \times \frac{1\,\mathrm{mmol}\,\mathrm{Cl^-}}{1\,\mathrm{mmol}\,4-\mathrm{CP}} \times \frac{\mathrm{molecular\ weight}\,\mathrm{Cl^-}}{1\,\mathrm{mmol}\,\mathrm{Cl^-}} \tag{3}$$

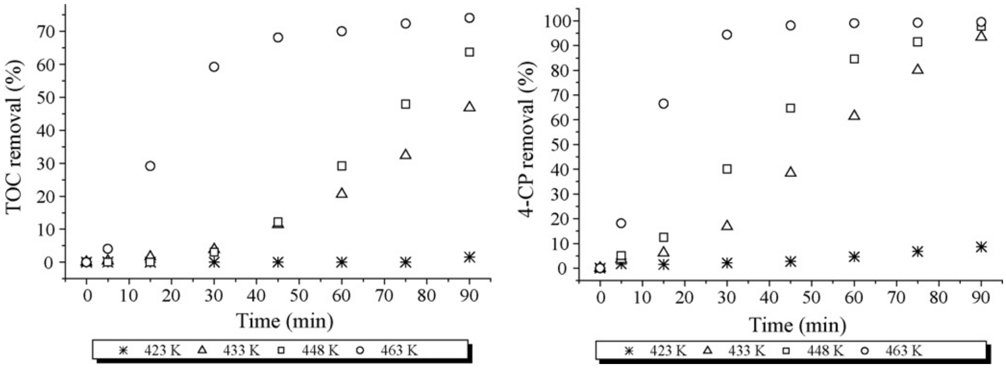

Fig. 2. TOC and 4-CP removal vs. time. WO carried out with an initial concentration of 500 ppm of 4-CP, at 10 bar of P_{O_2} and at different temperatures.

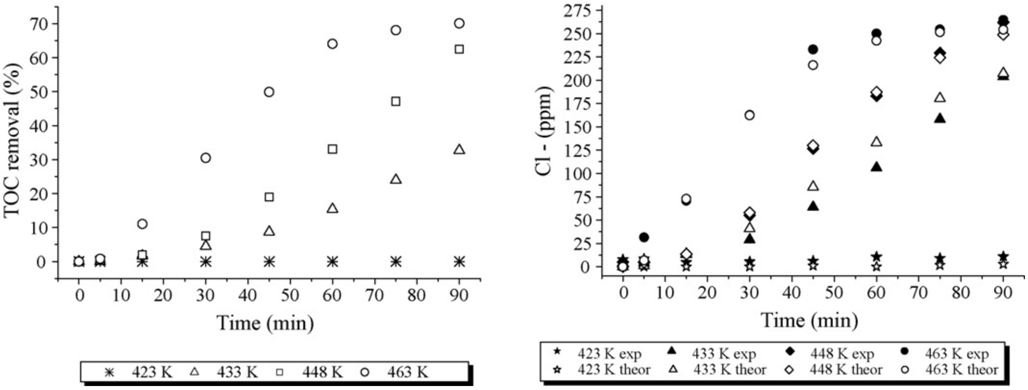

Fig. 3. Results of the WO at 10 bar of P_{O_2}, 1000 ppm of 4-CP and different temperatures. (a) TOC removal vs. time. (b) Cl^- measured by means of the ion chromatograph (exp) and the calculated from the 4-CP decomposed (theor) vs. time.

Table 1
TOC and 4-CP removals

Temperature (K)	1000 ppm of initial concentration of 4-CP		500 ppm of initial concentration of 4-CP	
	TOC removal (%)	4-CP removal (%)	TOC removal (%)	4-CP removal (%)
432	0	1.1	1.56	8.61
433	32.7	76.6	46.8	93.4
448	62.5	95.1	63.7	97.7
463	70.1	96.7	74.1	99.5

Wet oxidation reactions at different temperatures and different initial concentrations of 4-CP.

where molecular weight of 4-CP is 128.5 g/mol and molecular weight of Cl^- is 35.5 g/mol.

In Fig. 3b, the values of the chloride concentration measured by the IC and the calculated from the destroyed 4-CP are depicted.

Samples from the experiments carried out with an initial concentration of 500 ppm and at the following temperatures: 423, 433, 448 and 463 K were analyzed for BOD in order to know the influence of the reaction temperature in this parameter. In Fig. 4, the results of these analyses are depicted. It can be concluded that an increase of the temperature involves and increase of the biodegradability, making then feasible the use of a biological post-treatment to couple the oxidation.

As for the influence of the oxygen partial pressure, wet oxidation reactions at 5, 7.5, 10 and 15 bar of pressure, with an initial solution containing 500 ppm of 4-CP and at a temperature of 448 K were carried out. According to the results of this set of experiments it can be affirmed that from 10 bar onwards the oxygen is in excess respect the organic matter's need, and consequently an increase in the pressure does not make the reaction any faster. On the other hand, when increasing the partial pressure of oxygen from 5 until 10 a progressive increase in the TOC and 4-CP removals was observed (see Fig. 5).

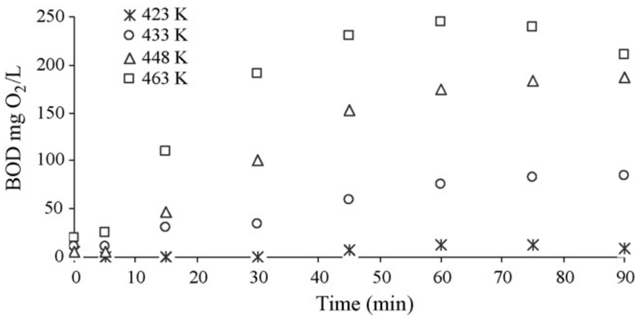

Fig. 4. BOD_5 vs. time. WO conditions: 500 ppm of 4-CP, 10 bar of P_{O_2} and different temperatures.

3.2. Kinetic study

In order to establish the reaction mechanism and the kinetic model, the results of the wet oxidation reaction carried out with initial solutions containing 1000 and 500 ppm of 4-CP, at 10 bar of P_{O_2} and at different temperatures (423, 433, 448 and 463 K) were taken under evaluation.

The results of the HPLC allowed the identification and quantification of hydroquinone and quinone as the most important intermediates of the wet oxidation of solutions containing 4-chlorophenol. Two low molecular weight acids were identified as well: maleic and oxalic acids. Considering the obtained results a reaction pathway based on the initial degradation of the 4-chlorophenol into hydroquinone, which further decomposes into quinone is suggested. The oxidation of quinone is then assumed to give rise to the formation of low molecular weight acids. From this reaction mechanism and considering that the reactions followed a pseudo-first order kinetic model, the variation of the concentration of these compounds with time can be described with Eqs. (4)–(6).

$$\frac{d[4-\mathrm{CP}]}{dt} = -k_1[4-\mathrm{CP}] \tag{4}$$

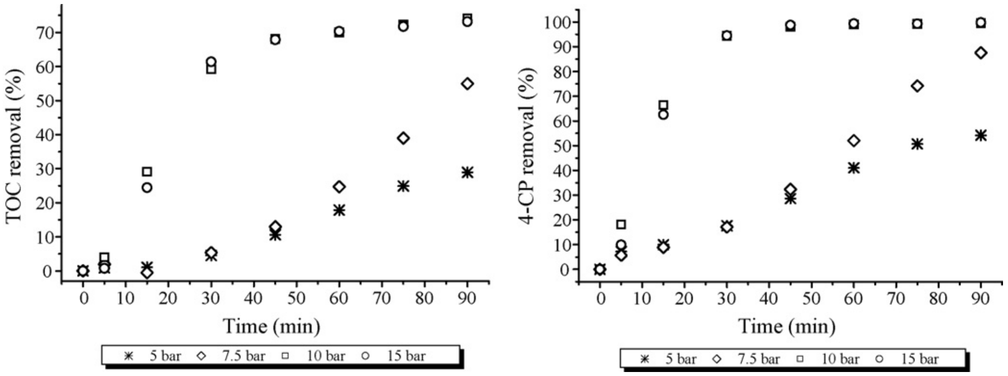

Fig. 5. TOC and 4-CP removal vs. time. WO carried out with 500 ppm of 4-CP at 463 K and different partial pressures of oxygen.

$$\frac{\mathrm{d}[\mathrm{HQ}]}{\mathrm{d}t} = k_1[4-\mathrm{CP}] - k_2[\mathrm{HQ}] \tag{5}$$

$$\frac{\mathrm{d}[Q]}{\mathrm{d}t} = k_2[\mathrm{HQ}] - k_3[Q] \tag{6}$$

The integration of the previous equations was made using the Mathematica 4.1.2.0 (Wolfram Research, Inc.) software which allowed the obtaining of the following expressions:

$$[4-\mathrm{CP}] = [4-\mathrm{CP}]_\mathrm{o}\,\mathrm{e}^{[-k_1(t-j)]} \tag{7}$$

where *j* is the induction period of time

$$[\mathrm{HQ}] = \frac{-[4-\mathrm{CP}]_\mathrm{o}\,\mathrm{e}^{(jk_1+k_2t)}(-1+\mathrm{e}^{(-k_1+k_2)t})k_1}{k_1-k_2} \tag{8}$$

To check if the mechanistic model fitted the experimental data, an optimization process was made using the initial concentration of the 4-CP and Eqs. (7)–(9). This way, the concentration of the target compound and the intermediates was found and then, compared with the experimental concentrations. Tool Solver (Microsoft Excel) was used in order to find initial feasible values of the pseudo-kinetic rate constants (k_1, k_2 and k_3) and the induction time (*j*). This initial solution was then taken as a starting point to find the optimum values of these kinetic parameters, which correspond to the minimum difference between the calculated concentrations and the experimental ones. The simulation was made using Mathematica 4.1.2.0 (Wolfram Research, Inc.). The calculations were made using the results of the wet

$$[Q] = \frac{k_2\,\mathrm{e}^{(jk_1-(k_2+k_3)t)}k_1k_2(\mathrm{e}^{k_2(j+t)}(k_1-k_3)+\mathrm{e}^{jk_1+(-k_1+k_2+k_3)t}(k_2-k_3)+\mathrm{e}^{(jk_2+k_3t)}(-k_1+k_3)+\mathrm{e}^{(jk_1+k_3t)}(-k_2+k_3))}{(k_1-k_2)(k_1-k_3)(k_2-k_3)} \tag{9}$$

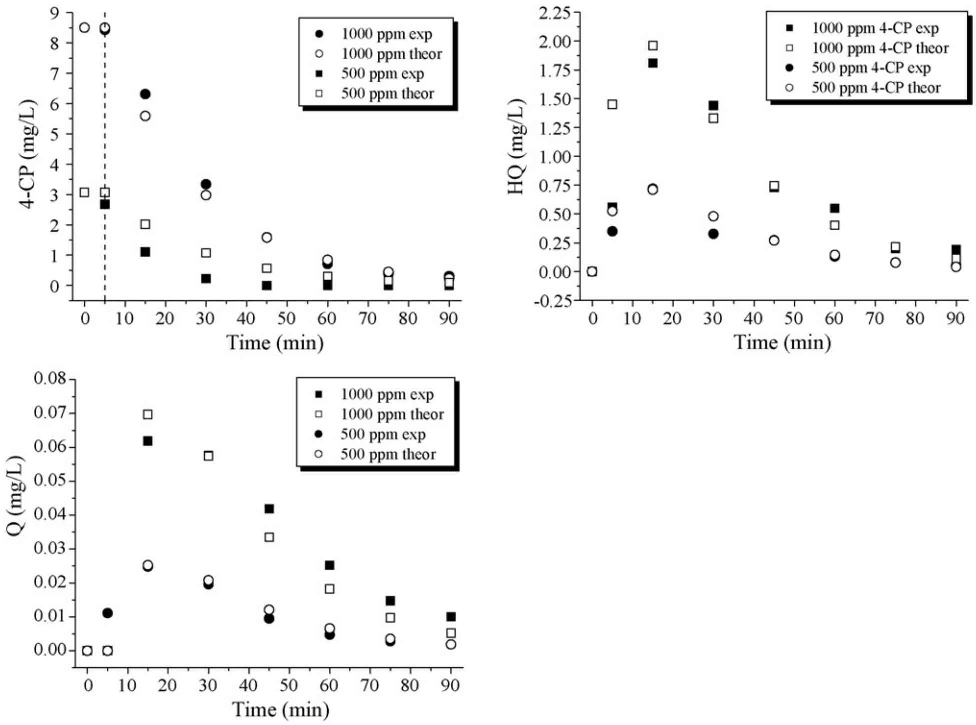

Fig. 6. Modelled and experimental concentrations of 4-chlorophenol (4-CP), hydroquinone (HQ) and quinone (Q) vs. time. Wet oxidation at 463 K and 10 bar of P_{O_2} and two different concentrations of 4-CP: 500 and 1000 ppm.

Table 2
Pseudo-first order kinetic constants and induction times

Temperature (K)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	j (min)
433	$1.15 \times 10^{-2} \pm 1.4 \times 10^{-3}$	$7.72 \times 10^{-2} \pm 4.95 \times 10^{-3}$	$2.83 \pm 1.58 \times 10^{-2}$	23.4 ± 2.65
448	$2.38 \times 10^{-2} \pm 2.6 \times 10^{-3}$	$8.40 \times 10^{-2} \pm 7.45 \times 10^{-3}$	$3.00 \pm 1.67 \times 10^{-2}$	10.01 ± 2.81
463	$4.2 \times 10^{-2} \pm 4.17 \times 10^{-3}$	$12.95 \times 10^{-2} \pm 4.39 \times 10^{-3}$	$3.57 \pm 1.58 \times 10^{-2}$	5.02 ± 1.17

Wet oxidation reactions at 10 bar of P_{O_2}, 750 rpm of stirring speed, initial solution of 1000 ppm of 4-CP and different temperatures (433, 448 and 463 K).

oxidation reactions carried out at 433, 448 and 463 K, 10 bar of partial pressure of oxygen and with initial solutions containing 1000 and 500 ppm of 4-CP. The experimental data at 423 K was not considered for the modeling of the kinetics since the temperature was too low to observe any changes in the composition of the solution.

The result of these calculations proved that the mechanistic pathway suggested is suitable to describe the wet oxidation of solutions containing 4-chlorophenol under the operating conditions studied. In Fig. 6, the results of the experimental and calculated concentrations of the main compounds involved in the process at 463 K are depicted. In addition, in Table 2 the values of the pseudo-first order reaction rate constants and the induction times are presented. The values of the kinetic constants are higher than the temperature, which is in agreement with the experimental data obtained from the reactions. In addition, it was found out that the induction period is longer the lower the temperature. This fact can be explained taking into account that the initiation of the radicalary system is favored at the highest temperatures.

4. Conclusions

- Wet oxidation appears to be a suitable process to treat effluents containing 4-CP since high removals of the target compound and TOC were achieved when working at 10 bar of partial pressure of oxygen and 448 K. A pseudo-first order kinetic model appeared to be suitable to describe the mechanistic pathway of the process, where hydroquinone and quinone are the main intermediate compounds of the process. In addition, no intermediates containing chloride were detected.
- The degradation of the 4-CP has an induction period in which hydroxyl radicals are formed. This induction period is longer the lower the temperature.
- An increase of the operating temperature in the studied range (423–463) involved a faster degradation rate and the biodegradability was favored. Below 423 K, no remarkable changes of the solution during the process were observed.
- The reaction rate was faster when increasing the partial pressure of oxygen from 5 to 10 bar. However, no improvement was observed when the pressure was increased from 10 to 15 bar, meaning thus, an excess of oxygen under this conditions.

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