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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 dodecyldiphenyloxide disulfonate) under conventional Fenton reaction conditions (Fe(II) plus H_2O_2 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^{-1} 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.

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 ($HO^\bullet$), 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_2O_2, which is reduced in the process to the hydroxide ion and a hydroxyl radical (Eq. (1)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \quad k_1 = 76\,M^{-1}\,s^{-1} \tag{1}$$

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_2O_2 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_2) also can act as the electron acceptor, being reduced by the semiquinone radical to superoxide/hydroperoxide radicals, $O_2^{\bullet-}/HO_2^\bullet$, that can be converted into H_2O_2. 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*-hydroxylbenzoic acid > *m*-hydroxylbenzoic 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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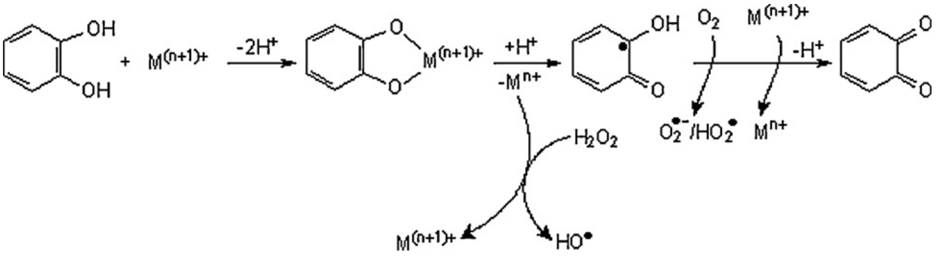


Scheme 1. Catechol oxidation by transition metals (M = Fe or Cu) and formation of $HO^{\bullet}$ as proposed by Aguiar et al. [9].

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 Fe (III) to Fe (II).

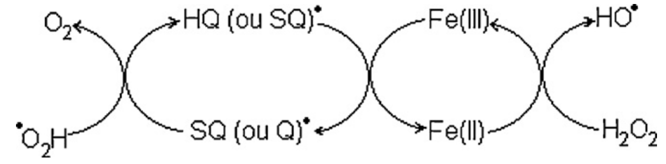
Although degradation of surfactants via the conventional Fenton reaction is well-known (e.g., [1]), we could find no reports of surfactant degradation via a catechol-accelerated Fenton reaction. In the present work, therefore, we report an investigation of the acceleration of the Fenton degradation and mineralization of DowFax^{TM} 2A1 by added catechol. The anionic surfactant DowFax^{TM} 2A1 (sodium dodecyldiphenyloxide 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^{TM} 2A1 (furnished as a 45% solution in water) was kindly provided by Dow Brazil, São Paulo. Hydrogen peroxide (30%) and the inorganic salts $FeClO_4$ were obtained from Synth (Labsynth, Brazil) and H_2SO_4 and 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 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 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^{TM} 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 × 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^{TM} 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^{TM} 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 H_2O_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 $Ag/AgCl/Cl^-$ as the reference electrode. A solution of 0.50 M aqueous Na_2SO_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 Fe(II) and H_2O_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.



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

3. Results and discussion

3.1. Degradation efficiency

The efficiency of the Fenton reaction for the complete degradation of the anionic surfactant DowFax^{TM} 2A1 (initial concentration 250 ppm of organic carbon) was determined as a function of the total added concentration of H_2O_2 in the absence (Fig. 1A) and presence (Fig. 1B) of catechol. In both cases, H_2O_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 H_2O_2 or with the resultant product, the hydroperoxyl radical [5]. Fig. 2 shows the temporal variation of the net concen-