Comparison of the chemical precipitation, UV/H$_2$O$_2$ and Fenton processes to optimize removal of chronic toxicity from kraft mill effluents

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ABSTRACT

Secondary Treatment Effluents (STE) from Kraft mill effluents are discharged into aquatic ecosystems with high color and chronic toxicity contents owing to the recalcitrance of compounds in the effluents. The goal of the study was to evaluate the chemical precipitation, UV/H$_2$O$_2$, and the Fenton processes (H$_2$O$_2$/Fe^{2+}) for chemical oxygen demand (COD) and for removing chronic toxicity from STE. A circumscribed central composite model and a response surface methodology were used to evaluate the effects of variables such as Al$_2$(SO$_4$)$_3$, Fe(II), and H$_2$O$_2$ concentration and pH range for each treatment. The optimal conditions were 984.2 mg Al$_2$(SO$_4$)$_3$/L and pH 5.2 for chemical precipitation; 51.4 mM H$_2$O$_2$ and pH 5.1 for UV/H$_2$O$_2$; and 5.5 mM Fe(II): 25 mM H$_2$O$_2$ concentration and pH 2.8 for H$_2$O$_2$/Fe^{2+}. Under such optimal conditions, COD removal was 84.7, 80.0, and 93.6%, with reaction times of 57, 75, and 10 min for the chemical precipitation, UV/H$_2$O$_2$, and H$_2$O$_2$/Fe^{2+} methods, respectively. This study recorded chronic toxicity in STE and sludge formed during chemical precipitation with maximum reductions in percentages of Allometric Growth Rate (AGR) of 11.5 for STE without dilution (100%, $p < 0.05$). For chemical precipitation sludge, the maximum reduction of AGR was 3.4% for a dilution of 75%. We concluded that all the assessed treatments effectively removed chronic toxicity in the treated effluents.

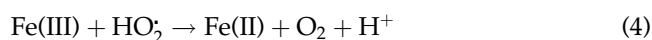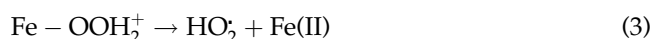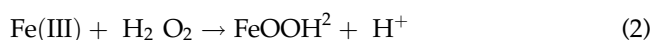*Keywords:* AOPs; COD; Chemical precipitation; Chronic toxicity; Kraft mill effluents

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1. Introduction

Kraft mill effluents require primary treatment to remove suspended solids (80–90%) and secondary treatment for organic matter measured as biological oxygen demand, (BOD$_5$) and COD (chemical oxygen demand). Secondary treatment removes BOD$_5$ and COD in the ranges of 73–99% and 30–50%, respectively [1–3]. However, some refractory compounds have been found even after secondary treatment (aerated lagoon, activated sludge). For example, phytosterols have been found in concentrations ranging between 0.01 and 3.4 mg/L [4]. Xavier et al. [5] reported phytosterols removal of between 41 and 99% after activated sludge treatment, although the removal mechanism is not well understood. Phytosterols can be absorbed by sludge due to hydrophobic affinity (log $K_{ow} > 6$) and has been identified as a potential source of chronic toxicity expressed as estrogenic activity in exposed organisms [6,7]. The estrogenic effects of these effluents have been evaluated in invertebrates, such as *Daphnia magna*, and effects on growth, reproduction and development of sex characteristics have been found [7,8], although Chamorro et al. [4] reported removing between 80 and 83% of estrogenic activity after Moving Bed Biofilm Reactor (MBBR) treatment.

In order to remove potential sources of chronic toxicity from STE, post-treatment is needed. Currently, chemical precipitation treatment based on the addition of coagulants is mainly used in the industry, accounting for 90–96% color removal. However after chemical precipitation, there are several refractory compounds remaining in solution [9]. Advanced Oxidation Processes (AOPs) could be used as an alternative tertiary treatment [10]. In the last decade, AOPs have been used as efficient methods for transforming pollutants, based on the *in situ* generation of hydroxyl radicals ($\cdot$HO) for mineralization of organic and recalcitrant compounds due to their high reduction potential of 2.8 V [11,12]. Previous studies of treating Kraft mill effluents with AOPs have mainly been focused on color removal (82–85%) and organic matter removal, with COD removal of over 60% and between 20 and 94% for TOC (Total Organic Carbon) removal using different AOPs: UV/H$_2$O$_2$, the Fenton process (H$_2$O$_2$/Fe^{2+}), UV/H$_2$O$_2$/Fe^{2+}, and O$_3$, UV/TiO$_2$ [13–15]. Although AOPs have proven highly effective, there have been few studies assessing the removal of chronic toxicity with AOP technologies. Studies have found effects on the reproduction of *Ceriodaphnia dubia*, with decrease in concentration from 19.2 to 6 UTc (UTc: concentration that could inhibit 25% of reproduction).

Among the AOPs, H$_2$O$_2$/Fe^{2+} (Fenton reaction) and UV/H$_2$O$_2$ are alternatives for tertiary treatment of Kraft mill effluents by removing potential sources of chronic toxicity. The H$_2$O$_2$/Fe^{2+} system produces $\cdot$HO by interaction of H$_2$O$_2$ with ferrous salts (Eq. (1)). Additionally, Fe(III) can react with H$_2$O$_2$ in Fenton-like reactions (Eqs. (2)–(4)) regenerating Fe(II). The advantage of this system is the low cost of reagents and the low energy demand. On the other hand, the UV/H$_2$O$_2$ system (Eq. (5)) generates $\cdot$HO by splitting hydrogen peroxide by UV radiation with concomitant energy consumption [14,16]. The main drawback of the Fenton reaction is the formation of iron sludge that ultimately requires disposal, while the UV/H$_2$O$_2$ system can be adversely affected by the high levels of turbidity found in Kraft mill effluents [12,17].

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + \cdot HO + {}^- HO \tag{1}$$

$$Fe(III) + H_2O_2 \rightarrow FeOOH^2 + H^+ \tag{2}$$

$$Fe - OOH_2^+ \rightarrow HO_2^{\cdot} + Fe(II) \tag{3}$$

$$Fe(III) + HO_2^{\cdot} \rightarrow Fe(II) + O_2 + H^+ \tag{4}$$

$$H_2O_2 + h\nu \rightarrow 2 \cdot HO \tag{5}$$

Consequently, the goal of this work was to optimize the reaction conditions of three treatments (chemical precipitation treatment, UV/H$_2$O$_2$, and H$_2$O$_2$/Fe^{2+}) to remove COD and chronic toxicity in Kraft mill effluents. Optimization was obtained with a Circumscribed Central Composite (CCC) model.

2. Experimental

2.1. Effluent

The Kraft mill effluents used in this study were obtained after secondary treatment by a local Kraft mill industry that processes *Pinus radiata* with an Elementary Chlorine Free bleaching system. The effluent was stored in darkness at 4°C ± 1 [18]. The following parameters of the effluent were characterized: COD, BOD$_5$ (biological oxygen demand), volatile suspended solids (VSS), total nitrogen (TN), total phosphorus (TP), TOC, Total phenolic compounds (UV$_{215}$), aromatics compounds (UV$_{254}$), lignin derivates (UV$_{272}$, UV$_{280}$), color (VIS$_{440}$) and chronic toxicity.

2.2. Tertiary treatments

2.2.1. Chemical precipitation

Chemical precipitation was determined in a Test Jar (VELP ScientificaFC4S) with 1 L sample and $Al_2(SO_4)_3$ as a coagulant at 20 ± 1.1℃. The experimental pH ranged from 5.0 to 6.5. The samples were stirred for 4 min at 200 rpm followed by coagulation for 8 min at 45 rpm and flocculation for 13 min at 15 rpm. The samples were allowed to settle for 30 min. The aqueous phase and solid phase were stored at 4℃ ± 1 for subsequent physicochemical analysis and toxicity tests.

2.2.2. UV/H₂O₂

Direct irradiation was applied in Petri dishes (0.2 L) with 4×8 W lamps (UVC, λ 254 nm). The radiation energy was 500 µW/cm^2 (measured with a UVX radiometer with a UV dosage of 200 kW h/m^3, Shortwave Meter UVP J—225) at a distance of 0.2 m from the lamp above the solution at $25.4 \pm 1.7°$ C, adding a H_2O_2 concentration with constant stirring. The experimental pH ranged from 3.0 to 7.0 and 75 min of reaction time.

2.2.3. H₂O₂/Fe²⁺

This treatment was performed in Petri dishes (0.2 L) using $FeSO_4 \cdot 7H_2O$ and H_2O_2 at a temperature of 19.4 ± 1.1℃ with constant stirring and protected from light. The experimental pH was 2.8, with a reaction time of 10 min.

In each experiment, pH was adjusted with NaOH (1.0 N) or HCl (1.0 N) solutions.

2.3. Optimization and response surface modeling

A CCC model (2^2) was used to optimize reaction conditions for the chemical precipitation, UV/H₂O₂, and H₂O₂/Fe²⁺ treatments, resulting in a polynomial equation and a three-dimensional representation with a response factor (Y) for COD removal. Two variables were studied for each treatment, each at two levels (high and low, or +1 and −1) and the interaction between the variables was assessed. Eleven experiments were conducted including three central points (0) to give the model statistical consistency and star point (+1.4, −1.4). Different variables were considered for each treatment: (a) $Al_2(SO_4)_3$ concentration and pH for chemical precipitation; (b) H_2O_2 concentration and pH UV/H₂O₂; (c) Fe(II) and H_2O_2 concentration for H₂O₂/Fe²⁺. Mode 7.0^{TM} software was used for data analysis and determination of the polynomial response surfaces and optimizations. Statistical validity for each treatment was determined by ANOVA with a confidence level of 95% [16].

2.4. Analytical determinations

COD, BOD₅, VSS, TSS, TN, and TP were measured according to Standard Methods [19]. TOC was determined by ANOVA kit spectrophotometer. Aromatic compounds (UV₂₅₄), lignin derivatives (UV₂₇₂, UV₂₈₀), and color (VIS₄₄₀) were determined by spectrophotometer Model Spectronic Unicam UV–visible Genesys TM Series 10 [1]. Total phenolic compounds (UV₂₁₅) concentration was measured by UV absorbance in a 1-cm quartz cell at 215 nm, pH 8.0 (0.2 M KH_2PO_4 buffer) and transformed into concentrations using a calibration curve with phenol as a standard solution. The pH level was determined with a selective electrode (Model inoLab® Level1/pH). Samples were membrane filtered through 0.45-µm pore size filters.

2.5. Chronic toxicity

Chronic toxicity was determined in Kraft mill effluents before and after tertiary treatments with female *D. Magna* (neonates < 24 h) following standard procedures for chronic toxicity bioassays [20]. Stock cultures and bioassays were maintained at 20.0 ± 1.1℃ with 16 h light: 8 h dark-photoperiods. The Daphnids were fed three times weekly with unicellular green algae *Selenastrum capricornatum* and supplemented with a baker's yeast suspension, trout chow, and alfalfa with an equivalent carbon content of 7.2 mg C/L on Mondays and Wednesdays, and 10.8 mg C/L on Fridays. To minimize test organism mortality, the ranges of dilution of Kraft mill effluents for chronic toxicity studies were established after acute toxicity testing (data not shown). Each bioassay of chronic toxicity consisted of 10 replicates of 70 mL (containing one organism) was established for each dilution, including control. The dilutions used for STE were 25, 50, and 100% (diluted with reconstituted water), while for Kraft mill effluent after tertiary treatment the dilutions were 12.5, 25, 50, and 75% (diluted with reconstituted water). Only sludge from chemical precipitation was used in bioassays [20,21]. Chronic toxicity was assessed by reproduction (neonate production) and variations in the proportions of body length to width, expressed as the percentage of the Allometric Growth Ratio (% AGR), calculated according to López et al. [7], as shown in Eq. (6).

$$AGR(\%) = \left[\left(\frac{\text{Body Length}}{\text{Body Width}} \right) - 1 \right] \times 100 \qquad (6)$$

Data obtained were processed statistically by checking the normality (χ^2 test) and homogeneity of variances (Bartlett's test). The significance of differences in reproductive parameters and allometric growth was determined by an ANOVA, followed by Tukey's test, all with the TOXSTAT statistical package [20].

3. Results and discussion

Table 1 shows the physicochemical characterization of STE. The pH values ranged from 6.9 to 7.6. The average values for COD, TOC, and BOD_5 were 268.9, 116.2, and 30.0 mg/L, respectively. The calculated biodegradability index (BOD_5/COD ratio) was low, between 0.09 and 0.13, which indicates the presence of recalcitrant organic matter in this kind of effluent [22,23]. To clarify which pollutant groups are present in STE, the specific compounds were measured by a spectrophotometer in the UV–Vis region. However, some compounds, especially saturated hydrocarbons and carbohydrates, either do not absorb or only absorb below 200 nm, and thus cannot be detected by UV spectrophotometry [2]. Total phenolic compounds concentrations were between 25.6 and 35.1 mg/L, color 2.6 (AU), concentration of 0.2-mg TSS/L and lignin derivatives (UV_{272} and UV_{280}) and aromatic compounds (UV_{254}). The values recorded in this study are consistent with other research [3,24,25]. Furthermore, the STE presented low nutrient concentrations, corresponding to 0.5 mg/L for TP, while TN concentration was below the detection limit (0.50 mg/L). The

presence of nutrient is generally related to their addition during the secondary treatment to ensure performance of micro-organisms in removing BOD_5 [24].

UV/H_2O_2 and H_2O_2/Fe^{2+} treatments were applied to remove COD to determine the minimum reaction time needed for maximum COD removal prior to the factorial experimental design (Fig. 1). The ranges used in this study for COD removal were based on previous investigations with Kraft mill effluents [14,22,26]. The experiments for UV/H_2O_2 were conducted at pH 3 and 35 mM H_2O_2, reaching a maximum at 75 min with 50.7 and 78.7% COD removed at pH 3 and 7, respectively. The H_2O_2/Fe^{2+} experiments were conducted at pH 2.8 at a concentration of 4.2 mM Fe(II) and 42.5 mM H_2O_2 (1: 10), reaching a maximum at 10 min with 74.4% COD removed. Chemical precipitation required 57 min [27].

The CCC model used to optimize the reaction conditions for chemical the precipitation, UV/H_2O_2, and H_2O_2/Fe^{2+} methods are described in Table 2. The variables chosen for chemical precipitation had ranges of 500–1,500 mg $Al_2(SO_4)_3$/L and pH 5.0–6.5. The range of variables for the UV/H_2O_2 and H_2O_2/Fe^{2+} treatments were based on the literature on the oxidation of Kraft mill effluents, and were 10.5–60 mM H_2O_2 and pH 3.0–7.0 for UV/H_2O_2 and 1.5–8.0 mM Fe (II) and 7.0–40.0 mM H_2O_2 for H_2O_2/Fe^{2+}. Columns 1 and 2 (chemical precipitation), 5 and 6 (UV/H_2O_2), and 9 and 10 (H_2O_2/Fe^{2+}) present the real and codified values (in parenthesis) for the studied variables. Columns 4, 8, and 12 indicate the factor response (COD removal) for chemical precipitation (Y_{CHP}), UV/H_2O_2 (Y_H), and H_2O_2/Fe^{2+} (Y_{FP}), respectively. Eqs. (6)–(8) present the polynomials describing the

Table 1
Physicochemical characterization of secondary treatment outlet effluent (STE)

Parameters	Unit	Range	Average
pH		6.9–7.6	7.2 ± 0.5
COD	mg/L	267.7–270.1	268.9 ± 1.7
BOD5	mg/L	25.7–34.2	30.0 ± 6.0
TOC	mg/L	112.5–120.0	116.2 ± 5.2
Total phenolic compounds (UV_{215})	mg/L	25.6–35.1	30.3 ± 6.6
Aromatics compounds (UV_{254})	abs	4.5	4.5 ± 0.0
Lignin derivates (UV_{272})	abs	2.3—2.6	2.4 ± 0.2
Lignin derivates (UV_{280})	abs	2.1—2.3	2.2 ± 0.1
Color (VIS440)	abs	2.6	2.6 ± 0.0
Total Nitrogen (TN)	mg/L	LDT	LDT
Total Phosphorus (TP)	mg/L	0.5	0.5 ± 0.0
TSS	mg/L	0.2—0.3	0.2 ± 0.0

LDT: Low detection time (<0.5).
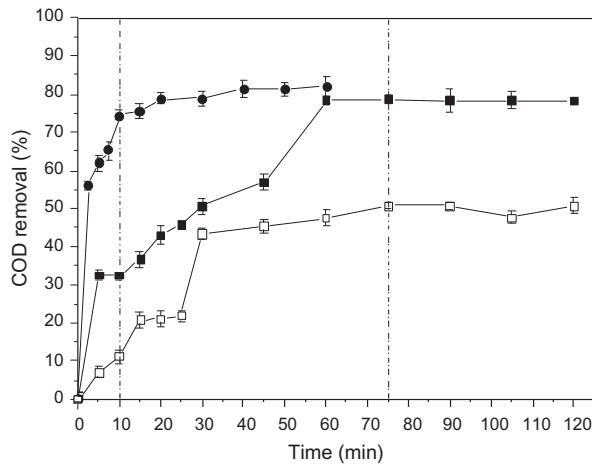
Fig. 1. COD removal kinetics in STE.UV/H_2O_2 experiment 35 mM H_2O_2: pH 7 (■) and pH 3 (□). $T = 25.4 \pm 1.7$℃ (UV dosage of 500 μW cm^{-2}). H_2O_2/Fe^{2+}experiment 4.2 mM Fe (II): 42.5 mM H_2O_2 (●). pH 2.8, $T = 19.4 \pm 1.1$℃.

response factor calculated by Mode 7.0^{TM} software. Each term in the polynomial consists of a coefficient that represents the variable's weight, a codified value of the variable, and the relative error associated with the coefficient. In the case that the relative error is greater than the coefficient, this term is not represented in the polynomial due to the lack of statistical consistency [28]. In the case of chemical precipitation, pH is the most important variable for removing COD, while $Al_2(SO_4)_3$ concentration is the least significant. For the UV/H_2O_2 and H_2O_2/Fe^{2+} systems, the most important variables are H_2O_2 and Fe(II) concentrations, respectively. Fig. 2 shows a contour diagram that represents the polynomials.

The optimal variables for maximum COD removal in the treatments were: (a) between 918.9 and 1049.4 mg of $Al_2(SO_4)_3$/L and pH 5.0–5.3 for chemical precipitation, achieving 76.3% COD removal (Fig. 2(a)) and (b) between 48.3 and 54.5 mM H_2O_2 and pH 4.6–5.6 for UV/H_2O_2, achieving 74.0% COD

Table 2
Circumscribed central composite (2^2) for chemical precipitation, UV/H_2O_2 and H_2O_2/Fe^{2+}

	Chemical precipitation				UV/H_2O_2				H_2O_2/Fe^{2+}			
Column	1	2	3	4	5	6	7	8	9	10	11	12
Run	$Al_2(SO_4)_3$ mg/L	pH	Y_{CHP} calc. %	Y_{CHP} exp. %	H_2O_2 mM	pH	Y_H calc. %	Y_H exp. %	Fe(II) mM	H_2O_2 mM	Y_{FP} calc. %	Y_{FP} exp. %
1	500(−1)	5.0 (−1)	62.6	56.8	10.5 (−1)	3.0 (−1)	34.4	35.7	1.5 (−1)	7.0 (−1)	43.0	46.1
2	1,500(+1)	5.0 (−1)	55.9	60.9	60.0 (+1)	3.0 (−1)	72.3	71.2	8.0 (+1)	7.0 (−1)	81.5	82.1
3	500(−1)	6.5 (+1)	25.9	23.8	10.5 (−1)	7.0 (+1)	55.1	56.5	1.5 (−1)	40.0 (+1)	52.7	50.4
4	1,500(+1)	6.5 (+1)	53.0	61.7	60.0 (+1)	7.0 (+1)	68.7	67.7	8.0 (+1)	40.0 (+1)	86.0	81.2
5	293(−1.4)	5.8(0)	33.0	39.3	0.3 (−1.4)	5.0(0)	32.5	30.7	0.2 (−1.4)	23.5 (0)	32.2	31.3
6	1,707 (+1.4)	5.8(0)	47.4	38.3	70.2 (+1.4)	5.0(0)	68.9	70.4	9.3 (+1.4)	23.5 (0)	82.9	85.6
7	1,000(0)	4.7 (−1.4)	72.5	73.7	35.3 (0)	2.2 (−1.4)	58.6	58.5	4.8(0)	0.2 (−1.4)	69.0	66.1
8	1,000(0)	6.8 (+1.4)	44.4	40.4	35.3 (0)	7.8 (+1.4)	70.6	70.4	4.8(0)	46.8 (+1.4)	79.1	83.9
9	1,000(0)	5.8(0)	73.2	76.8	35.3 (0)	5.0(0)	69.8	68.7	4.8(0)	23.5 (0)	82.5	80.8
10	1,000(0)	5.8(0)	73.2	73.1	35.3 (0)	5.0(0)	69.8	71.8	4.8(0)	23.5 (0)	82.5	81.7
11	1,000(0)	5.8(0)	73.2	69.8	35.3 (0)	5.0(0)	69.8	68.8	4.8(0)	23.5 (0)	82.5	85.1

Response factor: Y is defined as COD removal for Chemical precipitation (Y_{CHP}), UV/H_2O_2 (Y_H) and H_2O_2/Fe^{2+} (Y_{FP}) after 57, 75 and 10 min, respectively. Y calc.: Y calculated for software; Y exp.: Y experimental.
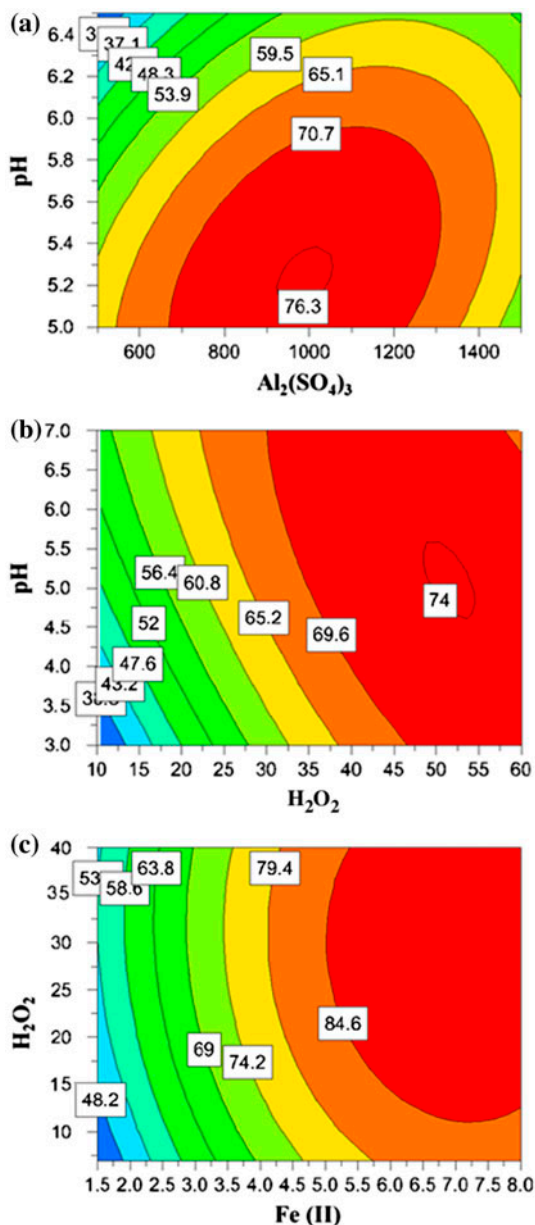
Fig. 2. Contour diagram of response surface models for (a) chemical precipitation, (b) UV/H_2O_2 and (c) H_2O_2/Fe^{2+}.

removal (Fig. 2(b)) and (c) between 10.9 and 39.7 mM H_2O_2 and 4.9–7.0 mM Fe(II) for H_2O_2/Fe^{2+}, achieving 84.6% COD removal (Fig. 2(c)). Rodrigues et al. [22] noted that the variable pH plays an important role in treating Kraft mill effluents by chemical precipitation to remove TSS, turbidity, and color. As mentioned above, Stephenson and Duff [29] determined pH ranges for different coagulants: 4.0–6.5 for $FeCl_3$, over 7.4 for $FeSO_4$, 5.0–6.0 for $AlCl_3$ and between 5.5 and 6.8 for $Al_2(SO_4)_3$, although these values depend on the characteristics of the effluent

to be treated. For UV/H_2O_2, Jamil et al. [12] indicated that ·HO generated from the direct photolysis of H_2O_2 is the main species responsible for COD removal, but noted that above 147-mM H_2O_2, it can combine with hydrogen peroxide or react with these radicals, thus inhibiting COD removal. Excess H_2O_2 or Fe(II) may be detrimental since these species can react with intermediaries like ·HO, which is responsible for the direct oxidation of organic matter [16,30]. However, according to Lucas et al. [23], the presence of Fe(II) is the main factor slowing down the H_2O_2/Fe^{2+} process because the regeneration of Fe(II) from Fe(III) is slower that the consumption of ferrous iron [17]. Consequently, the typical range for H_2O_2/Fe^{2+} reactants is about 1 part Fe(II) per 5–25 parts H_2O_2.

$$Y_{CHP} = 73.2(\pm 4.5) + 5.1[Al_2(SO_4)_3](\pm 2.7) \\ - 9.9[pH](\pm 2.7) - 16.4[Al_2(SO_4)_3]^2(\pm 3.3) \\ - 7.3[pH]^2(\pm 3.3) + 8.4[Al_2(SO_4)_3][pH](\pm 3.8)$$

(7)

$$Y_H = 69.7(\pm 1.1) + 12.8[H_2O_2](\pm 0.6) + 4.2[pH](\pm 0.6) \\ - 9.5[H_2O_2]^2(\pm 0.7) - 2.5[pH]^2(\pm 0.7) \\ - 6.1[H_2O_2][pH](\pm 0.9)$$

(8)

$$Y_{FP} = 82.5(\pm 2.4) + 17.9[Fe(II)](\pm 1.4) + 3.5[H_2O_2](\pm 1.4) \\ - 12.4[Fe(II)]^2(\pm 1.7) - 4.2[H_2O_2]^2(\pm 1.7)$$

(9)

The mid-points of the optimal variables obtained with the contour diagram of the response surface were selected to analyze the kinetics of COD removal. Fig. 3 depicts the COD removal profile obtained with the selected optimal reaction variables for UV/H_2O_2 and H_2O_2/Fe^{2+}. In these experiments, the UV/H_2O_2 system reaches a maximum COD removal of 80% after reaction time of 75 min,51.4-mM H_2O_2 concentration and pH 5.1. For the Fenton reaction (H_2O_2/Fe^{2+}), maximum COD removal was 93.6% after a reaction time of 10 min using 5.5-mM Fe(II) and 25-mM H_2O_2. In the case of chemical precipitation, after 57 min, 84.7% of COD was removed using 984.2 mg $Al_2(SO_4)_3$/L and pH 5.2. These results are summarized in Table 3. Srivastava et al. [31] and Garg et al. [32] determined COD removal between 63 and 74% for chemical precipitation using $Al_2(SO_4)_3$ at concentrations above 2 g/L, pH 5.0, with a reaction time of 120 min. Jamil et al. [12] reported COD removal of over 50% by UV/H_2O_2 under conditions of pH 3.0 and 147.1 mM of H_2O_2 at 75 min [12]. While for H_2O_2/Fe^{2+}, COD removal is
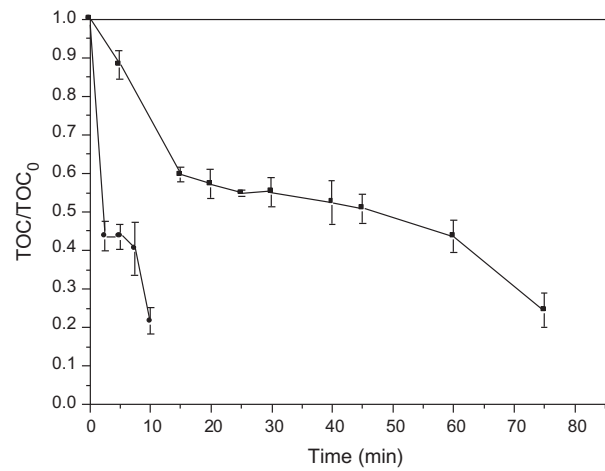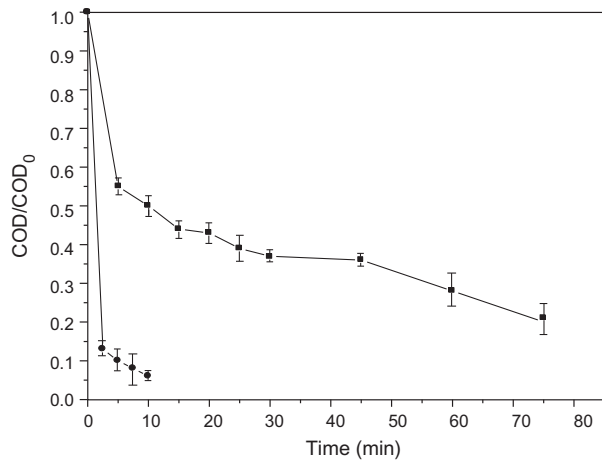
Fig. 3. COD removal with the optimal variables obtained with the Contour diagram of response surface, (■) UV/H_2O_2 system, conditions: 51.4-mM H_2O_2: pH 5.1; (●) H_2O_2/Fe^{2+} system, conditions 5.5-mM Fe(II): 25-mM H_2O_2, pH 2.8.

Fig. 4. TOC mineralization by UV/H_2O_2 (■) and H_2O_2/Fe^{2+} (●).

between 55 and 90% with 0.9–13.6 mM Fe(II) and 29.4 and 58.8-mM H_2O_2 at pH 3 [12,17]. In summary, in the present work we have improved the removal of COD using fewer reagents and shorter treatment time, thus reducing the cost of treatment.

As shown in Fig. 4, the two AOP methods reached similar levels of mineralization, with TOC/TOC$_o$ ratios of almost 80%, but with very different reaction times; 10 min for H_2O_2/Fe^{2+} and 75 min for UV/H_2O_2. These results could be because Fe(II) consumption takes only a few minutes, allowing most of the TOC to mineralize rapidly [28]. Garcia-Segura and Brillas [33] noted that the effectiveness of AOPs in mineralizing organic matter is limited by the formation of refractory carboxylic acids, such as oxalic acid. Oxalic acid is the most common byproduct of aromatic compounds in Kraft mill effluents. An Average Oxidation State (AOS) near 2.4 is characteristic of short-chain carboxylic acids, achieving a higher level of mineralization [34]. In this study, an AOS value of 1.2 was obtained by the H_2O_2/Fe^{2+} system (calculated with
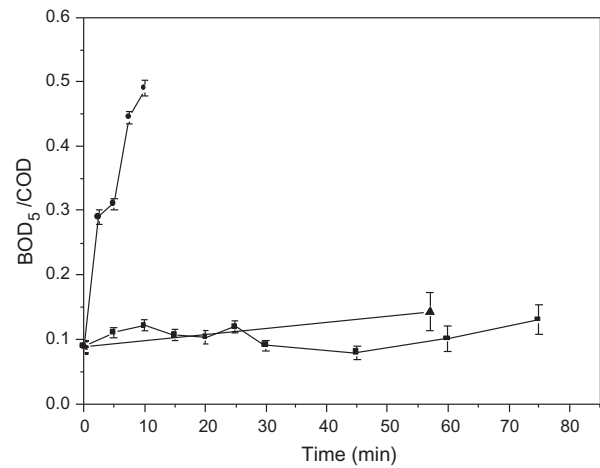

Fig. 5. Biodegradability index (BOD$_5$/COD) evolution in chemical precipitation (▲), UV/H_2O_2 (■) and H_2O_2/Fe^{2+} (●).

Table 3
Optimized values for variables and maximum COD removal for each treatment

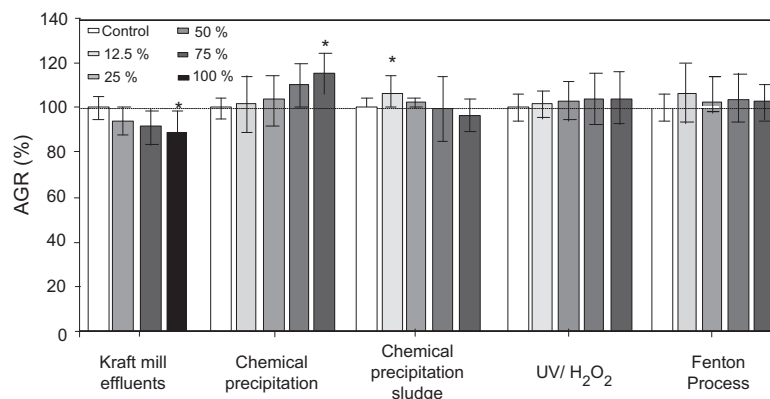| Variables	Unit	Chemical precipitation	UV/H_2O_2	H_2O_2/Fe^{2+}
pH	–	5.2	5.1	–
$Al_2(SO_4)_3$	mg/L	984.2	–	–
H2O2	nM	–	51.4	25
Fe(II)	nM	–	–	5.5
COD	%	84.7	80.0	93.6

Fig. 6. Evaluation of chronic toxicity in different effluents by *D. magna*.

Eq. (9)), indicating incomplete oxidation and probably obtaining aldehyde or keton intermediates.

Previous studies with UV/H_2O_2 have determined TOC removal rates between 8.0 and 45%, with concentrations of H_2O_2 between 25 and 50 mM and a pH of 3–11 [14,26]. In the case of H_2O_2/Fe^{2+}, TOC removal has been reported to range from 20 to 40%, with concentrations between 147.1 mM H_2O_2–294.1 mM H_2O_2, both at 1.8 mM Fe(II) and pH 3.0 [28], while Catalkaya and Kargi [14] registered TOC removal between 63.4 and 84.6%, with 5-mM Fe(II) and 50-mM H_2O_2 and a pH of 3.0–5.0. This study shows that AOPs are more efficient (in terms of TOC removal) than chemical precipitation. Chemical precipitation obtained TOC removal of 43.6%. Fig. 5 shows the biodegradability index BOD_5/COD). When the effluent was submitted to H_2O_2/Fe^{2+}, the BOD_5/COD index rapidly increased to 0.49, indicating that recalcitrant compounds in the COD decreased. In contrast, with the chemical precipitation and UV/H_2O_2 processes, the BOD_5/COD index was more or less unchanged after an hour of treatment. With AOPs, BOD_5/COD removal rates were 22.65 and 46.82% for the UV/H_2O_2 and H_2O_2/Fe^{2+} processes, respectively. In conclusion, H_2O_2/Fe^{2+} seems to be the most efficient treatment, because recalcitrant compounds are transformed into biodegradable compounds. Furthermore, Eskelinen et al. [15] and Rodrigues et al. [22] obtained BOD_5/COD ratios between 0.14 and 0.22 after chemical precipitation, whereas the UV/H_2O_2 and photocatalysis processes resulted in ratios of 0.11 and between 0.63 and 0.71, respectively, confirming the levels of refractory organic matter removal by AOPs.

$$AOS = \frac{4(TOC - COD)}{TOC} \qquad (10)$$

Although AOPs are highly effective, there have been few studies of chronic toxicity removal by these technologies. One exception is the work of Eskelinen et al. [15], who obtained phytosterol removal of over 90%, specifically for β-sitosterol and stigmastanol with 5-g CaO/L and pH 12. AOPs are a promising alternative for mineralizing recalcitrant compounds due to the high potential for ·HO reduction [11,12]. Fig. 6 shows chronic toxicity in *D. magna* obtained in this study for STE before and after tertiary treatment. López et al. [7] determined the presence of chronic toxicity by variations in length-to-width body proportions expressed as reductions in the AGR. Chronic toxicity was observed in STE with AGR reductions of between 6.1 and 11.5%, presenting significant differences with respect to the control only for undiluted STE (100%, $p < 0.05$). Furthermore, chemical precipitation sludge shows AGR reductions of 0.6 and 3.4% for dilutions of 50 and 75%. Nevertheless, the UV/H_2O_2 and H_2O_2/Fe^{2+} treatments did not register % AGR reductions and therefore are efficient in removing chronic toxicity.

López et al. [7] studied different combinations of STE (*P. radiata*, mixture *P. radiata* 50: 50% *Eucalyptus globulus*) containing added phytosterols (β-sitosterol, stigmasterol), and obtained AGR reductions of 17 and 27% at days 14 and 21, respectively. Olmstead and LeBlanc [8] found increases of 20 and 2% in body width relative to body length when *D. magna* were exposed to STE of 10 and 20%, respectively. These results may be associated with recalcitrant compounds remaining in the STE, such as phytosterols, because of which chronic toxicity has been found in effluent discharge in concentrations between 0.16 and 0.33 mg/L for β-sitosterol, 0.02–0.07 mg/L for stigmasterol, and 0.06 mg/L for campesterol [4,5]. These effluents are a potential source of chronic toxicity in aquatic

ecosystems because they are associated with particles or dissolved organic matter and sediment [35,36].

4. Conclusions

The chemical precipitation, UV/H_2O_2, and H_2O_2/Fe^{2+} methods were tested under optimal conditions for the CCC model and found to be efficient in removing COD, achieving 84.7, 80.0, and 93.6% removal with reaction times of 57, 75, and 10 min, respectively. Further, these treatments were able to remove chronic toxicity from the STE, although chronic toxicity was recorded in both treated STE and sludge formed during chemical precipitation, with maximum AGR reductions of 11.5% for undiluted STE (100%, $p < 0.05$) and reductions of 3.4% for 75% diluted STE.

Acknowledgements

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