

# The effect of a catechol chelator as a redox agent in Fenton-based reactions on degradation of lignin-model substrates and on COD removal from effluent of an ECF kraft pulp mill

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## Abstract

We evaluated the effect of a catechol chelator as a redox agent in Fenton-based reactions (known as chelator-mediated Fenton reaction—CMFR), in the presence of three different transition metals ions ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ ) by determining the oxidative capability of CMFR towards lignin-model substrates. The potential application of mediated Fenton-based reactions as a novel process to treat pulp mill effluent was evaluated and monitored by chemical oxygen demand (COD) and total phenol removals from a combination of the effluents generated during an ECF bleaching stage. The catechol chelator 3,4-dihydroxyphenylacetic acid (DOPAC) reduced both  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , in addition, the maximum  $\text{Cu}^{2+}$  reduction activity was reached in a shorter time than for  $\text{Fe}^{3+}$  reduction, however, the highest metal reduction activity was observed with  $\text{Fe}^{3+}$ . When DOPAC was added to Fenton-based reactions ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{Cu}^{2+}/\text{H}_2\text{O}_2$ ) an increase in oxidative activities of these reactions were found as they resulted in great degradation improvement of the lignin-model substrates azure B, phenol red and syringaldazine. The same increase in oxidative capability of Fenton-based reactions in the presence of DOPAC was observed after effluent treatment, expressed by the increase in COD removal, namely, an increase in the range of about 70% in COD removal when  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  was the catalytic metal and about 25% for  $\text{Cu}^{2+}$ . However CMFR lead to an increase in total phenol content. As COD removal by CMFR system using  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was not significantly different and that  $\text{Fe}^{3+}$  ions promoted lesser increase in total phenol content,  $\text{Fe}^{3+}$  was chosen for experimental optimization. At optimum conditions, 75% of COD and 30% of total phenol removal were achieved.

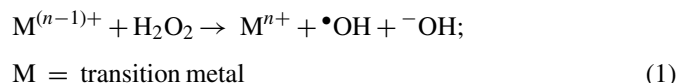
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**Keywords:** Catechol; Transition metal; COD; ECF kraft effluent; Chelator-mediated Fenton reaction

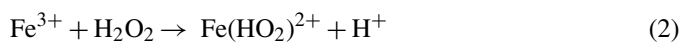
## 1. Introduction

A powerful method for remediation of wastewater is chemical oxidation, in which reactive chemical species such as the hydroxyl radical ( $\bullet\text{OH}$ ) is generated in aqueous solution. The hydroxyl radical is often chosen because it is a non-specific oxidant that reacts with most organic compounds at near diffusion-limited rates. A common source of  $\bullet\text{OH}$  is the catalytic decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) by soluble ferrous iron ( $\text{Fe}^{2+}$ ) at low pH (2–3), known as Fenton reaction, which results in the near-stoichiometric generation of  $\bullet\text{OH}$  [1].

It is well known that other transition metals such as copper [3] can undergo Fenton-based reaction as the following general equation (Eq. (1)):



Moreover, the newly formed oxidized metal (or if it is originally presented in the system) also undergoes Fenton reactions, as the reduced metal can be slowly generated as shown for  $\text{Fe}^{2+}$  in the following simplified equations (Eqs. (2) and (3)) [2]:



The major advantage of Fenton process is that highly complicated apparatus and pressurized systems are not required for the

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oxidation process [4], besides the fact that iron is very abundant and non-toxic and  $\text{H}_2\text{O}_2$  is safe to handle and to the environment [5,6]. All these advances make this oxidative process a feasible technology to be applied directly from laboratory to large scale [4]. Furthermore, it has been found that the degradation efficiency of Fenton reaction can be accelerated by UV light (photo-Fenton) [5,6]. On the other hand, application of Fenton oxidative process is rare in practice as the sludge produced contains high amount of iron which needs to be managed by a safe disposal method [7], the narrow effective pH range (2–3) [8,9] and costly photo-based process limit its applicability.

As an attempt to overcome this limitations, the use of catecholate-type chelator along with Fenton's reagent (referred as chelator mediated-Fenton reactions—CMFR), based on the mechanism displayed by brown-rot fungi to degrade wood contents, involving the participation of  $\text{Fe}^{3+}$ , an iron chelator (with iron reducing capability), and  $\text{H}_2\text{O}_2$  to produce  $\bullet\text{OH}$ , has recently been suggested as an alternative oxidative process [10,11], and reported to significantly increase the oxidation efficiency of Fenton and Fenton-like systems, and to perform over a wide range of pH (3–9) [10]. In this process, the catecholate compound assists in the redox cycling of iron, which then in turn enhances the production of hydroxyl radicals via Fenton chemistry, by acting as a reducing agent of  $\text{Fe}^{3+}$  originally presented or generated in the system, thus, the generation of  $\bullet\text{OH}$  by CMFR consists of a chain reaction where the iron cycles between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  as  $\text{H}_2\text{O}_2$  is consumed and the chelator is oxidized [10], producing additional  $\bullet\text{OH}$  and leading to the regeneration of the catalyst.

In two recent works, we have shown that catecholate chelator-mediated Fenton reactions not only clearly degraded cellulosic and hemicellulosic substrates and a biodegradable-resistant polymeric dye, but also significantly accelerated and increased the effectiveness of degradation reactions [10,12]. In this work, we evaluated the effect of a catecholate-type chelator in Fenton-based reactions (using three metal ions) on degradation of lignin-model substrates commonly used to determine oxidative activity of lignin-degrading enzymes, with the objective to evaluate both the effect of CMFR towards lignin and also to determine the oxidative capability of this process using different transition metals. Thereafter, these mediated reactions were used to treat a combination of effluents generated during the bleaching stage of an elemental chlorine free (ECF) kraft pulp mill. Treatment effectiveness was evaluated and monitored by chemical oxygen demand (COD) and total phenol removals.

## 2. Material and methods

### 2.1. Material

The synthetic catecholate-type chelator 3,4-dihydroxyphenylacetic acid (DOPAC) was chosen as it has previously been used as a model chelator compounds to mimetic chelator-mediated Fenton reaction systems displayed by wood decaying fungi [10].

The lignin-model substrates used in this work were the non-phenolics diammonium salt of 2,2-azinobis-3-

ethylbenzothiazoline-6-sulfonic acid (ABTS), azure B and *o*-dianisidine, and the phenolics 2,6-dimethoxyphenol (DMP), syringaldazine and phenol red. Chemical structures of substrates are shown in Fig. 1.

The ECF effluent used in this study was a combination (1:1) of the acid and alkaline effluents generated in the Oa(Ze)DP bleaching stage, obtained from a kraft pulp mill industry in the state of São Paulo, Brazil. The effluent was stored at 4 °C in glass flasks and used without filtration. The combined effluent had the following characteristics: total phenol  $54.1 \pm 3.8 \text{ mg L}^{-1}$ ; COD  $1612.5 \pm 36.8 \text{ mg L}^{-1}$ ; pH 5.6.

### 2.2. Methods

#### 2.2.1. $\text{Fe}^{3+}$ and $\text{Cu}^{2+}$ reduction activity

The ability of 3,4-dihydroxyphenylacetic acid (DOPAC) to reduce  $\text{Fe}^{3+}$  was evaluated in a reaction mixture containing 800  $\mu\text{L}$  of 50 mM sodium acetate buffer at pH 5.6, 200  $\mu\text{L}$  of 200  $\mu\text{M}$  DOPAC, 400  $\mu\text{L}$  of 1% ferrozine and 50  $\mu\text{L}$  of 20 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (freshly prepared). The volume was completed to 2 mL with distilled water. Concentrations of  $\text{Fe}^{2+}$  was determined by complexation with ferrozine ( $\epsilon_{562 \text{ nm}} = 27900 \text{ M}^{-1} \text{ cm}^{-1}$ ) [13], during 30 min.  $\text{Cu}^{2+}$  reduction was determined as described by  $\text{Fe}^{3+}$ , except that neocuproine ( $\epsilon_{454 \text{ nm}} = 7500 \text{ M}^{-1} \text{ cm}^{-1}$ ) [14] and  $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$  were used instead of ferrozine and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , respectively. Readings were made against a blank solution where chelator was replaced by distilled water.

#### 2.2.2. Degradation of lignin-model substrates

The oxidative properties of Fenton-based reactions in the presence and absence of DOPAC were determined by monitoring the oxidation of several lignin-model substrates at two pH values (3.0 and 5.6). The reaction mixture contained 0.6 mM syringaldazine (0.6 mM ABTS, 0.6 mM DMP, 0.6 mM *o*-dianisidine, 0.016 mM azure B or 0.056 mM phenol red), 100  $\mu\text{L}$  of 2 mM DOPAC, 50  $\mu\text{L}$  of 40 mM  $\text{H}_2\text{O}_2$  and 50  $\mu\text{L}$  of transition metal solution 4 mM (freshly prepared— $\text{Cu}^{2+}$  as  $\text{CuSO}_4$ ;  $\text{Fe}^{2+}$  as  $\text{FeSO}_4$  or  $\text{Fe}^{3+}$  as  $\text{FeCl}_3$ ), and the pH was adjusted with  $\text{H}_2\text{SO}_4$  or NaOH (prior to addition of metal ions and  $\text{H}_2\text{O}_2$ ). The transition metal was added last to initiate the reaction. Readings were taken after 30 min. Four controls were made (all in the presence of substrate): (i)  $\text{M}^{n+}/\text{H}_2\text{O}_2$ ; (ii)  $\text{M}^{n+}/\text{DOPAC}$ ; (iii)  $\text{M}^{n+}$ ; (iv) DOPAC. All controls were conducted at identical experimental conditions as mediated reactions. All samples were run in duplicate. Results are expressed as the average of two replicates.

#### 2.2.3. Effluent treatment

2.2.3.1. Effect of a catecholate compound in Fenton-based reactions. The treatments were carried out in an open beaker containing 5 mL of effluent, 1.2 mM DOPAC, 3.38 mM metal ( $\text{Cu}^{2+}$  as  $\text{CuSO}_4$ ;  $\text{Fe}^{2+}$  as  $\text{FeSO}_4$  or  $\text{Fe}^{3+}$  as  $\text{FeCl}_3$ ) and 134 mM  $\text{H}_2\text{O}_2$  in a final volume of 9 mL, at room temperature (25 °C) for 1 h. After treatment, effluent samples were heated in closed tube for 30 min to eliminate residual  $\text{H}_2\text{O}_2$ .

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