

# Assessment of Catalytic Performance of Fe<sup>2+</sup>, Fe<sup>3+</sup> and Fe<sup>2+</sup>:Cu<sup>2+</sup> In Fenton and Photo-Fenton Treatment of Pulp Bleaching Wastewater

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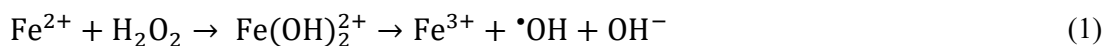
**Abstract** - Fenton process has been widely studied for the abatement of recalcitrant pollutants, such as adsorbable organic halides (AOX), from industrial wastewaters. In this work, Fenton and photo-Fenton processes were applied to remove AOX from real pulp bleaching wastewater. The catalytic performance of different oxidation states of iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>) and a combination of Fe<sup>2+</sup>:Cu<sup>2+</sup> were studied. Advantages, limitations, and operating cost of the different solutions studied were discussed. At the optimum operating condition adopted for AOX removal, side effect on organic load (COD and BOD<sub>5</sub>) was also assessed. Iron catalysts Fe<sup>2+</sup> and Fe<sup>3+</sup> were firstly compared. For that purpose, response surface methodology (RSM) was applied to find the operating conditions yielding maximum AOX removal at minimum cost, for both iron species. After defining the most suitable iron catalyst load, a second round of experiments were conducted, to study Cu<sup>2+</sup> as Fenton (co)catalyst. In those experiments, the optimum load of catalyst previously found was maintained, and different Fe:Cu ratios were studied, namely: 0:100; 25:75, 50:50, 75:25 and 100:0 % (mol/mol). Fe<sup>2+</sup> proved to be a more cost-effective iron catalyst than Fe<sup>3+</sup>, with photo-Fenton process allowing for better performance with lower chemical, and lower operating cost. Fe<sup>2+</sup> showed superior catalytic performance than Cu<sup>2+</sup>, yielding around twice the AOX removal. In Fenton process, up to 50 % Cu<sup>2+</sup> was successfully included in the catalyst mixture, with no significant loss of catalytic activity neither increase in operating cost. On the other hand, no synergetic effect between metals was registered. The photolytic regeneration of Cu<sup>2+</sup> was not effective, which may have hindered •OH production in photo-Fenton process, leading to a decrease efficacy with a decrease in the Fe:Cu molar ratio.

**Keywords:** Fenton, Photo-Fenton, AOX, Iron, Copper, Bleaching Wastewater

## 1. Introduction

Over 185 million tonnes of paper pulp were produced in 2018, meaning 25 kg per capita [1]. In Europe, almost 20 million tonnes of wood pulp were imported and over 17 million tonnes were exported [1]. During pulp production, pulp bleaching probably produces the most concerning wastewater stream, presenting low biodegradability and high contents of chemical oxygen demand (COD), suspended solids, dissolved lignin, colour and organochlorine compounds, namely adsorbable organic halides (AOX) [2]. The latter pose serious environmental hazard to fish and zooplankton, including respiratory stress, liver damage, effect on sexual maturation and ability to reproduce, carcinogenicity, mutagenicity, and even lethal effects [3]–[5].

Fenton process has been widely studied for the abatement of recalcitrant pollution from industrial wastewaters, including pulp mill wastewater (e.g. [6]–[8]). Its conventional form is based on the Fe<sup>2+</sup>-catalysed decomposition of H<sub>2</sub>O<sub>2</sub> into •OH – Equation (1) – which non-selectively attacks organic compounds. Further details on the principles and reaction system of Fenton process may be found elsewhere [9]. UV irradiation can be used to enhance iron catalyst's regeneration and •OH production – Equations (2) – (3) – increasing the removal efficacy. This variant is known as photo-Fenton and has also been subject of research focusing on pulp mill wastewater treatment (e.g. [7], [8], [10]).



The use of iron as Fenton catalyst presents several advantages, such as its high abundance, low-cost, environmental compatibility and low-toxicity [11]. On the other hand, both  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  may also act as Fenton catalyst (e.g. [12], [13]), although the  $\bullet\text{OH}$  production rate is 104 – 105 folds faster when  $\text{Fe}^{2+}$  is used, as reviewed by Ganiyu et al. [14]. The chemical reactivity of iron is strictly dependent on the speciation of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and ferric hydroxides, which determines the suitability of  $\text{Fe}^{3+}$ -catalysed Fenton [11]. When photo-Fenton process is used, the increase in  $\text{Fe}^{3+}$ -to- $\text{Fe}^{2+}$  conversion may allow for successful  $\text{Fe}^{3+}$ -catalysed process to be conducted (e.g.[15]).

Fenton and photo-Fenton processes perform better at pH around 3, where Fe(III) hydroxyl complexes are more soluble and  $\text{Fe}(\text{OH})^{2+}$  is more photoactive [16]. For pH above 3.5 – 4.0, iron precipitates as  $\text{Fe}(\text{OH})_3$ , decreasing catalyst availability, hindering  $\text{Fe}^{3+}$ -to- $\text{Fe}^{2+}$  regeneration cycle, and increasing solid sludge generation, despite coagulation of ferric species may contribute positively to the treatment [9], [11], [16]. To avoid the need to correct pH, and the high chemical costs associated, research efforts have been put to search for alternative metal catalysts to replace iron [11]. Copper seems to be a viable alternative, receiving increased attention lately. Wang et al. [16] reviewed Fenton-like processes for wastewater treatment and concluded that although around 85 % of the works published dealt with iron-related catalysts, copper was the second most cited element (around 11 %). The interest in copper as a Fenton catalyst is based on the reactivity towards  $\text{H}_2\text{O}_2$  that both the monovalent  $\text{Cu}^+$  and divalent  $\text{Cu}^{2+}$  show, according to the basic mechanism presented in Equations (4) – (8), analogous to the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  Fenton processes, respectively [17]–[19].



At acidic conditions, copper may show lower catalytic activity than iron, but the opposite occurs at circumneutral and alkaline conditions, mainly due to the higher solubility of copper ion. While the iron aquo complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is insoluble at  $\text{pH} > 5$ , its corresponding copper complex  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is predominant in neutral pH conditions [11], [19]. The  $\text{Cu}^{2+}$ -catalysed Fenton process may produce cupryl ion ( $\text{Cu}^{3+}$ ) as the main oxidant instead of  $\bullet\text{OH}$  under neutral pH conditions, which is believed to be a more selective oxidant than  $\bullet\text{OH}$  [19]. When Cu is used together with Fe as a co-catalyst, the  $\text{Cu}^{2+}/\text{Cu}^+$  couple may even enhance the  $\text{Fe}^{3+}$ -to- $\text{Fe}^{2+}$  regeneration cycle, according to Equation (9) [17], [18]. Therefore, under specific conditions, that is the possibility of a synergistic effect between iron and copper.



Primo et al. [20] reported similar COD removal (58 – 64 %) from landfill leachate applying Fenton process with  $15 \text{ g}\cdot\text{L}^{-1} \text{H}_2\text{O}_2$  and  $1 \text{ g}\cdot\text{L}^{-1} \text{Cu}^{2+}$  than with  $0.015 \text{ g}\cdot\text{L}^{-1} \text{H}_2\text{O}_2$  and  $2 \text{ g}\cdot\text{L}^{-1} \text{Fe}^{2+}$ . When the two metals were used simultaneously ( $1 \text{ g}\cdot\text{L}^{-1} \text{Cu}^{2+}$  plus  $2 \text{ g}\cdot\text{L}^{-1} \text{Fe}^{2+}$ ), up to 69 % COD removal was achieved with the same  $15 \text{ g}\cdot\text{L}^{-1}$  of  $\text{H}_2\text{O}_2$ . Those authors also concluded that photo-Fenton process was more effective than Fenton, increasing COD reduction to 78 %. Dealing with olive mill wastewater, Iboukhoulef et al. [21] applied microwave-assisted Fenton-like process with  $\text{Cu}^{2+}$  as catalyst, achieving 77.7 % and 89.2 % removal of phenolic compounds and colour, respectively after 12 minutes of treatment.

Despite growing interest in Cu, most works dealt with the removal of target compounds from synthetic wastewater, rather than treating real industrial wastewater, with much more complex matrices [11]. Moreover, and to the best of our knowledge, no attempt has been made to removal recalcitrant compounds such as AOX from actual industrial wastewater with this alternative catalyst, despite the known environmental hazard that AOX pose. Therefore, in this work copper and iron were used as co-catalysts in Fenton and photo-Fenton processes to remove AOX from real pulp paper (PP) bleaching wastewater. At the optimum operating condition adopted for AOX removal, side effect on COD and  $\text{BOD}_5$  was also assessed. Operating cost of the studied solutions was also compared.

## 2. Materials and Methods

Pulp bleaching wastewater was collected after the first chlorine dioxide bleaching stage (D<sub>0</sub>) of a Portuguese PP industry that produces kraft pulp, mainly from *Eucalyptus globulus*. The collected wastewater presented  $93.1 \pm 2.0 \text{ mg}\cdot\text{L}^{-1}$  of AOX, COD of  $3695 \pm 162 \text{ mg}\cdot\text{L}^{-1}$ , BOD<sub>5</sub> of  $174.3 \pm 4.0 \text{ mg}\cdot\text{L}^{-1}$  and pH  $2.8 \pm 0.2$ .

Batch experiments (0.5 L) were conducted in a quartz photoreactor, equipped with a 150W UV medium pressure UVA+UVB (297 - 436 nm) TQ150 lamp and 200 rpm magnetic stirring. Considering that the wastewater was acidic, no correction was made before the oxidation experiments. Regarding temperature, since the wastewater is generated at  $60 \pm 5 \text{ }^\circ\text{C}$ , the experiments were performed at  $60 \pm 2 \text{ }^\circ\text{C}$  to avoid additional costs. When the wastewater reached the desired temperature, catalyst and oxidant were added. In the photo-Fenton experiments, the UV lamp was turned on immediately after adding the chemicals (oxidant – H<sub>2</sub>O<sub>2</sub> – and catalyst). Preliminary results showed that AOX removal was not influenced by treatment time (t) ranging 10 – 60 minutes (data not shown), so all experiments lasted for 10 minutes. At the end of treatment, samples of the treated wastewater were collected and immediately quenched with sodium sulphite (1.50 M aq. solution of Na<sub>2</sub>SO<sub>3</sub> – Fisher 99%).

Iron catalysts Fe<sup>2+</sup> and Fe<sup>3+</sup> were firstly compared. For that purpose, central composite design (CCD) and response surface methodology (RSM) were applied to find the operating conditions yielding maximum AOX removal at minimum cost, for both iron species. For two variables, a matrix of 11 experiences was performed, including three repetitions at the central point, to allow for statistical inference. Further details on CCD and RSM methodology and its application to pulp bleaching wastewater by Fenton processes may be found in a previous work [7]. Experimental ranges are listed in Table 1.

Table 1: Experimental range for CCD and RSM optimisation of Fe<sup>2+</sup>-catalysed and Fe<sup>3+</sup>-catalysed Fenton and photo-Fenton processes.

Variable	Minimum	Maximum
[H <sub>2</sub> O <sub>2</sub> ] (mM)	20	250
[Fe] (mM)	1	16
t (min)		10
T (°C)		$60 \pm 2$
pH		$2.8 \pm 0.2$
Irradiance <sup>#</sup> (W·m <sup>-2</sup> )		142
<sup>#</sup> photo-Fenton		

After defining the most suitable iron catalyst load, a second round of experiments were conducted, to study the effect of Cu<sup>2+</sup> as Fenton (co)catalyst (with Fe<sup>2+</sup>). In those experiments, the optimum load of catalyst previously found was kept, and different Fe:Cu ratios were studied, namely: 0:100; 25:75, 50:50, 75:25 and 100:0 % (mol/mol). Experimental conditions for those experiments are shown in Table 2 and were obtained from the results of the Fe<sup>2+</sup> and Fe<sup>3+</sup> experiments – see Section 3.

Table 2: Experimental conditions tested for Fe:Cu-catalysed Fenton and photo-Fenton processes.

Variable	Fenton	Photo-Fenton
[H <sub>2</sub> O <sub>2</sub> ] (mM)	169	178
[Catalyst] (mM)	12.5	1
t (min)		10
T (°C)		$60 \pm 2$
pH		$2.2 \pm 0.2$
Irradiance (W·m <sup>-2</sup> )	-	142

Hydrogen peroxide solution ( $\text{H}_2\text{O}_2$  30 % – Panreac) was used as received; iron(II) sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  – Panreac), iron(III) sulphate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  – Panreac) and copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  – Fisher) were used as aqueous of approximately 0.5 M, 0.2 M and 0.5 M, respectively. AOX was measured according to EN 16166:2012, ISO and EPA Method 1650C. COD and  $\text{BOD}_5$  were measured according to Standard Methods 5220D and 5210D [22].

Operating costs presented represent the cheapest condition to achieve each AOX removal target, and were computed based on average lab-scale market prices of  $\text{H}_2\text{O}_2$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  of  $2.0 \text{ €} \cdot \text{L}^{-1}$ ,  $9.6 \text{ €} \cdot \text{kg}^{-1}$ ,  $20.0 \text{ €} \cdot \text{kg}^{-1}$  and  $10.2 \text{ €} \cdot \text{kg}^{-1}$ . For photo-Fenton process, electricity cost of  $70 \text{ €} \cdot \text{MWh}^{-1}$  was considered.

### 3. Results and Discussion

#### 3.1. $\text{Fe}^{2+}$ vs $\text{Fe}^{3+}$ -catalysed (photo-)Fenton processes

Response-surface of AOX removal by Fenton and photo-Fenton processes is depicted in Fig. 1.

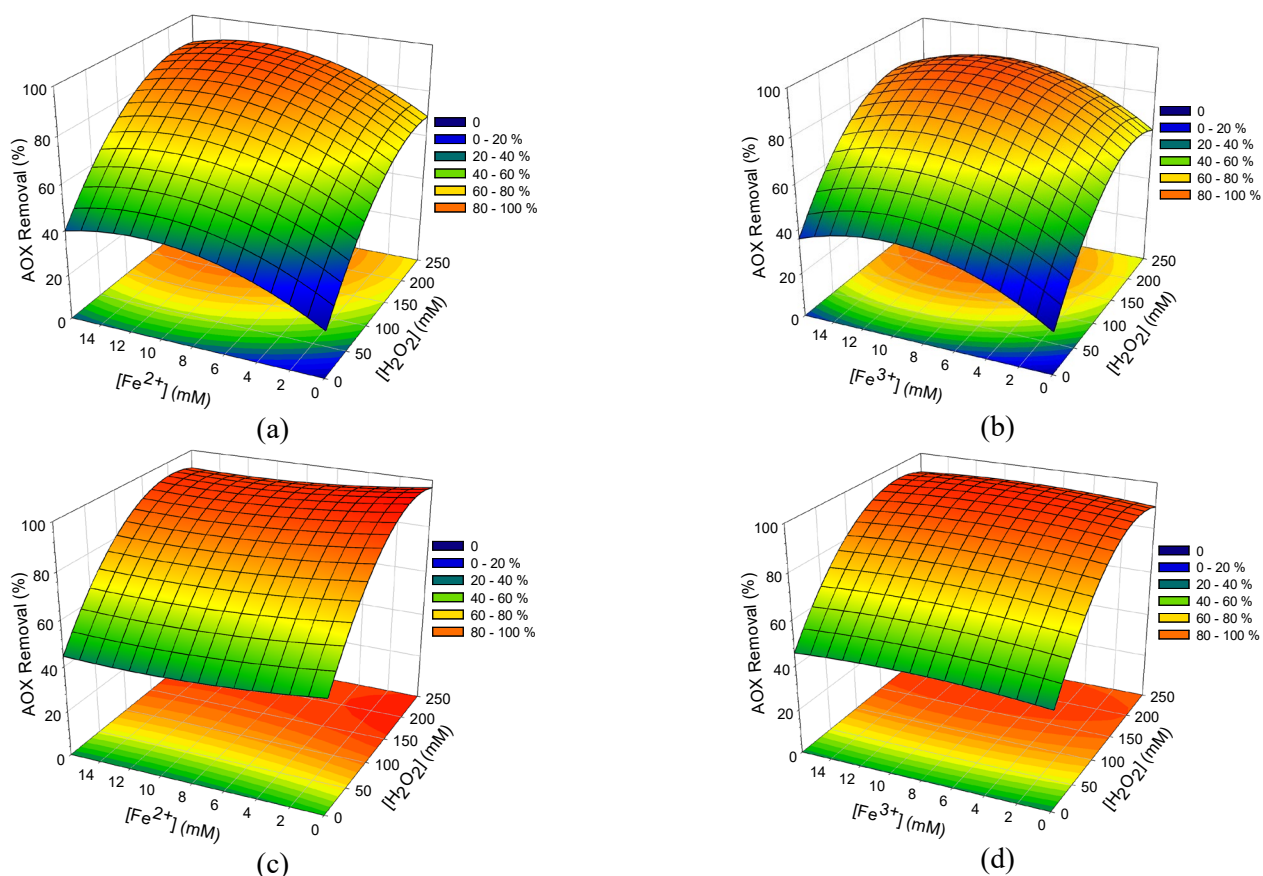


Fig. 1: AOX removal by (a)  $\text{Fe}^{2+}$ -catalysed Fenton process, (b)  $\text{Fe}^{3+}$ -catalysed Fenton process, (c)  $\text{Fe}^{2+}$ -catalysed photo-Fenton process, and (d)  $\text{Fe}^{3+}$ -catalysed photo-Fenton process.

AOX removal by Fenton and photo-Fenton processes increased with  $[\text{H}_2\text{O}_2]$ , the only variable statistically influencing the response ( $p < 0.05$ ). Fenton process yielded a region of maximum AOX removal for  $[\text{H}_2\text{O}_2] > 150 \text{ mM}$  and a minimum  $[\text{Fe}] > 4 \text{ mM}$ , regardless of the oxidation state of Fe. For both iron catalysts, maximum AOX removal ranged 82 – 88 %. Photo-Fenton process yielded higher AOX removal than Fenton process with lesser consumption of chemicals: the region of maximum removal was attained for  $[\text{H}_2\text{O}_2] > 125 \text{ mM}$  and a minimum  $[\text{Fe}] > 1 \text{ mM}$ . Maximum AOX removal registered ranged 88 – 92 %, regardless of the oxidation state of Fe. Given the similar technical

performance, the choice of Fe-catalyst would depend on the operating cost of the different (photo-)Fenton processes studied. Fig. 2 shows the cost of Fenton and photo-Fenton processes using  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  catalysts.

For AOX removal up to 90 %, Fenton process is always more costly than photo-Fenton process, meaning that the lower demand of chemicals in photo-Fenton process surpassed the higher demand of electricity. For both processes,  $\text{Fe}^{2+}$ -catalysed oxidation was more cost-effective than  $\text{Fe}^{3+}$ -catalysed oxidation, due to higher demand of chemicals to achieve equal AOX removal. For higher treatment times (> 60 min),  $\text{Fe}^{3+}$ -catalysed processes could eventually reach the same AOX removal than the  $\text{Fe}^{2+}$ -catalysed ones with similar amount of chemicals, but that would entail significant disadvantage in the reactor volume needed to treat wastewater flow of hundreds of  $\text{m}^3$  per hour.

It must be noted that all costs presented are based on lab-scale purchase of chemicals. Moreover, it was also assumed that the UV lamp efficacy would only be valid for 0.5 L of wastewater, which is an unrealistic worst-case scenario. Therefore, full-scale implementation on these processes would allow for several times lower costs to be practiced. Nevertheless, the results presented in Figure 2 allow the conclusion that the  $\text{Fe}^{2+}$ -catalysed Fenton and photo-Fenton processes was more cost-effective than the  $\text{Fe}^{3+}$ -catalysed ones. Therefore, subsequent experiments, aiming at the replacement of iron by copper as Fenton catalyst, were performed with different of  $\text{Fe}^{2+}:\text{Cu}^{2+}$  molar ratios.

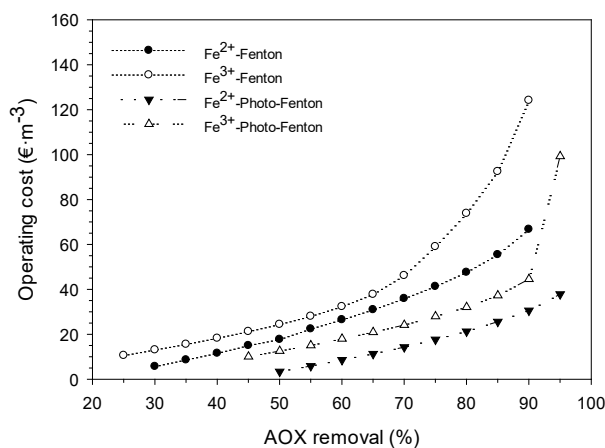


Fig. 2: Operating cost for increasing AOX removal target, for  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -catalysed Fenton and photo-Fenton processes.

### 3.2. Fe:Cu-catalysed (photo-)Fenton processes

AOX removal achieved with different  $\text{Fe}^{2+}:\text{Cu}^{2+}$  molar ratios is shown in Fig. 3.

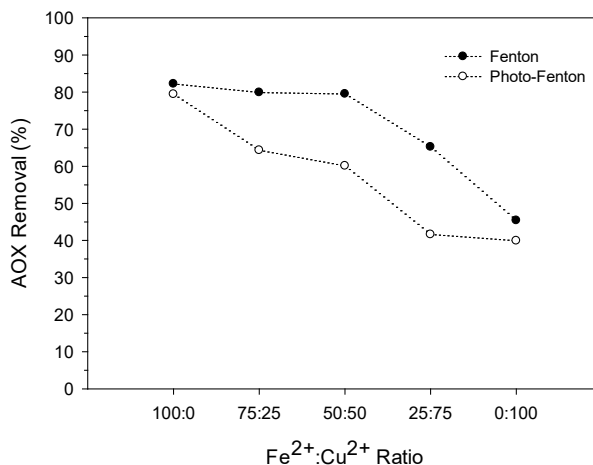


Fig. 3: AOX removal by  $\text{Fe}^{2+}:\text{Cu}^{2+}$ -catalysed Fenton and photo-Fenton processes, for different  $\text{Fe}^{2+}:\text{Cu}^{2+}$  catalyst molar ratios.

For 100 % Fe<sup>2+</sup> or Cu<sup>2+</sup> catalyst, AOX removal was very similar between Fenton and photo-Fenton experiments. When mixed catalyst was used, the performance of Fenton and photo-Fenton processes was noticeably different. In Fenton process, up to 50 % Cu<sup>2+</sup> was successfully included in the catalyst mixture, with no significant efficacy loss. Above that threshold, AOX removal decreased to a minimum around 40 % for 100 % Cu<sup>2+</sup> catalyst. On the other hand, the removal achieved with mixed catalyst was always lower than the one achieved by 100 % Fe<sup>2+</sup>. Results show superior catalytic performance of Fe<sup>2+</sup> (in the experimental range studied), as was expected in acidic medium [11], [19]. However, no synergetic effect between metals was registered, unlike what was theoretically expected – Equation (9). Higher treatment time could allow for some Fe<sup>3+</sup>-to-Fe<sup>2+</sup> regeneration and enhanced Fenton reaction's extent, since some residual H<sub>2</sub>O<sub>2</sub> was detected at the end of the 10-min treatment. In photo-Fenton process, the decay in AOX removal efficacy was more pronounced with decreasing Fe:Cu ratio. The photolytic regeneration of Cu<sup>2+</sup> was not effective and the amount of regenerated Fe<sup>2+</sup> was decreased with lower Fe:Cu ratio, so the production of •OH may have been hindered.

Dealing with oxalic and oxamic acids by means of Fenton-like processes using iron and copper, Garcia-Segura et al. [18] reported slower photodecomposition of Fe and Cu complexes for Cu proportion above 25 %, given the smaller proportion of Fe and the lower photoactivity of Cu, which hindered the treatment's efficacy. Analogous effect was discussed by Salazar et al. [17]. On the other hand, Primo et al. [20] reported similar effectiveness between Fe<sup>2+</sup>-catalysed and Cu<sup>2+</sup>-catalysed Fenton and photo-Fenton processes in the treatment of landfill leachate. However, those authors were targeting general COD reduction, and the treatment time was 60 minutes. Another factor that may contribute to this loss of efficacy with increasing Cu<sup>2+</sup> proportion is that reaction (Equation (8)) is hindered by molecular oxygen (O<sub>2</sub> oxidizes Cu<sup>+</sup> to Cu<sup>2+</sup> in acidic and circumneutral media) decreasing •OH production [11]. This effect could be tackled by increasing H<sub>2</sub>O<sub>2</sub>, but this would be counterproductive, since it would increase the cost of treatment, COD and •OH scavenging – see Equation (10) [9], [11], [16].



COD increased with decreasing Fe<sup>2+</sup>:Cu<sup>2+</sup> molar ratio (see Fig. 4), due to lower catalytic activity of that metal and consequent lower •OH production. Moreover, excessive H<sub>2</sub>O<sub>2</sub> could have increased COD of the wastewater; in the presence of stronger oxidants (such as dichromate ion Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), H<sub>2</sub>O<sub>2</sub> may behave as reductant and be oxidised, contributing to the COD [16], [21]. As already discussed, lower photoactivity of Cu<sup>2+</sup> led to higher COD after photo-Fenton process. BOD<sub>5</sub> increased mainly with Fenton process, due to the formation of readily biodegradable intermediates during treatment. Downstream biological abatement of readily biodegradable organic matter was favoured especially by Fenton process, since the BOD<sub>5</sub>/COD, which is a direct marker for biodegradability of a wastewater, increased from 0.05 in the original bleaching wastewater to 0.10 – 0.18.

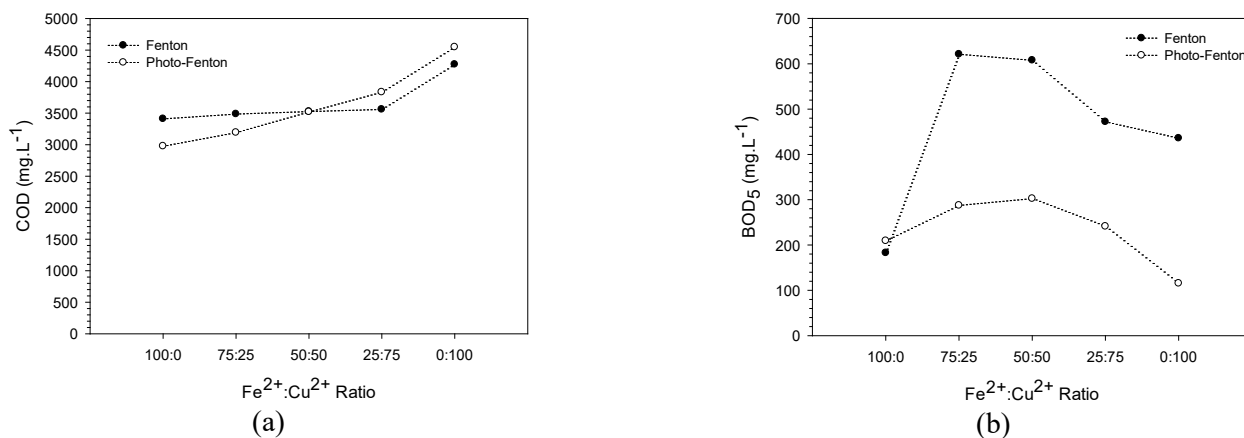


Fig. 4: (a) COD and (b) BOD<sub>5</sub> of the wastewater after treatment by Fe<sup>2+</sup>:Cu<sup>2+</sup>-catalysed Fenton and photo-Fenton processes.

Operating cost of  $\text{Fe}^{2+}:\text{Cu}^{2+}$ -catalysed photo-Fenton process was 30 – 35 % lower when compared with Fenton process at the same conditions (see Fig. 5). Once again, the reduction in chemical demand surpassed the additional cost of UV irradiation, making photo-Fenton a more cost-effective solution. Increasing the  $\text{Cu}^{2+}$  proportion in the catalyst mixture did not significantly change the cost of treatment, since the prices of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were in fact very similar.

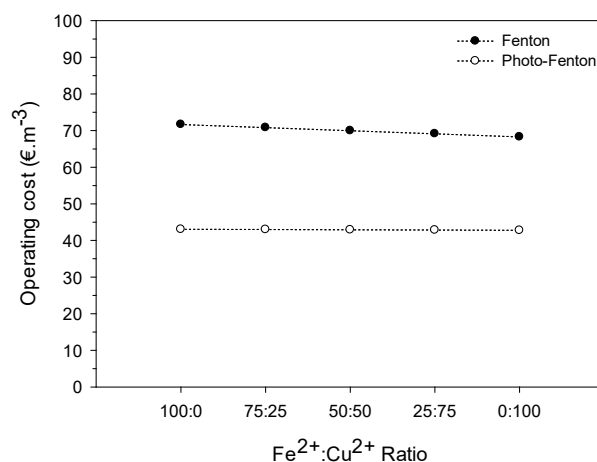


Fig. 5: Operating cost by  $\text{Fe}^{2+}:\text{Cu}^{2+}$ -catalysed Fenton and photo-Fenton processes, for different  $\text{Fe}^{2+}:\text{Cu}^{2+}$  catalyst molar ratios.

#### 4. Conclusions

Results showed similar catalytic activity between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  for AOX removal, although  $\text{Fe}^{2+}$  proved to be more cost-effective. Photo-Fenton process allowed for better performance with lower operating cost than Fenton process. Although  $\text{Fe}^{2+}$  showed higher catalytic activity than  $\text{Cu}^{2+}$ , up to 50 %  $\text{Cu}^{2+}$  was successfully included in the Fenton catalyst mixture. However, no synergetic effect between metals was registered. The photolytic regeneration of  $\text{Cu}^{2+}$  was not effective, which may have hindered  $\bullet\text{OH}$  production in photo-Fenton process, leading to decreased efficacy with decreased  $\text{Fe}^{2+}:\text{Cu}^{2+}$  molar ratio. Biodegradability of the wastewater was improved especially by Fenton process, with  $\text{BOD}_5/\text{COD}$  increasing from 0.05 to 0.10 – 0.18. Increasing the  $\text{Cu}^{2+}$  proportion in the catalyst mixture did not significantly change the cost of treatment. On the other hand, and despite being less effective in removing AOX, the  $\text{Fe}^{2+}:\text{Cu}^{2+}$ -catalysed photo-Fenton process was 30 – 35 % cheaper, meaning that for lower AOX removal target, that process may still be an promising alternative.

This work highlighted the advantages of Fenton and photo-Fenton processes to remove recalcitrant pollutants such as AOX from industrial wastewaters, at levels which would be impossible to achieve by conventional treatment technologies.  $\text{Fe}^{2+}$  proved to be the most effective (photo-)Fenton catalyst, although its partial replacement by  $\text{Cu}^{2+}$  was proven to be feasible up to 50 %, with no catalytic loss and no increase in operating cost.

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