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Response to Reviewers: ANSWER TO REVIEWERS'S COMMENTS:

Reviewer #1:

This paper is very interesting and relevant to the scientific community that has developed researches about environmental problems. This paper gives scientific information to the readers and some recent research topics that are being carried out. It is well written and has scientific and technological relevance.

I recommend this paper for publication in Chemical Engineering Journal. My feeling is that it is a good paper. I didn't make many comments, just a few comments.

Page 3 - line 8: Merk to be changed to Merck

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Page ten: line 7- 12 -Is it that the Cl⁻ ions and SO₄²⁻ ions inhibit the Fenton process

Cork boiling wastewater treatment at pilot plant scale: comparison of solar photo-Fenton and ozone (O₃, O₃/H₂O₂). Toxicity and biodegradability assessment

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Abstract

Remediation of cork boiling wastewater was studied as an example of complex industrial wastewater treatment by applying a protocol based on a combination of advanced technologies and chemical-biological assays. Solar photo-Fenton and ozone (alone or in combination with hydrogen peroxide at different pH conditions), at pilot plant scale have been used as chemical oxidation step. Additionally, the effect of a physic-chemical pre-treatment using different flocculants (FeSO₄ and FeCl₃) was evaluated. Although physic-chemical pre-treatment with Fe³⁺ provided good removals of COD, DOC and TSS, it was found that it did not enhance solar photo-Fenton post-treatment. On the contrary, ozone-based process was improved after physic-chemical pre-treatment with Fe³⁺, attaining higher degradation efficiencies with lower ozone consumptions for the combination O₃/initial pH 7. Toxicity and biodegradability assays were performed to evaluate possible variations along the oxidation processes. After solar photo-Fenton treatment, toxicity and biodegradability remained constant at their initial values. Then, Zahn-Wellens test was carried out to study long term biodegradability and possible biomass adaptation to the partially photo-treated effluent. Decrease in toxicity values and short term biodegradability enhancement were observed for cork boiling wastewater treated by ozonation systems.

Keywords: Biodegradability, cork boiling wastewater, industrial wastewater, ozonation, solar photo-Fenton.

1. Introduction

Industrial wastewater's characteristics depend on the industry where it is generated and with process variations. This implies that industrial wastewater treatment is a complex problem due to the wide variety of compounds it may contain as well as their concentration. Thus, selection of the best treatment option for remediation of a specific industrial wastewater is a highly complicated task provided that the choice of one or more processes to be combined in a certain situation depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost.

In general, the possibilities and capabilities of the conventional treatments available are widely known. However, information on the efficiency of the new technologies (Advanced Oxidation Processes, AOPs) for eliminating certain specific pollutants present in wastewater compared to conventional options is necessary. For this reason, bench-scale and pilot-plant studies are required to develop the technologies and generate information on new industrial wastewater treatment processes. Such scaled studies are even more decisive when combining several technologies for decontamination or reuse of a specific industrial wastewater [1].

A perfect example of the challenge on the treatment and reuse of a complex industrial wastewater is cork boiling wastewater. Cork processing includes a stage in which slabs are immersed in boiling water during one hour in order to improve their physic-chemical characteristics. In addition, the same water is normally used for several boiling cycles, and so it concentrates in persistent compounds. As a consequence, the resulting wastewater contains undesirable corkwood extracts (phenolic acids, tannic fraction, 2,4,6-trichloroanisol, pentachlorofenol, ~~etc.~~) which are not easily removed by conventional treatments. Therefore, this wastewater cannot be discharged into public water courses [2]. Despite of their characteristics, these effluents are usually released directly without any previous treatment in the environment or in municipal wastewater treatment plants (MWTP), involving active sludge low efficiencies, along with real environmental impacts to superficial and underground aquatic/soil systems. Furthermore, great volumes of wastewater are generated during cork boiling processes (about 400 L of wastewater per ton of raw cork) and, consequently, its treatment has some technical and economic constraints [3]. Therefore, wastewater generated during cork boiling is representative of typical industrial effluents with high contents of DOC (higher than 500 mg/L^{-1}) and COD (higher than 1000 mg/L^{-1}), with low pH, low toxicity and biorecalcitrant nature. In this sense, and taking into account that conventional biological processes cannot satisfactorily deal with this kind of wastewater due to the

presence of compounds potentially inhibitory for activated sludge, one feasible option is the use of Advanced Oxidation Processes (AOPs). These advanced technologies can degrade organic recalcitrant pollutants present in wastewater by forming hydroxyl radicals [4,5]. Some AOPs have been demonstrated to be efficient treatments for complex effluents such as those generated in the winery sector, which have similar characteristics to the cork boiling wastewaters [1]. For instance, the effectiveness of different ozone-based advanced oxidation processes (O_3 , O_3/UV and $O_3/UV/H_2O_2$) was investigated in a pilot-scale bubble column reactor, attaining significant COD and DOC removals for such specific industrial wastewater[64]; another example is winery wastewater remediation using some AOPs ($TiO_2/H_2O_2/UV$ and $Fe^{2+}/H_2O_2/UV$ and solar photo-Fenton) tested at a pilot plant equipped with an immobilized biological reactor (IBR) and a photocatalytic system with compound parabolic collectors (CPCs), which is reported to be an alternative to a conventional biological, achieving good COD eliminations- [75]. As far as we know, little researching work related to the treatment of cork boiling wastewater can be found in literature. Some reported processes are: flocculation/flotation/ultrafiltration, used as a pre-treatment [86]; oxidation using Fenton reagent [97]; integrated Fenton reagent and coagulation/-flocculation processes [108]; and photo-oxidation ($H_2O_2/UV-vis$, $H_2O_2/Fe^{2+}/UV-vis$, $TiO_2/UV-vis$ and $TiO_2/H_2O_2/UV-vis$) using a batch photo-reactor with a mercury vapor lamp emitting in the 200–600 nm range [911]. All of them were proved to be effective for COD removal and biodegradability and toxicity enhancement, although, in general, treatment's efficiency was improved when a physic-chemical pre-treatment was performed. Some other AOPs have been applied for cork boiling wastewaters remediation. For instance, ozonation with the addition of H_2O_2 and solar photo-Fenton processes have been previously studied considering the possible combination with a final conventional biological post-treatment [129, 134].

Nevertheless, it is not usual to find real application case studies dealing with a sequential approach for giving a complete solution for the treatment and reuse of a complex industrial wastewater. Then, the objective of this study is defining the best treatment line for real cork boiling wastewater remediation and reuse, emphasizing the complex chemical and biological analytical tools that should be applied to obtain reliable design data for up-scaling purposes. With this aim, the application of ozone alone (at natural and higher pH) and in combination with hydrogen peroxide, and solar photo-Fenton process at pilot plant scale have been evaluated. Additionally, this work analyses the convenience of performing a physic-chemical pre-treatment of the industrial effluent, as well as the study of toxicity and biodegradability throughout the

different oxidation processes. This approach is also intended to find the proper operating conditions to achieve sufficient biodegradability enhancement of the cork boiling wastewater for being discharged into a conventional activated sludge system, which could be installed on-site allowing its reuse in the cork processing factory.

2 Materials and methods

2.1 Cork boiling wastewater characterization. Reagents and chemicals.

Real cork boiling wastewater used in this study was collected at a cork-processing plant located in San Vicente de Alcántara (Extremadura, Spain). All tests were performed at Plataforma Solar de Almería (Tabernas, Spain). Cork boiling wastewater is dark brown liquor due to a high polyphenols concentration and other corkwood extracts. As a consequence, it presents a high turbidity value which can affect solar photo-Fenton process efficiency. Characterization was carried out following the procedures described below. Table 1 shows the values for the main characterization parameters. This sample exhibited a high organic content and a low biodegradability level (organic carbon can be considered recalcitrant and possibly inhibitory to microbial metabolism of a biological oxidation system), though it is non-toxic. High levels of potassium ions can be attributed to the boiling process.

TABLE 1

Experiments were performed using reagent-grade iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), reagent-grade hydrogen peroxide (30% w/v), sulphuric acid and sodium hydroxide (for physic-chemical pre-treatment and pH adjustment), all provided by Panreac and Merck.

2.2 Analytical determinations

Immediately after sampling and filtering through 0.2- μm [nylon](#) syringe-driven filters ([Millipore Millex®-GM](#)), dissolved organic carbon (DOC) was measured with a Shimadzu TOC-VCN analyser. Dissolved nitrogen (TN) was quantified in a TC-TOC-TN analyser coupled with a TNM-1 unit (Shimadzu, model TOC-V_{CSN}). Total iron concentration was determined using the 1,10-phenanthroline method following ISO 6332, and hydrogen peroxide was measured using titanium (IV) oxysulfate according to DIN 38402H15. Anions concentrations (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) were determined with a Dionex DX-600 ion chromatograph system using a Dionex Ionpac AS11-HC

4×250-mm column. The gradient program for anion determination was pre-run for 5 min with 20 mM NaOH, an 8-min injection of 20 mM of NaOH, and 7 min with 35 mM of NaOH, at a flow rate of 1.5 mL_{min}⁻¹. Cations concentrations (Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺) were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4-mm×250-mm column. Isocratic elution was performed with H₂SO₄ (10 mM) at a flow rate of 1.2 mL_{min}⁻¹. COD was determined using Merck Spectroquant kits (ref: 1.14541.0001). Turbidity was measured in a Hach 2100N turbidimeter. Total suspended solids (TSS) and volatile suspended solids (VSS) were quantified according to the American Standard Methods [124]. Conductivity was measured using a conductivity meter Crison GLP31.

2.3 Toxicity and Biodegradability assays

Acute toxicity and short term biodegradability assays were carried out in a BM-T Advance respirometer (Surcis S.L.), which consists of a 1_L capacity vessel, equipped with a temperature and pH control system. It also has an oxygen probe (Protos 3400, Knick Elektronische Messgeräte GmbH & Co. KG) for respirometric determination of the activated sludge activity based on the oxygen uptake rate (OUR). The ultimate biodegradability was evaluated using an adaptation of the Zahn-Wellens test EC protocol.

The activated sludge used in the bioassays came from the municipal wastewater treatment plant of El Bobar (Almería). After reception, the sludge was characterized through DOC, ammonium, nitrate and nitrite concentrations, TSS and VSS measurements. Prior to biological tests, the excess of H₂O₂ present in the samples was removed by adding catalase solution (2500 U_{mg}⁻¹ bovine liver) after adjusting the pH between 6.5 and 7.5.

For toxicity analyses, the respirometer was loaded with 1L of endogenous activated sludge. Temperature was controlled at 20° C and the system was continuously aerated and agitated. This analysis compares maximum bacterial oxygen uptake rate (OUR_{max}) in a reference with that of the target sample. The reference was 30 mL of distilled water with 0.5 g of sodium acetate_g⁻¹ VSS. Moreover, 30 mL of sample was added to obtain the OUR_{max-sample}. The inhibition percentages were calculated using (Eq. 1):

$$\text{Inhibition (\%)} = 100 \times (1 - \text{OUR}_{\text{max-sample}} / \text{OUR}_{\text{max-ref}}) \quad (\text{Eq. 1})$$

In short-term biodegradability assays, 700 mL of endogenous activated sludge were introduced in the respirometer and aerated until saturation. At that moment, 300 mL of oxygen-saturated target sample were added and the test started. The ratio COD/COD_b

(total chemical oxygen demand/easily biodegradable chemical oxygen demand) allows to assess the percentage of COD_b removed from the total COD and, thus, to establish the biodegradable character of the sample. A sample is considered to be very highly biodegradable when COD/COD_b is greater than 0.8; biodegradable, when it is comprised between 0.7 and 0.8; slightly slowly biodegradable when the ratio is 0.3-0.7, slightly biodegradable when the ratio is between 0.1-0.3 and 0.3 and non-biodegradable when it is lower than 0.13 (according to instructions given by the respirometer's manufacturer, SURCIS S.L.).

The ultimate biodegradability of raw wastewater and partially treated samples obtained at different photo-oxidation times were evaluated using an adaptation of the Zahn-Wellens test EC protocol, Directive 88/303/EEC (1992). After pH adjustment to 6.5-7.5, a volume of 240 mL of each sample was added to an open glass bottle, along with mineral nutrients (KH₂PO₄, K₂HPO₄, Na₂HPO₄, NH₄Cl, CaCl₂, MgSO₄ and FeCl₃) and the required amount of activated sludge according to each sample's DOC. Each bottle was kept in the dark, with magnetic stirring and aeration during 28 days. Diethylene glycol was used as a reference compound. Blank controls contained activated sludge, distilled water and mineral nutrients. The biodegradation percentage (D_t) was determined by Eq. (2):

$$D_t = \left(1 - \frac{C_t - C_B}{C_A - C_{BA}} \right) \cdot 100 \quad (\text{Eq. 2})$$

Where C_A and C_{BA} are the DOC values (mg C/L) in the mixture and in the blank control measured 3 hours after the beginning of the experiment; and C_t and C_B are the DOC values (mg C/L) in the mixture and in the blank control at the sampling time, respectively. The samples are considered to be biodegradable when D_t is higher than 70%.

2.4 Experimental equipment

Homogeneous photocatalysis was performed in a CPC solar collector pilot plant installed in the Plataforma Solar de Almería (PSA). The hydraulic circuit of the reactor consists of a recirculation tank, a centrifugal pump and four CPC modules with a total irradiated area of 4.16 m². The photo-reactor is equipped with a temperature control system. This pilot plant operates in batch mode, it has a total volume of 82 L (V_T) and a total illuminated volume inside the absorber tubes of 44.6 L (V_i). The four CPC

concentrator modules are mounted on a metal frame tilted 37° (latitude of the PSA) and facing the south. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same angle as the CPCs). Comparison of different photocatalytic assays under different solar conditions is possible by means of Eq. (3)

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot UV \cdot \frac{A_r}{V_T} \quad (\text{Eq. 3})$$

$$\Delta t_n = t_n - t_{n-1}$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during the period Δt_n , A_r is the illuminated area (m^2), and $Q_{UV,n}$ is the accumulated energy per unit of volume ($kJ \cdot L^{-1}$) at t_n .

The illumination time, t_{30W} , allows to combine the data from several days' experiments as well as their comparison with other photocatalytic assays [135]. It can be calculated using Eq. 4.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{UV}{30} \cdot \frac{V_i}{V_T} \quad (\text{Eq. 4})$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation ($\lambda < 400$ nm) measured between t_{n-1} and t_n , and t_{30W} is a “normalized illumination time”. In this case, time refers to a constant solar UV power of $30 \text{ W} \cdot m^{-2}$ (typical solar UV power on a perfectly sunny day around noon).

Cork boiling wastewater (after pre-treatment) was introduced into the CPC photo-reactor and homogenised in darkness by turbulent recirculation during 15 min. Then, pH was adjusted to 2.6-2.8. Afterwards, iron salt ($FeCl_3 \cdot 6H_2O$ or $FeSO_4 \cdot 7H_2O$) was added to reach an initial concentration of $20 \text{ mg iron} \cdot L^{-1}$ in solution. Finally, the first dose ($200 \text{ mg} \cdot L^{-1}$) of hydrogen peroxide was added, the CPCs were uncovered and the photo-Fenton process started. Samples were taken at pre-defined times to evaluate the degradation process. The hydrogen peroxide concentration was monitored to keep concentration around $200\text{-}300 \text{ mg} \cdot L^{-1}$ (by regular additions of $100 \text{ mg} \cdot L^{-1}$).

The ozonation system is an Anseros PAP-pilot (Anseros Klaus Nonnenmacher GmbH, Germany) for batch operation. The ozonation tank is a 10 L Pyrex cylindrical vessel with a magnetic stirrer for proper homogenisation. The system is also equipped with two non-dispersive UV analysers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone concentration. The oxygen generator supplies a maximum gas flow of $6 \text{ L} \cdot \text{min}^{-1}$

with an oxygen concentration up to 90%. Besides, ozone production can be adjusted providing a maximum concentration of $8.82 \text{ g O}_3 \text{ L}^{-1} \text{ h}^{-1}$ for a gas flow of $0.2 \text{ Nm}^3 \text{ L}^{-1} \text{ h}^{-1}$. Therefore, inlet ozone concentration average was around $36 \text{ g O}_3 \text{ m}^{-3}$ in all the experiments, while ozone outlet concentration average changed from $18 \text{ g O}_3 \text{ m}^{-3}$ at the beginning of the degradation process, to around $30 \text{ g O}_3 \text{ m}^{-3}$ when the system attained saturated conditions. A thermic ozone destructor has been coupled to the reactor exhaust in order to avoid its release to the atmosphere. In those experiments in which ozonation was tested with the addition of H_2O_2 , three doses of 200 mg L^{-1} were added in each one, as this reagent was consumed during the reaction.

3 Results and discussion

3.1 Physic-chemical pre-treatment

In general, physic-chemical pre-treatment aimed to stabilize industrial wastewater, to eliminate suspended solids (accompanied to a small portion of DOC and COD), as well as to decrease turbidity, in order to increase efficiency of the subsequent chemical oxidation treatment. The evaluation of the effect of a physic-chemical pre-treatment on the later oxidation processes for the case study of cork boiling wastewater was studied by testing two coagulants. For this purpose, cork boiling wastewater was divided into three fractions: a raw gross (RW, characteristic parameters shown in [Table 1](#)); and two pre-treated fractions: PW1 using Fe^{3+} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and PW2 using Fe^{2+} ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Pre-treatment consisted of a coagulation and filtration process. In a first stage, pH was adjusted to 2.8 (optimum pH for photo-Fenton process). Secondly, Fe^{3+} or Fe^{2+} was added until reaching a final dissolved concentration of $20 \text{ mg iron L}^{-1}$. Water was allowed to stand for about 8 hours and, finally, the supernatant was filtered through a $75\text{-}\mu\text{m}$ silex filter. Measurements of the main parameters were performed before and after pre-treatment. Results are shown in [Table 2](#). After pH adjustment, an initial dose of iron (40 mg L^{-1} , according to previous tests performed at bench-scale, data not shown) was added to PW1 and PW2 in order to reach a final dissolved iron concentration of 20 mg L^{-1} for the subsequent solar photo-Fenton experiments. Precipitated iron was removed with settled solids. In both cases, only one addition was enough to have the appropriate final concentration of iron, although iron precipitation was more important for PW1 (23.7 mg L^{-1} of non-dissolved iron) than for PW2 (22.2 mg L^{-1} of non-dissolved iron).

TABLE 2

The reductions of the analysed parameters for PW1 and PW2 were: 50.6% and 33.2% for DOC; 61.3% and 45.2% for COD; 75.9% and 58.2% for TSS, respectively. Thus, it can be concluded that using Fe^{3+} as a coagulation agent at acid pH provided the best results compared with Fe^{2+} for this specific wastewater, without adding other coagulants or flocculants such as aluminium sulphate [146, 157], sodium aluminate [168], polyaluminium chloride [179] or polyelectrolytes [2018].

It is important to highlight the increase in toxicity values after the pre-treatment step (pH was always adjusted between 6.5-7.5 for bioassays). It is obvious that physico-chemical process provoked the real wastewater concentration on the most toxic species.

3.2 Solar photo-Fenton process

Solar photo-Fenton treatment was applied to RW, PW1 and PW2. Regarding the experiments performed with RW, pH was adjusted to 2.6-2.8 before adding the required amount of Fe^{3+} to achieve an initial concentration of 20 mg L^{-1} , optimal for solar photo-Fenton treatment according to the photo-reactor glass tubes external diameter. All the experiments were performed at a constant temperature of 35°C and adding 100 mg L^{-1} of hydrogen peroxide doses so as to maintain a concentration of around $200 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$ during the assay.

RW and PW1 were treated by solar photo-Fenton process using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a Fe^{3+} source (see Figure 1). RW DOC suffered a remarkable reduction of 39%, while PW1 DOC was mineralized only 16% (data not shown). In addition, maximum COD removals were 59% and 52%, respectively, after receiving an accumulative energy of about 64 kJ L^{-1} . Besides H_2O_2 consumption was similar for the two tests: 750 mg L^{-1} for RW (after 377 474 min of illumination time) and 780 mg L^{-1} for PW1 (after 435 227 min of illumination time).

COD decreasing and increasing behaviour observed for RW obeyed to foam formation at the beginning of the assay. After the third sample ($Q_{UV} = 10 \text{ kJ L}^{-1}$), foam started to re-dissolve involving rising COD values. However, an important reduction of COD was observed from $Q_{UV} = 50 \text{ kJ L}^{-1}$ onwards. This occurred after the first stage of the treatment governed by Fenton process, while once wastewater's characteristics were improved, light penetration increased and so photo-Fenton process acquired importance through the end of the test.

According to these results, the pre-treatment with Fe^{3+} did not improve treatment efficiency of the subsequent solar photo-Fenton oxidation process. Indeed, physico-

chemical pre-treatment increased hydrogen peroxide and UV energy requirements for attaining similar degradation percentages as in RW.

PW2 was also treated by solar photo-Fenton but using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a Fe^{2+} source (see Figure 1). It is important to highlight that in this case, after $60 \text{ kJ} \cdot \text{L}^{-1}$ of accumulative energy (comparing with RW and PW1), the mineralization percentage was about 21% and COD elimination was 26% (much lower than those figures obtained when Fe^{3+} was used).

FIGURE 1

If a common treatment point is considered for the three wastewater fractions, as for example, 50% of COD elimination, differences in energy requirements can be observed: $59.3 \text{ kJ} \cdot \text{L}^{-1}$ ($t_{30w}=206\text{--}375$ min) were necessary for RW and $62 \text{ kJ} \cdot \text{L}^{-1}$ ($t_{30w}=409\text{--}35$ min) for PW1, but $80.5 \text{ kJ} \cdot \text{L}^{-1}$ ($t_{30w}=508$ min) for PW2. Additionally, the highest H_2O_2 consumption was also measured for PW2 treatment: $1100 \text{ mg} \cdot \text{L}^{-1}$; in contrast to $698 \text{ mg} \cdot \text{L}^{-1}$ for RW and $780 \text{ mg} \cdot \text{L}^{-1}$ for PW1.

Globally, it can be concluded that the pre-treatment step does not benefit the efficiency of the subsequent solar photo-Fenton process for this specific real wastewater. Most promising results were obtained within the solar photo-Fenton treatment of the raw wastewater fraction. Anyway, using Fe^{3+} as a coagulation agent provided better results than Fe^{2+} in terms of COD, DOC and TSS removals, jointly with lower H_2O_2 consumption and accumulative energy requirement to attain the same remediation point in the photo-Fenton process.

3.3 Ozonation treatment

Ozone can be used alone as an oxidant agent or in combination with hydrogen peroxide and/or at high pH to act as an AOP by generating hydroxyl radicals.

RW and PW1 were treated by ozonation alone and in combination with H_2O_2 at two different initial pH values (7 and 10). Ozonation was not tested on PW2 as better results were obtained when using Fe^{3+} as coagulant. All these assays were carried out using a gas flow of $0.1 \text{ Nm}^3 \cdot \text{h}^{-1}$ and a 50% level of ozone production, providing an inlet concentration of $3.5 \text{ g} \cdot \text{L}^{-1}$. RW treatment by ozonation at natural pH (around 7) showed a COD removal of 15% after 4.5 hours (DOC remained constant) and an ozone consumption of $400 \text{ mg} \cdot \text{L}^{-1}$. Due to the low degradation achieved, the rest of the experiments were carried using PW1 as it was concluded that ozonation was not adequate for treating RW.

Ozonation of PW1 at initial pH 7 and 10

When ozonation is applied at pH between 4 and 9 the organic matter degradation can occur through direct ozone attack or indirect free radical attack. However, when it is applied at pH 10 the indirect pathway (HO^\bullet) prevails (reactions 1-3) [219-224]:



As it can be observed in Figure 2, no important changes in COD and DOC were detected along 4.5 hours of ozonation at initial pH of 7 (13.5% and 16% of elimination, respectively), by consuming 400 mg L^{-1} of ozone and reaching a final pH of 5.1 (free pH during the reaction). Nevertheless, better results were achieved when initial pH was increased to a value of 10. Although mineralization percentage did not improve (9% of DOC reduction), a COD elimination of 33% was attained after 4.5 h with an ozone consumption of $460 \text{ mg O}_3 \text{ L}^{-1}$. Ozonation was extended for 15 hours under pH 10, COD and DOC removals of 62% and 47%, respectively, were detected after a total ozone consumption of 1.1 g L^{-1} , lowering the final pH to 6.4.

The results shown are in concordance with the fact that when water with high DOC (like cork boiling wastewater) is treated by ozonation at pH higher than 9, an increase on the process efficiency can be observed. However, in the case of other wastewaters with low organic matter concentration, a decrease in the oxidation capacity of the system is detected at high pH due to the high occurrence of reaction 3 [224].

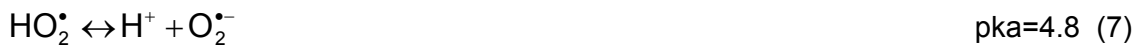
FIGURE 2

Ozonation/ H_2O_2 of PW1 at initial pH 7 and 10

Finally, PW1 was treated by $\text{O}_3/\text{H}_2\text{O}_2$ (doses of 200 mg L^{-1}) at initial pH 7 and 10. Results are presented in Figure 3. When working at pH 7, DOC and COD reductions of 56% and 57%, respectively, were observed after 11 h of treatment along with an ozone consumption of $0.824-26 \text{ g L}^{-1}$, reaching a final pH of 6.7. On the other hand, when working under pH 10 conditions, DOC and COD removals were 60% and 82%,

respectively, for a 15 h treatment, an ozone consumption of 1.89 g/L^{-1} and a final pH equal to 7.7.

The presence of H_2O_2 in the ozonation system favours the generation of hydroxyl radicals by reaction 4 and, depending on the pH and the equilibrium of reaction 5, through reactions 6-10 too [235].



Taking into account that pH in the experiments was never higher than 10, hydroxyl radicals extra generation thanks to the addition of H_2O_2 occurred only through reaction 4. This is why only a slight efficiency improvement in DOC degradation percentage was observed between ozonation at pH 10 and $\text{O}_3/\text{H}_2\text{O}_2$ at pH 7 or 10. Nevertheless, best COD elimination percentages measured during ozonation at pH10, compared with $\text{O}_3/\text{H}_2\text{O}_2$, highlight a possible interaction between reagents (O_3 and H_2O_2) through reaction 3. This effect could be translated into a low efficient use of H_2O_2 probably provoked by an excess of this reagent at the initial stage of the treatment.

FIGURE 3

Ozonation treatments comparison

Table 3 shows the results attained after ozonation of PW1 under different pH conditions with and without hydrogen peroxide addition. A common treatment time of 4.5 hours has been selected given that the main objective was maintaining the oxidation process until changes in toxicity and enhancement of biodegradability were observed (see section 3.4). As it can be seen, the best COD degradation percentage was obtained with ozonation at pH 10. The rest of treatments tested were quite similar

in terms of COD and DOC elimination. In addition, O_3/H_2O_2 at initial pH of 10 did not improve degradation of PW1 while a higher consumption of reagents was required (0.68 g/L^{-1} of O_3 and 200 mg/L^{-1} of H_2O_2). The comparison between experiments with and without hydrogen peroxide addition, revealed that efficiency improvement was not enough to justify the use of H_2O_2 ; besides ozone consumptions are very similar except for $O_3(pH\ 10)/H_2O_2$.

TABLE 3

3.4 TOXICITY AND BIODEGRADABILITY ASSAYS

The main role of a chemical pre-treatment, such as AOPs, is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of mineralization should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. Therefore, and with the aim to identify the best possible combination point between the chemical and biological treatment steps, toxicity and biodegradability analysis must be performed.

Solar Photo-Fenton treatment

Table 4 collects acute toxicity and short-term biodegradability results obtained from cork boiling wastewater treatment with solar photo-Fenton under different conditions, considering a COD elimination of 50% in all the cases. First of all, it is important to highlight how physic-chemical pre-treatment worsened raw wastewater's characteristics as initial toxicity increased considerably for PW1 and PW2. Furthermore, only a great reduction in acute toxicity was detected after the photo-Fenton treatment of PW2. Regarding biodegradability, a slight enhancement was observed at the end of the treatment of RW and PW2, whilst PW1 remained non-biodegradable.

TABLE 4

The still high values of acute toxicity after solar photo-Fenton pre-treatment of PW1, jointly with the low biodegradability according to respirometric analysis, made it interesting to perform a long term biodegradability study by applying a Zahn-Wellens test. This assay allowed evaluating the behaviour of a conventional activated sludge in contact with the real wastewater for a long time (28 days). Besides, information about possible biomass adaptation, making PW1 biological treatment feasible as a post-

treatment step, could be obtained from the test. As it is observed in Figure 4, only the last sample with a COD of 317233 mg/L^{-1} ($Q_{UV}=36.262.4 \text{ kJ/L}^{-1}$ and $560780 \text{ mg H}_2\text{O}_2/\text{L}^{-1}$ consumed) nearly achieved the 70% of biodegradability threshold after 6 days of bio-treatment. In consequence, combination of chemical-biological oxidation technologies seems not to be the best treatment option for this kind of industrial wastewater due to the long treatment time (640 minutes) required for the photo-Fenton process as a first step.

FIGURE 4

Ozonation treatment

Table 5 presents toxicity and biodegradability results when ozonation under different conditions was applied. In all cases a treatment time of 4.5 h was considered. As it is shown, RW remained non-toxic and the inhibition percentage of PW1 decreased sharply to 33% after ozonation treatment at pH 7. On the contrary, PW1 ozonation at pH 10 and $\text{O}_3/\text{H}_2\text{O}_2$ treatment at pH 7 and 10 showed just a slight toxicity decrease, although it was maintained over 50% of inhibition.

Regarding biodegradability, all the wastewater fractions shifted from non-biodegradable to slightly biodegradable independently of the experimental conditions. This means that RW and PW1 are sensitive to be further treated by a biological system after being partially oxidized by ozonation.

These short term toxicity and biodegradability favourable results made it unnecessary to carry out long term biodegradability assays by Zahn-Wellens test. The significant decrease in toxicity inhibition percentages and the important increase in short term biodegradability analysis highlight a feasible combination between ozonation (RW (pH7), whose toxicity and biodegradability values after the treatment were 0% and 0.28, respectively; and PW1 (pH7) whose toxicity and biodegradability final values were 33% and 0.19, respectively) and a conventional bio-treatment for the remediation of the industrial wastewater under study.

TABLE 5

4 CONCLUSIONS

After cork boiling wastewater physic-chemical pre-treatment, an improvement of the main measured parameters took place, observing better results when Fe^{3+} was used

as a coagulant agent. However, raw wastewater (RW) exhibited the best results after the solar photo-Fenton process, given that it required lower energy and hydrogen peroxide consumption (main parameters considered in an industrial plant design) than PW1 and PW2 treatment.

From the point of view of toxicity and biodegradability, no physic-chemical pre-treatment would be necessary for the treatment real cork boiling wastewater by ozonation. Accordingly, the treatment line would be RW ozonation at pH 7 and final DOC elimination in an advanced biological process.

Comparing solar photo-Fenton and ozonation processes, both advanced oxidation processes tested have been clearly demonstrated to be able to increase biodegradability of cork boiling wastewater.

Finally, it is necessary to highlight the increase of toxicity values for the real wastewater after the physic-chemical pre-treatment while biodegradability remained constant. Biodegradability for RW and PW2 slightly improved after photo-Fenton treatment, but not for PW1. On the other hand, after ozonation treatments, toxicity showed slight decrease, except for RW that remained non-toxic. Better results were observed regarding biodegradability enhancement. This means that RW and PW1 could be further treated by a biological system after being partially oxidized by ozonation.

This work presents a general protocol for identifying the best combined treatment line for a specific industrial wastewater. This protocol should include preliminary physic-chemical studies followed by the combination of chemical and biological processes. As it is widely approved within the scientific community, toxicity and biodegradability assays must complete chemical analysis for determining the best combination strategy. The decision between one and other treatment (in this case solar photo-Fenton or ozonation) must be based on a deep economic assessment that should be performed for the specific industrial emplacement, taking into account solar irradiance, specific water discharge normative, electricity costs, etc. Results extracted from the application of this protocol should constitute the basis of a future viability study for these technologies scaling-up.

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Table 1. [Cork boiling Ww](#)astewater characterization

Parameter	Value (mg/L⁻¹)
pH	7.2
Conductivity (mS/cm ⁻¹)	1.1
Turbidity (NTU)	163
TSS	290
COD	1240
DOC	586
Total nitrogen	27.8
Total iron	3.3
Na ⁺	60.1
NH ₄ ⁺	15.1
K ⁺	224.6
Mg ²⁺	20.3
Ca ²⁺	99.3
Cl ⁻	134
SO ₄ ²⁻	4.9
PO ₄ ³⁻	<DL
NO ₃ ⁻	<DL
Biodegradability	0.13 (Slightly biodegradable)
Toxicity	8.6% (Non-toxic)

Biodegradability=(CODb/COD)

DL= detection limit

Table 2. Comparison of different pre-treatments [for cork boiling wastewater](#).

	PW1	PW2
COD (mg O₂/L⁻¹)	480	680
DOC (mg/L⁻¹)	290	391
pH	2.8	3.1
Conductivity (mS/cm⁻¹)	0.8	1.1
Turbidity (NTU)	116	136
TSS (mg/L⁻¹)	70	120
Final total iron (mg/L⁻¹)	19.6	21.1
Toxicity (%I)	90	100
Biodegradability	0.08	0.13

[PW1 pre-treated using FeCl₃·6H₂O](#)

[PW2 pre-treated using FeSO₄·7H₂O](#)

Table 3. Comparison of ozonation under different operating conditions after 4.5 h of PW1 fraction treatment ~~of PW1 fraction.~~

	O ₃ (pH 7)	O ₃ (pH 10)	O ₃ (pH 7)/H ₂ O ₂	O ₃ (pH 10)/H ₂ O ₂
COD (Elimination %)	13.5	33	18.5	13
DOC (Elimination %)	16	11.5	19	17
pH_i-pH_{f(4.5h)}	7.2-5.1	10-6.2	7.1-5.8	9.8-7.6
O₃ (g/L⁻¹)	0.4	0.48	0.43	0.68
H₂O₂ consumed (mg/L⁻¹)	--	--	200	200

Table 4. Toxicity and biodegradability corresponding to solar photo-Fenton tests (50% of COD removal) [for RW, PW1 and PW2 treatment.](#)

Wastewater Fraction	Toxicity* (%Inhibition)	Biodegradability**	Q_{UV} (kJ L⁻¹)	H₂O₂ consumed (mg L⁻¹)
RW	8.6 – 0	0.13 – 0.30	59.3	698
PW1	90 - 86	0.08 - 0.08	62	780
PW2	100 – 62	0.13 - 0.33	80.5	1100

*Toxicity: Initial Toxicity– Toxicity when 50 % of COD was removed.

**Biodegradability: Initial biodegradability-biodegradability when 50 % of COD was removed.

Table 5. Toxicity and biodegradability corresponding to ozonation [tests of RW and PW1](#) (treatment time of 4.5 h) [for RW and PW1](#).

Experimental conditions	Toxicity* (%Inhibition)	Biodegradability**	O ₃ consumed (g/L ⁻¹)	H ₂ O ₂ consumed (g/L ⁻¹)
RW (pH 7)	8.6 – 0	0.13 – 0.28	0.38	-
PW1 (pH 7)	90 – 33	0.08 - 0.19	0.40	-
PW1 (pH 7)/H ₂ O ₂	90 - 76	0.08 - 0.26	0.43	0.20
PW1 (pH 10)	90 - 76	0.08 - 0.22	0.48	-
PW1 (pH 10)/H ₂ O ₂	90 – 67	0.08 – 0.19	0.68	0.20

*Toxicity (%): Toxicity₀ (%) – Toxicity_{4.5h} (%)

**Biodegradability: Biodegradability₀ – Biodegradability_{4.5h}

FIGURES CAPTION

Figure 1. Evolution of COD and H₂O₂ consumption for solar photo-Fenton treatment of RW, PW1, PW2 (Experimental conditions: pH=2.6-2.8, [Fe³⁺]=20 mg L⁻¹, T=35°C, [H₂O₂]=200 mg L⁻¹).

Figure 2. Evolution of COD and O₃ consumption at initial pH of 7 and 10 for PW1 treatment by ozonation.

Figure 3. Evolution of COD and O₃ consumption at initial pH 7 and 10 for PW1 treatment by O₃/H₂O₂ (three doses of 200 mg/L).

Figure 4. Long term biodegradability study of PW1 photo-Fenton samples by Zahn-Wellens test.

Cork boiling wastewater treatment at pilot plant scale: comparison of solar photo-Fenton and ozone (O₃, O₃/H₂O₂). Toxicity and biodegradability assessment

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Abstract

Remediation of cork boiling wastewater was studied as an example of complex industrial wastewater treatment by applying a protocol based on a combination of advanced technologies and chemical-biological assays. Solar photo-Fenton and ozone (alone or in combination with hydrogen peroxide at different pH conditions), at pilot plant scale have been used as chemical oxidation step. Additionally, the effect of a physic-chemical pre-treatment using different flocculants (FeSO₄ and FeCl₃) was evaluated. Although physic-chemical pre-treatment with Fe³⁺ provided good removals of COD, DOC and TSS, it was found that it did not enhance solar photo-Fenton post-treatment. On the contrary, ozone-based process was improved after physic-chemical pre-treatment with Fe³⁺, attaining higher degradation efficiencies with lower ozone consumptions for the combination O₃/initial pH 7. Toxicity and biodegradability assays were performed to evaluate possible variations along the oxidation processes. After solar photo-Fenton treatment, toxicity and biodegradability remained constant at their initial values. Then, Zahn-Wellens test was carried out to study long term biodegradability and possible biomass adaptation to the partially photo-treated effluent. Decrease in toxicity values and short term biodegradability enhancement were observed for cork boiling wastewater treated by ozonation systems.

Keywords: Biodegradability, cork boiling wastewater, industrial wastewater, ozonation, solar photo-Fenton.

1. Introduction

Industrial wastewater's characteristics depend on the industry where it is generated and with process variations. This implies that industrial wastewater treatment is a complex problem due to the wide variety of compounds it may contain as well as their concentration. Thus, selection of the best treatment option for remediation of a specific industrial wastewater is a highly complicated task provided that the choice of one or more processes to be combined in a certain situation depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost.

In general, the possibilities and capabilities of the conventional treatments available are widely known. However, information on the efficiency of the new technologies (Advanced Oxidation Processes, AOPs) for eliminating certain specific pollutants present in wastewater compared to conventional options is necessary. For this reason, bench-scale and pilot-plant studies are required to develop the technologies and generate information on new industrial wastewater treatment processes. Such scaled studies are even more decisive when combining several technologies for decontamination or reuse of a specific industrial wastewater [1].

A perfect example of the challenge on the treatment and reuse of a complex industrial wastewater is cork boiling wastewater. Cork processing includes a stage in which slabs are immersed in boiling water during one hour in order to improve their physic-chemical characteristics. In addition, the same water is normally used for several boiling cycles, and so it concentrates in persistent compounds. As a consequence, the resulting wastewater contains undesirable corkwood extracts (phenolic acids, tannic fraction, 2,4,6-trichloroanisol, pentachlorofenol) which are not easily removed by conventional treatments. Therefore, this wastewater cannot be discharged into public water courses [2]. Despite of their characteristics, these effluents are usually released directly without any previous treatment in the environment or in municipal wastewater treatment plants (MWTP), involving active sludge low efficiencies, along with real environmental impacts to superficial and underground aquatic/soil systems. Furthermore, great volumes of wastewater are generated during cork boiling processes (about 400 L of wastewater per ton of raw cork) and, consequently, its treatment has some technical and economic constraints [3]. Therefore, wastewater generated during cork boiling is representative of typical industrial effluents with high contents of DOC (higher than 500 mg L^{-1}) and COD (higher than 1000 mg L^{-1}), with low pH, low toxicity and biorecalcitrant nature. In this sense, and taking into account that conventional biological processes cannot satisfactorily deal with this kind of wastewater due to the presence of compounds

potentially inhibitory for activated sludge, one feasible option is the use of Advanced Oxidation Processes (AOPs). These advanced technologies can degrade organic recalcitrant pollutants present in wastewater by forming hydroxyl radicals [4, 5]. Some AOPs have been demonstrated to be efficient treatments for complex effluents such as those generated in the winery sector, which have similar characteristics to the cork boiling wastewaters [1]. For instance, the effectiveness of different ozone-based advanced oxidation processes (O_3 , O_3/UV and $O_3/UV/H_2O_2$) was investigated in a pilot-scale bubble column reactor, attaining significant COD and DOC removals for such specific industrial wastewater [6]; another example is winery wastewater remediation using some AOPs ($TiO_2/H_2O_2/UV$ and $Fe^{2+}/H_2O_2/UV$ and solar photo-Fenton) tested at a pilot plant equipped with an immobilized biological reactor (IBR) and a photocatalytic system with compound parabolic collectors (CPCs), which is reported to be an alternative to a conventional biological, achieving good COD eliminations [7]. As far as we know, little researching work related to the treatment of cork boiling wastewater can be found in literature. Some reported processes are: flocculation/flotation/ultrafiltration, used as a pre-treatment [8]; oxidation using Fenton reagent [9]; integrated Fenton reagent and coagulation/flocculation processes [10]; and photo-oxidation ($H_2O_2/UV-vis$, $H_2O_2/Fe^{2+}/UV-vis$, $TiO_2/UV-vis$ and $TiO_2/H_2O_2/UV-vis$) using a batch photo-reactor with a mercury vapor lamp emitting in the 200–600 nm range [11]. All of them were proved to be effective for COD removal and biodegradability and toxicity enhancement, although, in general, treatment's efficiency was improved when a physic-chemical pre-treatment was performed. Some other AOPs have been applied for cork boiling wastewaters remediation. For instance, ozonation with the addition of H_2O_2 and solar photo-Fenton processes have been previously studied considering the possible combination with a final conventional biological post-treatment [12, 13].

Nevertheless, it is not usual to find real application case studies dealing with a sequential approach for giving a complete solution for the treatment and reuse of a complex industrial wastewater. Then, the objective of this study is defining the best treatment line for real cork boiling wastewater remediation and reuse, emphasizing the complex chemical and biological analytical tools that should be applied to obtain reliable design data for up-scaling purposes. With this aim, the application of ozone alone (at natural and higher pH) and in combination with hydrogen peroxide, and solar photo-Fenton process at pilot plant scale have been evaluated. Additionally, this work analyses the convenience of performing a physic-chemical pre-treatment of the industrial effluent, as well as the study of toxicity and biodegradability throughout the different oxidation processes. This approach is also intended to find the proper

operating conditions to achieve sufficient biodegradability enhancement of the cork boiling wastewater for being discharged into a conventional activated sludge system, which could be installed on-site allowing its reuse in the cork processing factory.

2 Materials and methods

2.1 Cork boiling wastewater characterization. Reagents and chemicals.

Real cork boiling wastewater used in this study was collected at a cork-processing plant located in San Vicente de Alcántara (Extremadura, Spain). All tests were performed at Plataforma Solar de Almería (Tabernas, Spain). Cork boiling wastewater is dark brown liquor due to a high polyphenols concentration and other corkwood extracts. As a consequence, it presents a high turbidity value which can affect solar photo-Fenton process efficiency. Characterization was carried out following the procedures described below. Table 1 shows the values for the main characterization parameters. This sample exhibited a high organic content and a low biodegradability level (organic carbon can be considered recalcitrant and possibly inhibitory to microbial metabolism of a biological oxidation system), though it is non-toxic. High levels of potassium ions can be attributed to the boiling process.

TABLE 1

Experiments were performed using reagent-grade iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), reagent-grade hydrogen peroxide (30% w/v), sulphuric acid and sodium hydroxide (for physic-chemical pre-treatment and pH adjustment), all provided by Panreac and Merck.

2.2 Analytical determinations

Immediately after sampling and filtering through 0.2- μm nylon syringe-driven filters (Millipore Millex®-GM), dissolved organic carbon (DOC) was measured with a Shimadzu TOC-VCN analyser. Dissolved nitrogen (TN) was quantified in a TC-TOC-TN analyser coupled with a TNM-1 unit (Shimadzu, model TOC- V_{CSN}). Total iron concentration was determined using the 1,10-phenanthroline method following ISO 6332, and hydrogen peroxide was measured using titanium (IV) oxysulfate according to DIN 38402H15. Anions concentrations (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) were determined with a Dionex DX-600 ion chromatograph system using a Dionex Ionpac AS11-HC 4×250-mm column. The gradient program for anion determination was pre-run for 5 min with 20 mM NaOH, an 8-min injection of 20 mM of NaOH, and 7 min with 35 mM of

NaOH, at a flow rate of 1.5 mL min⁻¹. Cations concentrations (Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺) were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4-mm×250-mm column. Isocratic elution was performed with H₂SO₄ (10 mM) at a flow rate of 1.2 mL min⁻¹. COD was determined using Merck Spectroquant kits (ref: 1.14541.0001). Turbidity was measured in a Hach 2100N turbidimeter. Total suspended solids (TSS) and volatile suspended solids (VSS) were quantified according to the American Standard Methods [14]. Conductivity was measured using a conductivity meter Crison GLP31.

2.3 Toxicity and Biodegradability assays

Acute toxicity and short term biodegradability assays were carried out in a BM-T Advance respirometer (Surcis S.L.), which consists of a 1 L capacity vessel, equipped with a temperature and pH control system. It also has an oxygen probe (Protos 3400, Knick Elektronische Messgeräte GmbH & Co. KG) for respirometric determination of the activated sludge activity based on the oxygen uptake rate (OUR). The ultimate biodegradability was evaluated using an adaptation of the Zahn-Wellens test EC protocol.

The activated sludge used in the bioassays came from the municipal wastewater treatment plant of El Bobar (Almería). After reception, the sludge was characterized through DOC, ammonium, nitrate and nitrite concentrations, TSS and VSS measurements. Prior to biological tests, the excess of H₂O₂ present in the samples was removed by adding catalase solution (2500 U mg⁻¹ bovine liver) after adjusting the pH between 6.5 and 7.5.

For toxicity analyses, the respirometer was loaded with 1L of endogenous activated sludge. Temperature was controlled at 20° C and the system was continuously aerated and agitated. This analysis compares maximum bacterial oxygen uptake rate (OUR_{max}) in a reference with that of the target sample. The reference was 30 mL of distilled water with 0.5 g of sodium acetate g⁻¹ VSS. Moreover, 30 mL of sample was added to obtain the OUR_{max-sample}. The inhibition percentages were calculated using (Eq. 1):

$$\text{Inhibition (\%)} = 100 \times (1 - \text{OUR}_{\text{max-sample}} / \text{OUR}_{\text{max-ref}}) \quad (\text{Eq. 1})$$

In short-term biodegradability assays, 700 mL of endogenous activated sludge were introduced in the respirometer and aerated until saturation. At that moment, 300 mL of oxygen-saturated target sample were added and the test started. The ratio COD/COD_b (total chemical oxygen demand/easily biodegradable chemical oxygen demand) allows to assess the percentage of COD_b removed from the total COD and, thus, to establish

the biodegradable character of the sample. A sample is considered to be highly biodegradable when COD/COD_b is greater than 0.8; biodegradable, when it is comprised between 0.7 and 0.8; slowly biodegradable when the ratio is 0.3-0.7, slightly biodegradable when the ratio is between 0.1-0.3 and non-biodegradable when it is lower than 0.1 (according to instructions given by the respirometer's manufacturer, SURCIS S.L.) .

The ultimate biodegradability of raw wastewater and partially treated samples obtained at different photo-oxidation times were evaluated using an adaptation of the Zahn-Wellens test EC protocol, Directive 88/303/EEC (1992). After pH adjustment to 6.5-7.5, a volume of 240 mL of each sample was added to an open glass bottle, along with mineral nutrients (KH_2PO_4 , K_2HPO_4 , Na_2HPO_4 , NH_4Cl , $CaCl_2$, $MgSO_4$ and $FeCl_3$) and the required amount of activated sludge according to each sample's DOC. Each bottle was kept in the dark, with magnetic stirring and aeration during 28 days. Diethylene glycol was used as a reference compound. Blank controls contained activated sludge, distilled water and mineral nutrients. The biodegradation percentage (D_t) was determined by Eq. (2):

$$D_t = \left(1 - \frac{C_t - C_B}{C_A - C_{BA}} \right) \cdot 100 \quad (\text{Eq. 2})$$

Where C_A and C_{BA} are the DOC values ($mg\ C\ L^{-1}$) in the mixture and in the blank control measured 3 hours after de beginning of the experiment; and C_t and C_B are the DOC values ($mg\ C\ L^{-1}$) in the mixture and in the blank control at the sampling time, respectively. The samples are considered to be biodegradable when D_t is higher than 70%.

2.4 Experimental equipment

Homogeneous photocatalysis was performed in a CPC solar collector pilot plant installed in the Plataforma Solar de Almería (PSA). The hydraulic circuit of the reactor consists of a recirculation tank, a centrifugal pump and four CPC modules with a total irradiated area of $4.16\ m^2$. The photo-reactor is equipped with a temperature control system. This pilot plant operates in batch mode, it has a total volume of 82 L (V_T) and a total illuminated volume inside the absorber tubes of 44.6 L (V_i). The four CPC concentrator modules are mounted on a metal frame tilted 37° (latitude of the PSA) and facing the south. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same

angle as the CPCs). Comparison of different photocatalytic assays under different solar conditions is possible by means of Eq. (3)

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot UV \cdot \frac{A_r}{V_T} \quad (\text{Eq. 3})$$

$$\Delta t_n = t_n - t_{n-1}$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during the period Δt_n , A_r is the illuminated area (m^2), and $Q_{UV,n}$ is the accumulated energy per unit of volume (kJ L^{-1}) at t_n .

The illumination time, t_{30W} , allows combining the data from several days' experiments as well as their comparison with other photocatalytic assays [15]. It can be calculated using Eq. 4.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{UV}{30} \cdot \frac{V_i}{V_T} \quad (\text{Eq. 4})$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation ($\lambda < 400 \text{ nm}$) measured between t_{n-1} and t_n , and t_{30W} is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

Cork boiling wastewater (after pre-treatment) was introduced into the CPC photo-reactor and homogenised in darkness by turbulent recirculation during 15 min. Then, pH was adjusted to 2.6-2.8. Afterwards, iron salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added to reach an initial concentration of $20 \text{ mg iron L}^{-1}$ in solution. Finally, the first dose (200 mg L^{-1}) of hydrogen peroxide was added, the CPCs were uncovered and the photo-Fenton process started. Samples were taken at pre-defined times to evaluate the degradation process. The hydrogen peroxide concentration was monitored to keep concentration around $200\text{-}300 \text{ mg L}^{-1}$ (by regular additions of 100 mg L^{-1}).

The ozonation system is an Anseros PAP-pilot (Anseros Klaus Nonnenmacher GmbH, Germany) for batch operation. The ozonation tank is a 10 L Pyrex cylindrical vessel with a magnetic stirrer for proper homogenisation. The system is also equipped with two non-dispersive UV analysers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone concentration. The oxygen generator supplies a maximum gas flow of 6 L min^{-1} with an oxygen concentration up to 90%. Besides, ozone production can be adjusted providing a maximum concentration of $8.82 \text{ g O}_3 \text{ h}^{-1}$ for a gas flow of $0.2 \text{ Nm}^3 \text{ h}^{-1}$. Therefore, inlet ozone concentration average was around $36 \text{ g O}_3 \text{ m}^{-3}$ in all the

experiments, while ozone outlet concentration average changed from 18 g O₃ m⁻³ at the beginning of the degradation process, to around 30 g O₃ m⁻³ when the system attained saturated conditions. A thermic ozone destructor has been coupled to the reactor exhaust in order to avoid its release to the atmosphere. In those experiments in which ozonation was tested with the addition of H₂O₂, three doses of 200 mg L⁻¹ were added in each one, as this reagent was consumed during the reaction.

3 Results and discussion

3.1 Physic-chemical pre-treatment

In general, physic-chemical pre-treatment aimed to stabilize industrial wastewater, to eliminate suspended solids (accompanied to a small portion of DOC and COD), as well as to decrease turbidity, in order to increase efficiency of the subsequent chemical oxidation treatment. The evaluation of the effect of a physic-chemical pre-treatment on the later oxidation processes for the case study of cork boiling wastewater was studied by testing two coagulants. For this purpose, cork boiling wastewater was divided into three fractions: a raw gross (RW, characteristic parameters shown in Table 1); and two pre-treated fractions: PW1 using Fe³⁺ (FeCl₃·6H₂O), and PW2 using Fe²⁺ (FeSO₄·7H₂O). Pre-treatment consisted of a coagulation and filtration process. In a first stage, pH was adjusted to 2.8 (optimum pH for photo-Fenton process). Secondly, Fe³⁺ or Fe²⁺ was added until reaching a final dissolved concentration of 20 mg iron L⁻¹. Water was allowed to stand for about 8 hours and, finally, the supernatant was filtered through a 75-µm silex filter. Measurements of the main parameters were performed before and after pre-treatment. Results are shown in Table 2. After pH adjustment, an initial dose of iron (40 mg L⁻¹, according to previous tests performed at bench-scale, data not shown) was added to PW1 and PW2 in order to reach a final dissolved iron concentration of 20 mg L⁻¹ for the subsequent solar photo-Fenton experiments. Precipitated iron was removed with settled solids. In both cases, only one addition was enough to have the appropriate final concentration of iron, although iron precipitation was more important for PW1 (23.7 mg L⁻¹ of non-dissolved iron) than for PW2 (22.2 mg L⁻¹ of non-dissolved iron).

TABLE 2

The reductions of the analysed parameters for PW1 and PW2 were: 50.6% and 33.2% for DOC; 61.3% and 45.2% for COD; 75.9% and 58.2% for TSS, respectively. Thus, it can be concluded that using Fe³⁺ as a coagulation agent at acid pH provided the best

results compared with Fe^{2+} for this specific wastewater, without adding other coagulants or flocculants such as aluminium sulphate [16, 17], sodium aluminate [18], polyaluminium chloride [19] or polyelectrolytes [20].

It is important to highlight the increase in toxicity values after the pre-treatment step (pH was always adjusted between 6.5-7.5 for bioassays). It is obvious that physico-chemical process provoked the real wastewater concentration on the most toxic species.

3.2 Solar photo-Fenton process

Solar photo-Fenton treatment was applied to RW, PW1 and PW2. Regarding the experiments performed with RW, pH was adjusted to 2.6-2.8 before adding the required amount of Fe^{3+} to achieve an initial concentration of 20 mg L^{-1} , optimal for solar photo-Fenton treatment according to the photo-reactor glass tubes external diameter. All the experiments were performed at a constant temperature of 35°C and adding 100 mg L^{-1} of hydrogen peroxide doses so as to maintain a concentration of around $200 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$ during the assay.

RW and PW1 were treated by solar photo-Fenton process using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a Fe^{3+} source (see Figure 1). RW DOC suffered a remarkable reduction of 39%, while PW1 DOC was mineralized only 16% (data not shown). In addition, maximum COD removals were 59% and 52%, respectively, after receiving an accumulative energy of about 64 kJ L^{-1} . Besides H_2O_2 consumption was similar for the two tests: 750 mg L^{-1} for RW (after 377 min of illumination time) and 780 mg L^{-1} for PW1 (after 435 min of illumination time).

COD decreasing and increasing behaviour observed for RW obeyed to foam formation at the beginning of the assay. After the third sample ($Q_{\text{UV}} = 10 \text{ kJ L}^{-1}$), foam started to re-dissolve involving rising COD values. However, an important reduction of COD was observed from $Q_{\text{UV}} = 50 \text{ kJ L}^{-1}$ onwards. This occurred after the first stage of the treatment governed by Fenton process, while once wastewater's characteristics were improved, light penetration increased and so photo-Fenton process acquired importance through the end of the test.

According to these results, the pre-treatment with Fe^{3+} did not improve treatment efficiency of the subsequent solar photo-Fenton oxidation process. Indeed, physico-chemical pre-treatment increased hydrogen peroxide and UV energy requirements for attaining similar degradation percentages as in RW.

PW2 was also treated by solar photo-Fenton but using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a Fe^{2+} source (see Figure 1). It is important to highlight that in this case, after 60 kJ L^{-1} of accumulative energy (comparing with RW and PW1), the mineralization percentage was about 21% and COD elimination was 26% (much lower than those figures obtained when Fe^{3+} was used).

FIGURE 1

If a common treatment point is considered for the three wastewater fractions, as for example, 50% of COD elimination, differences in energy requirements can be observed: 59.3 kJ L^{-1} ($t_{30w}=206 \text{ min}$) were necessary for RW and 62 kJ L^{-1} ($t_{30w}=409 \text{ min}$) for PW1, but 80.5 kJ L^{-1} ($t_{30w}=508 \text{ min}$) for PW2. Additionally, the highest H_2O_2 consumption was also measured for PW2 treatment: $1100 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$; in contrast to $698 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$ for RW and $780 \text{ H}_2\text{O}_2 \text{ mg L}^{-1}$ for PW1.

Globally, it can be concluded that the pre-treatment step does not benefit the efficiency of the subsequent solar photo-Fenton process for this specific real wastewater. Most promising results were obtained within the solar photo-Fenton treatment of the raw wastewater fraction. Anyway, using Fe^{3+} as a coagulation agent provided better results than Fe^{2+} in terms of COD, DOC and TSS removals, jointly with lower H_2O_2 consumption and accumulative energy requirement to attain the same remediation point in the photo-Fenton process.

3.3 Ozonation treatment

Ozone can be used alone as an oxidant agent or in combination with hydrogen peroxide and/or at high pH to act as an AOP by generating hydroxyl radicals.

RW and PW1 were treated by ozonation alone and in combination with H_2O_2 at two different initial pH values (7 and 10). Ozonation was not tested on PW2 as better results were obtained when using Fe^{3+} as coagulant. All these assays were carried out using a gas flow of $0.1 \text{ Nm}^3 \text{ h}^{-1}$ and a 50% level of ozone production, providing an inlet concentration of $3.5 \text{ g O}_3 \text{ h}^{-1}$. RW treatment by ozonation at natural pH (around 7) showed a COD removal of 15% after 4.5 hours (DOC remained constant) and an ozone consumption of $400 \text{ mg O}_3 \text{ L}^{-1}$. Due to the low degradation achieved, the rest of the experiments were carried using PW1 as it was concluded that ozonation was not adequate for treating RW.

Ozonation of PW1 at initial pH 7 and 10

When ozonation is applied at pH between 4 and 9 the organic matter degradation can occur through direct ozone attack or indirect free radical attack. However, when it is applied at pH 10 the indirect pathway (HO^\bullet) prevails (reactions 1-3) [21-22]:



As it can be observed in Figure 2, no important changes in COD and DOC were detected along 4.5 hours of ozonation at initial pH of 7 (13.5% and 16% of elimination, respectively), by consuming 400 mg L^{-1} of ozone and reaching a final pH of 5.1 (free pH during the reaction). Nevertheless, better results were achieved when initial pH was increased to a value of 10. Although mineralization percentage did not improve (9% of DOC reduction), a COD elimination of 33% was attained after 4.5 h with an ozone consumption of $460 \text{ mg O}_3 \text{ L}^{-1}$. Ozonation was extended for 15 hours under pH 10, COD and DOC removals of 62% and 47%, respectively, were detected after a total ozone consumption of 1.1 g L^{-1} , lowering the final pH to 6.4.

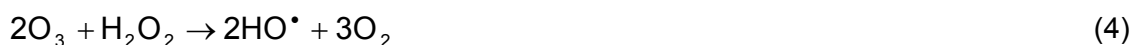
The results shown are in concordance with the fact that when water with high DOC (like cork boiling wastewater) is treated by ozonation at pH higher than 9, an increase on the process efficiency can be observed. However, in the case of other wastewaters with low organic matter concentration, a decrease in the oxidation capacity of the system is detected at high pH due to the high occurrence of reaction 3 [24].

FIGURE 2

Ozonation/ H_2O_2 of PW1 at initial pH 7 and 10

Finally, PW1 was treated by $\text{O}_3/\text{H}_2\text{O}_2$ (doses of 200 mg L^{-1}) at initial pH 7 and 10. Results are presented in Figure 3. When working at pH 7, DOC and COD reductions of 56% and 57%, respectively, were observed after 11 h of treatment along with an ozone consumption of 0.82 g L^{-1} , reaching a final pH of 6.7. On the other hand, when working under pH 10 conditions, DOC and COD removals were 60% and 82%, respectively, for a 15 h treatment, an ozone consumption of 1.89 g L^{-1} and a final pH equal to 7.7.

The presence of H₂O₂ in the ozonation system favours the generation of hydroxyl radicals by reaction 4 and, depending on the pH and the equilibrium of reaction 5, through reactions 6-10 too [25].



Taking into account that pH in the experiments was never higher than 10, hydroxyl radicals extra generation thanks to the addition of H₂O₂ occurred only through reaction 4. This is why only a slight efficiency improvement in DOC degradation percentage was observed between ozonation at pH 10 and O₃/H₂O₂ at pH 7 or 10. Nevertheless, best COD elimination percentages measured during ozonation at pH10, compared with O₃/H₂O₂, highlight a possible interaction between reagents (O₃ and H₂O₂) through reaction 3. This effect could be translated into a low efficient use of H₂O₂ probably provoked by an excess of this reagent at the initial stage of the treatment.

FIGURE 3

Ozonation treatments comparison

Table 3 shows the results attained after ozonation of PW1 under different pH conditions with and without hydrogen peroxide addition. A common treatment time of 4.5 hours has been selected given that the main objective was maintaining the oxidation process until changes in toxicity and enhancement of biodegradability were observed (see section 3.4). As it can be seen, the best COD degradation percentage was obtained with ozonation at pH 10. The rest of treatments tested were quite similar in terms of COD and DOC elimination. In addition, O₃/H₂O₂ at initial pH of 10 did not improve degradation of PW1 while a higher consumption of reagents was required (0.68 g L⁻¹ of O₃ and 200 mg L⁻¹ of H₂O₂). The comparison between experiments with

and without hydrogen peroxide addition, revealed that efficiency improvement was not enough to justify the use of H_2O_2 ; besides ozone consumptions are very similar except for $O_3(pH 10)/H_2O_2$.

TABLE 3

3.4 TOXICITY AND BIODEGRADABILITY ASSAYS

The main role of a chemical pre-treatment, such as AOPs, is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of mineralization should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. Therefore, and with the aim to identify the best possible combination point between the chemical and biological treatment steps, toxicity and biodegradability analysis must be performed.

Solar Photo-Fenton treatment

Table 4 collects acute toxicity and short-term biodegradability results obtained from cork boiling wastewater treatment with solar photo-Fenton under different conditions, considering a COD elimination of 50% in all the cases. First of all, it is important to highlight how physico-chemical pre-treatment worsened raw wastewater's characteristics as initial toxicity increased considerably for PW1 and PW2. Furthermore, only a great reduction in acute toxicity was detected after the photo-Fenton treatment of PW2. Regarding biodegradability, a slight enhancement was observed at the end of the treatment of RW and PW2, whilst PW1 remained non-biodegradable.

TABLE 4

The still high values of acute toxicity after solar photo-Fenton pre-treatment of PW1, jointly with the low biodegradability according to respirometric analysis, made it interesting to perform a long term biodegradability study by applying a Zahn-Wellens test. This assay allowed evaluating the behaviour of a conventional activated sludge in contact with the real wastewater for a long time (28 days). Besides, information about possible biomass adaptation, making PW1 biological treatment feasible as a post-treatment step, could be obtained from the test. As it is observed in Figure 4, only the last sample with a COD of 317 mg L^{-1} ($Q_{UV}=36.2 \text{ kJ L}^{-1}$ and $560 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$ consumed) nearly achieved the 70% of biodegradability threshold after 6 days of bio-

treatment. In consequence, combination of chemical-biological oxidation technologies seems not to be the best treatment option for this kind of industrial wastewater due to the long treatment time (640 min) required for the photo-Fenton process as a first step.

FIGURE 4

Ozonation treatment

Table 5 presents toxicity and biodegradability results when ozonation under different conditions was applied. In all cases a treatment time of 4.5 h was considered. As it is shown, RW remained non-toxic and the inhibition percentage of PW1 decreased sharply to 33% after ozonation treatment at pH 7. On the contrary, PW1 ozonation at pH 10 and O₃/H₂O₂ treatment at pH 7 and 10 showed just a slight toxicity decrease, although it was maintained over 50% of inhibition.

Regarding biodegradability, all the wastewater fractions shifted from non-biodegradable to slightly biodegradable independently of the experimental conditions. This means that RW and PW1 are sensitive to be further treated by a biological system after being partially oxidized by ozonation.

These short term toxicity and biodegradability favourable results made it unnecessary to carry out long term biodegradability assays by Zahn-Wellens test. The significant decrease in toxicity inhibition percentages and the important increase in short term biodegradability analysis highlight a feasible combination between ozonation (RW (pH7), whose toxicity and biodegradability values after the treatment were 0% and 0.28, respectively; and PW1 (pH7) whose toxicity and biodegradability final values were 33% and 0.19, respectively) and a conventional bio-treatment for the remediation of the industrial wastewater under study.

TABLE 5

4 CONCLUSIONS

After cork boiling wastewater physico-chemical pre-treatment, an improvement of the main measured parameters took place, observing better results when Fe³⁺ was used as a coagulant agent. However, raw wastewater (RW) exhibited the best results after the solar photo-Fenton process, given that it required lower energy and hydrogen peroxide consumption (main parameters considered in an industrial plant design) than PW1 and PW2 treatment.

From the point of view of toxicity and biodegradability, no physic-chemical pre-treatment would be necessary for the treatment real cork boiling wastewater by ozonation. Accordingly, the treatment line would be RW ozonation at pH 7 and final DOC elimination in an advanced biological process.

Comparing solar photo-Fenton and ozonation processes, both advanced oxidation processes tested have been clearly demonstrated to be able to increase biodegradability of cork boiling wastewater.

Finally, it is necessary to highlight the increase of toxicity values for the real wastewater after the physic-chemical pre-treatment while biodegradability remained constant. Biodegradability for RW and PW2 slightly improved after photo-Fenton treatment, but not for PW1. On the other hand, after ozonation treatments, toxicity showed slight decrease, except for RW that remained non-toxic. Better results were observed regarding biodegradability enhancement. This means that RW and PW1 could be further treated by a biological system after being partially oxidized by ozonation.

This work presents a general protocol for identifying the best combined treatment line for a specific industrial wastewater. This protocol should include preliminary physic-chemical studies followed by the combination of chemical and biological processes. As it is widely approved within the scientific community, toxicity and biodegradability assays must complete chemical analysis for determining the best combination strategy. The decision between one and other treatment (in this case solar photo-Fenton or ozonation) must be based on a deep economic assessment that should be performed for the specific industrial emplacement, taking into account solar irradiance, specific water discharge normative, electricity costs, etc. Results extracted from the application of this protocol should constitute the basis of a future viability study for these technologies scaling-up.

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Table 1. Cork boiling wastewater characterization.

Parameter	Value (mg L⁻¹)
pH	7.2
Conductivity (mS cm ⁻¹)	1.1
Turbidity (NTU)	163
TSS	290
COD	1240
DOC	586
Total nitrogen	27.8
Total iron	3.3
Na ⁺	60.1
NH ₄ ⁺	15.1
K ⁺	224.6
Mg ²⁺	20.3
Ca ²⁺	99.3
Cl ⁻	134
SO ₄ ²⁻	4.9
PO ₄ ³⁻	<DL
NO ₃ ⁻	<DL
Biodegradability	0.13 (Slightly biodegradable)
Toxicity	8.6% (Non-toxic)

Biodegradability=(CODb/COD)

DL= detection limit

Table 2. Comparison of different pre-treatments for cork boiling wastewater.

	PW1	PW2
COD (mg O₂ L⁻¹)	480	680
DOC (mg L⁻¹)	290	391
pH	2.8	3.1
Conductivity (mS cm⁻¹)	0.8	1.1
Turbidity (NTU)	116	136
TSS (mg L⁻¹)	70	120
Final total iron (mg L⁻¹)	19.6	21.1
Toxicity (%I)	90	100
Biodegradability	0.08	0.13

PW1 pre-treated using FeCl₃·6H₂O

PW2 pre-treated using FeSO₄·7H₂O

Table 3. Comparison of ozonation under different operating conditions after 4.5 h of PW1 fraction treatment.

	O₃(pH 7)	O₃(pH 10)	O₃(pH 7)/H₂O₂	O₃(pH 10)H₂O₂
COD (Elimination %)	13.5	33	18.5	13
DOC (Elimination %)	16	11.5	19	17
pH_i-pH_{f(4.5h)}	7.2-5.1	10-6.2	7.1-5.8	9.8-7.6
O₃ (g L⁻¹)	0.4	0.48	0.43	0.68
H₂O₂ consumed (mg L⁻¹)	--	--	200	200

Table 4. Toxicity and biodegradability corresponding to solar photo-Fenton tests (50% of COD removal) for RW, PW1 and PW2 treatment.

Wastewater Fraction	Toxicity* (% Inhibition)	Biodegradability**	Q_{UV} (kJ L⁻¹)	H₂O₂ consumed (mg L⁻¹)
RW	8.6 – 0	0.13 – 0.30	59.3	698
PW1	90 - 86	0.08 - 0.08	62	780
PW2	100 – 62	0.13 - 0.33	80.5	1100

*Toxicity: Initial Toxicity– Toxicity when 50 % of COD was removed.

**Biodegradability: Initial biodegradability-biodegradability when 50 % of COD was removed.

Table 5. Toxicity and biodegradability corresponding to ozonation of RW and PW1 (treatment time of 4.5 h).

Experimental conditions	Toxicity* (% Inhibition)	Biodegradability**	O₃ consumed (g L⁻¹)	H₂O₂ consumed (g L⁻¹)
RW (pH 7)	8.6 – 0	0.13 – 0.28	0.38	-
PW1 (pH 7)	90 – 33	0.08 - 0.19	0.40	-
PW1 (pH 7)/H₂O₂	90 - 76	0.08 - 0.26	0.43	0.20
PW1 (pH 10)	90 - 76	0.08 - 0.22	0.48	-
PW1 (pH 10)/H₂O₂	90 – 67	0.08 – 0.19	0.68	0.20

*Toxicity (%): Toxicity₀ (%) – Toxicity_{4.5h} (%)

**Biodegradability: Biodegradability₀ – Biodegradability_{4.5h}

FIGURES CAPTION

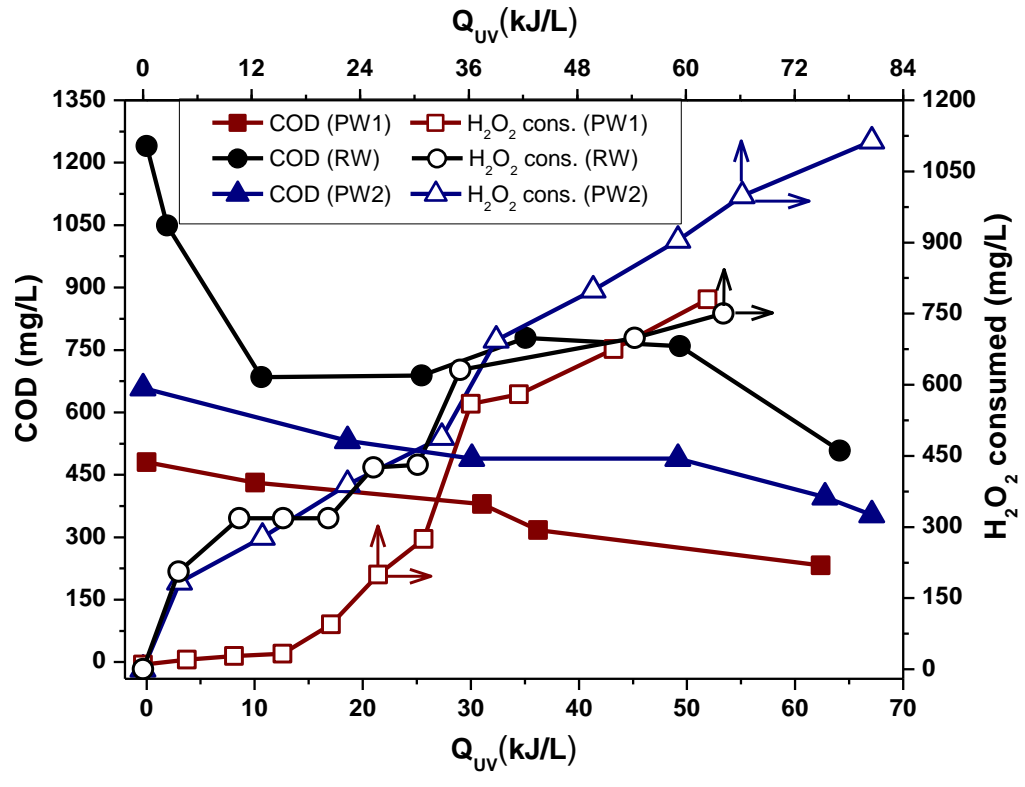
Figure 1. Evolution of COD and H₂O₂ consumption for solar photo-Fenton treatment of RW, PW1, PW2 (Experimental conditions: pH=2.6-2.8, [Fe³⁺]=20 mg L⁻¹, T=35°C, [H₂O₂]=200 mg L⁻¹).

Figure 2. Evolution of COD and O₃ consumption at initial pH of 7 and 10 for PW1 treatment by ozonation.

Figure 3. Evolution of COD and O₃ consumption at initial pH 7 and 10 for PW1 treatment by O₃/H₂O₂ (three doses of 200 mg/L).

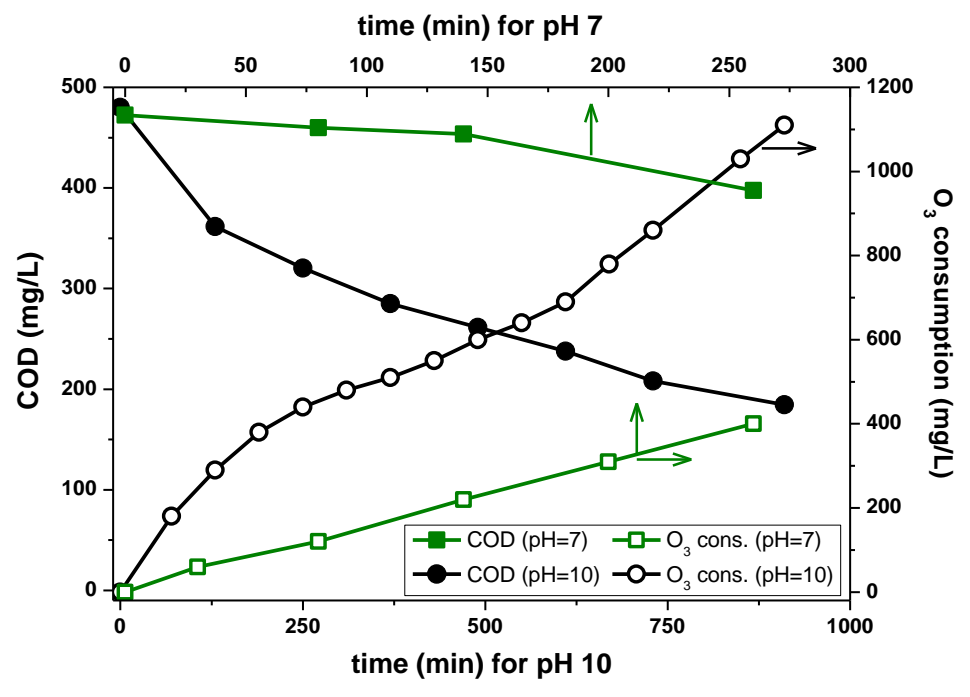
Figure 4. Long term biodegradability study of PW1 photo-Fenton samples by Zahn-Wellens test.

1 Figure 1.



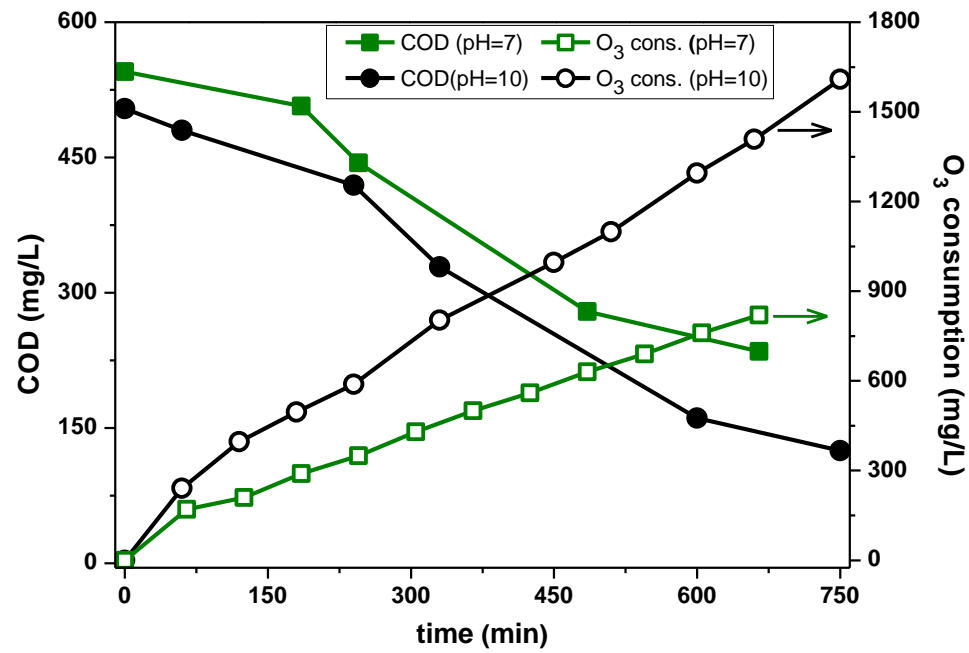
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1 Figure 2.



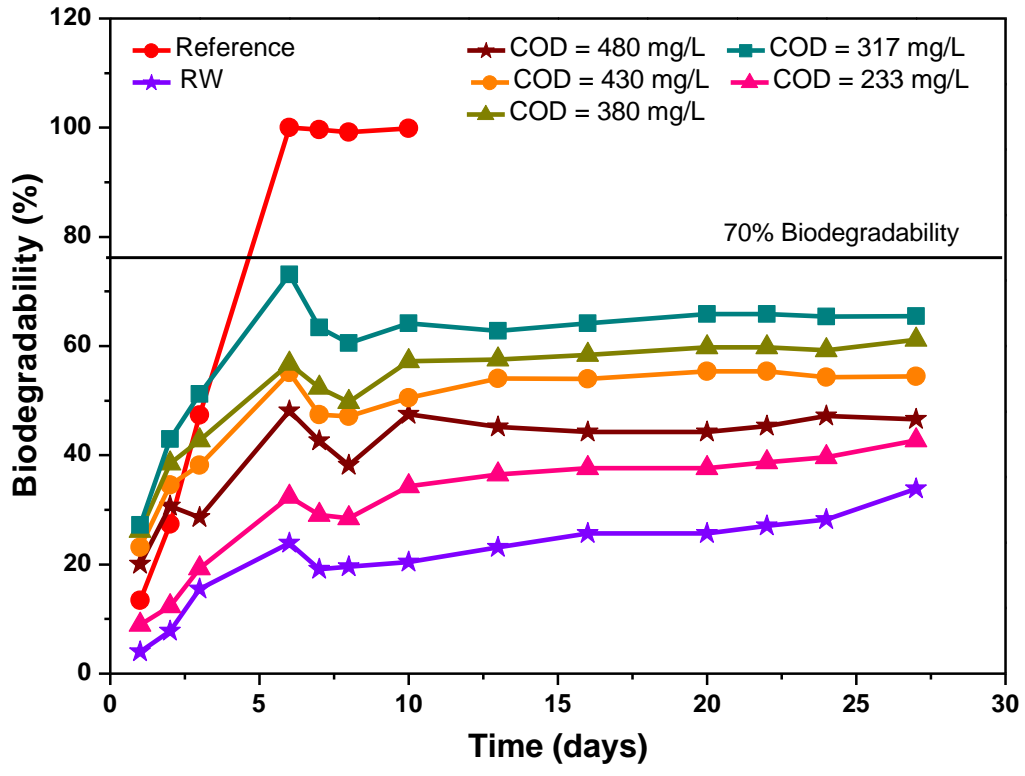
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1 Figure 3.



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1 Figure 4.



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