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Sequential Solar Photo-Fenton-Biological System for the Treatment of Winery Wastewaters

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In this study, winery wastewaters are considered for degradation using heterogeneous photo-Fenton as a preliminary step before biotreatment. The heterogeneous photo-Fenton process assisted by solar light is able to partially degrade the organic matter present in winery wastewaters. When an initial hydrogen peroxide concentration of 0.1 M is used over 24 h of treatment, a degradation yield of organic matter (measured as TOC) of around 50% is reached. The later treatment (activated sludge process) allows the elimination of 90% of the initial TOC present in pretreated winery wastewaters without producing nondesired side-effects, such as the bulking phenomenon, which is usually detected when this treatment is used alone. The final effluent contains a concentration of organic matter (measured as COD) of 128 mg O_2/L. The coupled system comprising the heterogeneous photo-Fenton process and biological treatment based on activated sludge in simple stage is a real alternative for the treatment of winery wastewater.

KEYWORDS: Winery wastewaters; sequential system; solar photo-Fenton; biological treatment

INTRODUCTION

Winery wastewaters are generated during the different activities carried out for wine elaboration, mainly originating from washing and rinsing operations of fermentation tanks, barrels, and other items. The treatment of this type of effluent by means of biological options presents some difficulties due to the high organic substance concentrations (3000−15000 mg O_2/L, measured as COD) and their load fluctuations (*1*).

In recent years, the winery sector has faced increasing pressure in order to fulfill legal environmental requirements while maintaining a competitive position in the global market. Aragón is one of the most important wine-producing regions in Spain. A typical vineyard usually produces about 17 300 tons of grapes per year. The winery industry located in the Aragón region must conform to Decree 38/2004, BOA n°30, March 10th 2004 (*2*) relating to the discharge of wastewater in collection systems, in accordance with European Council Directive 91/271/EEC (*3*). To this end, wineries must install their own wastewater treatment plants in order to observe the maximum contamination level limits and to ensure the correct operation of the collecting systems and urban wastewater treatment plants.

Because of the high biodegradability of winery wastewaters, some medium-scale wineries are equipped with aerobic biological treatments. However, the majority of them operate unsatisfactorily because of their seasonal variability, composition, and high organic matter concentration. The biological process by activated sludge, based on the growth of a microbial population in the form of flocs, is generally the most appropriate because of its low costs and simplicity, reproducing and accelerating the natural process. However, its effectiveness is closely related to the quality of the separation of sludge in the secondary settling tank (*4*).

Previous studies carried out by our research group (*5*) with the same wastewater show that when the activated sludge process is directly fed with winery wastewaters containing a concentration of organic matter higher than 1500 mg O_2/L (organic loads higher than 9.37 kg O_2/(m^3 d)), the proliferation of filamentous bacteria appears in a few hours. This growth produces undesirable side effects such as foams and bulking phenomena, which interfere with the treatment efficiency. A previous stage to the biological process is required in order to decrease the content of organic matter in winery wastewaters.

A possible alternative could be the application of advanced oxidation processes (AOPs) as pretreatment in order to produce the partial degradation of organic matter and decrease the concentration of inhibitor compounds in aerobic biological treatments, such as polyphenol compounds (*6, 7*).

Advanced oxidation processes (AOPs) are based on the in situ generation of highly potent chemical oxidants such as the hydroxyl radical ($OH^{\bullet}$), a powerful nonselective chemical oxidant, which has a strong oxidation potential and acts very rapidly with most organic compounds. They offer a particularly useful alternative for the treatment of effluents with high organic matter content.

Many systems are classified under the broad definition of AOPs. Among them, Fenton, photo-Fenton, photocatalysis, ozonation, and wet oxidation can be mentioned. Most of the AOPs use a combination of strong oxidants (e.g., O_3 and H_2O_2)

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Table 1. Main Features of Real Winery Wastewaters

pH	COD (mg O_2/L)	BOD5/COD	TOC (mg C/L)	tartaric acid (g/L)	malic acid (mg/L)	polyphenols (mg gallic acid/L)	ethanol (g/L)	glucose + fructose (g/L)
3.5	3300	0.45	969	1.21	10	99	1.2	0.1

with catalysts (e.g., transition metal ions or photocatalysis) and irradiation (e.g., ultraviolet or visible). The Fenton process involves the reaction of ferrous ions (catalyst) and hydrogen peroxide (oxidizing agent) to form the active hydroxyl radicals (Fenton process). The Fenton reaction is markedly accelerated by light so the photo-Fenton reaction typically gives faster rates and a higher degree of mineralization (*8*). Furthermore, the photo-Fenton reaction can be driven with low energy photons in the visible part of the spectrum. Thus, photo-Fenton processes are potential low cost AOPs that can be achieved under solar irradiation (*9*).

Previous studies carried out by our research group (*10–12*) show that heterogeneous and homogeneous photo-Fenton processes, using radiation sources such as a Xenon lamp, which simulates the solar radiation, are appropriate treatments for winery wastewaters.

In addition, in a previous study the homogeneous and heterogeneous photo-Fenton processes of winery wastewaters were also compared as a preliminary step to a biological treatment (*13*). The degradation of organic matter was higher for homogeneous process, although a concentration of 250 mg/L iron was required. In this case, the remaining iron concentration is excessive for microorganism activity and would require the precipitation and separation of iron. For this reason, the heterogeneous process was selected as more appropriate in this study. The use of heterogeneous Fenton catalyst avoids the necessity of a separation step.

The development of supported Fenton catalysts has recently become important in the emerging field of advanced oxidation technologies (*14–17*).

The photo-Fenton processes activated by sunlight could decrease the cost of the treatment, providing an advantage for industrial applications. Moreover, several authors have reported the use of natural sunlight as radiation source in photocatalytic processes (*9, 18*).

Previous studies have attempted the strategy of combining chemical and biological processes to treat contaminants in wastewaters. These studies, extensively reviewed by Mantzavinos and Psillakis (*19*), suggest potential advantages of this strategy for water treatment (*20*).

The aim of this report therefore is to study the degradation of winery wastewaters by a heterogeneous solar assisted photo-Fenton process and activated sludge treatment combined system. Furthermore, it examines the influence of different factors such as the methodology of hydrogen peroxide addition and the use of natural solar light (with better illumination and dark periods) on the evolution of the degradation of organic matter during the heterogeneous solar assisted photo-Fenton process.

MATERIALS AND METHODS

Materials. The winery wastewaters used in this study came from a typical winery industry located in the Aragón region of Spain. **Table 1** summarizes the main features of these winery wastewaters, which have low pH, high biodegradability, and a high concentration of organic matter, mainly composed of organic acids, ethanol, glucose, fructose, and polyphenols.

The heterogeneous Fenton catalyst used in this research work, developed by our research group, consists of clay, commercial iron salt (5 wt. % in water, Scharlau), and colloidal silica (30%, wt. % suspension in water, Ludox SM-30). The solid material used as initial support of the heterogeneous catalyst is clay supplied by SAMCA S.A. This clay has a surface area of 20.5 m^2/g and contains different amounts of metals (Fe 4.6 wt %, Al 12.4 wt %, Ti 0.4 wt %, etc.). In order to condition the catalyst, the following procedure is used (*21*): (1) Clays are impregnated with an aqueous solution composed of colloidal silica and Fe_2Cl_3. It was previously checked that the addition of iron to the natural clay improved the efficiency of the catalyst (*5*). (2) The catalyst is dried at room temperature and calcined at 500 °C during 3 h. (3) The catalyst is rinsed with boiling water and dried in air at room temperature.

The heterogeneous Fenton catalyst and the initial clay used as support were characterized using scanning electron microscopy (SEM), surface area and pore measurements (BET) as well as Fourier transform infrared spectroscopy (FTIR). The main features of the Fenton catalyst are the following: (1) The BET area reaches a value of 52 m^2/g. (2) When the infrared spectra of initial clay and heterogeneous Fenton catalyst are compared, it is observed that, for heterogeneous Fenton catalyst, two bands at 973 and 800 cm^{-1} appear. These probably originate from $Fe_n(OH)_n$ and Fe_nO_n compounds (*22*). On the other hand, the bands found close to 600 cm^{-1} are related to vibrations of bond Fe−O (*23*). (3) The quantitative microanalysis achieved by SEM shows that the heterogeneous Fenton catalyst contains 10% wt of Fe.

Analytical Methodology. The amount of organic matter is quantified by means of two different parameters: total organic carbon (TOC) and chemical oxygen demand (COD). TOC is determined using a TOC-VCSH Shimazdu analyzer, and COD is measured by the open reflux method, method 5520B (*24*). H_2O_2 in solution is controlled during and after the treatment using a Merck peroxide test (O_2^{2-}) (0−25 mg H_2O_2/L and 0−100 mg H_2O_2/L). The pH is tested with a pH meter (Crison 507). Biochemical oxygen demand (BOD_5) is measured during 5 days using an Hg free WTW 2000 Oxitop unit thermostatted at 20 °C. Experiments are carried out according to the 5210D standard method (*24*). Ethanol is determined by gas chromatography with a FID detector HP5890. The total polyphenolic content is measured by UV−vis spectrophotometry at 765 nm by the Folin−Ciocalteau method, using gallic acid (mg GAE/L) as standard (*25*). Tartaric acid is measured at 505 nm by the Metavanadate method (*26*). Malic acid, glucose, and fructose are measured at 340 nm by enzymatic methods (*26*). The spectrophotometer used is a Thermo Spectronic Helios α. Iron in solution is analyzed by induced coupled plasma by method 3111B (*24*). The total Kjeldahl nitrogen is measured by method 4500-N (*24*) and the total phosphorus by method 4500-P (*24*). Volatile suspended solids (VSS) are measured by method 2540 (*24*). Sludge volume index (SVI), sludge settling rate (SSR), and oxygen uptake rate (OUR) are measured according to methods 2710D, 2710E, and 2710B (*24*). The microorganisms were viewed on optical microscope (Axiostar Plus Zeiss) using fresh preparations.

Experimental Procedure. *Heterogeneous Photo-Fenton Process.* Experiments were performed during sunny days in June at the University of Zaragoza (Spain) located at 247 m above sea level, 41°39′N, 1°00′29E, using natural solar light as the radiation source. In Zaragoza (Spain), the mean daily global irradiation is close to 4500 Wh/m^2, and the mean total sunshine duration is about 3200 h/year (*27*).

The reaction system consisted of an open Pyrex vessel of 10 L (length (cm) × width (cm) × depth (cm) = 40 × 15 × 15) with a stirring system. A bed of heterogeneous Fenton catalyst (31 g catalyst/L wastewater) was placed inside the reactor and filled with 5 L of winery wastewaters. The addition of hydrogen peroxide (30% (v/v), Carlo Erba) was carried out by two different methodologies: (1) One addition of 0.1 M H_2O_2 at initial time. (2) Three additions of 0.03 M H_2O_2 at different times.

The concentrations of both hydrogen peroxide and Fenton catalyst were chosen taking into account a previous and detailed study of the heterogeneous photo-Fenton process applied to the treatment of winery wastewaters using as radiation source a Xenon lamp (*11*).

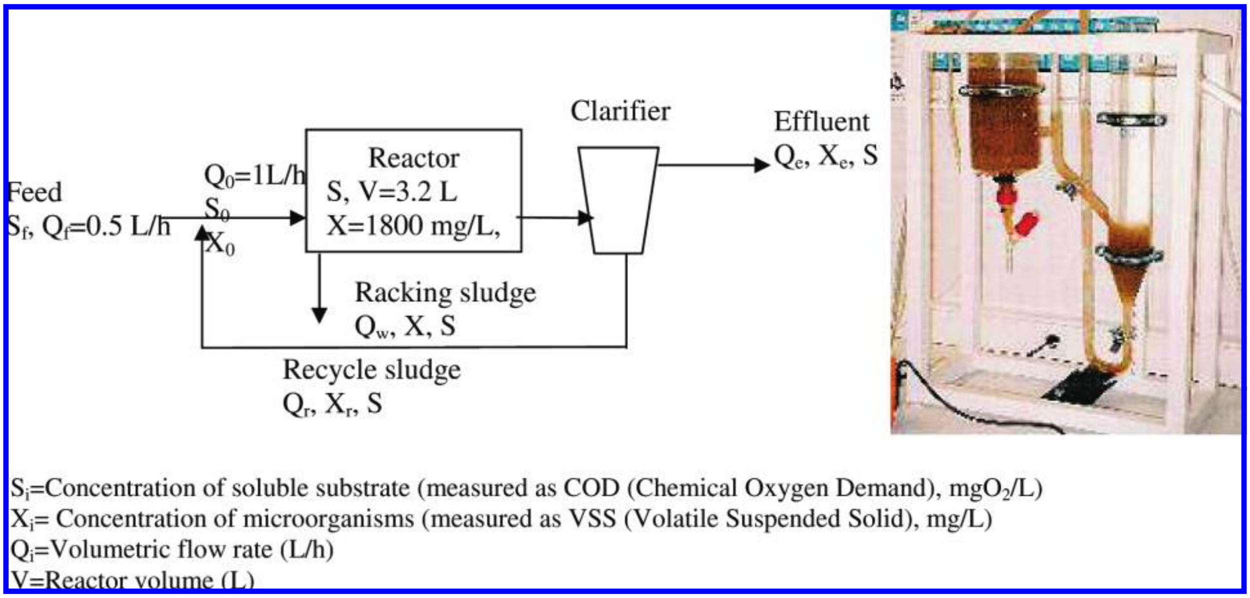

Figure 1. Diagram and picture of the activated sludge laboratory-scale plant.

The aqueous solutions were magnetically stirred in order to have a completely mixed reactor. The temperature in the reactor during these experiments increased up to 30 °C.

All experiments were performed in duplicate. In order to consider possible interferences, a control experiment was also performed without the addition of hydrogen peroxide and Fenton catalyst (Fenton reagents) to know the possible photolysis of the winery wastewaters and to quantify possible losses of organic matter by volatilisation.

Measurements of total organic carbon, presence of hydrogen peroxide, pH, and concentration of polyphenols were carried out in order to follow the evolution of the solar assisted heterogeneous photo-Fenton process. The duration of the experiments depended on the results of organic matter degradation taking into account the operational range of our biological process based on activated sludge (*5*).

Biological Treatment Based on Activated Sludge Process. The aerobic degradation process was conducted by means of a conventional activated sludge system, comprising an aeration reactor (completely mixed, 3.2 L) and a clarifier (2.2 L). Diffusers were installed in the aeration tank for providing both the necessary dissolved oxygen for the degradation process and mixing. **Figure 1** shows the schematic representation and the picture of the activated sludge pilot-scale plant, which is located in the laboratory of Environmental Technologies at the University of Zaragoza (Spain). The temperature was fixed at 25 °C by means of a thermostatic unit.

As winery wastewaters do not contain the required microorganisms for aerobic degradation, an activated sludge was taken from a municipal wastewater treatment plant as a source of microorganisms. They were previously acclimatized to this substrate, using diluted phototreated solutions as a feed, during a period of 30 days. Several laboratory-scale biological experiments were carried out in continuous flow and completely mixed reactor after the acclimatization period using as feed the phototreated winery wastewaters. These phototreated effluents were obtained taking into account the operational conditions selected because of the results related to photo-Fenton experiments.

The winery wastewaters showed a low content of nutrients (phosphorus: 0.7 mg/L; nitrogen: 14 mg/L), which has already been demonstrated by other authors (*28*). For an activated sludge process, a suitable ratio must be considered of the influent degradable matter expressed as ultimate BOD or COD to nitrogen and phosphorus. It should be (on a mass basis) COD/N/P = 100:5:1 (*29*). Additions of urea and phosphate salt are needed to guarantee the process of cellular synthesis.

As is indicated in **Figure 1**, the biomass concentration in the reactor was fixed at 1800 mg/L (measured as volatile suspended solids, VSS). The selected volumetric flow rate of the influent (Q_f) and the combined feed (Q_0) were 0.5 and 1 L/h, respectively.

RESULTS AND DISCUSSION

Oxidation of Winery Wastewaters by Heterogeneous Photo-Fenton Process. A study was carried out to know the application of the heterogeneous photo-Fenton process assisted by natural solar light. **Figure 2** shows the yield of degradation of organic matter, defined as: $Y = [(TOC_0 - TOC_f)/TOC_0) \times 100]$, where TOC_f = TOC in the sample after treatment and TOC_0 = initial value of TOC in the sample. The profiles of this parameter versus time for the photo-Fenton experiment and the control experiment are represented in this figure. In order to know the influence of the methodology of hydrogen peroxide addition, the profile of the degradation yield of organic matter (defined as *Y*) for the photo-Fenton treatment with stepwise addition is represented in **Figure 2**, as well. The presence of hydrogen peroxide was regularly checked in solution. In the case of the experiment with stepwise addition of H_2O_2, the addition of this reactive took place at initial time and at any time that H_2O_2 was not detected. The photo-Fenton and control experiments started at 1.00 p.m.

The results obtained show the following considerations: (1) During the control experiment, there was no decrease in organic matter concentration, verifying that the photolysis of winery wastewaters was not detected thus discounting any possible photochemical effect associated with the organic matter content in this effluent alone. Furthermore, the reaction system used to carry out the photo-Fenton process did not produce any loss by volatilisation. (2) During the heterogeneous photo-Fenton process, the dissolution of the iron present in the heterogeneous catalyst reached a concentration in solution of 7 mg/L. The homogeneous process can be considered negligible, since a previous study (*12*) showed that the yield of organic matter degradation for winery wastewaters was 3% when the iron concentration in solution was 5 mg/L. (3) The evolution of the degradation process depends on the solar radiation. During the night or period without illumination, the "dark period" (reaction time: 6 h−19 h), a slight degradation was produced. On the other hand, during the period of better illumination, the degradation of organic matter was higher. After 24 h of treatment, a final concentration of organic matter of 324 mg C/L (measured as TOC) and 986 mg O_2/L (measured as COD) was reached in the case of the photo-Fenton experiment with one addition of hydrogen peroxide at initial time. The degrada-

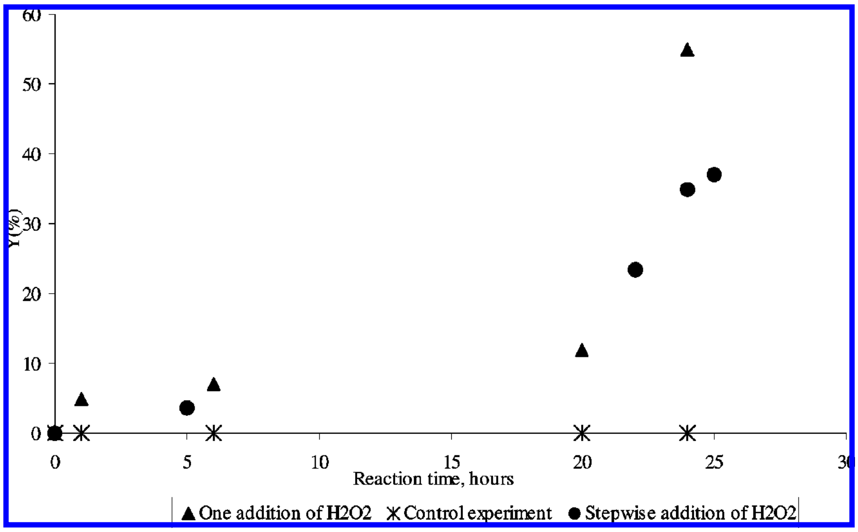

Figure 2. Evolution of the degradation yield of organic matter (*Y* parameter) versus time for the control experiment and for the heterogeneous photo-Fenton processes with one addition of hydrogen peroxide at initial time and stepwise addition. Experimental conditions: initial time, 1.00 p.m.; 31 g/L catalyst; one addition of 0.1 M H_2O_2 at initial time or three additions of 0.03 M H_2O_2 at different times.

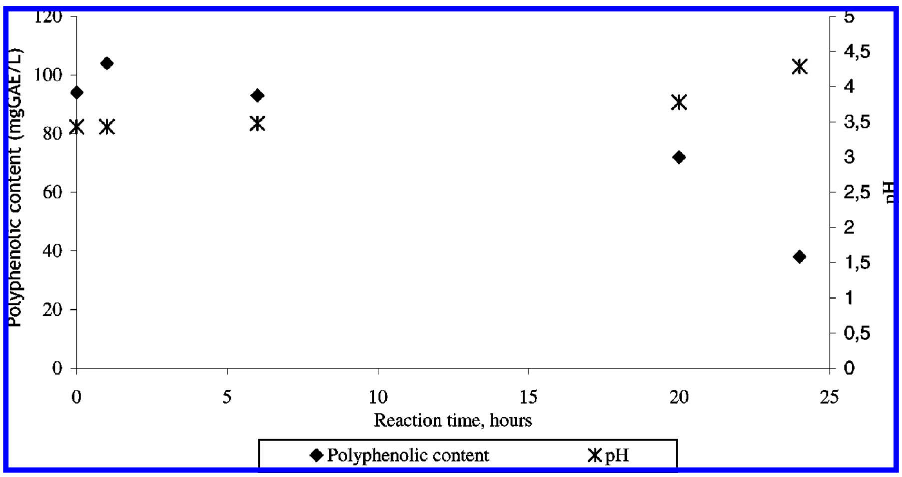

Figure 3. Evolution of the pH and polyphenolic content during the photo-Fenton process with one addition of hydrogen peroxide at initial time. Experimental conditions: initial time, 1.00 p.m.; 31 g/L catalyst.

tion yield of organic matter (measured as TOC) was about 55%. Therefore, using sunlight during the photo-Fenton process is a technique capable of decreasing the concentration of organic matter present in winery wastewaters to a stage where the organic matter contents can be treated by the activated sludge process, as indicated in the Introduction section (*5*). (4) The difference between degradation yields for better illumination periods is due to the fact that organic compounds are turned into smaller molecules during the first better illumination period; therefore, in the majority of cases, the mineralization of organic matter is easier during the second better illumination period. (5) During the photo-Fenton experiment with one addition of hydrogen peroxide at initial time, analyses of this reagent showed that H_2O_2 was always in solution, and the final concentration was in the range 10−25 mg H_2O_2/L. The total consumption of hydrogen peroxide was around 99%. In the case of the experiment with stepwise addition of H_2O_2, the measurements of H_2O_2 concentration at 20 and 24 h indicated that this reactive was in solution. Hydrogen peroxide analyses indicated that there was no reactive in solutions at 22 and 25 h, therefore new additions of H_2O_2 were carried out at those moments. (6) Kosaka (*31*) showed that the stepwise addition of hydrogen peroxide during advanced oxidation processes can be more efficient than the use of one hydrogen peroxide addition at initial time. However, a direct addition of the oxidant is more effective for long reaction times, as it can be observed in **Figure 2**. This is due to the fact that there is always sufficient organic matter present in solution and there is no inefficient hydrogen peroxide use.

The evolution of the pH and polyphenolic content during the photo-Fenton process with one addition of hydrogen peroxide at initial time is reflected in **Figure 3**. The polyphenols compounds have inhibitor characteristics toward aerobic biological processes, so it is considered of interest to know the behavior of these compounds during the photo-Fenton process. The experiments started at 1.00 p.m., with direct solar radiation on the reactor.

The results obtained show the following considerations: (1) The amount of polyphenols increases at the beginning of the treatment. This is due to the hydroxylation of the aromatic rings. Further oxidation opens the rings. Aerobic biological treatments are able to treat effluents with a polyphenolic content of 50−100 mg GAE/L (*30*), and in this photocatalytic experiment, polyphenols have been reduced down to 40 mg GAE/L. (2) The pH analyses indicated that the evolution of this parameter during photo-Fenton experiments is not significant, since the initial and final pHs were 3.5 and 4.1, respectively. The evolution of the

Table 2. Average Values Obtained for Each Control Parameter for the Biological Treatment[a]

S_f (mg O_2/L)	S_0 (mg O_2/L)	S_e (mg O_2/L)	X (mg/L)
995	561	128	1800
OUR (mg/(L · min))	SSR (m/h)	SVI (mL/g)	X_e (mg/L)
6	1.58	109	73

[a] Sludge volume index (SVI), sludge settling rate (SSR), oxygen uptake rate (OUR), concentrations of soluble substrate (S_i) (measured as COD), concentration of microorganisms (X_i).

pH during the treatment shows a slight increase mainly due to the degradation of the different acids present in winery wastewaters (tartaric acid, malic acid, etc.) in intermediate compounds.

Degradation of Pretreated Winery Wastewaters by Activated Sludge Process. Aerobic degradation experiments of winery wastewaters, pretreated by the heterogeneous photo-Fenton process, were performed in the activated sludge pilot-scale plant described in the section Experimental Procedure. Once the steady state was achieved, parameters such as chemical oxygen demand (COD), oxygen uptake rate (OUR), sludge volume index (SVI), and so forth were measured during three weeks in order to study the behavior of this aerobic biological treatment. The phototreated effluents used as feed presented concentrations of organic matter in the range 826−1200 mg O_2/L (measured as COD). Summarizing, the pretreated winery wastewaters contain an average concentration of organic matter of 320 mg C/L (measured as TOC) and 1000 mg O_2/L (measured as COD), amounts which can be assimilated by the microorganisms present in the biological reactor. As indicated previously, the performance of the simple stage activated sludge process is adequate for the feeding of winery wastewaters containing a concentration of organic matter lower than 1500 mg O_2/L (organic loads higher than 9.37 kg $O_2/(m^3$ d)) (*5*). Moreover, previous studies carried out in our research group show that the byproduct generated during this heterogeneous process is not toxic for the microorganisms.

The average values obtained for each control parameter are shown in **Table 2**. The parameters sludge volume index (SVI) and settling velocity reached average values of 109 mL/g and 1.58 m/h, respectively. The oxygen uptake rate was 6 mg/(L min). Furthermore, the concentration of volatile suspended solids in the clarified effluent was 73 mg/L, a lower value than the maximum contamination level limit specified in Decree 38/2004m BOA n°30, March 10^{th} 2004 (*2*).

A yield of degradation of organic matter of around 90% (measured as TOC) was achieved by activated sludge treatment, and the final effluent presented an average organic matter concentration (measured as COD) of 128 mg O_2/L (**Table 2**). In accordance with Decree 38/2004, BOA n°30, March 10^{th} 2004 (*2*) of Aragón, the winery wastewaters treated by heterogeneous solar assisted photo-Fenton process and activated sludge treatment can be discharged into the wastewaters collecting system.

Microbiological analyses showed a balance between the different types of microorganisms detected in the biological reactor (bacterium, protozoes, filamentous microorganisms, etc.) producing a correct flocculation and a good settleability of sludge. During this biological experiment, the settleability and compactibility of sludge were very good. Neither bulking nor foaming phenomena appeared during the experimentation. These operational problems are very usual when the activated sludge process is applied to the treatment of winery wastewaters (*1*).

Summarizing, as a consequence of the results obtained during this research work, the coupled system composed of the heterogeneous photo-Fenton process and biological treatment based on the activated sludge process can be seen as a real alternative for the treatment of winery wastewaters due mainly to the following: (1) Real winery wastewaters are partially degraded by the solar assisted heterogeneous photo-Fenton process (24 h, $[H_2O_2] = 0.1$ M, 31 g catalyst/L). The organic matter concentration in the pretreated effluent was sufficiently low, close to 1000 mg O_2/L, to enable it to be treated by the biological process. Yields of degradation of organic matter (measured as TOC) of 50−60% are achieved. Furthermore, the evolution of the degradation of organic matter depends on the solar radiation. (2) The activated sludge treatment, using as feed phototreated winery wastewaters, operates correctly. The microbial population detected in the reactor is adequate for the degradation of organic matter present in wastewaters. The yield of degradation of organic matter obtained by this biological process is close to 90% (measured as TOC). The sludge settleability is good, since average values of VSZ = 1.58 m/h and SVI = 109 mL/g are obtained. (3) The total yield of organic matter degradation by the combined heterogeneous photo-Fenton process and activated sludge system is 96% (measured as COD). The final effluent contains a concentration of organic matter of 128 mg O_2/L (measured as COD), which is lower than the maximum allowed limit (1000 mg O_2/L) indicated in the Decree 38/2004 relative to the discharge of wastewaters in collection systems.

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