Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.966333

57 (2016) 431–439
January

Taylor & Francis
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Behavior of dihydroxybenzenes and gallic acid on the Fenton-based decolorization of dyes

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Received 25 May 2014; Accepted 12 September 2014

ABSTRACT

Dihydroxybenzenes (DHBs) are used as mediators to increase the degradation of recalcitrant organic pollutants by Fenton reaction. DHBs regenerate Fe^{2+} ions, resulting in the formation of OH radicals in a more intense and continuous manner than the classical Fenton reaction. The present work investigates the behavior of different DHBs and gallic acid (a trihydroxybenzene) on the decolorization of dye solutions by Fenton systems (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2). For the majority of DHBs and gallic acid, pro-oxidant properties were observed on the decolorization of methylene blue, chromotrope 2R, methyl orange, and phenol red. These properties were dependent on the hydroxyl position in the aromatic ring and were highly influenced by the structure and redox potential of the target pollutant. The dye decolorization by Fenton-like reaction (Fe^{3+}/H_2O_2) in the presence of 2,5-dihydroxybenzoic acid as mediator was more efficient than classical Fenton reaction. For example, Fe^{3+}/H_2O_2/2,5-dihydroxybenzoic acid system provided 60% of phenol red decolorization against 40% by Fe^{2+}/H_2O_2 after 60 min of reaction. DHBs and gallic acid increased the decolorization of dyes, requiring the highest H_2O_2 consumption. However, H_2O_2 consumption occurred even when the dye solutions were not extensively decolorized, suggesting that part of the generated OH radicals reacted with either DHBs, H_2O_2 or other reactive species in solution.

Keywords: Dye; Fenton reaction; Dihydroxybenzene; Iron; Hydrogen peroxide; Gallic acid

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1. Introduction

Dyes contained within industrial effluents are often highly persistent to biodegrade and must therefore be treated before discharge. Other conventional treatments such as activated carbon adsorption, coagulation, and reverse osmosis are not also effective for treatment of those dye pollutants. These treatments only transfer dye from liquid phase to solid adsorbent [1,2]. As a promising alternative, the Fenton reaction has been an effective method to treat a wide range of dyes and other organic pollutants in wastewater, because it is cost–effective, it presents low toxicity and it is easy to operate. Moreover, no energy input is necessary to activate hydrogen peroxide [3,4].

The Fenton reaction generates reactive species with high oxidation potential such as hydroxyl radical

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($^{\bullet}$OH) from hydrogen peroxide using Fe^{2+} as homogeneous catalyst (Eq. (1)). However, a number of drawbacks limit its widespread application including the accumulation of Fe^{3+}. The Fenton-like reaction uses Fe^{3+} as catalyst and it is considered as a slower reaction when compared to the classical Fenton reaction (with Fe^{2+}) and the former forms other radicals of lower redox potentials such as hydroperoxyl ($^{\bullet}O_2H$); Eq. (2)) [3–5]. The Fe^{2+} generated in the reaction 2 then converts another molecule of H_2O_2 to OH radical via reaction 1. However, the slower reaction is the rate-determining step of Fenton reaction. To degrade the pollutant quickly and effectively, the input of Fe^{2+} must be compared to that of H_2O_2.

$$\begin{aligned} &Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \\ &\quad k = 40 - 80\,\text{mol}^{-1}\,\text{ls}^{-1} \end{aligned} \tag{1}$$

$$\begin{aligned} &Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}O_2H + H^{+} \\ &\quad k = 9.1 \times 10^{-7}\,\text{mol}^{-1}\,\text{ls}^{-1} \end{aligned} \tag{2}$$

To enhance the formation of OH radicals via Fenton systems, Fe^{3+}-reducing dihydroxybenzenes (DHBs) have been evaluated as mediators in reactions designed to degrade recalcitrant compounds and contaminated wastewaters [6–12]. Recently, diluted wood extracts containing DHBs have increased azure B decolorization through Fenton-like reactions [13]. In a DHB-driven Fenton reaction, the OH radicals are formed at highest levels and for long periods of time due to the constant regeneration of Fe^{2+} ions by passing reaction 2 [6,7,14]. When regenerating Fe^{2+}, DHBs are oxidized in two steps. Initially, Fe^{3+} ions convert the DHB to semiquinone radical, which is then oxidized to the respective quinone by another Fe^{3+} or also O_2, reducing to the superoxide radical ($O_2^{\bullet -}$) [5,15]. *Para*-quinone intermediates are more stable [16] and may be regenerated to its original form [7,17] while *ortho*-quinones are converted to carboxylic acids and CO_2 by Fe^{3+} [16]. From practical perspectives, degradation and mineralization of DHBs and their intermediates during Fenton-based treatment can be desirable, because these compounds increase the total organics concentration. DHBs or gallic acid can also react with OH radicals [5,7]. Thus, the concentration of mediators during treatment must be lower than the concentration of the target pollutant.

Many studies in the literature have aimed the degradation of a single recalcitrant compound as target pollutant, the catechol (1,2-dihydroxybenzene) or 2,3-dihydroxybenzoic acid being the most evaluated DHBs as mediators [6,7,11,12]. In the present work, we investigated the decolorization of four dyes by classical Fenton reaction (Fe^{2+}/H_2O_2), Fenton-like reaction (Fe^{3+}/H_2O_2), and DHB-driven Fenton systems using five DHB mediators: catechol, 2,3-dihydroxybenzoic, 2,4-dihydroxybenzoic, 2,5-dihydroxybenzoic, and 3,4-dihydroxyphenylacetic acids; gallic acid (3,4,5-trihydroxybenzoic acid) is a trihydroxybenzene and was also evaluated as mediator. Commercial synthetic dyes having different chemical structures (two azo dyes-methyl orange and chromotrope 2R; a triphenylmethane dye-phenol red; and a heterocyclic cationic dye-methylene blue) were used as target pollutants.

2. Materials and methods

2.1. Reagents

Reagents were obtained as follows and are used without further purification: chromotrope 2R, 2,3-dihydroxybenzoic, 2,4-dihydroxybenzoic, 2,5-dihydroxybenzoic, and 3,4-dihydroxyphenylacetic acids from Sigma-Aldrich Chemical Co. (Milwaukee WI, USA); catechol from Fluka Chemie (Buchs, Switzerland); Fe $(NO_3)_3$, methyl orange, gallic acid, phenol red, and H_2O_2 (30% m/m) from Vetec (Rio de Janeiro, Brazil). Other reagents purchased from diverse suppliers were of analytical grade. All stock solutions were prepared using deionized water. The structures of the DHBs (including gallic acid) and dyes investigated in this work are shown in Figs. 1 and 2, respectively.

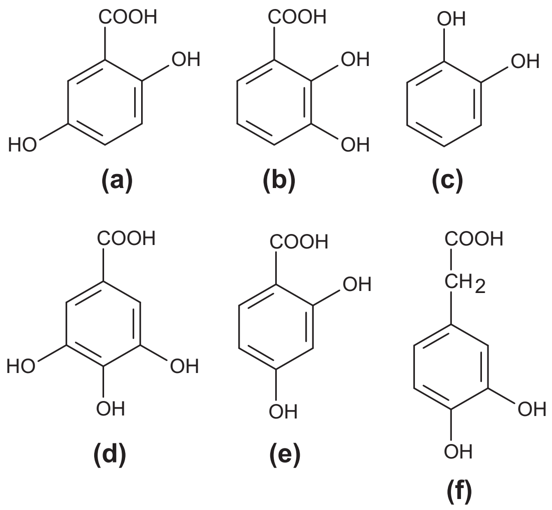

Fig. 1. Structures of the DHBs and gallic acid investigated in the present work: (a) 2,5-dihydroxybenzoic acid; (b) 2,3-dihydroxybenzoic acid; (c) catechol; (d) gallic acid; (e) 2,4-dihydroxybenzoic acid; and (f) 3,4-dihydroxyphenylacetic acid.

2.2. Dye decolorization by Fe^{3+}/H_2O_2 systems

The reactions of dye decolorization were performed under optimal conditions as previously described using azure B dye as target pollutant without causing Fe^{3+} precipitation (pH 2.5–3.0) [9]. The reactions were carried out inside 3 ml quartz cuvettes containing 10 μmol l^{-1} freshly prepared DHB (or gallic acid), 30 μmol l^{-1} dye, 450 μmol l^{-1} H_2O_2, 30 μmol l^{-1} freshly prepared $Fe(NO_3)_3$, and 1 mmol l^{-1} H_2SO_4 (to adjust pH). Decolorization assays were also performed with 0.5 l of reaction volume and the results obtained were similar to those performed in 3 ml quartz cuvettes (data not shown). Thus, we selected the volume of 3 ml because it consumed less reagent solutions. For all the analysis, the ion solutions were last added to the mixture to initiate the reaction. All the reagents were soluble under these experimental conditions. Duplicate reactions were monitored spectrophotometrically at 0, 5, 10, 20, 40, and 60 min intervals. All experiments were carried out at room temperature and in the dark. The decolorization was expressed as a decrease in absorbance at the wavelength at which each dye shows absorbance maximum (λ_{max}): 435 nm for phenol red, 508 nm for methyl orange, 513 nm for chromotrope 2R, and 665 nm for methylene blue. The reference cell in the spectrophotometer contained all reagents except the dye and Fe^{3+} solutions. Decolorization reactions in the absence of DHBs and gallic acid (Fenton-like reaction) were also performed.

In another set of experiments, reactions in the absence of dyes were carried out as controls to investigate the possible interference of DHB and gallic acid degradation products on the decolorization of dyes.

2.3. Dye decolorization by Fe^{2+}/H_2O_2 systems

Decolorization of dyes by classical Fenton reaction (Fe^{2+}/H_2O_2) was also performed. In this set of experiments, $Fe(NO_3)_3$ was replaced by $FeSO_4$ solution. The effect of DHBs or gallic acid on the classical Fenton reaction was also evaluated using methyl orange dye as target compound. Reactions in the absence of dye were also performed in this case to investigate the possible interference of DHB and gallic acid degradation products on the Fe^{2+}/H_2O_2 decolorization of methyl orange.

2.4. Determination of H_2O_2

The residual H_2O_2 was quantified with NH_4VO_3 and the peroxovanadium cation generated in the reaction medium was detected at 450 nm [18]. Reaction mixture (1 ml) was treated with 1 ml of 1.24 g l^{-1} NH_4VO_3 dissolved in 1.92% (v/v) of H_2SO_4. The reference cell in the spectrophotometer contained deionized water replacing the sample. Absorbance values from the solutions containing all reagents, except NH_4VO_3, were subtracted from the values of the entire reaction mixture. All the analyses were performed using an UV/visible spectrophotometer (Biochrom Libra S50).

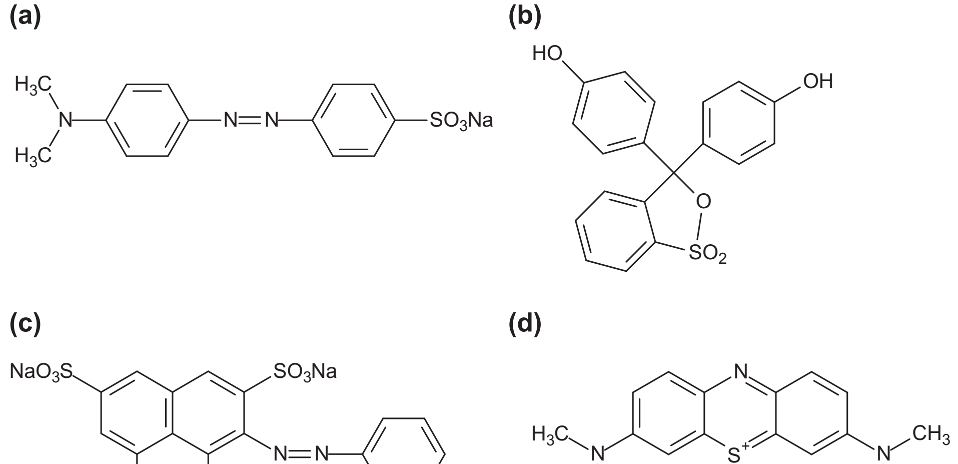

Fig. 2. Structures of the dyes investigated in the present work: (a) methyl orange; (b) phenol red; (c) chromotrope 2R; and (d) methylene blue.

3. Results and discussion

UV/visible spectra of the dye-containing solutions presented significant reduction of the absorbance in the visible range and increase in the UV range below 250 nm. In the region from 400 to 450 nm, a small increase in the absorbance was observed for methyl orange, methylene blue, and chromotrope 2R solutions (Fig. 3). Reactions performed in the absence of dyes did not show appearance of colorization after 60 min of reaction. Thus, DHB and gallic acid degradation products did not interfere in the analysis of dye decolorization.

The decrease in the absorbance peak in the visible range corresponds to the destruction of chromophoric groups by OH radicals [19,20]. The increase in absorbance in the UV range below 250 nm suggests possible dye conversion into lighter and lower molecular mass compounds [20,21], whereas small increase in the region from 400 to 450 nm can correspond to formation of quinone structures [16]. Some colorless degradation intermediates, aliphatics and aromatics, from these dyes degraded by OH radicals were previously identified [22–24]. Although only the decolorization of the solutions containing the dyes was analyzed in this work, the literature shows that chromophoric groups are firstly destroyed and then the dye molecule is mineralized by Fenton reagents [19,20,22,25].

The dye solutions were not decolorized in the presence of 10% (v/v) ethanol, which is OH radical scavenger, confirming the participation of this radical in the decolorization reactions [6,9]. Additionally, the dye decolorization was not detected when incubated with either H_2O_2 or Fe^{3+} solutions only.

Figs. 4–7 show the dye decolorization by classical Fenton reaction (Fe^{2+}/H_2O_2), Fenton-like reaction (Fe^{3+}/H_2O_2), and Fe^{3+}/H_2O_2/mediator systems with the treatment time. Generally, the dye decolorization by Fe^{2+}/H_2O_2 proceeds by two stages: a first and fast stage, and a second much slower stage. According to Nakagawa et al. [26], the first stage is attributed to the action of OH radicals formed quickly by Fenton reaction and the second stage is ascribed to other radicals with low redox potential, which are formed by the slow reaction between Fe^{3+} accumulated and H_2O_2 (Fenton-like reaction). This second stage may be due to the balance between generation and disappearance

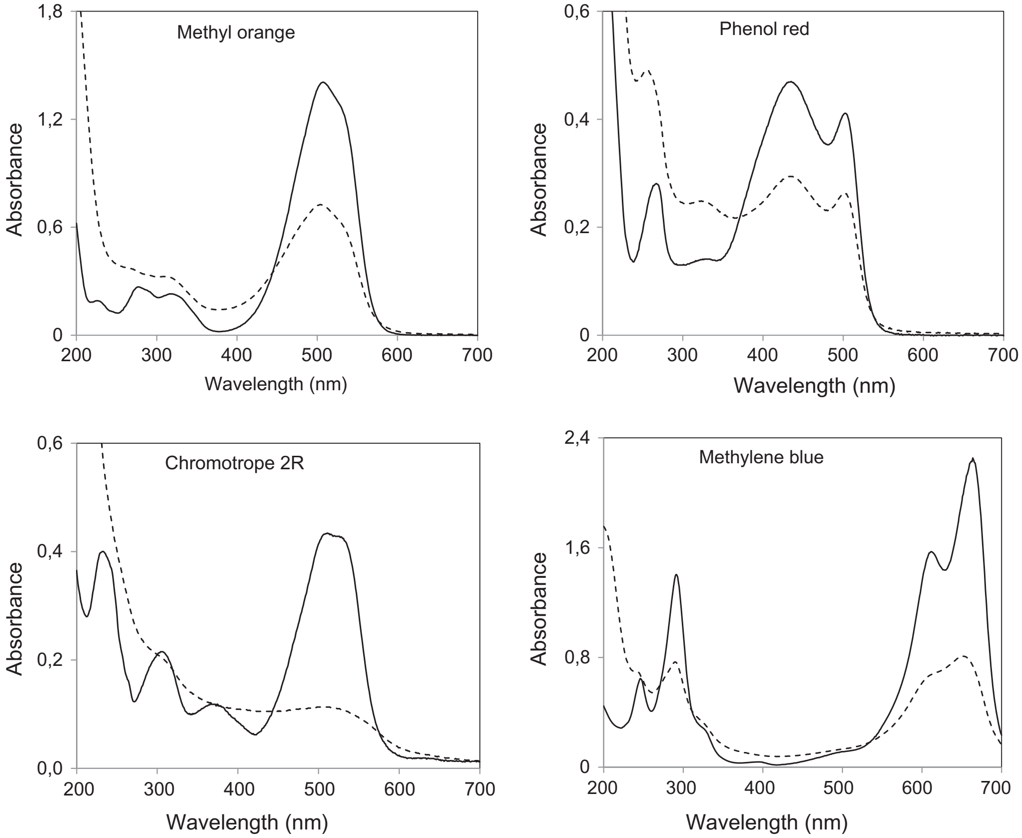

Fig. 3. UV–visible spectra of dye solution, untreated (full line) and treated by Fe^{2+}/H_2O_2 at pH 2.5–3.0 for 60 min (dashed line).

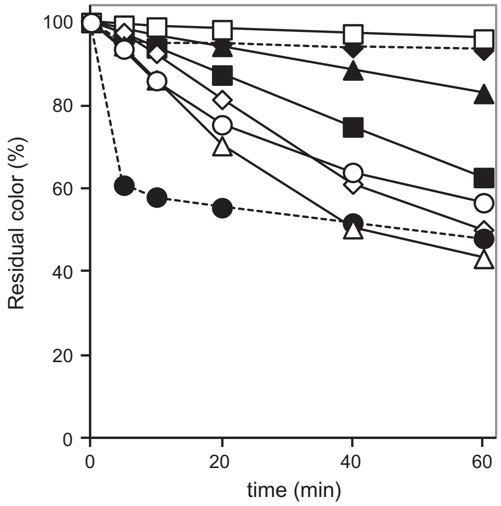

Fig. 4. Time-course of decolorization of 30 μmol l^{-1} methyl orange by Fenton systems at pH 2.5–3.0. Classical Fenton reaction (●), Fenton-like reaction (Fe^{3+}/H_2O_2,♦), Fe^{3+}/H_2O_2 in the presence of: 3,4-dihydroxyphenylacetic acid (■), catechol (▲), gallic acid (○), 2,3-dihydroxybenzoic acid (◊), 2,4-dihydroxybenzoic acid (□), and 2,5-dihydroxybenzoic acid (△). Fe^{3+} reactions contained 450 μmol l^{-1} H_2O_2, 10 μmol l^{-1} DHB (or gallic acid), and 30 μmol l^{-1} freshly prepared Fe^{3+}; Fe^{2+} reactions were performed at 450 μmol l^{-1} H_2O_2 and 30 μmol l^{-1} freshly prepared Fe^{2+}. Duplicate decolorization experiments presented error values lower than 5% of the average values.

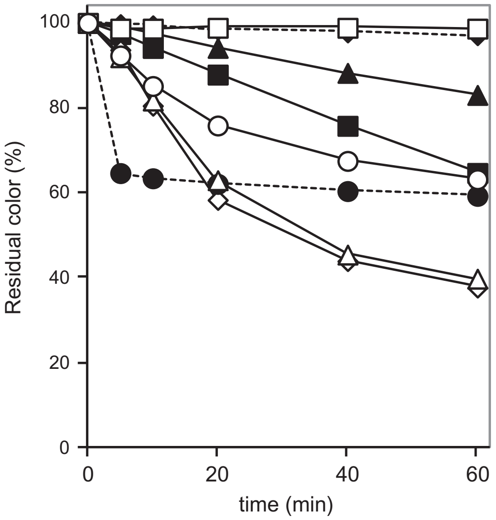

Fig. 5. Time-course of decolorization of 30 μmol l^{-1} phenol red by Fenton systems at pH 2.5–3.0. Classical Fenton reaction (●), Fenton-like reaction (Fe^{3+}/H_2O_2, ♦), Fe^{3+}/H_2O_2 in the presence of: 3,4-dihydroxyphenylacetic acid (■), catechol (▲), gallic acid (■), 2,3-dihydroxybenzoic acid (◊), 2,4-dihydroxybenzoic acid (□), 2,5-dihydroxybenzoic acid (△). Fe^{3+} reactions contained 450 μmol l^{-1} H_2O_2, 10 μmol l^{-1} DHB (or gallic acid), and 30 μmol l^{-1} freshly prepared Fe^{3+}; Fe^{2+} reactions were performed at 450 μmol l^{-1} H_2O_2 and 30 μmol l^{-1} freshly prepared Fe^{2+}. Duplicate decolorization experiments presented error values lower than 5% of the average values.

of OH radicals. However, this two-stage phenomenon did not fit the DHB-driven Fenton systems to dye decolorization.

The Fe^{2+}/H_2O_2 decolorization of methyl orange reached 52% after 60 min of reaction, whereas the decolorization by Fe^{3+}/H_2O_2 was negligible under the assay conditions. The DHBs and gallic acid improved the decolorization of this dye, except 2,4-dihydroxybenzoic acid. 2,3- and 2,5-dihydroxybenzoic acids were the most effective mediators to decolorize methyl orange. Fe^{3+}/H_2O_2/2,5-dihydroxybenzoic acid system reached higher decolorization (57%) than the classic Fenton reaction after 60 min (Fig. 4).

Decolorization of phenol red by Fe^{3+}/H_2O_2 was also negligible. The curve behaviors for the phenol red decolorization were similar to those observed for methyl orange. Catechol, 3,4-dihydroxyphenylacetic and gallic acids mediated decolorization of phenol red. 2,3- and 2,5-dihydroxybenzoic acids were the most effective mediators, both exhibited 60% of decolorization against 40% by Fe^{2+}/H_2O_2. On the other hand, 2,4-dihydroxybenzoic acid did not mediate the decolorization of phenol red (Fig. 5).

Chromotrope 2R was the second most susceptible dye to decolorization. Its decolorization by Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 reached 74 and 27% after 60 min, respectively. Gallic acid and the DHBs, including 2,4-dihydroxybenzoic acid, promoted 95% of decolorization of this dye after 60 min of reaction (Fig. 6).

Methylene blue was the most susceptible dye to decolorization, including Fe^{3+}/H_2O_2. The decolorization varied between the different reaction systems, but after 60 min the values achieved were similar. The classical Fenton reaction reached above 90% of decolorization at 40 min, whereas the Fenton-like reaction reached this same value after 60 min. For the last reaction, an induction period to decolorization (above 5 min) was observed. The DHBs and gallic acid accelerated methylene blue decolorization, and the 2,5-dihydroxybenzoic acid was the most effective mediator promoting above 90% of decolorization at 20 min of reaction. 2,4-dihydroxybenzoic acid did not mediate the decolorization of this dye (Fig. 7).

The effect of DHBs and gallic acid on the classical Fenton reaction to decolorize methyl orange, one of the least susceptible to decolorization, was also evaluated (Fig. 8). In this case, all the mediators were effective, reaching above 91% of decolorization after 60 min of reaction.

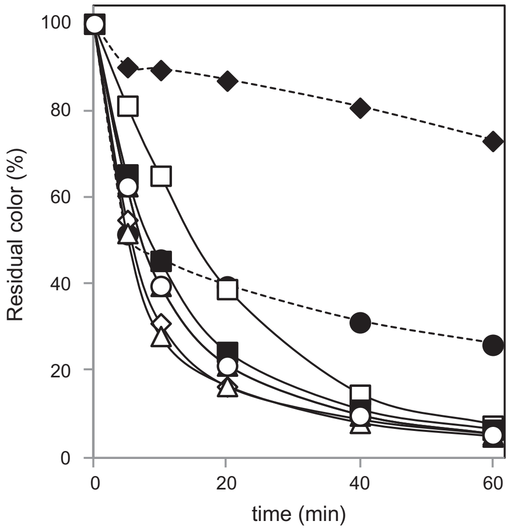

Fig. 6. Time-course of decolorization of 30 μmol l^{-1} chromotrope 2R by Fenton systems at pH 2.5–3.0. Classical Fenton reaction (●), Fenton-like reaction (Fe^{3+}/H_2O_2, ♦), Fe^{3+}/H_2O_2 in the presence of: 3,4-dihydroxyphenylacetic acid (■), catechol (▲), gallic acid (■), 2,3-dihydroxybenzoic acid (◇), 2,4-dihydroxybenzoic acid (□), and 2,5-dihydroxybenzoic acid (△). Fe^{3+} reactions contained 450 μmol l^{-1} H_2O_2, 10 μmol l^{-1} DHB (or gallic acid), and 30 μmol l^{-1} freshly prepared Fe^{3+}; Fe^{2+} reactions were performed at 450 μmol l^{-1} H_2O_2 and 30 μmol l^{-1} freshly prepared Fe^{2+}. Duplicate decolorization experiments presented error values lower than 5% of the average values.

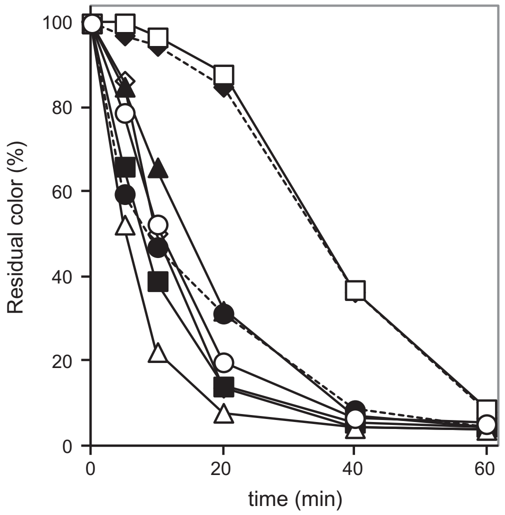

Fig. 7. Time-course of decolorization of 30 μmol l^{-1} methylene blue by Fenton systems at pH 2.5–3.0. Classical Fenton reaction (●), Fenton-like reaction (Fe^{3+}/H_2O_2, ♦), Fe^{3+}/H_2O_2 in the presence of: 3,4-dihydroxyphenylacetic acid (■), catechol (▲), gallic acid (○), 2,3-dihydroxybenzoic acid (◇), 2,4-dihydroxybenzoic acid (□), and 2,5-dihydroxybenzoic acid (△). Fe^{3+} reactions contained 450 μmol l^{-1} H_2O_2, 10 μmol l^{-1} DHB (or gallic acid), and 30 μmol l^{-1} freshly prepared Fe^{3+}; Fe^{2+} reactions were performed at 450 μmol l^{-1} H_2O_2 and 30 μmol l^{-1} freshly prepared Fe^{2+}. Duplicate decolorization experiments presented error values lower than 5% of the average values.

OH radical is a very active and strong oxidant that has the capability of breaking down organic molecules. However, it typically has a short life-time that limits its application [3]. Among the mediators evaluated in the present work to increase the formation of OH radicals and make it continuous, 2,3- and 2,5-dihydroxybenzoic acids promoted progressive and most intense decolorization for the majority of dyes, while the classical Fenton reaction was quick at the first stage, but slow by increasing the reaction time. The Fenton-like reaction showed the lowest decolorization values.

Previously, DHBs and gallic acid investigated in this work showed Fe^{3+}-reducing activity, except 2,4-dihydroxybenzoic acid. The 2,5-dihydroxybenzoic acid has two hydroxyls in *para* position in its structure, while the other Fe^{3+}-reducing DHBs and gallic acid have their hydroxyl groups in *ortho* position (see Fig. 1). In reacting with Fe^{3+}, DHB and gallic acid are converted into quinone-type structures. However, 2,4-dihydroxybenzoic acid is unable to be directly oxidized by Fe^{3+} ions into a quinone structure due its hydroxyl groups in *meta* position [5,7,16,17]. This explains its low efficiency on the decolorization of dyes. The pro-oxidant effect observed for the 2,4-dihydroxybenzoic acid on the decolorization of chromotrope 2R by Fe^{3+}/H_2O_2 and methyl orange by Fe^{2+}/H_2O_2 indicates that intermediates generated from its transformation by OH radical mediated these decolorization reactions. OH radicals are able to substitute aromatic rings creating new phenolic functions in its structure, generating 1,4-dihydroxybenzene- or 1,2-dihydroxybenzene-derivatives that are Fe^{3+}-reducers [5]. Previously, malachite green decolorization by Fe^{3+}/H_2O_2 was also increased in the presence of two non-reducer compounds, resorcinol (1,3-dihydroxybenzene), which is 2,4-dihydroxybenzoic acid analogous, and 2-hydroxybenzoic acid. Hydroxylated products from 2-hydroxybenzoic acid were identified, which increased the decolorization of malachite green according to Chen et al. [7].

The decolorization of methylene blue was very similar to the azure B, an analogous compound to methylene blue [9] and it was effective for all reaction systems, including Fe^{3+}/H_2O_2. Hydrogen peroxide also reduces Fe^{3+} (reaction 2), but the Fenton reagents are slowly produced [3,5]. Previously, Oliveira et al. [27] proposed the formation of hydroquinone intermediates from the oxidation of methylene blue via

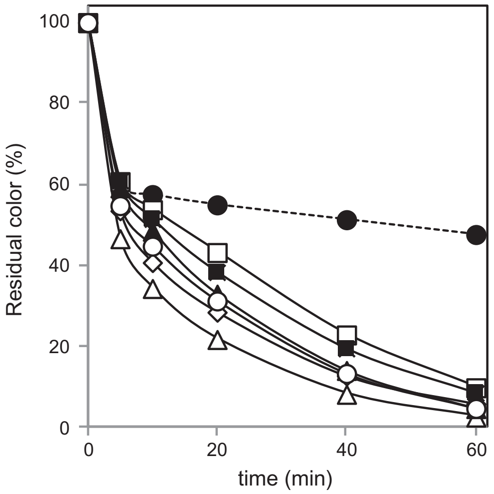

Fig. 8. Time-course of decolorization of 30 μmol l^{-1} methyl orange by Fenton systems at pH 2.5–3.0. Fe^{2+}/H_2O_2 (classical Fenton reaction) in the absence (●) and in the presence of: 3,4-dihydroxyphenylacetic acid (■), catechol (▲), gallic acid (○), 2,3-dihydroxybenzoic acid (◇), 2,4-dihydroxybenzoic acid (□), 2,5-dihydroxybenzoic acid (△). The reactions contained 450 μmol l^{-1} H_2O_2, 10 μmol l^{-1} DHB (or gallic acid), and 30 μmol l^{-1} freshly prepared Fe^{2+}. Duplicate decolorization experiments presented error values lower than 5% of the average values.

heterogeneous Fenton systems. In the present work, the decolorization of methylene blue by Fenton-like reaction has showed an induction period, which can be attributed to the formation of hydroquinone intermediates that mediated the decolorization of its precursor. Du et al. [28] also observed an induction period in the degradation of phenol, 4-chlorophenol or 4-nitrophenol by Fenton-like reaction, attributing to the appearance of Fe^{3+}-reducing DHB intermediates that accelerated the degradation of their precursors in the reaction medium.

With regard to the azo dyes, chromotrope 2R was more susceptible for decolorization than methyl orange. The decolorization of phenol red (triphenylmethane dye) and methyl orange presented similar behaviors. On the other hand, Fe^{3+}/H_2O_2 did not promote decolorization of methyl orange and phenol red, but it caused decolorization of chromotrope 2R and methylene blue (heterocyclic dye). These different behaviors of decolorization among the dyes investigated in this work can be attributed to the different reactivity of each chromophoric group and other reaction sites present in the dye molecules. The central methine carbon in the phenol red is an important site of attack by OH radicals, leading to its decolorization and cleavage and the aromatic rings can be hydroxylated or cleaved [20–22]. Decolorization of methylene blue begins with the cleavage of $C–S^{+}=C$ functional group [29], while the decolorization of azo dyes proceeds by the breaking of azo groups (–N=N–). However, the $–N(CH_3)_2$ substituent (non-chromophoric group) present in methylene blue and methyl orange is also an important site of attack by OH radicals [20,22,23,29]. In accordance with our results, Xu et al. [19] investigated the Fenton-based decolorization of twenty dyes, including azo, triphenylmethane, anthraquinone, heterocyclic and phthalocyanine groups, and they did not observe highest decolorization for a specific group of dyes. In addition, the different effects of DHBs and dyes may be also related to their redox potentials.

Table 1 shows the consumption of H_2O_2 for the decolorization reactions after 60 min. Comparing Fenton-like and classical Fenton reactions (both in the absence of DHBs or gallic acid), the latter exhibited the highest consumption of H_2O_2 and decolorization of dyes, which is attributed to its highest constant of reaction. In the presence of DHBs or gallic acid, the consumption of H_2O_2 was increased to decolorize all dyes. Among the mediators, the reactions containing 2,4-dihydroxybenzoic acid consumed less H_2O_2. For the reactions in the absence of dyes, the mediators also increased the consumption of H_2O_2, which was the lowest consumption observed. This indicates that intermediates generated from decolorization of dyes can affect the conversion of Fe^{2+}/Fe^{3+}, by increasing the consumption of H_2O_2.

The decolorization of methyl orange required high consumption of H_2O_2 in the presence of 2,5-dihydroxybenzoic acid, the most effective mediator in the decolorization of this dye. To our knowledge, this compound was not previously evaluated as a mediator for the Fenton degradation of organic pollutants. For the methylene blue, the consumption of H_2O_2 did not show significant difference between the DHBs, except for 2,4-dihydroxybenzoic acid that consumed less H_2O_2. The highest decolorization for chromotrope 2R and methylene blue can be related with the highest consumption of H_2O_2 during the reactions using these dyes as target compounds. Although the Fenton-like reaction has decolorized little chromotrope 2R and did not decolorize methyl orange and phenol red, high consumption of H_2O_2 was observed. This can be explained by the fact that: (1) if OH radicals were formed in significant quantities, they could also react with the DHBs (or gallic acid), with its own precursor (H_2O_2), Fe^{2+}, ($^{\cdot}O_2H$),and/or even may be autoscavenged (Eqs. (3)–(6)) [4]; and (2) the hydroperoxyl radicals from reactions 2 or 5, apparently do not have redox potential enough to decolorize these dyes.

Table 1
Consumption of H_2O_2 (%) after 1 h reaction in mixtures containing dyes, DHBs and Fenton reagents. Deviations from the average values are based on duplicate experiments

Reaction system	Dyes*						
				Methyl orange		Without dyes	
	Chromotrope 2R	Methylene blue	Phenol red	With Fe^{3+}	With Fe^{2+}	With Fe^{3+}	With Fe^{2+}
Classical Fenton reaction	77.6 ± 1.9	75.0 ± 0.6	59.1 ± 1.5	–	62.8 ± 1.2	–	48.3 ± 0.1
Fenton-like reaction	69.2 ± 0.3	62.8 ± 1.2	50.7 ± 1	52.1 ± 2	–	32.1 ± 1.5	–
2,4-Dihydroxybenzoic acid	78.5 ± 1.3	67.8 ± 0.9	48.0 ± 0.3	59.9 ± 1	76.9 ± 1	44.5 ± 0.4	71.2 ± 1.0
2,3-Dihydroxybenzoic acid	77.9 ± 0	79.7 ± 0.6	60.5 ± 0.6	68 ± 1.3	77.5 ± 0.3	54.4 ± 0.9	69.6 ± 0.3
2,5-Dihydroxybenzoic acid	79.2 ± 0	82.3 ± 2.0	59.9 ± 0.6	76.9 ± 0.6	83.9 ± 0.7	58.3 ± 0.6	71.4 ± 0.6
Gallic acid	76.9 ± 0.3	89.3 ± 1.5	62.2 ± 0.6	63.7 ± 0.3	75.9 ± 0	61.3 ± 0.6	70.2 ± 0
3,4-Dihydroxyphenylacetic acid	74.2 ± 0.3	81.7 ± 3.8	70.4 ± 1.2	65.3 ± 2	74.5 ± 0	64.1 ± 0.4	73.5 ± 0.3
Catechol	77.5 ± 0.3	78.2 ± 0.9	58.5 ± 0.9	63.5 ± 3.2	78.9 ± 1	57.1 ± 0.6	62.8 ± 0.3

*The effect of DHBs or gallic acid on the decolorization of chromotrope 2R, methylene blue, and phenol red was only carried out for Fe^{3+}/H_2O_2 systems.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + {}^{-}OH \qquad k = 2.5 - 5 \times 10^{8}\,\mathrm{mol^{-1}\,ls^{-1}} \tag{3}$$

$$ {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad k = 5 - 8 \times 10^{9}\,\mathrm{mol^{-1}\,ls^{-1}} \tag{4}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \qquad k = 1.7 - 4.5 \times 10^{7}\mathrm{mol^{-1}ls^{-1}} \tag{5}$$

$$ {}^{\bullet}OH + {}^{\bullet}O_2H \rightarrow H_2O + O_2 \qquad k = 1.4 \times 10^{10}\mathrm{mol^{-1}ls^{-1}} \tag{6}$$

It should be mentioned that the addition of DHBs or gallic acid in the Fenton system is not simple approach, because of the cost, toxicity, and biodegradability of these compounds. When react with Fe^{3+} (or other oxidant), these mediators can be degraded and mineralized [16] and this can be desirable. On the other hand, DHBs could be reutilized through immobilization onto solid supports. Recently, Pagano et al. [30] verified an increase in the Fenton degradation of a non-ionic surfactant by 1,4-hydroquinone adsorbed on granular activated carbon. In this study, only 3% of the DHB was desorbed from support after treatment.

4. Conclusions

The decolorization of synthetic dyes in aqueous solution by DHB-driven Fenton systems was investigated. The addition of DHBs or gallic acid can effectively increase the oxidation reactivity in dye decolorization. The position of the hydroxyl groups in the aromatic ring influenced the pro-oxidant properties of these mediators. Different behaviors were observed to the four dyes tested, suggesting that the effect of the target pollutant structure and redox potential also influenced the decolorizations. To increase the decolorization of dyes, the mediators increased the consumption of H_2O_2. It was also observed that a high consumption of H_2O_2 did not always provide an effective decolorization of the dyes, suggesting that OH radicals reacted with the DHBs (or gallic acid), H_2O_2 or other reactive species in solution.

Acknowledgments

We wish to thank R. Oliveira and A.A. Mendes for critical reading of this manuscript. This research has been supported by FAPEMIG (Process number APQ-01585-11). F. Barreto and C.S. Santana thank CNPq and FAPEMIG for their student fellowships, respectively.

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