

Changes in Solution Color During Phenol Oxidation by Fenton Reagent

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Fenton reaction is a highly effective treatment for degrading phenolic compounds in an aqueous solution. However, during phenol oxidation, the oxidized water takes on a dark brown color associated with increased toxicity. Then, although phenol can be completely removed, if the oxidation process is not carried out properly, the final wastewater will be brown in color and have higher toxicity, two parameters in which legislation imposes restrictions. This paper analyzes the development of the dark color observed in the solution under oxidation treatment and formulates a reaction mechanism to explain the color generation. The experiments were carried out following the batch-wise procedure, but with the solution pH being kept constant throughout the reaction at its optimum value for phenol removal, i.e., pH 3.0. It is checked experimentally that color is formed at the beginning of the reaction in less than five minutes, and follows the kinetic-path of a reaction intermediate. During the first steps of the reaction phenol is degraded to dihydroxylated rings (catechol, resorcinol, and hydroquinone). These aromatic intermediates generate higher colored compounds such as *ortho*- and *para*-benzoquinone. On the other hand the dihydroxylated rings can react with their own quinones to generate charge-transfer complexes (quinhydrone), compounds which take on a dark color at low concentrations. Moreover, when iron reacts with hydrogen peroxide, ferric ions are generated that can be coordinated to benzene rings to produce colored metal complexes. The observed color of the solution is not a fortuitous result depending on trace components of low significance, but depends directly on the main reaction intermediates, so it is concluded that observed color depends on the level of oxidation reached. The maximum color observable during oxidation treatment (A_0) depends only on initial phenol concentration and not on oxidant or catalyst doses.

Introduction

Many physical, chemical, and biophysical processes have been studied for their ability to destroy phenolic compounds, but conventional treatments use to be ineffective because this kind of species is refractory and poorly biodegradable. Besides this, phenol degradation occurred in chlorinating plants, producing chlorine-phenol compounds more toxic and resistant than phenol itself (1–3).

Advanced oxidation processes (AOPs) are applied to remove resistant, toxic, and poorly biodegradable pollutants

from water and wastewaters. AOPs have been defined as those oxidation treatments based on the reaction of hydroxyl radical in an aqueous solution; it is a powerful and extremely reactive oxidant agent that can destroy organic pollutants efficiently (2–7). Hydrogen peroxide is currently considered the most appropriate reactant used for these technologies. Transition metals (e.g., iron or copper), ozone, or UV-light are employed to activate its reaction.

Fenton reagent (H_2O_2/Fe^{2+}) activates the reaction between organic substances and hydrogen peroxide in the presence of ferrous sulfate operating at atmospheric pressure and room temperature. It breaks down organic pollutants into harmless compounds (acids, carbon dioxide, and water). So it requires neither additional equipment such as ozone systems or ultraviolet lamps nor expensive reagents because it uses ferrous salts as an activator agent.

During phenol oxidation with Fenton reagent numerous stable intermediates are generated which make it difficult to establish a reaction mechanism. Nowadays, it is accepted that phenol follows roughly the reaction mechanism proposed by Devlin (8) where a partial oxidation of phenol generates a great number of intermediate species of different nature. The intermediate compounds generated are mainly catechol, hydroquinone, benzoquinone, maleic acid, oxalic acid, and acetic acid. The oxidation sequence comprises a first stage where phenol is decomposed to aromatic compounds with two hydroxyl groups substituted in benzene rings (hydroquinone, resorcinol, and catechol). Their oxidation generates quinone compounds: *p*-benzoquinone and *o*-benzoquinone. In the next stage the rings open to form carboxylic acids with lower carbon numbers as oxidation lapses.

One peculiarity of phenol oxidation is that intermediate species generated during the process can be more toxic and less biodegradable than phenol itself. Current legislation controls phenol concentrations discharged into water systems, but it is also necessary to characterize and control these toxic compounds. The acids formed are numerous, but they are biodegradable, so their environmental impact is lower. They do not, therefore, need to be eliminated because they can be degraded later in biological treatments.

The basic control parameters of oxidation treatment are pH, the pollutant amount contained in water, and the hydrogen peroxide and catalyst dosages used, all of which have been investigated in depth in the relevant literature. However, little has been said about the changes in color observed during the phenol oxidation or, more relevantly, about the mechanism and the conditions for avoiding the formation of colored compounds or intermediates (9–10). Nevertheless, the production of colored wastewaters makes it difficult to implement this oxidation treatment, but the color shown by wastewaters during oxidation treatment could be used as an overall indicator of their oxidation state. Color generation during phenol oxidation is a fast reaction where the phenolic solution changes initially from colorless to brown, and later the color decays to a minimum level. This study analyzes the effect of the main reaction parameters on phenol oxidation with Fenton reagent, focusing on color changes and the possibility of obtaining low-toxicity colorless waters after treatment.

Experimental Method

Chemicals. Synthetic phenol solutions were prepared by dissolving pure phenol (Panreac PRS 90%) in distilled water, and preserving it in amber-colored bottles. Ferrous ion solutions were prepared from ferrous sulfate heptahydrated

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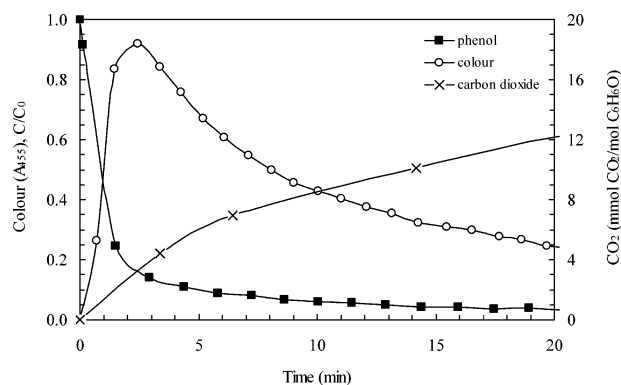


FIGURE 1. Example of experimental kinetic of phenol oxidation with Fenton Reagent at constant solution pH 3.0. Color solution (absorbance at 455 nm) and carbon dioxide generation are overplotted. $[\text{phenol}]_0 = 100 \text{ mg/L}$; $[\text{Fe(II)}]_0 = 9.9 \text{ mg/L}$; $R = 9.9 \text{ mol H}_2\text{O}_2/\text{mol phenol}$. Atmospheric pressure and room temperature.

(Panreac PRS) and hydrogen peroxide was used as the oxidant (Panreac PRS, 30% v/v), diluted in distilled water.

Setup of the Experiment. Synthetic phenol solutions (500 mL) were added in a batch reactor with the specific catalyst concentration to be studied in each case. The mixture was homogenized by magnetic agitation. The reaction starts after a predetermined dose of oxidant is added to the reactor. Experiments were carried out at atmospheric pressure and room temperature, and operational pH was controlled with an automatic buret that dosed NaOH 0.1 M or HCl 0.1 M. Phenol concentration and color level were monitored throughout the oxidation process and the solution temperature was measured.

Methods of Analysis. Phenol concentration was determined by the 4-aminoantipyrine Method using a UV/VIS Lambda 10-Perkin-Elmer spectrophotometer, coupled to a FIAS 300-Perkin-Elmer flow injection analysis system. Color was determined by the standard methods (11) using an Odyssey DR/2500 spectrophotometer, by direct measurement (without colorimetric additives) of the absorbance at 455 nm. Operation temperature was measured throughout the reactions, and pH was kept constant by a Titrimo 702 SM-Metrohm automatic buret. The amount of carbon dioxide was estimated through total organic carbon (TOC) measurements using a TOC-VCSN Shimadzu Analyzer. CO_2 formation was assumed as the decrease of TOC during the reaction.

Conditions of the Experiment. Results reported in the relevant literature clearly indicate that the operation pH determines the degree of oxidation reached in the treatment, with pH 3.0 being the most effective value (12). At higher pH levels, iron precipitates as hydroxides and at lower levels self-decomposition of hydrogen peroxide is promoted (13). So in this experimental study, all kinetic assays were carried out at constant pH throughout the reaction at the optimum level of $\text{pH } 3.0 \pm 0.05$.

Although the experiments were not controlled to run at a constant temperature, the maximum increment observed during experiments lasting many hours was 2°C .

Results of the Experiment and Discussion. Figure 1 shows experimental results for one assay-type where phenol concentration, color of the solution, and CO_2 formation are plotted throughout the oxidation reaction. This kinetic plot clearly resembles a pattern of series reaction. Phenol removal is a fast reaction, with almost complete elimination taking only few minutes. As a rule, and for the experimental conditions investigated here, 90% of phenol degradation occurs in the five first minutes of the reaction. The rest degrades slowly, taking around half an hour to attain oxidation efficiencies greater than 98%. There are several reasons for this behavior of the phenol oxidation rate, but

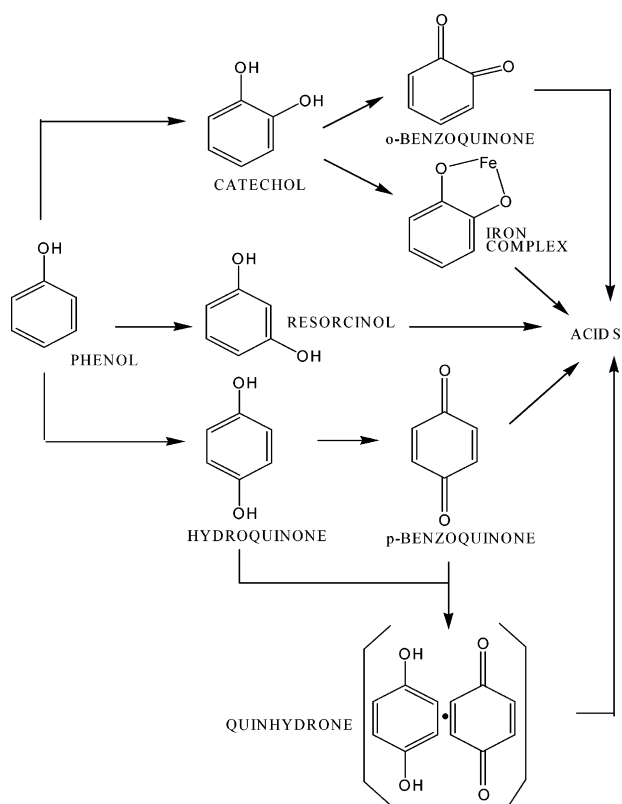


FIGURE 2. Scheme of the reaction pathway proposed to explain the colour changes observed in solution during the reaction.

generally, it is thought to be associated with the dynamics of hydroxyl radical generation. Thus, it is proposed that ferrous ions react quickly with hydrogen peroxide initially generating a large amount of hydroxyl radicals that give rise to a fast destruction of the aromatic rings (14). But afterward, as the reaction continues, the catalyst iron(II) is continuously regenerated and reacts again, so the regeneration rate keeps the concentration of radicals in the solution proportional to the actual concentration of hydrogen peroxide. Within the concentration tested, the decrease in the phenol oxidation rate is probably due to a decrease in iron activity, because iron(III) is forming complexes with organic intermediates.

The final product of reaction is carbon dioxide, which follows a monotonic increasing curve throughout oxidation, with its concentration being indicated by the degree of mineralization achieved. Figure 1 also plots the molar ratio of carbon dioxide to phenol for the first stages of the reaction. It can be observed here that, after 20 min, and most of the initial phenol contained in the water has been degraded, the degree of mineralization is very low at just $12 \text{ mmol CO}_2/\text{mol phenol}$. This very low mineralization (0.2% of phenol converted to phenol) is due to the fact that CO_2 molecules are mainly formed from the decarboxilation or chain-shortening of acid intermediates generated during the reaction whose reaction kinetic is very slow, and final acids are very difficult to bring down to carbon dioxide at the beginning of the reaction (3).

In the first minutes of the reaction, the phenol solution undergoes a fast color change from colorless to dark brown, reaching a peak level. Later the water begins to slowly clear up to a light brown, and even turns a pale yellow residual color in some experimental conditions.

The kinetic pathway (Figure 2) followed by the phenol oxidation reaction and the many experimental results reported here show that color is not a fortuitous result depending on trace components or parameters with low significance, but depends directly on the main reaction

intermediates. Indeed, in any experiment, color shows the path of a reaction intermediate which follows a slow kinetic that can continue for hours. So it might be possible to establish a relationship between the color level observed and the intermediate compounds generated during the oxidation.

The mechanism that we proposed for phenol oxidation Figure 2 states that during the first stages of oxidation, highly colored intermediate compounds such as p-benzoquinone (yellow) and o-benzoquinone (red) are generated (3, 8). Their color comes from their quinoidal structure, which contains chromophore groups substituted in benzene rings. Benzoquinones achieve their peak level during the first minutes, then disappear slowly because they are very stable species due to the conjugated carbonyl groups contained in their internal structure. To compare the color generated by benzoquinones, several single standards were prepared at low concentration and in the same conditions under which phenol oxidation was carried out. These single substances show a color level lower than that monitored during oxidation, which indicates that there must be a contribution by other intermediates or an interaction between reacting species. However, the mixture of single p-benzoquinone (yellow) and hydroquinone (colorless) solutions fits the color observed in the reacting mixture (brown), revealing occasional intermolecular interactions between quinones and dihydroxylated rings. These highly colored species are well-known in the literature (15, 16) as charge-transfer complexes called quinhydrones that are assumed here to be generated during oxidation treatment to explain the visible spectra and absorbance at 455 nm.

On the other hand, Fenton reaction involves a reaction between iron and hydrogen peroxide where ferric ions are generated (17–21). These species can bind to intermediate species with hydroxyl groups substituted in benzene rings generating metal complexes (22–27). Of all the mixtures of small amounts of iron(III) with colorless compounds generated during phenol oxidation such as phenol, hydroquinone, and carboxylic acids, only the catechol solution shows some color change, turning dark green. This suggests the formation of colored iron complexes.

Having stated the main contributions to color formation, we now go on to analyze the effect of the reaction parameters on color changes. Studies of oxidation using Fenton reagent indicate that the variables with most influence on the reaction rate are the initial amount of pollutant in wastewater, the catalyst, and oxidant dosage used in the treatment and the solution pH (28, 29).

Oxidant Molar Ratio. The effect of the initial hydrogen peroxide amount on color formation was tested in a set of assays with constant catalyst concentrations $\text{Fe}^{2+} = 9.9 \text{ mg/L}$ at constant pH 3.0. Results are reported in Figure 3, which shows the temporal absorbance at 455 nm using different concentrations of oxidant. For a wide range of conditions, the molar ratio of oxidant to phenol does not affect the maximum color at origin ($A_0 = 1.38 \text{ UA}$) observable in any time plot of color where all kinetic curves have the same ordinate at origin, given by eq 5.

Using oxidant molar ratios ranging from zero to the stoichiometry reference value of 14 mol $\text{H}_2\text{O}_2/\text{mol}$ phenol, the temporal profile of the solution color level follows the same path shown in Figure 1, i.e., a kinetic curve of color with two branches. The first, with a sharp positive slope, demonstrates that color generation takes place in parallel with phenol decay. After a while, but still during the first stage of the reaction, a peak appears at between 3 and 5 min and then gives way to the negative branch of the curve, indicating that colored intermediates start to degrade to colorless compounds. This degradation takes place slowly because quinone-type compounds seem to be a very stable species in this medium. The absolute value of this negative

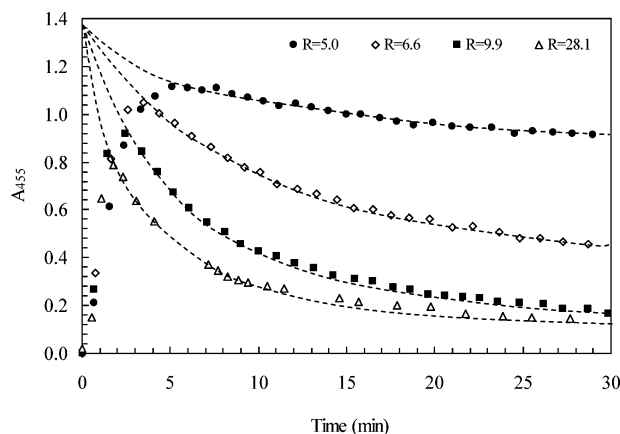
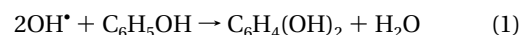


FIGURE 3. Temporal results of color changes (absorbance at 455 nm, A_{455}). Effect of the molar ratio of the oxidant on color formation and fading rate. $[\text{phenol}]_0 = 100 \text{ mg/L}$; $[\text{Fe(II)}]_0 = 9.9 \text{ mg/L}$.

slope shows that degradation reactions are much slower than color generation. The rate of this decolorization stage increases with the initial molar ratio of hydrogen peroxide. However the final color level achieved is similar at R values higher than 10, with water being fully decolorized at long reaction times. So higher oxidant amounts seem to reduce fading time but do not improve the final appearance of the oxidized water; they may even produce lower efficiency in oxidant use because hydroxyl radicals react with hydrogen peroxide, causing it to degrade itself.

With oxidant ratios lower than 4 mol $\text{H}_2\text{O}_2/\text{mol}$ phenol, the color generated during oxidation treatment increases in proportion to the oxidant molar ratio (see Figure A, Supporting Information), but overall, the decolorization step is almost negligible. Due to the very low stoichiometric ratio, phenol can only be degraded to quinone-type intermediates because hydroxyl radicals are attenuated before the complete degradation of the aromatic rings to open-chain acids. The color peaks at around 4 mol $\text{H}_2\text{O}_2/\text{mol}$ phenol, and then diminishes as the aromatic intermediates are broken down to form acids. This reaction is promoted by the high concentration of hydroxyl radicals.

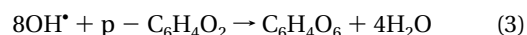
Considering the general proposals for these oxidation reactions (8) and reaction pathway we proposed in Figure 2, the first step is here described by eq 1, where the oxidation of phenol to dihydroxylated rings requires two hydroxyl radicals, i.e., $R = 1$, assuming that each hydrogen peroxide gives rise to two active hydroxyl radicals.



Later, dihydroxylated species such as pirocatechol degrade to benzoquinones, with this second step requiring additional hydroxyl radicals, as described by reaction 2. The overall stoichiometric consumption at this level, $R = 2$, is



The next reaction leads to the opening of the aromatic ring, but depending on the benzoquinone isomer considered, the reaction could yield 2,5-dioxo-3-hexendioic acid ($\text{C}_6\text{H}_4\text{O}_6$) or muconic acid (2,4-dihexendioic acid, $\text{C}_6\text{H}_6\text{O}_4$). Reaction 3 needs eight hydroxyl radicals, which means that the overall consumption of hydrogen peroxide is $R = 6$



Muconic acid requires much less oxidant, giving rise, if this were the only path for quinone destruction, to just 3 mol of hydrogen peroxide per mol of oxidized phenol ($R = 3$) to

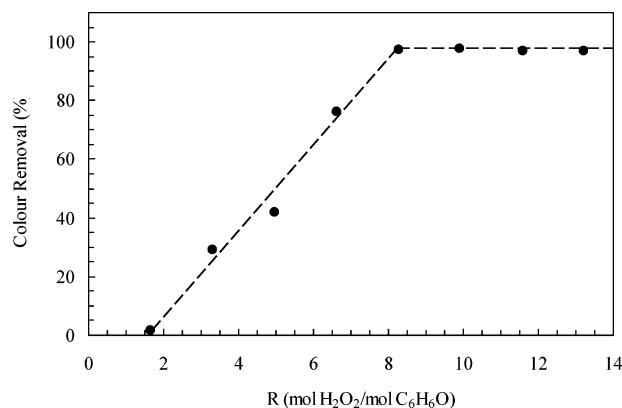
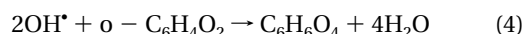


FIGURE 4. Decolorization level achieved after long reaction time as a function of the molar ratio of hydrogen peroxide to initial phenol.

obtain fully decolorized water:



Considering the experimental results reported in Figures 3 and 4, on the basis that the ring-opening yields uncolored compounds in any case and that reported consumption of oxidant is high, the reaction path is better described by reaction 3 than 4. That is, p-benzoquinone is the main reaction intermediate, although reaction 4 should not be entirely rejected because muconic acid, probably derived from an ortho-substituted aromatic ring, is frequently detected in this reacting medium (8, 30).

The relationship between the dose of hydrogen peroxide and the final color of the solution is therefore established, and it is concluded that the color observed depends on the level of oxidation reached. Consequently, it can be said that current color is a good indicator of the degree of oxidation achieved during the reaction. Using long reaction times, at least 10 mol of H₂O₂ per mol of initial phenol are required to obtain fully colorless oxidized waters. Working in these conditions some biodegradable acids would remain in the solution but the toxicity associated with aromatic intermediates and that of the phenol itself would be totally removed, although this point has not been experimentally proven.

On the other hand, Figure 4 represents the level of color removal ($1 - A_\infty/A_0$) achieved at the end of the experiments. Figure 4 gives a clear idea of the kinetic mechanism, stressing the importance of eqs 1–4. It should be noted that using a low molar ratio the color initially generated remains in the solution, so although the absolute amount of color increases with the molar ratio, these conditions are not enough to achieve the oxidation level required to turn the phenol to colorless acid. Consequently, the level of decolorization increases with the molar ratio, between $R = 1$ and $R = 8$, which indicates that Figure 4 should be read as the proportion of the aromatic rings that have been turned to open-chain acid or more degraded species.

Phenol Concentration. The influence of the initial concentration was evaluated between 10 and 200 mg of phenol/L by a series of assays using an oxidant ratio of 9.9 mol H₂O₂/mol phenol at a constant catalyst concentration of 9.9 mg Fe(II)/L. All kinetics follow the same path shown in Figure 3 and peak at similar reaction times of around 3 min, after which the water fades slowly. Higher phenol concentrations increase the color level of the reacting solution (see Figure B, Supporting Information).

These experimental results of color changes during the oxidation reaction of phenol were analyzed on the basis of the reaction pathway shown in Figure 2. At the beginning of the reaction phenol reacts with hydroxyl radicals catalytically

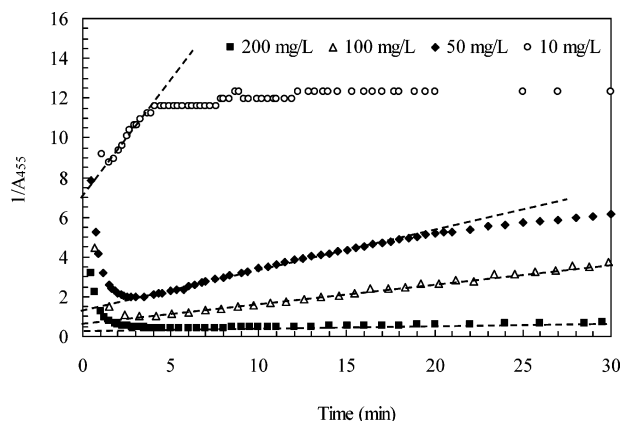


FIGURE 5. Second-order plot for different oxidation kinetic runs with different initial concentrations of phenol.

generated from hydrogen peroxide to form a dihydroxylated ring. These compounds easily oxidize to the quinone group, some of which are colored, but the latter can react with the former to form quinhydrone, a highly colored charge-transfer complex. Moreover, the final color can be deepened or modified by iron(III) that appears in the reacting medium due to the oxidation of Fenton reagent. From our point of view, quinone-type compounds are the main contributors to the color observed during the reaction, although the contribution of iron(III) is by no means negligible because the residual color of fully oxidized water increases with the total concentration of iron (see Figure 6).

During the first few minutes of the reaction, color increases following a first-order kinetic coupled with phenol removal, but this process is so fast that it cannot be analyzed in depth. However, the color formed during this time decreases slowly after peaking, and if the reaction conditions are not carefully controlled, it remains after the oxidation treatment. It is believed that this color-decreasing part of the reaction is coupled with the oxidation of quinone-type compounds, and after several attempts it has been fitted to a pseudo-second-order kinetic, shown in Figure 5, which is in agreement with other experimental studies of the degradation of intermediates (30).

The ordinate at origin calculated by extrapolating the linear part of the curve gives the maximum color observable (A_0), corresponding to the equivalent concentration of the reaction intermediates at the beginning of the reaction. These maximum absorbance figures should be proportional to the total amount of phenol in the solution, and are, therefore, plotted against the initial concentration, fitting an almost perfect linear relationship (see Figure C, Supporting Information) described by eq 5:

$$A_0 = \epsilon C_{\text{PhOH}} \quad (5)$$

where $\epsilon = 1300 \text{ AU/mol PhOH}$ at the experimental conditions tested in this work.

The kinetics of color removal follow the pseudo-second order approach, while the concentration of intermediates is high enough. This is clearly observable through the results obtained at the lowest phenol concentration, 10 mg/L, for which the color remains constant at the lowest level after 5 minutes of reaction. This discrepancy means that color only fits the second-order approach while quinone-type compounds are present in solution.

Effect of Iron Catalyst Dosage. Catalyst concentration increases the oxidation rate because iron activates the hydrogen peroxide to form hydroxyl radicals. Consequently, color formation is also promoted by higher iron concentration in the solution (see Figure D, Supporting Information). As

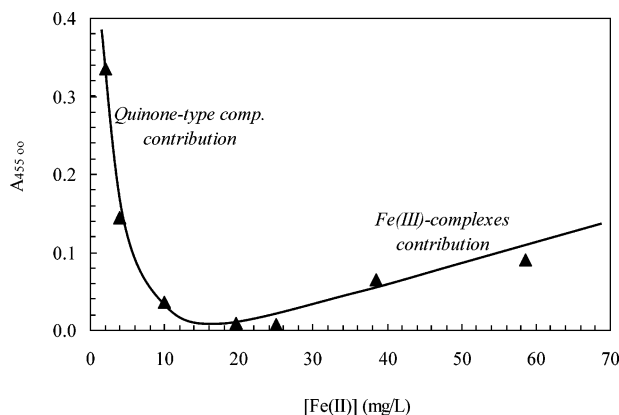


FIGURE 6. Color (A_{455}) of the phenolic solution after long reaction times as a function of initial iron(II) concentration.

explained above, the catalyst speeds up the degradation of phenol to quinone-type compounds and, consequently, increases the rate of color formation. When iron concentration in the solution is increased the rate of formation of colored compounds is also increased.

However, the effect of iron on the fading rate of water is not so clear. This can be better understood if one analyzes the residual color observed after long reaction times (Figure 6). An opposite tendency is observed for the effect of this variable on the final color. At low concentrations of iron, the solution has a high final coloration because intermediate compounds are not fully oxidized due to the poor reacting conditions. However with higher amounts of iron, the final color tends to increase from a minimum at around 20 mg Fe (II)/L. This behavior is due to the fact that iron reacts with hydrogen peroxide to produce free radicals and ferric ions, but these ions are extremely labile and can, therefore, react with almost any organic substrate present in water to form metal complexes. These complexes are colored species that persist throughout the process and generate more color in the oxidized water by the erratic tendency of the color-curve tails (These maximum absorbance figures should be proportional to the total amount of phenol in the solution, and are, therefore, plotted against the initial concentration, fitting an almost perfect linear relationship (see Figure D, Supporting Information).

To explain quantitatively the effect of iron on kinetics, the residual color experimentally measured—that reported in Figure 6 by a solid tendency curve—is split into contributions. The first is time-dependent and corresponds to quinone-type compounds. Its final level (residual color) shows a negative slope with iron concentration, and it is depicted in Figure 6 as following an hyperbolic relationship with iron concentration. The second contribution to the final color, denoted by a straight branch with positive slope, is only dependent on and proportional to the total iron concentration in the solution.

The temporal data on the color contribution of quinone-type compounds (A_Q) is calculated from experimentally measured values of solution color but with the contribution of the iron compound (A_{Fe}) given by the straight line in Figure 6 subtracted. Working in this way, color (A_Q) curves are almost overlapped and follows a similar path with slight differences between them. So slope of the second-order plot ($1/A_Q$ vs time) corresponding to the degradation of these compounds is slightly dependent on iron concentration (see Figure E, Supporting Information). This step (water fading) is mainly associated with the ring-opening reaction, and it can be concluded that this reaction progresses without a clear effect of the catalyst.

From these results, it is also concluded that the formation of metallic complexes between quinone-type compounds

and iron(III) stabilizes the aromatic structure, giving rise to a slower rate for the ring-opening reaction. Consequently, a higher concentration of iron does not imply a proportionally faster decolorization kinetic because the higher concentration of hydroxyl radicals is balanced by the chemical stabilization of the quinoidal intermediates. These complexes reduce the rate of iron(II) regeneration from iron(III), and consequently, the amount of free radicals (which should be proportional to iron(II) if the hydrogen peroxide concentration is assumed to be constant) reach a minimum when the concentration of quinone-type compounds is at its maximum (maximum of color). This fact would clearly explain the sudden cessation of phenol removal reported in Figure 1 when the maximum color is reached (at around 3 min). This behavior of Fenton reagent is very important in terms of oxidant efficiency because higher oxidation rates are always achieved with higher doses of catalyst, but the self-decomposition of hydrogen peroxide is also promoted, with no net increase in quinoidal-type compound removal. For practical design purposes, attention should be focused on introducing operational improvements in this way.

Supporting Information Available

Five figures with more detail about our results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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