Changes on dissolved oxygen in phenolic wastewaters during the oxidation by Fenton reagent

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Abstract. When dihydroxylated benzenes are oxidized, during the initial minutes there is an elevated consumption of dissolved oxygen (DO), achieving a minimum value. Next, DO increases following second order kinetics, whose reaction rates depend on the nature of the compounds. In this stage, occurs the catalyst regeneration that releases oxygen, being possible to establish a relation-ship between the rate of OD formation, \( k_{DO} \) (L\(^2\)/mg H\(_2\)O min \(^{-1}\)) and the iron regeneration. The OD release is greater during the oxidation of hydroquinone (k_{DO}=0.32) than catechol (k_{DO}=0.24), because the ortho-substituted benzenes may form organometallic complexes that act as chelator agents.

For resorcinol the OD formation is very slow (k_{DO}=0.04) because may form supramolecular structures with ferric ions impeding its regeneration. By the turbidity of the water, it has quantified the amount of iron involved in the formation of metal-complexes. At the maximum turbidity, in the case of hydroquinone all dissolved iron is as Fe\(^{3+}\). However, for catechol, 4% of catalyst is as Fe\(^{3+}\) and for resorcinol, 53%.

Keywords: dihydroxylated benzenes, dissolved oxygen, iron regeneration, iron complexes, turbidity

1. Introduction

Turbidity of phenolic solutions oxidized using the Fenton technology is affected by the iron species added as catalyst (Villota et al., 2016b; Villota et al., 2015). Thus, experiments performed on the oxidation of different dihydroxylated benzene compounds have established a relationship between the turbidity generated and the position of the hydroxyl substituents in the benzene ring (Villota et al., 2016a). Turbidity changes are also associated with possible reactions between iron species and organic contaminants (Villota et al., 2014).

When applying the Fenton reagent treatment, a cycle of iron catalyst regeneration takes place in parallel to the degradation process of the organic load. The approach consists of analyzing the oxygen released into the water when ferrous ions react with hydrogen peroxide. In this manner, the different stages of the Fenton reaction mechanism that produce oxygen are studied. Reactions are classified according to the process, whether oxygen is formed with the participation of ferric ion (Eqs. 3-5) or oxidizing radicals (Eqs. 6-14). The latter are produced by the main reaction between oxygen peroxide and ferrous ion (Eq. 1-2).

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO} + \text{OH}^- \\
\text{H}_2\text{O}_2 + \text{HO}^* & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
\text{Fe}^{2+} + \text{H}_2\text{O} & \leftrightarrow \text{FeOH}^{2+} + \text{H}^+ \\
\text{Fe}^{3+} + \text{2H}_2\text{O} & \leftrightarrow \text{Fe(OH)}_2^{+} + \text{2H}^+ \\
2\text{Fe}^{3+} + 2\text{H}_2\text{O} & \leftrightarrow [\text{Fe}_2(\text{OH})_2]^{4+} + 2\text{H}^+ \\
\text{Fe}^{3+} + \text{HO}^* & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \\
\text{Fe}^{3+} + \text{O}_2^{*-} & \rightarrow \text{Fe}^{2+} + \text{O}_2 \\
\text{Fe}^{2+} + \text{HO}^* & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{OH}^* + \text{O}_2^{*-} & \rightarrow \text{OH}^- + \text{O}_2 \\
\text{OH}^* + \text{HO}_2^{*-} & \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{HO}_2^{*} + \text{HO}_2^{*} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2^{*} + \text{O}_2^{*-} & \rightarrow \text{HO}_2^- + \text{O}_2 \\
\text{O}_2^{*} + \text{O}_2^{*-} & \rightarrow \text{O}_2 + \text{HO}_2^- \\
\text{HO}_2^{*} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^* 
\end{align*}
\]

Studies of phenol oxidation show that when phenol degrades (Devlin and Harris, 1984), organic matter may interact with iron ions in solution forming organometallic complexes (Yamahara et al., 2002). These species would consist of aromatic rings with substituents in ortho position linked to the ferric ions, that would bring in color and turbidity to the wastewater treated (Villota et al., 2016c; Mijangos et al., 2006) increasing its toxicity (Zazo et al., 2007; De Luis et al., 2001). Along these lines, there exist bibliography on the interactions between meta-substituted benzene rings and ferric ions, albeit their configuration is unknown (Habicht and Mäeorg, 2014; Lam et al., 2005). Moreover, when the byproducts of oxidation react, they...
could form large size structures. Thus, para-substituted rings in their dihydroxylated and quinoidal forms interact and yield charge transfer complexes such as quinhydriones (Song et al., 2009). Hence, polar carboxylic acids such as muconic acid (Rodríguez et al., 2009; Rodríguez et al., 2007) would establish hydrogen bonds with the benzene rings that contain meta-substituted groups generating supramolecular structures (Villota et al., 2016a; Rodríguez et al., 2008).

2. Materials and methods

2.1. Reaction system

The experimental assays utilizing Fenton Technology were carried out with 500 mL of aqueous solutions of catechol, hydroquinone and resorcinol (Panreac, 99%) with an initial concentration, \( C_0 =100 \text{ mg/L} \) and iron catalyst, added as ferrous ions (FeSO\(_4\) 2H\(_2\)O, Panreac 80%). The reaction mixture was homogenized with a stirrer at 500 rpm. Acidity was adjusted at pH=3.0 by dosing NaOH or HCl 0.2M (Probus, 99.9%). Temperature was controlled at \( T = 25.0^\circ \text{C} \) using a cryo-thermostat bath of 1150 watts (Selecta Frigiterm-10), pumping water through a cooling sheath. Oxidant (H\(_2\)O\(_2\), Foret 30%) was added at varying molar ratios over the initial pollutant in the wastewater. Treated samples were stored for five days to be analyzed at steady state.

2.2. Analytical methods

Solution turbidity (NTU) was measured with a turbidimeter (2100Qis Hach). Dissolved Oxygen concentration (DO, mg/L) was examined with a multiparameter (WTW Multi 304i). Iron concentration was analyzed by colorimetric method, using 1,10-phenanthroline at 510 nm (Fortune and Mellon, 1938), which allows distinction of total iron (Fe, mg/L), ferrous (Fe\(^{2+}\), mg/L) and ferric ions (Fe\(^{3+}\), mg/L).

3. Results and discussion

3.1. Turbidity changes during the degradation of organic pollutants

Substances considered in the study were phenol and its direct oxidation intermediates, such as isomers of hydroxyl di-substituted benzene rings in position ortho (catechol), meta (resorcinol) and para (hydroquinone). Publications on the oxidation mechanism of phenol show that the principal degradation pathways that cause turbidity take place along the hydroxyl meta-substituted intermediates that eventually lead to the formation of muconic acid (Rodriguez et al., 2009). Based on these results, the reactions were carried out at oxidant doses H\(_2\)O\(_2\)=4.0 mM, which correspond to the theoretical molar ratio leading to the degradation stage in the oxidation of phenol that ends in muconic acid (Villota et al., 2014).

![Figure 1. Changes of turbidity during the oxidation of phenolic compounds by Fenton reagent. Experimental conditions: \( C_0=100.0 \text{ mg/L} \); pH=3.0; \( \text{H}_2\text{O}_2=4.0 \text{ mM} \); Fe=20.0 \text{ mg/L} \); \( T = 25.0^\circ \text{C} \)

Figure 1 shows changes of turbidity with time during oxidation of dihydroxylated phenols under similar test conditions. The position of the hydroxyl substituents in the benzene ring produces a change in the evolution of turbidity along time. Thus, when a meta substituted benzene rings (resorcinol) is oxidized; a large level of turbidity is produced. In this case, the turbidity is mostly formed in the initial 30 minutes until a maximum (NTU\(_\text{max}=36.3\)) and slowly decreases until attaining steady state (NTU\(_\text{ss}=9.4\)).

In the initial five minutes of oxidation, solutions of catechol and hydroquinone show a rapid increase in turbidity until attaining a maximum. In the case of hydroquinone, NTU\(_\text{max}=12.0\), and for catechol NTU\(_\text{max}=24.7\). This difference suggests that the degradation of benzene rings with hydroxyl substituents placed in ortho position generates higher turbidity than the para-substituted. Once the maximum has been reached, turbidity rapidly diminishes at higher rate than for resorcinol. Besides, after 120 minutes of reaction, turbidity arrives at a steady state which corresponds for catechol to NTU\(_\text{ss}=5.6\), and for hydroquinone NTU\(_\text{ss}=0.9\).

3.2. Evolution of dissolved oxygen (DO) during the oxidation

The effect of iron species was characterized to analyze the causes of turbidity generated by oxidized solutions as a function of the hydroxyl-substituent position in the benzene ring. Then, the evolution of DO during the oxidation of phenolic intermediates was measured under the operating conditions shown in Figure 1.

Figure 2 reveals the evolution of DO during the oxidation of several degradation intermediates. DO exhibits a drastic decrease until it reaches a minimum close to 0 mg/L in the initial five minutes. This behavior is similar for all contaminants. Thereafter, DO increases following a second order kinetic (Figure 3) until it reaches steady state. In this second stage of the oxidation, DO production show a clear dependence on the species oxidized.

When the reactions that compose the regeneration cycle of iron (Eqs. 1-14) are examined, it can be surmised that the evolution of DO during oxidation could point to the nature of the iron species in solution. Hence, in its initial stage, the Fenton reaction takes place when ferrous ions are
oxidized to ferric (Eqs. 1-2) thus producing highly oxidizing radicals that would degrade the contaminant. This reaction is very fast and generates a highly oxidizing environment that would require a large consumption of oxidizing species. Considering the trends in Figure 1 at the initial reaction stage, a correspondence between the reactions described in Eqs. 1-2 and the fast consumption of DO during the first five minutes of reaction could be established. Thus, DO is consumed through oxidation reaction with organic matter.

Once all DO has almost been consumed, that would correspond to the maximum formation of ferric ions, a second stage involving catalyst regeneration would take place whereby ferric ions are converted into ferrous, reactivating the oxidation (Eq. 6). This stage comprises a complex system of radical reactions that occur in parallel (Eqs. 3-8) and implies oxygen release (Eqs. 6-7), where the DO increase was mainly due to slow consumption of hydroxyl radicals for oxidation process and rapid production of oxygen by the breakdown of peroxides catalysed by ferric ion (Kavita and Palanivelu, 2004). Kinetics in Figure 2 indicates that this second stage takes place when DO increases, that is, after the initial five minutes of reaction until reaching steady state.

Figure 2. Changes of dissolved oxygen (OD) during the oxidation of phenolic compounds by Fenton reagent. Experimental conditions: \( C_0=100.0 \text{ mg/L}; \) pH=3.0; \( H_2O_2=4.0 \text{ mM}; \) Fe=20.0 mg/L; T=25.0ºC.

Also important is the oxygen release through the reactions with radicals (Eqs. 9-12). However, the contaminant treatment is carried out at conditions involving oxidant shortage and catalyst surplus. Then, it is reasonable to assume that the oxidizing radicals generated would be consumed in the oxidation of contaminant matter. Therefore, inter-radical reactions that may generate oxygen would have a minor contribution when compared with the oxygen forming reactions of the iron regeneration cycle. Consequently, it can be surmised here that the kinetic pathways that correspond to the formation of DO as shown in Figure 2 would be determined by the reaction rates established by Eqs. 6-7.

Figure 3 reveals the second order kinetic profiles for the formation of DO in the oxidation of the phenolic compounds. The formation of DO follows the evolution established by Eq. 15, whereby \( k_{DO} (L^2/\text{mg}^2 \text{ min}) \) is the kinetic constant of DO generation and \( DO_0 \) the intercept (mg/L). The kinetic parameters for each contaminant are shown in Table 2.

\[
DO^2 = k_{DO} \cdot DO_0^2 \tag{15}
\]

As well, the iron regeneration rate in hydroquinone oxidation is greater than in catechol. The reason could be found in the interaction that ferric ions establish with ortho substituted benzene compounds producing metallic complexes (Yamahara et al., 2002). These interactions would hinder the iron regeneration cycle. Moreover, ferric ions and organometallic complexes in solution are colored and bring turbidity. This would explain the production of greater turbidity when catechol is decomposed than when hydroquinone is degraded.

The case of resorcinol is noteworthy as, in the oxidation of solutions; high turbidity is produced. To explain this, the kinetic constants of DO generation are considered. They are used to calculate the overall constant in resorcinol degradation which has around \( k_{DO}=0.041 \text{ (L}^2/\text{mg}^2 \text{ min)} \). This value indicates that the regeneration reaction rate from ferric to ferrous ions would be very small when compared with the kinetic constants for DO formation in the oxidation of ortho and para-substituted benzene compounds. Hence, iron in solution would mostly be present as ferric ion promoting high turbidity levels.

3.3. Effect of catalyst dosage

To confirm this hypothesis, the concentration of iron ions in their ferric and ferrous forms were analyzed at the maximum levels of turbidity encountered after the oxidation of phenolic solutions. To do this, several tests were performed in which solutions at concentration \( C_0=100 \text{ mg/L}, \) prepared with dihydroxylated isomers, were oxidized. The treatment was carried out at constant oxidant dose, \( H_2O_2=4.0 \text{ mM}, \) and varying the catalyst concentration from \( Fe_3^{+2}=0 \) to 50 mg/L.

Figure 4 shows the catalyst dose, expressed as ferrous ion concentration, \( (Fe^{+2}, \text{ mg/L}) \), versus ferrous ion analyzed at the point of maximum turbidity \( (Fe^{+2}_{max}, \text{ mg/L}) \). Ferrous ion concentration, \( (Fe^{+2}_{max}, \text{ mg/L}) \), at maximum turbidity
exhibits a linear dependence on the catalyst dose, \((\text{Fe}_o^{2+}, \text{mg/L})\), as defined by Eq. 16. The relation between these two variables is given by the dimensionless parameter \(\varepsilon_{\text{max}}\). The data also reveals that the relation of ferrous ions established by \(\varepsilon_{\text{max}}\) depends on the position of the hydroxyl groups in the aromatic ring. Table 2 shows the calculated parameters.

![Graph showing the concentration of dissolved ferrous ions when oxidized samples show maximum turbidity](link_to_graph)

**Figure 4.** Concentration of dissolved ferrous ions when oxidized samples show maximum turbidity. Experimental conditions: \(C_o=100.0 \text{ mg/L} ; \) pH=3.0; \(H_2O_2=4.0 \text{ mM} ; \) \(T=25.0\text{oC}\).

The value of \(\varepsilon_{\text{max}}\) for hydroquinone solutions reveals that when they are oxidized, ferrous ion concentrations show almost no alteration along the treatment and remain constant until maximum turbidity. This result indicates that no catalyst is lost in the oxidation by complexing reactions between iron and para substituted aromatic rings. As well, iron at the point of maximum turbidity would be present as ferrous ion.

In the oxidation of catechol solutions, the concentration of ferrous ions at maximum turbidity represents 96% of the catalyst initial load. That is, 4% of the initial ferrous ions is present as ferric. The latter species brings in color and turbidity. Alternatively, they could interact with the ortho substituted benzene rings in solution, leading to the formation of metallic complexes that would also enhance both parameters.

\[
\text{Fe}^{2+}_{\text{max}} = \varepsilon_{\text{max}} \text{Fe}_o^{2+}
\]

(16)

**Table 2.** Empirical parameters estimated during the oxidation of dihydroxylated phenolic compounds. Experimental conditions: \(C_o=100.0 \text{ mg/L} ; \) pH=3.0; \(H_2O_2=4.0 \text{ mM} ; \) \(\text{Fe}=20.0 \text{ mg/L} ; \) \(T=25.0\text{oC}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>DO</th>
<th>(k_{\text{DO}})</th>
<th>(r^2)</th>
<th>(\varepsilon_{\text{max}})</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>1.95</td>
<td>0.3246</td>
<td>0.992</td>
<td>1.02</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>5</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Catechol</td>
<td>1.78</td>
<td>0.2439</td>
<td>0.995</td>
<td>0.96</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td>4</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.57</td>
<td>0.0407</td>
<td>0.886</td>
<td>0.47</td>
<td>0.971</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>1</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Finally, oxidized solutions of resorcinol display a ferrous ion decrease down to 47% of the initial value at the point of maximum turbidity. This implies that 53% of the initial ferrous ion concentration is present as ferric, which is much larger than in the case of catechol. As a consequence, resorcinol oxidation brings in greater color and turbidity. Nevertheless, possible interactions between meta-substituted benzene rings and ferric ions, which would explicate the high turbidity produced, ought to be considered as well.

4. Conclusions

The highest turbidity is achieved when oxidizing resorcinol (NTU_{max}=48.1), followed by catechol (NTU_{max}=24.6) and hydroquinone (NTU_{max}=12.0). In the beginning, there is a high consumption of dissolved oxygen (DO), attributed to the oxidation of \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\), generating oxidizing radicals. Thereafter, DO increases following a second order kinetic depending on the specific contaminant. In this stage, iron regeneration would occur and oxygen would release.

Hence, the kinetic constant \(k_{\text{DO}}\) \((L^2/mg\text{min})\) could be considered an indicator of the regeneration rate of iron species. Ferrous regeneration is faster for hydroquinone \((k_{\text{DO}}=0.32)\) than for catechol \((k_{\text{DO}}=0.24)\). This can be caused by the formation of organometallic complexes between \(\text{Fe}^{2+}\) and ortho substituted aromatic rings, which would slow down the iron regeneration cycle. These complexes bring in high turbidity in the oxidation of catechol.

This fact in the case of resorcinol can be attributed to a much smaller value of the oxygen formation rate \((k_{\text{DO}}=0.041)\) than for catechol and hydroquinone, inferring that iron regeneration proceeds at a much slower pace and iron remain in \(\text{Fe}^{3+}\) state. When turbidity reaches its maximum, \(\text{Fe}^{2+}\) linearly enlarges with increasing catalyst initial dose. This relation is established by the dimensionless parameter, \(\varepsilon_{\text{max}}\), that depends on the hydroxyl groups position in the aromatic ring. In the oxidation of hydroquinone \(\varepsilon_{\text{max}}=1.0\), meaning that the catalyst concentration supplied is as \(\text{Fe}^{2+}\). For catechol, \(\varepsilon_{\text{max}}=0.96\), implying that 4% if the iron is as \(\text{Fe}^{3+}\) which may form metallic complexes and increase turbidity. In the case of resorcinol, \(\varepsilon_{\text{max}}=0.47\), 53% of iron exists as \(\text{Fe}^{3+}\) and turbidity is the greatest.

References


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