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# Phenolic Wastewaters: Definition, Sources and Treatment Processes

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Additional information is available at the end of the chapter

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## Abstract

This chapter aims the state of the art concerning the development of advanced oxidation processes (AOPs) for treatment of organic-aqueous effluent for the reuse of liquid water. It presents the major oxidative processes applied for industrial and domestic treatment, where the effluents are often contaminated by phenolic compounds. A special emphasis is given to a relatively new technique called direct contact thermal treatment (DiCTT) that has the advantages of conventional AOP without its inconveniences. The DiCTT process is characterized by the generation of hydroxyl radicals ( $\bullet\text{OH}$ ) by combustion of natural gas, its compact installation and easy operation, being able to be used in offshore oil-exploration platforms, where natural gas is available and the space is reduced. Also, in this chapter, original results on the treatment of the DiCTT technique are presented, which are considered unconventional, by evaluating the oxidation and the conversion of the total organic carbon (TOC) of phenolic compounds at low temperature and atmospheric pressure, with identification and quantification of the intermediate compounds, using high-performance liquid chromatography (HPLC), which may be more toxic than the original pollutants.

**Keywords:** phenolic compounds, natural gas, AOP, DiCTT, TOC

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## 1. Introduction, definitions and concepts

Water is an important renewable natural resource; however, it is also reusable. For humans, its employment becomes a problem due to demographic growth and its application in agricultural and industrial enterprises. Thus, the limited availability of water for an eventual reuse appears to be the unique solution. In the past few years, wastewater treatment is the adopted solution in the majority of countries. Traditionally, industrial effluents are frequently contaminated by

hazardous organic substances, such as phenolic compounds and aromatic intermediates, as well as other halogenated or volatile organic substances, metals (mainly, Sb, Cu, Pb, Zn, Cd, Cr, Ni, Hg) and other chemical species, such as cyanide ( $\text{CN}^-$ ), benzene and chloroform [1]. The presence of these compounds in wastewater and drinking water, due to their toxicity, become a serious problem affecting the ecosystem and causing, for example, health problems [2].

The phenolic compounds are harmful to human health, causing necrosis, digestive problems, and liver and kidney damages. The presence of phenols in drinking water may cause serious public health problems, and the death of fishes, even at concentrations in the range of  $1 \text{ mg L}^{-1}$ . At concentrations of less than  $1 \text{ mg L}^{-1}$  (ppm), they are also toxic to other biological species and destroy the aquatic environment [3].

Phenolic substances are widely employed as industrial chemicals for wood preservation; in petroleum refineries and petrochemical plants; coke gasifiers; in manufacturing of pulp and paper; pharmaceutical plants; food industry; minerals; plastics; metals and organic chemical plants, as well as in agricultural activities as pesticides. However, several research studies indicated that some of these phenolic organic substances are recalcitrant and persistent in treated water as they are refractory to conventional treatment [4, 5]. The most detected organic pollutants in those wastewater are presented in **Table 1** [1].

Phenols are compounds derived from aromatic hydrocarbons by replacing hydrogen atoms with hydroxyls. These compounds are generally solids and are obtained from coal tar distillation and heating of chloro-benzene with water [6]. Phenols can be classified according to the number of hydroxyls into monophenols, diphenols and triphenols. Phenol is less volatile than water and sparingly soluble in it, since the phenol-water system forms an azeotrope to 9.2% by mass of phenol [7].

The toxicity of these organic substances contaminants in different water bodies, including wastewater, surface water, groundwater and drinking water, at environmental levels of  $\text{mg L}^{-1}$

Groups	Phenolic compounds
Phenol ( $\text{C}_6\text{H}_5\text{OH}$ )	2-Chloro-phenol; 2,4-di-chloro-phenol; 2,6-di-chloro-phenol; 2,4,5-tri-chloro-phenol; 2,4,6-tri-chloro-phenol; 2,3,4,5-tetra-chloro-phenol; 2,3,4,6-Tetra-chloro-phenol; 2,3,5,6-tetra-chloro-phenol; penta-chloro-phenol
Cresols ( $\text{C}_7\text{H}_8\text{O}$ )	2-Methyl-phenol; 3-methyl-phenol; 4-methyl-phenol; 2,4-di-methyl-phenol
Nitrophenols ( $\text{C}_6\text{H}_5\text{NO}_2$ )	2-Nitro-phenol; 4-nitro-phenol; 2,4-di-nitro-phenol
Aminophenols ( $\text{C}_6\text{H}_7\text{NO}$ )	4-Amino-phenol
Others	2-Chloro-3-methyl-phenol; 4-chloro-3-methyl-phenol; 2-methyl-4,6-di-nitro-phenol; 2-cyclo-hexyl-4,6-di-nitro-phenol; 2-sec-butyl-4,6-di-nitro-phenol (Dinoseb)

**Table 1.** The main phenolic pollutants more detected in effluents.

significantly affect the organoleptic properties of water [8]. Resolution 430 of the Conselho Nacional do Meio Ambiente—CONAMA (National Council on the Environmental), Brazil set a maximum of total phenols concentration at  $0.5 \text{ mg L}^{-1}$  for all effluents originating from any polluting source that can be disposed of in water bodies as of 13 May 2011 [9].

According to literature review, phenolic and petroleum wastewater are recalcitrant compounds. Wastewater is generally characterized by the biological oxygen demand (BOD), chemical oxygen demand (COD), pH and total organic carbon (TOC) [10]. Petroleum wastewater contains a COD range from 850 to  $1020 \text{ mg L}^{-1}$ , a BOD range from  $570 \text{ mg L}^{-1}$ , a TOC range from 300 to  $440 \text{ mg L}^{-1}$  and a pH range from 8 to 8.2, showing that it contains large amounts of non-biodegradable organic matter [11]. Petro-chemical wastewater contains an initial COD range of 300–600  $\text{mg L}^{-1}$ , a BOD range of 150–360  $\text{mg L}^{-1}$  and a pH range of 7–8 [12]. Conventional treatment of these substances is difficult because biologically resistant organic compounds do not induce oxygen depletion in receiving water [13].

Several biological and chemical methods have shown a low efficiency to degrade the contaminants completely. As biological and chemical methods degrade only up to 60% of the recalcitrant components and in addition they require larger operation area and more chemical processes to reduce the sludge [14].

There are a number of studies of industrial effluents treatments via conventional methods that are combined with chemical, biological and physical methods and also advanced oxidation processes (AOPs), shared with reactors for complete degradation of highly recalcitrant industrial wastewater. Section 2 discusses the AOP theory and the possibility of enhancement in reactor performance when implemented in the processes.

## 2. Theory of advanced oxidation processes (AOPs)

The need for an efficient treatment of phenolic compounds in water is very important. When conventional treatment methods such as biological processes fail due to the recalcitrant nature of the contaminants, physical and chemical methods are a good solution. Therefore, oxidation processes are preferred to degrade such organics present. For example, the chemical processes are commonly used to degrade recalcitrant substances. High degradation efficiencies are possible with direct oxidation methods. However, pollution load, process limitation and operation condition are the more important factors considered during the selection for most oxidation processes [15]. The main treatment methods of industrial effluents with biological processes are aerobic, anaerobic and enzymatic. The physical processes are decantation, filtration and adsorption. The chemical methods are incineration, electrochemical and advanced oxidation processes (AOP), for example, photocatalysis, ozonation, Fenton/photo-Fenton and direct contact thermal treatment (DiCTT) [4].

The AOPs have been a viable alternative method for the wastewater treatment containing toxic and refractory organic pollutants, being studied in various combinations and are mainly based on intermediate reactions of hydroxyl radicals ( $\bullet\text{OH}$ ), an unstable and very reactive

species, resulting in the degradation of toxic organic contaminants due to its high oxidizing potential of 2.8 V under acidic conditions and these processes have the major advantage of being a destructive treatment. Depending on the species to be degraded the hydroxyl radicals of reactive species, which attack the main part of organic molecules with a rate constant frequently in the order of  $10^6$ – $10^9$  L mol<sup>-1</sup>s<sup>-1</sup>, and reacts  $10^6$ – $10^{12}$  times faster than ozone [16]. According to Tisa et al. [10] apud Bach et al. [17] and Garrido-Ramírez et al. [18], the principles of •OH generation is based on various combinations of strong oxidants, such as oxygen, ozone, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ultra-violet (UV) and electron beam.

The AOPs are classified according to the reactive phase (homogeneous and heterogeneous). The homogeneous including: ozone (O<sub>3</sub>), ozone/ultraviolet (O<sub>3</sub>/UV), ozone/hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV), and (H<sub>2</sub>O<sub>2</sub>/UV) processes, as well as Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), Fenton-like (Fe<sup>3+</sup>/m<sup>n+</sup>/H<sub>2</sub>O<sub>2</sub>), photo-Fenton (UV/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), sono-Fenton (US/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), electro-Fenton, sono-electro-Fenton, photo-electro-Fenton, sono-photo-Fenton. The heterogeneous includes: (TiO<sub>2</sub>/ZnO/CdS+UV), (TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>), (H<sub>2</sub>O<sub>2</sub>+Fe<sup>2+</sup>/Fe<sup>3+</sup>/m<sup>n+</sup>-solid), (H<sub>2</sub>O<sub>2</sub>+Fe<sup>0</sup>/Fe-nano-zero valente iron) and (H<sub>2</sub>O<sub>2</sub>+immobilized nano-zero valente iron). The non-conventional AOPs include ionizing radiation, microwaves and pulsed plasma techniques. Depending on the matrix and on the pollutant, degradation kinetics of AOPs can be zero order, first order and second order. First-order kinetics constant is achieved for pollutant degradation due to concentration of hydroxyl radicals within 1–10<sup>-4</sup> s<sup>-1</sup> [15, 4]. The mechanisms of different AOPs are presented in **Table 2**.

In the AOPs, oxygen and their reactive species (O<sub>x</sub>, HO<sub>x</sub>, x = 1, 2, 3, 4) act as main precursors during the oxidation that occurs in step of degradation of the organic component [23].

Devlin and Harris [24] proposed in their experimental trials that levels of O<sub>2</sub> decrease quickly in accordance with the rates of degradation of aromatic compounds, due to the high concentrations of phenol, in the temperature range from 420 to 498 K, near or above the stoichiometric conditions. These results led to demonstrate that the concentration of radicals (•O) is the dominant mechanism for this temperature range, in which the intermediate rings resulting from the oxidation of phenol are degraded.

Section 3 indicates that the direct contact thermal treatment technology is recent, with a limited investigation and was initially developed in Canada by Benali et al. [25, 26], being the unique experimental results available in the literature, until this moment. The DiCTT process provides a promising novel means to induce degradation and mineralization of organic pollutants in water being an AOP treatment method with respective advantages and limitations. Since combining AOP treatment process with reactors can be more promising in industrial applications, this research area needs to be explored further. Section 3 describes the DiCTT technique with applications in degradation and mineralization of the organic pollutant, being elaborated to highlight the important factors and their effects, as also a detailed investigation of the effective design and operating parameters are summarized.

The actual work evaluated the liquid phase flow rate (Q<sub>L</sub>) of 100 and 170 L h<sup>-1</sup> and the effect of initial phenol concentration (C<sub>Pho</sub>) of 500, 2000 and 3000 mg L<sup>-1</sup>. The experiments studies were performed using a molar stoichiometric ratio of phenol/hydrogen peroxide (R<sub>p/H</sub>) of 50%, an air excess (E) of 40%, a recycle rate of gaseous thermal wastes (Q<sub>RC</sub>) of 50%, and, a natural gas

Name of the AOP	Types	Mechanism reaction	Highlights	References
Fenton oxidation	Homogeneous	$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$	- Degradation of pollutant happens in acidic aqueous mixture - High efficiency	Lucas and Peres [19]
	Heterogeneous	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$ $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{FeHOO}^{2+} + \text{H}^+$ $\text{FeHOO}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \bullet\text{HO}_2$ $\bullet\text{OH} + \text{organics} \rightarrow \text{products}$ $\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{H}_2\text{O} + \bullet\text{HO}_2$ $\text{Fe}^{2+} + \bullet\text{OH} \rightarrow \text{Fe}^{3+} + \bullet\text{OH}$ $\text{Fe}^{2+} + \bullet\text{HO}_2 \rightarrow \text{Fe}^{3+} + \text{OH}_2^-$ $\text{Fe}^{3+} + \bullet\text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	- Reaction is possible in pH 5–7 - Catalyst reusability is possible - Lag phase is observed that happens in activating the catalyst	Bach et al. [17] Garrido-Ramírez et al. [18]
Ozone	$\text{O}_3/\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2 + 2\text{O}_3 \rightarrow 2\bullet\text{OH} + 3\text{O}_2$	- This combined AOP works better in higher pH values - Degrades the pollutants into smaller cycle particles - Inactive in reducing COD - Oxidation rate is higher - Follows direct pathway for pollutant degradation	Esplugas et al. [20]
	$\text{O}_3/\text{UV}$	$\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\bullet\text{OH} + \text{O}_2$	- UV accelerates ozone molecules and produces oxidizing radical	Esplugas et al. [19]
UV	$\text{UV}/\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2 \xrightarrow{\lambda > 300\text{nm}} 2\bullet\text{OH}$	- UV irradiation supplies energy to the chemical compounds as radiation	Esplugas et al. [19]

Name of the AOP	Types	Mechanism reaction	Highlights	References
	UV/Fe <sup>2+</sup>	$\text{Fe(OH)}^{2+} + \text{UV} \rightarrow \text{Fe}^{2+} + \bullet\text{OH}$ $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \bullet\text{OH}$	<ul style="list-style-type: none"> <li>- Reaction molecules reaches their excited state absorbing UV and promotes further reaction</li> <li>- Effectively can be applied in variety of pollutant degradation [21]</li> <li>- High synergy effect between the ozone and the UV radiation has been noted</li> </ul>	
Photo catalysts	Photo catalysts	$\text{TiO}_2 \xrightarrow{\lambda < 400\text{nm}} e^-_{(cb)} + h^-_{(vb)}$ $e^-_{(cb)} + h^-_{(vb)} \rightarrow \text{heat}$ $\text{H}_2\text{O} + h^-_{(vb)} \rightarrow \bullet\text{OH} + \text{H}^+$ $\bullet\text{OH} + \text{dyes} \rightarrow \text{colourless}$	<ul style="list-style-type: none"> <li>- Degradation of pollutant takes place by redox Oxidation [22]</li> <li>- First-order kinetics are observed</li> </ul>	Chen and Chou (1994)

**Table 2.** Mechanisms of different advanced oxidation processes.

flow ( $Q_{GN}$ ) of  $4 \text{ m}^3 \text{ h}^{-1}$ , on the oxidation of phenolic effluents by DiCTT process. The phenol concentration and mineralization content were obtained by high-performance liquid chromatography (HPLC) and mineralization Total Organic Carbon (TOC), respectively. A new data bank was compiled in this work by optimizing the operation conditions for the degradation/mineralization of phenol by the DiCTT process. (Phenol was used as a model compound for liquid organic wastes.)

### 3. Concepts of DiCTT-AOPs in degradation and mineralization of organic pollutants

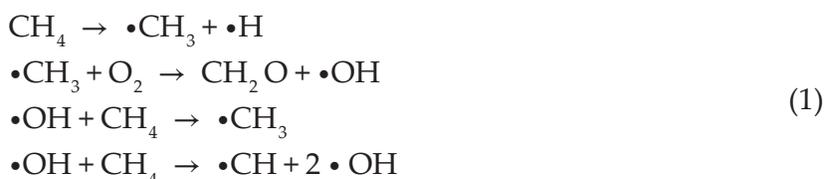
#### 3.1. Pilot plant and experimental procedure

Currently, a non-conventional AOP called Direct Contact Thermal Treatment (DiCTT) process has been investigated, whose main attraction are the use of natural gas as the energy source, the demonstrated ability to oxidize phenolic compounds at low temperatures and atmospheric pressure, and the generation of free radicals ( $\bullet\text{OH}$ ,  $\bullet\text{H}$ ,  $\bullet\text{CH}_3$  and  $\bullet\text{CHO}$ ) resulting from combustion of natural gas (methane). The installation of the DiCTT technology presents a compact reactor configuration that involves maintaining the reactor in a vertical position, favouring the immediate application of this technology in off-shore oil platforms, where natural gas is available and space is limited [4, 27].

The experimental unit used is mainly composed of a vertical stainless steel reactor, being 1.359 mm high and 203 mm internal diameter, a gas-liquid separator, a first tank (Tank 1) for preparation of phenol synthetic solutions, 400 L volume, a second tank (Tank 2) for feeding in polluted waters, also of 400 L volume, and a natural gas burner with 50 kW maximum power. The combustion air is provided by an axial fan with 0.3 HP power. The output pressure of the natural gas supply is  $2 \times 10^5 \text{ Pa}$ , followed by a reduction to  $1 \times 10^5 \text{ Pa}$  for combustion in the burner.

In this process, the effluent is tangentially injected into the reactor to produce a helical flow in its inner walls. The helical flow allows an intimate contact between the effluent and free radicals produced in the combustion flame of the natural gas, resulting in a thermochemical oxidation in the liquid phase, while avoiding their incineration. The high flame temperature contributes to the oxidation performance of the effluent in the presence of free radicals and works for the oxidation process to be carried out in completely liquid phase, by transferring some of the excess oxygen present in the flame.

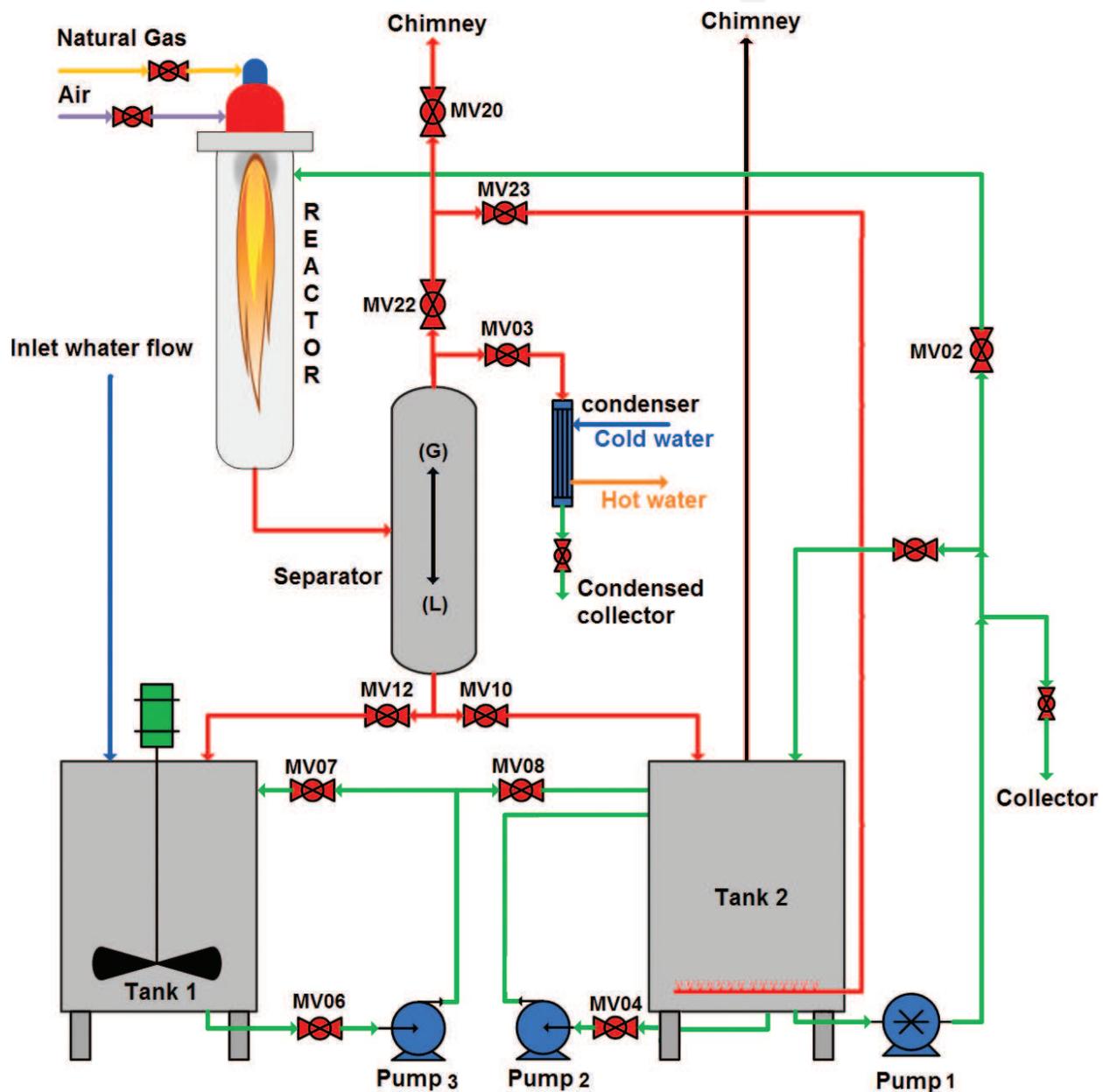
The DiCTT process is a thermochemical oxidation method in aqueous medium, and generating free radicals resulting from the combustion of natural gas (methane) according to the reaction mechanism described by the whole of Eq. (1) following [27]:



This technique presents operational and capital costs 2.5 times lower than those of wet air oxidation (WAO) and 4.1 times lower than those of electric plasma oxidation (EPO) [27].

**Figure 1** show a schematic representation of the pilot plant used in the experiments that was composed of a vertical, stainless-steel reactor and a gas-liquid separator.

The phenol solution was prepared in Tank 1. The operation of the system was stabilized by heating the water to almost 70°C for an hour and a half; phenol was subsequently added to Tank 1, and the synthetic effluent was transferred from Tank 1 to Tank 2. The reactor had an internal helical groove with a rectangular shape, in the axial direction, through which the liquid effluent flowed. Wastewater polluted with phenol was injected into the reactor



**Figure 1.** Pilot plant using the DiCTT process.

tangentially to produce a liquid helical stream on its inner walls. The combustion gases were vented to the atmosphere through a chimney; a fraction of recycled combustion gases (of the total flow rate  $Q_{RC}$ ) was immediately injected into Tank 2 by adjusting an open valve to heat the solution in the recirculation tank (Tank 2) more rapidly and to dissolve a fraction of the residual oxygen from combustion into the reaction liquid, thereby inducing the thermochemical oxidation of the phenolic compounds. For the experiments, 250L of effluent was prepared. For each experiment 250mL samples of effluent in black plastic bottles were collected at previously chosen points and put to cool in a refrigerator. For the analyses, 250mL of treated drinking water was employed as a reference. To initiate the oxidation reaction, some millilitres of phenol/hydrogen peroxide with a mole ratio,  $R_{PH}$  was introduced into Tank 2. Liquid samples were withdrawn for analysis through a collector located at the entrance of the tubes connecting the feed tank (Tank 2) to the reactor inlet (**Figure 1**).

### 3.2. Analytical methods

For the experiments, a phenol solution of analytical grade and oxygenated water 35% PA were employed. For the chromatographic analysis, methanol UV/HPLC grade and for TOC analysis phosphoric acid 25% PA were used.

The concentrations of phenol, catechol and hydroquinone were monitored using an HPLC instrument (Shimadzu, model LC-20AT, with integrated data acquisition using a UV detector and a CLC-ODS column (M)/(C-18) that was 250 mm in length and 4.6 mm in diameter, also from Shimadzu). An isocratic elution mode was used under the following conditions: oven temperature of 35°C; flow rate of 0.75 mL min<sup>-1</sup> for the mobile phase; injection volume of 20 µL; mobile phase consisting of 10% methanol and 90% phosphoric acid/deionised water with pH adjusted to 2.2; and operation of the UV detector at a wavelength of 270 nm to detect phenol, catechol and hydroquinone [4].

The TOC content was measured using a TOC analyser (TOC-Vcsh model, Shimadzu) to analyse phenolic mineralisation quantitatively [28].

### 3.3. Parameters and calculated data

Phenol oxidation is a common reaction stoichiometry described in Eq. (2):



From Eq. (2) others relations were calculated.

Molar ratios other than 100% were calculated proportionally using the reaction stoichiometry in Eq. (2).

In this work, natural gas (89.24% of methane) supplied by COPERGAS (Pernambuco, Brazil) was employed [29]. Stoichiometrically 9.881 mol of air reacts with one mol of methane. So, the excess air (E) in the combustion and the equivalent ratio ( $\Phi$ ) may be evaluated employing Eqs. (3) and (4) [30, 31].

$$E = \frac{1}{9.881} \left( \frac{Q_{AR}}{Q_{GN}} \right) - 1, \quad (3)$$

$$\varphi = 9.881 \left( \frac{Q_{GN}}{Q_{AR}} \right), \quad (4)$$

where  $Q_{AR}$  denotes the volumetric flow rate of air, and  $Q_{GN}$  denotes the volumetric flow rate of natural gas.

The power dissipated by the burner ( $P$ ) was calculated using Eq. (5):

$$P = Q_{GN} \cdot PCM, \quad (5)$$

where  $PCM$  denotes the average heat of combustion of natural gas, which has a value of  $34,740 \text{ kJ m}^{-3}$  [29].

The percent degradation of phenol ( $X_F$ ) was calculated using Eq. (6):

$$X_F = \left( \frac{Q_L \cdot C_{Ph_0} - Q_L \cdot C_{Ph} - F_G \cdot C_{Phv}}{Q_L \cdot C_{Ph_0}} \right) \times 100, \quad (6)$$

where  $Q_L$  represents the volumetric flow rate,  $C_{ph_0}$  the initial phenol concentration,  $C_{ph}$  the phenol concentration at time  $t$ ,  $F_G$  the dry air mass flow rate,  $C_{phv}$  the phenol concentration in the condensate at time  $t$ . TOC conversion was evaluated via Eq. (7).

The TOC conversion ( $X_T$ ) was evaluated via Eq. (7):

$$X_T = \left( \frac{Q_L \cdot \text{TOC}_0 - Q_L \cdot \text{TOC} - F_G \cdot \text{TOC}_v}{Q_L \cdot (\text{TOC}_0 - \text{TOC}_B)} \right) \cdot 100, \quad (7)$$

where  $\text{TOC}_0$  denotes the initial total organic carbon concentration,  $\text{TOC}$  and  $\text{TOC}_v$  denote the total organic carbon and the total organic carbon in the condensate, respectively, at a time point  $t$  of the process and  $\text{TOC}_B$  denotes the total organic carbon in the blank.

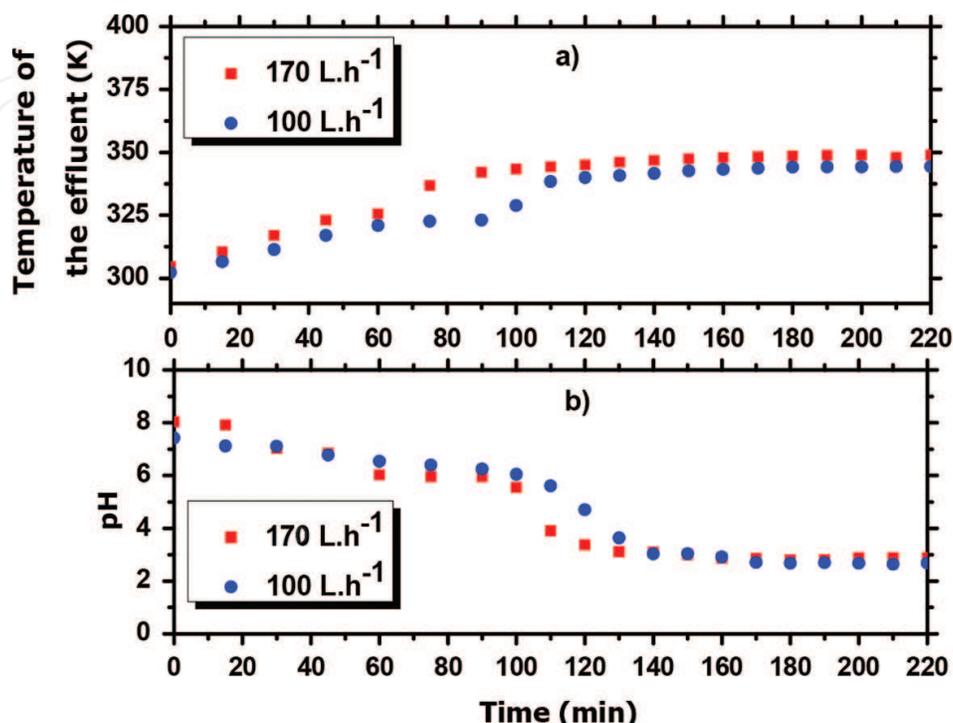
### 3.4. Effect of the liquid phase flow rate

This work was to evaluate the influence of the liquid phase flow rate on the level of phenol oxidation, settling other process variables. These operational parameters are listed in **Table 3**.

Tests	$Q_L$ (L h <sup>-1</sup> )	$Q_{GN}$ (m <sup>3</sup> h <sup>-1</sup> )	E (%)	$C_{ph_0}$ (mgL <sup>-1</sup> )	$Q_{RG}$ (%)	$R_{p/H}$ (%)
E1	170	4	40	500	50	50
E2	100	4	40	500	50	50

**Table 3.** Operational parameters for the study of the influence of the liquid phase flow rate.

**Figure 2a** and **b** show, respectively, the evolution of the temperature and pH of the liquid effluent present in the feed tank (Tank 2) during the process, varying the volumetric flow of the same.

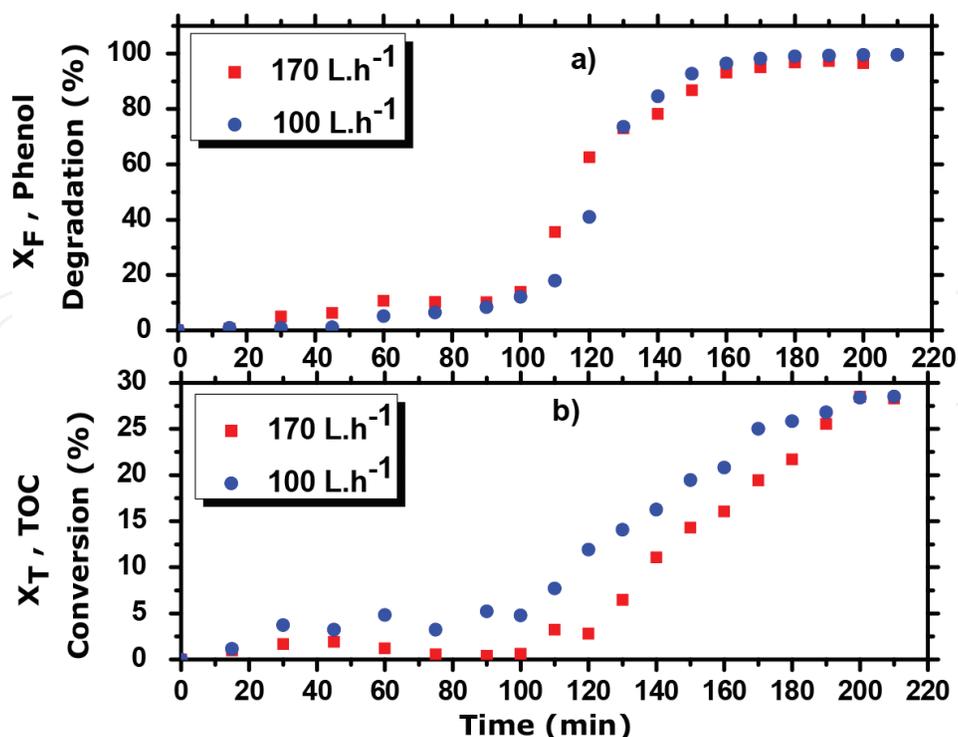


**Figure 2.** (a) Evolution of temperature of the liquid effluent as a function of the operating time. (b) Evolution of pH as a function of the operating time.  $E = 40\%$ ,  $Q_{GN} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $C_{\text{pho}} = 500 \text{ mg L}^{-1}$ ,  $R_{\text{p/H}} = 50\%$  and  $Q_{\text{RC}} = 50\%$ .

**Figure 2a** indicates that the elevation of effluent flow affects the heating curve of liquid effluent, getting it faster to obtain steady-state temperature in Tank 2. **Figure 2a** also show that for the larger effluent flow ( $170 \text{ L h}^{-1}$ ), the same reaches a maximum temperature of  $348 \text{ K}$ , quite greater than the temperature of the effluent flow of the  $100 \text{ L h}^{-1}$  ( $344 \text{ K}$ ), featuring a small effect, since the difference in these temperatures reaches an order of magnitude lower than the measurement uncertainty by thermocouples.

The oxidation process indicates that the heating profile is characterized by two distinct steps, a first, approximately  $110 \text{ min}$ , characterized by a rapid temperature rise and a second, after  $110 \text{ min}$  of operation, showing a temporal increase rate of low temperature. **Figure 2b** show that the evolution of pH also identifies these two steps, the first of about  $110 \text{ min}$ , characterized by a decreased less than hydrogen potential as a function of time, and the second-fastest where the temporal decay profile of pH is more significant. It is shown a low influence in liquid flow in the dynamics of acid formation [24].

**Figure 3a** and **b** show, respectively, the profile of phenol degradation and residual fraction of the TOC as a function of time for the two flows of liquid effluent studied,  $100$  and  $170 \text{ L h}^{-1}$ .

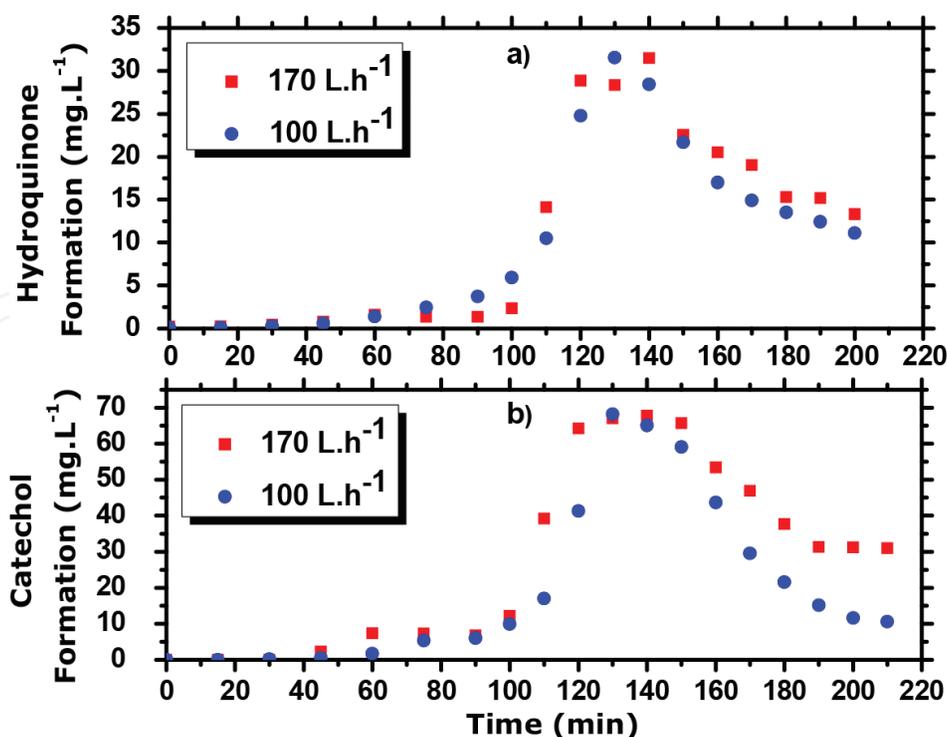


**Figure 3.** (a) Evolution of phenol degradation as a function of the operating time. (b) Evolution of TOC conversion as a function of the operating time.  $E = 40\%$ ,  $Q_{GN} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $C_{Ph0} = 500 \text{ mg L}^{-1}$ ,  $R_{p/H} = 50\%$  and  $Q_{RG} = 50\%$ .

**Figure 3a** indicates that, in the range studied, the variation of the effluent flow does not affect the profile of phenol degradation and total degradation of the same is almost completely achieved in 180 min of operation, reaching values of 99.5 and 97.4%, respectively, at effluent flow of 100 and 170 L h<sup>-1</sup>. **Figure 3b** indicates that the increase of the effluent flow of 100 to 170 L h<sup>-1</sup> allows a higher speed of phenol mineralization, due the acceleration of the lowest value of the pH, but not interfering in the maximum value TOC conversion, around 28% with an operating time of 210 min.

**Figure 4a** and **b** indicates, respectively, the time profiles of the hydroquinone and catechol formed by thermochemical phenol oxidation, for the two flows of liquid effluent, 100 and 170 L h<sup>-1</sup>. Analysing the same figures, it can be seen that the rate of formation of these species becomes appreciable after the induction period, approximately 110 min, previously observed by the curves of the evolution of pH, phenol degradation and TOC conversion.

The evolution of the hydroquinone and catechol concentrations happened quickly because of the thermochemical oxidation reaction of phenol with high speed, regardless of the flows of liquid effluent studied. It has been observed that hydroquinone and catechol concentrations are reached when phenol consumption rate is maximum, which is identified in the process time between 140 and 150 min. After reaching the maximum hydroquinone and catechol formation, an immediate reduction in the concentration of these two species is observed, indicating that to achieve the maximum consumption of phenol, the oxidation rate of these two organic compounds becomes greater than its rate of formation, enabling to be degraded, thus favouring the formation of other organic compounds that are not acids, because the pH remained almost constant at 2.5–2.8, after



**Figure 4.** (a) Evolution of hydroquinone formation as a function of the operating time. (b) Evolution of catechol formation as a function of the operating time.  $E = 40\%$ ,  $Q_{GN} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $C_{Ph0} = 500 \text{ mg L}^{-1}$ ,  $R_{p/H} = 50\%$  and  $Q_{RG} = 50\%$ .

140–150 min of operation. The products resulting from the oxidation of hydroquinone and catechol are probably aldehydes (Glyoxal, for example, in the case of hydroquinone and catechol) and alkenes (1,4-dioxo-2-butene, for example, in the case of hydroquinone) [24].

**Figure 4a** and presents the results obtained in the quantification of concentrations of hydroquinone and catechol, respectively. It also show a speed of formation and consumption of these species not significantly affected by variation of the flows of liquid effluent. It is also observed a rate of production and disappearance slightly larger (especially in the case of catechol) with use of effluent flow rate  $170 \text{ L h}^{-1}$ , similarly what was evidenced in the evolution of pH, being less for the flow rate of  $170 \text{ L h}^{-1}$ , allowing more oxidation of phenol to hydroquinone and catechol. However, regardless of the flow of the liquid studied, catechol concentrations were approximately two times higher compared to those obtained in relation to the hydroquinone.

### 3.5. Effect of initial phenol concentration

In order to evaluate the effect of initial concentration of the organic pollutant on the efficiency of the process DiCTT on thermochemical phenol oxidation, three initial concentrations of the aromatic contaminant ( $C_{Ph0}$ ): 500, 2000 and  $3000 \text{ mg L}^{-1}$ , were employed keeping all other variables constant. The operating conditions used in this study are presented in **Table 4**.

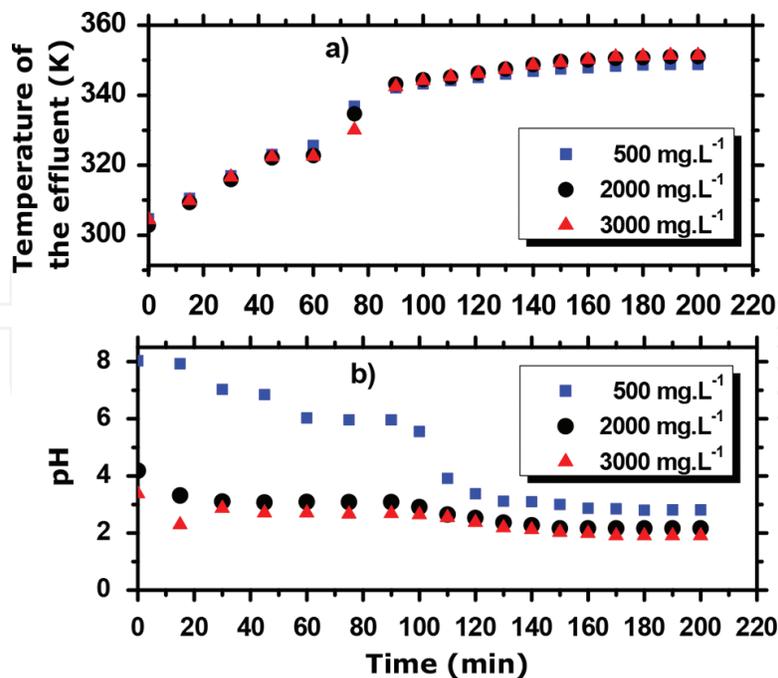
**Figure 5a** and **b** presents, respectively, the evolution of the temperature and pH of the liquid effluent in the perfect mixing tank (Tank 2) during the process, varying only the initial concentration of phenol. From **Figure 5a** it can be seen that the concentration of phenol does

Tests	$C_{\text{Ph}_0}$ (mgL <sup>-1</sup> )	$Q_{\text{GN}}$ (m <sup>3</sup> h <sup>-1</sup> )	E (%)	$Q_L$ (Lh <sup>-1</sup> )	$Q_{\text{RG}}$ (%)	$R_{\text{p/H}}$ (%)
E3	500	4	40	170	50	50
E4	2000	4	40	170	50	50
E5	3000	4	40	170	50	50

**Table 4.** Operational parameters for the study of the influence of the initial concentration of phenol.

not influence the heating curve of the liquid phase, reaching a temperature of approximately 350 K (77°C). An expected behaviour since the variation of concentration, in different experiments, it is not enough to significantly change the chemical and thermophysical properties of the effluent, since the natural gas flow in the process is the same for all cases, as well as the excess air and effluent flow which remained constant during these essays.

**Figure 5b** show the curves of the evolution of pH for concentrations of phenol 2000 and 3000 mg L<sup>-1</sup>. It can be seen that the initial pH value already show low values, 4 and 3, respectively, while for a  $C_{\text{Ph}_0}$  equal 500 mg L<sup>-1</sup>, pH presents an initial value of 8. This can be explained due to the amount of hydrogen peroxide added. In the procedure adopted for the preparation of the synthetic effluent, the peroxide is mixed with the phenol solution in the preparation tank, causing uncontrolled reactions. As the molar stoichiometric ratio of the mix is kept constant, to higher concentrations of phenol oxidant availability in the reaction medium is greater, increasing the effect and decreasing the initial pH due to a possible premature oxidation of phenol to form organic acids.

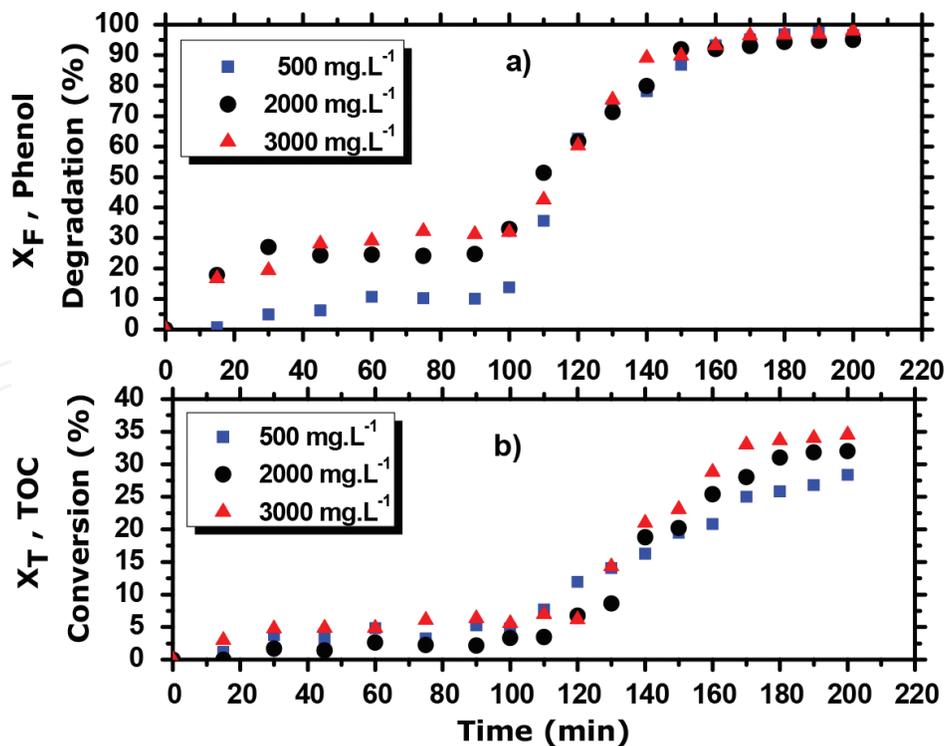


**Figure 5.** (a) Evolution of temperature of the liquid effluent as a function of the operating time. (b) Evolution of pH as a function of the operating time.  $E = 40\%$ ,  $Q_{\text{GN}} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $Q_L = 170 \text{ L h}^{-1}$ ,  $R_{\text{p/H}} = 50\%$  and  $Q_{\text{RG}} = 50\%$ .

**Figure 6a** and **b** presents, respectively, the profile of phenol degradation and TOC conversion as a function of time, for different initial concentrations of phenol studied.

**Figure 6a** show that the increase of the initial concentration of phenol from 500 to 3000 mg L<sup>-1</sup> does not affect the duration of the first step of the reaction, called induction period, and does not have a significant effect on the phenol degradation after a time of approximately 130 min. After the induction period, around 110 min, the speed of the reaction becomes more pronounced, as was expected, reaching values of  $X_F$  practically the same after an operating time of around 130 min, regardless of the initial concentration of phenol. Phenol degradation around 99% is obtained after an operating time of 180 min.

**Figure 6b** show the evolution of TOC conversion, identifying a time of induction period also approximately 110 min, and show a slight increase in the TOC conversion with increasing of the initial phenol concentration, reaching  $X_T$  values of 27.5; 31.5 and 33.5% to initial concentration of phenol of 500, 2000 and 3000 mg L<sup>-1</sup>, respectively, after an operating time of 210 min. Regardless of the value of the initial phenol concentration, the process presents maximum rates of phenol degradation almost 100% after 170 min of operation, in addition to providing a TOC conversion, between a range of 27.5–33.5%, after 210 min, within the range of the initial concentration of phenol, being the air excess used of 40% and a combustion gases recycling rate of 50%.

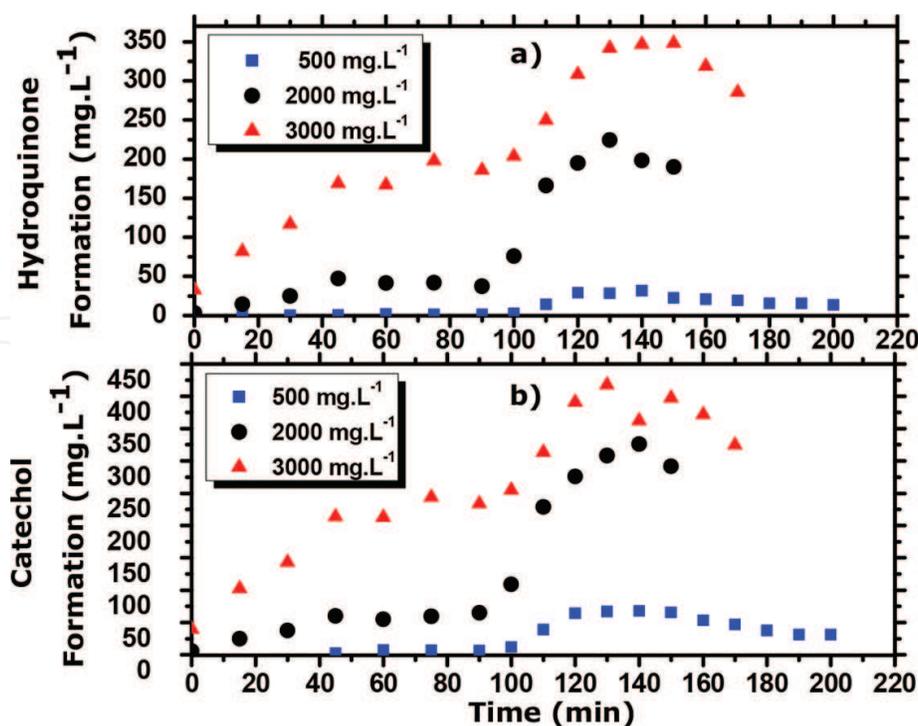


**Figure 6.** (a) Evolution of phenol degradation as a function of the operating time. (b) Evolution of TOC conversion as a function of the operating time.  $E = 40\%$ ,  $Q_{GN} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $Q_L = 170 \text{ L h}^{-1}$ ,  $R_{PH} = 50\%$  and  $Q_{RC} = 50\%$ .

**Figure 7a** and **b** show, respectively, the results obtained in the quantification of the concentrations of hydroquinone and catechol formation. The evolution of the concentration profiles of hydroquinone and catechol in function of the time confirm clearly the induction time of reaction, around 110 min, identified initially by the curves of time evolution of the phenol degradation (**Figure 6a**) and TOC conversion (**Figure 6b**). It can be that maximum values of hydroquinone and catechol concentration formed in approximately 140 min operating time, reaching the maximum speed of phenol degradation and TOC conversion and that the catechol concentrations are always higher than the hydroquinone concentration.

After 140 min, both hydroquinone and catechol concentrations decrease, thus allowing the formation of other organic compounds that are not acids, because the pH becomes practically constant (pH = 3) after 140 min of operation (**Figure 5b**). It can be that the products resulting from the oxidation of hydroquinone and catechol are possibly aldehydes (Glyoxal, for example, in the case of hydroquinone and catechol) and alkenes (1,4-dioxo-2-butene, for example, in the case of hydroquinone).

The phenol oxidation produces catechol and hydroquinone [20]. Analyses indicated a higher catechol production than hydroquinone. This may be explained by the mesomeric effect. This signifies an electron re-distribution to the ortho position, which increases its reactivity at this position of the molecule due to the proximity of opposing charges [4, 27].



**Figure 7.** (a) Evolution of hydroquinone formation as a function of the operating time. (b) Evolution of catechol formation as a function of the operating time.  $E = 40\%$ ,  $Q_{GN} = 4 \text{ m}^3 \text{ h}^{-1}$ ,  $Q_L = 170 \text{ L h}^{-1}$ ,  $R_{p/H} = 50\%$  and  $Q_{RG} = 50\%$ .

## 4. Conclusions and recommendations

The Advanced Oxidation Processes (AOPs) are found to be an environmental friendly process for the degradation and mineralization of refractory compounds. The limitations of conventional processes in wastewater treatment necessitate study on the AOPs. Thus, applications of the Direct Contact Thermal Treatment (DiCTT) process is a promising technique increasingly used to remove phenolic compounds in water. The method advantages are operational and capital costs lower than other process and ability to allow total degradation and higher mineralization of target compounds when compared to conventional AOPs. On the other hand, further efforts are conducted to overcome the empirical aspect by studying the operating parameters, as well as the optimization of the process.

The complete degradation of phenol (almost 100%) was obtained independently of the flows of liquid effluent, 100 and 170 L h<sup>-1</sup>, and, of the initial phenol concentrations, 500, 2000 and 3000 mg L<sup>-1</sup> over a 180-min period. A TOC conversion of almost 35% was observed corresponding to an operational time of approximately 210 min at a  $Q_L$  of 170 L h<sup>-1</sup>, which allows the speed of phenol mineralization is faster, but without interfering in the final value of almost 28% TOC conversion after 210 min of operation process. The flows of liquid effluent of 170 L h<sup>-1</sup> was considered to be the best operating condition for the DiCTT process. An induction time of approximately 110 min was identified from the concentration profiles of hydroquinone and catechol. The concentrations of these intermediates tended to decrease independently of the flows of liquid effluent and of the initial phenol concentrations, indicating the formation of the other organic compounds, which were not acids (constant pH) according to data reported in the literature.

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