



## Optimisation of Fenton's reagent usage as a pre-treatment for fermentation brines

Francisco J. Rivas\*, Fernando J. Beltrán,  
Olga Gimeno, Pedro Alvarez

*Departamento de Ingeniería Química y Energética, Universidad de Extremadura,  
Avenida de Elvas S/N, 06071 Badajoz, Spain*

Received 19 July 2001; received in revised form 25 July 2002; accepted 28 July 2002

---

### Abstract

Pre-treatment of fermentation brines from green olives has been carried out by the Fe(II)/Fe(III)/H<sub>2</sub>O<sub>2</sub> system. Reagent concentration exerted a positive influence on chemical oxygen demand (COD) removal. Hydrogen peroxide uptake showed values in the range 0.3–1.6 mol of COD eliminated per mol of H<sub>2</sub>O<sub>2</sub> consumed depending on operating conditions. The optimum working pH was found to be in the interval 2.0–3.5. Reaction temperature increased the COD degradation rate, although similar COD conversion values were obtained after 5 h of treatment regardless of the value of this parameter. An analysis of the biodegradability of this type of effluent demonstrated the beneficial effect of the chemical pre-oxidation. According to the experimental results, it is suggested that there is an inhibitory effect of the wastewater due to its COD content and nature rather than attributable to the presence of high amounts of sodium chloride. Biodegradation efficiency increased as temperature was raised up to 30 °C. A further increase of this parameter up to 40 °C resulted in the death of the microorganisms.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Brines; Fenton; Aerobic biodegradation; Olive wastewater; Wastewater treatment

---

### 1. Introduction

A considerable number of effluents are characterised by a high content of inorganic salts, especially sodium chloride and in some cases sodium hydroxide [1,2]. Some examples can be found in the manufacturing of pesticides, herbicides, pharmaceutical products, dyes, etc. Other processes that generate an important amount of brines are related to gas oil recovery

---

\* Corresponding author. Tel.: +34-924-289385; fax: +34-924-271304.

E-mail address: fjrivas@unex.es (F.J. Rivas).

operations, landfill leachates, meat-packing wastewater, etc. [3]. Disposal and management of this type of effluent is not an easy task. Traditionally, biological processes have been considered to be the most economical and simple option to treat these aqueous wastes [4–10]. However, this technique is not always feasible due to the toxic nature of high concentrations of, on the one hand, sodium and/or chloride and, on the other hand, the presence of a significant organic contaminant load. Woolard and Irvine [2] have recently reviewed studies carried out on the biological treatment of brines. In general, it has been demonstrated that this method does not constitute a suitable choice even when using acclimated seeds. Therefore, chemical oxidation processes seem to be appropriate to reduce the contaminant load of this kind of effluent and hence render them more biodegradable. In this sense, Lin et al. [3], based on the high conductivity of brines, have proposed an electrochemical method of treatment. Also, Rearick et al. [11] have used the Fenton system in conjunction with a series of membranes to re-use wastewater generated in the manufacturing of dyestuff.

In this study, the chemical oxidation of wastewater from the fermentation brines of table olives has been investigated. Fermentation brines are characterised by a low pH (3.5–4.5) and a high content of NaCl (6–10%). Few works have dealt with this type of wastewater. Some authors have tested a physico-chemical method based on a previous neutralisation followed by an adsorption step on activated carbon or an ionic resin [12]. Other processes, however, have been addressed to disposal of the waste into impermeable layers with no aquifers [13] or into low deep aerated lagoons. Also, the direct dumping of the saline effluents into the sea has been proposed [14].

In the present work, Fenton's reagent has been studied for the treatment of fermentation brines. It has been demonstrated that this treatment allows for large reductions of the organic load of wastewaters at acceptably low costs [15,16]. In addition, effluents similar in composition have already been treated with promising results. Thus, wastewater from the manufacturing of olive oil has been processed by using Fenton's reagent, showing considerable reductions of the chemical oxygen demand (COD) of the effluent [17].

After the chemical oxidation has taken place, aerobic biological experiments have been carried out by using non-treated and Fenton's pre-treated effluents. A comparative study has been completed to ascertain the positive or negative effects of this integrated treatment.

## 2. Materials and methods

Chemical oxidation experiments were carried out in a 500 ml glass reactor under sunlight conditions, batchwise and (unless otherwise specified) in the presence of oxygen. The aqueous solution of reactants was homogenised by magnetic agitation to avoid concentration gradients. Systematically, samples were withdrawn and immediately analysed after sampling (in less than 2 min). Immediate analysis of samples allowed for the analytical procedure to be completed without interference from reducing or scavenging substances (quenchers).

Fermentation brines were taken from a factory located in Navalvillar de Pela in the province of Badajoz (southwest of Spain). Table 1 shows the characterisation of this type of wastewater. Most experiments were carried out after dilution of the raw wastewater with synthetic urban wastewater with a dilution factor of 2 (one part brines + one

Table 1  
Characteristics of fermentation brines from the manufacturing of table olives used in this work

COD ( $\text{g l}^{-1}$ )	30.9
BOD <sub>5</sub> ( $\text{g l}^{-1}$ )	18.0
BOD <sub>f</sub> ( $\text{g l}^{-1}$ )	23.6
TC ( $\text{g l}^{-1}$ )	10.3
TOC ( $\text{g l}^{-1}$ )	10.2
pH	4.25
NaCl ( $\text{g l}^{-1}$ )	10.0

part synthetic urban wastewater). Synthetic urban wastewater composition was: glucose ( $216 \text{ mg l}^{-1}$ ), peptone ( $46 \text{ mg l}^{-1}$ ),  $\text{K}_2\text{HPO}_4$  ( $138 \text{ mg l}^{-1}$ ),  $\text{KH}_2\text{PO}_4$  ( $69 \text{ mg l}^{-1}$ ),  $\text{NH}_4\text{Cl}$  ( $52 \text{ mg l}^{-1}$ ),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  ( $26 \text{ mg l}^{-1}$ ),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $1 \text{ mg l}^{-1}$ ),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  ( $1 \text{ mg l}^{-1}$ ),  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$  ( $1 \text{ mg l}^{-1}$ ),  $\text{CaCl}_2$  ( $7 \text{ mg l}^{-1}$ ) and  $\text{NaHCO}_3$  ( $83.2 \text{ mg l}^{-1}$ ). The purpose of the dilution was to simulate the conditions obtained if the Fenton process were integrated in a real plant for municipal wastewater treatment.

All chemicals were provided by Aldrich and used without further purification. Analysis of chemical oxygen demand was determined in a Dr. Lange spectrophotometer, the method based on the dichromate standard procedure [18]. The positive interference derived from the presence of hydrogen peroxide was corrected by considering the correction factor proposed by Talinli and Anderson [19]. Final (BOD<sub>f</sub>) and 5 days (BOD<sub>5</sub>) biological oxygen demand was determined by the respirometric method. In this case, 300 ml glass bottles containing known amounts of inocula were used. The polyphenols content was measured using the Folin Ciocalteu reagent after liquid–liquid extraction of the sample with ethyl acetate. Results were expressed as equivalent phenol concentration. Total peroxides concentration was determined iodometrically. Ferrous ion in the solution was analysed by the 2,4,6-tripyridyl-s-triazine (TPTZ) method. This analysis was carried out after hydrogen peroxide removal through decomposition with excess of catalase (1 unit decomposes  $1 \mu\text{mol}$  of hydrogen peroxide per minute at pH 7 and  $25^\circ\text{C}$  while the concentration falls from 10.3 to 9.2 mM. Catalase contains 51100 units per milligram of protein and 47.7 mg of protein per millilitre). Details of the analytical procedure can be found elsewhere [17,20]. The pH of the reaction media was followed by means of a Radiometer Copenhagen pH-meter (HPM82). When needed, initial pH of the solution was varied by the corresponding addition of HCl or NaOH.

Biodegradation of fermentation brines was carried out in a 500 ml glass sequencing batch reactor (SBR) containing a given amount of suspended activated sludge. The reactor was operated with cycles comprising filling, reacting, settling and drawing periods. Reaction time was the limiting step, being of 24 h. Therefore, the controlling step (biological reaction) governs the time of the overall process. In this sense, it can be said that, in a real process, the time consumed in filling and withdrawing will depend on the flow-rate capacity of the pumps used. Additionally, settling time will depend on characteristics and nature of microorganisms and geometry of the biological tank. In this work, microorganisms showed a sludge volumetric index (SVI) of  $129 \text{ ml g}^{-1}$  of VSS, and a zone settling velocity (ZSV) of  $5 \times 10^{-4} \text{ m s}^{-1}$ . To check for any substrate or biomass inhibition, experimental conditions of input wastewater, and initial microorganism concentration were selectively varied for each

cycle. Control analysis was conducted on the SBR for temperature, pH and dissolved oxygen. During the reaction period, samples of the mixed liquor were steadily withdrawn and centrifuged. The liquid and solid phases thus obtained were analysed for volatile suspended solids (VSS) and chemical oxygen demand, respectively.

In biodegradation experiments, biomass concentration was related to the concentration of VSS which were measured following ‘Standard Methods’ [18].

### 3. Results and discussion

#### 3.1. Influence of operating conditions on Fenton’s oxidation

##### 3.1.1. Influence of hydrogen peroxide initial concentration

In this work, the influence of the initial concentration of hydrogen peroxide was assessed. For that purpose, experiments were conducted at similar operating conditions but different amounts of  $\text{H}_2\text{O}_2$  added at the beginning of the process, in the range 0.01–1.0 M. Fig. 1 depicts the evolution of COD and  $\text{H}_2\text{O}_2$  conversion for the aforementioned experimental series.

From Fig. 1, an increase of the COD removal rate as the  $\text{H}_2\text{O}_2$  initial concentration is raised from 0.2 to 1.0 M is observed. Additionally, in all cases a roughly 10 K increase of the reaction temperature was experienced indicating the exothermic nature of the oxidation.

Also, from Fig. 1, a 100% hydrogen peroxide conversion for the experiments carried out with the lowest  $\text{H}_2\text{O}_2$  concentrations is observed, decreasing these to 50–60% for runs

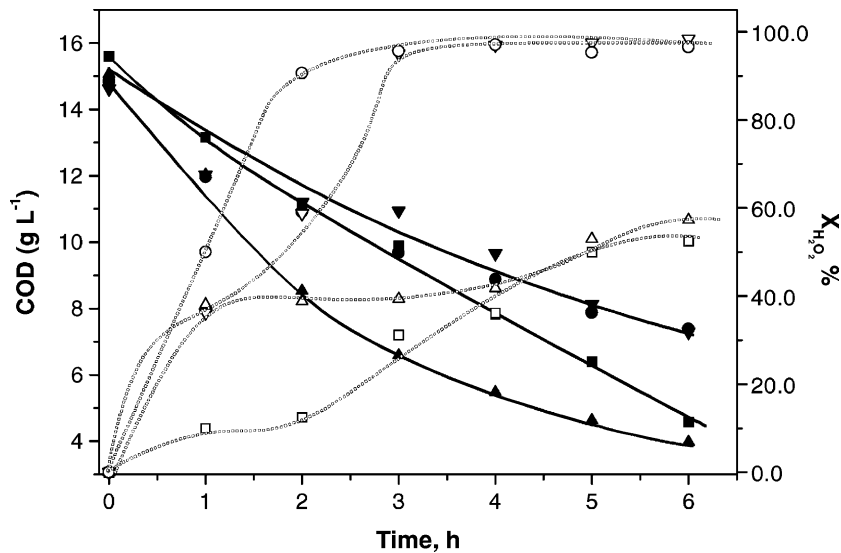


Fig. 1. Fe(II)/ $\text{H}_2\text{O}_2$  treatment of table olive fermentation brines. Evolution of COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of  $\text{H}_2\text{O}_2$  initial concentration. Conditions:  $T_0 = 293$  K;  $\text{pH}_0 = 3.5$  (average value);  $C_{\text{Fe(II)}_0} = 0.01$  M;  $\text{COD}_0 = 15 \text{ g l}^{-1}$  (approximate value);  $C_{\text{H}_2\text{O}_2(0)} = 1.0$  M (▲, △), 0.5 M (■, □), 0.25 M (●, ○), 0.20 M (▼, ▽).

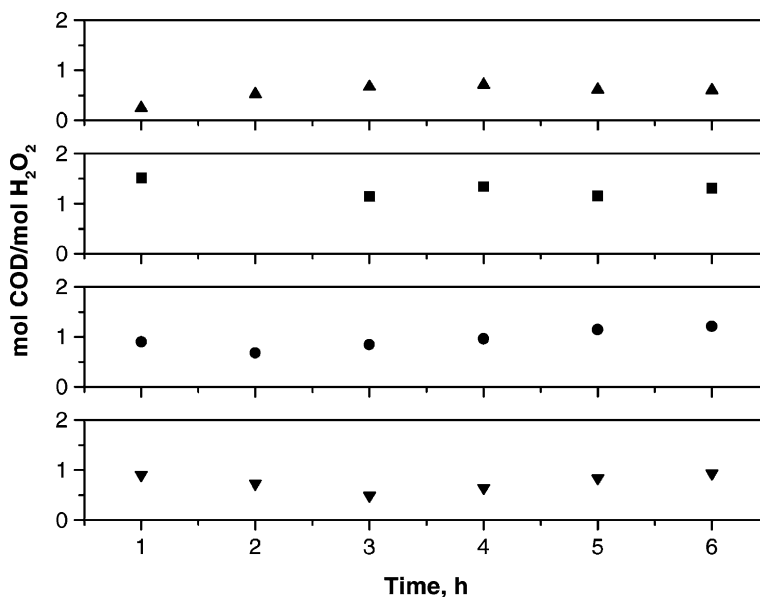


Fig. 2. Fe(II)/ $H_2O_2$  treatment of table olive fermentation brines. Evolution of removed COD/hydrogen peroxide consumption ratio with time. Influence of  $H_2O_2$  initial concentration. Conditions:  $T_0 = 293$  K;  $pH_0 = 3.5$  (average value);  $C_{Fe(II)_0} = 0.01$  M;  $COD_0 = 15$  g l $^{-1}$  (approximate value);  $C_{H_2O_2(0)} = 1.0$  M (▲), 0.5 M (■), 0.25 M (●), 0.20 M (▼).

initially conducted with 0.5 and 1.0 M of  $H_2O_2$ . It is obvious that for identical remaining operating conditions, the lower the amount of  $H_2O_2$  used, the faster its conversion (not its reaction rate). However, increasing the concentration of this reagent does not necessarily mean a higher COD removal. Parallel inefficient decomposition routes may contribute to wastage of hydrogen peroxide. These results suggest that there may be an optimum in hydrogen peroxide consumption related to the amount of COD removed from the reaction media. Thus, the ratio of COD eliminated to  $H_2O_2$  consumed is represented in Fig. 2. At the sight of the apparent stoichiometric coefficients calculated, it can be realised that at the end of the reaction period (6 h), the ratio COD/ $H_2O_2$  is in the range between 0.6 and 1.2 with values close to 1. A slight improvement of this coefficient was noticed for the experiment conducted with  $C_{H_2O_2(0)} = 0.5$  M, experiencing the lowest values for the run carried out with  $C_{H_2O_2(0)} = 1.0$  M. In contrast to the evolution of hydrogen peroxide, ferrous iron reacted completely in the first few minutes of the experiments showing concentrations in the interval  $10^{-4}$  to  $10^{-3}$  M over almost the entire reaction period.

Also, from this experimental series it was found that Fenton's reagent is an effective technology to reduce the phenolic content of this type of wastewater. Thus, in all cases, a reduction for these substances was experienced from roughly 650 mg l $^{-1}$  of phenol to amounts slightly above of 200 mg l $^{-1}$  of phenol after 6 h of the oxidative treatment ( $\approx 65\%$  conversion).

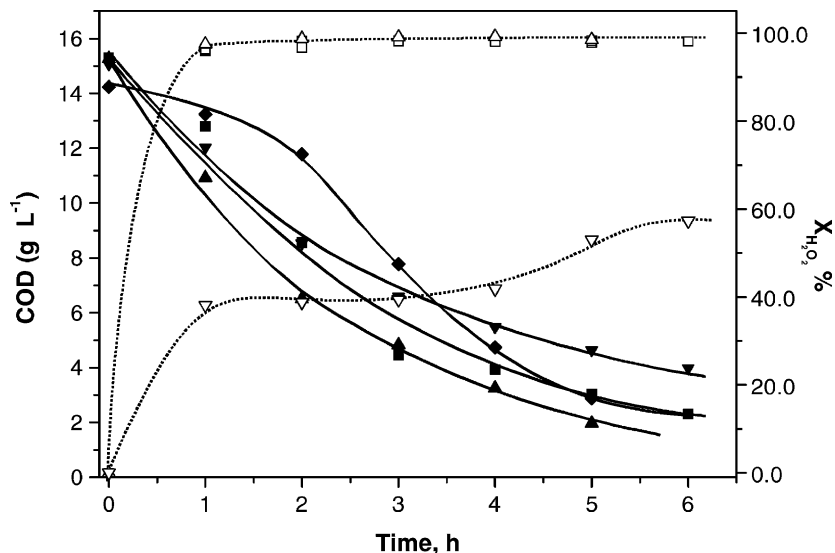


Fig. 3. Fe(II)/Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of Fe(II)/Fe(III) initial concentration. Conditions:  $T_0 = 293$  K;  $pH_0 = 3.5$  (average value);  $C_{H_2O_2(0)} = 1.0$  M;  $COD_0 = 15$  g l<sup>-1</sup> (approximate value);  $C_{Fe(II)} = 0.01$  M (▼, ▽), 0.03 M (■, □), 0.05 M (▲, △);  $C_{Fe(III)} = 0.03$  M (◆).

### 3.1.2. Influence of ferrous iron initial concentration

To ascertain the effect of the initial ferrous iron on the effectiveness of the oxidation, a series of experiments was conducted by varying this parameter from 0.01 to 0.05 M while keeping constant the remaining operating conditions.

As observed from Fig. 3, the higher the initial amount of Fe(II), the higher the COD conversion obtained after 5 h. Also, the phenolic content elimination was improved showing conversions of 80 and 95% for experiments conducted with 0.03 and 0.05 M of Fe(II), respectively. In addition, it is striking that for Fe(II) concentrations above 0.01 M, the decomposition of hydrogen peroxide achieved was in all cases 100% in the first hour of reaction. Because of this, the stoichiometric coefficients obtained for this series were lower than those obtained for catalyst concentrations below 0.01 M (see Fig. 4).

Based on the experimental results obtained, the following considerations can be drawn:

- At least for Fe(II) concentrations above 0.01 M ( $C_{H_2O_2} = 1$  M), the hydrogen peroxide acts as an initiator rather than as a direct source of oxidant species.
- The fast oxidation of Fe(II) to Fe(III) suggests that the oxidation system studied should be better described as the hydrogen peroxide decomposition by the red-ox couple Fe(II)/Fe(III). The latter statement could be experimentally corroborated by conducting an experiment in the presence of ferric iron with no addition of the reduced species (see Fig. 3, diamond symbols). As deduced from Fig. 3, after an initial lag period of 2 h, the final COD conversion obtained was similar to the value obtained when using Fe(II) at

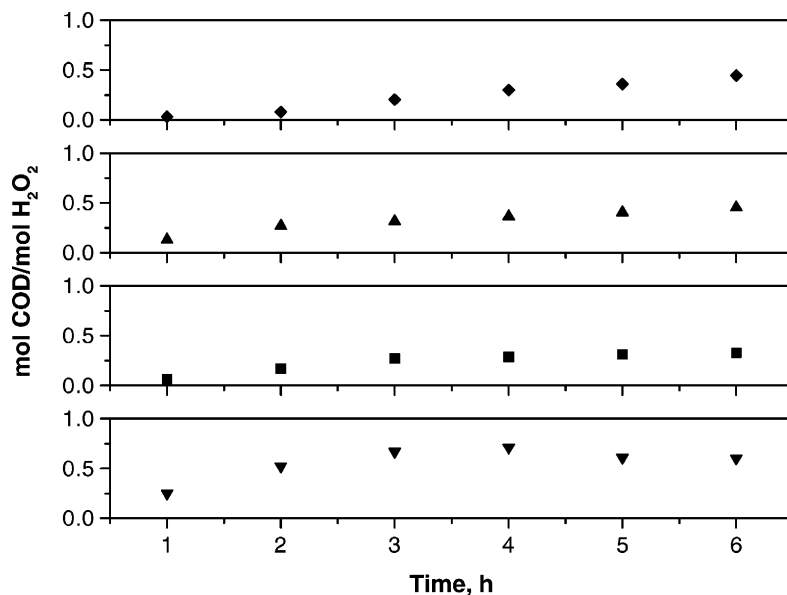


Fig. 4. Fe(II)/Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of removed COD/hydrogen peroxide consumption ratio with time. Influence of Fe(II)/Fe(III) initial concentration. Conditions:  $T_0 = 293$  K;  $\text{pH}_0 = 3.5$  (average value);  $\text{C}_{\text{H}_2\text{O}_2(0)} = 1.0$  M;  $\text{COD}_0 = 15 \text{ g l}^{-1}$  (approximate value);  $\text{C}_{\text{Fe(II)}} = 0.01$  M (▼),  $0.03$  M (■),  $0.05$  M (▲);  $\text{C}_{\text{Fe(III)}} = 0.03$  M (◆).

the same operating conditions. The induction period experienced may be attributed to the lower catalytic activity of Fe(III) in comparison to Fe(II).

Therefore, with a view to savings in operating costs (disappearance of a reduction step to recover the catalysts), the rest of the present study was completed with the addition of Fe(III) instead of Fe(II).

### 3.1.3. Influence of ferric iron initial concentration

The influence of the initial Fe(III) concentration was tested in the interval  $5 \times 10^{-3}$  to  $3 \times 10^{-2}$  M for a constant concentration of hydrogen peroxide of 1.0 M. Similarly, to results obtained in the case of the use of Fe(II), a slight positive effect of this parameter was observed in the range of concentrations studied (see Fig. 5). Nevertheless, the enhancement of the process was less pronounced if compared to the experimental series conducted with the reduced form of the metallic cation. Also, the evolution of the remaining hydrogen peroxide in the reaction media followed a comparable trend to the one observed for the Fe(II) catalysed experiments. Thus, the rapid total conversion of this reagent was experienced when the amount of iron was equal or above 0.02 M.

### 3.1.4. Influence of pH

The reaction pH is probably the most influential parameter regarding the effectiveness of Fenton process. There are several pH-related factors affecting the efficacy of Fenton

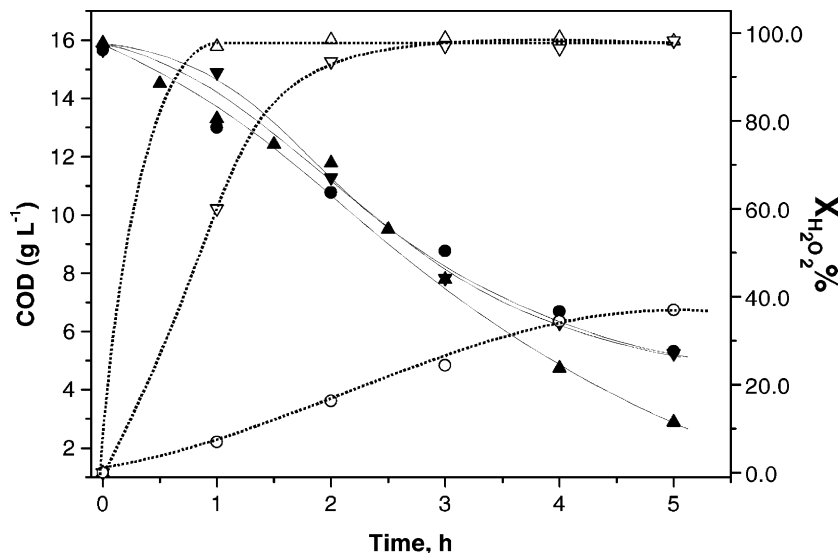


Fig. 5. Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of Fe(III) initial concentration. Conditions:  $T_0 = 293$  K;  $\text{pH}_0 = 3.5$  (average value);  $C_{\text{H}_2\text{O}_2(0)} = 1.0$  M;  $\text{COD}_0 = 15 \text{ g l}^{-1}$  (approximate value);  $C_{\text{Fe(III)}} = 0.03$  M (▲, △), 0.02 M (▼, ▽), 0.005 M (●, ○).

oxidation; however, the stability of reagents is likely the predominant effect to take into consideration. Most studies reported on Fenton and Fenton-like systems claim that the optimum working pH is situated in the range 3–4, the efficiency of the treatment experiencing strong reductions as the pH is set out of this interval. In contrast, other authors have reported neutral conditions to be the most appropriate to remove some kinds of compounds [21,22].

In this work, no differences were obtained for experiments carried out at acidic conditions from pH 2.0 to 3.5 (see Fig. 6). However, a strong inhibition of the COD removal was observed when the starting pH value was 6.0. Similar results have been reported for wastewater from olive oil mills [17]. Analogously, hydrogen peroxide depletion also underwent a significant deceleration when the pH was adjusted to 6.0. Nevertheless, in the latter case, H<sub>2</sub>O<sub>2</sub> was not more effectively used since the stoichiometric coefficients calculated at any time approached the value 0.3–0.4 reported previously for acidic conditions ( $C_{\text{Fe(II)}} = 0.03$  M and  $C_{\text{H}_2\text{O}_2} = 1.0$  M).

### 3.1.5. Influence of reaction temperature

As stated previously, for the experiments carried out in this study with no temperature control, an average of 10–20 K temperature increase in the reaction media was observed depending on operating conditions. Thus, in Fig. 7, it can be observed how this parameter rapidly increases up to a maximum value, gradually decreasing, afterwards, due to heat exchange with the surroundings.



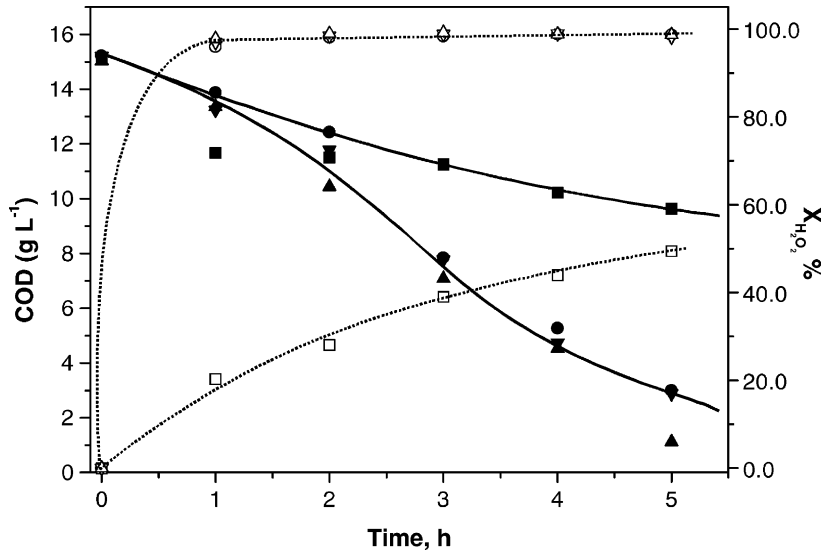


Fig. 6. Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of initial pH. Conditions:  $T_0 = 293$  K;  $C_{\text{H}_2\text{O}_2(0)} = 1.0$  M;  $\text{COD}_0 = 15 \text{ g l}^{-1}$  (approximate value);  $C_{\text{Fe(III)}} = 0.03$  M;  $\text{pH}_0 = 6.0$  (■, □), 3.5 (▼, ▽), 3.0 (●, ○), 2.0 (▲, △).

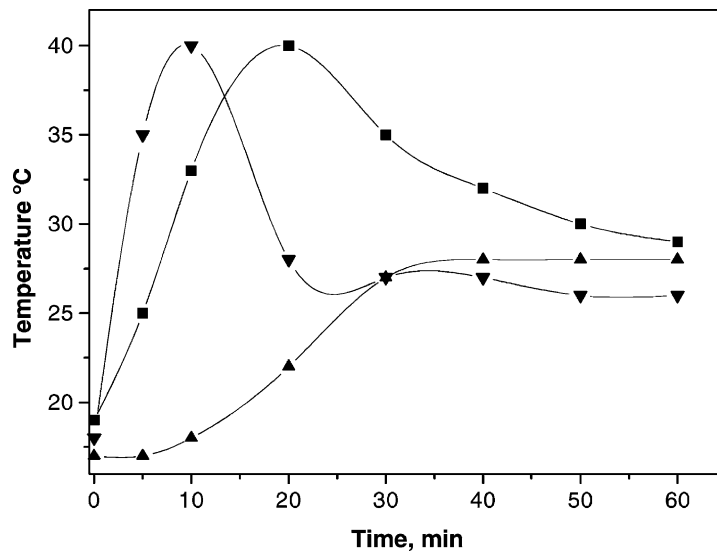


Fig. 7. Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of temperature with time. Influence of Fe(III) initial concentration. Conditions:  $T_0 \approx 291$  K;  $\text{pH}_0 = 3.5$  (average value);  $C_{\text{H}_2\text{O}_2(0)} = 1.0$  M;  $\text{COD}_0 = 15 \text{ g l}^{-1}$  (approximate value);  $C_{\text{Fe(III)}} = 0.01$  M (▲), 0.02 M (■), 0.03 M (▼).

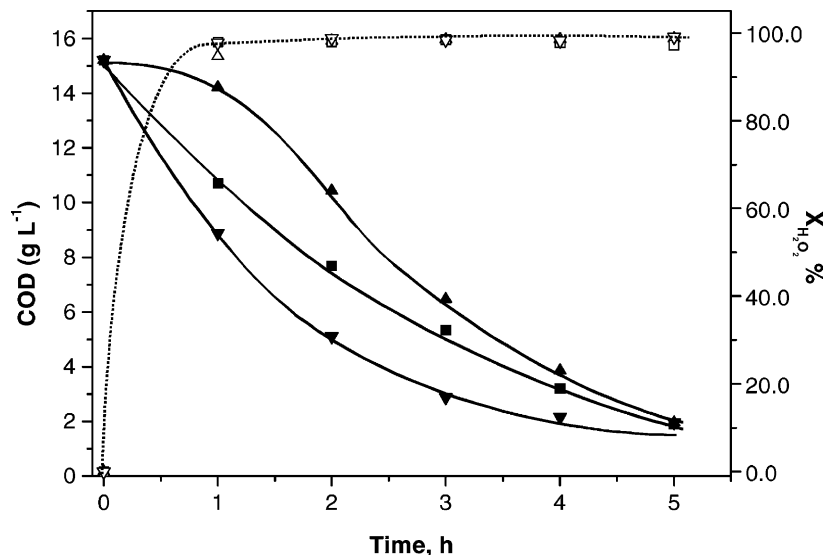


Fig. 8. Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of initial temperature. Conditions: pH<sub>0</sub> = 3.5; C<sub>H<sub>2</sub>O<sub>2</sub>(0)</sub> = 1.0 M; COD<sub>0</sub> = 15 g l<sup>-1</sup> (approximate value); C<sub>Fe(III)</sub> = 0.03 M; T = 298 K (▲, △), 313 K (■, □), 333 K (▼, ▽).

Therefore, a series of experiments was conducted at different temperatures (298–333 K) by keeping this parameter constant throughout the reaction period. From Fig. 8, it can be observed that for the experiments carried out at 313 and 333 K, the inhibition period totally disappeared leading to significant COD conversions if compared to results obtained at 298 K. Nevertheless, after 5 h of treatment, the final COD value achieved was almost identical (≈2000 mg l<sup>-1</sup>). These results suggest either the existence of a fraction of refractory substances towards the oxidation by the Fe(III)/H<sub>2</sub>O<sub>2</sub> system, or the formation–accumulation of low molecular weight oxygenated species which cannot undergo further oxidation. Experiments carried out in the presence of a higher hydrogen peroxide concentration (2.0 M) did not lead to COD reductions below 2000 mg l<sup>-1</sup>.

### 3.1.6. Influence of the initial COD concentration

The role of the initial COD concentration was investigated by using different dilution factors of the wastewater with synthetic urban wastewater. Thus, experiments with initial COD of 31, 15 and 7.5 g l<sup>-1</sup> were completed and the results shown in Fig. 9. As observed from this figure, the experiments conducted with 15 and 7.5 g l<sup>-1</sup> COD led to similar results after 5 h of treatment. In contrast, a higher value of the final COD was obtained (approximately 14.4 g l<sup>-1</sup>) when the starting COD was set at 31 g l<sup>-1</sup>. Nevertheless, it should be noted that the apparent stoichiometric coefficient calculated, measured as COD removed per mol of hydrogen peroxide consumed, increased as the initial concentration of COD was raised. Values of this ratio of 0.54, 0.35 and 0.13 were calculated after 5 h for experiments carried out with initial COD of 31, 15 and 7.5 g l<sup>-1</sup>, respectively (see inset in Fig. 9).

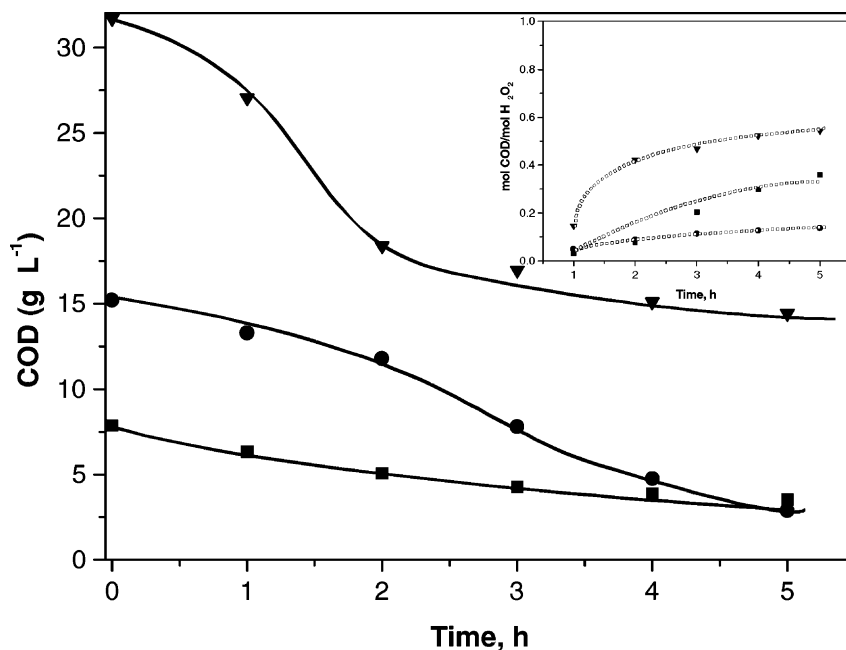


Fig. 9. Fe(III)/H<sub>2</sub>O<sub>2</sub> treatment of table olive fermentation brines. Evolution of COD (solid symbols) and removed COD/hydrogen peroxide consumption ratio (embedded figure) with time. Influence of initial COD. Conditions: pH<sub>0</sub> = 3.5; C<sub>H<sub>2</sub>O<sub>2</sub>(0)</sub> = 1.0 M; T = 293 K; C<sub>Fe(III)</sub> = 0.03 M; COD<sub>0</sub> = 7.5 g l<sup>-1</sup> (■), 15 g l<sup>-1</sup> (●), 31 g l<sup>-1</sup> (▼).

Also, the final conversion achieved for the phenolic content of the effluent was lower for the experiment initiated with the highest contaminant load, albeit the amount of these compounds eliminated was substantially higher (three to four times higher) for this experiment (i.e. the reaction rate increased).

Based on a normal stoichiometric coefficient for H<sub>2</sub>O<sub>2</sub> consumption (2 g of H<sub>2</sub>O<sub>2</sub> consumed per gram of COD degraded), the price of hydrogen peroxide, and the amount of COD reduced (around 9000 mg l<sup>-1</sup> in a typical Fenton's experiment with Fe(III) = 0.03 M and H<sub>2</sub>O<sub>2</sub> = 1.0 M), operating costs attributed to H<sub>2</sub>O<sub>2</sub> were found to be US\$ (1.2 × 10<sup>-3</sup>) per cubic meter of wastewater treated and ppm of COD removed. If H<sub>2</sub>O<sub>2</sub> is assumed to constitute the 75% of operating costs, the final value of the operation would be US\$ (1.6 × 10<sup>-3</sup>) per cubic meter of wastewater treated and ppm of COD removed. These results are quite similar to other calculations for this treatment, confirming the economic feasibility of the process [17].

### 3.2. Aerobic biodegradation experiments

As suggested by previous studies [1,2], biodegradation experiments were carried out using microorganisms acclimated to the saline environment of brines. Thus, before proper operation of the SBR, a number of cycles were completed to acclimate bacteria to the saline

nature of the effluent. For doing so, the reactor was first loaded with activated sludge from a municipal wastewater treatment plant and synthetic domestic wastewater. The content of fermentation brines in the feed was progressively increased throughout successive cycles. When the content of brines in the mixture exceeded 1:10 by volume, inhibitory effects were noticed (i.e. decrease in overall substrate utilisation rate). Therefore, in order to avoid these inhibitory effects, the dilution ratio 1:10 was chosen. Diluted wastewater had a COD of approximately  $2.5\text{--}3\text{ g l}^{-1}$ . Cycles were repeated with the same wastewater load and keeping a constant biomass concentration by appropriate sludge wasting at the withdrawing step. When consistency in COD depletion profiles with time was achieved, the biomass was assumed to be acclimated to the applied effluent.

First of all, two series of experiments were carried out in parallel with untreated brines and with brines previously subjected to chemical pre-treatment by Fenton's oxidation. In the latter case, the final COD achieved by chemical oxidation was about  $2.5\text{ g l}^{-1}$ . Inhibition by substrate was not observed when this effluent was subjected to direct biodegradation. Taking into account the fraction of COD removed by means of the chemical oxidation, the percentages by volume of initial brines in the wastewater to be biodegraded varied from 10 to 50% for non-treated and pre-treated wastewater, respectively. Therefore, the chemical pre-oxidation allows for reducing the volume of water for dilution purposes and also suggests that biological oxidation was inhibited by high COD content rather than by the salinity of the wastewater (i.e. salinity was five times higher for the pre-treated effluent). Fig. 10 shows the evolution of remaining COD and the VSS concentration profiles during the reaction period of comparative experiments. The evolution of VSS shows typical log-growth and stationary phases. Lag and log-death phases were not clearly observed in all cases because of the use of acclimated seeds and the limited time of the reaction step, respectively. Regarding COD

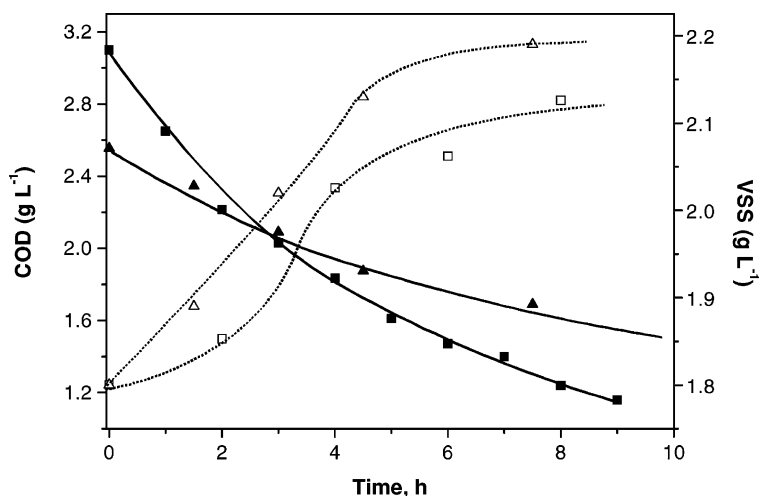


Fig. 10. Biological treatment of table olive fermentation brines before and after Fenton's pre-oxidation. Evolution of COD (solid symbols) and VSS (open symbols) with time. Conditions:  $\text{pH}_0 = 7.0$ ;  $T = 20^\circ\text{C}$ ; no Fenton's treatment (■); after Fenton's treatment (▲).

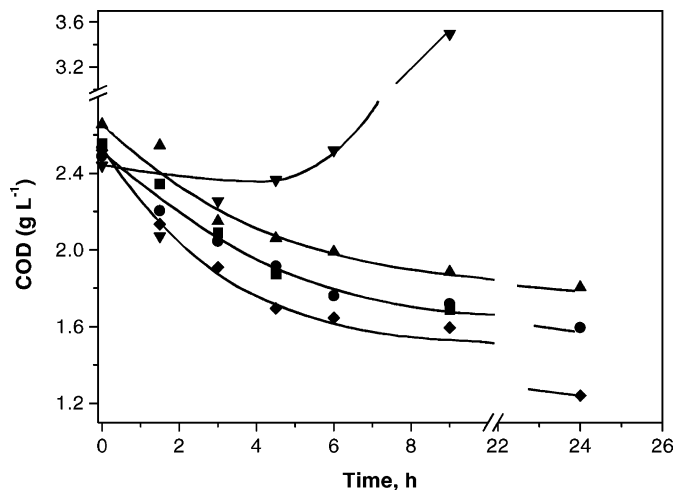


Fig. 11. Biological treatment of table olive fermentation brines after Fenton's pre-oxidation. Evolution of COD with time. Influence of temperature. Conditions:  $\text{pH}_0 = 7.0$ ;  $\text{VSS} = 1.8 \text{ g l}^{-1}$ ;  $T = 40^\circ\text{C}$  (▼),  $30^\circ\text{C}$  (◆),  $20^\circ\text{C}$  (■),  $10^\circ\text{C}$  (●),  $5^\circ\text{C}$  (▲).

profiles, it is observed that the biological activity of microorganisms is quite similar for the non-treated and Fenton's pre-oxidised effluents, some slight enhancement is observed for the non-treated wastewater, although, as stated previously, when the chemical step is used, considerable reductions in dilution water needs are obtained. Moreover, microorganisms were acclimated to the raw diluted wastewater, not to the effluent generated after Fenton oxidation, this may have contributed to the difference in the biodegradation performance.

The effect of temperature on the biodegradation rate of effluent from Fenton's oxidation was also studied. Fig. 11 shows the evolution of residual COD with reaction time. As expected, biodegradation rate was temperature dependent. As a rule, the higher the temperature, the higher the substrate utilisation rate in the range  $5\text{--}30^\circ\text{C}$ . In this temperature range, settling characteristics of biological solids were not significantly affected. At  $40^\circ\text{C}$ , bacterial inhibition was clearly evident.

#### 4. Conclusions

From the present study, the following conclusions can be drawn:

- Usage of Fenton's reagent allows for a significant reduction of the COD content of fermentation brines.
- Both Fe(II) and/or Fe(III) can act as a catalyst of the hydrogen peroxide decomposition. Use of ferric iron instead of the reduced form may contribute to the improvement of the process economy.
- Optimum working pH was situated at acidic conditions, similar to the natural pH found for this type of effluents.

- Fenton's reagent pre-treatment allows for a considerable reduction in water dilution needs if a conventional biodegradation step is further applied.
- Aerobic biodegradation of the pre-treated effluent is best performed in the proximity of 30 °C, experiencing a total inhibition of the process if temperature is increased to 40 °C.

### Acknowledgements

This work has been supported by the Junta de Extremadura and Fondo Social Europeo (Project IPR00A002).

### References

- [1] C.R. Woolard, R.L. Irvine, *Water Environ. Res.* 66 (1994) 230.
- [2] C.R. Woolard, R.L. Irvine, *Water Res.* 29 (1995) 1159.
- [3] S. Lin, T. Shyu, M. Sun, *Water Res.* 32 (1998) 1059.
- [4] F. Ludzack, D. Noran, *J. WPCF* 37 (1965) 1404.
- [5] M. Hamoda, I. Al-Attar, *Water Sci. Technol.* 31 (1995) 61.
- [6] D. Kincannon, F. Gaudy, *J. WPCF* 38 (1966) 1148.
- [7] M. Stewart, H. Ludwig, W. Kearns, *J. WPCF* 34 (1962) 1161.
- [8] G. Feijoo, M. Soto, R. Mendez, J.M. Lema, *Enzyme Microb. Technol.* 17 (1995) 180.
- [9] R. Mendez, J. Lema, M. Soto, *Water Environ. Res.* 67 (1995) 33.
- [10] F. Omil, R. Mendez, J. Lema, *ISSN 0378-4738 Water SA* 22 (1996) 173.
- [11] W. Rearick, L. Farias, H. Goettsch, *Textile Chemist Colorist* 29 (1997) 10.
- [12] A. Garrido, M. Brenes, P. Garcia, *Grasas y Aceites* 43 (1992) 291.
- [13] R. Batina, L. McNeill, in: *Proceedings of the 48th Annual Technical Report of California Olive Association*, Monterrey, USA, 1969, pp. 67–72.
- [14] R. Kennedy, in: *Proceedings of the 48th Annual Technical Report of California Olive Association*, Monterrey, USA, 1969, pp. 13–19.
- [15] R.J. Bidga, *Chem. Eng. Prog.* December (1995) 62.
- [16] R.J. Bidga, *Environ. Technol.* May/June (1996) 34.
- [17] F.J. Rivas, F.J. Beltran, J. Frades, O. Gimeno, *J. Agric. Food Chem.* 49 (2001) 1873.
- [18] APHA: *Standard Methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington, DC, 1995.
- [19] I. Talinli, G. Anderson, *Water Res.* 26 (1992) 107.
- [20] F.J. Rivas, F.J. Beltran, J. Frades, P. Buxeda, *Water Res.* 35 (2001) 387.
- [21] E. Lypczinska-Kochani, in: A. Bowers, J. Roth (Eds.), *Chemical Oxidation Technologies for the Nineties*, vol. 4, Technomic Publishing Co., Basel, Switzerland, 1994, pp. 12–27.
- [22] F.J. Beltrán, M. González, F.J. Rivas, P. Alvarez, *Water Air Soil Pollut.* 105 (1998) 685.