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# AOX removal from pulp and paper wastewater by Fenton and photo-Fenton processes: a real case-study

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## Abstract

D<sub>0</sub> bleaching wastewater from *E. globulus* Kraft pulping industry was treated by Fenton and photo-Fenton processes. The aim was to optimise the operational conditions for adsorbable organic halides (AOX) removal, namely oxidant concentration, [H<sub>2</sub>O<sub>2</sub>], catalyst concentration, [Fe<sup>2+</sup>], and treatment time, using the central composite experimental design (CCED) tool. Temperature and pH were set at 60 °C and 2, respectively, which are similar to the natural values of the D<sub>0</sub> bleaching wastewater. Both processes showed potential to remove AOX from D<sub>0</sub> with 177 - 178 mM H<sub>2</sub>O<sub>2</sub> and 10 min reaction time. Maximum AOX removal was 85 % for the Fenton process with 8.5 mM Fe<sup>2+</sup>, and 95 % for the photo-Fenton process with 2.0 mM Fe<sup>2+</sup> and UV irradiance 142 W.m<sup>-2</sup>. For both methods, the only statistically significant variable (p=0.05) was the concentration of oxidant, [H<sub>2</sub>O<sub>2</sub>].

*Keywords:* AOX; Bleaching wastewater; CCED; Fenton; Photo-Fenton; Pulp and Paper industry

## 1. Introduction

Amongst the variety of potentially toxic compounds found in wastewater from pulp and paper industry (PP), possibly the most concerning ones are adsorbable organic halides (AOX) which are a family of environmentally persistent, bioaccumulative chemicals produced when the halogens react with organic matter. Reported AOX toxic effects on fish and zooplankton included respiratory stress, mixed function oxygenase activity, carcinogenicity and mutagenicity, liver damage, effect on sexual maturation and ability to reproduce, and even lethal effects (Oller et al., 2011; Pokhrel and Viraraghavan, 2004; Ranganathan et al., 2007; Savant et al., 2006).

Advanced oxidation processes (AOP) have been reported to reduce organic load, toxicity and the content of recalcitrant compounds such as AOX from wastewaters (Hermosilla et al., 2012; San Sebastián Martínez et al., 2003). Such remediation techniques involve the generation of highly reactive and non-selective hydroxyl radicals that attack the organic compounds (Babuponnusami and Muthukumar, 2014). The major drawback of AOP are the large amounts of chemical reagents and electrical energy required (Merayo et al., 2013; Pérez et al., 2002; Torrades et al., 2003).

Fenton process is a fast and effective AOP based on the catalytic (Fe<sup>2+</sup>) dissociation of the oxidant (H<sub>2</sub>O<sub>2</sub>) into hydroxyl radicals (OH<sup>•</sup>) capable of oxidizing strong organic pollutants (Babuponnusami and Muthukumar, 2014; Neyens and Baeyens, 2003; Torrades et al., 2003; Van Aken et al., 2013). The generally accepted mechanism of the Fenton reaction is well described by equations (1)-(4), as stated by Torrades et al. (2003).



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The main disadvantages of the Fenton process are the high cost associated to chemicals and the formation of an iron (oxidized) sludge that requires a management strategy and additional cost to be handled/disposed (Balabanič et al., 2012; Poyatos et al., 2010; Van Aken et al., 2013). UV light is an efficient way to improve regeneration of  $\text{Fe}^{2+}$  by photo-reduction of  $\text{Fe}^{3+}$  (equation (5)) increasing the production of  $\text{OH}^\bullet$  (Babuponnusami and Muthukumar, 2014; Poyatos et al., 2010; Torrades et al., 2003).



This variation to the conventional Fenton is known as photo-Fenton and has been reported to improve the degradation of organic pollutants while reducing the consumption of  $\text{Fe}^{2+}$ , the turbidity and the production of iron sludge (Hermosilla et al., 2012).

This work aimed to optimize the application of Fenton and photo-Fenton processes to maximize AOX removal from a real PP wastewater. Since AOX is formed essentially in the pulp bleaching stage, this work focused only on AOX removal from acidic bleaching streams before mixing with the other process wastewaters. This is a novel feature that could mean lower volumes of wastewater to treat, less chemical consumption and lower economic cost.

## 2. Materials and Methods

The wastewater was collected in a Portuguese PP industry processing *Eucalyptus globulus* Kraft pulps in a 4-stage elemental chlorine-free bleaching process ( $\text{D}_0\text{E}_p\text{D}_1\text{D}_2$ ). The wastewater from the first chlorine dioxide (D) bleaching stage,  $\text{D}_0$ , had an AOX content of  $124 \pm 12.0 \text{ mg.L}^{-1}$ .

Central composite experimental design (CCED) was used to plan the experiments aiming to assess the conditions that will yield the most desirable response (AOX removal) without performing unnecessary experiments, thus minimizing resource consumption and costs (Torrades et al., 2011, 2003).

Considering the underlying principles of the Fenton and photo-Fenton processes, the independent variables (factors) that may affect AOX removal from the  $\text{D}_0$  bleaching stream are pH, temperature,  $[\text{H}_2\text{O}_2]$ ,  $[\text{Fe}^{2+}]$  and reaction time. However, pH of the  $\text{D}_0$  bleaching stream was between 2-2.5, which falls within the optimum range reported in the literature for these processes (Babuponnusami and Muthukumar, 2014; Hermosilla et al., 2015; Poyatos et al., 2010); moreover, temperature seems to have little effect on Fenton/photo-Fenton removal efficiency (Babuponnusami and Muthukumar, 2014; Torrades et al., 2011), so the experiments were carried out at the usual temperature of  $\text{D}_0$  streams in the PP industry, i.e. at  $60 \pm 2 \text{ }^\circ\text{C}$ . Accordingly, the independent variables optimized in this work were  $[\text{H}_2\text{O}_2]$ ,  $[\text{Fe}^{2+}]$  and reaction time. The tested ranges for each factor are shown in Table 1, according to CCED methodology.

Table 1. Predefined levels of variables  $[\text{H}_2\text{O}_2]$ ,  $[\text{Fe}^{2+}]$  and treatment time (t) used in the CCED experiments for optimisation of response AOX removal (%).

Variable	-1.68	-1	0	+1	+1.68
$[\text{H}_2\text{O}_2]$ (mM)	25	70.5	137.5	204.5	250
$[\text{Fe}^{2+}]$ (mM)	1	4	8.5	13	16
t (min)	5	10	17.5	25	30
pH	$2.2 \pm 0.2$				
Temperature T ( $^\circ\text{C}$ )	$60 \pm 2$				

Experiments were performed in a quartz Peschl MPDS Basic Batch-L Photoreactor equipped with a 150W UV TQ150 lamp, using 0.5 L wastewater in each experiment.  $\text{H}_2\text{O}_2$  was used as an analytical grade 30% solution (w/v), while  $\text{Fe}^{2+}$  was used as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . After the pre-established treatment time, samples were taken from the photoreactor and sodium sulphite  $\text{Na}_2\text{SO}_3$  was immediately added for reaction quenching.

AOX quantification was performed by adsorption into activated carbon, combustion of the loaded carbon and coulometric titration, in accordance with EN 16166:2012, ISO 9562:2004 and EPA Method 1650C. For this purpose, a Thermo TOC 1200 AOX/Total Carbon Analyser was used.

Regarding data treatment, results from experiments were fitted to a second order polyonomy, according to equation (6), where  $Z$  is the fitted response;  $k, a, b, c, (\dots)$  to  $i$  are regression coefficients; and  $x, y, z$  are the independent variables studied.

$$Z = k + a.x + b.x^2 + c.y + d.y^2 + e.z + f.z^2 + g.x.y + h.x.z + i.y.z \quad (6)$$

Analysis of variance (two-way ANOVA) was performed to test whether the variables and interactions between them significantly influenced the measured response.

### 3. Results and discussion

The results for AOX removal from the  $D_0$  bleaching wastewater stream by Fenton process are shown in Figure 1. The fitted model had an  $R^2 = 0.70$ .

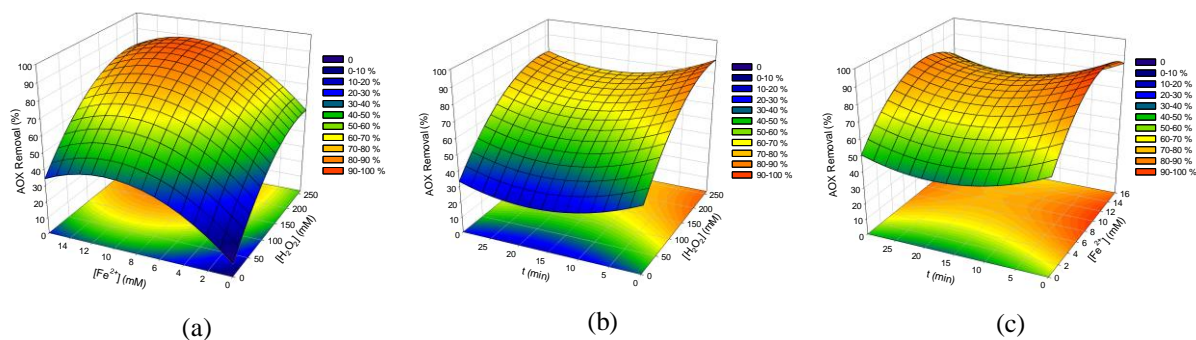


Fig 1. AOX removal (%) from  $D_0$  bleaching wastewater ( $C_{AOX, D_0} \approx 124 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{pH}=2$ ,  $T=60^\circ\text{C}$ ) by Fenton process, as function of: (a)  $[\text{H}_2\text{O}_2]$  and  $[\text{Fe}^{2+}]$ , for  $t=10 \text{ min}$ ; (b)  $[\text{H}_2\text{O}_2]$  and  $t$ , for  $[\text{Fe}^{2+}]=4 \text{ mM}$ ; (c)  $[\text{Fe}^{2+}]$  and  $t$ , for  $[\text{H}_2\text{O}_2]=137.5 \text{ mM}$ .

It seems that  $[\text{Fe}^{2+}]$  only influenced AOX removal for  $[\text{H}_2\text{O}_2] \leq 70\text{-}80 \text{ mM}$ , as shows Figure 1(a). For oxidant concentrations above those values, AOX removal increased mainly with increasing  $[\text{H}_2\text{O}_2]$ , which indeed was the only statistically significant variable ( $p < 0.01$ ) with 95% confidence ( $p = 0.05$ ). This is not an unprecedented result for different substrates degraded (Babuponnusami and Muthukumar, 2014; Pérez et al., 2002; Van Aken et al., 2013). The influence of each variable in the response is well represented by the Pareto chart of effects (Figure 2).

Maximum AOX removal around 90% was reached for  $[\text{H}_2\text{O}_2] \geq 140 \text{ mM}$ . Similar response surfaces were obtained for treatment times above 10 min showing the little effect of time on AOX removal ( $p \geq 0.45$ ). Moreover, Figure 1(b) shows that for treatment times below 30 min the increment of  $[\text{H}_2\text{O}_2]$  clearly promotes higher AOX removal, from removals below 30% to a maximum around 80-85% for a fixed  $[\text{Fe}^{2+}]$  of 4 mM. These results were similar to those reported by Catalkaya and Kargi (2007) - 89% AOX removal for biologically treated pulp mill wastewater for  $t=30 \text{ min}$  - and better than those obtained by Van Aken et al. (2013) - 66% AOX removal from graphical industry wastewater for  $t=24 \text{ h}$ . Figure 1(c) shows the effect of the  $[\text{Fe}^{2+}]$  on AOX removal at a fixed  $[\text{H}_2\text{O}_2] = 137.5 \text{ mM}$ . Although it seems that  $[\text{Fe}^{2+}]$  between 6 and 12 mM improves AOX removal, this variable was not statistically significant ( $p \approx 0.10$ ). The fitted polynomial model had however a weak  $R^2$  of  $\approx 0.70$ , which means it only explains 70% of the response variability. Nevertheless, it must be stated that the apparent decrease treatment efficiency for higher  $[\text{Fe}^{2+}]$  would not be unprecedented - Pérez et al. (2002) observed that iron concentration above  $\approx 7 \text{ mM}$  would be detrimental to TOC removal.

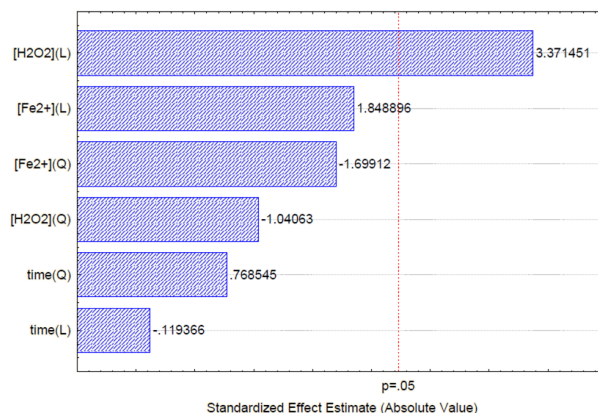


Figure 2. Pareto chart of effects of  $[\text{H}_2\text{O}_2]$ ,  $[\text{Fe}^{2+}]$  and treatment time on AOX removal from  $\text{D}_0$  bleaching stream by Fenton process.

The results obtained for AOX removal from  $\text{D}_0$  bleaching wastewater by the photo-Fenton process are shown in Figure 3. The fitted model had an  $R^2 = 0.95$ .

AOX removal by photo-Fenton process was mainly affected by  $[\text{H}_2\text{O}_2]$  ( $p < 0.0001$ ): the higher the oxidant concentration, the higher the AOX removal from the  $\text{D}_0$  bleaching wastewater. The Pareto chart of effects depicted in Figure 4 highlights the dependence of AOX removal on the oxidant concentration.

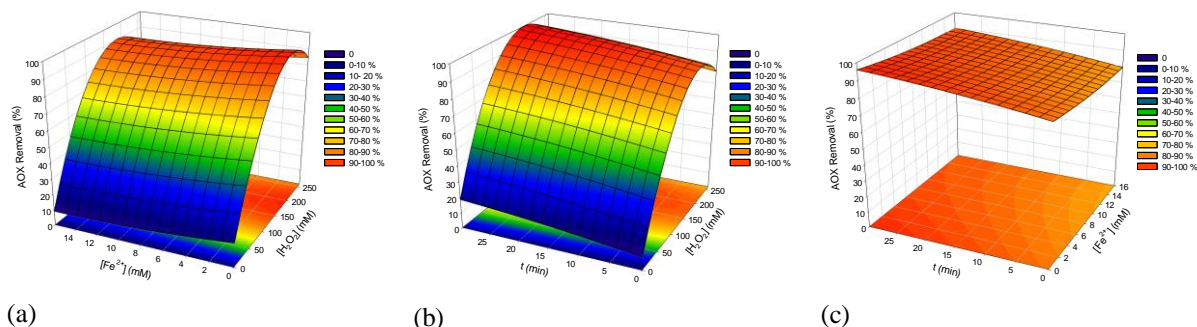


Fig 3. AOX removal (%) from the  $\text{D}_0$  bleaching wastewater ( $C_{\text{AOX}, \text{D}_0} \approx 124 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{pH}=2$ ,  $T=60^\circ\text{C}$ ) by photo-Fenton process, as function of: (a)  $[\text{H}_2\text{O}_2]$  and  $[\text{Fe}^{2+}]$ , for  $t=10 \text{ min}$ ; (b)  $[\text{H}_2\text{O}_2]$  and  $t$ , for  $[\text{Fe}^{2+}]=4 \text{ mM}$ ; (c)  $[\text{Fe}^{2+}]$  and  $t$ , for  $[\text{H}_2\text{O}_2]=137.5 \text{ mM}$

Figure 3 (a), corresponding to  $t=10 \text{ min}$ , shows maximum AOX removal  $\approx 90\%$  obtained for  $[\text{H}_2\text{O}_2] \geq 100 \text{ mM}$ , regardless of  $[\text{Fe}^{2+}]$ . This means that equal AOX removal by the photo-Fenton process can be attained with smaller amounts of chemicals when comparing to Fenton process. For the later,  $\approx 90\%$  removal required for  $[\text{H}_2\text{O}_2] \geq 140 \text{ mM}$  and  $[\text{Fe}^{2+}] \geq 4 \text{ mM}$  (see Figure 1).

Similar response surfaces were obtained for  $t > 10 \text{ min}$ , with maximum AOX removal reaching 95%. Catalkaya and Kargi (2007) recorded 93% AOX removal from biologically treated pulp mill wastewater using a 16 W UV lamp and  $[\text{H}_2\text{O}_2]=50 \text{ mM}$ ,  $[\text{Fe}^{2+}]=2.5 \text{ mM}$ , and  $t=5 \text{ min}$ . In this work, for  $t=10 \text{ min}$  and 150 W UV lamp, the same  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  conditions could only remove about 50% AOX. This was probably due to the biological treatment (Catalkaya and Kargi, 2007) and to inherent characteristics of each wastewater, highlighting the importance of adjusting the AOP operational conditions to the wastewater stream being treated.

Figure 3 (b) and (c) show some benefit in using higher treatment times, especially when using higher oxidant concentrations, allowing for 95% AOX removal to be attained ( $p=0.10$ ).  $[\text{Fe}^{2+}]$  was the less significant variable when applying photo-Fenton process ( $p > 0.25$ ) (see also Figure 4).

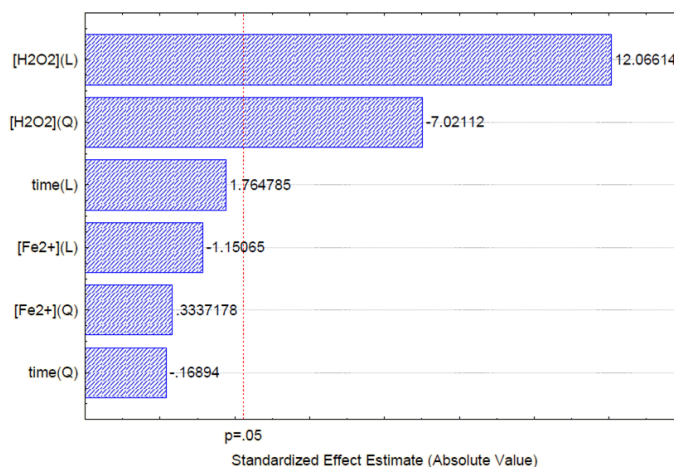


Figure 4. Pareto chart of effects of [H<sub>2</sub>O<sub>2</sub>], [Fe<sup>2+</sup>] and treatment time on AOX removal from D<sub>0</sub> bleaching stream by photo-Fenton.

#### 4. Conclusion

Both Fenton and photo-Fenton processes proved to be efficient for AOX removal from *Eucalyptus globulus* Kraft ECF bleaching wastewater, depending mainly of [H<sub>2</sub>O<sub>2</sub>] (only statistically significant variable at 95% confidence level). For the Fenton process maximum AOX removal was 85 % with [H<sub>2</sub>O<sub>2</sub>] = 177 mM, [Fe<sup>2+</sup>] = 8.5 mM, pH≈2, 60 °C and 10 minutes treatment time. Photo-Fenton process reached higher efficiency combined with lower chemical consumption. For this method, maximum AOX removal was 95% for [H<sub>2</sub>O<sub>2</sub>] = 178 mM, [Fe<sup>2+</sup>] = 2.0 mM, UV irradiance 142 W.m<sup>-2</sup>, pH≈2, 60 °C and 10 min. The short treatment times of these methods are very attractive for industrial-scale application. However, further investigation is required to assess the “side-effects” these methods may have namely in what concerns the organic load (COD/BOD), colour, ecotoxicity, etc. of the treated wastewaters.

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