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Nature of the degradation products of phenol which produce high levels of color in the wastewater oxidized in a photo-Fenton system

N. Villota*, J.M. Lomas, L.M. Camarero

Department of Chemical and Environmental Engineering, Escuela Universitaria de Ingeniería de Vitoria-Gasteiz, University of the Basque Country UPV/EHU, Nieves Cano, 12, 01006 Vitoria-Gasteiz, Spain, Tel. +34 646261951; Fax: +34 945013270; emails: natalia.villota@yahoo.es (N. Villota), josemaria.lomas@ehu.es (J.M. Lomas), luismiguel.camarero@ehu.es (L.M. Camarero)

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ABSTRACT

This work completes the step of the mechanism of phenol oxidation, where the wastewater shows the maximum color levels, considering the formation of trihydroxybenzene rings and quinoidal compounds of hydroxylated nature as degradation intermediates. They have been determined experimentally by the stoichiometric ratios of oxidant to degrade phenol until the intermediate species generated during the oxidation (R = mol H_2O_2/mol C_6H_6O). Hence, catechol forms at $R = 1.0$, resorcinol at $R = 1.3$ and hydroquinone at $R = 2.0$. The addition of these ratios, $R = 4.3$, corresponds to the minimum dosage required to oxidize the initial phenol contained in the solution. p-benzoquinone is formed at $R = 1.0$. The formation of trihydroxylated rings with substituents in ortho-position (pyrogallol) and meta-(phloroglucinol), which makes them more unstable, needs a lower dosage of oxidant, $R = 4.0$, than the para-substituted (hydroxyhydroquinone), that requires $R = 5.5$. Muconic acid formation reaches its maximum at $R = 6.0$ while the formation of benzoquinones substituted by hydroxyl groups (dihydroxybenzoquinone) require $R = 8.0$. These results suggest that oxidation of p-benzoquinone would yield dihydroxybenzoquinone species, whereas muconic acid would be an oxidation byproduct of ortho- and meta-substituted species. The oxidation intermediates generated during the first steps of the oxidation pathway determine the color of oxidized wastewater, although iron species in solution may enhance its intensity. Maximum color is obtained at $R = 4.0$ and is produced by intermediates that are generated during the oxidation of pyrogallol and phloroglucinol-type compounds. A drastic decrease in color happens between $R = 4.0$ and 6.0 which corresponds to the formation of muconic acid. Finally, the color increases slightly at R greater than 7.0 which can be related to the formation of dihydroxylated benzoquinones. As the color and toxic compounds are degraded to biodegradable acids of colorless nature, the color intensity diminishes to colorless at $R > 13.0$.

Keywords: Dihydroxylated benzene; Hydroxylated benzoquinone; Phenol; Photo-Fenton; Trihydroxylated benzene

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*Corresponding author.

1. Introduction

This work aims to extend the understanding of phenol oxidative pathways. To this purpose, the analysis of the formation of phenol degradation intermediates has been considered to complete the studies available in the literature [1–5]. Although, the decomposition of phenol using Advanced Oxidation Processes (AOPs) has been widely studied, the mechanism of oxidation that occurs has not been fully elucidated yet. As described in the bibliography, phenol oxidation proceeds through quite a complex radical mechanism in which complex species are formed [6]. The identification of these species is critical yet and it remains still incomplete because of the intricate nature of the reaction mechanism [7,8]. Therefore, the challenge in these kind of studies involves the identification of phenol degradation intermediates that are formed during the early stages of oxidation.

In simple terms, the oxidation of phenol with hydrogen peroxide to yield carbon dioxide and water embodies a global process of reactions in series that lead to the formation of products of an intermediate oxidation state. During the early stages of oxidation, phenol degrades into dihydroxybenzene rings, ortho-, meta-, and para-substituted (catechol, resorcinol, and hydroquinone). These species are in equilibrium with their corresponding benzoquinones (para and ortho). In the case of resorcinol, the substitution of the hydroxyl groups in the meta position does not lead to the formation of stable meta-substituted benzoquinone instead resorcinol will decompose producing diresorcinol-type molecules [9]. Fig. 1 displays the resonant forms of the dihydroxylated intermediates depending on the position of the substituent hydroxyl groups.

In the early stages of phenol oxidation, as phenol degrades, the treated waters acquire toxicity [10,11]. In fact the oxidized waters show higher toxicity than that corresponding to equivalent samples of the initial pollutant [12–14]. This result could be directly related to the formation of intermediate compounds presenting high chemical stability and hard to be mineralized [15]. In this way, although phenol can be effectively removed, it does not imply that the toxicity level of the effluent is adequate [16]. Moreover, the oxidized samples show a strong coloration, and its intensity can be related to the presence of intermediates of quinoidal nature [17].

When reaching high oxidation levels, the opening of the aromatic rings takes place. At this point, it is shown that the dosage of oxidant used in the treatment determines the selectivity of the reaction. In this manner, the degradation via ortho-substituted compounds leads to the formation of muconic acid [18,19]. As well, the oxidation via para-substituted species results in the formation of 2,5-dioxohexenoic acid. Since the ortho-substituted structures are more unstable than the para-substituted, it is shown that to be degraded to the corresponding acidic species the former requires lower dosages of oxidant than the latter. At this oxidant level, as the oxidation proceeds, the toxicity of treated water progressively decreases [14].

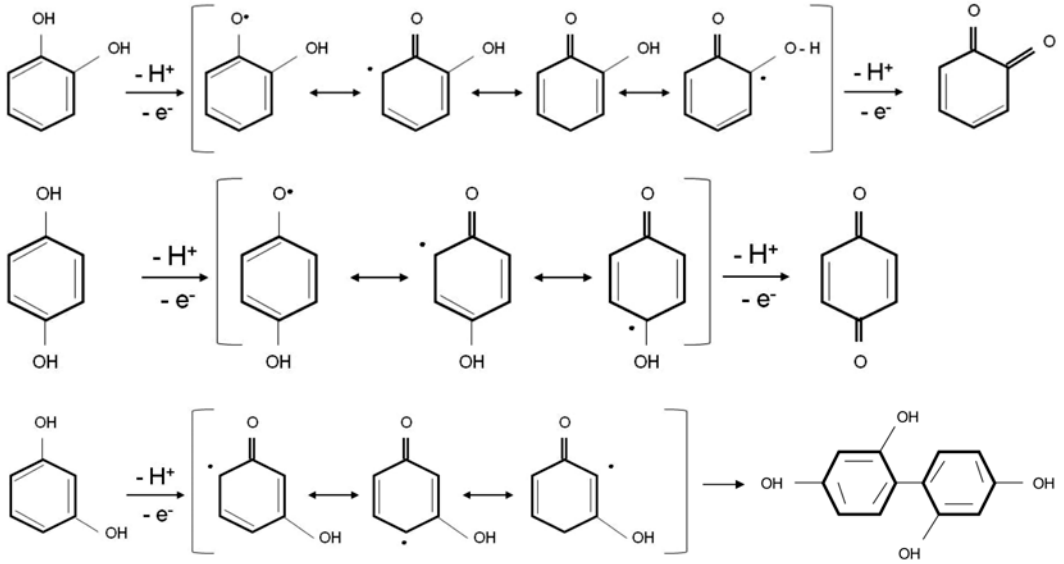

Fig. 1. Resonant forms of the dihydroxylated benzene rings depending on the position of the hydroxyl substituents.

This behavior may be attributed to the decomposition of the aromatic rings to carboxylic acids which are biodegradable species. Furthermore, since these acids are colorless species, the toxicity reduction of the solutions is associated to loss of coloring.

2. Materials and methods

The experimental assays utilizing photo-Fenton process were carried out with 500 mL of aqueous phenol solutions with an initial concentration, Ph_o = 100.0 mg L^{-1} (C_6H_6O Panreac, 99%), and iron catalyst added as ferrous ions ($FeSO_4 \cdot 2H_2O$, Panreac 80%) at concentration, Fe = 20.0 mg L^{-1}. These reagents were mixed in a reactor equipped with a medium pressure mercury lamp of 150 W (TQ-150, Heraeus), that provided a large emission band in the UV and increased intensity in the visible. This lamp emitted an adequate emission range, having 95% transmission between 300 and 570 nm, and it was jacketed either with a water-cooled quartz filter or a Pyrex filter. This arrangement permitted the study of the photodegradation using irradiation at wavelengths greater than 290 nm. The reaction mixture was homogenized by a magnetic stirrer, set at 500 rpm. Acidity was adjusted at pH 3.0 by dosing NaOH or HCl 0.2 M (Probus, 99.9%) with an automatic burette (Dosimat 665-Metrohm). Temperature was controlled at T = 25.0℃ using a cryo-thermostat bath of 1,150 watts (Selecta Frigiterm-10), and pumping water through the cooling sheath. The oxidant was added (H_2O_2, Foret 30%), at varying molar ratios of oxidant over the initial phenol in the water (R = 0–14.0 mol H_2O_2/mol C_6H_6O). These operation conditions favor the fenol degradation forming colored species [17].

At the addition time, the oxidation started and the reaction mixture was irradiated with UV light for 120 min. After irradiation, samples were stored for 10 d to analyze the corresponding values at steady state.

The oxidation tests with Fenton reagent were conducted in a mixed reactor fitted with a cooling jacket, and agitated by a magnetic stirrer. Oxidation using ultrasonic (US) waves was performed in a reactor (Bandelin electronic type DK 156 BP), 6L capacity and 0.72 kWh irradiation, 720 W US output power, 600 W heat power, and 35 kHz average frequency. The mixed tank reactor with the Fenton reagent was then introduced in the larger unit. The samples were agitated at 175 rpm with a magnetic stirrer (Heidolph RZR 2101). The temperature was controlled at 25.0℃, using a thermostatic bath (Selecta Frigiterm-10). After the reaction had begun, the samples were irradiated with US waves for 120 min.

The solution color was measured with a spectrophotometer UV/vis (Uvikon Kontron 930), 455 nm (Mijangos et al.). The degree of mineralization was measured with a Total Organic Carbon analyzer (TOC-VCSN Shimadzu). The concentration of organic species was analyzed by High Performance Liquid Chromatography HPLC (Agilent Technologies 1200 Series) attached to a spectrophotometer UV/vis. Analytic standards and detection setups were as follows: At 280 nm-phenol (Panreac, 99%), hydroquinone (Panreac, 99%), catechol (Baker Organic Chemical, 99%), resorcinol (Panreac, 99%), and phloroglucinol (Acros Organics, 99%). At 242 nm: ZZ-muconic acid (Acros Organics, 98%) and EE-muconic acid (Acros Organics, 97%). At 210 nm: p-benzoquinone (Alfa Aesar, 98%), hydroxyhydroquinone (Aldrich, 99%), pyrogallol (Sigma, 98%), and 2,5-dihydroxy-1,4-benzoquinone (Acros Organics, 98%). Table 1 displays the calibration curves of the aforementioned compounds. Analysis was performed by manually injecting 20 μL samples that were dragged by a carrier current of 1.0 mL min^{-1} flow, consisting of a mixture of methanol and distilled water, MeOH/H_2O: 20/80, through a column C_{18}, XBridge Phenyl 5 μm 4.6 × 250 mm (Bridge Waters), and the limit of detection (LOD) was 0.1 mg L^{-1}.

3. Results and discussion

The chemical pathway for phenol oxidation currently accepted is based on the classic reaction scheme established by Devlin and Harris [5] in which the process mechanism is expressed as a combination of series–parallel reactions. The main objective of this study is to complement the existing knowledge of the process as proposed in the literature by analyzing the formation of species according to their characteristic properties. And, additionally, to determine experimentally, the oxidant stoichiometric ratios are necessary to degrade phenol to its oxidation intermediates.

The approach of the work is based on a literature review of the species analyzed in oxidation systems that present similar characteristics to phenol oxidation [20–23]. These studies show that the oxidation of benzene rings of dihydroxylated nature, through the formation of para-substituted species, can lead to the creation of hydroxyhydroquinone. Alternatively, the oxidation through ortho-and meta-substituted benzene rings could produce pyrogallol [22]. Studies including the reactions with benzoquinones have revealed the formation of hydroxyhydroquinone and pyrogallol-type compounds [3]. Following these initial considerations, this paper analyzes the formation reactions of benzene rings of trihydroxylated nature, evaluating

Table 1
Calibration curve of the analyzed compounds (C_0 = 100.0 mg L^{-1}; T = 25.0°C)

Compound	λ (nm)	Slope (mg UA^{-1} L^{-1})	r^2
Phenol	280	0.132	0.9950
Catechol	280	0.125	0.9996
Resorcinol	280	0.172	0.9912
Hydroquinone	280	0.113	0.9975
Pyrogallol	280	0.918	0.9991
	210	0.020	0.9944
Phloroglucinol	280	2.006	0.9986
	210	0.013	0.9962
Hydroxyhydroquinone	280	0.106	0.9974
	210	0.097	0.9970
p-Benzoquinone	280	0.599	0.9992
Dihydroxybenzoquinone	210	1.193	0.9246
EE-muconic acid	242	0.014	0.9952
ZZ-muconic acid	242	0.011	0.9913

the oxidative pathways as a function of the position of the hydroxyl groups on the benzene rings. The formation of hydroxylated compounds of quinoidal nature is also assessed.

3.1. Effect of the oxidant to phenol molar ratio on the oxidation

Fig. 2 shows the phenol decomposition (Ph/Ph$_o$) and total organic carbon (TOC/TOC$_o$) at steady state as a function of the oxidant to phenol molar ratio (R, mol H_2O_2/mol C_6H_6O) using a photo-Fenton treatment [24]. Furthermore, a small figure is inserted, displaying the reduction of NPOC (Non-Purgeable Organic Carbon, mg C L^{-1}) during the early period of phenol degradation, under the stoichiometric conditions (R = 14.0 mol oxidant mol/phenol).

Results indicate that, although phenol is fully degraded in 30 min of reaction, NPOC undergoes a slight decrease (around 10%). This can be due to the intermediate species of decomposition, generated in the former stages of oxidation, which are quite

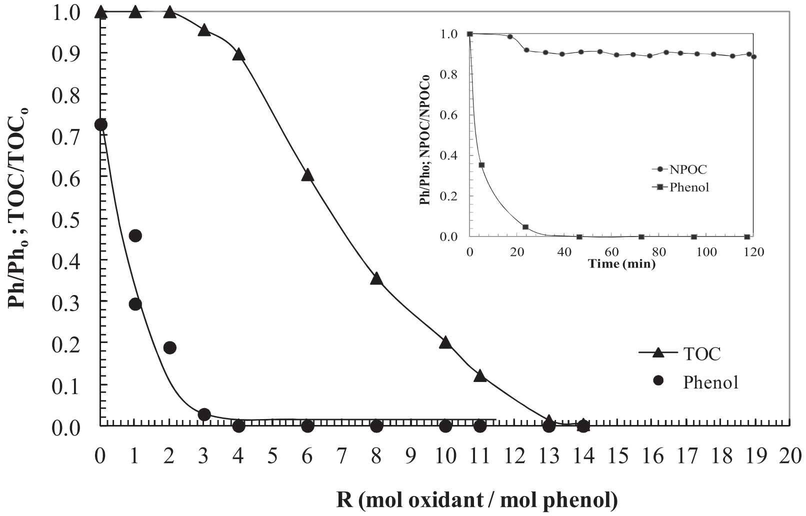

Fig. 2. Effect of the oxidant molar ratio on phenol degradation (Ph/Ph$_o$) and Total Organic Carbon (TOC/TOCo) in a Photo-Fenton system. Experimental conditions: Ph$_o$ = 100.0 mg L^{-1}; pH 3.0; Fe = 20.0 mg L^{-1}; T = 25.0°C; t = ∞. Small picture: Kinetic of NPOC removal during the phenol degradation. Experimental conditions: Ph$_o$ = 100.0 mg L^{-1}; pH 3.0; R = 14.0 mol oxidant/mol phenol; Fe = 20.0 mg L^{-1}; T = 25.0°C.

recalcitrant and require long reaction times for being degraded.

During the steady state the oxidant molar ratios ranged between *R* = 0–14.0. The reaction proceeded until reaching at *R* = 13.0 the maximum degradation of phenol to carbon dioxide and water. In all trials, acidity was fixed at pH 3.0, constant dosage of catalyst Fe = 20.0 mg L^{-1} and UV radiation. Thus, the possible interferences that may cause iron species in the solution are avoided.

Examining the degree of phenol oxidation reached, it may be concluded that it is possible to completely degrade the initial phenol load using oxidant molar ratios above 4.0. This result is obtained by radiating the system with a 150 W UV lamp for 120 min, allowing the samples to stand until steady state. By operating with $R < 4.0$, although phenol does not completely decomposed, the degree of phenol oxidation increases with the oxidant ratio following an exponential trend. It is noteworthy that *R* = 4.0 corresponds to the theoretical ratio of oxidant leading to the formation of muconic acid [2].

Fig. 2 also shows the degree of wastewater mineralization in the oxidized samples expressed as total organic carbon ratio (TOC/TOC_o). TOC undergoes an induction period when operating at oxidant ratios $R < 4.0$. In this range, levels of water mineralization up to 10% are reached. When the ratio, *R*, is greater than 4.0, wastewater mineralization exponentially increases with the oxidant molar ratio. Within this range, phenol is degraded to high oxidation stages generating carboxylic acids of cyclic chain, eventually leading to ring opening. These structures will further break down, leading to carboxylic acids of linear chain. During this process, chain shortening of acidic species happens and carbon is released as CO_2. In this way, carrying out the treatment with oxidizing ratios *R* = 14.0, all organic matter contained in the water is released to the atmosphere as carbon dioxide as shown in Fig. 2.

3.2. *Effect of oxidant dosage in the formation of phenol oxidation intermediates*

The oxidant dosage determines the oxidation state that can be reached. Using this approach, the phenol degradation intermediates that are generated at different stages of oxidation were analyzed. Fig. 3 displays the formation of dihydroxylated intermediates (Hy: hydroquinone, mg L^{-1}; Ca: catechol mg L^{-1}; Re: resorcinol, mg L^{-1}), and p-benzoquinone (pBq, mg L^{-1}), as a function of the oxidant to phenol molar ratio. It is remarkable that the values of maximum concentration for these species correspond to the experimental stoichiometric ratio.

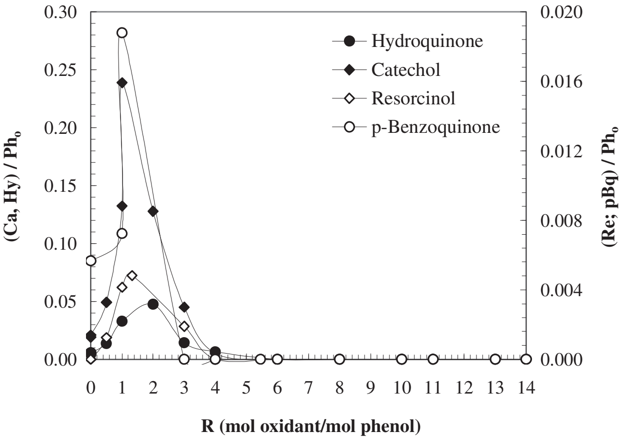

Fig. 3. Effect of the oxidant molar ratio employed in a photo-Fenton treatment on the formation of reaction intermediates during the early stages of phenol degradation. Experimental conditions: Ph_o = 100.0 mg L^{-1}; pH 3.0; Fe = 20.0 mg L^{-1}; *T* = 25.0°C; *t* = ∞.

Results show that dihydroxylated benzene rings form during the early phases of the reaction. At this stage, the most unstable species require lower oxidant ratios for their formation. Thus, Fig. 3 shows that catechol formation is maximum when using dosages of *R* = 1.0, while resorcinol requires *R* = 1.3 and hydroquinone *R* = 2.0. The addition of these molar ratios corroborates the stoichiometric oxidant ratio that is experimentally obtained for phenol oxidation (Fig. 2), which corresponds to *R* = 4.3. On the other hand, the selectivity of the reaction species reveals that the main path for the oxidation of phenol involves the ortho-substituted species.

Para-benzoquinone experiences maximum formation when using ratios *R* = 1.0. The ortho-and para-substituted benzoquinones are species in equilibrium with the dihydroxylated compounds, with substituents in the same positions in the benzene ring. In the particular case of hydroquinone and p-benzoquinone, they can establish charge transfer linkages, generating compounds like quinhydrone [17,25]. It is noteworthy that, equally to the oxidation in the case of phenol, these species are degraded completely when using oxidant ratios *R* above 4.0. This corresponds to the total ratio that is required to degrade phenol to its immediate degradation intermediates, namely the dihydroxylated benzene rings in their ortho-, meta-, and para-substituted forms.

Fig. 4 reveals the formation of trihydroxylated benzene rings in different configurations: ortho-, meta-, and para-(Py: pyrogallol, mg L^{-1}; Phloro:

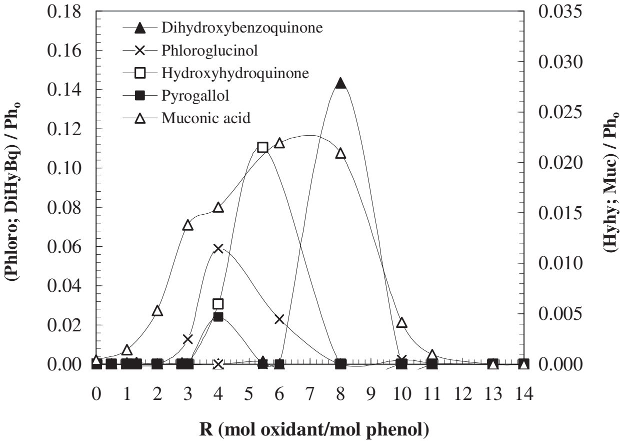

Fig. 4. Effect of the oxidant molar ratio using in the photo-Fenton treatment on the formation of reaction intermediates during higher stages of the phenol degradation. Experimental conditions: Ph_o = 100.0 mg L^{-1}; pH 3.0; Fe = 20.0 mg L^{-1}; T = 25.0°C; $t = \infty$.

phloroglucinol, mg L^{-1}; Hy: hydroxyhydroquinone, mg L^{-1}), and the formation of the dihydroxylated species of p-benzoquinone (DiHyBq: dihydroxybenzoquinone, mg L^{-1}) and that of muconic acid (Muc: ZZ-muconic acid, mg L^{-1}) in function of the oxidant to phenol ratio.

Fig. 4 shows that the formation of compounds with unstable molecular structures requires lower oxidant dosage ratios. Thus, the production of trihydroxylated rings with substituents in ortho-(pyrogallol) and meta-(phloroglucinol) positions demand oxidant ratios around R = 4.0. However, the formation of trihydric rings with para-substituted hydroxyl groups (hydroxyhydroquinone) needs oxidant ratios above R = 5.5. From the reaction selectivity, it is ascertained that the predominant oxidation pathway in this state proceeds through trihydroxylated para-substituted species. This indicates that the more stable trihydroxylated species are those that are found in large concentrations in the resistant residue of treated water.

The analysis of benzoquinones substituted by hydroxyl groups has revealed the presence of dihydroxybenzoquinone in the final residue of the treated samples. The results show that dihydroxybenzoquinones are species that require oxidant ratios around R = 8.0. These ratios that are higher than those for the ortho- and meta-substituted oxidation routes can be explained in terms of the higher stability of the aromatic ketones, which is enhanced when there are substituted hydroxyl groups in the ring.

Muconic acid in treated water is detected within a wide operating range of the oxidant ratio (R = 0–13.0 mol H_2O_2/mol C_6H_6O), in which the maximum concentration value is obtained when at R = 6.0. These results indicate that the formation of muconic acid requires the use of oxidant dosage ratios lower than those for generating dihydroxybenzoquinone. Therefore, it would be reasonable to conclude that the oxidation of p-benzoquinone species could result in dihydroxybenzoquinone, whereas muconic acid would be formed as a result of an oxidation process through ortho- and meta-substituted species. These conclusions would be consistent with the mechanism put forward by Devlin and Harris [5] which states that oxidation through para-substituted species could generate 2,5-dioxo-hexenoic-type acids while the oxidation by ortho-substituted species would lead to the formation of muconic acid.

3.3. Mechanism proposed for phenol degradation

Fig. 5 proposes the mechanism of phenol oxidation based on the experimental results, in which the ratios of oxidant to generate the specific oxidation intermediates are estimated.

The mechanism proposed is consistent with the structure of the mechanisms presented in the references mentioned above. Hence, it should be considered that the diagram in Fig. 5 shows, in a simple and schematic manner, the formation of the oxidation intermediates. However, given the radical nature of the reaction system being analyzed, it is likely that additional reactions of intermediate formation would simultaneously take place. Nevertheless, certain deviations are observed when comparing the oxidant ratios experimentally obtained, with the theoretical proportions estimated by the stoichiometry of the various reactions [2]. These discrepancies become more important at higher oxidation levels.

Experimental oxidant ratios are generally somewhat higher than those theoretically estimated. This may be attributed to the existence of additional pathways involving reactions between iron salts, added as catalyst, and hydrogen peroxide [26] that occurs in parallel to phenol degradation. Therefore, some hydroxyl radicals generated in the reaction system are consumed in the regeneration cycle of iron [27]. Furthermore, iron ions can interact with the organic matter in the system resulting in the formation of metal complexes [28–31]. These species, which possess some stability, would create an additional radical sump.

3.4. Effect of the presence of intermediates on wastewater coloring

Fig. 6 shows the color of treated wastewaters as a function of the oxidant molar ratio operating by

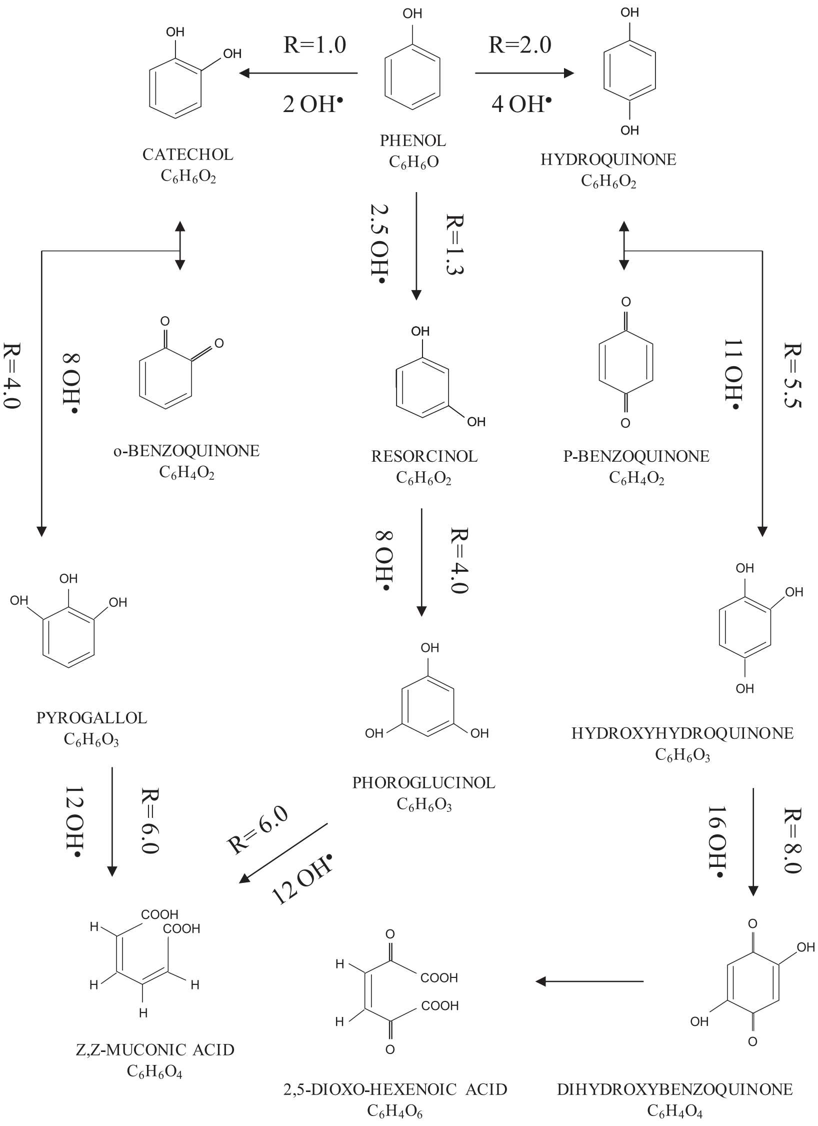

Fig. 5. Molar ratios of oxidant (R = mol H_2O_2/mol C_6H_6O) employed to degrade phenol to reaction intermediates generated during the initial stages of the oxidation pathway.

different Fenton technologies. The color will be determined by the nature of the oxidation intermediates [32].

Results show that the kind of treatment affects the intensity of the color of the oxidized samples. Several factors may influence the water color and iron species in solution are important contributors. Although tests were performed at constant dosages of catalyst, the combined action of UV light and US waves may have directly affected iron speciation [33]. On the other hand, the contribution to the color that is provided by the oxidation intermediates should also be examined. To this purpose, Table 2 exhibits the color shown by aqueous solutions of the studied intermediate species, adjusted to the experimental conditions, pH 3.0 and T = 25.0°C. The main species that generate colored solutions are: pyrogallol, yellow; p-benzoquinone, orange; hydroxyhydroquinone, dark orange, and dihydroxybenzoquinone, red.

The evolution of color, as a function of the oxidant ratio showed a similar trend to that observed in the treatments of the oxidation intermediates. This suggests that, although iron compounds can affect color intensity, the oxidation intermediates are the principal source of color evolution. When analyzing

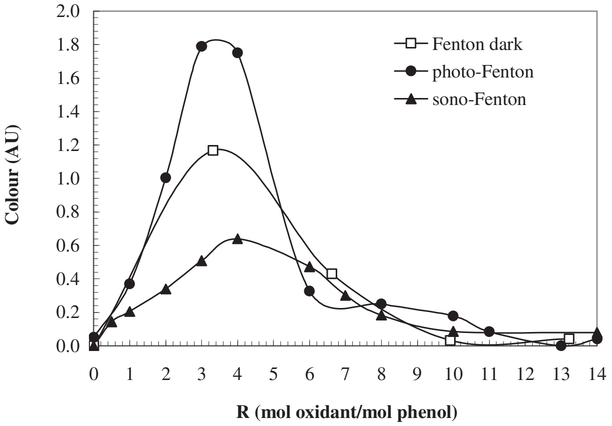

Fig. 6. Effect of the oxidant molar ratio on the induction of color in phenol solutions treated by different Fenton technologies. Experimental conditions: Ph_o = 100.0 mg L^{-1}; pH 3.0; Fe = 20.0 mg L^{-1}; T = 25.0°C; $t = \infty$.

the color development as shown in Fig. 6, it is necessary to consider the results displayed in Figs. 3 and 4 which confirm the intermediates formation. In doing this, it can be established that the water color increases in intensity with increasing oxidant dosage until it reaches its maximum at R = 4.0. This stage may be associated with the degradation reactions of phenol that lead to the formation of species with similar characteristics to pyrogallol and phloroglucinol. Once this maximum has been attained, water color diminishes with increasing oxidant dosage, treated water becoming colorless at R > 13.0. The drastic decrease in color that is observed between R = 4.0–6.0 corresponds to the muconic acid formation. A slight increase at dose ratios greater than R = 7.0 can be related to the formation of dihydroxylated benzoquinones.

4. Conclusions

This work confirms previously published studies of the mechanism of phenol oxidation by analyzing the formation of trihydroxylated benzene rings. In this way, it considers the degradation pathways depending on the position occupied by the hydroxyl groups on the benzene rings, and the formation of quinoidal compounds of hydroxylated nature. Additionally, the oxidant molar ratios necessary to produce the intermediates generated at different stages of the mechanism is experimentally established.

The study of dihydroxylated benzene rings can prove that the formation of the most volatile species needs lower oxidant ratios. Thus, catechol is obtained at R = 1.0, resorcinol at R = 1.3 and hydroquinone at R = 2.0. The addition of these ratios, R = 4.3, corresponds to that required to oxidize all the starting phenol contained in the water. On the other hand, the p-benzoquinone is created at R = 1.0. Forming trihydroxylated rings with ortho- (pyrogallol) and meta-substituents (phloroglucinol), which presents more unstable structures, needs a lower ratio, R = 4.0, than para-substituted rings (hydroxyhydroquinone) that demand R = 5.5.

The presence of muconic acid in the treated water is detected in a wide operating range (R = 0–13.0) in which the maximum production occurs at R = 6.0 whereas benzoquinones substituted by hydroxyl groups (dihydroxybenzoquinone) need R = 8.0. These results lead to the conclusion that oxidation of p-benzoquinone would result in dihydroxybenzoquinone species. Meanwhile, muconic acid would be formed as a result of an oxidation process through ortho- and meta-substituted species.

The mechanism of phenol oxidation experimentally obtained shows concordance with the studies presented in the literature. However, the oxidant ratios

Table 2
Color analyzed in aqueous solutions of phenol degradation intermediates (C_0 = 100.0 mg L^{-1}; T = 25.0°C)

Compound	Color (AU) pH 3.0	Color (AU) pH natural
Phenol	0.081	0.087
Catechol	0.084	0.084
Resorcinol	0.080	0.081
Hydroquinone	0.080	0.080
Pyrogallol	0.160	0.160
Phloroglucinol	0.087	0.090
Hydroxyhydroquinone	0.461	0.477
p-Benzoquinone	0.205	0.231
Dihydroxybenzoquinone	0.642	0.642
EE-muconic acid	0.089	0.089
ZZ-muconic acid	0.087	0.085

applied are somewhat higher than those estimated by reaction stoichiometry. This may be caused by alternate parallel mechanisms which would involve reactions between iron salts and hydrogen peroxide thereby providing a radical sump.

The oxidation intermediates determine the color of treated water although iron species may enhance its intensity. Color is maximum when operating at $R = 4.0$. And it may be concluded that it would be produced by intermediates possessing structural features of the type of pyrogallol and phloroglucinol. A decrease in color happens between $R = 4.0–6.0$, which corresponds to the formation interval of muconic acid. Then, the color increases slightly at $R > 7.0$, and decreases gently until rendering colorless samples at $R > 13.0$. This trend could be associated with the formation of dihydroxylated benzoquinones.

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