Original Article

Degradation of xanthate in waters by hydrogen peroxide, fenton and simulated solar photo-fenton processes

Bruno García-Leiva a, Luiz Alberto Cesar Teixeira b,*, Mauricio Leonardo Torem c

a Pontifícia Universidade Católica do Rio de Janeiro, Dept. of Chemical and Materials Engineering, Rua Marquês de S. Vicente, 225–5011, Rio de Janeiro, 22451-900, Brazil
b Pontifícia Universidade Católica do Rio de Janeiro, Dept. of Chemical and Materials Engineering and Peróxidos do Brasil Ltda. (Solvay Group), Rua Marquês de S. Vicente, 225–5011, Rio de Janeiro, 22451-900, Brazil
c Pontifícia Universidade Católica do Rio de Janeiro, Dept. of Chemical and Materials Engineering, Rua Marquês de S. Vicente, 225–5011, Rio de Janeiro, 22451-900, Brazil

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A B S T R A C T

This work reports the findings of a preliminary study of oxidative degradation of ethyl xanthate (EX) in aqueous solutions comparing hydrogen peroxide, the Fenton process, and photo-Fenton process driven by simulated solar radiation. Kinetic runs were carried out following a factorial design using a synthetic effluent with initial [EX] = 100 mg/L, H2O2 was dosed at the stoichiometric amount required for complete mineralization of EX. The variables studied were: initial pH: 5 and 9; [Fe2+]:[H2O2] molar ratio: 0.0 and 1.40, and irradiance: 0 and 30 mW/cm2. An initial fast step breaks down more than 90% of the xanthate, forming intermediates that still contain unoxidized carbon and sulphur. Additional steps occur in which organic carbon and reduced sulphur from the intermediates may ultimately be converted to bicarbonate and sulphate. The progress of the reaction is indicated by reduction in TOC, gain in sulphate (SO4), and H2O2 consumption. Overall the optimum conditions for the breakdown of EX were those using the photo-Fenton process: initial pH = 5; [Fe2+]:[H2O2] molar ratio = 1.40; and irradiance = 30 mW/cm2. After 2 h the best results were: xanthate breakdown > 98.6%; TOC reduction = 39.2%; SO4 generation = 43.1%. The experiments were conducted batchwise and this led to partial mineralization of the xanthate’s organic and sulphur contents. The statistical design using simulated solar radiation enabled us to conclude that tailings ponds could be used as treatment reactors, where their efficiency is enhanced by sunlight.

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* Corresponding author.
E-mails: bgarcilev@gmail.com (B. García-Leiva), teixeira@puc-rio.br (L.A. Teixeira), torem@puc-rio.br (M.L. Torem).

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1. Introduction

It is estimated that about 2 billion tons of minerals are processed by flotation annually [1] including almost all of the copper, lead, zinc, nickel and molybdenum produced in the world. Xanthate salts are amongst the most commonly used flotation collectors.

The wastewater from the sulphide mineral flotation processes collected in dams may contain residual xanthates as well as dissolved metals and non-metals, and other organics such as frothers. Without adequate treatment, its contact with the environment can cause pollution of underground and surface waters. Although many flotation plants recycle a high percentage of the water accumulated in tailings dams, some discharge may occur on a regular or seasonal basis. Thus, there is interest in studying processes for removing xanthates from such plant tailings to prevent environmental contamination. The breakdown of residual xanthate and other organics from flotation effluents also facilitates the recycling of the effluents in the plant, by reducing the interference of such compounds on flotation selectivity [2,3]. This contributes to minimizing the intake of raw water, particularly important in regions of water scarcity.

As to the environmental aspects, xanthates show high toxicity to biota especially in aqueous media as reported in data compiled by Alto et al. [4]. The highest toxicity is due to carbon bisulfide (CS₂), an intermediate product of the natural breakdown of xanthate [5–7], so an eventual discharge of wastewater containing residual xanthate can cause environmental damage. In the toxicity data reported by Alto et al. [4], LC₅₀ values for 96h ranged from 0.1 mg/L for Daphnia magna to 100 mg/L for fish species Salmo gairdneri (rainbow trout). In a more recent study Guerrero [8] analysed the acute toxicity in Guppy fish and found a significantly lower LC₅₀ (96h) = 1.5 mg/L.

In recent years various wastewater treatment techniques to remove residual xanthate have been studied. These include oxidation using hydrogen peroxide, ozone, photolysis and Fenton [2,9–15], precipitation, decomposition, acid neutralisation [16], biodegradation [17], and adsorption on bentonite [3].

Of the techniques studied, the breakdown of xanthate by oxidation using hydrogen peroxide has considerable advantages as the xanthate could ideally be converted into innocuous products, carbonate and sulphate, both acceptable for effluent discharge into rivers, or for in-plant recycling. Hydrogen peroxide is a chemical well established in the treatment of mining effluents.

In a study of xanthate oxidation with H₂O₂, Silvester et al. [9] proposed that the EX anion reacting with H₂O₂ is oxidised to ethyl perxanthate (C₂H₅OCS₂O⁻) (EPX), according to Eq. (1). And EPX is further oxidised to ethyl thiosulphate and sulphate (Eq. 2). An overall reaction was proposed with sulphate being the final sulphur containing product (Eq. 3).

\[
\text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + \text{H}_2\text{O}_2 = \text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + \text{H}_2\text{O} \quad (1)
\]

\[
\text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + \text{H}_2\text{O}_2 = \text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + \text{SO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \quad (2)
\]

\[
\text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + 8\text{H}_2\text{O}_2 = \text{C}_2\text{H}_5\text{OH} + \text{CO}_3^{2-} + 2\text{SO}_4^{2-} + 5\text{H}_2\text{O} + 5\text{H}^+ \quad (3)
\]

In a more recent and detailed study, Chen et al. [13] established a new reaction path for the degradation of EX with H₂O₂ after identifying thiosulphate as a reaction intermediate resulting from the oxidation of EPX according to Eq. (4) (not balanced).

\[
\text{C}_2\text{H}_5\text{OCS}_2\text{O}^- + \text{pH}_2\text{O}_2 = \text{S}_2\text{O}_3^{2-} + 3\text{CO}_3^{-} \quad (4)
\]

In this proposed reaction path, the thiosulphate ion can be further oxidized to sulphate according to Eq. (5) at pH > 7, or to elemental S at pH < 7.

\[
\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O}_2 = \text{SO}_4^{2-} + \text{H}_2\text{O} \quad (5)
\]

Although the use of uncatalyzed hydrogen peroxide for xanthate degradation is an attractive proposition, it may not be a powerful enough oxidant for extensive mineralization (total conversion of the xanthate ion into carbonate and sulphate), and so more powerful oxidation techniques such as the advanced oxidation processes (AOPs) may be required. In the AOPs, the H₂O₂ molecule added to the effluent splits and generates the very powerful oxidant HO· radical which in turn is able to breakdown various refractory organic compounds.

Of the advanced oxidation techniques studied, the Fenton process and its variations have shown good results. This led us to investigate the potential effectiveness of a variation of the Fenton process: the photo-Fenton process, with a view to evaluate the possibility of using tailings dams as solar-photolytic Fenton reactors for the breakdown of xanthates.

The Fenton advanced oxidation system was discovered in 1894 [18] but it was only in the 1980s that it started to be studied for the degradation of aqueous refractory organics, resistant to uncatalyzed chemical oxidation by O₂, Cl₂, or H₂O₂ [19,20].

Fenton’s main reactions and their kinetic constants are:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^{-} + \text{OH}^- \quad k_1 = 76 \text{ L/mol.s} \quad (6)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad k_2 = 0.001\text{upto0.01L/mol.s} \quad (7)
\]

Eq. (6) is the primary generator of the powerful HO· radical. It works fast provided there is sufficient H₂O₂ and Fe²⁺ present to drive the reaction. Once the catalyst Fe²⁺ is converted to Fe³⁺, this is recycled back to Fe²⁺ by H₂O₂ as shown.
in Eq. (7). But since the reduction of Fe$^{3+}$ by hydrogen peroxide (Eq. 7) is about 7000 times slower than the oxidation of Fe$^{2+}$, the breakdown speed (and efficiency) of compounds in the Fenton reaction typically decreases with time. In practice, in a conventional Fenton process, one usually compensates for the reduction of [Fe$^{2+}$] during the course of the reaction by increasing the initial Fe$^{2+}$ dose; this implies a higher cost.

The photo-Fenton process evolved in 1993 when Ruppert et al. [21], Sun & Pignatello [22,23], and Zepp et al. [24], started experimenting with radiation, adding photons to the Fenton process. They found that the efficiency of the Fenton reaction was greatly improved by the use of ultraviolet/visible radiation.

Chong et al. [25] suggested homogeneous photo-catalysis of the photo-Fenton process according to Eqs (8) and (9), by combining Fenton reagent with UV/visible light of wavelength lower than 580 nm.

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} + \text{hv} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}.$$  
(8)

$$\text{Fe}^{3+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{HO}. + \text{H}^+.$$  
(9)

The use of light is interesting as it promotes the reduction of Fe$^{3+}$ by photons, rapidly reducing ferric ions to their initial oxidation state (Fe$^{2+}$). The Fe$^{2+}$ can react again with H$_2$O$_2$ giving rise to a continuous source of hydroxyl radicals HO$_2$, increasing the speed and efficiency of the photo-assisted process by comparison to the conventional Fenton process, by generating a higher rate of hydroxyl radicals [25]. In addition to the photo-Fenton reactions, the action of UV radiation of wavelength less than 300 nm on solutions containing H$_2$O$_2$ also results in generating HO radicals through cleavage of the molecule according to Eq. (10) [26,27]:

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{HO}.$$  
(10)

As described above, the present exploratory study aimed at evaluating the removal/degradation and mineralization of ethyl xanthate by a simulated solar-like photo-Fenton advanced oxidation process. The objective was the eventual possibility of using tailings ponds as degradation reactors enhanced by solar radiation. We also compared the main differences of that process with those of direct oxidation by hydrogen peroxide on its own, and the conventional Fenton process.

2. Methods

The study was carried out using a $2^3$ factorial experimental design with three factors at two levels and three centre point replication runs (CPRs) as follows: Variable A (initial pH) = 5 and 9; Variable B ([Fe$^{2+}$]:[H$_2$O$_2$] molar ratio) = 0.0 and 1:40; Variable C (Irradiance) = 0 and 30 mW/cm$^2$. Runs were carried out in random order. CPRs were done to estimate the standard error and allow statistical analysis of the significance of the effects of the studied variables.

All the EX degradation experiments carried out in aqueous solutions by direct oxidation with hydrogen peroxide or by Fenton and photo-Fenton processes were batch runs carried out in glass beakers. The initial volume of synthetic effluent was 500 mL, with a concentration of 100 mg/L of EX ion, made up from the K-EX salt (from Sigma–Aldrich). The experiments were carried out at room temperature (T=25 °C ± 1 °C) with vigorous stirring using a 3 cm magnetic bar.

Initially the pH was adjusted to the desired initial value with sulphuric acid (0.1 M) or sodium hydroxide (0.1 M) (no more than 10 drops). In the experiments carried out using the Fenton and photo-Fenton processes, iron II sulphate heptahydrate was pre-weighed and added to the solution to achieve a concentration of 16.1 mg/L of Fe$^{2+}$. We note that in the present study the chosen reaction conditions do not favour the precipitation of insoluble iron-xanthate, given that the solubility product of metal Fe$^{2+}$-xanthate is $8.0 \times 10^{-8}$ [28].

Hydrogen peroxide (from Solvay, H$_2$O$_2$ 50% grade) was added and the timer started. Once the reaction was started aliquots were collected at 5, 30 and 120 min. Each sample was treated with 1 mg of catalase to cause immediate decomposition of H$_2$O$_2$ in the sample, and to stop the reaction. The concentration of xanthate was determined by spectrophotometry at 301 nm (Varian model Cary 100 UV-Vis). The concentration of residual hydrogen peroxide was determined using Merck analytical Spectroquant strips (116974) with a Merck RQFlex reflectometer. Fe was determined at 120 min by atomic absorption (Analytikjena model 700), and TOC at 120 min using a TOC-VCPN Shimadzu analyser. Sulphate was determined at 30 min and at 120 min by ion chromatography (Thermo Scientific Ion Chromatography System (Dionex ICS-90)). Visible precipitation of Fe(OH)$_3$ was observed in all the Fenton/photo-Fenton runs. At the end of each experiment pH and temperature were recorded.

For the experiments carried out with incident radiation, a conical Osram 8 WLED lamp with a 25° illumination angle was used, at a vertical distance of 13 cm from the surface of the solution in the beaker, which was comparable to the average solar irradiance of 30 mW/cm$^2$. The centre point runs were carried out at a vertical distance of 20 cm.

The amount of hydrogen peroxide added was the same for all experiments and was determined according to the chemical equation (Eq. 11) assuming complete mineralization of EX.

$$\text{C}_2\text{H}_3\text{OCS}^{2-} + 14\text{H}_2\text{O}_2 + 60\text{OH}^- = 18\text{H}_2\text{O} + 3\text{HCO}_3^{2-} + 2\text{SO}_4^{2-}.$$  
(11)

The equation shows that the progress of the mineralization reaction is related to the formation of bicarbonate and sulphate, and consumption of H$_2$O$_2$. The reaction stoichiometry indicates that 14 moles of H$_2$O$_2$ are needed to mineralize 1 mole of xanthate. This means that the full oxidation of 100 mg/L of EX requires 392.9 mg/L of H$_2$O$_2$, and that was used in all experiments.

It is known that the conventional Fenton process depends on the concentration of the catalyst pair Fe$^{2+}$/Fe$^{3+}$. It operates at optimal performance in the pH range around 3.5 to 4.5. This prevents the precipitation of Fe(OH)$_3$, as it would impair the regeneration of Fe$^{2+}$. Nevertheless, the range of initial pH chosen for the present work was set at 5–7–9, with a
view to exploring the possibility of operating the Fenton and photo-Fenton processes at near neutral pH, without having to acidify the flotation effluents, which are typically near neutral to slight alkaline—even if this reduced the reaction speed.

A decrease in pH is expected to occur during the reaction. The simplified overall mineralization reaction (Eq. 11) indicates a consumption of OH\(^{-}\) ions. But the HCO\(_3\)^{-} generated, combined with the natural alkalinity of effluents contained in dams, will provide a buffer effect that is expected to offer some resistance to pH variation. The buffer effect together with the basicity resulting from the main Fenton reaction step (Eq. 6) will likely lead to a slight reduction in the treated solution pH, even if there is some counteraction generated by the acidity of the hydrolytic precipitation of Fe(OH)\(_2\) during the progress of the overall reaction.

The range of the [Fe\(^{2+}\)]/[H\(_2\)O\(_2\)] molar ratio included the zero value to cover the uncatalyzed oxidation condition, and the upper level of 1:40 (16.1 mg/L Fe\(^{2+}\)). This was obtained from a set of preliminary runs (not shown here) which revealed that a figure of 98% of EX breakdown was achieved in the range 1:80 to 1:40, after 30 min of reaction time, at initial pH 5, without irradiation.

3. Results and discussion

As indicated by the reactions that take place in the breakdown of EX (Eqs 1 to 10), this is a fairly complex reaction system. The experimental format of the present work was a statistical factorial analysis of variance (ANOVA) to identify the significant effects of the studied independent variables and their factor interactions on the extent of mineralization of the EX species. The possible advantage in using solar irradiation in the breakdown process was studied. The following results and corresponding discussion will be limited and do not allow for detailed mechanistic considerations. For each response variable considered (initial EX% Breakdown; TOC% Reduction; SO\(_4\)% Formation; and H\(_2\)O\(_2\)% Consumption) only the ANOVA results are presented. The preparation of surface response graphics, was carried out at a confidence level of 95% (\(\alpha = 0.05\)) using TIBCO’s Statistica software.

3.1. Breakdown of EX

Table 1 shows the results of the breakdown of EX (measured as absorbance at \(\lambda = 301\) nm) in the factorial design experiments. Experiments 1, 2, 5 and 6 refer to the direct oxidation using hydrogen peroxide on its own (without Fe\(^{2+}\)), with and without irradiation. Experiments 3 and 4 refer to the oxidation using the conventional Fenton process and experiments 7 and 8 were carried out using the photo-Fenton process. Corresponding kinetic curves are shown in Fig. 1.

Taking into consideration the experimental error estimated from the central point replications, and assuming that the initial reaction speed in each experiment was taken as constant in the interval \(t = 0\) to \(t = 5\) min, this analysis revealed that the molar ratio [Fe\(^{2+}\)] : [H\(_2\)O\(_2\)] was the only statistically significant variable affecting the rate of breakdown of EX. The mean initial rate for the experiments with [Fe\(^{2+}\)]/[H\(_2\)O\(_2\)] = 0 was

13.8 mg/L.min, versus 19.7 mg/L.min for the Fenton/photo-Fenton experiments.

As to the xanthate % breakdown in 120 min of reaction time, the ANOVA revealed the statistically significant main factors initial pH (positive effect) and [Fe\(^{2+}\)]/[H\(_2\)O\(_2\)] (positive effect), as well as the negative interaction of these two factors. The EX% breakdown for the experiments with [Fe\(^{2+}\)]/[H\(_2\)O\(_2\)] = 0 was on average 89.3%, versus 98.9% for the Fenton/photo-Fenton experiments, as illustrated in the surface plot in Fig. 2. These findings indicate that for the breakdown of EX, the Fe-catalysed processes are more powerful than the direct oxidation with H\(_2\)O\(_2\), which is to be expected. The irradiance did
Table 1 – Results of the factorial design experiments. Calculated standard errors: % EX breakdown ± 0.2; % TOC reduction ± 4.0; % Sulphate formation ± 9.1; % H$_2$O$_2$ consumption ± 2.5.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH</th>
<th>[% Fe$^{2+}$]: [% H$_2$O$_2$] (Molar ratio)</th>
<th>Irradiance (mW/cm$^2$)</th>
<th>% EX breakdown</th>
<th>% TOC reduction</th>
<th>% Sulphate formation</th>
<th>% H$_2$O$_2$ consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0 min</td>
<td>5 min</td>
<td>30 min</td>
<td>120 min</td>
</tr>
<tr>
<td>Exp 1</td>
<td>5</td>
<td>0 : 40</td>
<td>0</td>
<td>68.9</td>
<td>90.0</td>
<td>88.3</td>
<td>14.6</td>
</tr>
<tr>
<td>Exp 2</td>
<td>9</td>
<td>0 : 40</td>
<td>0</td>
<td>67.1</td>
<td>91.8</td>
<td>90.3</td>
<td>15.0</td>
</tr>
<tr>
<td>Exp 3</td>
<td>5</td>
<td>1 : 40</td>
<td>0</td>
<td>99.5</td>
<td>99.3</td>
<td>99.0</td>
<td>46.4</td>
</tr>
<tr>
<td>Exp 4</td>
<td>9</td>
<td>1 : 40</td>
<td>0</td>
<td>97.5</td>
<td>98.8</td>
<td>98.9</td>
<td>31.3</td>
</tr>
<tr>
<td>Exp 5</td>
<td>5</td>
<td>0 : 40</td>
<td>30</td>
<td>69.7</td>
<td>89.5</td>
<td>88.9</td>
<td>36.2</td>
</tr>
<tr>
<td>Exp 6</td>
<td>9</td>
<td>0 : 40</td>
<td>30</td>
<td>69.8</td>
<td>91.5</td>
<td>89.7</td>
<td>32.7</td>
</tr>
<tr>
<td>Exp 7</td>
<td>5</td>
<td>1 : 40</td>
<td>30</td>
<td>98.6</td>
<td>99.0</td>
<td>98.6</td>
<td>39.2</td>
</tr>
<tr>
<td>Exp 8</td>
<td>9</td>
<td>1 : 40</td>
<td>30</td>
<td>99.1</td>
<td>99.0</td>
<td>99.0</td>
<td>48.0</td>
</tr>
<tr>
<td>CPR1</td>
<td>7</td>
<td>0.5 : 40</td>
<td>15</td>
<td>90.4</td>
<td>99.1</td>
<td>98.8</td>
<td>29.4</td>
</tr>
<tr>
<td>CPR2</td>
<td>7</td>
<td>0.5 : 40</td>
<td>15</td>
<td>95.3</td>
<td>99.1</td>
<td>98.7</td>
<td>28.6</td>
</tr>
<tr>
<td>CPR3</td>
<td>7</td>
<td>0.5 : 40</td>
<td>15</td>
<td>89.6</td>
<td>99.1</td>
<td>99.0</td>
<td>29.4</td>
</tr>
</tbody>
</table>
not show a significant effect, possibly because the initial EX breakdown step is faster than the photolytic reaction steps.

These results agree reasonably well with the findings of Chen et al. [12,13] in terms of the reaction time of 120 min. The breakdown of the EX anion using H₂O₂ on its own as oxidant achieved 90%. The higher performance of the Fenton process (about 99% removal of xanthate anion) in the present study also agrees reasonably well with the results of Ai et al. [10] using a synthetic effluent with a [EX] = 120 mg/L (Fig. 3).

3.2. TOC reduction

The reduction in Total Organic Carbon (TOC) is an indication of the mineralization achieved during xanthate oxidation. It is also a convenient direct indicator of the reduction of the chemical oxygen demand (COD) of an effluent, which is a parameter commonly employed in setting and monitoring the compliance of treated wastewaters to legal discharge limits.

Table 1 shows the results of the % reduction of TOC for the reaction time of 120 min.

The ANOVA revealed that for the % reduction of TOC there are two significant main variables: the [Fe³⁺]:[H₂O₂] molar ratio; and the irradiance (as seen in Fig. 4), as well as two factor interaction between these variables.

Average TOC reduction in the experiments with [Fe³⁺]:[H₂O₂] = 0 was 24.6%, versus 41.2% for the Fenton/photo-Fenton processes. Average TOC reduction in the experiments at pH 5 was 34.1% versus 31.8% at pH 9, a non-significant difference compared to the standard error calculated by the central point replicate runs (CPRs). Average TOC reduction for experiments with irradiance = 0 mW/cm² was 26.8% versus 39.0% for irradiance = 30 mW/cm². In these experiments the use of irradiance showed a significant effect on TOC reduction, comparable to that of the [Fe³⁺]:[H₂O₂] molar ratio. However, the significant effect of irradiance was observed for the uncatalyzed oxidation and the Fenton / photo-Fenton processes. This may be in part related to the action of HO.

generated by UV photolytic splitting of H₂O₂ in aqueous solutions (according to Eq. (10)) [26,27], as well as to direct photolysis of the EX ion [2].

3.3. Sulphate formation

Besides the extent of the TOC reduction, the degree of sulphate anion formation is also an indicator of the progress of the xanthate mineralization during the oxidation reaction with hydrogen peroxide on its own and with the Fenton and photo-Fenton processes.

The highest formation of sulphate anion in all experiments was 72.2 mg/L (Exp. 2), which is equivalent to an oxidation efficiency of 45.6%, based on the assumption that the theoretical value to achieve total oxidation of one mole of xanthate, yielding two moles of sulphate, is 158.5 mg/L, according to Eq. (11).

The results of the formation of sulphate anion SO₄²⁻ are shown in Table 1 for 30 and 120 min of reaction. This is a slower step compared to the initial xanthate breakdown step, as seen in Table 2. In most experiments, sulphate formation carried on increasing after 30 min. The effect of initial pH could be assessed by the difference in the average % sulphate formation at initial pH 5, 38.8%, and at initial pH 9, 33.7%. Similarly, the effect of irradiation may be assessed by the difference between the average % sulphate formation at zero irradiance: 38.6%, and at 30 mW/cm²: 33.9%. The effect of the Fe catalyst may be assessed by the difference in % sulphate formation at zero Fe, 37.3%, and at 1:40, 35.2%. Unfortunately, these differences using the 95% confidence level could not be taken as significant, due to the large experimental error indicated by the three central point replicate runs (CPRs). However, the interaction between variables initial pH and irradiance was found significant and negative, despite the large experimental error. In the present case this results from the fact that the effect of irradi-
Table 2 – Significance of isolated main variable’s effects at 95% confidence level in each step of the overall reaction.

<table>
<thead>
<tr>
<th>Rate of initial xanthate breakdown</th>
<th>Initial pH</th>
<th>[Fe²⁺]:[H₂O₂]</th>
<th>Irradiance</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of xanthate breakdown in the initial step</td>
<td>Not significant</td>
<td>Positive but only at [Fe]:[H₂O₂] = 0</td>
<td>Positive</td>
</tr>
<tr>
<td>% TOC reduction</td>
<td>Not significant</td>
<td>Positive</td>
<td>Not significant</td>
</tr>
<tr>
<td>% SO₂ generation</td>
<td>Not significant</td>
<td>Positive</td>
<td>Not significant</td>
</tr>
<tr>
<td>H₂O₂ consumption</td>
<td>Not significant</td>
<td>Positive</td>
<td>Not significant</td>
</tr>
</tbody>
</table>

* But significant and negative as the interaction between irradiance and [Fe]:[H₂O₂].
** But significant and negative as the interaction between pH and [Fe]:[H₂O₂].

Fig. 5 – Surface plot of % H₂O₂ consumption after 120 min as a function of variation in pH (non-significant as a main variable) and significant [Fe]:[H₂O₂] molar ratio, showing the significance of two-factor interaction between these variables. Initial [EX] = 100 mg/L.

thus decreasing markedly the speed of the main Fenton reaction (Eq. 6).

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}.
\] (6)

The monitoring of [H₂O₂] during the reaction is presented in Table 1. The ANOVA revealed the main factor [Fe²⁺]:[H₂O₂] molar ratio as statistically significant for the % consumption of H₂O₂, as well as the (negative) two-factor interaction initial pH - [Fe²⁺]:[H₂O₂]. Average H₂O₂ consumption in the absence of Fe²⁺ was 26.7%. With the Fenton / photo-Fenton experiments the highest value was 32.2%. The lower initial pH 5 favours H₂O₂ consumption, averaging 36.1%, as compared to the figure at high initial pH 9, averaging 28.3% consumption. Average H₂O₂ consumption for experiments with irradiance = 0 was 30.4%, versus 28.5% with irradiance = 30 mW/cm², a difference comparable to the experimental error.

The consumption of H₂O₂ during the reaction reflects its participation in the various steps of the EX breakdown reaction, regardless of each reaction step involving or not the HO radical and other active oxygen species. The main consumption of H₂O₂ will be associated to the Fenton reactions (Eq. 6–8). As such, the ANOVA revealed the expected behaviour of any Fenton process with respect to the concentrations of H₂O₂, Fe²⁺, and the initial pH.

3.5. Overall remarks

The interest of treating a flotation effluent containing xanthate is not limited to the breakdown of the xanthate ion, but also to a more thorough mineralization reaction in which the xanthate species get converted into bicarbonate, sulphate and water. Table 2 maps the significance of the effects of each main variable, for each of the components of the overall EX breakdown reaction.

The limited extent of mineralization indicated by the 39.2% TOC reduction and the 43.1% sulphate generation was reached at the end of 120 min of reaction time, even with a residual H₂O₂ of about 63% of the initial dose still present unreacted in solution. The difference between the consumption of H₂O₂ of 37% and the maximum mineralization figures of 39 and 43% may be within the experimental error and suggests reasonably good consistency in the results. The reaction slows down considerably, even in the presence of a reasonably high residual unreacted [H₂O₂]. This is compatible with the observation that during the reaction the catalyst Fe²⁺ oxidizes to Fe³⁺ and its total Fe²⁺/Fe³⁺ concentration falls from 16.1 to below 1 mg/L,
as a catalytically inactive Fe(OH)₃ precipitate. It also indicates that the remaining sulphur-organic intermediates were not amenable to H₂O₂ direct oxidation – with and without the aid of irradiation.

4. Conclusions

The kinetic study of the breakdown of EX in aqueous solutions using hydrogen peroxide, Fenton and simulated solar photo-Fenton processes leads to the following conclusions:

The process proceeds via a fast-initial oxidation step that breaks down the EX into intermediate species (according to previous authors: ethyl xanthate), which still contains unoxidized carbon and unoxidized sulphur. In this first reaction step, oxidation of the xanthate is significantly affected by initial pH and the presence of Fe²⁺, which acts as catalyst in both the Fenton and photo-Fenton processes. Light of similar irradiance to sunlight does not have a significant effect on that first reaction step. The highest xanthate degradations were obtained by the Fenton and photo-Fenton processes, reaching 99% breakdown of the xanthate ion in just 5 min.

Additional and slower oxidation reaction steps occur in which organic carbon and reduced sulphur from the intermediates are converted into bicarbonate and sulphate. The progress of those reaction steps is indicated by the slower increase in sulphate and reduction in TOC, as well as the consumption of H₂O₂.

There were three main factors affecting the progress of the overall reaction after 120 min of reaction time. These were, initial pH, [Fe²⁺]:[H₂O₂] molar ratio, and irradiance. The two-factor interactions were, initial pH with molar ratio [Fe²⁺]:[H₂O₂] and initial pH with irradiance.

The most favourable conditions for the overall xanthate breakdown reaction were initial pH = 5, [Fe²⁺]:[H₂O₂] = 1:4, and irradiance = 30 mW/cm². In such conditions, a single batch oxidation, after 120 min of reaction time, resulted in:

- % of xanthate breakdown in the initial step = 98.6
- % TOC reduction = 39.2
- % SO₄ generation = 43.1
- % H₂O₂ consumption = 37.4

These results indicated a partial destruction of the organic xanthate content achieved in a single run and the corresponding existence of organic breakdown degradation by-products. These levels have been achieved, even with 62.6% of the initial H₂O₂ still present unreacted in solution. That was not enough to keep the reaction progressing, as the concentration of the catalyst pair Fe²⁺/Fe³⁺ fell from 16.1 to less than 1 mg/L due to the precipitation of a catalytically inactive Fe(OH)₃, formed as a reaction product in the Fenton/photo-Fenton reactions in the studied initial pH range of 5 to 9. This limitation on the mineralization achieved suggests the need for further studies to expand the effect of the [Fe]:[H₂O₂] molar ratio in the initial pH range of 5 to 9.

The beneficial effect of solar-like irradiation on the TOC removal suggests the possibility of using tailings ponds as solar photolytic oxidative degradation reactors for xanthates, both for direct oxidation with H₂O₂ and for photo-Fenton processes. These conclusions indicate the opportunity for further study.

Conflicts of interest

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The authors declare that the present manuscript has not been submitted to any other journal.

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