

This is an author generated post-print of the article:

João Peres Ribeiro, Catarina Costa Marques, Inês Portugal, Maria Isabel Nunes, 2020.

Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: optimisation of operating conditions and cost assessment. Journal of Environmental Chemical Engineering 8, 104032.

The final publication is available on <https://doi.org/10.1016/j.jece.2020.104032>

Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: optimisation of operating conditions and cost assessment

João Peres Ribeiro^a, Catarina Costa Marques^a, Inês Portugal^b, Maria Isabel Nunes^{*a}

^aCESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193, Aveiro, Portugal

^bCICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal

*Corresponding author: Maria Isabel Nunes

isanunes@ua.pt; +351 234370200. Departamento de Ambiente e Ordenamento, Universidade de Aveiro. Campus Universitário de Santiago, 3810-193, Aveiro, Portugal

Abstract

AOX emissions to water are a key environmental aspect in the pulp and paper industry being limited by EU Ecolabel criteria. In this work, response surface methodology was used to optimise Fenton and photo-Fenton processes for AOX removal from a kraft pulp mill bleaching wastewater. Focus on the specific stream where AOX is higher reduces the wastewater volume to treat and the associated costs. Moreover, there is a need to assess the effect of treatment in parameters other than AOX, such as BOD₅, COD and colour content, which were also quantified in this work. Operational costs were determined for both processes, including chemical consumption and energy input (in the case of photo-Fenton process). The photo-Fenton process exhibited better performance than the classic Fenton process, achieving 90 % AOX removal against 80 % for the Fenton process, higher colour content removal and enhanced wastewater's biodegradability (BOD₅/COD ratio). Moreover, photo-Fenton process showed lower operational costs for maximum AOX removal: 46.5 €·m⁻³ wastewater treated or 0.45 €·g⁻¹ AOX removed, against 70.0 €·m⁻³ wastewater treated or 0.78 €·g⁻¹ AOX removed by the Fenton process.

Keywords: Fenton; Photo-Fenton; AOX; operational cost; bleaching wastewater

Declaration of interest: NONE

1. INTRODUCTION

Pulp and paper industry (PP) is one of the main producers of wastewater worldwide. Kraft pulping is the prevalent chemical pulping process accounting for 90 % of the worldwide paper production [1]. From the different stages of the pulping process, bleaching process produces probably the most toxic wastewater stream, exhibiting high chemical oxygen demand – COD ($1 - 7 \text{ g}\cdot\text{L}^{-1}$), high content of suspended solids ($0.5 - 2 \text{ g}\cdot\text{L}^{-1}$), low biodegradability ratio of BOD_5/COD (0.02 to 0.07, with BOD_5 meaning 5-day biochemical oxygen demand), dissolved lignin, colour, complexing agents like EDTA, an array of inorganic elements (e.g. Ca, K, Mg, P and Al) and hundreds of organochlorine compounds, such as dioxins, furans, chlorophenols, chloroform, chloromethane, phenols, chlorinated hydrocarbons, *etc.* [2–7]. However, the most concerning pollutant found in PP wastewater is perhaps the adsorbable organic halogens – AOX – which show extremely concerning effects on fish and zooplankton, including respiratory stress, mixed function oxygenase activity, carcinogenicity and mutagenicity, liver damage, effect on sexual maturation and ability to reproduce, and even lethal effects [3,4,8,9]. Therefore, AOX emissions from the pulp and paper industry are regulated with the EU Ecolabel imposing a maximum of $0.17 \text{ kg}\cdot\text{ton}^{-1}$ of air-dried pulp at the point of discharge [10].

The toxic and recalcitrant nature of the PP bleaching wastewater makes conventional biological processes insufficient to ensure efficient treatment [11–16]. Regarding AOX removal, Ranganathan et al. [8] cited more than one study reporting biological processes' efficiencies below 50 % in removing these compounds from wastewaters, even with hydraulic retention time of 15 h.

The Fenton process is one of the most widely studied advanced oxidation process (AOP) for recalcitrant compounds removal. It is based on the catalytic effect of Fe^{2+} on the dissociation of the oxidant, H_2O_2 , into hydroxyl radicals, HO^\bullet , which is a strong and non-selective oxidant capable of oxidizing highly recalcitrant organic pollutants [11,17–20]. The main drawbacks of the Fenton process are the high consumption of chemicals and the formation of a dark iron sludge that requires additional costs for separation from the treated wastewater and subsequent disposal [21–24]. Adding UV light to the treatment (the so called photo-Fenton process) has been proved effective for regenerating the catalytic Fe^{2+} ion by photo-reduction of Fe^{3+} (reducing the consumption of Fe^{2+}), simultaneously improving the production of HO^\bullet and the degradation of organic pollutants [7,11,19,22,23,25,26].

The efficiency of Fenton processes is mainly ruled by the conditions of operation, namely oxidant and catalyst concentrations, pH, temperature, and time of treatment [18,23]. Moreover, the choice of the most suitable experimental conditions to treat any particular wastewater depends mainly on the characteristics of that wastewater [19]. Fenton processes are strongly influenced by pH mainly due to the speciation of iron [11,25,26], with the optimum pH being around 2.5 – 3 [11,22,27]. At lower pH values, complex iron species like $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ react with H_2O_2 at slower rates, reducing HO^\bullet formation and changing quantum yield of light absorption (in the case of photo-Fenton) [11,28,29]. On the other hand, higher pH values can favour: (i) H_2O_2 decomposition to O_2 and H_2O [26,28], and (ii) the formation and precipitation of iron oxides/hydroxides, meaning less iron ions are available to react with H_2O_2 and form HO^\bullet [2,11,26]. Temperature has been reported to have a negligible effect on Fenton/photo-Fenton efficiency [11,28,30] given the low activation energy of the first steps of the reaction mechanism [31].

In this work, response surface methodology (RSM) was used to find the optimal operating conditions to remove AOX from a real kraft pulp bleaching wastewater by Fenton and photo-Fenton processes. Since AOX arises essentially in pulp bleaching operations, this work focused on AOX removal from the bleaching stage wastewater before mixing with other wastewater streams and being sent to the wastewater treatment plant. This strategy reduces the volumes to be treated by the Fenton processes and thus reduces the consumption of chemicals and the capital and operational costs. Despite focusing on AOX removal, and contrasting to what is sometimes found in the literature, in this work an integrated analysis has been performed to assess also the “side-effects” of the Fenton/photo-Fenton treatment, regarding COD, BOD_5 and colour reduction, plus the operational cost associated with the Fenton and photo-Fenton processes.

2. EXPERIMENTAL

2.1 WASTEWATER

The bleaching wastewater was provided by a Portuguese PP industry that produces kraft pulp, mainly from *Eucalyptus globulus*, using a 4-stage elemental chlorine free bleaching process comprising three chlorine dioxide (D) stages and an intermediate alkaline extraction with H_2O_2

addition (Ep) – D₀EpD₁D₂. The wastewater samples were collected (grab sample) from the industrial plant, immediately after the D₀ bleaching stage, and stored in the dark at 0 – 4 °C. The wastewater samples were used within one month and characterized by standard methods (see Section 2.4). The parameters listed in Table 1 represent mean and standard deviation values of replicate analysis performed monthly throughout two years.

Table 1. Characteristic parameters of D₀ bleaching wastewater from a Portuguese Kraft PP industry.

Parameter	Mean ± s
AOX (mg·L ⁻¹)	123.2 ± 28.2
COD (mg O ₂ ·L ⁻¹)	3100 ± 299
BOD ₅ (mg O ₂ ·L ⁻¹)	178 ± 16.8
pH	2.2 ± 0.2
Colour (mg Pt·L ⁻¹)	1530 ± 227

2.2 EXPERIMENTAL DESIGN

The experimental work was planned and executed according to central composite experimental design (CCED). This method allows to assess the effect of *a priori* established factors (independent variables) on a target response (dependent variable). Factors are studied within a predefined range (minimum “-1”, median “0” and maximum “1”), originating a matrix of experiments to perform, to which at least 3 replicates of the central point (performed at the “0” values of each factor) and 2 axial points (± “1.42”) are added, to allow for statistical inference and quadratic effects assessment, respectively. In this work, the response was AOX removal from the D₀ bleaching wastewater and the independent variables tested were concentration of the oxidant [H₂O₂] and concentration of the catalyst [Fe²⁺], for both Fenton and photo-Fenton processes. Considering that the pH of the wastewater used in this work (2.2 ± 0.2, see Table 1) was within the optimal pH range (2.5 – 3.0) for Fenton processes [11,22,27,32], the experiments were performed without pH correction. Regarding temperature, since the wastewater is generated at 60 ± 5 °C the experiments were performed at 60 ± 2 °C envisioning a future industrial implementation (i.e. to avoid additional costs related to temperature adjustment). The treatment time (t) was set at 10 min based on preliminary experiments that revealed treatment

times above 10 minutes have no statistically significant effect on AOX removal for this wastewater [33].

Table 2 presents the values of the factors at the defined levels for the CCED experiments along with the fixed operating parameters. A total of 11 experiments were performed including 3 repetitions at the central point.

Table 2. Predefined levels of studied variables [H₂O₂] and [Fe²⁺] used in the CCED experiments for optimisation of response AOX removal by Fenton and photo-Fenton processes.

Variable	-1.42	-1	0	+1	+1.42
[H ₂ O ₂] (mM)	20	51.8	137.5	223.3	250
[Fe ²⁺] (mM)	1	3.2	8.5	13.8	16
t (min)			10		
pH			2.2 ± 0.2		
Temperature, T (°C)			60 ± 2		
Irradiance* (W·m ⁻²)			142		

*Photo-Fenton process (medium pressure UVA+UVB lamp)

2.3 EXPERIMENTAL SETUP

Experiments were performed in a 0.7 L quartz photoreactor, equipped with a 150W UV medium pressure UVA+UVB (297 - 436 nm) TQ150 lamp (for the photo-Fenton experiments) and magnetic stirring. For each experiment, 0.5 L of bleaching wastewater was placed inside the reactor and, after reaching the pre-set temperature for the essay, H₂O₂ (30 % w/v, Panreac) and Fe²⁺ (0.8 M aqueous solution of FeSO₄·7H₂O, Panreac, 97% purity) were added under constant stirring (200 rpm) to initiate the Fenton reaction. In the photo-Fenton experiments, the UV lamp was turned on immediately after adding the chemicals. After the pre-set treatment time, samples were taken from the reactor and immediately quenched by adding an aqueous solution of sodium sulphite (1.5 M aq. solution of Na₂SO₃, Fisher, 98% purity). Each sample was split into three subsamples, which were preserved as follows: (i) acidification (pH < 2) for AOX and COD analysis; (ii) neutralization (pH ≈ 7) for BOD₅ analysis; (iii) no pH adjustment for colour measurement. The three subsamples were stored below 4 °C until analysis.

2.4. ANALYTIC METHODS

AOX was quantified by coulometric titration, in accordance with EN 16166:2012, ISO 9562:2004 and EPA Method 1650C, using a Thermo TOC 1200 AOX/Total Carbon Analyser. COD and BOD₅ measurements were performed using an Aqualytic® COD photometer and a WTW Oxitop® Control equipment, respectively, following the commonly accepted methodologies 5220D and 5210D [34]. pH was measured with a Denver Instrument® model 25 pH/ION METER. Colour was determined by absorbance measurements at 410 nm, according to ISO 7887:2015, using a T80+ UV/VIS spectrometer from PG instruments.

2.5. STATISCAL DATA TREATMENT

RSM was used to analyse the experimental results, allowing to explore the relationships between the variables and the studied response from a reduced number of experiments. It is used for mapping a response surface over a special region of concern, or for selecting operating conditions to obtain purpose requirements [35].

In this work, a regression model (second order polynomial function, equation (1)) was fitted to the experimental results.

$$Z = k + a.x + b.x^2 + c.y + d.y^2 + e.x.y \quad (1)$$

where Z is the fitted response, in this work AOX removal; k , a , b , (...) to e are the regression coefficients; and x and y are the independent variables, in this work $[H_2O_2]$ and $[Fe^{2+}]$, respectively. The last term corresponds to the interaction between the two dependent variables. Additionally, for both set of results - Fenton and photo-Fenton experiments - simplifications of equation (1) were tested (e.g. model without the interaction term), in order to obtain a suitable model that predicts the efficiency of AOX removal as a function of $[H_2O_2]$ and $[Fe^{2+}]$.

The adequacy of the suggested regression model was evaluated by carrying out an analysis of variance (ANOVA) of the regression; p-value and Lack of Fit parameters were used, as well as the determination coefficients (R^2 and R^2_{adj}). A 95 % confidence level was adopted in this study. The validation of the model assumptions was done through a residuals plots analysis. First, the residuals were normalized with respect to their standard deviations (studentized) and its distribution was analysed to determine if they followed a normal distribution (i.e. a normal distribution function was fitted to the residuals) and were random (the observed residuals were plotted against predicted AOX removal). An outlier plot was also assessed to determine if any of

the experiments had particularly large residuals; usually a cut-off of ± 3.5 standard deviations is used to define an outlier. All statistical analyses were performed with StatSoft Statistica® v. 8.0 software.

3. RESULTS AND DISCUSSION

The bleaching wastewater sample used in this work had $113.9 \text{ mg}\cdot\text{L}^{-1}$ AOX, $3703 \text{ mg}\cdot\text{L}^{-1}$ COD, $174.3 \text{ mg}\cdot\text{L}^{-1}$ BOD₅ and $1804 \text{ mg Pt}\cdot\text{L}^{-1}$ colour. These values are within the average values of the bleaching wastewater from the industrial plant as shown in Table 1.

3.1 Fenton process

The second-order polynomial model of equation (1) and three simplifications of this model were fitted to the experimental results for the Fenton process – see Table S1 in the Supplementary Material. Since the interaction between the independent variables was not significant ($p = 0.37$) and decreased the quality of the fitting (decreasing R^2_{adj}), the polynomial fitting was performed disregarding the interaction term from equation (1).

The ANOVA results and the regression coefficients of the fitted model (without interactions) are shown in Table 3 and Table 4, respectively. The determination coefficient ($R^2 \approx 0.815$) indicated the model explains 81.5 % of the response variability (see Figure 1d). This value is very close to the minimum value ($R^2 = 0.80$) usually pointed out as acceptable [36,37]. Most important, the Lack of Fit was not significant relatively to pure error (p -value = 0.08), which proves that the quadratic model without the interaction term fits well to the data for the Fenton process.

Therefore, the model fitted to the experimental results was obtained according to Eq. (2).

$$Z = 22.0 + 0.453x - 0.001x^2 + 1.12y - 0.011y^2 \quad (2)$$

The linear effect of the oxidant concentration, $[\text{H}_2\text{O}_2]$, was the only statistically significant variable, meaning that AOX removal increases linearly with increasing $[\text{H}_2\text{O}_2]$ ($p < 0.01$, see Table 3).

Table 3. ANOVA table for AOX removal from kraft bleaching wastewaters by the Fenton process.

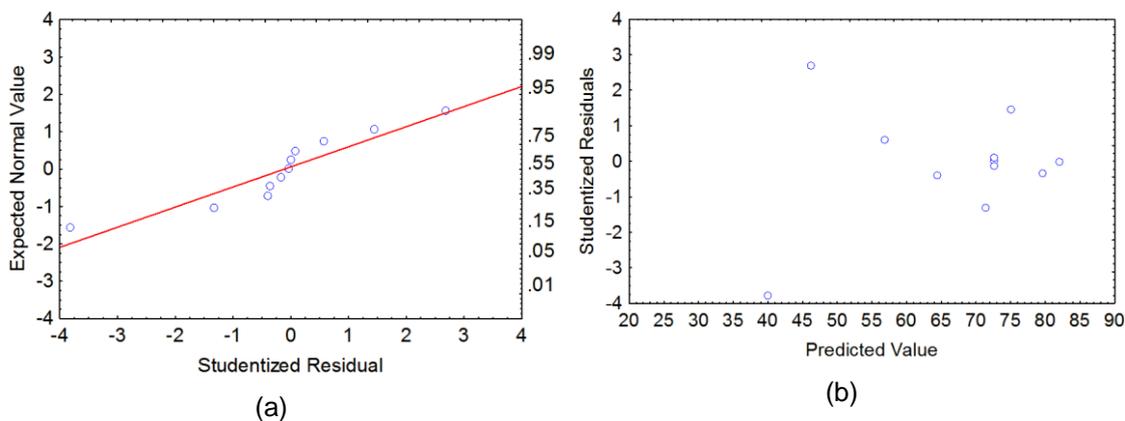
Variable	SS	df	MS	F	p-value
$[\text{H}_2\text{O}_2]$ (mM) - Linear	1207.776	1	1207.776	17.36556	0.005897

[H ₂ O ₂] (mM) - Quadratic	323.824	1	323.824	4.65599	0.074305
[Fe ²⁺] (mM) – Linear	229.707	1	229.707	3.30275	0.119057
[Fe ²⁺] (mM) – Quadratic	0.538	1	0.538	0.00773	0.932784
Lack of Fit	415.594	4	103.899	121.794	0.081600
Pure Error	1.706	2	0.853		
Total SS	2256.734	10			

Table 4. Regression coefficients for the second-order polynomial model fitting AOX removal by the Fenton process.

Variable	Regression coefficient	Std. error	p-value	95% Confidence interval	
Mean	22.034	12.854	0.137	-9.418	53.485
[H ₂ O ₂] (mM) - Linear	0.453	0.144	0.020	0.099	0.806
[H ₂ O ₂] (mM) - Quadratic	-0.001	0.001	0.074	-0.002	0.000
[Fe ²⁺] (mM) – Linear	1.196	2.178	0.603	-4.132	6.524
[Fe ²⁺] (mM) – Quadratic	-0.011	0.124	0.933	-0.314	0.292

Concerning the validation of the model assumptions, the residual plot shown in Figure 1a shows small deviation from the straight line, indicating that the studentized residuals may be considered to follow a normal distribution. Figure 1b shows a random scatter approximately centred on zero throughout the range of predicted values, indicating the residuals are random and the variance of the observations is constant for all response values. Moreover, no outliers were identified in Figure 1c since all values lied within the range ± 3.5 standard deviations around the mean.



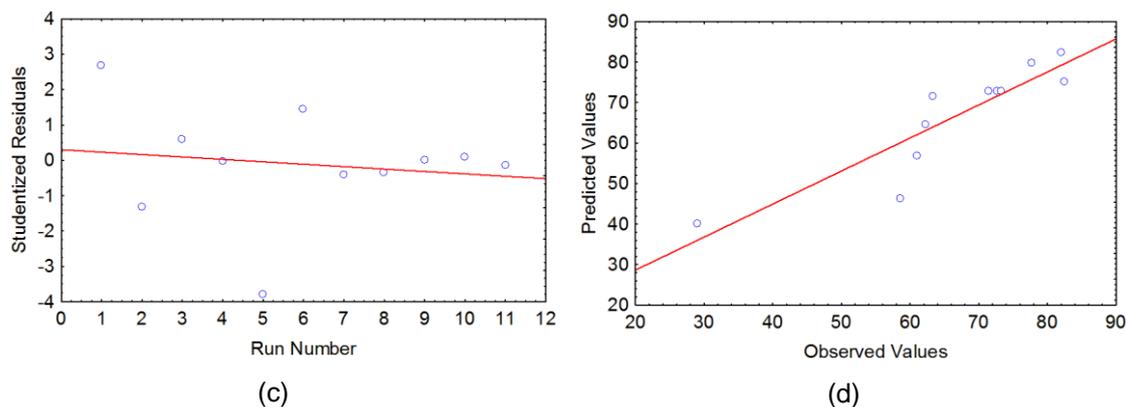
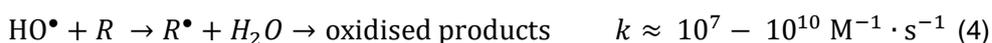
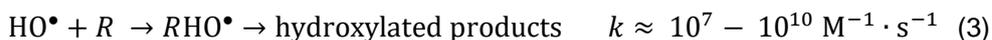


Figure 1. AOX removal by Fenton process: (a) studentized residuals and normal (%) probability; (b) studentized residuals and predicted response; (c) outlier t plot; (d) predicted and experimental values.

Figure 2 depicts the response surface predicted by the model, which can be used to analyse and predict the AOX removal for any given operating condition within the experimental range of this work, and within that range only (see Table 2). Results showed increasing AOX removal for increasing $[H_2O_2]$, which is in accordance with several published works (e.g. [11,17,29]) dealing with Fenton processes. Enough H_2O_2 will maximize the production of HO^\bullet , which is the driving force of the main reactions of degradation of organics (R) involved in Fenton processes: hydroxylation, dehydrogenation or hydrogen abstraction, and redox reactions – see equations (3)-(4) [27,38,39].



The general degradation pathways of the organics show that hydroxylation of organic aromatic pollutants leads to the cleavage of the aromatic moieties yielding short-linear aliphatic carboxylic and dicarboxylic acids, which chain is shortened, giving rise to the accumulation of oxalic and formic acid that are finally mineralized to CO_2 [38,40]. Care must be taken to prevent excess use of H_2O_2 given its counter-productive effect of HO^\bullet scavenging; moreover, unused H_2O_2 will increase COD and toxicity of the treated wastewater, which may pose environmental threats and/or hinder Fenton application prior to biological treatment [2,11,19]. In fact, Bautista et al. [39] recorded an EC_{50} value of $12 \text{ mg} \cdot \text{L}^{-1}$ of H_2O_2 for marine bacterium *Vibrio fischeri*. Moreover, for short treatments times, the intermediates in the solution may still be structurally close to the initial recalcitrant compounds [41], contributing to toxicity, although Xie et al registered that 28 out of 33 kinds of organic compounds, among which 11 out of 13 kinds of

AOX were completely removed by the Fenton process applied to pharmaceutical wastewater [42].

In this work, maximum AOX removal ($\approx 80\%$) was attained for $[\text{H}_2\text{O}_2] \geq 160\text{ mM}$. Considering the associated operational costs (see Section 3.3), the optimal solution for maximum AOX removal by Fenton process would be $[\text{H}_2\text{O}_2] = 169\text{ mM}$ and $[\text{Fe}^{2+}] = 12.5\text{ mM}$. A validation experiment was performed under these conditions, yielding 82.2% AOX removal which differs less than 3% from the predicted result (80.1% AOX removal). Catalkaya and Kargi [43] achieved even better results for pulp mill wastewater treatment by Fenton process: 89% AOX removal, for $[\text{H}_2\text{O}_2] = 50\text{ mM}$ and $[\text{Fe}^{2+}] = 2.5\text{ mM}$, with $\text{pH} = 5$, ambient temperature and $t = 30\text{ min}$. The higher AOX removal yield for lower concentrations of H_2O_2 and Fe^{2+} might be due to the biological pre-treatment undergone by the wastewater before the Fenton treatment [43]. Hence, easily biodegradable compounds had already been removed from the wastewater matrix and did not compete for HO^\bullet . These findings prove the influence of the wastewater composition on the treatment efficiency, and the need for optimization procedures such as those performed in this work.

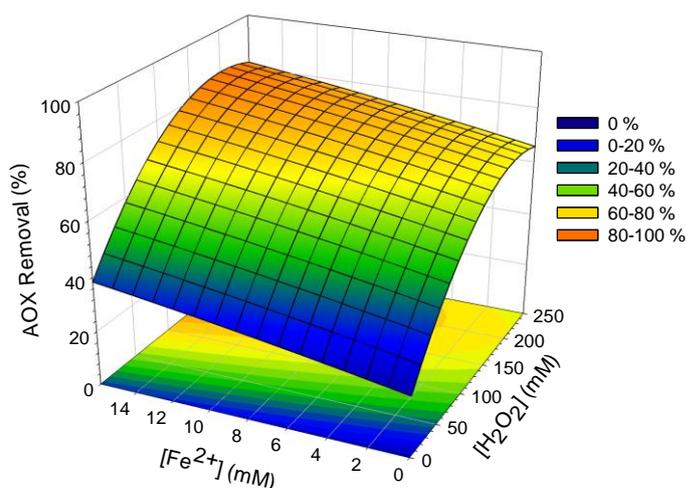


Figure 2. Influence of $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$ on AOX removal from the D_0 bleaching stream wastewater ($C_{\text{AOX}_D0} = 113.9\text{ mg}\cdot\text{L}^{-1}$), for 10 min treatment by the Fenton process.

Figure 3 shows the side-effect of the Fenton process on: (a) COD, (b) BOD_5 , (c) BOD_5/COD ratio and (d) colour of the D_0 bleaching wastewater. As stated before, the goal of this work was not to optimise these parameters, but rather to quantify any side-effect caused by the Fenton process performed under optimised conditions for AOX removal.

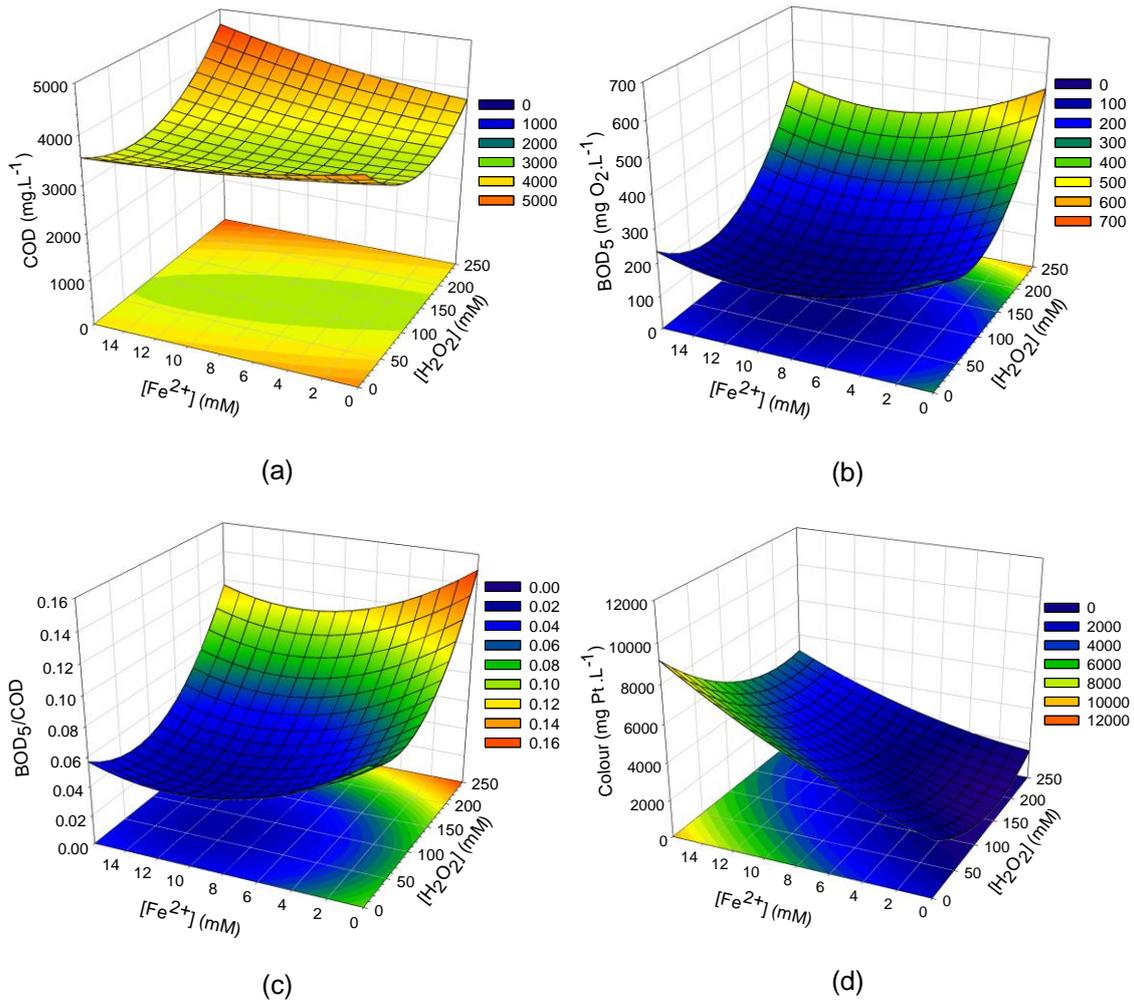


Figure 3. (a) COD, (b) BOD₅, (c) BOD₅/COD ratio and (d) colour of the D0 bleaching stream wastewater for 10 min treatment by the Fenton process. COD_{D0} ≈ 3703 mg O₂·L⁻¹ ; BOD₅_{D0} ≈ 174.3 mg O₂·L⁻¹ ; colour_{D0} ≈ 1804 mg Pt·L⁻¹

The experimental results for COD ranged between 2500 and 4500 mg·L⁻¹. Within the range of operating conditions evaluated, the highest COD removal was achieved for [Fe²⁺] < 6 mM and [H₂O₂] between 100 and 150 mM, corresponding to 0.89 and 1.38 g H₂O₂ / g COD_{initial}, respectively, and to AOX removal between 50-70 %. These results corroborate the findings of Van Aken et al. [17], who reported optimum COD removal (up to 67 %) from a graphical industry wastewater, for an oxidant dose between 0.2 and 2 g H₂O₂ / g COD_{initial}. On the other hand, Torrades et al. [28] registered a maximum COD removal (around 95 %) from synthetic black liquor at pH = 3, T = 25 °C, [Fe²⁺] = 4.66 mM and a much lower concentration of oxidant ([H₂O₂] = 44.1 mM). Altogether, these results highlight the importance of using real samples to identify the optimum operating conditions for treating real wastewaters.

For [Fe²⁺] > 6 mM and [H₂O₂] > 150 mM, COD of the treated wastewater increased. This means that, for maximum AOX removal condition, predicted COD removal below 10% would be

achieved (a confirmation experiment was performed yielding 8% COD removal). For the highest $[\text{H}_2\text{O}_2]$ tested in this work, maximum COD (around $4500 \text{ mg O}_2\cdot\text{L}^{-1}$) in the treated wastewater was registered, which would correspond to an increase in COD (around 20%). This is in agreement with Babuponnusami and Muthukumar [11], who also observed that excess chemicals would contribute to increase COD in the substrate. The explanation for this fact is probably related to the auto-scavenging of HO^\bullet radicals, which forms water and perhydroxyl radicals (OH_2^\bullet) reducing the efficiency of the process [20,38,44,45]. Indeed, a decrease in AOX removal in the region of higher oxidant concentrations was also observed in this work (see Figure 2).

Increasing the oxidant concentration increased BOD_5 in the treated wastewater up to more than twice. Maximum BOD_5 recorded surpassed $450 \text{ mg O}_2\cdot\text{L}^{-1}$ for $[\text{H}_2\text{O}_2] > 200 \text{ mM}$. Thus, the conditions for maximum AOX removal ($[\text{H}_2\text{O}_2] > 160 \text{ mM}$) are prone to increase BOD_5 of the treated wastewater. In practice, the BOD_5/COD ratio is more relevant than the final BOD_5 , since it expresses the biodegradable organic fraction in the total organic load. In this work, for highest AOX removal conditions, the predicted BOD_5/COD ratio slightly increased to 0.06-0.09 against 0.05 in the original wastewater, which was validated by a confirmation experiment that yielded 0.07. These findings show that the higher AOX removals achieved by the Fenton process would also entail some biodegradability enhancement. This is a very positive feature assuming that this process would be applied prior to any biological treatment. Corroborative results of this strategy have been reported in the literature. For instance, Balcioglu et al. [12] recorded an increase of the BOD_5/COD ratio of a photoprocessing wastewater, from 0.20 to 0.55, after 60 min of Fenton treatment with $[\text{H}_2\text{O}_2] = 180$ and $[\text{Fe}^{2+}] = 10 \text{ mM}$. In another work, Van Aken et al. [17] recorded an increase in BOD_5/COD ratio from 0.10 to almost 0.40 for increasing $[\text{H}_2\text{O}_2]$ (up to 30 mM, with $[\text{Fe}^{2+}]$ around 60 mM), when treating graphical industry wastewater with the Fenton process. However, that increase was mainly due to the reduction in COD since no significant effect on BOD_5 was registered.

Regarding colour intensity, the highest values were recorded for lower $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ pairs. In these conditions, corresponding to AOX removal below 60 %, the colour of the wastewater became more than four times worse than before treatment, mainly due to the oxidation of iron which leads to the formation and precipitation of ferric compounds such as $\text{Fe}(\text{OH})_3$. On the

other hand, conditions of high [H₂O₂] and low [Fe²⁺] produced the lowest colour intensities: ≤ 1200 mg Pt·L⁻¹, corresponding to more than 30 % colour reduction. This result is, however, lower than those found in the literature (85-90 %) for different wastewaters [29,43]. At optimal oxidant and catalyst concentrations for AOX removal, model prediction (confirmed experimentally) showed that colour became around two-fold the colour of the untreated wastewater, which is a disadvantage of the Fenton process.

3.2 Photo-Fenton Process

The second-order polynomial model of equation (1) and three simplifications of this model were fitted to the experimental results for the photo-Fenton process; Table S2 in the Supplementary Material resumes the determination coefficients and mean square residual of these regression model fittings. The best fitting model was the second-order polynomial model disregarding the interaction effect of the two independent variables (Eq. (5)) since it was not significant and did not improve R²_{adj}.

$$Z = 40.1 + 0.462x - 0.001x^2 - 0.124y + 0.003y^2 \quad (5)$$

The p-value of the Lack of Fit (see Table 5) indicates that the fit of the regression model is significant. Moreover, the R² of this model was also quite good (≈0.99) which highlights the quality of the fit (see also Figure 4d). Table 5 and Table 6 present the ANOVA results and the regression coefficients, respectively, for the fitted model.

Table 5. ANOVA table for AOX removal (%) from kraft bleaching wastewaters by the photo-Fenton process.

Variable	SS	df	MS	F	p-value
[H ₂ O ₂] (mM) - Linear	1872.208	1	1872.208	1330.703	0.000751
[H ₂ O ₂] (mM) - Quadratic	268.821	1	268.821	191.069	0.005193
[Fe ²⁺] (mM) – Linear	1.425	1	1.425	1.013	0.420214
[Fe ²⁺] (mM) – Quadratic	0.031	1	0.031	0.022	0.895546
Lack of Fit	19.212	4	4.803	3.414	0.239184
Pure Error	2.814	2	1.407		
Total SS	2256.435	10			

Table 6. Regression coefficients for the second-order polynomial model fitting for AOX removal by the photo-Fenton process.

Variable	Regression coefficient	Std. error	p-value	95% Confidence interval	
Mean	40.089	2.953	0.000	32.864	47.315
[H ₂ O ₂] (mM) - Linear	0.462	0.033	0.000	0.381	0.543
[H ₂ O ₂] (mM) - Quadratic	-0.001	0.000	0.000	-0.001	-0.001
[Fe ²⁺] (mM) – Linear	-0.124	0.500	0.812	-1.348	1.100
[Fe ²⁺] (mM) – Quadratic	0.003	0.028	0.930	-0.067	0.072

With regard to the influence of the independent variables in the response, from Table 5 it is clear that both linear and quadratic terms of the oxidant concentration ([H₂O₂]) have significant effects on the AOX removal (p-values < 0.01). The catalyst concentration in the range tested has a non-significant effect.

The model adequacy was checked by residual plots analysis. The normal probability plot presented in Figure 4a shows that residuals mainly follow a normal distribution. The random scatter of the residuals in Figure 4b indicates that the regression model is an appropriate description of the process. In Figure 4c all observations lied in the interval ± 3.5 , thus no outliers were identified in this set of experiments.

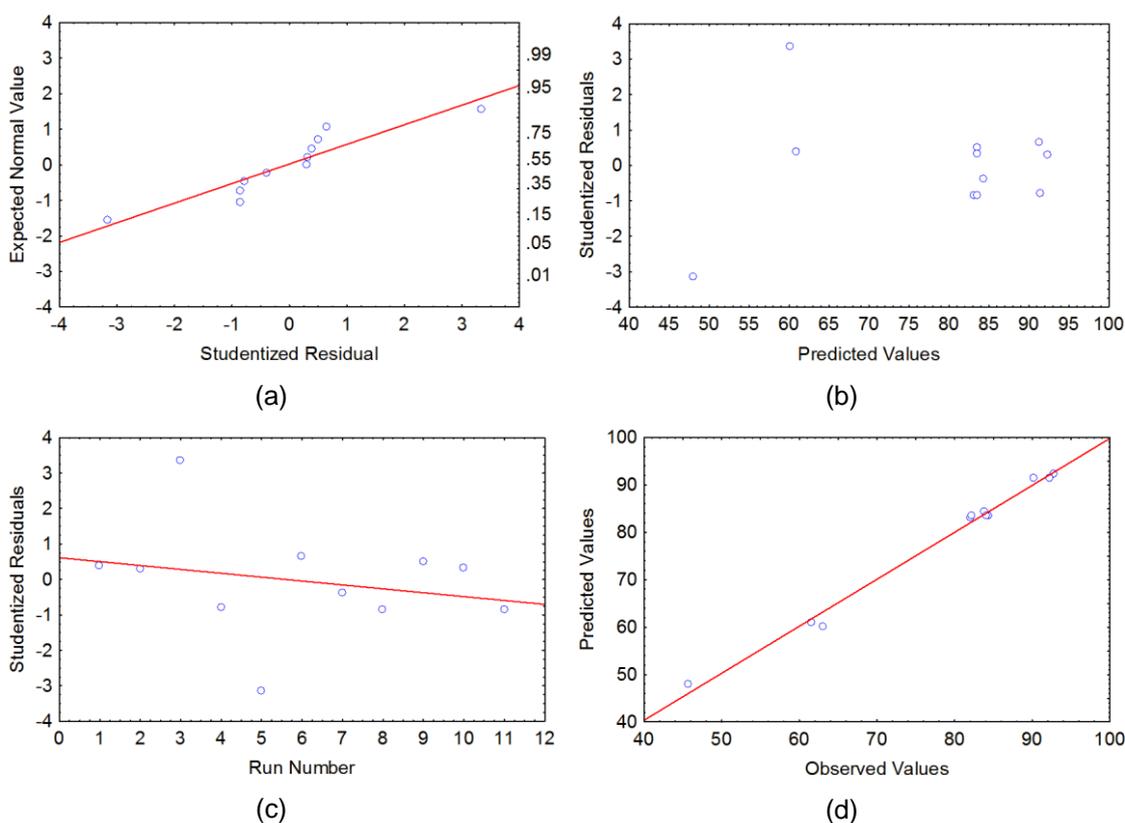


Figure 4. AOX removal by photo-Fenton process: (a) Studentized residuals and normal (%) probability; (b) Studentized residuals and predicted response; (c) Outlier t plot; (d) predicted and experimental values.

The response surface obtained from the photo-Fenton experiments, concerning the AOX removal efficiency, is shown in Figure 5, and can be used to analyse and predict the AOX removal for any given operating condition within the experimental range of this work, and within that range only (see Table 2).

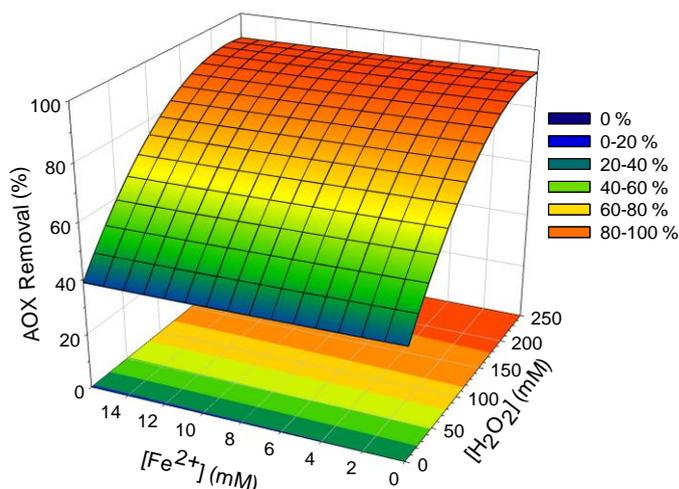


Figure 5. Influence of $[H_2O_2]$ and $[Fe^{2+}]$ on AOX removal from the D_0 bleaching stream wastewater ($C_{AOX_D0} = 113.9 \text{ mg}\cdot\text{L}^{-1}$), for 10 min treatment by photo-Fenton process.

AOX removal by photo-Fenton process increased with increasing $[H_2O_2]$ ($p < 0.0001$).

Significance of both linear and quadratic effects shows that this dependence is well described by a second-order relationship. Maximum AOX removal attained was around 90 %, for $[H_2O_2] \geq 178 \text{ mM}$, and providing a minimum $1 \text{ mM } Fe^{2+}$, which is substantially lower than for Fenton process. Under these conditions, the predicted AOX removal for the Fenton process was only 68 % (see also Figure 2).

Catalkaya and Kargi [43] recorded 93 % AOX removal from a biologically treated pulp mill wastewater for much lower concentrations of chemicals, namely $[H_2O_2] = 50 \text{ mM}$ and $[Fe^{2+}] = 2.5 \text{ mM}$, with $t = 5 \text{ min}$ and a 16 W UV lamp. In this work, those $[H_2O_2]:[Fe^{2+}]$ conditions would only remove about 50 % AOX, even considering higher operating times ($t = 10 \text{ min}$) and UV irradiation (142 W UV lamp), which highlights the influence of the prior biological treatment and the characteristics of the wastewater itself.

A validation experiment was performed with $[\text{H}_2\text{O}_2] = 178 \text{ mM}$ and $[\text{Fe}^{2+}] = 1 \text{ mM}$, leading to 89.4 % AOX removal, which differs only 1 % from the predicted result – 90.1 % AOX removal. This confirms the predictive quality of the fitted model.

The effect of the photo-Fenton process on COD, BOD_5 , BOD_5/COD ratio and colour content of the bleaching wastewater is shown in Figure 6. Lowest COD of around $2600 \text{ mg}\cdot\text{L}^{-1}$ was recorded for $[\text{H}_2\text{O}_2]$ ranging between 100 and 150 mM, corresponding to 0.89 and $1.38 \text{ g H}_2\text{O}_2 / \text{g COD}_{\text{initial}}$, respectively ($p < 0.01$), for the tested range of $[\text{Fe}^{2+}]$.

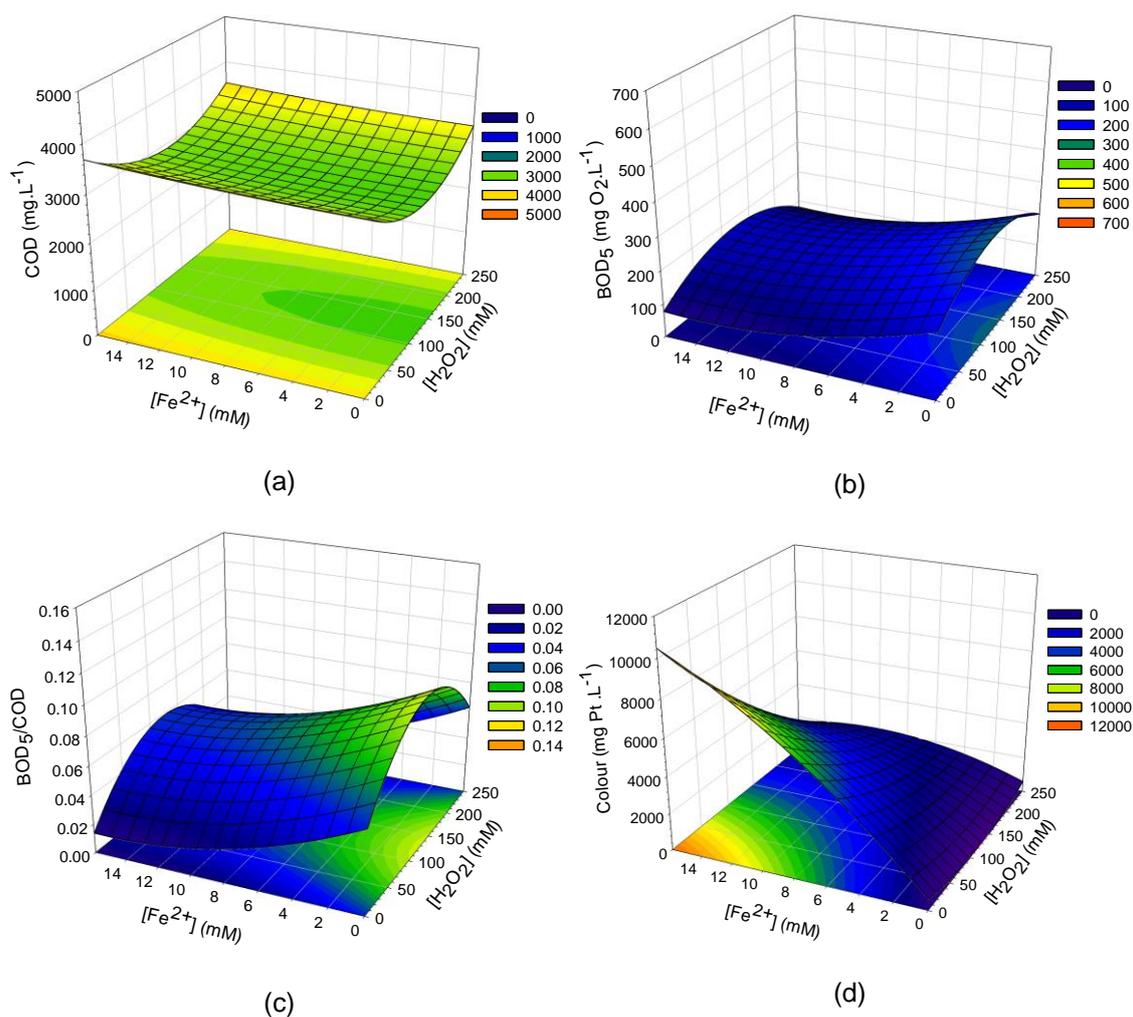


Figure 6. (a) COD, (b) BOD_5 , (c) BOD_5/COD ratio and (d) colour of the D0 bleaching stream wastewater for 10 min treatment by photo-Fenton process. $\text{COD}_{\text{D0}} \approx 3703 \text{ mg O}_2\cdot\text{L}^{-1}$; $\text{BOD}_{5,\text{D0}} \approx 174.3 \text{ mg O}_2\cdot\text{L}^{-1}$; $\text{colour}_{\text{D0}} \approx 1804 \text{ mg Pt}\cdot\text{L}^{-1}$

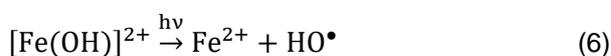
Any adopted solution for AOX removal by the photo-Fenton process would also result in some COD removal, but always below 30 %. At optimum conditions for AOX removal, 15 - 25 % COD removal was expected, and confirmed experimentally (20 % achieved experimentally). This suggests that the organic compounds attacked by HO^\bullet are possibly being transformed into

other compounds (dichromate-oxidizable) that contribute equally for COD. Accordingly, Hermosilla et al. [46] reported equal COD removal of a landfill leachate with photo-Fenton using a 32-fold lower concentration of iron when compared with Fenton. Torrades and García-Montaño [36] recorded 60 % COD removal from a dye wastewater after 120 min of treatment by photo-Fenton process under the following conditions: pH = 3; T = 25 °C; $[Fe^{2+}] \approx 2$ mM and $[H_2O_2] = 73.5$ mM. In this work, those concentrations would only yield around 30 - 35 % COD removal. This difference may be due to the nature of the wastewater treated and to the temperature. In fact, very high temperature may reduce treatment efficiency due to decomposition of H_2O_2 into O_2 and H_2O [11,47].

Maximum BOD_5 (> 280 mg $O_2 \cdot L^{-1}$) was recorded in the region of low $[Fe^{2+}]$ and $[H_2O_2]$ in the range 90-150 mM. For higher oxidant concentration a decrease of BOD_5 was recorded, up to a maximum of about 40 %. Hence, for the conditions of maximum AOX removal ($[H_2O_2] > 150$ mM and $[Fe^{2+}] = 1$ mM) BOD_5 of the treated wastewater would be around 270 mg $O_2 \cdot L^{-1}$. In that experimental range, BOD_5/COD ratio would increase from 0.05 in the untreated wastewater to 0.07 - 0.12, meaning some biodegradability rising. This was verified by an experiment at optimal conditions for AOX removal ($[H_2O_2] = 178$ mM and $[Fe^{2+}] = 1$ mM) that yielded 20% BOD_5 increase, meaning BOD_5/COD ratio increasing to 0.09. These results highlight the low biodegradable fraction of the wastewater and the importance of adjusting the oxidant concentration for AOX removal by the photo-Fenton process so that it can benefit a downstream biological treatment. Similarly, Morais and Zamora [48] observed an increase in the BOD_5/COD ratio from 0.13 to 0.40 for photo-Fenton treatment of landfill leachate, under 58.8 mM of H_2O_2 and 0.18 mM of Fe^{2+} , with $t = 60$ min, pH = 2.8, ambient temperature and a 125 W lamp as UV radiation source.

As previously observed for the Fenton process, the colour intensity of the photo-Fenton treated bleaching effluents was higher for lower $[H_2O_2]$ and $[Fe^{2+}]$. In this range of conditions, corresponding to AOX removal ≤ 70 %, the colour of the treated wastewater would be more than four-fold the value before treatment. On the other hand, pairs of high $[H_2O_2]$ and low $[Fe^{2+}]$ produced the lowest colour intensities: around 300 mg Pt $\cdot L^{-1}$, corresponding to more than 80 % colour removal. These results were similar to the ones obtained by Catalkaya and Kargi [43] for biologically treated pulp mill wastewater – 82 % colour removal after 5 min. Finally, it should be

noted that ranges of oxidant/catalyst concentrations that yielded the higher AOX removal also yielded the highest colour removal (model prediction of at least 70 % colour reduction, experimentally verified – 76 % reduction registered), which is another promising result. These results show the higher efficiency of the photo-Fenton process, associated to the UV light effect. Such improvement is due to the fact that under light irradiation $[\text{Fe}(\text{OH})]^{2+}$, which is the dominant Fe^{3+} form at pH 2.8-3.5 [23,49], undergoes metal charge transfer excitation, producing HO^\bullet and regenerating Fe^{2+} , that catalyses the decomposition of H_2O_2 into even more HO^\bullet (equation (6)). In addition, a different (but slower) pathway of HO^\bullet production takes place under photo-Fenton conditions, which is the direct photolysis of H_2O_2 , according to equation (7) [23,50,51].



3.3 Operational cost analysis

The experimental results presented in this work show that it is possible to attain a certain value for AOX removal by more than one combination of $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$. Therefore, the final decision about the operating conditions will be ruled by economic criteria, namely operational cost analysis. In this work, the Fenton and photo-Fenton model equations were used to determine all combinations that would yield AOX removal equal to 25, 30, 35, 40, ..., up to 90 %. Operational costs were computed in order to determine the cheapest combination to achieve each target AOX removal based on lab-scale average market prices for H_2O_2 30 % (w/v) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ of 2 $\text{€} \cdot \text{L}^{-1}$ and 9.5 $\text{€} \cdot \text{kg}^{-1}$, respectively, and electricity cost of 70 $\text{€} \cdot \text{MWh}^{-1}$ (for the UV light supply in photo-Fenton process), based on typical energy market prices for Portuguese PP industry. Considering a 150 W of UV-lamp power, 10 min of treatment, and assuming that the recorded removals would only be valid for 0.5 L (which reflects an unrealistic worst-case scenario), a cost of electricity per cubic meter of treated wastewater was computed (3.50 $\text{€} \cdot \text{m}^{-3}$) for the photo-Fenton process operational cost. Figure 7 shows the minimum attainable cost for the different AOX removal targets from the bleaching wastewater by both Fenton and photo-Fenton processes.

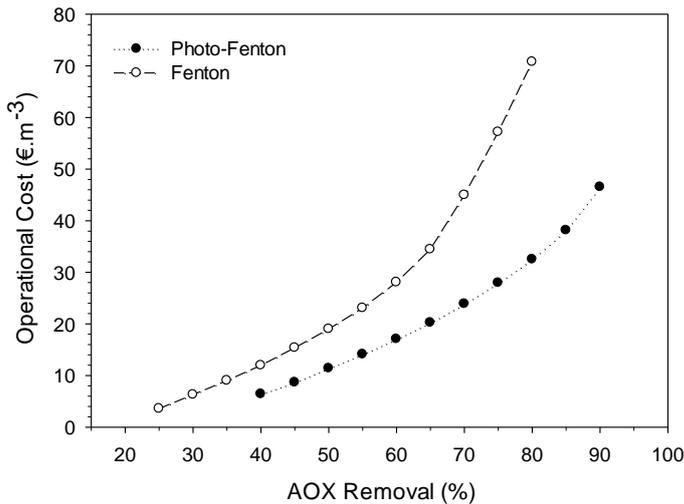


Figure 7. Operational costs for AOX removal from D0 bleaching wastewater by Fenton and photo-Fenton processes.

To achieve higher AOX removal, higher chemical concentrations are necessary, namely H_2O_2 , as proved experimentally. Using the Fenton process, 50 % AOX removal would cost $18.99 \text{ €}\cdot\text{m}^{-3}$; for maximum AOX removal (around 83 %) the cost would be more than $70 \text{ €}\cdot\text{m}^{-3}$. For the studied wastewater ($C_{\text{AOX}} = 113.9 \text{ mg}_{\text{AOX}}\cdot\text{L}^{-1}$), this would represent costs from $0.13 \text{ €}\cdot\text{g}^{-1}$ AOX removed (for 25 % removal) up to $0.78 \text{ €}\cdot\text{g}^{-1}$ AOX removed (for 80 % removal).

As stated before, AOX removal by photo-Fenton process depended only on $[\text{H}_2\text{O}_2]$ so the most economical solution for each AOX removal target was achieved by increasing only $[\text{H}_2\text{O}_2]$, while providing the minimum $[\text{Fe}^{2+}]$ studied: 1 mM. According to Figure 7, the operational costs associated with the photo-Fenton process are systematically lower than with the Fenton process for any desired removal efficiency. For instance, considering 50 % AOX removal the operational cost would be $11.38 \text{ €}\cdot\text{m}^{-3}$ (against $18.99 \text{ €}\cdot\text{m}^{-3}$ for the Fenton process). Considering maximum achievable AOX removal of around 90 % for the photo-Fenton process (against around 80% for Fenton process), the operational cost would be $46.5 \text{ €}\cdot\text{m}^{-3}$, which would be the cost of removing only 70 % AOX by the Fenton process. Moreover, the lower cost of iron sludge disposal should also be considered as a positive aspect of the photo-Fenton process, since it requires much less Fe^{2+} .

The increase of cost associated with the increase of removal target was less sharp in the photo-Fenton process, which was clear by the economic indicator *cost per g of AOX removed*, that increased only from 0.14 to $0.45 \text{ €}\cdot\text{g}^{-1}$ AOX removed for 40 % and 90 % AOX removal,

respectively. Belalcázar-Saldarriaga et al. [52] computed 1.0 USD·m⁻³ as the cost for photo-Fenton treatment of a commercial dye in a raceway reactor, using 0.65 mg H₂O₂ and 0.05 mg Fe²⁺ per mg of dye, with solar irradiation and t = 60 min. However, that work focused on the removal of dye from the synthetic wastewater containing only the target compound, which increases several times the removal efficiency. In another work, Cañizares et al. [53] reported 5 €·m⁻³ as the cost to achieve 70 % COD removal from olive oil mill wastewater, considering 18 g·L⁻¹ H₂O₂ and 0.7 g·L⁻¹ Fe²⁺ as chemical input. One should note, however, that the costs presented in this work were based in lab-scale prices for the chemical reagents. At full-scale, market prices of the chemicals used would be several times lower, which would mean much lower costs would be attained. For instance, Belalcázar-Saldarriaga et al. [52] considered market price of H₂O₂ as half of the one considered in this work and the price of FeSO₄ was almost 10-fold lower. Cañizares et al. [53] also considered prices for H₂O₂ and FeSO₄ around ten-fold lower than the prices considered herein.

4. CONCLUSION

Photo-Fenton process proved to be more efficient than conventional Fenton in removing AOX from kraft pulp bleaching wastewater, showing higher AOX removal with lower chemical consumption: 90 % removal for [H₂O₂] = 178 mM and [Fe²⁺] = 1.0 mM under photo-Fenton conditions, against 80 % removal for [H₂O₂] = 169 mM and [Fe²⁺] = 12.5 mM with conventional Fenton. For both methods, [H₂O₂] was the only operating parameter statistically affecting AOX removal, for fixed pH (2 ± 0.2), temperature (60 ± 2 °C) and treatment time (10 min).

Besides allowing for higher AOX removal efficiencies, the photo-Fenton process provided higher colour removal, increased biodegradability of the wastewater, lower operational costs, and has the potential to reduce the formation of iron sludge. This is still the main drawback of the Fenton processes and still requires further investigation. For maximum AOX removal, BOD₅/COD ratio (i.e., the biodegradability) slightly increased from 0.05 to 0.09 for photo-Fenton treated wastewater, against 0.07 using Fenton process; colour decreased almost 80 % for photo-Fenton, while for Fenton it became almost two-fold higher than in the untreated wastewater. The operational cost was also an advantage of the photo-Fenton process: under

optimal operating conditions, the costs were estimated to be around 70 €·m⁻³ or 0.78 €·g⁻¹ AOX removed for photo-Fenton, against around 46.5 €·m⁻³ or 0.45 €·g⁻¹ AOX removed for Fenton. Finally, this work highlighted the advantages of (photo-)Fenton processes over other technologies regarding AOX removal, such as the higher removal efficiencies compared with biological treatment (usually between 50 - 60 % [54,55]), and the lower cost and shorter treatment time when compared to other AOP such as ozonation or photocatalysis [21,56]. The coupling between Fenton processes and biological treatment is probably the most suitable to treat PP wastewater, due to the coupled efficiency in removing recalcitrant pollutants in a first AOP stage, followed by strong mineralization of organic matter by biological processes. The results from this work prove the suitability of Fenton processes to be applied prior to biological treatment, which could help solving the issue of wastewater treatment for industries that generate very high amounts of wastewaters.

ACKNOWLEDGEMENTS

This work was financed by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of Operational Competitiveness and Internationalization Programme (POCI) in the scope of Project PROTEUS - POCI-01-0247-FEDER-017729. Thanks also due to FCT/MCTES for the financial support to CESAM (UIDP/50017/2020+UIDB/50017/2020), through national funds. This work was also developed within the scope of CICECO (UIDB/50011/2020 & UIDP/50011/2020), financed by national funds through the FCT/MCTES and when appropriate co-financed by ERDF under the PT2020 Partnership Agreement). Finally, J. P. Ribeiro acknowledges FCT – Fundação para a Ciência e a Tecnologia, I.P. for his PhD Grant (SFRH/BD/141133/2018).

REFERENCES

- [1] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Liquid fuels, hydrogen and chemicals from lignin: A critical review, *Renew. Sustain. Energy Rev.* 21 (2013) 506–523. doi:10.1016/j.rser.2012.12.022.
- [2] K. Eskelinen, H. Särkkä, T.A. Kurniawan, M.E.T. Sillanpää, Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: A comparative study, *Desalination*. 255 (2010) 179–187. doi:10.1016/j.desal.2009.12.024.
- [3] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater - A review, *Sci. Total Environ.* 333 (2004) 37–58. doi:10.1016/j.scitotenv.2004.05.017.

- [4] D. V. Savant, R. Abdul-Rahman, D.R. Ranade, Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater, *Bioresour. Technol.* 97 (2006) 1092–1104. doi:10.1016/j.biortech.2004.12.013.
- [5] R. Toczyłowska-Mamińska, Limits and perspectives of pulp and paper industry wastewater treatment - A review, *Renew. Sustain. Energy Rev.* 78 (2017) 764–772. doi:10.1016/j.rser.2017.05.021.
- [6] O. Ashrafi, L. Yerushalmi, F. Haghghat, Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission, *J. Environ. Manage.* 158 (2015) 146–157. doi:10.1016/j.jenvman.2015.05.010.
- [7] M.A. Hubbe, J.R. Metts, D. Hermosilla, M.A. Blanco, L. Yerushalmi, F. Haghghat, P. Lindholm-Lehto, Z. Khodaparast, M. Kamali, A. Elliott, Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities, *BioResources.* 11 (2016) 7953–8091. doi:10.15376/biores.11.3.hubbe.
- [8] K. Ranganathan, S. Jeyapaul, D.C. Sharma, Assessment of water pollution in different bleaching based paper manufacturing and textile dyeing industries in India, *Environ. Monit. Assess.* 134 (2007) 363–372. doi:10.1007/s10661-007-9628-z.
- [9] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination - A review, *Sci. Total Environ.* 409 (2011) 4141–4166. doi:10.1016/j.scitotenv.2010.08.061.
- [10] M. Kowalska, S. Donatello, O. Wolf, Revision of the EU Ecolabel criteria for Paper products Final Technical Report, Seville, 2019. https://ec.europa.eu/environment/ecolabel/documents/tissue_paper_tr_2019.pdf.
- [11] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, *J. Environ. Chem. Eng.* 2 (2014) 557–572. doi:10.1016/j.jece.2013.10.011.
- [12] I.A. Balcioglu, I. Arslan-Alaton, M. Otker, R. Bahar, N. Bakar, M. Ikiz, Application of advanced oxidation processes to different industrial wastewaters, *J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng.* 38 (2003) 1587–1596. doi:10.1081/Ese-120021482.
- [13] M. Trapido, T. Tenno, A. Goi, N. Dulova, E. Kattel, D. Klauson, K. Klein, T. Tenno, M. Viisimaa, Bio-recalcitrant pollutants removal from wastewater with combination of the Fenton treatment and biological oxidation, *J. Water Process Eng.* 16 (2017) 277–282. doi:10.1016/j.jwpe.2017.02.007.
- [14] J.M. Ochando-Pulido, S. Pimentel-Moral, V. Verardo, A. Martinez-Ferez, A focus on advanced physico-chemical processes for olive mill wastewater treatment, *Sep. Purif. Technol.* 179 (2017) 161–174. doi:10.1016/j.seppur.2017.02.004.
- [15] X. Zhu, J. Tian, R. Liu, L. Chen, Optimization of Fenton and electro-Fenton oxidation of biologically treated coking wastewater using response surface methodology, *Sep. Purif. Technol.* 81 (2011) 444–450. doi:10.1016/j.seppur.2011.08.023.
- [16] P.A. Soloman, C. Ahmed Basha, M. Velan, N. Balasubramanian, P. Marimuthu, Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM, *Sep. Purif. Technol.* 69 (2009) 109–117. doi:10.1016/j.seppur.2009.07.002.
- [17] P. Van Aken, K. Van Eyck, J. Degreève, S. Liers, J. Luyten, COD and AOX Removal and Biodegradability Assessment for Fenton and O₃/UV Oxidation Processes: A Case Study from a Graphical Industry Wastewater, *Ozone-Science Eng.* 35 (2013) 16–21. doi:10.1080/01919512.2013.720552.
- [18] E. Neyens, J. Baeyens, A Reivew of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50. doi:10.1016/S0043-1354(02)00461-X.

- [19] F. Torrades, M. Pérez, H.D. Mansilla, J. Peral, Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions, *Chemosphere*. 53 (2003) 1211–1220. doi:10.1016/S0045-6535(03)00579-4.
- [20] J.M.P. Ramos, N.M. Pereira-Queiroz, D.H.S. Santos, J.R. Nascimento, C.M. de Carvalho, J. Tonholo, C.L.P.S. Zanta, Printing ink effluent remediation: A comparison between electrochemical and Fenton treatments, *J. Water Process Eng.* 31 (2019) 100803. doi:10.1016/j.jwpe.2019.100803.
- [21] D. Balabanič, D. Hermosilla, N. Merayo, A.K. Klemenčič, A. Blanco, Comparison of different wastewater treatments for removal of selected endocrine-disruptors from paper mill wastewaters., *J. Environ. Sci. Heal. Part A Toxic/Hazardous Subst. Environ. Eng.* 47 (2012) 1350–1363. doi:10.1080/10934529.2012.672301.
- [22] J.M. Poyatos, M.M. Muñoz, M.C. Almecija, J.C. Torres, E. Hontoria, F. Osorio, Advanced oxidation processes for wastewater treatment: State of the art, *Water. Air. Soil Pollut.* 205 (2010) 187–204. doi:10.1007/s11270-009-0065-1.
- [23] M. Zhang, H. Dong, L. Zhao, D. Wang, D. Meng, A review on Fenton process for organic wastewater treatment based on optimization perspective, *Sci. Total Environ.* 670 (2019) 110–121. doi:10.1016/j.scitotenv.2019.03.180.
- [24] S. Sun, H. Yao, W. Fu, L. Hua, G. Zhang, W. Zhang, Reactive Photo-Fenton ceramic membranes: Synthesis, characterization and antifouling performance, *Water Res.* 144 (2018) 690–698. doi:10.1016/j.watres.2018.08.002.
- [25] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review, *Water Res.* 139 (2018) 118–131. doi:10.1016/j.watres.2018.03.042.
- [26] D. Hermosilla, N. Merayo, R. Ordóñez, Ángeles Blanco, Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill, *Waste Manag.* 32 (2012) 1236–1243. doi:10.1016/j.wasman.2011.12.011.
- [27] D. Hermosilla, N. Merayo, A. Gascó, Á. Blanco, The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review, *Environ. Sci. Pollut. Res.* 22 (2015) 168–191. doi:10.1007/s11356-014-3516-1.
- [28] F. Torrades, S. Saiz, J.A. García-Hortal, Using central composite experimental design to optimize the degradation of black liquor by Fenton reagent, *Desalination*. 268 (2011) 97–102. doi:10.1016/j.desal.2010.10.003.
- [29] M. Pérez, F. Torrades, X. Domènech, J. Peral, Removal of organic contaminants in paper pulp effluents by AOPs: An economic study, *J. Chem. Technol. Biotechnol.* 77 (2002) 525–532. doi:10.1002/jctb.610.
- [30] K. Lal, A. Garg, Utilization of dissolved iron as catalyst during Fenton-like oxidation of pretreated pulping effluent, *Process Saf. Environ. Prot.* 111 (2017) 766–774. doi:10.1016/j.psep.2017.09.005.
- [31] A. V. Vorontsov, Advancing Fenton and photo-Fenton water treatment through the catalyst design, *J. Hazard. Mater.* 372 (2019) 103–112. doi:10.1016/j.jhazmat.2018.04.033.
- [32] Y. Guo, Q. Xue, H. Zhang, N. Wang, S. Chang, H. Wang, H. Pang, H. Chen, Treatment of real benzene dye intermediates wastewater by the Fenton method: Characteristics and multi-response optimization, *RSC Adv.* 8 (2018) 80–90. doi:10.1039/c7ra09404c.
- [33] J.P. Ribeiro, C.C. Marques, I. Portugal, M.I. Nunes, AOX removal from pulp and paper wastewater by Fenton and photo-Fenton processes: A real case-study, *Energy Reports*. 6 (2020) 770–775. doi:10.1016/j.egy.2019.09.068.
- [34] A. Greenberg, L. Clesceri, A. Eaton, eds., *Standard methods for the examination of water and wastewater*, 20th ed., American Public Health Association; American Water

- Works Association; Water Environment Federation, Baltimore, 1999.
- [35] H. Majdi, J.A. Esfahani, M. Mohebbi, Optimization of convective drying by response surface methodology, *Comput. Electron. Agric.* 156 (2019) 574–584. doi:10.1016/j.compag.2018.12.021.
- [36] F. Torrades, J. García-Montaña, Using central composite experimental design to optimize the degradation of real dye wastewater by Fenton and photo-Fenton reactions, *Dye. Pigment.* 100 (2014) 184–189. doi:10.1016/j.dyepig.2013.09.004.
- [37] A.M. Joglekar, A. May, Product excellence through design of experiments, *Cereal Food World.* 32 (1987) 857–868.
- [38] S. Garcia-Segura, L.M. Bellotindos, Y.-H. Huang, E. Brillas, M.-C. Lu, Fluidized-bed Fenton process as alternative wastewater treatment technology - A review, *J. Taiwan Inst. Chem. Eng.* 67 (2016) 211–225. doi:10.1016/j.jtice.2016.07.021.
- [39] P. Bautista, A.F. Mohedano, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, Application of Fenton oxidation to cosmetic wastewaters treatment, *J. Hazard. Mater.* 143 (2007) 128–134. doi:10.1016/j.jhazmat.2006.09.004.
- [40] M. Munoz, G. Pliego, Z.M. Pedro, J.A. Casas, J.J. Rodriguez, Application of intensified Fenton oxidation to the treatment of sawmill wastewater, *Chemosphere.* 109 (2014) 34–41. doi:10.1016/j.chemosphere.2014.02.062.
- [41] W. Bae, H. Won, B. Hwang, R.A. de Toledo, J. Chung, K. Kwon, H. Shim, Characterization of refractory matters in dyeing wastewater during a full-scale Fenton process following pure-oxygen activated sludge treatment, *J. Hazard. Mater.* 287 (2015) 421–428. doi:10.1016/j.jhazmat.2015.01.052.
- [42] Y. Xie, L. Chen, R. Liu, Oxidation of AOX and organic compounds in pharmaceutical wastewater in RSM-optimized-Fenton system, *Chemosphere.* 155 (2016) 217–224. doi:10.1016/j.chemosphere.2016.04.057.
- [43] E.C. Catalkaya, F. Kargi, Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study, *J. Hazard. Mater.* 139 (2007) 244–253. doi:10.1016/j.jhazmat.2006.06.023.
- [44] K. Sivagami, K.P. Sakthivel, I.M. Nambi, Advanced oxidation processes for the treatment of tannery wastewater, *J. Environ. Chem. Eng.* 6 (2018) 3656–3663. doi:10.1016/j.jece.2017.06.004.
- [45] A. Brink, C.M. Sheridan, K.G. Harding, The Fenton oxidation of biologically treated paper and pulp mill effluents: A performance and kinetic study, *Process Saf. Environ. Prot.* 107 (2017) 206–215. doi:10.1016/j.psep.2017.02.011.
- [46] D. Hermosilla, M. Cortijo, C.P. Huang, Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes, *Sci. Total Environ.* 407 (2009) 3473–3481. doi:10.1016/j.scitotenv.2009.02.009.
- [47] I. Gulkaya, G.A. Surucu, F.B. Dilek, Importance of H₂O₂/Fe²⁺ ratio in Fenton's treatment of a carpet dyeing wastewater, *J. Hazard. Mater.* 136 (2006) 763–769. doi:10.1016/j.jhazmat.2006.01.006.
- [48] J.L. De Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, *J. Hazard. Mater.* 123 (2005) 181–186. doi:10.1016/j.jhazmat.2005.03.041.
- [49] S. Miralles-Cuevas, I. Oller, A. Agüera, J.A. Sánchez Pérez, S. Malato, Strategies for reducing cost by using solar photo-Fenton treatment combined with nanofiltration to remove microcontaminants in real municipal effluents: Toxicity and economic assessment, *Chem. Eng. J.* 318 (2017) 161–170. doi:10.1016/j.cej.2016.06.031.
- [50] I. Arslan-Alaton, F. Gurses, Photo-Fenton-like and photo-fenton-like oxidation of Procaine Penicillin G formulation effluent, *J. Photochem. Photobiol. A Chem.* 165 (2004)

165–175. doi:10.1016/j.jphotochem.2004.03.016.

- [51] E. Hernández-Francisco, J. Peral, L.M. Blanco-Jerez, Removal of phenolic compounds from oil refinery wastewater by electrocoagulation and Fenton/photo-Fenton processes, *J. Water Process Eng.* 19 (2017) 96–100. doi:10.1016/j.jwpe.2017.07.010.
- [52] A. Belalcázar-Saldarriaga, D. Prato-García, R. Vázquez-Medrano, Photo-Fenton processes in raceway reactors: Technical, economic, and environmental implications during treatment of colored wastewaters, *J. Clean. Prod.* 182 (2018) 818–829. doi:10.1016/j.jclepro.2018.02.058.
- [53] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes, *J. Environ. Manage.* 90 (2009) 410–420. doi:10.1016/j.jenvman.2007.10.010.
- [54] A. Schnell, P. V. Hodson, P. Steel, H. Melcer, J.H. Carey, Enhanced biological treatment of bleached kraft mill effluents - II. Reduction of mixed function oxygenase (MFO) induction in fish, *Water Res.* 34 (2000) 501–509. doi:10.1016/S0043-1354(99)00161-X.
- [55] P. Singh, I.S. Thakur, Colour removal of anaerobically treated pulp and paper mill effluent by microorganisms in two steps bioreactor, *Bioresour. Technol.* 97 (2006) 218–223. doi:10.1016/j.biortech.2005.02.022.
- [56] A.D. Bokare, W. Choi, Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes, *J. Hazard. Mater.* 275 (2014) 121–135. <http://www.sciencedirect.com/science/article/pii/S0304389414003239>.