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Application of biological oxidation and solar driven advanced oxidation processes to remediation of winery wastewater

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ABSTRACT

Biological oxidation and solar driven advanced oxidation processes (AOPs) applied as a single stages were tested at a pilot plant equipped with an immobilized biological reactor (IBR) and a photocatalytic system with compound parabolic collectors (CPCs) for the remediation of a winery wastewater ($DOC_{average}$ = 882 mg L^{-1}; pH 4.1). Due to the variable nature of winery wastewater composition and quantity, the application of AOPs as a single or as preliminary stage can be an effective alternative to only conventional biological treatment. Regarding the AOPs systems tested ($TiO_2/H_2O_2/UV$ and $Fe^{2+}/H_2O_2/UV$), the solar photo-Fenton reaction (optimized at pH 2.8 and 55 mg Fe^{2+} L^{-1}) showed the highest efficiency, being necessary an UV dose of 100 kJ_{UV} L^{-1} and 338 mM H_2O_2 (15 mg H_2O_2 mg C^{-1}) to achieve a COD value lower than 150 mg O_2 L^{-1}, which is agreement with the discharge limits into receiving waters imposed by the Portuguese Legislation (Decree-law n° 236/98). To achieve the same COD target value using only the IBR system or the combination of solar-photo-Fenton (22 kJ_{UV} L^{-1}; 80 mM H_2O_2 consumed) and biological systems, approximately 10 and 6 days (time necessary for the biological oxidation) are required. The efficiency of the AOPs in the treatment of simulated and real winery wastewaters was also compared.

1. Introduction

Portugal is one of the most renowned producers of wine in the world, with 600,000 L of wine produced in 2009 [1]. After wine grape harvest, the industrial production of the wine involves a series of steps, such as: separation, crushing and pressing of grapes, vintage sulfating, alcoholic fermentation, aging respite and finally the bottling for launching in the market. Winery wastewaters production is inevitable, achieving values of 3000–5000 L ton^{-1} of grapes crushed [2], resulting essentially from product loss and many different cleaning operations, including washing activities during the crushing/maceration and pressing of grapes, as well as the rinsing of fermentation tanks, barrels and other items of equipment, with singular characteristics depending on process activities [3]. In particular, the winery wastewater production is seasonable, influenced by flexibility of wine crop, where the spatiotemporal variations are very significant, affecting directly the composition and the volume of the effluent generated. In addition, the bio-fermentation step may take advantage of different types of yeast to consume the sugars present in the grapes and converts them into alcohol and CO_2. Thus, different varieties of grapes and strains of yeasts result in different types of wine and consequently winery wastewaters with different characteristics. In general, the typical raw winery wastewater presents a pH between 3 and 4, COD ranges from 320 to 296,119 mg O_2 L^{-1} and BOD_5 values around 125–130,000 mg O_2 L^{-1} [4]. The main organic compounds present in this kind of wastewaters are soluble sugars (fructose and glucose), organic acids (tartaric, lactic and acetic), alcohols (glycerol and ethanol) and high-molecular-weight compounds, such as polyphenols, tannins and lignin [5]. The treatment and management of this wastewater causes a considerable apprehension, especially considering the environmental restrictions required to discharge into water bodies (Portuguese legislation, Decree-law n° 236/98 – Table 1). One of most antique technique used to treat this type of wastewater is the septic tank leach field, however this practice suffers from serious problems related to plugs originated by the high solid loading rate, apart from significance odor release problems [6]. Although the conventional biological reactor system can reduce significantly the organic carbon matter content, the challenge when applied to variable nature of winery wastewater composition and quantity can be associated with the series of start-up and shut-down operations, including periods of inactivity [7].

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Table 1
Characteristics of the winery wastewater samples and discharge limits established by the Portuguese legislation (Decree-Law n° 236/98).

Parameter	Discharge limits (Decree-law n° 236/98)	Winery wastewater			
		Real	Simulated	After solar photo-Fenton treatment[d]	After biological treatment[e]
pH	6.0–9.0	4.1 ± 0.2	6.3 ± 0.3	2.8	8.1
IC (mg C L^{-1})	–	10 ± 1	39 ± 5	8.4	169
DOC (mg C L^{-1})	–	882 ± 81	1030 ± 40	73	39
COD (mg O_2 L^{-1})	150	2958 ± 67	–	145	120
BOD_5 (mg O_2 L^{-1})	40	1500 ± 100	–	120	–
BOD_5/COD	0.27	0.51 ± 0.05	–	0.82	–
Polyphenols (mg caffeic acid L^{-1})	–	12 ± 3	11.4 ± 0.4	<1.6	2.4
Abs_{254}[c]	–	0.24 ± 0.04	0.35 ± 0.05	–	–
Total dissolved iron (mg (Fe^{2+} + Fe^{3+}) L^{-1})	2[a]	3.3 ± 0.9	–	45.3	–
Sulfate (mg SO_4^{2-} L^{-1})	2000	7 ± 1	–	661	229
Chloride (mg Cl^- L^{-1})	–	26.9 ± 0.3	–	24	53
Total dissolved nitrogen (mg N L^{-1})	15[b]	5 ± 3	–	14	5.9
Ammonia (mg N-NH_4^+ L^{-1})	7.8	0.8 ± 0.1	–	6.5	0.1
Nitrate (mg N-NO_3^- L^{-1})	11.3	0.6 ± 0.2	–	0.5	<0.02
Nitrite (mg N-NO_2^- L^{-1})	–	3 ± 1	–	<0.03	4.7

– Value not measured.
[a] Total iron.
[b] Total nitrogen.
[c] Using a cuvette with path length of 1 cm.
[d] Using $[Fe^{2+}]_0$ = 55 mg L^{-1} and pH 2.8.
[e] After 6 days of treatment.

Another inconvenient, is the possible presence of high concentration of polyphenols in the wastewater (0–1450 mg L^{-1} [4]), which can reduces significantly the microbial activity [8]. Therefore, given the dynamic nature of wine production, the direct use of AOPs as a single stage to remediate the winery wastewater without passing firstly by the classical biological treatment is not entirely unexpected. The AOPs are based on the generation of powerful reactive chemical species, such as hydroxyl radicals (•OH), degrading even the most recalcitrant molecules into biodegradable compounds or completely mineralize them into CO_2, H_2O and inorganic ions [9,10]. There are numerous options and different approaches and technologies to treat winery wastewater with AOPs, such as: (i) ozone-based (O_3, O_3/UV and O_3/UV/H_2O_2) [11,12]; (ii) photocatalytic/photolytic reaction with titanium dioxide and artificial light (λ = 310–435 nm) [6]; (iii) photo-Fenton reaction in heterogeneous (natural clay with Fe 4.58 wt%, Al 12.42 wt%, Ti 0.41 wt% as the mainly metals) [13] and homogeneous phase [14]; and (iv) Fenton's reagent [15].

The main goal of this work is to evaluate the remediation efficiency of a real winery wastewater using two treatment strategies at pilot plant scale: (i) biological oxidation in an immobilized biological reactor (IBR); (ii) heterogeneous (TiO_2/H_2O_2/UV) and homogeneous (Fe^{2+}/H_2O_2/UV) solar driven AOPs, using compound parabolic collectors (CPCs); and (iii) pre-oxidation using a solar photo-Fenton system and possible combination with a further biological treatment. In addition, the efficiency of the AOPs was compared using real and synthetic (dilution of red wine in distilled water) winery wastewaters.

2. Experimental methodology

2.1. Chemicals

AOPs were performed employing titanium dioxide (Degussa, P25, 80% anatase and 20% rutile), hydrogen peroxide (50% (w/v), 1.10 g cm^{-3}, Quimitécnica, S.A.), iron sulfate heptahydrated (Panreac) and sulfuric acid (96%, 1.84 g cm^{-3}, Pronalab) for pH adjustment. Photo-treated wastewater was neutralized with commercial grade sodium hydroxide (30% (w/v), 1.33 g cm^{-3}, Quimitécnica, S.A.). The pH control in the biological reactor was achieved with sodium hydroxide and sulfuric acid. Ultrapure and pure water for analyses was obtained using a Millipore® system (Direct-Q model) and a reverse osmosis system (Panice®), respectively.

2.2. Analytical determinations

Sulfate, chloride, nitrate, phosphates, nitrite and low-molecular-weight carboxylate anions (acetate, propionate, formate, pyruvate, valerate, malonate, maleate, oxalate, phthalate and citrate) were measured by ion chromatography (Dionex ICS-2100) using a Dionex Ionpac (column AS 11-HC 4× 250 mm; suppressor ASRS®300 4 mm). Sodium, potassium, ammonium, magnesium and calcium were also analyzed by ion cromatography (Dionex DX-120), using a Dionex Ionpac (column: CS12A 4× 250 mm; suppressor: CSRS®300 4 mm). The analyses of anions/cations were performed at isocratic elution mode, using 30 mM NaOH/20 mM methanesulfonic acid at a flow rate of 1.5/1.0 mL min^{-1}, respectively. The gradient program used for low-molecular-weight carboxylate anions comprised a pre-run for 8 min with 1 mM NaOH, 20 min with 30 mM NaOH and 10 min with 60 mM NaOH, at a flow rate of 1.5 mL min^{-1}, using an eluent generator cartrige (Dionex, RFICTM). Dissolved organic carbon (DOC) was measured in a TC-TOC-TN analyzer equipped with a NDIR detector calibrated with standard solutions of potassium hydrogen phthalate (total carbon) and a mixture of sodium hydrogen carbonate/sodium carbonate (inorganic carbon) and coupled with an ASI-V autosampler (Shimadzu, model TOC-VCSN). Total dissolved nitrogen was measured in the same TC-TOC-TN analyzer coupled with a TNM-1 unit (Shimadzu, model TOC-VCSN) calibrated with standard solutions of potassium nitrate, after thermal decomposition and NO detection by chemiluminescence method. COD concentration was measured by Merck®Spectroquant kits (Ref.: 1.14541.0001). Evaluation of H_2O_2 concentration during experiments was performed by the metavanadate method, based on the reaction of H_2O_2 with ammonium metavanadate in acidic medium, which results in the formation of a red-orange color peroxovanadium cation, with maximum absorbance at 450 nm

[16]. Iron concentration was determined by colorimetry with 1,10-phenantroline according to ISO 6332 [17]. Total polyphenols concentration was measured by spectrophotometry at 765 nm using the Folin-Ciocalteau reagent (Merck) [18]. Polyphenols content is expressed as mg of caffeic acid L^{-1}. Absorbance at 450 nm (vanadate method), 510 nm (phenantroline method) and 765 nm (Folin–Ciocalteau method) were measured in a UNICAM Helios α spectrophotometer. All samples were pre-filtrated through 0.45 μm Nylon membrane filters from VWR before analysis. pH and temperature were measured using a pH meter HANNA HI 4522. The quantification of total suspended solids and volatile suspended solids was carried out according to the Standard Methods [19].

2.3. Biodegradability assays

Before biological tests and other analyses involving chemical oxidation, excess H_2O_2 present in samples was removed using a small volume of 0.1 g L^{-1} solution of catalase (2500 U mg^{-1} bovine liver) after adjusting sample pH to 6.5–7.5. DOC, COD and BOD_5 determinations were performed before the addition of catalase.

Biochemical oxygen demand (BOD_5) was determined according to OECD-301F test using an OxiTop (manometric respirometry), described in Standard Methods [19]. A 28 days biodegradability Zahn-Wellens test was performed according to EC protocol, Directive 88/303/EEC [20]. 250 mL of pre-treated samples at different photo-Fenton times, without hydrogen peroxide, were added to an open glass vessel, magnetically stirred and kept in the dark at 25 °C. Activated sludge from a WWTP in Porto, previously centrifuged, and mineral nutrients (KH_2PO_4, K_2HPO_4, Na_2HPO_4, NH_4Cl, $CaCl_2$, $MgSO_4$ and $FeCl_3$) were added to samples. Control and blank experiments were prepared using glucose as carbon source, to which mineral nutrients and activated sludge were also added. The percentage of biodegradation (D_t) was determinate by the following equation:

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \quad (1)$$

where C_A and C_{BA} are DOC (mg L^{-1}) in sample and in blank, measured 3 h after starting the experiment, C_t and C_B are DOC (mg L^{-1}) in sample and in blank, measured at sampling time t.

The average oxidation state (AOS) and carbon oxidation state (COS) were also calculated using Eqs. (2) and (3), which allow evaluating the oxidation degree and effectiveness of the oxidative process [4].

$$\mathrm{AOS} = 4 - 1.5\left[\frac{\mathrm{COD}}{\mathrm{DOC}}\right] \quad (2)$$

$$\mathrm{COS} = 4 - 1.5\left[\frac{\mathrm{COD}}{\mathrm{DOC_0}}\right] \quad (3)$$

where DOC is the dissolved organic carbon at time t (mg C L^{-1}), DOC_0 is the initial dissolved organic carbon of the solution (mg C L^{-1}), and COD is the chemical oxygen demand at time t (mg O_2 L^{-1}). AOS and COS take values between +4 for CO_2, the most oxidized state of carbon, and −4 for CH_4, its most reduced state. AOS takes into consideration the organic matter in solution, while in COS calculation, the CO_2 eliminated from the solution is also considered [2].

For biodegradability tests, the photocatalytic experiment was performed maintaining all parameters (pH 2.8; $[Fe^{2+}]$ = 55 mg L^{-1}), except the H_2O_2 dose. In this case, a specific amount of H_2O_2 was added to the photo-reactor, and after H_2O_2 total consumption, a sample was taken for bioassays and a new dose of H_2O_2 was added. This procedure of "addition-total consumption-sample collection-addition" is very important since it prevents any reaction in dark conditions after sample collection, during storage and possible interferences in bioassays. Considering this procedure, experimental data must be expressed in terms of H_2O_2 consumption and not accumulated UV energy L^{-1} of winery wastewater.

2.4. Winery wastewater samples

The winery wastewater was collected in September 2011 at a red wine company located in the northeast of Portugal after the vintage season. A volume of 250 L of winery wastewater was stocked in appropriate containers under dark and low temperature. The simulated winery effluent was prepared by diluting common red wine obtained in a local supermarket with pure water (DOC = 1030 mg L^{-1}), in the proportion required to obtain an initial DOC similar to the real wastewater (around 1000 mg C L^{-1}), which led to a polyphenols content of 11 mg caffeic acid L^{-1}. Table 1 presents the main chemical-physical characteristics of winery samples used in this work.

2.5. Experimental set-up

2.5.1. Solar CPC reactor

All the solar driven AOPs' experiments were carried out in a CPC pilot plant located at the roof of Faculty of Engineering of Porto University (FEUP), Portugal (Lat.: 41°10′41″N, Long.: 8°35′50″W). The solar facility consists of a CPC illuminated area of 4.16 m^2, two recirculation tanks (45 and 100 L), two recirculation pumps (25 L min^{-1}) (ARGAL, model TMB), two flowmeters (Stübe, model DFM 165-350), polypropylene valves (FIP) and connecting tubing, being operated in batch mode. The solar collectors are made up of four CPC units (1.04 m^2) with five borosilicate tubes each (Schott-Duran type 3.3, Germany, cut-off at 280 nm, internal diameter 46.4 mm, length 1500 mm and thickness 1.8 mm) connected by polypropylene junctions. The plant is mounted on a fixed platform titled 41° (local latitude) with south orientation and can be operated in two ways: using the CPCs total area of 4.16 m^2 or using 2.08 m^2 individually, which makes possible to perform two different experiments at the same time using identical solar radiation conditions. The intensity of solar UV radiation is measured by a global UV radiometer (ACADUS 85-PLS) placed at the top of the pilot plant at the same angle, which provides UV data in terms of incident W m^{-2}.

Eq. (4) allows to obtain the amount of accumulated UV energy ($Q_{UV,n}$ kJ L^{-1}) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (4)$$

where t_n is the time corresponding to n-water sample, V_t is the total reactor volume, A_r is the illuminated collector surface area, and $\overline{UV}_{G,n}$ is the average solar ultraviolet radiation measured during the period Δt_n.

2.5.2. Biological system

The biological system is composed by a conditioner flat-bottom tank (50 L) and an immobilized biomass reactor (45 L). The conditioner tank is equipped with a pH control unit (CRISON, electrode and PH27P controller) and a mechanical stirrer (TIMSA) for pH adjustment, using either H_2SO_4 or NaOH dosed by means of two metering pumps (DOSAPRO MILTON ROY, GTM series, model A). The IBR is a flat-bottom container packed with 62 units of propylene rings (nominal diameter 50 mm), colonized by activated sludge from a municipal wastewater treatment plant (Freixo WWTP). The bioreactor is also equipped with a dissolved oxygen control unit (CRISON, electrode and OXI49P controller) and air is supplied by a blower (compressor-HAILEA model V-20; air flow

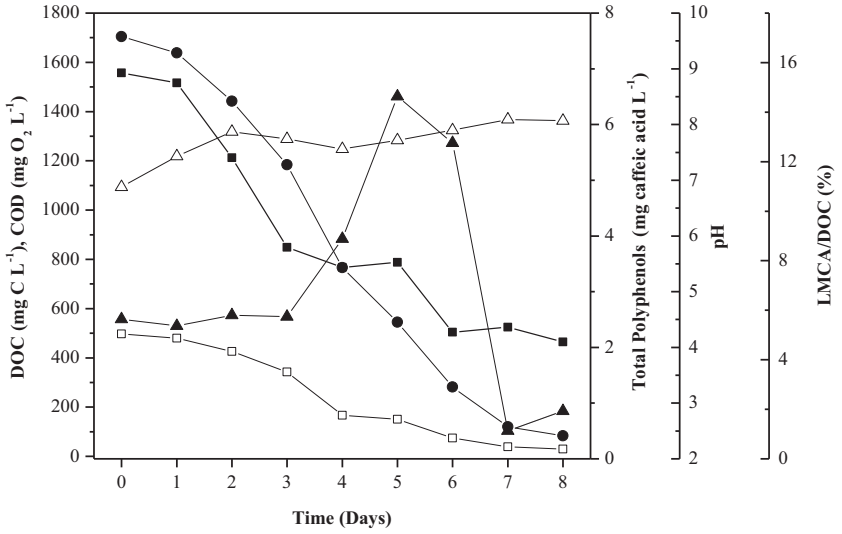

Fig. 1. Evaluation of winery wastewater degradation using an IBR process: □ – DOC; ● – COD; ■ – total polyphenols; △ – pH; ▲ – LMCA/DOC ratio.

rate = 20 L min^{-1}; ceramic air diffuser) for maintaining dissolved oxygen concentration in the system in the selected range (0.5–2 mg O_2 L^{-1}).

2.6. Experimental procedure

2.6.1. Solar driven AOPs

A volume of 40 L of winery wastewater (real or simulated) was added to one recirculation tank of the CPC units (2.08 m^2) and homogenized by turbulent recirculation during 15 min in darkness (a first control sample was taken to characterize the wastewater). For the heterogeneous photocatalytic tests (TiO_2/H_2O_2/UV) using the simulated wastewater, after taking the first sample, the pH was adjusted to 4.5 with H_2SO_4, the mixture was recirculated for more 15 min and a second sample was collected to confirm the pH. TiO_2 (200 mg L^{-1}) was added, and after recirculation for more 15 min, a third sample was collected and a first dose of H_2O_2 (50% (w/v)) was added to the mixture, just before uncovering the CPCs. For the photo-Fenton tests, the pH was adjusted with H_2SO_4 to 2.6–2.9 and a second sample was collected after 15 min of recirculation. Afterwards, iron salt ($FeSO_4 \cdot 7H_2O$) was added and well homogenized for 15 min and a third sample was taken for iron concentration control. Finally, the first dose of H_2O_2 was added and the CPCs were uncovered. For the UV-photolysis test (real wastewater), no acidification, no iron and no H_2O_2 addition were performed. In all cases, samples were taken at different time intervals to evaluate the progress of the oxidation. The H_2O_2 concentration was maintained between 200 and 500 mg L^{-1} during the entire run, by adding amounts to compensate the consumed ones, as determined by analysis throughout the experiments.

2.6.2. Biological process

A volume of winery wastewater sample was added into the neutralization tank, where pH was neutralized with NaOH to a pH around 7 (controlled in a range between 6.5 and 7.5). Following this preliminary step, the neutralized effluent was pumped to the IBR tank previously colonized by activated biomass, which operated as an up-flow reactor at a recirculation rate of 6.6 L min^{-1} and a hydraulic residence time of 7.6 min. The main chemical parameters of the winery wastewater during the biological treatment were evaluated at different days.

3. Results and discussion

3.1. Winery wastewater characterization

The winery wastewater used in this study presented a rosette color and strong odour, a high organic content (DOC = 882 mg C L^{-1}; COD = 2958 mg O_2 L^{-1}), considerable biodegradability (BOD_5 = 1500 mg O_2 L^{-1}; BOD_5/COD = 0.5), pH slightly acidic (4.1), low nitrogen content (5 mg N L^{-1}; 0.8 mg N-NH_4^+ L^{-1}; 0.6 mg N-NO_3^- L^{-1}; 3 mg N-NO_2^- L^{-1}) and low total polyphenols content (12 mg caffeic acid L^{-1}) (Table 1). The characteristics of the winery wastewaters can vary widely mainly due to the type of wine grapes and strains of yeasts used to fermentation steps. Petruccioli et al. [3] characterized two different wineries, Lungarotti (Torgiano, Perugia, Italy) and Coop Vitivinicola of Orvieto (Orvieto, Italy), obtaining values of COD = 800–11,000 mg O_2 L^{-1}; BOD_5 = 500–6900 mg O_2 L^{-1}; N-NH_3 = 0.001–2 mg L^{-1} and total polyphenols content = 5.8–33.6 mg L^{-1}, which are in agreement with the characteristics of the effluent used in this work.

3.2. Evaluation of biological treatment

Since the effluent presents a considerable biodegradability, a biological treatment using an IBR was performed (Fig. 1). A volume of 77 L of neutralized winery wastewater and 12 L of suspended biomass used as inoculum (total suspended solids – TSS = 5170 mg L^{-1} and volatile suspended solids – VSS = 4300 mg L^{-1}) were added to the IBR, resulting in a suspension with an initial DOC value of 496 mg C L^{-1} (dilution effect). A significant decay in COD (95%) and DOC (94%) was observed after 7 days of treatment, achieving final values of DOC and COD of 30 mg C L^{-1} and 84 mg O_2 L^{-1}, respectively, which is agreement with the discharge limits into natural waters according to the Portuguese Legislation (Decree-law n° 236/98). The biodegradation rate constant observed between the 1st and 7th days was approximately 268 mg O_2 L^{-1} day^{-1} and 79 mg C L^{-1} day^{-1} (the amount of biomass fixed in the polypropylene supports was not possible to quantify). On the other hand, in the same period of treatment time (7 days), the IBR process showed a lower effectiveness in the elimination of polyphenols, achieving a residual concentration of 2.1 mg caffeic acid L^{-1}. The low molecular-weight carboxylate anions (LMCA)/DOC ratio values were almost constant during the first 3 days, followed by an increase up to a maximum of 14% in

Table 2
Kinetic constants for solar photo-Fenton (pH 2.8) and TiO_2/H_2O_2 systems.

$[Fe^{2+}]_0$ (mg L^{-1})	$[Fe^{2+}]_{average}$ (mg L^{-1})	$T_{average}$ (°C)	k^a (L kJ^{-1})	$r_o{}^b$ (mg C kJ^{-1})	k^c (mmol kJ^{-1})
Solar photo-Fenton experiments using real winery wastewater sample					
30	18.7	20	0.018 ± 0.001	14 ± 1	1.7 ± 0.2
55	31.1	29	0.033 ± 0.002	24 ± 1	3.5 ± 0.1
75[d]	61.5	22	0.028 ± 0.004	20 ± 3	2.5 ± 0.3
75[e]	–	24	0.053 ± 0.004	47 ± 4	9.1 ± 0.6
Solar photo-Fenton experiment using synthetic winery wastewater sample					
55	37.5	35	0.027 ± 0.002	26 ± 2	6.2 ± 0.3

Sample	$pH_{average}$	$T_{average}$ (°C)	k^a (L kJ^{-1})	$r_o{}^b$ (mg C kJ^{-1})	k^c (mmol kJ^{-1})
Solar TiO_2 experiments					
Synthetic	3.3	28	0.009 ± 0.001	6.7 ± 0.4	7.4 ± 0.3
Real	4.9	21	0.008 ± 0.001	9.7 ± 0.6	3.3 ± 0.2

– Value not measured.
[a] Pseudo-first order kinetic constant for DOC degradation (Q_{UV} > 17 kJ L^{-1}).
[b] Initial DOC reaction rate.
[c] H_2O_2 consumption rate (Q_{UV} > 17 kJ L^{-1}).
[d] Reaction carried out in $[H_2O_2]$ = 200–500 mg L^{-1}.
[e] Reaction carried out in $[H_2O_2]$ = 1000–5000 mg L^{-1}.

the day 5, and then decreased in the subsequently days due its high biodegradability. In terms of nitrogen species, the total dissolved nitrogen and nitrite content remained almost constant during the treatment (below 7.5 and 4.7 mg N L^{-1}, respectively). In the clarifier, after 7 days of biological process, the TSS and VSS were 7.1 and 3.4 mg L^{-1}, respectively, meaning that the suspended biomass added to the wastewater was fixed in the inert support.

Petruccioli et al. [3] applied a packed-bed bioreactor (PBB) with Rachig rings and a fluidized-bed bioreactor (FBB) to the treatment of different winery wastewaters with the characteristics reported above. Considering a hydraulic retention time of 1.2 days and a microbial biomass concentration of 0.08 kg m^{-3} for PBB and 2.2 days and microbial biomass of 0.6 kg m^{-3} for FBB, a final COD value below 500 mg L^{-1} was reached, representing a COD removal efficiency of 90.1 and 88.7%, respectively, as the best result.

3.3. Evaluation of solar driven AOPs treatment

Solar driven AOPs were tested as an alternative approach to winery wastewater remediation. The results obtained using only direct solar radiation (photolysis) showed negligible effect on DOC removal (real winery wastewater sample), attaining a removal of only 8% after 105 kJ L^{-1} (data not showed).

A first approach to the treatment of the winery wastewater with AOPs was the solar photo-Fenton process. A pH value of 2.8 was selected for reaction not only because the predominant iron species in solution is $FeOH^{2+}$, which is the most photoactive ferric ion-water complex [21], but also because it avoids iron(III) precipitation. According to Malato Rodriguez et al. [22], a dissolved iron concentration of 20 mg L^{-1} is enough to absorb all the solar photons in a photoreactor with a 5-cm light path length. This concentration value is also more advisable, as the effluent is more compatible with the subsequent biotreatment [23]. However, as color winery wastewaters present different light-absorbing species, the amount of iron needed to absorb the maximum of solar photons must be optimized. Fig. 2a presents the mineralization of the winery wastewater at three different initial iron concentrations (30, 55 and 75 mg Fe^{2+} L^{-1}), showing an "induction period" of approximately 17 kJ_{UV} L^{-1} due to wastewater color, which competes as photons absorbers with H_2O_2 and iron species, and to partial oxidation of the organics. The second part of the DOC degradation curve shows a first-order kinetic behavior (Table 2), associated to a DOC reduction of 80%, requiring 3.2, 4.1 and 2.7 mg H_2O_2 per mg of carbon mineralized, respectively for the experiments with 30, 55 and 75 mg Fe^{2+} L^{-1}. The H_2O_2 consumption profile (data not showed) suggests

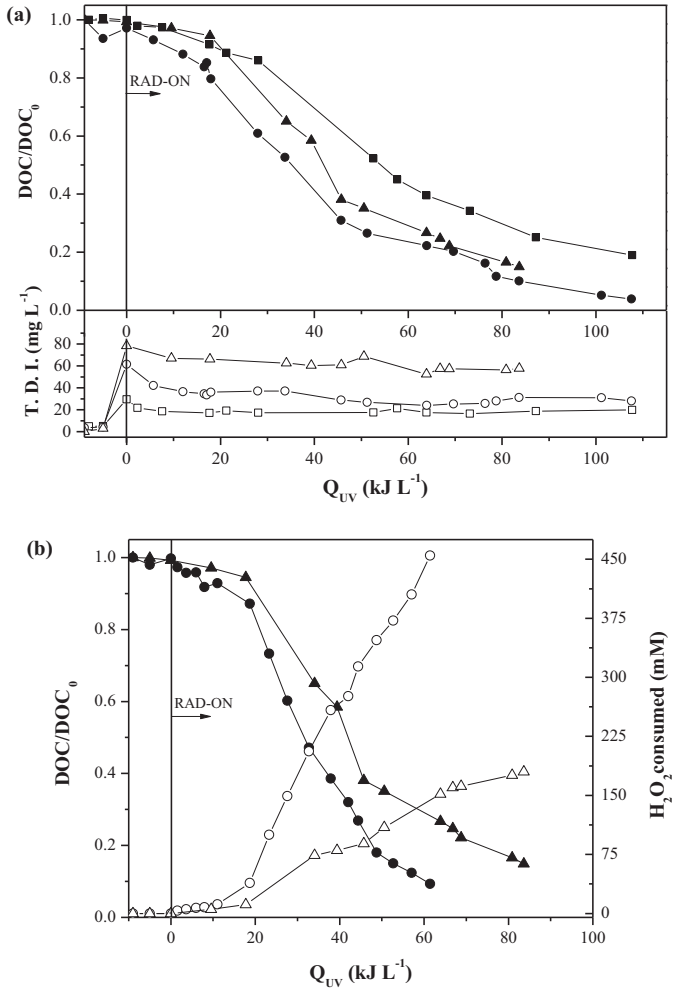

Fig. 2. Solar photo-Fenton reaction of a winery wastewater at pH 2.8. (a) (■,□) $[Fe^{2+}]_0$ = 30 mg L^{-1}; (●,○) $[Fe^{2+}]_0$ = 55 mg L^{-1}; (▲,△) $[Fe^{2+}]_0$ = 75 mg L^{-1}. (b) $[Fe^{2+}]_0$ = 75 mg L^{-1} with $[H_2O_2]$ = 1000–4000 mg L^{-1} (●,○) and $[H_2O_2]$ = 200–500 mg L^{-1} (▲,△). Solid symbols: DOC/DOC_0; Open symbols: $[H_2O_2]$ consumed and total dissolved iron (TDI) concentration.

a linear correlation with the UV energy accumulated unit of volume of wastewater during the second reaction period (Table 2). The total dissolved iron concentration decreased after H_2O_2 addition, suggesting the formation of strong complexes between Fe^{3+} and organic/inorganic constituents of the winery wastewater. Similar DOC abatement is observed for the two experiments with higher initial iron concentration (55 and 75 mg L^{-1}), achieving a fast decay of DOC (reduction of 80%) using a UV dose of 70 kJ_{UV} L^{-1}. Lucas et al. [14] reported a similar behavior in the treatment of a synthetic wastewater prepared with wine and grape juice, and iron doses higher than 55 mg L^{-1} showed a negligible improvement of the photo-Fenton reaction.

According to the kinetic constant values presented in Table 2, considering a pseudo-first order reaction, the optimum initial iron concentration for the treatment of this winery wastewater using a solar photo-Fenton reaction is 55 mg Fe^{2+} L^{-1} (average dissolved iron concentration of 31 mg L^{-1}).

The photo-Fenton reaction rate depends greatly on H_2O_2 concentrations, where too low concentrations can be the rate-limiting step and too high concentrations can compete with pollutants for the •OH and self-decomposition of H_2O_2 into O_2 and H_2O can also occur [24]. Fig. 2b shows the DOC profile for two different H_2O_2 concentration ranges (200–500 and 1000–5000 mg L^{-1}). To achieve 85% mineralization, a UV dose of 52 and 84 kJ_{UV} L^{-1} was necessary (or 8.4 and 14.8 mg H_2O_2 mg C^{-1}), respectively for the H_2O_2 concentration ranges between 200–500 and 1000–5000 mg L^{-1}. Although the photo-Fenton reaction rate increases when employing higher H_2O_2 doses (Table 2), the consumption of H_2O_2 increases by a factor of four, which is not an attractive option due to the high costs.

A second experimental approach to winery wastewaters treatment with solar driven AOPs was heterogeneous photocatalysis with TiO_2 in combination with H_2O_2, which can work as an electron scavenger, avoiding the electron/hole recombination and further increasing the reaction rates [25]. The TiO_2 concentration used was 200 mg L^{-1}, corresponding to the optimum concentration for the photoreactors used in this work, with an internal diameter of 46.4 mm [26]. Recently, Colina-Márquez et al. [27] showed by the accurate modeling of the radiation field in a CPC solar photoreactor by a six-flux absorption scattering model (SFM), that TiO_2 in the concentration of 200 mg L^{-1} is able to absorb 100% of the solar UV photons.

Fig. 3a and b shows the DOC removal profile for both real and simulated winery wastewaters using the TiO_2/H_2O_2 and Fe^{2+}/H_2O_2/UV solar systems. As observed, to achieve 60% mineralization of the synthetic and real winery wastewaters was necessary 31 and 44 kJ L^{-1}, consuming 150 and 161 mM H_2O_2 (or 9 and 11 mg H_2O_2 mg C^{-1}) using the Fe^{2+}/H_2O_2/UV solar systems, respectively. For the TiO_2/H_2O_2/UV system was necessary 80 and 92 kJ L^{-1}, consuming 220 and 311 mM H_2O_2 (or 12 and 18 mg H_2O_2 mg C^{-1}), respectively for synthetic and real winery wastewaters. According to these results, the solar photo-Fenton process is much more efficient than TiO_2/H_2O_2/UV solar photocatalysis, showing an initial reaction rate more than 2.5 times higher and a consumption of H_2O_2 2 times lower, considering the same mineralization. Synthetic wastewater is oxidized at a higher rate than real wastewater, which is associated mainly to the complex matrix of the real winery wastewater. For example, in terms of total polyphenols content, to achieve a residual concentration below 1.6 mg caffeic acid L^{-1} using the solar photo-Fenton reaction it was necessary a solar UV energy dose of 12 and 16 kJ L^{-1}, respectively for synthetic and real wastewaters. Considering these results and the fact that the majority of works reported in literature uses only synthetic wastewaters, a cautiously analysis of the results must be performed, regarding the possible process scale-up using the optimized parameters obtained for the synthetic wastewaters.

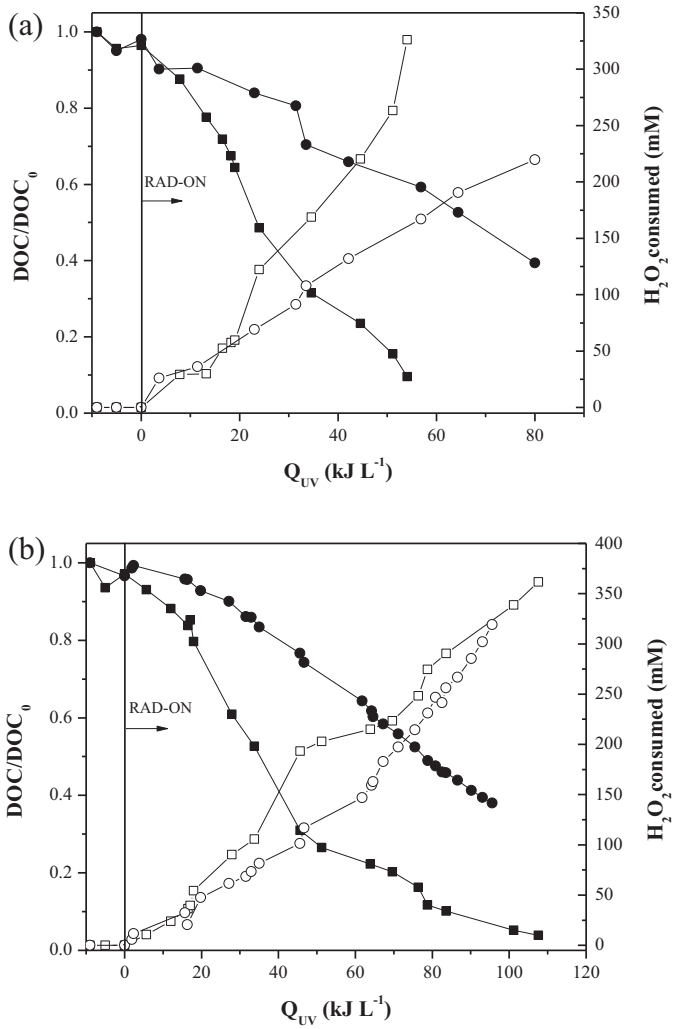

Fig. 3. Mineralization and H_2O_2 consumed during the treatment of a synthetic (a) and real (b) winery wastewater using the photo-Fenton (pH 2.8, $[Fe^{2+}]_0$ = 55 mg L^{-1}) (□,■) and TiO_2/H_2O_2/UV ($[TiO_2]_0$ = 200 mg L^{-1}) processes (○,●). Open symbols: $[H_2O_2]$ consumed; Solid symbols: DOC.

3.4. Biodegradability enhancement during solar photo-Fenton reaction

Although the winery wastewaters can be effectively treated using individually biological or chemical oxidation processes, different challenges must be overcome such as: (i) the need of series of start-up and shut-down operations, including periods of inactivity, when using biological processes due to variable nature of winery wastewater composition and quantity; (ii) the possible presence of high concentration of polyphenols in the wastewater, which can reduces significantly the microbial activity when using biological processes; (iii) high residence times and aeration demands in the biological reactor in order to achieve the discharge limits; (iv) the need of high energy doses and reactants, principally H_2O_2, when using the solar photo-Fenton process as single step.

In order to assess the viability of using a combined solar photo-Fenton (pH 2.8; $[Fe^{2+}]$ = 55 mg L^{-1}; 200 < $[H_2O_2]$ < 500 mg L^{-1}) with a biological process in the treatment of a real winery wastewater, the biodegradability of the effluent at different phototreatment times, was assessed. COD, total polyphenols and total dissolved nitrogen analyses were also performed in order to have a more comprehensive assessment of each step of the phototreatment.

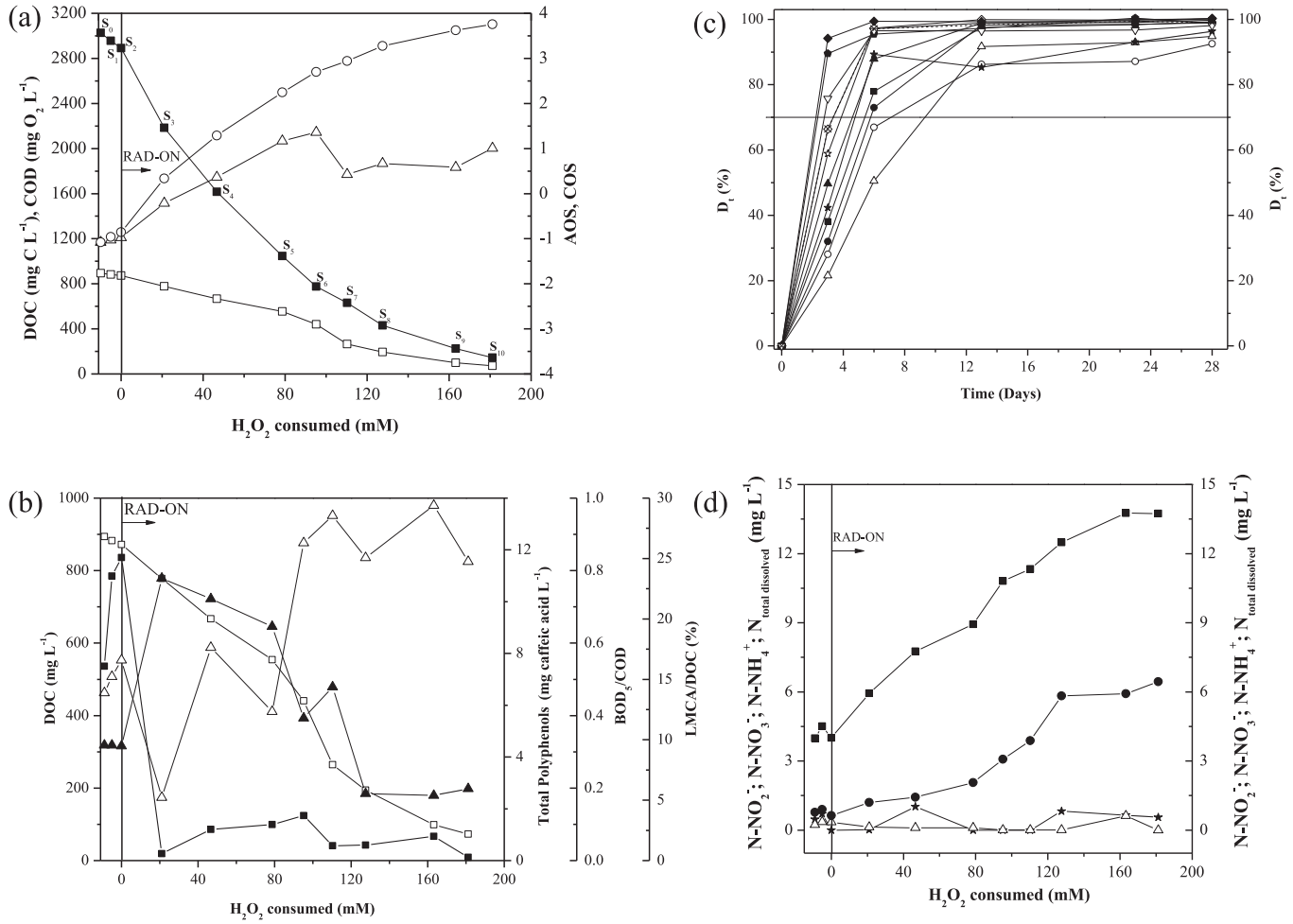

Fig. 4. Solar photo-Fenton treatment of winery effluent as a function of hydrogen peroxide consumed (pH 2.8; $[Fe^{2+}]_0 = 55\ mg\ L^{-1}$): (a) □ – DOC, ■ – COD, △ – AOS and ○ – COS; (b) □ – DOC, ■ – total polyphenols, △ – BOD_5/COD ratio, ▲ – LMCA/DOC ratio; (c) Zahn-Wellens test: ■ – S_0, DOC = 894 mg L^{-1}; ● – S_1, DOC = 882 mg L^{-1}, ▲ – S_2, DOC = 872 mg L^{-1}, △ – S_3, DOC = 778 mg L^{-1}, ○ – S_4, DOC = 667 mg L^{-1}, ★ – S_5, DOC = 554 mg L^{-1}; ☆ – S_6, DOC = 441 mg L^{-1}; ◊ – S_7, DOC = 265 mg L^{-1}, ♦ – S_8, DOC = 194 mg L^{-1}, ⬟ – S_9, DOC = 99 mg L^{-1}, ▽ – S_{10}, DOC = 73 mg L^{-1}, × – reference, DOC = 339 mg L^{-1}; (d) ★ – Nitrate (NO_3^--N); Δ – nitrite (NO_2^--N); ● – ammonia (NH_4^+-N); ■ – total dissolved nitrogen.

Fig. 4a shows a significant increase of the oxidation degree parameter (AOS), from −1 to 1.4 after 95 mM H_2O_2 consumption, and remained almost constant for further doses of H_2O_2. The increase of AOS suggests that more oxidized organic species are formed during the treatment and, afterwards AOS value reaches a plateau, the structure of the intermediates generated do not vary significantly [8]. Fig. 4a also shows an abatement of 95% on the COD (from 3026 to only 145 mg O_2 L^{-1}), showing a strong oxidation of the organic matter, which is well correlated with the COS parameter, which increased from −1.1, indicating the presence of rather reduced organic compounds, to +3.8 at the end of treatment, which means strong mineralization and generation of highly oxidized intermediates.

Fig. 4b shows a very fast degradation of the polyphenols followed by a significant increase of the low-molecular carboxylate anions, achieving a maximum concentration of 162 mg C L^{-1} (propionate > acetate > maleate > pyruvate > valerate > formate), corresponding to 17.6% of DOC, for a H_2O_2 dose of 47 mM H_2O_2.

Although the winery wastewater can be considered biodegradable, the oxidation capacity of •OH can enhance the biodegradability of the recalcitrant compounds, such as the polyphenols. For a H_2O_2 dose of 20 mM, corresponding to sample 3, it was observed a decrease of the BOD_5/COD (Fig. 4b) ratio when comparing to the initial wastewater, which is in agreement with the profile of the Zahn-Wellens test (Fig. 4c), indicating that the generated oxidized compounds strongly inhibit the activated sludge, which needed a longer adaptation period to yield the same mineralization. However, as expected, the biodegradability of the winery wastewater increased during the photo-Fenton reaction, leading to BOD_5/COD ratios higher than 0.9, after 80 mM H_2O_2, corresponding to the decay of the LCMA/DOC ratio values. According to the Zahn-Wellens results, after six days the biodegradation percentage increased from 78% to 89% and 97%, respectively for the raw wastewater (DOC = 894 mg L^{-1}), phototreated wastewater consuming 78 mM (22 kJ_{UV} L^{-1}) and 95 mM (35 kJ_{UV} L^{-1}) of H_2O_2. The pre-oxidation step enhances the biodegradability of the winery wastewater, increasing the microbial degradation rate, which consequently decreases the aeration demands and the retention time in the aeration tank. The possibility of performing a preliminary biological treatment followed by a solar photo-Fenton process was not evaluated because the Zahn-Wellens test of the winery wastewater showed that after 28 days the residual DOC was 10.1 mg L^{-1}, which is already in agreement with the discharge limits.

The concentration of nitrates and nitrites remained approximately constant during the phototreatment (Fig. 4d). On the other hand, the concentration of dissolved nitrogen and ammonium increased during the photo-Fenton reaction possible due to

nitrogen compounds oxidation present in the particulate phase and oxidation of organic nitrogen.

4. Conclusion

Although real winery wastewater showed a high biodegradability, the biological treatment of seasonable winery wastewaters, with high variability in terms of composition and quantity, is a big challenge, associated with the series of start-up and shut-down operations, including periods of inactivity. The proposed solar heterogeneous ($TiO_2/H_2O_2/UV$) and homogeneous ($Fe^{2+}/H_2O_2/UV$) AOPs, showed a good effectiveness as single stage for remediation of winery wastewater or used as pre-oxidation step enhancing the microbial activity. The photo-Fenton reaction presents the highest degradation rate, more than 2.5 times higher than the heterogeneous photocatalysis combined with H_2O_2. Considering a target COD value of 150 mg $O_2\,L^{-1}$, in agreement with Portuguese legislation for discharge into water bodies (Decree-Law n° 236/98), 290 mM of H_2O_2 and an UV solar dose of 100 kJ L^{-1} (pH 2.8, $[Fe^{2+}]_0 = 55\,mg\,L^{-1}$) are necessary, which corresponds to an H_2O_2 consumption/DOC oxidized ratio of 13.4 mg H_2O_2 per mg DOC. To achieve the same COD target value using only the IBR process or the combination of solar-photo-Fenton (80 mM H_2O_2 consumed) and biological systems, approximately 10 and 6 days (time necessary for the biological oxidation) are required. According to the Zahn-Wellens test of the winery wastewater, a residual DOC of 10.1 mg L^{-1} after 28 days was obtained, which is in agreement with the discharge limits, showing that the possible combination of a biological oxidation with a photo-Fenton reaction is not adequate to the treatment of this winery wastewater.

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