

# The effect of a catecholite 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

Valdeir Arantes, Adriane Maria Ferreira Milagres\*

Department of Biotechnology, Faculdade de Engenharia Química de Lorena, FAENQUIL, CP 116-12.600-970 Lorena, SP, Brazil

Received 2 March 2006; received in revised form 29 May 2006; accepted 30 June 2006

Available online 7 July 2006

## Abstract

We evaluated the effect of a catecholite 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 catecholite 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.

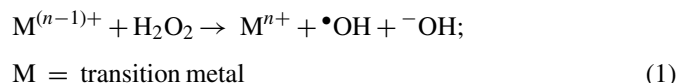
© 2006 Elsevier B.V. All rights reserved.

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

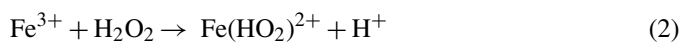
## 1. Introduction

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

\* Corresponding author. Tel.: +55 1231595000; fax: +55 1231533165.

E-mail addresses: arantes@debiq.fauenquil.br (V. Arantes), adriane@debiq.fauenquil.br (A.M.F. Milagres).

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  $\text{H}_2\text{O}_2$ .

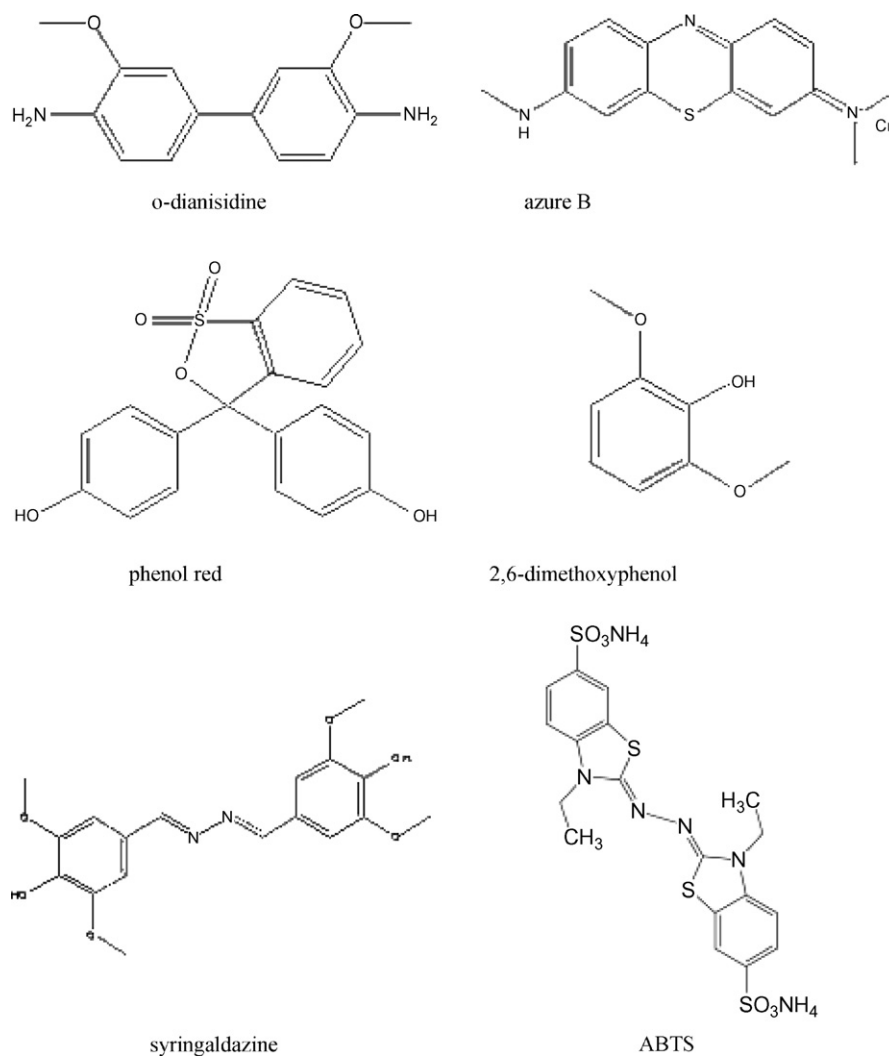


Fig. 1. Chemical structure of lignin-model substrates. Non-phenolics (2,2-azinobis-3-ethylbenzothiazoline-6-sulfonic acid, azure B and *o*-dianisidine) and phenolics (syringaldazine, phenol red and 2,6-dimethoxyphenol).

**2.2.3.2. Experimental design and statistical analysis.** To verify the influence of DOPAC, metal ( $\text{Fe}^{3+}$ ) and  $\text{H}_2\text{O}_2$  concentrations on COD and total phenol removals from the effluent, a  $2^3$  full factorial design with three repetitions at the centre point was employed (Table 1). For each of the three factors, high (coded value: +1), center (coded value: 0), and low (coded value: -1) set points were selected. Effluent treatment was carried out as described above and the data obtained were analyzed by the software STATGRAPHICS.

### 2.3. Analytical methods

The efficiency of effluent treatment was monitored by the extent of chemical degradation, measured spectrophotometrically as COD removal. Parallel to COD determination, total phenol content was also monitored by the spectrophotometric Folin–Ciocalteous method. Both determinations were carried out according to the Standard Methods for the Examination of Water and Wastewater [15].

## 3. Results and discussion

It is known that at weak acid and alkaline conditions Fenton-based reactions is generally unfavorable due to formation of metal complexes (hydrox)oxide precipitates. However, in a previously work [10] we found that CMFR displayed highly oxidative efficiency over a wide range of pH (3–9), and that this was likely due to the presence of the chelator in the reaction mixture, which would sequester the metal as soluble chelator–metal

Table 1  
Coded and level of variables chosen for the trials

Factor	Coded variable levels		
	-1	0	1
DOPAC (mM)	0	0.45	0.9
$\text{Fe}^{3+}$ (mM)	1.2	2.4	3.6
$\text{H}_2\text{O}_2$ (mM)	49.3	61.7	74.0

complex rather than forming (hydrox)oxide complexes. Therefore, in this work we have chosen to carry out all assays at pH 5.6, because this was the pH of the combined effluent without any adjustment, which is only slightly lower than the permitted limit of final effluent discharge. In addition, during the study of the oxidative capability of CMFR and Fenton-based reactions toward lignin-model substrates, experiments were also carried out at pH 3.0, which is approximately the pH commonly used to detect oxidative activity employing the substrates used in this work.

### 3.1. $Fe^{3+}$ and $Cu^{2+}$ reduction by DOPAC

It has been proposed that the enhancement of the degradation efficiency of some organic pollutants by catecholate-iron-chelators along with Fenton's reagent compared to Fenton and Fenton-like reactions is attributed to the ability of catecholate compounds to promote a redox cycling activity to continually reduce the transition metal and maintaining a high level of its reduced stage in the system, and so, permitting Fenton reactions to proceed more rapidly. In this matter, the reduction of  $Fe^{3+}$  and  $Cu^{2+}$  by DOPAC was determined, based on the formation of ferrozine- $Fe^{2+}$  and neocuproine- $Cu^{1+}$  complexes.

Reduction of both  $Cu^{2+}$  and  $Fe^{3+}$  by DOPAC followed a similar behavior as it can be seen from the reduction kinetics (Fig. 2), however, DOPAC reduced more  $Fe^{3+}$  than  $Cu^{2+}$  and both reductions were higher than the supposed stoichiometric amount. Non-stoichiometric  $Fe^{3+}$  reduction by other catecholate-type chelators have been reported and explained elsewhere [10,11,16]. In addition, as the reduction kinetic of  $Cu^{2+}$  by DOPAC was similar to the  $Fe^{3+}$  reduction kinetic, it is likely that the reduction of both transition metals follows a similar manner.

### 3.2. Degradation of lignin model substrates

The effect of DOPAC in Fenton-based reaction was evaluated by their ability to oxidize synthetic compounds commonly used to determine the oxidative activity of the major lignin-degrading enzymes – lignin peroxidase (LiP), manganese per-

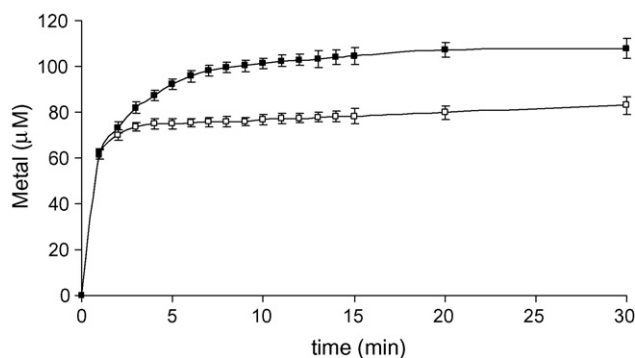


Fig. 2. Kinetics of  $Fe^{3+}$  (●) and  $Cu^{2+}$  (○) reduction by DOPAC (20  $\mu$ M) using ferrozine and neocuproine as complexing agent of the reduced stage of the transition metals, respectively.

oxidase (MnP) and laccase – produced by white-rot fungi (the only group of organisms that developed the ability to mineralize lignin to carbon dioxide).

The oxidative capability of CMFR and Fenton-based systems could not be evaluated using the substrates ABTS, *o*-dianisidine and DMP as the metal itself oxidized them. When azure B, phenol red and syringaldazine were used, the addition of DOPAC in Fenton-based reactions ( $Fe^{3+}/H_2O_2$ ,  $Fe^{2+}/H_2O_2$  and  $Cu^{2+}/H_2O_2$ ) resulted in great improvement of substrate degradation (specially for  $Fe^{3+}$  reactions) as the degradation reactions proceeded significantly more rapidly and efficiently than in the absence of DOPAC. The highest oxidation activities were detected either with  $Fe^{2+}$  or  $Fe^{3+}$  ions as catalyst (Table 2) and pH change from 3.0 to 5.6 did not seem to influence the effectiveness of DOPAC mediated Fenton reactions, as indicated by the highest decrease in absorbance for azure B and phenol red and increase for syringaldazine due to substrate degradation. In addition, no oxidative activity was detected when the assay was carried out in the presence of  $M^{n+}/DOPAC$  or only in the presence of DOPAC.

The increased oxidative activity of CMFR over Fenton-based reactions could be attributed to the formation of additional activated species, specially for the system in the presence of iron, as DOPAC has a strong  $Fe^{3+}$  and  $Cu^{2+}$  reducing activity (Fig. 2), and so, redox cycling activity would be expected by continually

Table 2

Degradation of lignin-model substrates (expressed in absorbance values) by Fenton-based reaction in the presence and absence of DOPAC

Substrates <sup>a</sup>	$\lambda_{max}$	pH	Control <sup>b</sup>	DOPAC- $M^{n+}/H_2O_2$ <sup>c</sup>			$M^{n+}/H_2O_2$ <sup>c</sup>		
				$Fe^{3+}$	$Fe^{2+}$	$Cu^{2+}$	$Fe^{3+}$	$Fe^{2+}$	$Cu^{2+}$
Azure B <sup>d</sup>	651	3.0	0.086	0.048	0.385	0.803	0.785	0.735	0.874
		5.6	0.637	0.080	0.101	0.432	0.836	0.220	0.544
Phenol red <sup>e</sup>	610	3.0	0.977	0.333	0.169	0.729	0.938	0.250	0.905
		5.6	0.832	0.177	0.277	0.790	0.786	0.334	0.789
Syringaldazine <sup>d</sup>	525	3.0	0.003	0.154	0.164	0.018	0.108	0.101	0.055
		5.6	0.003	0.269	0.204	0.033	0.218	0.116	0.015

<sup>a</sup> Substrate degradation is indicated by decrease in absorbance for Azure B and Phenol red, and by increase in absorbance for Syringaldazine.

<sup>b</sup> Control—only substrate.

<sup>c</sup>  $M^{n+}$ —transition metal.

<sup>d</sup> Non-phenolic substrate.

<sup>e</sup> Phenolic substrate.

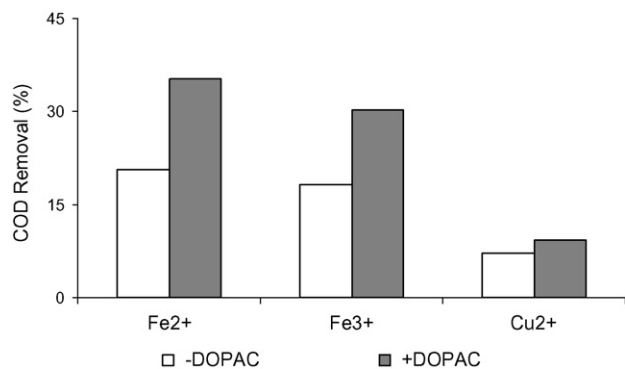


Fig. 3. Effect of DOPAC in Fenton-based reactions of three metal ions on COD removal of a kraft pulp mill effluent. [metal]=3.38 mM, [H<sub>2</sub>O<sub>2</sub>]=134 mM, [DOPAC]=1.2 mM.

reduce the metal and maintaining a high level of the reduced metal in the system, permitting Fenton-based reactions to proceed more rapidly. Although kinetic reductions of Fe<sup>3+</sup> and Cu<sup>2+</sup> by DOPAC showed to be very similar, the enhancement of lignin-model substrates degradation and also COD removal results as described below were very different between iron and copper.

### 3.3. COD and total phenol removals from a kraft effluent

Wastewaters generated by the bleaching of wood pulp are rich in organic matter, such as lignin degradation compounds and carbohydrates released during the bleaching stage, which account for the characteristic high chemical oxygen demand values. Here we show the effect of catecholate-type chelator in a Fenton-based reaction on COD and total phenol removals from an effluent of an ECF kraft pulp mill, with an initial total phenol concentration of  $54.1 \pm 3.8 \text{ mg L}^{-1}$  and high COD  $1612.5 \pm 36.8 \text{ mg L}^{-1}$ . The former likely due to phenols and polyphenolic compounds originated mainly from degradation and dissolution of residual lignin.

The results of COD removal are shown in Fig. 3. The effect of DOPAC in the systems where either Fe<sup>2+</sup> or Fe<sup>3+</sup> were the catalytic metals on COD removal was very similar, namely, an increase in the range of 70% over only Fenton-based reactions, without addition of DOPAC. When Cu<sup>2+</sup> was the catalytic metal, COD removal was also enhanced, however, this enhancement (about 25%) was comparatively lower than for Fe<sup>3+</sup> and Fe<sup>2+</sup>. These results indicate that iron species act as better catalysts than does Cu<sup>2+</sup>.

In this study, one of the possible explanations for the lower COD removal obtained with CMFR in the presence of copper would be the lower formation of oxidizing species compared to the systems in the presence of iron. Using a similar CMFR, Qian et al. [17] reported that the addition of the catecholate-type chelator 2,3-dihydroxybenzoic acid (2,3-DHBA) to Fenton-based reactions significantly enhance the formation of hydroxyl radical in the presence of iron, on the contrary, the formation of these radicals was inhibited in the presence of copper. In this way, this factor might explain why, in our study, COD removal and degradation of lignin-model substrates enhancement were

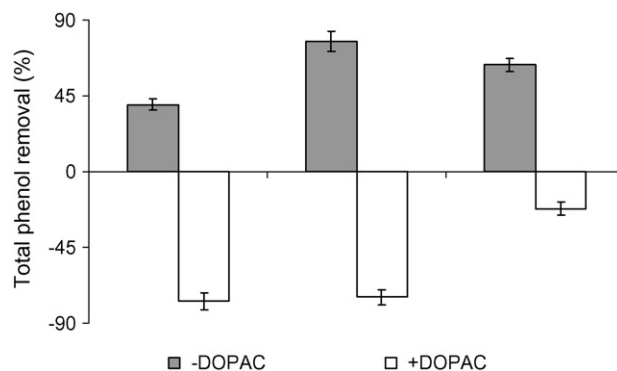


Fig. 4. Effect of DOPAC on Fenton-based reactions of three metal ions on total phenols content in the effluent. [metal]=3.38 mM, [H<sub>2</sub>O<sub>2</sub>]=134 mM, [DOPAC]=1.2 mM.

very low when copper was used as catalyst, as shown in Fig. 3 and Table 2.

The results of total phenols determinations are shown in Fig. 4. Differently from the effect observed in COD determinations, total phenols content in the effluent increased about 90% when it was treated by Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> and about 20% by Cu<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> in the presence of DOPAC. Considering that DOPAC is a dihydroxybenzene-type compound, it is expected that it would also react positively with the Folin phenol reagent if some amount of DOPAC remains in the reaction mixture after the reaction period, increasing the total phenols values. Although Folin–Ciocalteu phenol reagent has been widely used for the determination of phenolic and polyphenolic compounds in wastewaters, a number of substances that reacts with Folin phenol reagent, and so interferes in total phenol determination has been reported [18]. Among them there are a wide range of aromatic substances, such as catechol, hydroquinone, hydroxybenzoic acid, benzoic acid and benzoquinone [18]. In addition, semiquinone and benzoquinone are the likely intermediated compounds formed during reduction of transition metals by dihydroxybenzenes, which will also react positively with Folin assay, increasing total phenol content.

These factors may be the main reasons that account to the increase in total phenol content, however another factor, that may also explain in part the increase in total phenol content could be the addition of •OH to the lignin derivatives compounds presented in the effluent, considering that •OH can attack organic molecules by abstracting hydrogen from aliphatic structures or by adding as an electrophile to aromatic ones. Studies with lignin-model compounds indicate that when •OH adds to aromatic rings, hydroxylated cyclohexadienyl radical is formed and that this oxidized intermediate is more likely to decay to other products in which the aromatic ring becomes hydroxylated [19]. For example, when •OH addition occurs at unsubstituted ring positions, the radical is further oxidized and loses a proton to introduce a new phenolic hydroxyl group [19].

However, how to explain the increase in the total phenol content only when DOPAC was added to Fenton-based reactions? In the system with DOPAC it is expected that more reactive radicals would be generated, and this fact may be one of the reasons why total phenol content increased; that is, in presence of higher •OH

concentration, the organic matter present in the effluent would be oxidized to a higher extent, for example by the addition of  $\bullet\text{OH}$  to the rings, lowering the COD values (as shown in Fig. 3) and on the other hand, increasing the total phenol content. It has also to be considered that pulp and paper mill effluents are also characterized by a high molecular mass fraction, and as the oxidation process goes on, more low molecular mass compounds would be produced in the system, consequently, more sites where  $\bullet\text{OH}$  could be added would be generated.

### 3.4. Optimization of COD and total phenol removals

Considering that COD removal by CMFR using  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  were not significantly different, that the systems with  $\text{Fe}^{3+}$  ions promoted lower increase in total phenols content than  $\text{Fe}^{2+}$  and also that various methods have been introducing the rather cheap  $\text{Fe}^{3+}$  salts to  $\text{Fe}^{2+}$  [20]  $\text{Fe}^{3+}$  was chosen as the catalytic metal for further experimental evaluation, which aimed to better evaluate the effect of DOPAC in Fenton-based reactions based on both COD and total phenol removals by using statistical analyses. The design matrix of the variables in both natural and coded values along with COD and total phenol removals are shown in Table 3 and the estimated effect of each factor and their interactions are in Table 4.

From Table 3, it is clear that COD removals were higher than total phenol removals, and from Table 4 that all three factors studied, DOPAC,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  concentrations seem to have played a critical role in both COD and total phenol removals. It can be seen for COD removal that the coefficients for the linear effect  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ , the quadratic effect of DOPAC and the interactive effect of DOPAC and  $\text{H}_2\text{O}_2$  were significant. On the other hand, for total phenol removal the significant coefficients for the linear effect were DOPAC and  $\text{H}_2\text{O}_2$ , and the interactive effect was DOPAC and  $\text{H}_2\text{O}_2$ . Both models representing COD and total phenol removals showed statistically insignificant lack of fit ( $p > 0.05$ ), however only for COD removal a good deter-

Table 4

Estimated effects,  $F$  and  $p$  values for COD and total phenol removals

Factor	COD removal		Total phenol removal	
	Coefficient	$p > F$	Coefficient	$p > F$
Average	61.54	–	0.24	–
$x_1$	–4.6	0.3312	–120.8	0.0012
$x_2$	13.4	0.0188	–9.6	0.6899
$x_3$	15.6	0.0095	78.0	0.0118
$x_1^2$	–47.873	0.0008	33.7	0.4750
$x_2^2$	–7.873	0.3858	–24.3	0.6022
$x_3^2$	3.126	0.7242	–60.3	0.2181
$x_1 \cdot x_2$	–0.25	0.9609	1.0	0.9702
$x_1 \cdot x_3$	12.25	0.0418	73.0	0.0255
$x_2 \cdot x_3$	3.25	0.5305	9.5	0.7237

mination coefficient was determined (COD,  $R^2 = 0.9231$ ; total phenol,  $R^2 = 0.8243$ ).

Fig. 5 is the response surface plot and shows both COD and total phenol removals over independent variables DOPAC and  $\text{H}_2\text{O}_2$  when concentration of the metal is kept constant. From COD removal plot, it can be seen a degree of curvature due to the squared term of DOPAC. COD removal increased (75%) as DOPAC concentration increased to its central point (0.45 mM). Thereafter, it decreases as the DOPAC concentration increases. Recently, we have reported a similar observation when this oxidative system was employed to decolorize the biodegradable-resistant polymeric dye Poly R-478 [10]. From total phenol removal plot, a reverse effect in the presence of DOPAC was observed, as total phenol removal decreased as DOPAC concentration increased, however, at the optimum conditions for COD removal (75%), about 30% of total phenol removal was achieved. The application of response surface methodology showed that the optimum point for COD and total phenol removals were obtained under the following conditions: [DOPAC] = 0.45 mM; [ $\text{Fe}^{3+}$ ] = 3.6 mM and [ $\text{H}_2\text{O}_2$ ] = 74.0 mM.

Table 3  
Matrix and results of a  $2^3$  full factorial design with center point

Run no.	Actual values			Coded values			Removal (%)	
	DOPAC (mM)	$\text{Fe}^{3+}$ (mM)	$\text{H}_2\text{O}_2$ (mM)	DOPAC	$\text{Fe}^{3+}$	$\text{H}_2\text{O}_2$	COD	TPC
1	0	1.2	49.3	–1	–1	–1	34	49
2	0.90	1.2	49.3	+1	–1	–1	13	–88
3	0	3.6	49.3	–1	+1	–1	41	30
4	0.90	3.6	49.3	+1	+1	–1	31	–104
5	0	1.2	74.0	–1	–1	+1	25	56
6	0.90	1.2	74.0	+1	–1	+1	40	–24
7	0	3.6	74.0	–1	+1	+1	50	45
8	0.90	3.6	74.0	+1	+1	+1	53	–22
9	0	2.4	61.7	–1	0	0	40	38
10	0.90	2.4	61.7	+1	0	0	30	30
11	0.45	1.2	61.7	0	–1	0	53	–4
12	0.45	3.6	61.7	0	+1	0	57	14
13	0.45	2.4	49.3	0	0	–1	46	–45
14	0.45	2.4	74.0	0	0	+1	75	20
15	0.45	2.4	61.7	0	0	0	63	–30
16	0.45	2.4	61.7	0	0	0	67	–1
17	0.45	2.4	61.7	0	0	0	65	–16

TPC: total phenol content.

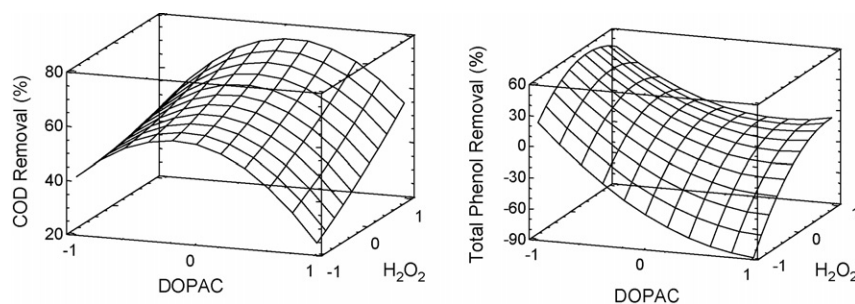


Fig. 5. Response surface plot of the effect of [DOPAC] and [H<sub>2</sub>O<sub>2</sub>] holding constant Fe<sup>3+</sup> (0.338 mM) on COD and total phenol removals.

#### 4. Conclusion

The results presented here indicate that DOPAC increases significantly the oxidative activity of Fenton-based reactions (H<sub>2</sub>O<sub>2</sub> and transition metal, specially iron), as observed by the oxidation of phenolic and non-phenolic synthetic compounds and ECF kraft pulp mill effluent, on the other hand, the same effect was not observed for total phenol removal as an increase was detected when DOPAC was added to Fenton-based reactions. Statistical analysis showed that DOPAC concentration is crucial for both COD and total phenol removals. Moreover, considering the wood biodegradation process our results of phenolic and non-phenolic substrates degradation contribute to better understand the CMFR as a nonenzymatic process that brown-rot fungi use to modify lignin in wood.

#### Acknowledgment

This research has been supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP Proc. 04/12080-0).

#### References

- [1] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [2] C. Walling, A. Goosen, Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide: effects of organic substrate, *J. Am. Chem. Soc.* 95 (1973) 2987–2991.
- [3] L. Pecci, G. Montefoschi, D. Cavallini, Some new details of the copper-hydrogen peroxide interaction, *Biochem. Biophys. Res. Commun.* 235 (1997) 264–267.
- [4] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere* 55 (2004) 1235–1243.
- [5] E.G. Solozhenko, N.M. Soboleva, V.V. Goncharuk, Decolorization of azo dye solutions by Fenton's oxidation, *Water Res.* 29 (1995) 2206–2210.
- [6] L.A. Pérez-Estrada, M.I. Maldonado, W. Gernjak, A. Agüera, A.R. Fernández-Alba, M.M. Ballesteros, S. Malato, Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale, *Catal. Today* 101 (2005) 219–226.
- [7] S. Meriç, D. Kaptan, T. Ölmez, Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, *Chemosphere* 54 (2004) 435–441.
- [8] M. Cheng, W. Ma, J. Li, Y. Huang, J. Zhao, Visible-light-assisted degradation of dye pollutants over Fe(III)-loaded resin in the presence of H<sub>2</sub>O<sub>2</sub> at neutral pH values, *Environ. Sci. Technol.* 38 (2004) 1569–1575.
- [9] W. Chu, C.K. Law, Treatment of trichlorophenol by catalytic oxidation process, *Water Res.* 37 (2003) 2339–2346.
- [10] V. Arantes, C. Baldocchi, A.M.F. Milagres, Degradation and decolorization of a biodegradable-resistant polymeric dye by chelator-mediated Fenton reactions, *Chemosphere* 63 (2006) 1764–1772.
- [11] B. Goodell, J. Jellison, J. Liu, G. Daniel, A. Paszczyński, F. Fekete, S. Krishnamurthy, L. Jun, G. Xu, Minireview: low molecular weight chelators and phenolic compounds isolated from wood decay fungi and their role in the fungal biodegradation of wood, *J. Biotechnol.* 53 (1997) 133–162.
- [12] V. Arantes, A.M.F. Milagres, Degradation of cellulosic and hemicellulosic substrates using a chelator-mediated Fenton reaction, *J. Chem. Technol. Biotechnol.* 81 (2006) 413–419.
- [13] L.L. Stookey, Ferrozine—A new spectrophotometric reagent for iron, *Anal. Chem.* 42 (1970) 779–781.
- [14] G. Johnson, N. Nazhat, R. Saadalla-Nazhat, Reaction of the aquacopper (I) ion with hydrogen peroxide, *J. Chem. Soc. Faraday Trans. 1* (1988) 501–510.
- [15] A.E. Greenberg, R.R. Trusell, L.S. Clesceri, *Standard Methods for the Examination of Water and Wastewater* (APHA), 17th ed., American Public Health Association, Washington, DC, 1989.
- [16] J. Pracht, J. Boenigk, M. Isenbeck-Schröter, F. Keppler, H.F. Schöler, Abiotic Fe(III) induced mineralization of phenolic substrates, *Chemosphere* 44 (2001) 613–619.
- [17] Y. Qian, B. Goodell, J. Jellison, C.C. Felix, The effect of hydroxyl radical generation on free-radical activation of TMP fibers, *J. Polym. Environ.* 12 (2004) 147–155.
- [18] J.D. Box, Investigation of the Folin–Ciocalteu phenol reagent for the determination of polyphenolic substances in natural waters, *Water Res.* 17 (1983) 511–525.
- [19] K.E. Hammel, A.N. Kapich, K.A. Jensen Jr., Z.C. Ryan, Reactive oxygen species as agents of wood decay by fungi, *Enzyme Microb. Technol.* 30 (2002) 445–453.
- [20] C. Minero, M. Lucchiari, D. Vione, V. Maurino, Fe(III)-enhanced sonochemical degradation of methylene blue in aqueous solution, *Environ. Sci. Technol.* 29 (2005) 8936–8942.