Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement

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ABSTRACT

A mixture of six phenolic acids, corresponding to an initial TOC of 370 mgC/L, was studied by Fenton's peroxidation aiming to improve the biodegradability of agro-industrial wastewaters. Input operating variables including the concentration of pollutants, iron and hydrogen peroxide as well as the reaction time were used to assess the mineralization degree through a factorial experimental methodology. A TOC removal in the range of 15.0–58.8% was attained within the operational conditions used. A reduced model was achieved using the statistically important independent factors and interactions to predict TOC degradation. On the hydrogen peroxide injection methodology, the results showed that the continuous introduction of small volumes is advantageous when compared with one single addition of the overall volume at the zero reaction time with a mineralization improvement of 11%. The use of $FeSO_4 \cdot 7H_2O$ correspondent to a Fe^{2+} load of 271 mg; $[H_2O_2] = 488.0$ mM, injected in twelve aliquots each 30 min during 6 h of reaction reached optimal efficiencies with the parent compounds (quantified by HPLC and the Folin–Ciocalteau method) quickly totally removed and TOC, COD and BOD_5 final values of 123 mgC/L, 180 mgO_2/L and 146 mgO_2/L, respectively. Toxicity assessment by *Vibrio fischeri* light inhibition revealed that Fenton's process reduces the effluent ecological impact related with the decomposition of the toxic phenolic acids. Indeed, EC_{50} changed from 32.2% dilution to no-dilution needed. The analysis of BOD_5/COD ratio pointed out a high improvement of the treated wastewater biodegradability from 0.30 to 0.80 meaning that the application of Fenton's oxidation as a pre-treatment enables a further application of an efficient post-biological technology which was also confirmed by respirometry.

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1. Introduction

During the last decades, Fenton's process has been studied in order to optimize its efficiency in the depuration of liquid effluents [1,2]. This Advanced Oxidation Process (AOP) is based on the generation of strongly oxidant hydroxyl radicals from the decomposition of hydrogen peroxide in the presence of iron ions at acidic conditions (according to Eq. (1)), which will react with organic matter [3].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^- \qquad (1)$$
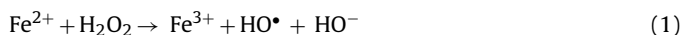
Additionally, the catalytic decomposition of hydrogen peroxide follows a radical mechanism involving hydroperoxyl radicals as well, Eqs. (2) and (3):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (2)$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H^+ \qquad (3)$$
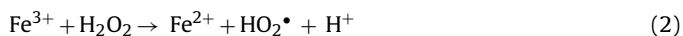
Radical chain oxidations will be then initiated by the hydroxyl radicals that will react non-selectively with the organic matter present in the wastewater [4]. Nevertheless, some radical scavenger effect is also attributed to hydrogen peroxide [5] and iron [6] as shown by Eqs. (4) and (5), respectively:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad (4)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^- \qquad (5)$$

The main advantage of this method is related with the fact that the reaction takes place at room conditions of pressure and temperature which makes the treatment less expensive. Moreover, generally short reaction times are necessary, requiring easy-to-use reagents [7].

Among the liquid effluents, the agro-industries wastewaters like Olive Mill Wastewaters (OMWs) are of particular concern since, due to their seasonal and toxic character, they are not suitable to be treated by the traditional biological systems [8]. This bio-refractory character is mainly caused by the high concentration of phenolic compounds which are toxic to microorganisms and plants [9]. The environmental legislation is increasingly restrictive, and the

Table 1
Synthetic wastewater characterization.

TOC/ppm	COD/mgO$_2$/L	TPh/mgGAeq/L	BOD$_5$/mgO$_2$/L	BOD$_5$/COD
370.0 ± 7.4	970 ± 78	350 ± 35	291 ± 58	0.30

remediation plants have to warrant proper effluents disposal. In this context, the AOPs and in particular the Fenton's process can have an important role [10–13], either to promote the wastewater treatment in order to accomplish the environmental parameters to a safe discharge into the natural water courses, or to minimize the effluent toxicity and enhance its biodegradability to allow an efficient post-biological depuration in municipal wastewater treatment plants.

The current experimental work aims to analyse the different effects of the operating parameters and their interactions over the efficiency of Fenton's oxidation in the treatment of a synthetic effluent comprised by six phenolic acids typically present in OMWs. A statistical technique encompassing a Design of Experiments methodology was implemented for this purpose while the wastewater toxicity and biodegradability were also measured in order to predict the possibility of using this chemical oxidation as a pre-treatment to obtain an effluent suitable to be further biologically depurated.

2. Materials and methods

2.1. Wastewater preparation and Fenton's process methodology

Six phenolic acids usually present in OMWs were selected to simulate these effluents, since it is well known that one of the major drawbacks regarding the application of the traditional biological depuration systems is related with the bio-toxicity and anti-microbial character of these compounds [11]. In this context, a synthetic phenolic mixture was prepared using 100 ppm of protocatechuic, syringic, veratric, vanillic, 4-hydroxybenzoic and 3,4,5-trimethoxybenzoic acids and Table 1 summarizes its main characteristics.

Fenton's process was carried out in the following way: 300 mL of the wastewater were stirred in a glass reactor with baffles paddles at 200 rpm, the pH was set at 3 and the necessary amount of an iron salt, FeSO$_4$·7H$_2$O was introduced into the reactor. The experiments begun when hydrogen peroxide (35%) was added into the previous mixture. Afterwards, samples were withdrawn and NaOH (3 M) was added to quench hydrogen peroxide in order to avoid interferences on the analytical methods and to promote iron precipitation before the subsequent analysis.

2.2. Analytical techniques

Total organic carbon (TOC) was determined using a Shimadzu TOC-5000 analyser with autosampler. TC calibration was performed using potassium acid phthalate standard solutions, while for IC hydrogen carbonate and carbonate solutions were prepared.

Chemical oxygen demand (COD) was obtained by the dichromate method according to the Standard Methods [14], being the samples digested during 2 h in a WTW CR3000 thermoreactor and the COD directly given by the absorbance measured on a photometer WTW MPM3000. The COD of a standard potassium acid phthalate solution was periodically measured to assure the method accuracy.

Biochemical oxygen demand was assessed by determining oxygen consumption (using a WTW InoLab 740 dissolved oxygen sensor equipped with a strirrOx) after 5 days of incubation of a microorganism culture obtained from garden soil [15].

The effluent phenolic content was determined by the Folin–Ciocalteau method and, since the calibration curve was based upon standard solutions of gallic acid, the polyphenolic content (TPh) was expressed as mg/L of equivalent gallic acid. The detailed procedure is described elsewhere [16].

Each parent phenolic acid concentration was also measured before and after Fenton's treatment by HPLC using the method referred by Martins and Quinta-Ferreira [15].

The samples eco-toxicity was analysed using the commercial LUMIStox test (according to DIN/EN/ISO 11348-2) which is based on the light emission inhibition of the luminescent bacteria *Vibrio fischeri*. The eco-toxicity levels expressed as EC$_{20}$ and EC$_{50}$, representing samples concentrations causing 20% and 50% of bacteria inhibition, respectively were acquired using different dilutions of each sample. The initial bacteria luminescence intensity was compared with the one obtained after the culture being exposed during 15 min to the toxic sample at 15 °C. The error between repeated runs was always lower than 2%.

Respirometric analyses were performed using a liquid static–static (LSS) respirometer and samples were run in duplicate with a maximum error of 8%. The standard oxygen uptake rate (OUR$_{st}$) achieved during the assimilation of a completely biodegradable sample (acetic acid with the same COD that the reaction sample under study) by a microorganism culture (obtained from a winery wastewater treatment plant) was further compared with the OUR values of the degradation of the original and the Fenton's treated wastewaters. The biodegradability was, thus, defined as follows (Eq. (6)):

$$\% \, \text{Biodegradability} = \left(\frac{\text{OUR}}{\text{OUR}_{st}} \right) \times 100 \tag{6}$$

Respirometry allowed to predict the samples toxicity [17] as well by using the activated sludge which had been in contact with the potentially toxic sample, to assimilate the new completely biodegradable sample (acetic acid, OUR$'_{st}$) according to Eq. (7):

$$\% \, \text{Toxicity} = \left(\frac{\text{OUR}_{st} - \text{OUR}'_{st}}{\text{OUR}_{st}} \right) \times 100 \tag{7}$$

2.3. Design of experiments

Fenton's process efficiency is affected by several factors such as pH, temperature, pollutants, iron and hydrogen peroxide concentrations. According to specialized literature it is accepted that hydroxyl radicals are better generated at pH values between 2 and 4 [4]. For lower medium pH, the reactions between Fe^{3+} and H$_2$O$_2$ (Eq. (2)) are inhibited [18] while for higher pH values is promoted the quick degradation of hydrogen peroxide and therefore, in our experiments the pH was set at 3 which is around the pH value of the raw simulated effluent. Moreover, one of the main advantages of this process is the fact that it occurs at atmospheric conditions so that room temperature was used. Hence, pollutants, iron and hydrogen peroxide concentrations, as well as the reaction times were the operational parameters selected to optimize the Fenton's process for the degradation of the phenolic wastewater.

Generally, some optimization processes commonly used consist in changing one variable at a time, not taking into account the possible interaction between the various operational parameters, thus requiring a large amount of experiments [19,20]. Within this scenario, the design of experiments (DOE) is an interesting optimization tool, involving a minimal number of experiments to achieve a reduced regression model, combining the influence of the different independent variables and of their interactions, to predict the values of a desired factor which is in our case TOC removal. When the process to be optimized is affected by sev-

Table 2
Independent variables and their levels used.

Variable	Symbol	Variable values		
		−1	0	+1
[TOC] (ppm)	x_1	185.0	277.5	370.0
[H$_2$O$_2$] (mM)	x_2	122.0	305.0	488.0
Fe (II) (mg)	x_3	67.7	169.4	271.0
Time (h)	x_4	1.0	3.5	6.0

Table 3
2^4 full factorial with replication of the central point for the four independent variables tested and the results obtained for the response factor (TOC removal).

Experiment	x_1	x_2	x_3	x_4	TOC degradation (%)
1	+	+	+	+	55.3
2	+	+	+	−	41.0
3	+	+	−	−	35.2
4	+	−	−	−	34.6
5	−	−	−	−	40.6
6	−	−	−	+	50.6
7	−	−	+	+	53.8
8	−	+	+	+	58.8
9	−	+	−	+	15.0
10	+	−	−	+	40.3
11	−	+	+	−	55.7
12	−	−	+	−	45.0
13	+	+	−	+	37.9
14	+	−	+	+	52.4
15	−	+	−	−	14.7
16	+	−	+	−	46.3
17	0	0	0	0	44.9
18	0	0	0	0	45.7

eral variables, factorial designs are usually handled to study their effect over the response factor in order to determine which factors have significant effect and how it affects the process [21]. In this work a two-level factorial design (2^k) was used and four independent variables were selected: TOC concentration (x_1), hydrogen peroxide concentration (x_2), Fe^{2+} load (x_3) and time (x_4), which were coded at three levels as is expressed in Table 2 (−1, 0, +1). The minimum (−1) value for the hydrogen peroxide corresponds to the double of the stoichiometric quantity theoretically needed to totally oxidize the six phenolic compounds for the wastewater prepared with higher TOC (370 mgC/L), and the maximum (+1) was set equal to four times that value. The iron concentrations were chosen in order to obtain Fe^{2+}:H$_2$O$_2$ (w/w) ratios within the range of 0.01–0.2. In fact, Ramirez et al. [22] found that a Fe^{2+}:H$_2$O$_2$ ratio of 0.02 was the optimal condition to maximise TOC removal by Fenton's process in the degradation of a synthetic dye Orange II, while Ahmadi et al. [11] referred a most favourable ratio of 0.12 for the Fenton's peroxidation of olive oil mill wastewater.

3. Results and discussion

Table 3 shows the design matrix obtained with the commercial software STATISTICA 6.0 (StatSoft, Inc.) which was used to statistical analysis of the results including the mineralization degree achieved after each experiment. Comparing the degradation values measured for the repeated runs, the experimental error is lower than 2% which is the maximum deviation of the TOC analyser.

No parent phenolic acids were found in the HPLC chromatograms obtained after the several Fenton experiments. Moreover, the Folin–Ciocalteau method did not detect phenolic character in the treated samples. Therefore, Fenton's process revealed to be very efficient in the degradation of these compounds. In fact, even if the benzenic ring is not very reactive, the presence of
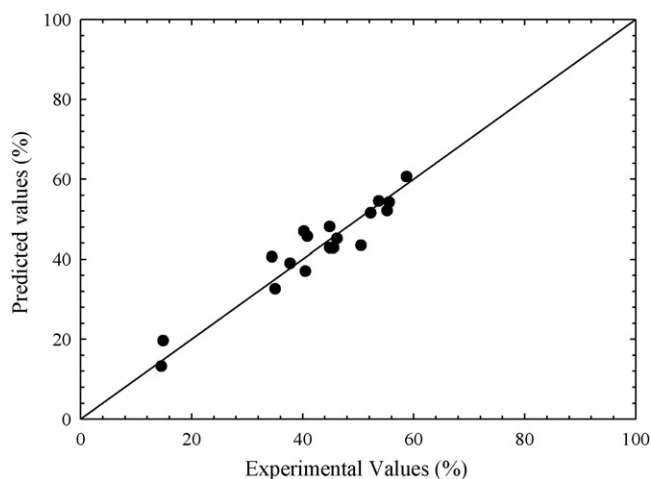
ring electro-donating groups, as is the case of the hydroxyl (–OH) and methoxy (–OCH$_3$) groups enhance the reactivity and allow a better attack of the hydroxyl radicals to oxidize the aromatic compounds which was also verified by Beltran De Heredia et al. [23]. Nevertheless, even if the parent compounds are totally removed whichever the experimental conditions in use, the same results are not envisaged for the mineralization level after each treatment. As it can be observed in Table 3 for the TOC removal, the mineralization is strongly dependent on the experimental conditions within a large range 15.0–58.8%, for the experiments 9 (with low initial TOC and Fe load and high hydrogen peroxide concentration and time) and 8 (low initial TOC and high Fe load, hydrogen peroxide concentration and time). In this ambit, a statistical approach was made to determine the influence of each variable as well as the importance of their interactions over TOC removal. From the results achieved it is clear that the Fe^{2+} load has the major weight on the wastewater mineralization. A similar result was obtained by Farré et al. [17] for the photo-Fenton degradation of herbicides. The same behaviour, but with lower impact, is detected when the reaction time and the initial effluent TOC are enlarged. On the contrary, when H$_2$O$_2$ concentration increases, a decrease is observed on the final mineralization. In fact, a radical scavenging effect is attributed to H$_2$O$_2$ (Eq. (3)) when the concentration is sufficiently high which reduces the amount of hydroxyl radicals available to organic compounds oxidation. Though other radicals are formed (hydroperoxide radicals, HO$_2$$^\bullet$), their oxidant power is much lower than the one attributed to HO$^\bullet$ [18].

The main importance of a statistical analysis of the results is related with the fact that it takes into consideration the interaction between the independent variables under study. There is interaction between two parameters if the variation of the response factor when one of them changes from its lower to its higher value is dependent on the level of the second one. Within our results, there is found high interaction between H$_2$O$_2$ concentration and Fe^{2+}. When Fe^{2+} load is at its lower level, the increase on H$_2$O$_2$ concentration leads to a decrease on TOC removal due to the hydrogen peroxide scavenger effect, as discussed earlier. Nevertheless, the increase on Fe^{2+} accelerates H$_2$O$_2$ conversion into hydroxyl radicals minimizing the hydrogen peroxide available to scavenge those radicals. Therefore, when Fe^{2+} is in its high level, the increase on hydrogen peroxide concentration allows achieving an effluent higher mineralized. A similar behaviour was found by Ormad et al. [24] in the study of the degradation of winery wastewaters by the photo-Fenton process. Some interaction is also seen between the wastewater initial TOC with the H$_2$O$_2$ and Fe^{2+} concentration.

From this sort of analysis of the results, it is possible to predict which of the independent parameters and respective interactions are statistically significant at a 5% probability level for the optimization of the response factor. Our results reveal that Fe^{2+}, [H$_2$O$_2$], time and the interactions [TOC]·[H$_2$O$_2$]·Fe^{2+}, [H$_2$O$_2$]·Fe^{2+}, [TOC]·Fe^{2+} and [TOC]·[H$_2$O$_2$] are significant for the Fenton's degradation of the phenolic wastewater.

A reduced multivariate model (Eq. (8)) can be written using the relevant variables and interactions to describe the TOC removal during the treatment of a synthetic phenolic wastewater. The coefficients of the model and the numeric error (between brackets) were calculated by multiple regression analysis using the STATISTICA 6.0 commercial software.

$$\begin{aligned} TOC_{Removal}(\%) =\ & 42.65(\pm 0.6) - 6.27x_2(\pm 1.3) + 17.43x_3(\pm 1.3) \\ & + 6.40x_4(\pm 1.3) + 5.20x_1x_2(\pm 1.3) - 5.67x_1x_3(\pm 1.3) \\ & + 9.61x_2x_3(\pm 1.3) - 9.73x_1x_2x_3(\pm 1.3) \end{aligned} \tag{8}$$

Fig. 1. Comparison between experimental and model predicted values for TOC removal.

Fig. 2. Effect of Fe^{2+} load on TOC degradation ($TOC_{initial} = 370$ mg/L; $[H_2O_2] = 488.0$ mM and 6 h of Fenton's reaction).

Fig. 3. COD, TOC and BOD_5 removal and BOD_5/COD ratio evolution along Fenton's process operating time ($TOC_{initial} = 370$ mg/L; $[H_2O_2] = 488.0$ mM; Fe^{2+} load = 271 mg and 6 h of Fenton's reaction).

Once the several independent parameters have different units, they are given in a dimensionless coded way, with (Eq. (9)):

$$x_1 = \frac{[TOC] - 277.5}{185.0} \quad x_2 = \frac{[H_2O_2] - 305.0}{366.0} \quad x_3 = \frac{Fe^{2+} - 169.4}{203.3}$$

$$x_4 = \frac{Time - 3.5}{5.0} \tag{9}$$

To verify the validity of this reduced model, Fig. 1 compares the experimental TOC values with those predicted by the model and a good fitting is found with an adjusted square correlation of 96%.
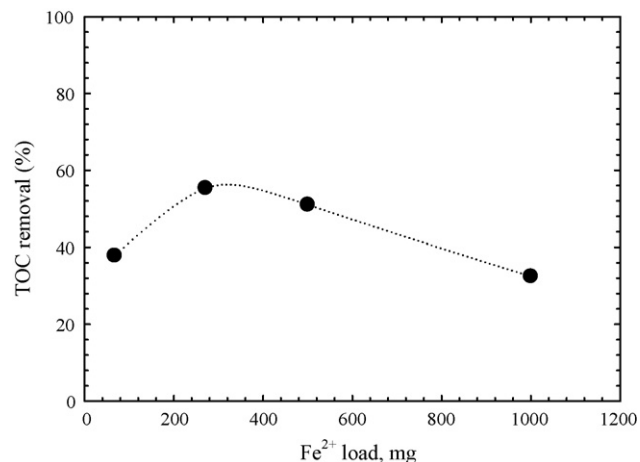
3.1. Optimization of the iron load

From the design of experiments, it was possible to conclude that the iron load had the highest impact on TOC removal of the phenolic wastewater after the Fenton's treatment. The positive sign of the coefficient for this variable (x_3) in Eq. (8) means that the increase on the catalyst load increases the production rate of the hydroxyl radicals which leads to a higher effluent mineralization level. Nevertheless, excess of iron can have a radical scavenger effect [6] (Eq. (5)).
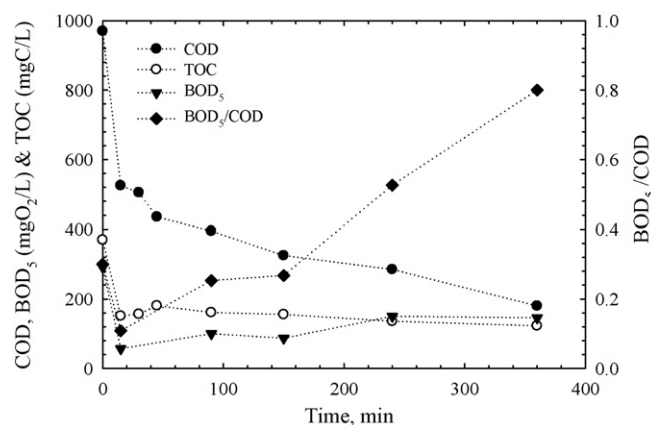
To find out the optimal iron load, several experiments were performed by increasing the catalyst concentration. For this, the initial effluent TOC, hydrogen peroxide concentration and reaction time were set at 370 mgC/L, 488.0 mM and 6 h, respectively. TOC removal increased 17.8%, from 37.9% to 55.7%, when the Fe^{2+} load rose from 67.6 to 271 mg (Fig. 2). However, the further augment on the catalyst concentration decreased the process efficiency. For example, when the amount of $FeSO_4 \cdot 7H_2O$ equivalent to an iron load of 1000 mg is introduced to the reactor the mineralization level was only 32.5%, lower than for the lowest catalyst concentration. Thus Fe^{2+} loads higher than 271 mg lead to a loss of $OH^\bullet$ by scavenge effect enhanced by the high catalyst concentration and, consequently, this value was taken for the following experiments.

3.2. Study of the H_2O_2 injection mode

The effect of the method of H_2O_2 addition was checked, for the best conditions achieved earlier ($FeSO_4 \cdot 7H_2O$ mass corresponding to 271 mg of Fe^{2+}; $[H_2O_2] = 488.0$ mM and 6 h of reaction). The necessary amount of H_2O_2 was, therefore, added by three different ways: (1) The H_2O_2 was initially totally introduced to the reactor; (2) the total volume of H_2O_2 was divided in six aliquots injected each hour (6 injections) to the reaction medium; (3) twelve injec-

tions of H_2O_2 were done each 30 min of reaction.

TOC removal increases from 55.7%, when the total volume of hydrogen peroxide is added at the beginning of the experiments, to 61.4% when the total amount is divided into 6 injections, and up to nearly 67% for 12 additions. This can be probably related with the radical scavenger effect of hydrogen peroxide when present on excess, reducing then the process depuration. Therefore, if low concentrations are added sequentially, H_2O_2 is quickly converted into hydroxyl radicals, not being available to scavenge part of the radicals produced.

3.3. Biodegradability and toxicity analysis

Aiming to analyse the potential use of coupled chemical-biological treatments [25] and to assess the possible impact of the discharged wastewaters over the aquatic ecosystems, the effluents biodegradability and toxicity were followed up along Fenton's oxidation for the best operational conditions obtained before ($FeSO_4 \cdot 7H_2O$ mass corresponding to 271 mg of Fe^{2+}; $[H_2O_2] = 488.0$ mM, injected in twelve aliquots each 30 min and 6 h of reaction).

Fig. 3 shows the effluent COD and BOD_5 along time and, as observed, even if a high degradation is initially detected with COD falling from 970 to 525 mgO_2/L after 15 min of reaction, corresponding to 46% reduction, the effluent still presents 180 mgO_2/L, after 6 h of chemical reactions which prevents its direct discharge

Table 4
EC_{20} and EC_{50} (LUMIStox) evolution along the treatment ($TOC_{initial} = 370$ mg/L; $[H_2O_2] = 930.0$ mM; Fe^{2+} load = 271 mg and 6 h of Fenton's reaction).

Experimental Time (min)	LUMIStox	
	EC_{20} (%)	EC_{50} (%)
0	4.5	32.2
15	9.9	28.1
30	33.2	[a]
90	27.8	[a]
150	[a]	[a]
360	[a]	[a]

[a] Values out of the scope of the instrument, meaning that a high toxicity removal occurred.

since this value is higher than the 150 mgO_2/L legal threshold. Also a prohibitive BOD_5 value of 146 mgO_2/L is found (above the legislated 40 mgO_2/L). In Fig. 3, one can observe a high TOC removal for the initial experimental times being achieved 123 mgC/L as final value. Notwithstanding, the parent phenolic compounds (confirmed by HPLC) and the wastewater phenolic character (determined by the Folin–Ciocalteau method) were totally removed within the first 15 min of reaction.

The ratio between BOD_5/COD along time is also depicted in Fig. 3 in order to follow the wastewater biodegradability. In this context, the initial synthetic phenolic mixture is not biodegradable presenting a low ratio BOD_5/COD of 0.3 and along the first 15 min of reaction this value still decreases. Nevertheless, after this, an increase on biodegradability is observed and at the end of 240 min of reaction the BOD_5/COD reaches 0.53 which means that this effluent is now easily biodegradable [26] achieving a final ratio of 0.80.

The effluent eco-toxicity was evaluated by its light inhibition over *Vibrio fisheri* bacteria (LUMIStox). Table 4 summarizes the wastewater EC_{20} and EC_{50} values for some treatment times. As expected, due to the presence of phenolic acids, the initial wastewater presents high toxicity with EC_{20} and EC_{50} correspondent to a dilution using only 4.5% and 32.2% of effluent, respectively. After 15 min of reaction, the treated wastewater toxicity is even higher than the one obtained for the parent solution (lower EC values). Nonetheless, after this experimental time a high toxicity removal occurs being obtained EC_{50} values out of the scope of the instrument, which means that even the undiluted treated solution can not provoke the inhibition of 50% of the bacteria. The same occurs for EC_{20} after 90 min.

The effluent toxicity and instantaneous biodegradability was also followed up by respirometric methods. The initial effluent with 2% of biodegradability was not able to be degraded by the activated sludge that was used. Moreover, it had negative impact over the bacteria since an OUR decrease was obtained when Acetic Acid was fed a second time after the biomass being in contact with the pollutant sample corresponding to 67% of toxicity. However, a quick and efficient toxicity removal occurred by the application of Fenton's process, with the effluent not presenting toxic character after 15 min of reaction. Also the wastewater biodegradability is enhanced along the chemical treatment process from 2% to 11% after 45 min followed by a slight decrease to 7% for the end of the reaction.

4. Conclusions

The efficiency of Fenton's peroxidation with a phenolic synthetic mixture composed by six phenolic acids was investigated through a factorial experiment design to evaluate the effect of iron load, hydrogen peroxide and pollutants concentrations as well as the reaction time. Firstly, among the input variables iron and hydrogen peroxide concentrations and the reaction time as well as the interactions: $[TOC] \cdot [H_2O_2] \cdot Fe^{2+}$, $[H_2O_2] \cdot Fe^{2+}$, $[TOC] \cdot Fe^{2+}$

and $[TOC] \cdot [H_2O_2]$ were found to be statistically relevant on the wastewater mineralization degree which led to a reduced model describing satisfactorily the TOC removal. Secondly, according to our results oxidation efficiency was slightly improved in about 11% when hydrogen peroxide is added to the reaction medium in small aliquots rather than being entirely introduced at the start of the experimental run. Fenton's process showed to be efficient for the removal of effluent toxicity as verified both by luminescent and respirometric methods. Finally, the instantaneous and long-term (for 5 days) biodegradable organic matter in effluent was inferred by respirometry and by the BOD_5/COD ratio analysis, respectively. Since a high biodegradability enhancement occurs during the chemical depuration process, even if the resulting effluent after 6 h does not accomplish the discharge environmental regulation, Fenton's peroxidation emerged as an interesting technology to be applied before a traditional biological treatment which will properly refine the wastewater until the legal emission values.

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