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Changes of turbidity during the oxidation of dihydroxylated benzenes by Fenton reagent and effect on dissolved oxygen

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ABSTRACT

The study seeks to relate turbidity with the nature of dihydroxylated benzene compounds. When these compounds are oxidized, maximum turbidity is 48 NTU for resorcinol, 25 NTU for catechol and 12 NTU for hydroquinone. During the initial minutes of the pollutants oxidation, there is an elevated consumption of dissolved oxygen (DO), achieving a minimum value. At this time, Fe^{2+} is oxidized to Fe^{3+}, being possible associate the maximum concentration of Fe^{3+} with the minimum DO. Next, DO increases following minus first-order kinetics, whose reaction rates depend on the benzene ring position where the hydroxyl groups are substituted. In this stage, occurs processes that involve the radicals participation and the catalyst regeneration that release oxygen, being possible to establish a relationship between the rate of DO formation, k_{DO} (L^2/mg^2 min) and these phenomena. The DO release is greater during the oxidation of hydroquinone, k_{DO} 0.16, than catechol, k_{DO} 0.12, because the ortho-substituted benzenes may form organometallic complexes that act as chelator agents that prevent the iron regeneration. For resorcinol, the DO formation is very slow, k_{DO} 0.02, because this may form supramolecular structures with ferric ions impeding its regeneration. Analyzing the maximum turbidity point, when hydroquinone is oxidized, all iron is present as Fe^{2+}. For catechol, the 4% of the catalyst is present as Fe^{3+} that can form organometallic complexes. In the case of resorcinol, the 53% of iron is as Fe^{3+} which would bring in even greater turbidity, proving that 0.15 mg Fe^{3+}/mg $C_6H_6O_2$ generates the maximum turbidity. At the steady state, for hydroquinone, all iron is regenerated as Fe^{2+} and for catechol, the 97%. However for resorcinol, the 28% of iron remains as Fe^{3+} that can form structures with the organic contaminants further increasing solution turbidity.

Keywords: Catechol; Dissolved oxygen; Fenton reagent; Hydroquinone; Resorcinol; Turbidity

1. Introduction

Turbidity of phenolic solutions oxidized using the Fenton technology [1] is affected by the iron species added as catalyst [2]. 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. Turbidity changes are also associated with possible reactions between iron species and organic contaminants.

When applying the Fenton reagent treatment, a cycle of iron catalyst regeneration takes place in parallel to the degradation process of the organic load [3]. 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

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oxygen are studied. Reactions are classified according to the process, whether oxygen is formed with the participation of ferric ion (Eqs. (2)–(4)) or oxidizing radicals (Eqs. (5)–(13)). The latter are produced by the main reaction between oxygen peroxide and ferrous ion (Eq. (1)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

- Processes of species formation:

$$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+ \quad (2)$$

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^{\ +} + 2H^+ \quad (3)$$

$$2Fe^{3+} + 2H_2O \leftrightarrow \left|Fe_2(OH)_2\right|^{4+} + 2H^+ \quad (4)$$

- Processes with ferric ion participation:

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2 \quad (6)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (7)$$

- Processes with radicals participation:

$${}^{\bullet}OH + O_2^{\bullet -} \rightarrow OH^- + O_2 \quad (8)$$

$${}^{\bullet}OH + HO_2^{\bullet -} \rightarrow H_2O + O_2 \quad (9)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (10)$$

$$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^{\ -} + O_2 \quad (11)$$

$$O_2^{\bullet} + O_2^{\bullet -} \rightarrow O_2 + HO_2^{\ -} \quad (12)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow H_2O + O_2 + {}^{\bullet}OH \quad (13)$$

Studies of phenol oxidation show that when phenol degrades [4,5] organic matter may interact with iron ions in solution [6,7], forming organometallic complexes. 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 water treated [8,9] increasing its toxicity [10–12]. Along these lines, there exist bibliography on the interactions between meta-substituted benzene rings and ferric ions, albeit their configuration is unknown [13,14]. Moreover, when the by-products 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 quinhydrones [15]. Hence, polar carboxylic acids such as muconic acid [16,17] would establish hydrogen bonds with the benzene rings that contain meta-substituted groups generating supramolecular structures [18].

2. Materials and methods

2.1. Reaction system

The experimental assays utilizing Fenton Technology were carried out with 500 mL of aqueous solutions with an initial concentration of pollutant, C_o 100 mg/L (catechol, Panreac 99.9%; hydroquinone, Panreac 99.9% and resorcinol, Panreac 99.9%), and iron catalyst, added as ferrous ions Fe^{2+} 0–60.0 mg/L ($FeSO_4$ $2H_2O$, 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 0.2 M (Probus 99.9%) with an automatic burette (Dosimat 665-Metrohm). Temperature was controlled at T 25.0°C using a cryothermostat bath of 1,150 W (Selecta Frigiterm-10), pumping water through a cooling sheath. Oxidant (H_2O_2, Foret 30%) was added at varying in the water H_2O_2 0–15.0 mmol/L. Treated samples were stored for 5 d to be analyzed at steady state.

2.2. Analytical methods

Dissolved oxygen (DO) concentration (mg/L) was examined with a multiparameter (WTW Multi 304i). Solution turbidity (NTU) was measured with a turbidimeter (2100Qis Hach). Iron concentration was analyzed by colorimetric method, using 1,10-phenanthroline at 510 nm, which allows distinction of total iron (Fe, mg/L), initial 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 isomers of hydroxyl disubstituted benzene rings in position ortho (catechol), meta (resorcinol) and para (hydroquinone). Publications on the oxidation mechanism of phenol shows that the principal degradation pathways that cause turbidity take place along the hydroxyl meta-substituted intermediates, which eventually lead to the formation of muconic acid. Based on these results, the reactions were carried out at oxidant doses H_2O_2 4.0 mmol/L, which correspond to the theoretical molar ratio leading to the degradation stage in the oxidation of phenol that ends in muconic acid [19].

Fig. 1 shows changes of turbidity with time during oxidation of the isomers under similar test conditions. During the oxidation, 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 ring (resorcinol) is oxidized, a large level of turbidity is produced. In this case, the turbidity is mostly formed in the initial 30 min until a maximum, 36.3 NTU, and slowly decreases until attaining steady state, 9.4 NTU. In the initial 5 min of oxidation, solutions of catechol and hydroquinone show

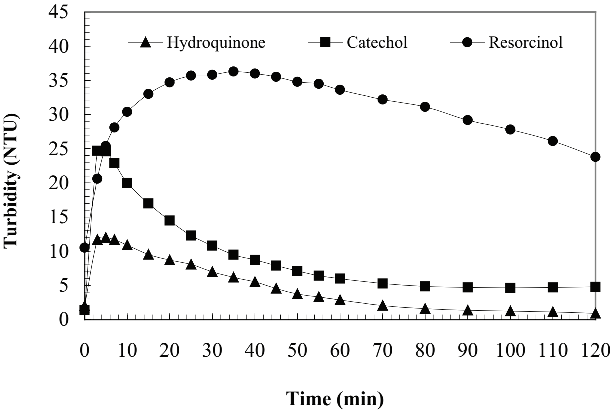

Fig. 1. Changes of turbidity during the oxidation of dihydroxylated benzenes by Fenton reagent. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM, Fe 20.0 mg/L and T 25.0°C.

a rapid increase in turbidity until attaining a maximum: in the case of hydroquinone, 12 NTU and for catechol, 25 NTU. This difference suggests that the degradation of benzene rings with hydroxyl substituents placed in ortho position generates higher turbidity than those para substituted. Once the maximum has been reached, turbidity rapidly diminishes at higher rate than for resorcinol. Besides, after 120 min of reaction, turbidity arrives at a steady state which corresponds for catechol to 5.6 NTU, and for hydroquinone 0.9 NTU.

3.2. Evolution of 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-substituted position in the benzene ring. Then, the evolution of DO during the oxidation of benzene isomers was measured under the operating conditions shown in Fig. 1. Fig. 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 5 min. This behavior is similar for all contaminants. Thereafter, DO increases following a minus first-order kinetic (Fig. 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)–(13)) 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 (Eq. (1)) 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 Fig. 1 at the initial reaction stage, a correspondence between the reaction described in Eq. (1) and the fast consumption of DO during the first 5 min 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. This stage comprises a complex system of radical reactions that occur in parallel (Eqs. (2)–(7)) and implies oxygen release (Eqs. (5) and (6)). Kinetics in Fig. 2 indicates that this second stage takes place when DO increases, that is, after the initial 5 min of reaction until reaching steady state.

Also important is the oxygen release through the reactions with radicals (Eqs. (8)–(11)). 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 Fig. 2 would be determined by the reaction rates established by Eqs. (5) and (6).

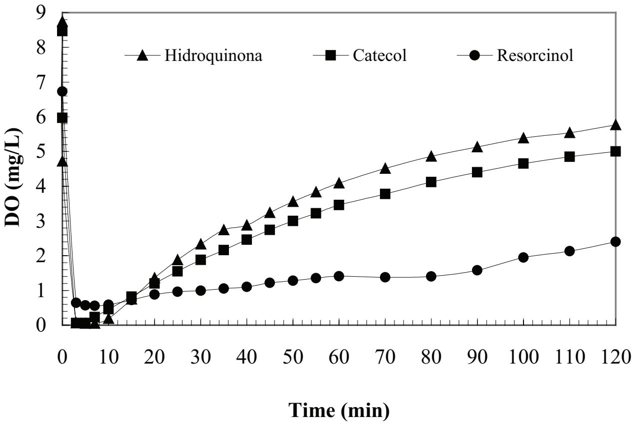

Fig. 2. Changes of dissolved oxygen (DO) during the oxidation of dihydroxylated benzenes by Fenton reagent. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM, Fe 20.0 mg/L and T 25.0°C.

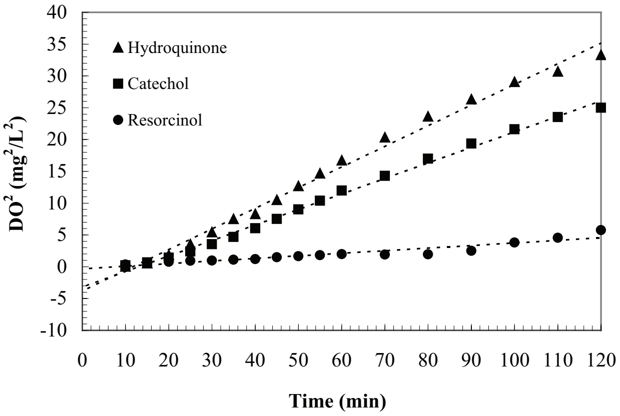

Fig. 3. Kinetic model of dissolved oxygen formation during the oxidation of dihydroxylated benzenes. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM, Fe 20.0 mg/L and T 25.0°C.

Fig. 3 reveals the minus first-order kinetics profiles for the formation of DO in the oxidation of the benzene compounds. The formation of DO follows the evolution established by Eq. (14), whereby k_{DO} (L^2/mg^2 min) is the kinetic constant of DO generation and DO_o the intercept (mg/L). The kinetic parameters for each contaminant are shown in Table 1.

These calculations facilitate the prediction of DO generation in the oxidation of dihydroxylated benzene compounds. However, the model deviates when applied to the phenol oxidation reaction. Based on the hypotheses proposed, the values calculated for the kinetic constant of DO generation, k_{DO} (L^2/mg^2 min), would be a kinetic parameter indicating the regeneration rate from ferric to ferrous ions.

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 [9]. 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 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} 0.04 (L^2/mg^2 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.

$$\mathrm{DO}^{(1-n)} = \mathrm{DO}_o^{(1-n)} + (n-1)\,k_{\mathrm{DO}}\,t \tag{14}$$

3.3. *Effect of catalyst dosage*

To confirm this hypothesis, the concentration of iron ions in their ferric and ferrous forms was analyzed at the maximum levels of turbidity encountered after the oxidation of solutions. To do this, several tests were performed in which solutions at concentration C_o 100 mg/L, prepared with dihydroxylated isomers, were oxidized. The treatment was carried out at constant oxidant dose, H_2O_2 4.0 mmol/L, and varying the catalyst concentration from Fe_o^{2+} 0 to 50 mg/L. Fig. 4 shows the catalyst dose, expressed as ferrous ion concentration, (Fe_o^{2+}, mg/L), vs. ferrous ion analyzed at the point of maximum turbidity (Fe_{max}^{2+}, mg/L).

Fig. 4 shows that ferrous ion concentration, (Fe_{max}^{2+}, mg/L), at maximum turbidity exhibits a linear dependence on the catalyst dose, (Fe_o^{2+}, mg/L), as defined by Eq. (15). The relation between these two variables is given by the dimensionless parameter ε_{max}. The data also reveal that the relation of ferrous ions established by ε_{max} depends on the position of the hydroxyl groups in the aromatic ring. Table 2 shows the calculated parameters.

$$\mathrm{Fe}^{2+}_{\mathrm{max}} = \varepsilon_{\mathrm{max}}\,\mathrm{Fe}^{2+}_{o} \tag{15}$$

The value of ε_{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.

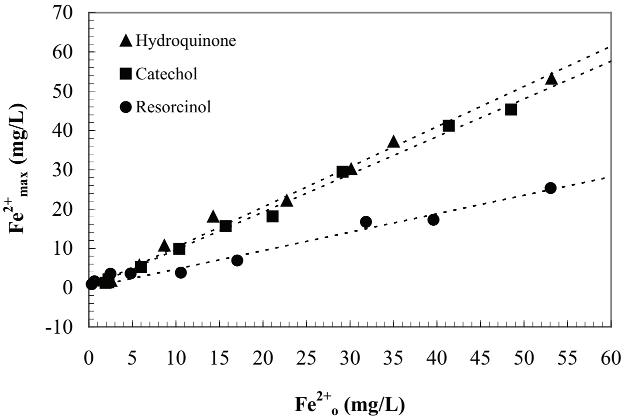

Fig. 4. Concentration of dissolved ferrous ions when oxidized samples show maximum turbidity. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM and T 25.0°C.

Table 1
Kinetic parameters estimated for DO formation (mg/L) during the dihydroxylated benzenes oxidation

Compound	DO_o (mg/L)	k_{DO}[$L^2/(mg^2$ min)]	r^2
Hydroquinone	1.9542	0.1623	0.9925
Catechol	1.7877	0.1219	0.9954
Resorcinol	0.5745	0.0203	0.8861

Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM, Fe 20.0 mg/L and T 25.0°C

Table 2
Empirical parameters estimated during the oxidation of dihydroxylated benzenes

Compound	ε_{max}	r^2	ε_{oo}	r^2
Hydroquinone	1.0	0.9910	0.964	0.9820
Catechol	0.96	0.9947	0.978	0.9904
Resorcinol	0.47	0.9717	0.726	0.9930

Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM and T 25.0°C.

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.

As a follow up, the relation between the initial concentration of ferrous ion (Fe_o^{2+}, mg/L) and its concentration when the oxidation reaction has reached steady state (Fe_{oo}^{2+}, mg/L) was tackled. Fig. 5 shows a linear dependence between these two parameters, established by the dimensionless factor, ε_{oo}, in Eq. (16). Table 2 includes the empirical values calculated.

This relation depends on the position of the substituted hydroxyl groups in the benzene rings. In the case of catechol and resorcinol, Fig. 5 exhibits their linear dependence. However, hydroquinone evidences a change in the slope that depends on the catalyst initial dose. Thus, at doses less than, $Fe_o^{2+} < 30$ mg/L, the correlation reveals a value close to one, (ε_{oo} 0.9640), which implies that iron is present as ferrous ions. However, at concentrations of catalyst greater than $Fe_o^{2+} > 30$ mg/L, the slope presents a significant decrease, ε_{oo} 0.2448.

This result suggests that since iron is presented both as ferrous and ferric, its regeneration cycle is incomplete. Hence, when hydroquinone solutions of concentration 100.0 mg/L are oxidized with 4.0 mmol/L of oxidant, a charge of oxidizing radicals is created capable of regenerating the catalyst if present under $Fe_o^{2+} < 30$ mg/L. At higher catalyst concentrations, the process takes place with an oxidant shortfall and some catalyst would remain in its oxidized state.

$$Fe^{+2}_{oo} = \varepsilon_{oo}\ Fe^{+2}_{o} \tag{16}$$

The oxidation of catechol solutions displays no significant variation between the initial concentration of ferrous ion and its concentration at steady state. In this case, part of the initial ferrous ions oxidizes to ferric and triggers turbidity and complexing reactions with the organic load. At steady state, however, these metallic complexes would have degraded to oxidation by-products, and ferric ions would have reduced to ferrous. This consideration suggests that when ortho-substituted benzene rings are oxidized, almost all the catalyst load employed would regenerate.

Resorcinol oxidation evidences that 28% of the initial concentration of catalyst is present as ferric ions at steady state. But when the oxidized water reaches its maximum turbidity, 53% of the initial iron is present as ferric. The steady state analysis reveals that only a fourth of the latter percentage remains in solution. These results indicate that in the oxidation of meta-substituted benzene, 28% of the initial catalyst load fails to be regenerated to ferrous ions. The failure to complete the iron regeneration cycle in all the operating range suggests the formation of structures with ferric ions that possess some stability and bring in significant turbidity.

3.4. Effect of iron species on the maximum turbidity formation

Fig. 6 shows maximum turbidity values (NTU_{max}) vs. the concentration of ferrous ions in solution (Fe_{max}^{2+}).

The oxidation of catechol and hydroquinone exhibits a linear correlation between the maximum turbidity and the concentration of ferrous ions. The ratio calculated for both contaminants is 0.06 (NTU L/mg Fe^{2+}). These results indicate that ferrous ions may generate turbidity but to a lower extent than ferric. The reason for this behavior is the low tendency of ferrous ions to form organometallic structures with ortho- and para-substituted benzene rings.

However, ferrous ions induce significant turbidity in resorcinol oxidation. Hence, maximum turbidity enlarges with increasing ferrous ion concentration until Fe_{max}^{2+} 15 mg/L, at which NTU_{max} 50 NTU. At ferrous ion greater than $Fe_{max}^{2+} > 20$ mg/L, the maximum turbidity starts decreasing to NTU_{max} 40 NTU. It is remarkable that the maximum concentration of ferrous ion in solution is Fe_{max}^{2+} 25 mg/L. This could correspond to the equilibrium factor between the iron

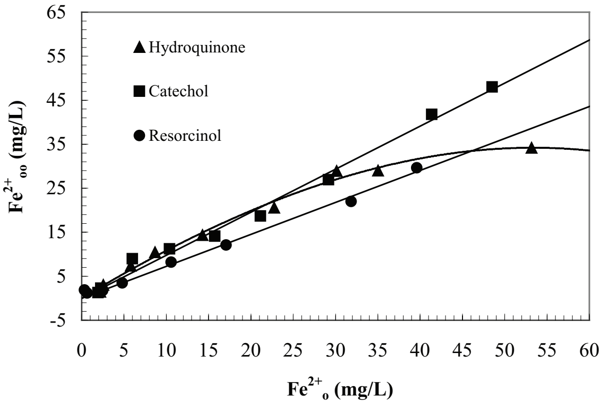

Fig. 5. Concentration of dissolved ferrous ions at steady state in relation to the catalyst dosage applied in the oxidation of dihydroxylated benzene rings. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM and T 25.0°C.

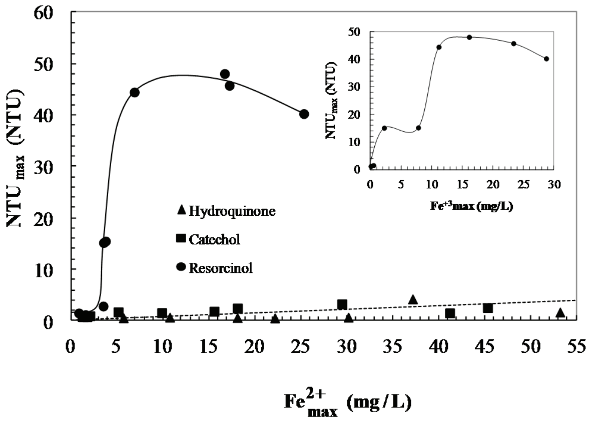

Fig. 6. Maximum turbidity vs. concentration of dissolved ferrous ions during the oxidation of dihydroxylated benzene rings. Small figure: Maximum turbidity vs. concentration of dissolved ferric ions during resorcinol oxidation. Experimental conditions: C_o 100.0 mg/L, pH 3.0, H_2O_2 4.0 mM and T 25.0°C.

species as established by the oxidant dose. Along these lines, when resorcinol is oxidized, the initial catalyst concentration undergoes a 50% speciation toward the formation of ferric ions. At the point of maximum turbidity, these ferric ions in solution could be precursors of supramolecular structures of large molecular weight and size capable of bringing in significant turbidity [20].

4. Conclusions

The highest turbidity is achieved when oxidizing resorcinol, 48 NTU, followed by catechol, 24.6 NTU and hydroquinone, 12.0 NTU. In the beginning, there is a high consumption of DO, generating oxidizing radicals, attributed to the oxidation of pollutants and Fe^{2+} to Fe^{3+}. The minimum DO would correspond to the maximum formation of Fe^{3+}. Thereafter, DO increases following a minus first-order kinetics depending on the specific contaminant. In this stage, iron regeneration would occur and oxygen would release. Hence, the kinetic constant k_{DO} (L^2/mg^2 min) could be considered as an indirect indicator of the regeneration rate of iron species.

Ferrous regeneration is faster for hydroquinone, k_{DO} 0.16 than for catechol, k_{DO} 0.12. This can be caused by the formation of organometallic complexes between Fe^{3+} 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_{DO} 0.02 than for catechol and hydroquinone, inferring that iron regeneration proceeds at a much slower pace and iron remain in Fe^{3+} state.

When turbidity reaches its maximum, Fe^{2+} linearly enlarges with increasing catalyst initial dose. This relation depends on the hydroxyl groups position in the aromatic ring. In the oxidation of hydroquinone and catechol, the catalyst concentration supplied is mainly as Fe^{2+}. In the case of resorcinol, 53% of iron exists as Fe^{3+} being higher turbidity.

Ferrous ions dosing and at steady state exhibit a linear correlation that depends on the position of the hydroxyl groups. For catechol, the iron is in Fe^{2+} form or that practically all is regenerated. For resorcinol, 28% of the catalyst remains as Fe^{3+} that can form supramolecular structures that impede its regeneration, producing high turbidity. About hydroquinone, when $Fe_o^{2+} < 30$ mg/L, the iron regeneration cycle is almost complete. However, if $Fe_o^{2+} > 30$ mg/L, there is a shortfall of oxidant, part of the catalyst cannot regenerate and remains in its oxidized state.

At the point of maximum turbidity formation, ferrous ion concentration linearly increases the turbidity. For catechol and hydroquinone, turbidity rises according to the ratio 0.06 (NTU L/mg Fe^{2+}). This suggests that Fe^{2+} brings in turbidity but at much lesser level than Fe^{3+}, because the former species cannot form intermetallic complexes with these contaminants. When resorcinol is oxidized, practically 50% of the catalyst is found as Fe^{3+} inducing high turbidity.

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