



## Surfactant degradation by a catechol-driven Fenton reaction

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### ABSTRACT

The addition of 0.5 mM catechol is shown to accelerate the degradation and mineralization of the anionic surfactant DowFax™ 2A1 (sodium dodecylphenyloxide disulfonate) under conventional Fenton reaction conditions (Fe(II) plus H<sub>2</sub>O<sub>2</sub> at pH 3). The catalytic effect causes a 3-fold increase in the initial rate (up to ca. 20 min) of conversion of the surfactant to oxidation products (apparent first-order rate constants of 0.021 and 0.061 min<sup>-1</sup> in the absence and presence of catechol, respectively). Although this catalytic rate increase persists for a certain amount of time after complete disappearance of catechol itself (ca. 8 min), the reaction rate begins to decline slowly after the initial 20 min towards that observed in the absence of added catechol. Total organic carbon (TOC) measurements of net mineralization and cyclic voltammetric and high performance liquid chromatographic (HPLC) measurements of the initial rate of reaction of catechol and the surfactant provide insight into the role of catechol in promoting the degradation of the surfactant and of degradation products as the eventual inhibitors of the Fenton reaction.

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### 1. Introduction

Preoccupation with the environment and, in particular, with pollution of water resources has led to the development of several new technologies for the treatment of urban and industrial residues. Among these new technologies, Advanced Oxidation Processes (AOPs) are considered to be the most promising alternative due to their high efficiency and versatility [1–5]. The AOP are based on the generation of hydroxyl radicals (HO•), which have a very high oxidation potential ( $E^\circ = +2.80$  V vs. NHE) and are capable of initiating a cascade of reactions that often results in the total degradation or mineralization of the organic substance [5]. The hydroxyl radical can be efficiently generated via the classical Fenton reaction, in which Fe(II) ions are oxidized to Fe(III) by H<sub>2</sub>O<sub>2</sub>, which is reduced in the process to the hydroxide ion and a hydroxyl radical (Eq. (1)).

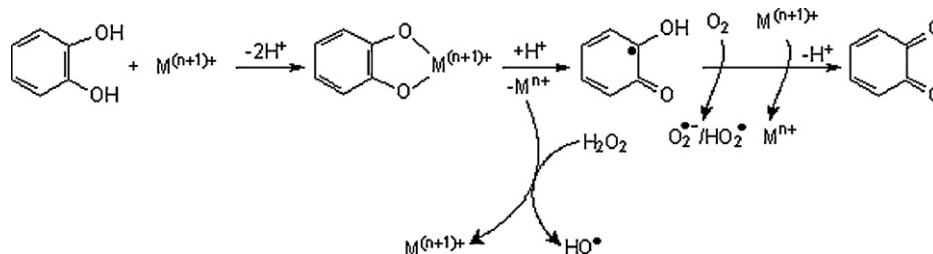


Although hydroxyl radicals are efficiently generated by the Fenton reaction, the reaction requires stoichiometric amounts of the Fe(II) ion and is relatively slow due to the sluggishness of the reaction of Fe(III) with H<sub>2</sub>O<sub>2</sub> to regenerate Fe(II). One strategy for increasing the rate of regeneration of Fe(II) consists of the addition of phenolic compounds such as dihydroxybenzenes (DHBs) that

have the ability to reduce Fe(III) to Fe(II) [6–8]. The mechanism proposed by Aguiar et al. [9] for the reduction of Fe(III) by catechol is outlined in Scheme 1. Thus, catechol forms a complex with Fe(III) and is oxidized to a semiquinone radical, which is subsequently oxidized to the corresponding quinone by another Fe(III). Molecular oxygen (O<sub>2</sub>) also can act as the electron acceptor, being reduced by the semiquinone radical to superoxide/hydroperoxide radicals, O<sub>2</sub>•<sup>-</sup>/HO<sub>2</sub>•, that can be converted into H<sub>2</sub>O<sub>2</sub>. Therefore, there are several pathways via which phenolic compounds can potentially increase the efficiency of the Fenton process [10–13].

Several authors have suggested that catechol or hydroquinone can be regenerated from the corresponding quinones, forming a catalytic redox cycle for the oxidation process [7,14,15]. The simple redox cycle mechanism proposed by Chen et al. [7] is shown in Scheme 2. These authors showed that the ability of a DHB to promote the Fenton reaction is directly related to the feasibility and ease of its transformation into the quinone (via the semiquinone). Thus, for example, the degradation of malachite green via the Fenton reaction was found to be catalyzed by catechol and by hydroquinone, but not by resorcinol, which cannot be oxidized to a quinone by iron (III). The relative activities of a series of organic catalysts followed the order: hydroquinone > salicylic acid > *p*-hydroxybenzoic acid > *m*-hydroxybenzoic acid > *p*-benzoquinone > aromatic carboxylic acids > aromatic carboxamides. For many compounds, an induction period was observed at the beginning of the degradation of malachite green, followed by rapid degradation of the dye. This

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**Scheme 1.** Catechol oxidation by transition metals ( $M = \text{Fe}$  or  $\text{Cu}$ ) and formation of  $\text{HO}^\bullet$  as proposed by Aguiar et al. [9].

induction period was attributed by Chen et al. [7] to the time necessary for the initial formation of hydroquinone or other DHB capable of initiating the redox cycle.

Analyzing phenol oxidation by the Fenton reaction, Du et al. [16] pointed out that the oxidation occurs in three phases. The initial stage of the reaction, analogous to the induction period observed by Chen, is slow and coincides with the generation of catalytic intermediates such as catechol and hydroquinone. This is followed by a fast intermediate stage in which phenol is oxidized quickly. In the third and final stage, the rate of degradation decreases drastically due to the consumption of most of the hydrogen peroxide and to the formation of aliphatic acids, such as acetic, formic, maleic and fumaric acids, that cannot readily reduce  $\text{Fe(III)}$  to  $\text{Fe(II)}$ .

Although degradation of surfactants via the conventional Fenton reaction is well-known (e.g., [1]), we could find no reports of surfactant degradation via a catechol-accelerated Fenton reaction. In the present work, therefore, we report an investigation of the acceleration of the Fenton degradation and mineralization of DowFax<sup>TM</sup> 2A1 by added catechol. The anionic surfactant DowFax<sup>TM</sup> 2A1 (sodium dodecyl-diphenyl-oxide disulfonate) is an acid-, base- and fairly oxidation-resistant dispersant and emulsion stabilizer with applications in household cleaning products, in emulsion polymerization and in the textile, pulp and paper, agrochemical and petroleum industries. Total organic carbon (TOC) measurements of net mineralization and cyclic voltammetric and high performance liquid chromatographic (HPLC) measurements of the decrease in the concentrations of catechol and the surfactant provide insight into the role of catechol in promoting the degradation of the surfactant.

## 2. Experimental

A commercial sample of DowFax<sup>TM</sup> 2A1 (furnished as a 45% solution in water) was kindly provided by Dow Brazil, São Paulo. Hydrogen peroxide (30%) and the inorganic salts  $\text{FeClO}_4$  were obtained from Synth (Labsynth, Brazil) and  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  were obtained from F. Maia (Brazil). All reagents were used as received.

The Fenton reactions were conducted in a simple reactor with a capacity of 500 mL that was protected from incident light in order to exclude the possibility of a contribution from photochemistry (photo-Fenton reaction). All experiments were carried out at ambient temperature with magnetic stirring. Initially, 200 mL of a solution containing the desired concentrations of iron(II), surfactant and catechol were added to the reactor. Hydrogen peroxide

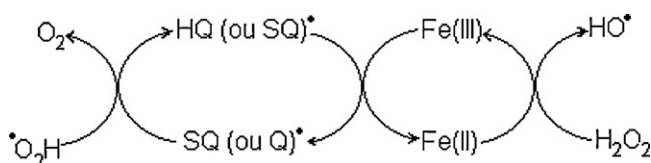
solution was added slowly over the first 40 min of reaction. The pH of the solution was maintained constant at pH 3.0 by addition of appropriate aliquots of aqueous  $\text{NaOH}$  as necessary. The ranges of variation of the reagent concentrations were: iron(II) from 0.3 to 1.0 mM, hydrogen peroxide from 0 to 200 mM (total concentration added) and catechol from 0 to 0.7 mM. At selected time intervals, aliquots of the solution were withdrawn and the Fenton reaction stopped by addition of aqueous  $\text{NaOH}$  (final pH of ca. 12) to precipitate iron oxides. After filtration, total organic carbon, TOC, of the samples was determined on a Shimadzu Model TOC-5000A TOC Analyzer. The concentrations of residual unreacted DowFax<sup>TM</sup> 2A1 surfactant or catechol were determined as a function of reaction time by following the decrease in peak area of these two compounds by HPLC on a Shimadzu Model LC-10ADVP chromatograph with a diode array detector equipped with a C18 column (25 cm  $\times$  4.60 mm). For HPLC analysis of catechol, the mobile phase (1 mL/min) was 18% acetonitrile:water for 3 min followed by a linear gradient from 18% to 56% acetonitrile for the next 9 min finalized by 1 min at 56% acetonitrile. For analysis of DowFax<sup>TM</sup> 2A1, the mobile phase (0.5 mL/min) was 50% acetonitrile:water. Good analytical sensitivity for both TOC and HPLC analysis required that the concentration of DowFax<sup>TM</sup> 2A1 used in the experiments (typically equivalent to 250 ppm of organic carbon) be substantially larger than that of catechol (0.5 mM catechol = 36 ppm organic carbon). The  $\text{H}_2\text{O}_2$  concentration was determined by spectrophotometric analysis with metavanadate following the methodology developed by Nogueira et al. [17].

The electrochemical experiments were conducted using a conventional cell with three electrodes without separation. A glassy carbon electrode 2 mm in diameter was used as the anode, a platinum wire as cathode and  $\text{Ag}/\text{AgCl}/\text{Cl}^-$  as the reference electrode. A solution of 0.50 M aqueous  $\text{Na}_2\text{SO}_4$  was employed as the supporting electrolyte. The pH of the solution was adjusted to approximately 3.0, similar to that employed for the Fenton reactions. Cyclic voltammograms of catechol were registered as a function of  $\text{Fe(II)}$  and  $\text{H}_2\text{O}_2$  concentrations with an Autolab PGSTAT 20 potentiostat-galvanostat apparatus. Voltammograms were also registered in situ in the Fenton reaction solution, monitoring the concentration of catechol as a function of time.

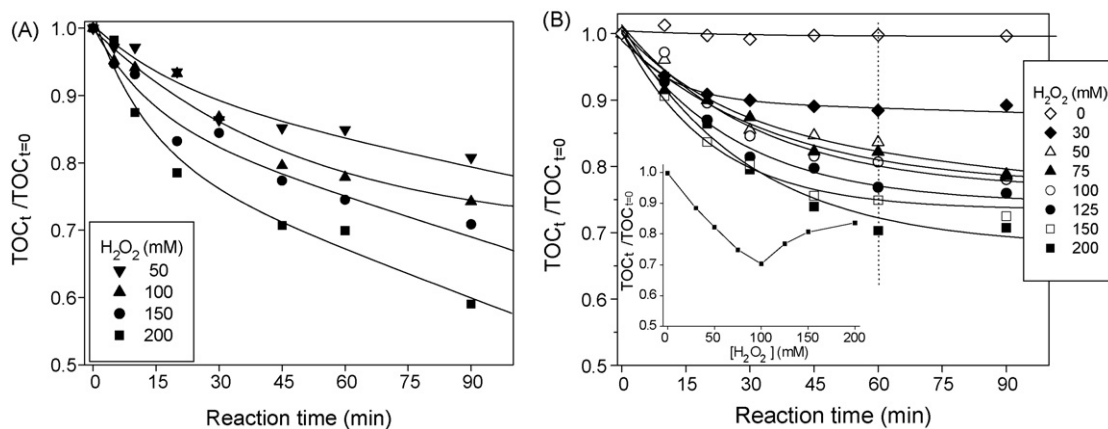
## 3. Results and discussion

### 3.1. Degradation efficiency

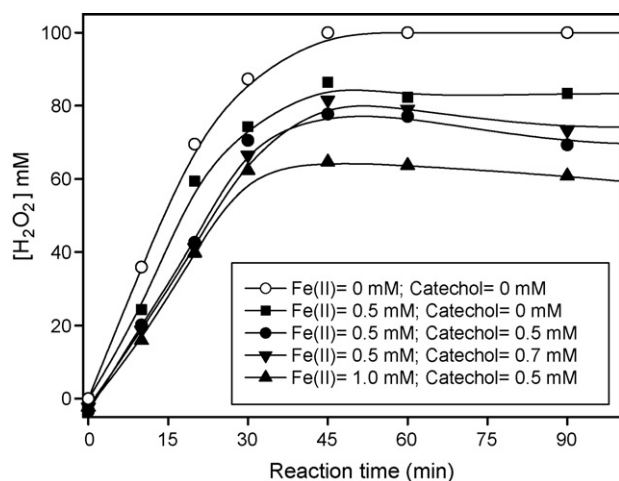
The efficiency of the Fenton reaction for the complete degradation of the anionic surfactant DowFax<sup>TM</sup> 2A1 (initial concentration 250 ppm of organic carbon) was determined as a function of the total added concentration of  $\text{H}_2\text{O}_2$  in the absence (Fig. 1A) and presence (Fig. 1B) of catechol. In both cases,  $\text{H}_2\text{O}_2$  was added over a period of 40 min in order to minimize the competitive reactions (Eqs. (2) and (3)) of the hydroxyl radicals generated by the Fenton reaction with  $\text{H}_2\text{O}_2$  or with the resultant product, the hydroperoxyl radical [5]. Fig. 2 shows the temporal variation of the net concen-



**Scheme 2.** The cyclic redox process proposed by Chen et al. [7] for regeneration of  $\text{Fe(II)}$  in the Fenton reaction catalyzed by DHB.

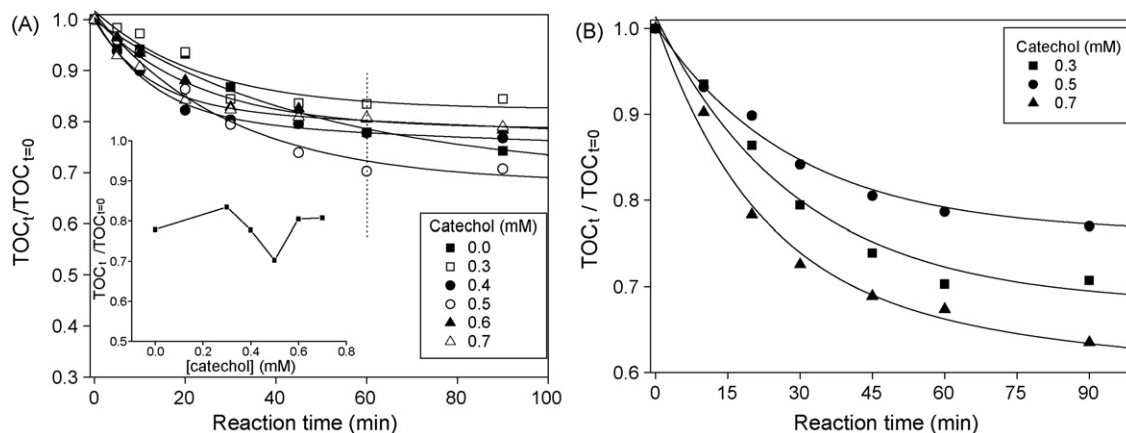
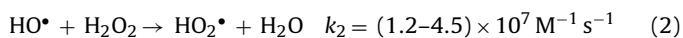


**Fig. 1.** (A) Fraction of TOC removal as a function of time at several total added  $H_2O_2$  concentrations in the absence of catechol.  $TOC_{t=0} = [\text{surfactant}]_{t=0} = 250$  ppm of carbon;  $[Fe(II)] = 0.5$  mM; pH 3.0. (B) Fraction of TOC removal as a function of time at several total added  $H_2O_2$  concentrations under the same conditions in the presence of 0.50 mM catechol (36 ppm organic carbon).  $TOC_{t=0} = [\text{surfactant}]_{t=0} + [\text{catechol}]_{t=0}$ . Inset: Fraction of TOC removal at  $t = 60$  min as a function of total added  $H_2O_2$



**Fig. 2.** Residual hydrogen peroxide concentration as a function of reaction time in the absence of surfactant. Total  $[H_2O_2]$  added over the first 40 min of reaction = 100 mM.

tration of  $H_2O_2$  in the reaction mixture with and without catechol, but in the absence of the surfactant.



**Fig. 3.** (A) Fraction of TOC removal as a function of time at various catechol concentrations.  $[\text{surfactant}]_{t=0} = 250$  ppm of carbon;  $[Fe(II)] = 0.5$  mM;  $[H_2O_2] = 100$  mM; pH 3.0.  $TOC_{t=0}$  as in Fig. 1B. Inset: Fraction of TOC removal at  $t = 60$  min as a function of  $[\text{Catechol}]$ . (B) Fraction of TOC removal as a function of time at various  $Fe(II)$  concentrations;  $[\text{catechol}] = 0.5$  mM, pH 3.0

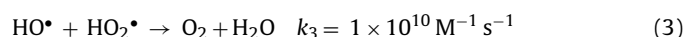
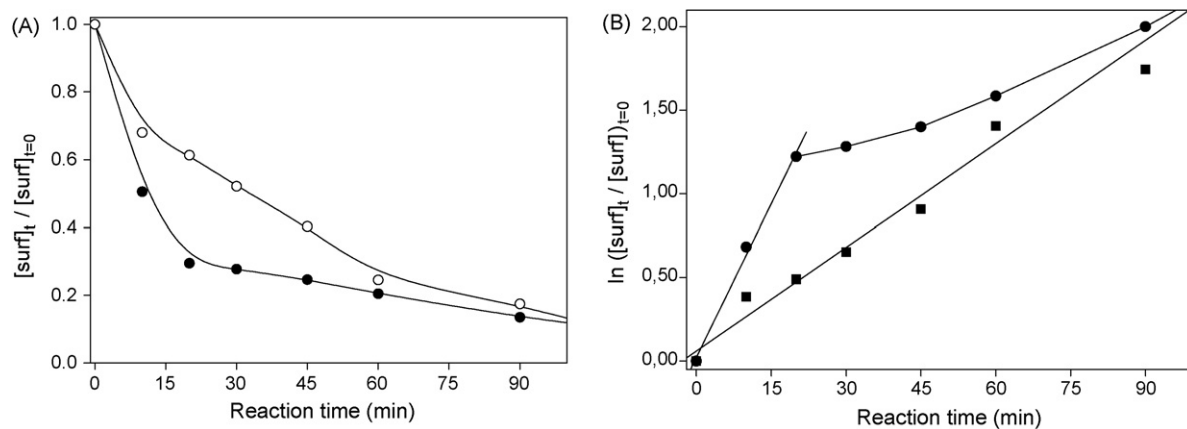


Fig. 1 shows that there is a clear difference in the efficiency of mineralization of the surfactant DowFax™ 2A1 in the absence and presence of catechol. Thus, in the absence of catechol, the degradation efficiency progressively increased with increasing total added  $H_2O_2$  concentration, approaching ca. 50% mineralization of the total organic carbon at 200 mM  $H_2O_2$  (Fig. 1A). In contrast, under the same conditions, but in the presence of 0.5 mM catechol (36 ppm organic carbon), the extent of surfactant mineralization increased with increasing total peroxide concentration up to 100 mM, followed by a marked decrease at higher peroxide concentrations (Fig. 1B). Similar behavior has been reported by Sun et al. [18] for the degradation of *p*-nitroaniline and by Mandal et al. [19] for the degradation of catechol.

Although the catalytic effect of catechol on the Fenton degradation process is not particularly evident in the overall rate of mineralization of the surfactant and there is no clear trend with increasing catechol concentration (Fig. 3A), the efficiency of mineralization does show a progressive increase with increasing  $Fe(II)$  concentration (Fig. 3B). In order to see the catalytic effect of catechol more clearly, however, one must examine the initial stages of the reaction and, in particular, the initial rate of conversion of the surfactant to products. Thus, as shown in Fig. 4A, the initial conversion of DowFax™ 2A1 to oxidation products is much faster in the presence than in the absence of catechol. In the absence



**Fig. 4.** (A) Decrease in DowFax 2A1 concentration as a function of reaction time in the absence (○) and presence (●) of 0.5 mM catechol.  $[\text{surfactant}]_{t=0} = 250$  ppm of carbon;  $[\text{H}_2\text{O}_2] = 100$  mM;  $[\text{Fe(II)}] = 0.5$  mM; pH 3.0. (B) First-order kinetic plot of  $\ln([\text{Surf}]_t / [\text{Surf}]_{t=0})$  vs. reaction time of the data of (A) in the absence (■) and presence (●) of catechol. The initial slopes provide apparent rate constants of 0.021 and 0.061  $\text{min}^{-1}$ , respectively, in the absence and presence of catechol

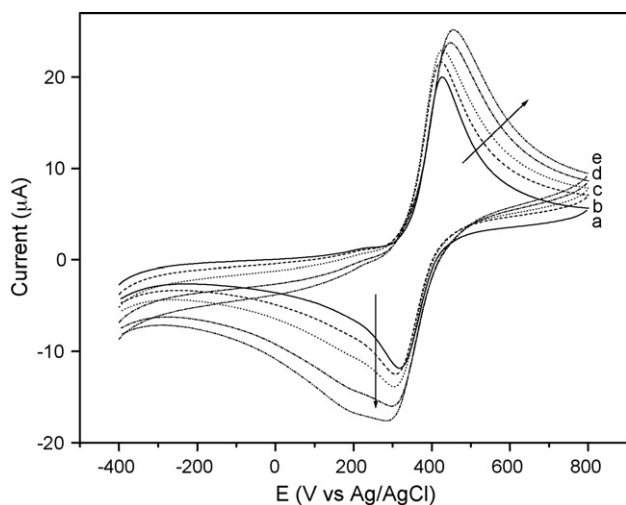
of catechol, a first-order kinetic plot of the data (Fig. 4B) shows that the conversion of the surfactant to products follows simple first-order kinetics (with an apparent first-order rate constant of 0.021  $\text{min}^{-1}$ , corresponding to a half life of ca. 34 min) over the entire first two hours of reaction. In the presence of catechol, however, the decrease in the DowFax™ 2A1 concentration is about three-fold faster during the initial 20 min of reaction (with an apparent first-order rate constant of 0.061  $\text{min}^{-1}$ , corresponding to a half life of ca. 11 min), followed by a gradual deceleration of the rate towards that observed in the absence of catechol (Fig. 4B).

### 3.2. Electrochemical studies

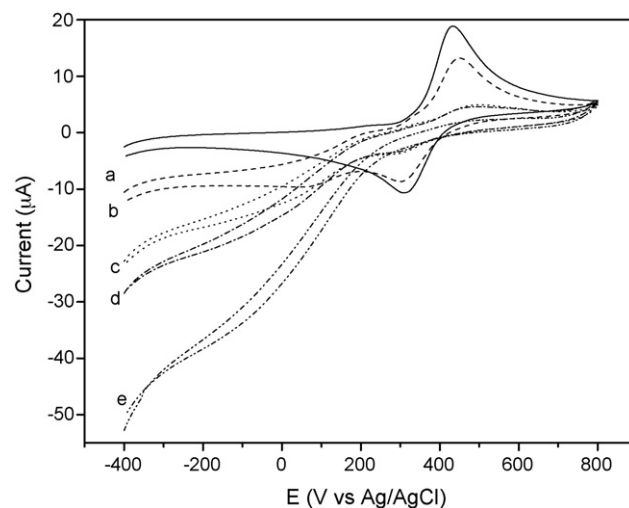
Initially, cyclic voltammograms of all of the reagents were registered individually in the supporting electrolyte. For  $\text{H}_2\text{O}_2$  and the surfactant, no electrochemical activity was observed in the range of potential analyzed ( $-0.4$  to  $1.0$  V vs.  $\text{Ag}/\text{AgCl}/\text{Cl}^-$ ). For catechol, a pair of quasi-reversible peaks corresponding to the transfer of two electrons was observed, reflecting the transformation of catechol into *o*-benzoquinone (Fig. 5) [20,21]. The addition of  $\text{Fe(II)}$  provokes an increase in the anodic and cathodic currents of catechol (Fig. 5), indicating a catalytic effect. This is suggestive of the presence of

$\text{Fe(III)}$  and of its participation in a cyclic process that regenerates quinone before the second electron transference (corresponding to an “ECE” mechanism). Quinone can be generated in two ways, i.e., via the two electron oxidation of catechol on the surface of the electrode and via the oxidation of catechol by  $\text{Fe(III)}$ . Similar behavior has been observed for the oxidation of 2,3-dihydroxybenzoic acid in the presence of  $\text{Cu(II)}$  [22].

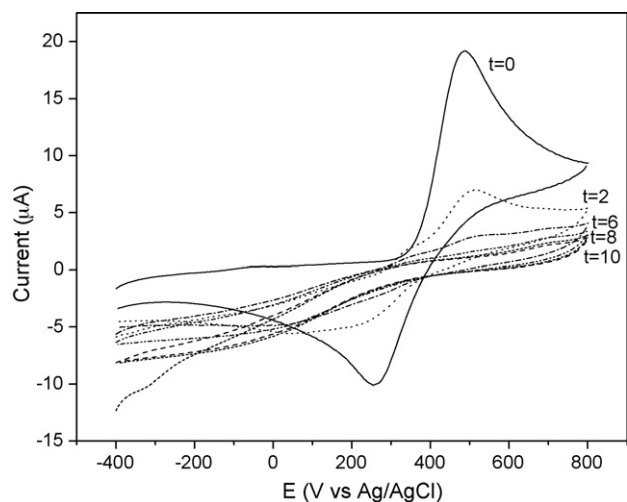
The addition of  $\text{H}_2\text{O}_2$  to a medium containing 0.5 mM catechol and 0.5 mM  $\text{Fe(II)}$  results in a significant increase in the cathodic current that can be associated with the reduction of the  $\text{O}_2$  that is generated as a by-product of the Fenton reaction [22,23]. At the same time, the addition of  $\text{H}_2\text{O}_2$  causes a steady decrease in the anodic peak corresponding to the catechol–quinone redox reaction (Fig. 6); this peaks eventually disappears completely upon total oxidation of all of the catechol initially present. Cyclical voltammograms were also registered *in situ* in the reactor during the degradation of DowFax™ 2A1 by the Fenton reaction under the same conditions employed for the TOC and product studies. Hydrogen peroxide was added at the same rate as in these other reactions and by 8 min, at which time the total added concentration of  $\text{H}_2\text{O}_2$  was ca. 30 mM, all of the catechol initially present had been oxidized, as indicated by the fact that the anodic and cathodic peaks of catechol were no longer observable (Fig. 7).



**Fig. 5.** Cyclic voltammograms of 0.5 mM catechol in 0.5 M  $\text{Na}_2\text{SO}_4$ , pH 3.0, in the: a, absence  $\text{Fe(II)}$ ; b–e, 0.50, 1.0, 1.5 and 2.0 mM  $\text{Fe(II)}$ , respectively.  $A = 0.031$   $\text{cm}^2$ ; scan rate 50  $\text{mV s}^{-1}$ .



**Fig. 6.** Cyclic voltammograms of 0.5 mM catechol and 0.5 mM  $\text{Fe(II)}$  in 0.5 M  $\text{Na}_2\text{SO}_4$ , pH 3.0 in the: a, absence  $\text{H}_2\text{O}_2$ ; b–e, 50, 100, 150 and 200 mM  $\text{H}_2\text{O}_2$ , respectively.  $A = 0.031$   $\text{cm}^2$ ; scan rate 50  $\text{mV s}^{-1}$ .

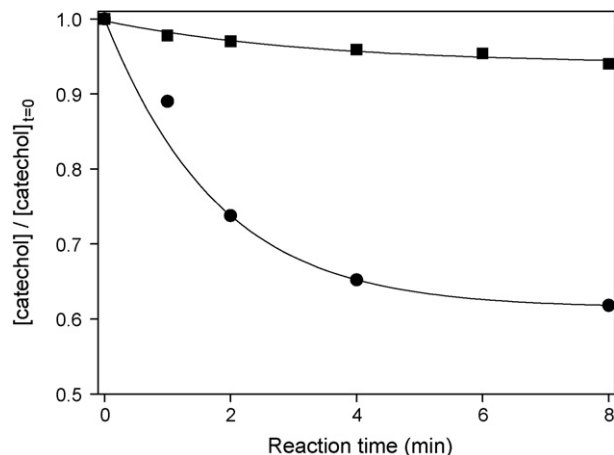


**Fig. 7.** Cyclic voltammograms registered *in situ* in the Fenton reaction reactor at function of reaction time. The solution contained 0.5 mM catechol, 200 ppm C of the surfactant and 0.5 mM Fe(II) at pH 3.0.  $\text{H}_2\text{O}_2$  was added continuously during the reaction (final net added concentration 30 mM).

These electrochemical results are consistent with the results for the disappearance of the surfactant in the same system (*vide supra*, Fig. 4), which show that the catalytic effect of catechol occurs primarily in the early stages of the reaction. However, the results in Fig. 4 suggest that the initial catalytic phase of the reaction continues for a certain period of time (up to ca. 20 min) even after all of the added catechol has been consumed. As in the case of the Fenton degradation of phenol, where one of the major initial reaction products is catechol, degradation of the surfactant can, and probably does result in the formation of hydroxyaromatic compounds that are also capable of promoting the Fe(III)/Fe(II) redox cycle.

### 3.3. Mechanistic aspects of the Fenton degradation in the presence of catechol

The present results confirm that catechol indeed exerts a catalytic effect on the degradation of the anionic surfactant DowFax™ 2A1, reflecting the acceleration of the Fe(III) to Fe(II) conversion by the catechol/*o*-benzoquinone redox pair. However, this catalytic effect is restricted to the early stages of the reaction due to the relatively fast degradation of catechol itself. In this regard, the observed minimum in the efficiency of the Fenton reaction as a function of hydrogen peroxide concentration in the presence of catechol (inset, Fig. 1B), which is not observed in the absence of catechol (Fig. 1A), is potentially significant. Although inhibition of Fenton reactions at high hydrogen peroxide concentrations is typically ascribed to competitive reaction of hydrogen peroxide with the hydroxyl radical (Eq. (2)), this clearly cannot be the case in our system since no such inhibition occurs in the absence of catechol. The important factor here appears to be the rapidity of the degradation of catechol in the early stages of the reaction, resulting in the formation of non-electroactive, non-aromatic products, such as oxalic acid, that can complex with Fe(III) but are incapable of reducing Fe(III) back to Fe(II). Complexation of Fe(III) by, for example, oxalic acid might be expected to prevent its reduction back to Fe(II) and, as a consequence, strongly inhibit the Fenton reaction [5]. This is indeed confirmed by the results shown in Fig. 8, which clearly demonstrate that the disappearance of catechol (initially 0.5 mM) is strongly inhibited by the addition of oxalic acid (1.0 mM) under conventional thermal Fenton reaction conditions. This stabilization of Fe(III) by oxalic acid or, potentially, by



**Fig. 8.** Degradation of catechol (0.5 mM) in the absence (●) and presence (■) of 1.0 mM oxalic acid; [Fe(II)] = 0.5 mM; pH 3.0.  $\text{H}_2\text{O}_2$  was added continuously during the reaction (final net added concentration 24 mM).

other aliphatic carboxylic acids formed as degradation products [5] would nicely explain the decreased efficiency of the Fenton reaction at high hydrogen peroxide concentrations observed in the presence of catechol. Thus, at progressively higher hydrogen peroxide concentrations, there is a correspondingly faster conversion of catechol into degradation products that can complex with Fe(III). In contrast, in the absence of catechol, the degradation of DowFax™ 2A1 is much slower and the rate of production of degradation products capable of stabilizing Fe(III) correspondingly much slower, leading to a monotonic dependence of the mineralization rate on  $\text{H}_2\text{O}_2$  concentration.

## 4. Conclusions

Normally, the rate limiting step in Fenton reactions at low added Fe(II) concentrations is the very slow  $\text{H}_2\text{O}_2$ -mediated reduction of Fe(III) back to Fe(II). The addition of catechol accelerates the initial rate of oxidation of the anionic surfactant DowFax™ 2A1 by the Fenton reaction and increases the overall efficiency of mineralization. However, the rate acceleration is transitory and the efficiency of mineralization decreases at higher  $\text{H}_2\text{O}_2$  concentrations. The rate acceleration in the early stages of the reaction is ascribed to catechol-mediated redox cycling of Fe(III) back to Fe(II), which is much faster than the corresponding  $\text{H}_2\text{O}_2$ -mediated reaction. However, the rapid competitive oxidation of catechol, especially at high added  $\text{H}_2\text{O}_2$  concentrations, results in the formation of degradation products like oxalic acid that strongly complex Fe(III) and block its reduction back to Fe(II). This appears to be responsible for the observed decrease in the mineralization efficiency at high  $[\text{H}_2\text{O}_2]$ . Further investigations of the mechanistic details of the catechol-mediated redox cycling process, which should permit further enhancements of the rate and efficiency of this process, are currently in progress in our laboratories.

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