

# Solar Photochemical Treatment of Winery Wastewater in a CPC Reactor

Marco S. Lucas,<sup>\*,†</sup> Rosa Mosteo,<sup>‡</sup> Manuel I. Maldonado,<sup>§</sup> Sixto Malato,<sup>§</sup> and José A. Peres<sup>†</sup>

<sup>†</sup>Centro de Química, Universidade de Trás-os-Montes e Alto Douro, Apartado 1013, 5001-801 Vila Real, Portugal, <sup>‡</sup>Department of Chemical Engineering and Environmental Technologies, University of Zaragoza, C/Pedro Cerbuna, 12, 50009, Zaragoza, Spain, and <sup>§</sup>Plataforma Solar de Almería—CIEMAT, Carretera Senés km 4, Tabernas (Almería), 04200 Spain

Degradation of simulated winery wastewater was studied in a pilot-scale compound parabolic collector (CPC) solar reactor. Total organic carbon (TOC) reduction by heterogeneous photocatalysis (TiO<sub>2</sub>) and homogeneous photocatalysis with photo-Fenton was observed. The influence of TiO<sub>2</sub> concentration (200 or 500 mg/L) and also of combining TiO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> on heterogeneous photocatalysis was evaluated. Heterogeneous photocatalysis with TiO<sub>2</sub>, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is revealed to be inefficient in removing TOC, originating TOC degradation of 10%, 11% and 25%, respectively, at best. However, photo-Fenton experiments led to 46% TOC degradation in simulated wastewater prepared with diluted wine (WV) and 93% in wastewater prepared with diluted grape juice (WG), and if ethanol is previously eliminated from mixed wine and grape juice wastewater (WW) by air stripping, it removes 96% of TOC. Furthermore, toxicity decreases during the photo-Fenton reaction very significantly from 48% to 28%. At the same time, total polyphenols decrease 92%, improving wastewater biodegradability.

KEYWORDS: CPC reactor; solar photocatalysis; photo-Fenton; titanium dioxide; toxicity; winery wastewater

## INTRODUCTION

Wine is the product of alcoholic fermentation of fresh grapes or of grape must. Wastewater from wine production, called winery wastewater, comes mainly from washing operations during grape crushing and pressing, and rinsing of fermentation tanks, barrels, bottles and other equipment or surfaces (1-3). Discharge and biological treatment of this type of effluent is a complex process due to the high concentration of organic matter, mainly composed of organic acids, ethanol, glucose, fructose and polyphenols with COD from 3000-15000 mg of O<sub>2</sub>/L. Furthermore, winery wastewater is seasonal, fluctuating widely in volume and composition.

Several physical and chemical processes are available for winery wastewater treatment, but the main one used is phase transfer of pollutants. Anaerobic treatments have been recognized as a possible way to significantly degrade wastewater with high organic content, such as winery effluents (4,5). However, the presence of compounds that are refractory and even toxic to the microorganisms along with the large quantities of sludge generated reduces the treatment's usability (6–8).

Advanced oxidation processes (AOPs) are based on chemical oxidation with hydroxyl radicals, which are very reactive shortlived oxidants. The radicals are produced in an on-site reactor, where they are capable of destroying a wide range of organic pollutants in water and wastewater (9, 10). Fenton's reagent oxidation is a homogeneous catalytic AOP that combines hydrogen peroxide and ferrous iron, as the catalyst, to oxidize specific contaminants or wastewaters. The overall reaction is

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet}$$
 (R1)

The ferrous ion catalyzes and triggers decomposition of  $H_2O_2$ , resulting in the generation of hydroxyl radicals, HO<sup>•</sup> (11, 12). Addition of UV radiation to Fenton's reagent allied in a photo-Fenton process could be of interest for wastewater treatment, because it directly influences the formation of HO<sup>•</sup> radicals (13). In photo-Fenton reaction, in addition to reaction 1, then hydroxyl radicals are also formed through the following reactions (reactions 2 and 3):

$$H_2O_2 + UV \rightarrow HO^{\bullet} + HO^{\bullet}$$
(R2)

$$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + HO^{\bullet} + H^+$$
 (R3)

Heterogeneous photocatalysis is based on irradiation of a catalyst, usually a semiconductor (e.g.,  $TiO_2$ ), which can be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites), providing them with wide scope as redox agents. Destruction or removal of contaminants takes place in the interfacial region between the excited solid particle and the solution, with no chemical change in the catalyst.

<sup>\*</sup>Corresponding author. E-mail: mlucas@utad.pt.

 Table 1. Winery Wastewater Characterization

wastewater	synthetic sample	pН	conductivity ( $\mu$ S/cm)	TOC (mg/L)	$COD \ (mg \ of \ O_2/L)$	total polyphenols (mg of gallic acid/L)
WV WG	wine grape juice	3.8 4.3	152 107	1155 1185	4440 4500	93 112
WW	wine $+$ grape juice (50:50)	4.1	124	1165	4474	103



Figure 1. Photo and schematic drawing of the CPC reactor used in the photochemical experiments.

Reactions 4, 5 and 6 are the main reactions in heterogeneous photocatalysis with  $TiO_2$  (14, 15):

$$\operatorname{TiO}_2 + h\nu \rightarrow \operatorname{TiO}_2 (e^- + h^+)$$
 (R4)

$$TiO_2 (e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -}$$
(R5)

$$TiO_2 (e^-) + H_2O_2 \rightarrow TiO_2 + HO^- + HO^{\bullet}$$
(R6)

Winery wastewater treatment by photo-Fenton and heterogeneous photocatalysis has been previously demonstrated (16, 17). Mosteo et al. (18) report that heterogeneous photo-Fenton, using natural sunlight as the radiation source, removed 50% TOC in 24 h, suggesting that this process can be used as a pretreatment for an aerobic biological process.

The purpose of this paper is to evaluate the performance of solar photochemical AOPs, such as heterogeneous photocatalysis (with TiO<sub>2</sub>, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and homogeneous photocatalysis with photo-Fenton, to treat winery wastewater in a compound parabolic collector (CPC) pilot solar plant. This is, to the best of our knowledge, the first study performed with winery wastewater in this type of solar collector.

## MATERIAL AND METHODS

**Winery Wastewater.** Because of the seasonal character of winery wastewater, the effluents had to be reproduced with synthetic samples prepared by diluting commercial grape juice (WG), commercial red wine (WV), and a mixture of both (wine and grape juice, WW) in Milli-Q water. WG is simulated wastewater characterized by its high sugar content that reproduces winery wastewater during fermentation. WV is wastewater with high ethanol content that attempts to imitate wastewater generated after fermentation. WW simulates the combination of both of the above in a mixture similar to the equalization tank in some wineries where all the effluents are mixed.

**Table 1** shows the main characteristics of the three types of winery wastewater: conductivity, pH, total organic carbon (TOC), chemical oxygen demand (COD) and total polyphenol content.

**Chemicals.** Heterogeneous photocatalytic degradation was carried out using a slurry suspension of Degussa (Frankfurt, Germany) P-25 titanium dioxide (surface area  $51-55 \text{ m}^2/\text{g}$ ) and sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) purchased from Panreac. The photo-Fenton experiments were performed using ferrous iron sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), hydrogen peroxide

(30% w/w) and sulfuric acid for pH adjustment (around 2.8–3.0), all supplied by Panreac.

The phototreated solutions were neutralized by means of NaOH (reagent grade, Panreac) for the toxicity test. Water used in the pilot plant was from the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10  $\mu$ S/cm, Cl<sup>-</sup> = 0.7–0.8 mg/L, NO<sub>3</sub><sup>-</sup> = 0.5 mg/L, organic carbon < 0.5 mg/L), in order to avoid possible analytical interference. Other chemicals used in these experiments were reagent grade and used as received.

**Analytical Determinations.** Organic matter concentration and mineralization were monitored by measuring the TOC by direct injection of filtered samples into a Shimadzu-5050A TOC analyzer, equipped with an ASI5000 autosampler, provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. The COD analysis was performed by Merck Spectroquant cuvette tests. Samples were prefiltered through 0.20  $\mu$ m syringe nylon filters (25 mm, Millex GN, Millipore). The COD and TOC are expressed in mg of O<sub>2</sub>/L and mg of C/L, respectively.

The initial hydrogen peroxide concentration was always 12 mM and controlled to avoid complete disappearance by adding small amounts as consumed. Hydrogen peroxide concentration was determined by the metavanadate method (19). Colorimetric determination of total iron concentration with 1,10-phenanthroline was used according to ISO 6332. Ultra pure distilled-deionized water was from a Milli-Q (Millipore Co.) system. The polyphenol content was measured in filtered samples by Folin-Ciocalteau reagent (20).

**Toxicity Measurements.** Toxicity was assessed using the Biofix Lumi-10 luminometer and the Biofix Lumi kit by Macherey-Nagel. The biological agent is a freeze-dried preparation of the marine bacterium *Vibrio fischeri* (formerly known as *Photobacterium phosphoreum*, NRRL number B-11177). Light emission was measured at 15 °C after a 15 min contact period. Hydrogen peroxide in the samples was removed prior to the toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg/L) from Fluka Chemie AG. All the samples were analyzed after adjusting the pH to 7. Careful control of temperature was essential because light emission is sensitive to temperature.

**Experimental Setup.** All experiments were carried out under sunlight, in a pilot plant installed at the Plataforma Solar de Almería (latitude 37°N, longitude 2.4°W). Photo-Fenton and titanium dioxide experiments were carried out in a compound parabolic collector (CPC) pilot solar plant (21) able to treat up to 40 L of wastewater (3.1 m<sup>2</sup> irradiated surface, 22 L irradiated volume).

The absorber tube has an internal diameter of 29.2 mm and an external diameter of 32.0 mm. Each experiment was repeated twice, and the data used for kinetic calculations correspond to the average of two different tests. The pilot plant (Figure 1) operates in batch mode. The



**Figure 2.** Total organic carbon in winery wastewater (WV and WG) during solar photolysis and heterogeneous photocatalysis (TiO<sub>2</sub>) in a CPC reactor. Experimental conditions:  $[TiO_2]_0 = 200 \text{ mg/L}$  and 500 mg/L; initial pH = 3.8.

solar collector is mounted on a fixed platform tilted 37° (local latitude). Solar ultraviolet radiation (UV  $\lambda < 400$  nm) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3), mounted on a platform tilted 37°, which provides data in terms of incident UV (W/m<sup>2</sup>). This gives an idea of the energy reaching any surface in the same position with regard to the sun.

With eq 1, the combination of the data from several days' experiments and the comparison between photoreactors installed at different emplacements are possible.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_{\rm T}}, \qquad \Delta t_n = t_n - t_{n-1}$$
(1)

where UV is the average solar ultraviolet radiation measured between  $t_n$  and  $t_{n-1}$  ( $\Delta t_n$ ),  $t_n$  is the experimental time for each sample,  $V_T$  is the total volume of water loaded in the pilot plant (35 L),  $V_i$  is the total irradiated volume (22 L, glass tubes) and  $t_{30W}$  is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m<sup>-2</sup> (typical solar UV power on a perfectly sunny day around noon). As the system is outdoors and is not thermally controlled, the temperature inside the reactor is continuously recorded by a PT-100 inserted in the tank. At the beginning of the process, the collectors were covered, the pH was adjusted and the TiO<sub>2</sub> or ferrous iron salt was added. After each addition of reagents, the synthetic wastewater was well homogenized by recirculation. Finally, a sample was taken (time zero), and after that the first amount of hydrogen peroxide was measured frequently and consumed reagent was continuously replaced to maintain the original concentration throughout the reaction.

#### **RESULTS AND DISCUSSION**

**Degradation of Winery Wastewater by TiO<sub>2</sub>. Figure 2** shows  $TOC/TOC_0$  during solar photolysis and heterogeneous photocatalysis (TiO<sub>2</sub>) of the simulated winery wastewater in the CPC reactor. The results reveal that solar photolysis, by itself, produces a very small decrease in TOC in the two studied samples of winery wastewater. However, in the synthetic sample with high sugar content (WG sample) the TOC content decreases slightly faster than in the synthetic WV sample.

In the experiments performed with heterogeneous photocatalysis (TiO<sub>2</sub>), degradation of two types of winery wastewater (WG or WV) was evaluated with two different amounts of catalyst (200 and 500 mg/L). In the experiments with 200 mg/L of TiO<sub>2</sub>, TOC decreased 8% in the WV sample and 10% in WG after a  $t_{30W}$  of 400 min. TOC removal from WV was not improved by increasing the amount of catalyst from 200 mg/L to 500 mg/L, which was again 10%. Thus, TiO<sub>2</sub> alone is insufficient, even when the amount of catalyst was more than doubled, to remove TOC

present in the winery wastewater. Therefore, a  $TiO_2$  concentration of 200 mg/L was selected as the best option and was used in following experiments.

Degradation of Winery Wastewaters by TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>/  $S_2O_8^{2^-}$ . Figure 3 shows experiments performed with TiO<sub>2</sub> combined with hydrogen peroxide or persulfate to evaluate the improvement in TOC removal generated by the addition of these oxidants to TiO<sub>2</sub>. No significant changes are observed in the data with either of the combinations  $(TiO_2/H_2O_2 \text{ or } TiO_2/S_2O_8^{-2})$ . With  $TiO_2/H_2O_2$ , TOC removal was 11% after a  $t_{30W}$  of 150 min, and with a single addition of 10 mM of  $S_2O_8^{2-}$  to TiO<sub>2</sub> at the beginning of the experiment, TOC degradation was 12% in both WV and WG samples. When the concentration of  $S_2 O_8^2$ (10 mM) in solution was kept constant throughout the reaction in a TiO<sub>2</sub>/ $S_2O_8^{2-}$  experiment, TOC removal was 25% after a  $t_{30W}$  of 440 min. Therefore, as a final comment on the heterogeneous photocatalysis experiments, it may be confirmed that no significant TOC degradation can be achieved with this process in either WV or WG even when the amount of  $TiO_2$  is increased or  $H_2O_2$ and  $S_2O_8^{2-}$  are added.

**Degradation of Winery Wastewater by Photo-Fenton Oxidation.** The effectiveness of photo-Fenton has previously been demonstrated using different sources of radiation and different types of winery wastewater (16, 18, 22). So, the next step in this study is to test the effectiveness of photo-Fenton in the treatment of a winery wastewater in a CPC reactor.

**Figure 4** shows the application of solar photo-Fenton to treatment of a sample of WV. The photo-Fenton experiments were done with a single dose of  $Fe^{2+}$  (55 mg/L) at a pH of 3. The hydrogen peroxide dose of 12 mM was maintained constant with successive additions throughout the experiment. The solar photo-Fenton experiments started when the CPC reactor was exposed to solar radiation. The results show that after a  $t_{30W}$  of 500 min with an added  $H_2O_2$  concentration of 151 mM TOC removal was 54%.

These results are not particularly exceptional since longer reaction time and higher dose of  $H_2O_2$  were used. A possible explanation could be the fast disappearance of iron from the reaction media, probably because the iron forms complexes with compounds present in the winery wastewater. **Figure 4** shows how fast iron disappears from the reaction media, especially in the first 100 min. So to find out whether this poor TOC removal could be explained by the very low iron concentration in solution, the amount of iron necessary to maximize solar photo-Fenton was specifically evaluated.



Figure 3. Influence of hydrogen peroxide ( $H_2O_2$ ) and sodium persulfate ( $Na_2S_2O_8$ ) in heterogeneous photocatalysis ( $TiO_2$ ) treatment of winery wastewater (WV or WG) in a CPC reactor. Experimental conditions: [ $TiO_2$ ]<sub>0</sub> = 200 mg/L; initial pH = 3.8.



**Figure 4.** Winery wastewater (WV) treatment by solar photo-Fenton using a CPC reactor. TOC ( $\Box$ ), hydrogen peroxide ( $\bullet$ ) and iron ( $\blacktriangle$ ) concentrations during reaction. Experimental conditions: [Fe<sup>2+</sup>]<sub>0</sub> = 55 mg/L; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 12 mM; initial pH = 3.0.

Influence of Ferrous Iron Concentration. Photo-Fenton experiments were carried out at two different  $Fe^{2+}$  concentrations, 55 mg/L and 110 mg/L. Figure 5 shows a photo-Fenton experiment performed with 110 mg/L. From the data shown, it may be observed that no significant improvement was achieved by increasing the iron concentration. In fact, contrary to what was expected, there is a small decrease in TOC removed. In the experiment with 55 mg/L of iron and a  $t_{30w}$  of 250 min, TOC degradation was 21% while with 110 mg/L of iron degradation was only 11%. This reduction in TOC removal may be explained by redox reactions in which HO<sup>•</sup> radicals are scavenged by reaction with other  $Fe^{2+}$  molecules as displayed in reaction 7 (23).

$$Fe^{2+} + HO^{\bullet} \rightarrow HO^{-} + Fe^{3+}$$
 (R7)

Thus, the large amount of ferrous iron added decreases the strength of the photo-Fenton reaction. It was also found that, even with a large initial amount of iron, the concentration in solution decreases very fast in the first minutes, just as it did in the experiment with 55 mg/L of iron.

Furthermore, the effect on TOC removal of several additions of iron during the reaction in an attempt to keep the amount of iron in solution constant at around 55 or 110 mg/L was studied. **Figure 6** shows the results of these experiments. In the experiment started with 55 mg/L of iron, TOC degradation was 44%, and in the experiment started with 110 mg/L, removal was 48% in around the same reaction time (400 min). These results reveal an improvement in TOC degradation compared to the experiments with single additions of iron, especially in the experiment started with 110 mg/L. Therefore, the continuous addition of ferrous iron throughout the reaction slightly improves the solar photo-Fenton degradation capacity, however, with continuous addition, the total amount of iron is obviously larger than with only one dose. Thus, in the experiment started with 15 mg/L of ferrous iron, at the end of reaction, the cumulative total of ferrous iron was 153 mg/L, and in the experiment started with 110 g/L, it was 323 mg/L.

Thus, around three times more ferrous iron was used than in the experiments with a single dosage, but this increment in iron does not directly correspond to an increment in TOC degradation, as the large amount of iron added in several additions does not lead to a clear improvement in TOC removal, because the difference between 55 mg/L and 110 mg/L on TOC degradation



**Figure 5.** Winery wastewater (WV) treatment by solar photo-Fenton in a CPC reactor. TOC ( $\Box$ ), hydrogen peroxide ( $\bullet$ ) and iron ( $\blacktriangle$ ) concentrations during reaction. Experimental conditions: [Fe<sup>2+</sup>]<sub>0</sub> = 110 mg/L; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 12 mM; initial pH = 3.0.



Figure 6. Effect of several additions of iron on TOC removal and accumulated iron concentration during photo-Fenton experiment. Experimental conditions: winery wastewater (WV);  $[Fe^{2+}]_{const} = 110 \text{ mg/L} (\bullet)$  and  $[Fe^{2+}]_{const} = 55 \text{ mg/L} (\Box)$ ;  $[H_2O_2] = 12 \text{ mM}$ ; initial pH = 3.0.

was only 4%. Therefore, the best ferrous iron dosage for solar photo-Fenton operation is a single dose of 55 mg/L. The next step in the study was an in-depth analysis of application of photo-Fenton to simulated winery wastewater.

Influence of Winery Wastewater Composition. Figure 7 shows the results of several experiments performed with photo-Fenton with different initial operating conditions. First, the effect of wastewater type (WV or WG) on the photo-Fenton experiment with a single 55 mg/L dose of ferrous iron was evaluated, and TOC removal was found to be higher in the WG sample than in the WV sample. TOC removal was 46% in a  $t_{30W}$  of 400 min in WV while in WG, degradation was 93%. So photo-Fenton treatment of winery wastewater is observed to be significantly affected by the composition of the wastewater, with a difference of up to 47%.

The next step was therefore to assess the application of photo-Fenton in wastewater containing a mixture of WV and WG (WW).

This simulates real wastewater treatment in some wineries that have retention tanks to store and equalize the seasonal effluent from the different stages of wine production before further treatment in a wastewater treatment plant. Photo-Fenton treatment of the wastewater with WG and WV was faster than with either WV or WG alone. TOC removal in the mixture was 90% for a  $t_{30W}$  of 150 min. This strong removal of the organic load present in the wastewater indicates that photo-Fenton was more efficient in terms of the iron dose applied. Therefore, another experiment was done with the mixture of wine and grape juice, but with a single dose of ferrous iron of only 20 mg/L.

**Figure 7** shows that there are no significant differences in TOC removal due to the smaller iron dosage, as after a  $t_{30W}$  of 150 min, degradation was 84%. Thus, for a 60% decrease in ferrous iron concentration, TOC removal is only 6% lower. Therefore, an interesting option may be to store and equalize such wastewater before photo-Fenton treatment, which would be significantly more economical in terms of ferrous iron consumption and TOC degradation.

Influence of the Ethanol in Winery Wastewater. The main difference between the two types of wastewater (WV and WG) is that WV has a large amount of ethanol and in WG there is a high concentration of sugars. Therefore, to evaluate the effect of ethanol on the photo-Fenton process and consequently on TOC removal, ethanol elimination from the winery wastewater was evaluated. Ethanol was removed from the wastewater made with diluted wine (WV) by air stripping using aquarium pumps and warming the solution to 35 °C for 24 h. By removing ethanol, the main volatile compound in the wastewater, the corresponding



Figure 7. Influence of winery wastewater composition on TOC removal during photo-Fenton oxidation. Experimental conditions:  $[H_2O_2]_0 = 12 \text{ mM}$ ; initial pH = 3.0. (**II**) WV with  $[Fe^{2+}]_0 = 55 \text{ mg/L}$ ; (**O**) WG with  $[Fe^{2+}]_0 = 55 \text{ mg/L}$ ; (**O**) WG with  $[Fe^{2+}]_0 = 55 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WG with  $[Fe^{2+}]_0 = 55 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WG with  $[Fe^{2+}]_0 = 55 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WG with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0 = 20 \text{ mg/L}$ ; (**O**) WW with  $[Fe^{2+}]_0$ 



Figure 8. Total polyphenols, COD and toxicity during photo-Fenton oxidation of winery wastewater. Experimental conditions:  $[Fe^{2+}]_0 = 20 \text{ mg/L}; [H_2O_2]_0 = 12 \text{ mM};$  initial pH = 3.0.

organic load, equivalent to 70% of the TOC present in the solution, was also removed, similar to other studies (24). Although the experiment was done with the same original TOC as the other experiments, a large volume of wine without ethanol was added so the initial TOC would be the same and only the ethanol concentration changed.

Photo-Fenton degradation of this ethanol-free winery wastewater was 96% after a  $t_{30W}$  of 130 min. Based on this assay, it should be stressed that ethanol significantly influences photo-Fenton efficiency. This can be explained by the ethanol degradation pathways during photo-Fenton. Since ethanol is transformed during photoxidation, e.g., as in photo-Fenton, into acetaldehyde and later into acetic acid (reaction 8) (25):

$$CH_{3}CH_{2}OH \xrightarrow{O_{2}} CH_{3}CHO \xrightarrow{O_{2}} CH_{3}COOH \quad (R8)$$
  
acetic acid

Acetic acid is a well-known hydroxyl radical scavenger, as can be observed in the following reaction (reaction 9):

$$CH_3COOH + HO^{\bullet} \rightarrow CH_2COOH^{\bullet} + H_2O$$
 (R9)

Therefore, the lower degradation capacity of the photo-Fenton process when applied to WV is because of the action of acetic acid on the hydroxyl radicals. Thus, if the wastewater contains a large amount of ethanol, an air stripping pretreatment prior to photo-Fenton significantly increases the efficiency of this advanced oxidation process.

COD, Total Polyphenols and Toxicity Evolution in Photo-Fenton Process. Winery wastewater contains significant concentrations of refractory and even toxic compounds. Figure 8 shows COD, total polyphenols and toxicity during the photo-Fenton experiment. This experiment was performed with winery wastewater prepared with ethanol-free WV and WG (curve \* in Figure 7).

Photo-Fenton removes 98% of the COD load in the winery wastewater after a  $t_{30W}$  of 82 min. This confirms the previous finding of 96% TOC after a  $t_{30W}$  of 130 min. The total polyphenol content, measured as the reduction in the concentration of gallic acid, was monitored during the photo-Fenton reaction. This model phenolic compound was selected since it is the most representative phenolic acid present in winery wastewater (26–28). Its concentration increases in the first  $t_{30W}$  of

30 min due to aromatic ring hydroxylation (7), but after that, during the rest of the reaction, it drops to 92% of the original polyphenol content.

The toxicity of the winery wastewater was measured with the luminescent bacteria *Vibrio fischeri*, which indicated that initial toxicity decreases after photo-Fenton, making the wastewater more acceptable for biological treatment. At first, after a  $t_{30W}$  of 15 min of contact with the winery wastewater, *Vibrio fischeri* showed 48% inhibition, but at  $t_{30W}$  of 25 min, the percentage of inhibition decreased to 44%, although afterward toxicity increased again to 82%. This small reduction in toxicity from 48 to 44% is probably due to some experimental error, since afterward it increases significantly. This can be explained by the higher total polyphenol content, making the wastewater more toxic. Afterward, as photo-Fenton progressed, toxicity dropped to 28% when COD when COD and total polyphenol content were reduced 98 and 92%, respectively.

As final remarks, this study shows that heterogeneous photocatalysis (TiO<sub>2</sub>, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) of simulated winery wastewater is inefficient in removing TOC, with best performance of only 25% TOC degradation. Homogeneous photocatalysis with solar photo-Fenton in the CPC reactor showed a TOC removal efficiency of 46% with simulated wine (WV) wastewater and 93% with grape juice (WG) in a  $t_{30W}$  of 400 min. However TOC removal was 90% in a 50:50 WV and WG mixture after a  $t_{30W}$  of 150 min.

If ethanol is previously removed from the winery wastewater mixture (WW) by air stripping, TOC degradation is 96% for a  $t_{30W}$  of 130 min. In addition to this high TOC degradation, toxicity also decreases significantly from 48% to 28%, which is related to the polyphenol content reduction by 92%. So, solar photo-Fenton may be considered an efficient treatment for winery wastewater treatment, if air stripping is previously applied to remove ethanol.

### ACKNOWLEDGMENT

The authors wish to thank Mrs. Deborah Fuldauer for English language correction.

## LITERATURE CITED

- Petruccioli, M.; Duarte, J. C.; Federici, F. High rate aerobic treatment of winery wastewater using bioreactors with free and immobilized activated sludge. J. Biosci. Bioeng. 2000, 90, 381–386.
- (2) Malandra, L.; Wolfaardt, G.; Zietsman, A.; Viljoen-Bloom, M. Microbiology of a biological contactor for winery wastewater treatment. *Water Res.* 2003, 37, 4125–4134.
- (3) Beck, C.; Prades, G.; Sadowski, A.-G. Activated sludge wastewater treatment plants optimization to face pollution overloads during grape harvest periods. *Water Sci. Technol.* 2005, *51*, 81–88.
- (4) Di Berardino, S.; Caetano, L.; Converti, A. Characterization and anaerobic pretreatment of the effluent from a wine cooperative. *Eng. Life Sci.* 2001, *3*, 127–131.
- (5) Brito, A. G.; Peixoto, J.; Oliveira, J. M.; Oliveira J. A.; Costa, C.; Nogueira, R.; Rodrigues, A. Brewery and winery wastewater treatment: some focal points of design and operation in utilization of by-products and treatment of waste in the food industry; Springer US: 2007; pp 109–131.
- (6) Benitez, F. J.; Beltran-Heredia, J.; Real, F. J.; Gonzalez, T. Aerobic and anaerobic purification of wine distillery wastewater in batch reactors. *Chem. Eng. Technol.* **1999**, *22*, 165–172.
- (7) Gernjak, W.; Krutzler, T.; Glaser, A.; Malato, S.; Cáceres, J.; Bauer, R.; Fernández-Alba, A. R. Photo-Fenton treatment of water containing natural phenolic pollutants. *Chemosphere* 2003, 50, 71–78.
- (8) Lucas, M. S.; Peres, J. A.; Lan, Y. B.; Li Puma, G. Ozonation kinetics of winery wastewater in a pilot-scale bubble column reactor. *Water Res.* 2009, 43, 1523–1532.

- (9) Kuo, W. G. Decolorizing dye wastewater with Fenton's reagent. Water Res. 1992, 26, 881–886.
- (10) Nogueira, R. F. P.; Silva, M. R. A.; Trovó, A. G. Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds. *Sol. Energy* **2005**, *79*, 384–392.
- (11) Chen, R.; Pignatello, J. Role of quinone intermediates as electron shuttles in Fenton oxidations of aromatic compounds. *Environ. Sci. Technol.* 1997, 31, 2399–2406.
- (12) Feng, J.; Hu, X.; Yue, P. L.; Zhu, H. Y.; Lu, G. Q. Discoloration and mineralization of Reactive Red HE-3B by heterogeneous photo-Fenton reaction. *Water Res.* 2003, *37*, 3776–3784.
- (13) Muruganandham, M.; Swaminathan, M. Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. *Dyes Pigm.* 2004, 63, 315–321.
- (14) Pirkanniemi, K.; Sillanpää, M. Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere* 2002, 48, 1047–1060.
- (15) Bahnemann, D. Photocatalytic water treatment: solar energy applications. Sol. Energy 2004, 77, 445–459.
- (16) Mosteo, R.; Ormad, P.; Mozas, E.; Sarasa, J.; Ovelleiro, J. L. Factorial experimental design of winery wastewaters treatment by heterogeneous photo-Fenton process. *Water Res.* 2006, 40, 1561– 1568.
- (17) Ormad, M. P.; Mosteo, R.; Ibarz, C.; Ovelleiro, José L. Multivariate approach to the photo-Fenton process applied to the degradation of winery wastewaters. *Appl. Catal. B: Environ.* **2006**, *66*, 58–63.
- (18) Mosteo, R.; Sarasa, J.; Ormad, M. P.; Ovelleiro, J. L. Sequential solar photo-Fenton-biological system for the treatment of winery wastewaters. J. Agric. Food Chem. 2008, 56, 7333–7338.
- (19) Nogueira, R. F. P.; Oliveira, M. C.; Paterlini, W. C. Simple and fast spectrophotometric determination of H<sub>2</sub>O<sub>2</sub> in photo-Fenton reactions using metavanadate. *Talanta* **2005**, *66*, 86–91.
- (20) Singleton, V. L.; Rossi, J. A. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* 1965, *16*, 144–158.
- (21) Kositzi, M.; Poulios, I.; Malato, S.; Cáceres, J.; Campos, A. Solar photocatalytic treatment of synthetic municipal wastewater. *Water Res.* 2004, *38*, 1147–1154.
- (22) Rodríguez, E.; Márquez, G.; Carpintero, J. C.; Beltrán, F. J.; Álvarez, P. Sequential use of bentonites and solar photocatalysis to treat winery wastewater. J. Agric. Food Chem. 2008, 56, 11956– 11961.
- (23) Malik, P. K.; Saha, S. K. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Sep. Purif. Technol.* 2003, *31*, 241–250.
- (24) Colin, T.; Bories, A.; Sire, Y.; Perrin, R. Treatment and valorisation of winery wastewater by a new biophysical process (ECCF<sup>®</sup>). *Water Sci. Technol.* 2005, *51*, 99–106.
- (25) Nimlos, M. R.; Wolfrum, E. J.; Brewer, M. L.; Fennell, J. A. Gas phase heterogeneous photocatalytic oxidation of ethanol: pathways and kinetic modelling. *Environ. Sci. Technol.* **1996**, *30*, 3102– 3110.
- (26) La Torre, G.; L., Saitta, M.; Vilasi, F.; Pellicano, T.; Dugo, G. Direct determination of phenolic compounds in Sicilian wines by liquid chromatography with PDA and MS detection. *Food Chem.* 2006, 94, 640–650.
- (27) Silva, M. N. B. S.; Coelho, A. V.; Vilas, L.; Bronze, M. R. Analysis of phenolic compounds in Muscatel wines produced in Portugal. *Anal. Chim. Acta* 2006, *563*, 84–92.
- (28) Lucas, M. S.; Dias, A. A.; Bezerra, R. M.; Peres, J. A. Gallic acid photochemical oxidation as a model compound of winery wastewaters. J. Environ. Sci. Health, Part A 2008, 43, 1288– 1295.

Received for review July 25, 2009. Revised manuscript received October 22, 2009. Accepted October 22, 2009. M.S.L. thanks the Fundação para a Ciência e a Tecnologia and Águas de Trás-os-Montes e Alto Douro for his Ph.D. grant (BDE/15576/2005). The authors thank the "Programa de Acceso y Mejora de Grandes Instalaciones Científicas Españolas" (Plataforma Solar de Almería, GIC-05-17).