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Treatment of real winery wastewater by wet oxidation at mild temperature

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Abstract

This study explores the treatment of high-strength real winery wastewater ($\text{COD}_0 \approx 35$ g/L, $\text{TOC}_0 \approx 11$ g/L) by wet oxidation processes. Wet air oxidation (WAO), catalytic wet air oxidation (CWAO), H_2O_2 -promoted CWAO, wet peroxide oxidation (WPO) and catalytic wet peroxide oxidation (CWPO) were the options tested using different carbon-based catalysts, *viz.* activated carbon, carbon black and graphite. Their suitability was analysed in terms of polyphenol, chemical oxygen demand (COD) and total organic carbon (TOC) abatement upon 4 h reaction time. The results showed that hydrogen peroxide was the unique oxidant capable of achieving an effective reduction of the organic load. The graphite tested was the most active catalyst, most probably due in great part to its Fe content (0.4 wt%), resistant to leaching.

CWPO with that graphite was tested at different conditions following the evolution of COD, TOC and ecotoxicity. The best results were obtained by using graphite at 5 g/L, the original pH of the wastewater (3.8), 125 °C and the stoichiometric amount of hydrogen peroxide distributed in stepwise additions. Under those conditions, 80% COD and TOC removals with 85% of hydrogen peroxide efficiency were achieved after 4 h reaction time, giving rise to colourless effluents of very low Microtox ecotoxicity.

Keywords

Winery wastewater; catalytic wet air oxidation; catalytic wet peroxide oxidation; carbon catalysts; ecotoxicity.

1. Introduction

The wine industry generates large volumes of wastewaters, between 1.3 and 1.5 L/L of wine [1]. These effluents are originated most in particular from the washing of the presses used for crushing the grapes and, in lesser extent, from the rinsing of fermentation tanks, barrels and other equipment components [2, 3]. Winery wastewater is characterized by a widely variable high organic strength (800 to 25,000 mg/L COD), high salinity (3,000-4,000 $\mu\text{S}/\text{cm}$) and sodicity ($\text{SAR}=8\text{-}9$). The typical components are suspended solids, polyphenols, organic acids, alcohols, sugars (maltose, glucose, fructose), aldehydes, soaps and detergents, nitrogen compounds and inorganics, including some traces of heavy metals [4, 5].

The wine industry recognizes the priority of the environmental and economical sustainable management of its wastewater [6] and, therefore, medium and large-scale wineries are usually equipped with biological treatment systems (aerobic, anaerobic or combinations of both). However, the seasonal variation of winemaking provokes important fluctuations in the quantity and quality of the effluents. This, in addition to the presence of recalcitrant compounds, especially polyphenols, make it difficult to find effective solutions capable of achieving a high reduction of the organic load [5, 7]. Advanced oxidation processes (AOPs) are currently being proposed as alternative to biological treatment for these wastewaters [4, 5].

Ozonation [2, 8-10], photocatalysis [3, 10, 11] and combined processes, *i.e.* $\text{O}_3/\text{TiO}_2/\text{UV}$ [10], $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ [2], $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$ [12] have been typically tested with synthetic

wastewaters prepared from commercial wine or grape juice, and only few studies have been conducted with real winery wastewater [2, 9, 12]. The combined processes have demonstrated to be more efficient. COD and TOC reductions close to 60% have been reported as the best results with real winery wastewater of moderate initial COD ($\approx 4,000$ mg/L) [2, 12].

The Fenton process is commonly characterized by its simplicity and low cost compared to other AOPs [13, 14]. However, fairly poor results have been obtained so far with winery wastewaters because of the refractoriness of a great part of the organic matter of those effluents under the common operating conditions of the conventional Fenton process. Combination with UV light radiation has been checked to improve the efficiency of that process [7, 11, 15-18]. Alternatively, Fenton oxidation has been proposed as post-treatment for the purpose of removing the complex organic molecules remaining after biological oxidation [19-21]. Wastewaters with a low initial COD (600 to 1,500 mg/L) have been treated by this way leading to COD reductions within a fairly wide range (60 to 90%) depending on the dose of hydrogen peroxide, the $[\text{H}_2\text{O}_2]/\text{Fe}$ ratio and the initial COD.

The current work investigates the treatment of high-strength real winery wastewater by wet oxidation processes for the purpose of identifying an effective solution capable of dealing with the seasonal fluctuations of the winemaking effluents allowing a high reduction of their organic load with almost complete depletion of polyphenols. Non-catalytic and catalytic wet air oxidation (WAO and CWAO, respectively) and wet peroxide oxidation (WPO and CWPO) have been tested. In WAO, high temperatures and pressures ($T=120\text{-}300$ °C, $P=0.8\text{-}20$ MPa) are required [22] while WPO works under relatively milder operating conditions ($T=50\text{-}125$ °C, $P=0.1\text{-}0.5$ MPa) using hydrogen peroxide [23]. Different carbon-based materials, *viz.* activated carbon, carbon black and

graphite have been tested as catalysts. Those materials have demonstrated to be active in CWAO [24] and CWPO [25, 26] of phenol. Hydrogen peroxide-promoted CWAO with the different carbon materials tested has also been studied. The beneficial effects of hydrogen peroxide as free-radicals promoter combined with oxygen in the presence of activated carbons have been proved in previous works for the treatment of phenolic wastewaters [27, 28]. Once selected the most efficient process in terms of COD and TOC removals, the operating conditions (temperature, pH, initial COD, hydrogen peroxide dose and the way of feeding the reagent) will be investigated for the sake of learning on their influence on the efficiency of the process by following the evolution of COD, TOC and ecotoxicity.

2. Experimental

2.1 Winery Wastewater

The winery wastewater was sampled from a wine factory located in Badajoz (Spain). It is a brownish acid effluent of unpleasant odor. A representative analysis is given by: pH=3.8, ecotoxicity=52 TU, conductivity=7.38 mS/cm, inorganic constituents=4.5 g/L (mainly N=0.32 g/L, K=2.5 g/L and P=0.28 g/L, S=0.12 g/L and Ca=0.16 g/L), COD=35 ± 2.2 g/L and TOC=11.3 ± 0.9 g/L. Close to 45% of the total organic carbon was identified as glycolic acid (5 g/L), acetic acid (3.5 g/L), malonic acid (1.2 g/L) and polyphenols (0.7 g/L equivalent phenol). Another acids (propanoic, 2-hydroxypropanoic, ethyl ester 2-hydroxypropanoic, butanoic, succinic, pentanoic, hexanoic, methyl phenylglyoxylate) and alcohols (ethanol, benzyl alcohol, phenylethyl alcohol, 2-ethyl-phenol, 2-butanol, glycerol) were detected in trace amounts. Moreover, several metals, such as Fe (5 mg/L), Mn (3 mg/L) and Zn (1 mg/L), are present in trace amounts, measured by TXRF (Extra-II Rich & Seifert spectrometer). Special attention must be paid to Fe, since this metal

catalyzes hydrogen peroxide decomposition into radical species.

2.2. Catalysts characterization

Three commercial carbon materials were tested as catalysts: activated carbon (AC, Panreac, ref.: 121237), carbon black (CB, Chemviron, ref.: 045527) and graphite (G, Sigma-Aldrich, ref.: 282863). Before use, the samples were sieved and the particle size ranging from 80 to 100 μm was selected for the experiments.

The specific surface area (S_{BET}) values were obtained from the 77 K N_2 adsorption/desorption isotherms using a Micromeritics Tristar apparatus. The micropore volume and the external or non-microporous surface area were obtained by the t -method. Elemental analyses of the as-received materials were performed in a LECO Model CHNS-932 apparatus. Elements identification and iron content in the carbon ashes were performed by TXRF (Extra-II Rich & Seifert spectrometer).

2.3. Oxidation experiments

The oxidation experiments were carried out in a 75 mL autoclave reactor (Berghof). The reactor consists of a stainless-steel pressure vessel (PTFE) placed on a magnetic stirrer and surrounded by an electric resistance heating block provided of the corresponding control system. Pressure was measured by a transducer. Six ports Valco valve VICI with two positions allows the gas flow pass through the reactor or bypass it. The inlet gas flow-rate (92 NmL/min of pure N_2 or O_2) bubbling into the liquid was adjusted by mass flow controllers (Hi-Tec Bronkhorst). In a typical CWAO experiment, 75 mL of wastewater at the testing pH and the catalyst were charged to the vessel. Then, the reactor was stoppered, heated and pressurized under nitrogen atmosphere to the desired conditions. After stabilization, the N_2 flow was switched into O_2 and the stirring was started at 1500 rpm. This was considered the starting reaction time. In the H_2O_2 -promoted CWAO and CWPO experiments, the experimental procedure was similar to the above described but 60 mL of wastewater were

charged to the reactor and, once established the selected operating conditions, 15 mL of hydrogen peroxide aqueous solution of the appropriate concentration were fed with a chromatographic pump (GILSON, model 307). The non-catalytic experiments were performed as in the corresponding catalytic process but obviously in the absence of catalyst.

Liquid samples were periodically withdrawn from the reactor and immediately injected in a vial (submerged in crushed ice) containing a known volume of cold distilled water. The diluted samples were filtered (0.45 μm Nylon filter) and subsequently analyzed by different techniques.

The operating conditions for the WAO, CWAO and H_2O_2 -promoted CWAO experiments were $\text{pH}=3.8$, $160\text{ }^\circ\text{C}$ and 1 MPa with a pure oxygen flow of 92 NmL/min. In the case of H_2O_2 promoted-CWAO, H_2O_2 was added at 20% of the stoichiometric amount relative to the initial COD. The WPO and CWPO runs were performed at $\text{pH}=3.8$, $80\text{ }^\circ\text{C}$, 0.1 MPa and 58 g/L H_2O_2 (100% of the stoichiometric amount of H_2O_2 relative to the initial COD). The catalyst, when used, was added in all cases at 5 g/L. Latter, the operational window tested for the CWPO with graphite was: $\text{pH}_0=2.2-7$, $T=80-125\text{ }^\circ\text{C}$, $P=0.1-0.7\text{ MPa}$, $[\text{COD}]_0=3.5-35\text{ g/L}$ and $[\text{H}_2\text{O}_2]_0=0-1.6$ times the stoichiometric amount. Two ways of feeding hydrogen peroxide were tested: once-through at the start of the experiment and stepwise upon the reaction time (4 h).

2.4. Chemical analyses

Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, model TOC VSCH). The hydrogen peroxide concentration was determined by colorimetric titration using the TiOSO_4 method [29]. Chemical oxygen demand (COD) measurements were performed by the Moore method [30]. The COD values were corrected discounting the contribution of the remaining hydrogen peroxide ($\text{COD}_{\text{corrected}}=\text{COD}_{\text{measured}}-$

0.4635·CH₂O₂, experimentally obtained from standard solutions of hydrogen peroxide within the range 10-1000 mg/L). Identification and quantification of inorganic constituents such as metals in the initial wastewater and in the reactor effluents was performed by TXRF. Polyphenolic compounds were measured by the Folin-Reagent test at 700 nm using a UV-VIS spectrophotometer (Shimadzu, mod. UV-1603). Short-chain organic acids were determined by Ionic Chromatography (IC) with anionic chemical suppression using a conductivity detector (Metrohm, mod. 883 BASIC IC Plus). A Metrosep A supp 5-250 column (25 cm long, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na₂CO₃ and 1 mM of NaHCO₃ as mobile phase.

The identification of species was performed by gas chromatography/ion trap mass spectrometry (GC/MS using a CP-3800/Saturn 2200, Varian apparatus equipped with an automatic injector CP-8200/SPME, solid-phase microextraction). The capillary column used was a Factor Four VF-5 ms, Varian (30 m length and 0.25 mm i.d.). The carrier gas (helium) flow rate in the GC was 1 mL/min. The solid-phase microextraction (SPME) was carried out with a fiber cartridge (poly(dimethylsiloxane) red), using adsorption and desorption times of 30 and 5 min, respectively. The sample injection was conducted at 220 °C. The temperature program used in the GC-MS analyses ramped as follows: 40 °C for 5 min, increased to 250 °C at 15 °C/min, held at 250 °C for 10 min, increased to 300 °C at 20 °C/min, and held at 300 °C for 2 min. Additional measurements were performed extracting the aqueous samples with solid-phase cartridges (C18, Waters), eluted with different organic solvents (n-hexane and methanol). The identifications were assessed with the aid of the database library NIST.

2.5. Ecotoxicity

The ecotoxicity of the effluents was determined in a Microtox M500 Analyzer (Azur

Environmental) following the standard Microtox test (ISO 11348-3, 1998). This bioassay is based on the decrease of light emission by *Photobacterium phosphoreum* as the result of exposure to a toxicant at 15 °C for 15 min. The toxicity units of the sample are calculated from: $TU=100/IC_{50}$, where IC_{50} is defined as the sample dilution percentage that yields 50% reduction of the light emitted by the microorganisms. Before measuring the toxicity, the residual hydrogen peroxide was removed with sodium bisulfite and the pH value of all the samples was adjusted between 6 and 8 according to the test specifications. The microorganisms were purchased from Microtox Acute Reagent supplied by I.O. Analytical. More detailed information about this assay and its application to wastewater can be found elsewhere [31].

3. Results and discussion

3.1. Catalyst characterization

The characterization of the carbon materials used as catalysts is summarized in Table 1. These materials show fairly different porous structure. The activated carbon has a well-developed microporosity but also an important contribution of mesoporosity, as indicates the high value of external or non-micropore surface area (A_{ext}) which represents more than one-half the BET surface area (S_{BET}). As expected, carbon black and graphite are non-microporous solids with low surface area, specially the second one.

The elemental analyses confirm that the three materials consist essentially of carbon. Some significant differences can be observed in the ash content, where it is important the presence of Fe in the graphite at 0.4% of the total dry weight. Special attention must be paid to this metal due to its catalytic activity for hydrogen peroxide decomposition into hydroxyl radicals.

3.2. Oxidation treatments

In a first attempt to reduce the organic load of the wastewater and then, the amount of oxidant (hydrogen peroxide or oxygen) required for the chemical oxidation, several pretreatments like adsorption with activated carbon and precipitation with $\text{Ca}(\text{OH})_2$ were checked. Fairly low COD and TOC reductions (less than 20%) and no significant ecotoxicity variation were observed, so that the raw wastewater was directly submitted to the different oxidation treatments investigated.

Figure 1 depicts the results obtained upon each of the oxidation processes tested after 4 h reaction time under the operating conditions indicated in the Experimental Section. Control experiments were also carried out to analyze the stability of the wastewater at the operating temperature. The thermal decomposition, breakdown of organic constituents without the addition of hydrogen peroxide or oxygen flow, was negligible at 80 °C but represented up to 20% of the initial COD at 160 °C.

The results show frankly low reductions of COD and TOC upon WAO at 160 °C and 1 MPa ($X_{\text{COD}} \approx 30\%$), moreover taking into account that a great part of this COD reduction can be attributed to the aforementioned thermal decomposition. The presence of a carbon catalyst did not particularly improve the performance of the process. Only polyphenols disappearance increased somewhat in the presence of activated carbon or carbon black, this being due mostly to adsorption [25]. A high reduction of polyphenols may be eventually important for a subsequent biological treatment since those compounds are resistant to biodegradation [5, 7].

The addition of hydrogen peroxide at only 20% of the stoichiometric amount improved significantly the COD and TOC removals (*c.f.* WAO and H_2O_2 -promoted WAO in Figure 1) allowing up to about 40% reduction of both. With the carbon materials tested the results were appreciably better, reaching 55-60% COD and TOC removals. These results are comparable to the reported from photo-assisted oxidation treatments like $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$,

$\text{O}_3/\text{UV}/\text{TiO}_2$ and $\text{H}_2\text{O}_2/\text{UV}/\text{TiO}_2$ [2, 10, 15]. H_2O_2 -promoted WAO and CWAO experiments performed under N_2 instead of O_2 flow showed no significant differences in terms of oxidation and mineralization, indicating that the improved degradation of the organic matter was essentially due to hydrogen peroxide without significant synergistic effects of this reagent and oxygen. Those synergistic effects had been demonstrated in previous works on H_2O_2 -promoted CWAO of phenol [27, 28] but do not seem to apply with this high strength winery wastewater.

Regarding polyphenols, almost complete conversion was observed in the H_2O_2 -promoted CWAO experiments with activated carbon and graphite. In the former, adsorption plays an important role while in the second the Fe content of the graphite tested (see Table 1) must have a determining effect.

CWPO with graphite leads to somewhat higher COD and TOC reductions and at substantially lower temperature than H_2O_2 -promoted CWAO (80 vs. 160 °C). As indicated before, the wastewaters tested is highly stable at 80 °C, therefore, the degradation of organic matter upon CWPO is essentially due to the oxidation process without significant contribution of thermal decomposition, which occurs in CWAO at 160 °C. Also, dissolved metals, particularly iron, could contribute in part to the oxidation/mineralization performance, as demonstrated by the results upon WPO.

The improved efficiency and the considerable reduction of temperature compensate the need of hydrogen peroxide in CWPO, which in the experiments of Figure 1 was added only at 20% of the stoichiometric amount relative to the initial COD. The higher activity of the graphite compared to the activated carbon and carbon black tested is consistent with the results obtained in a previous work [32] where the catalytic activity of these three materials for hydrogen peroxide decomposition was analysed by cyclic voltammetry. In that study, it was demonstrated that the iron content of the graphite tested, was the most

important feature explaining its higher activity in spite of its much lower surface area.

TXRF analyses of the fresh and used graphite, as well as of the corresponding CWPO effluents indicated that iron was not leached during the process. In fact, the activity of graphite was maintained upon three successive cycles where COD and TOC reductions remained invariable at around 60% after 4 h reaction time (Figure S1 of the Supplementary Data).

3.3. CWPO with graphite

The preceding results support the potential application of CWPO for the treatment of winery wastewater using the Fe-containing graphite as catalyst. To learn more on that potential application, the effect of temperature, *pH*, initial COD, hydrogen peroxide dose and the way of feeding this reagent, were investigated following the TOC and COD reductions as well as the ecotoxicity of the effluents.

3.3.1. Effect of temperature

Three different temperatures (80, 100 and 125 °C) were tested using the stoichiometric dose of hydrogen peroxide. The conversion profiles upon 1 h reaction time are given in Figure 2. The results show that increasing the temperature within the range tested improves significantly the oxidation rate in the early stages of the process, consistently with the faster decomposition of hydrogen peroxide. The final COD and TOC reductions after almost complete consumption of H₂O₂ (1 h reaction time at 100 and 125 °C and at 4 h at 80 °C) were similar (around 60%) since that is governed by the H₂O₂ dose. No Fe leaching was detected within the temperature range tested and no more than 5% of the COD and TOC removals can be attributed to thermal decomposition at the highest temperature tested (125 °C) after 4 h.

Figure 3 shows the Arrhenius plots of the initial rates of hydrogen peroxide decomposition and TOC and COD reductions. The corresponding values of the apparent

activation energy are included. The value obtained for H₂O₂ decomposition (60 kJ/mol, Figure 3) is in the upper limit of the range reported with Pd over different supports (AC, ZrO₂ and Al₂O₃) [33]. In case of TOC and COD, a wide spectrum of values has been reported likely due to the different nature of the wastewater and catalysts used. For TOC, the apparent activation energy obtained (70 kJ/mol, Figure 3) has the same value as the reported for cork processing wastewaters [34], whereas is higher than that given for cosmetic [35] both using Fe²⁺ catalyst (Fenton oxidation). The COD activation energy (61 kJ/mol, Figure 3) is, in general, higher than those reported with other industrial wastewater such as olive-oil mill with Fe²⁺ catalyst [36] and tannery water using both Fe²⁺ and activated carbon catalysts [37]. This can be due to the high concentration of organic acids (of refractory nature) present in our raw winery wastewater.

The temperature also affects to the distribution of by-products. It was seen that increasing the temperature from 80 to 125 °C reduced dramatically the percentage of the unidentified TOC after complete hydrogen peroxide consumption (42% at 80 °C vs. only around 5% at 100 and 125 °C). The identified TOC corresponds mainly to acetic acid (85% of the residual TOC), which is an expected by-product from the oxidation of ethanol [11] and from the breakdown of larger organic acids such as tartaric, malic and lactic [17] contained in the wastewater and some of them also formed upon oxidative degradation of more complex species.

Figure 4 shows the ecotoxicity of the resulting effluents after 4 h reaction time at different temperatures. Pictures of the corresponding samples are included where it can be seen that CWPO leads to almost colorless effluents from the dark brown initial wastewater. As observed, increasing the temperature has a marked beneficial effect on the reduction of ecotoxicity within the range 80-100 °C. Interestingly, the application of CWPO at 80 °C is accompanied by a remarkable increase of ecotoxicity in spite of the significant

reductions of COD, TOC and color. This fact indicates the formation of some reaction by-products of higher toxicity than the initial components of the wastewater. In addition, the ecotoxicity of the effluent from non-catalytic WPO at 80 °C was also determined, yielding a significantly higher value (925 TU). An attempt to identify the nature of the ecotoxic species, several effluent samples were analyzed by GC-MS. Most of the relevant peaks observed in the chromatograms of the raw wastewater (identified as phenylethyl alcohol, 4,4 dimethylbenzyl, methyl phenylglyoxylate, benzyl alcohol, 2-ethyl-phenol) did not appear in the effluents, while others corresponding to short chain organic acids, such as acetic and propanoic acid were increased (see Figure S2 in the Supplementary Data). It should be noted the presence of an unidentified peak in the ecotoxic effluents which was not observed in the raw wastewater and in the effluent from CWPO at 125 °C. The signal of that peak ($m/z=44$) increased according to the ecotoxicity of the effluent (see Figure S3 in the Supplementary Data).

3.3.2. Initial pH

It is well known that wet peroxide oxidation is sensitive to the pH and usually acid conditions are required [38]. The effect of this variable was explored within the range of 2.2 to 7. The starting pH value was adjusted (but not buffered) with 1M solution of HCl or NaOH. The results obtained at different initial pH values and 80 °C are depicted in Figure 5. As can be seen, at the lowest pH tested (2.2), the decomposition of hydrogen peroxide becomes much slower but this circumstance does not affect so dramatically to TOC and COD reductions. The best results were obtained at pH 3.8, which is that of the wastewater as received. This simplifies the potential application of CWPO to this type of waste. At neutral pH, the rate of hydrogen peroxide decomposition was similar as at 3.8, but fairly lower efficiency of TOC and COD reductions was observed due to the favored decomposition of hydrogen peroxide into oxygen and water.

3.3.3. Effect of the initial organic load

Winery wastewaters are characterized by fluctuations in flow-rate and organic loads which represent an inconvenience regarding the application of currently established technologies like anaerobic digestion. Thus, it is important to know how the organic load affects to the efficiency of the CWPO. With this purpose, wastewater with different initial COD values of 35, 17 and 3.5 g/L, prepared by dilution of the as received wastewater with distilled water have been charged to the reactor. Figure 6 shows that changes in the initial COD do not affect to the percentage reduction of TOC and COD achieved using the corresponding stoichiometric dose of hydrogen peroxide. This confirms the refractory character of a fraction of the organic matter of these wastewaters in terms of TOC. From the operational point of view, the same installation would be adequate for the treatment of any winery wastewater generated during the working season by adjusting the appropriate dose of hydrogen peroxide to the inlet organic load (COD, TOC). From a kinetic point of view, *pseudo* first-order with respect to COD and TOC can be inferred.

3.3.4. Hydrogen peroxide dose

Figure 7 shows the results obtained at 125 °C with different hydrogen peroxide doses within a wide range up to 1.6 times the stoichiometric. As can be seen, the TOC and COD reductions increased linearly with the amount of hydrogen peroxide up to the stoichiometric amount and beyond that a further small variation was observed. The asymptotic value at around 70% conversion is consistent with the existence of a refractory organic fraction corresponding to oxidation by-products and to initially present species, mainly short-chain organic acids, like acetic acid. The efficiency of hydrogen peroxide consumption (η), defined as the amount of COD removed per hydrogen peroxide consumed, progressively decreases from 0.9 to 0.45 values with the oxidant dose (Figure 7).

The effect of the hydrogen peroxide dose was also observed on the residual color of the effluent, which decreased progressively from brown to colorless when using at least the stoichiometric amount of hydrogen peroxide (Figure 7).

The dose of hydrogen peroxide showed a remarkable effect on the ecotoxicity of the resulting effluents as can be seen in Figure 8. At frankly substoichiometric doses highly toxic oxidation intermediates are formed which need further addition of hydrogen peroxide to be destroyed. These intermediates most probably include aromatic condensation by-products, responsible of the brownish color of the effluent (Figure 7), which finally breakdown as the hydrogen peroxide is increased.

The optimum dose of hydrogen peroxide can be established around the stoichiometric amount. This allows achieving more than 60% mineralization and complete color removal. Above the stoichiometric hydrogen peroxide dose, very low improvement is gained in terms of COD and TOC reductions due to the refractory character of the remaining organic matter.

The way of addition of hydrogen peroxide is also an important variable because it affects to the efficiency of hydrogen peroxide consumption. Figure 9 shows the TOC and COD conversions as well as hydrogen peroxide consumption and the efficiency values when the stoichiometric amount of hydrogen peroxide was stepwise added upon 4 h reaction time instead of in a simple addition at the start of the experiment as in the runs so far. As can be observed, this strategy is highly convenient since it allows achieving higher TOC and COD conversions with the same amount of H_2O_2 . The stepwise feeding allows maintaining a high (0.85-1) efficiency of hydrogen peroxide consumption *versus* the 60% achieved under once-through addition of the reagent at the start of the experiment.

4. Conclusions

Different oxidation processes (WAO, CWAO, H₂O₂ promoted WAO, H₂O₂ promoted CWAO, WPO and CWPO) have been tested for the treatment of high-strength real winery wastewater, being CWPO with Fe-bearing graphite the one yielding the best results. Fe leaching from the graphite catalysts was negligible.

Increasing temperature within the 80-125 °C range improves significantly the results obtained in terms of COD, TOC and ecotoxicity reductions. A similar effect was observed by increasing the hydrogen peroxide dose up to the stoichiometric amount relative to the initial COD. Further improvements beyond that those were very small. Complete degradation of polyphenols, 80% COD and TOC removals, total colour and odour elimination and very low ecotoxicity values were achieved with 85% hydrogen peroxide efficiency in 4 h reaction time at 125 °C, 0.7 MPa, 5 g/L of graphite, at the pH of the wastewater as received (3.8) and by stepwise distributed addition of the stoichiometric amount of hydrogen peroxide relative to the initial COD.

CWPO appears a promising option for the treatment of this type of wastewaters subjected to wide fluctuation of daily volumes and organic load. No significant changes on the percentage of COD and TOC reductions were observed within a broad range of initial COD (3.5-35 g/L) under the corresponding stoichiometric dose of hydrogen peroxide.

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Figure Captions

Figure 1. Results obtained upon treatment of the winery wastewater by the oxidation processes tested after 4 h reaction time. [(*) the presence of nitrogen instead of oxygen]

Figure 2. Effect of temperature on TOC and COD reductions and hydrogen peroxide decomposition upon CWPO with graphite. Operating conditions: $P=0.7$ MPa, $pH_0=3.8$, $C_{CAT}=5$ g/L and $H_2O_2:COD=stoichiometric$. (■) 80 °C (□) 100 °C (■) 125 °C.

Figure 3. Arrhenius plot from the CWPO experiments of Figure 2.

Figure 4. Ecotoxicity of the effluents from CWPO with graphite after 4 h at different temperatures ($P=0.7$ MPa, $pH_0=3.8$, $C_{CAT}=5$ g/L, $H_2O_2:COD=stoichiometric$).

Figure 5. Effect of initial pH on TOC and COD reductions and hydrogen peroxide decomposition upon CWPO with graphite. Operating conditions: $T=80$ °C, $P=0.1$ MPa, $C_{CAT}=5$ g/L and $H_2O_2:COD=stoichiometric$. (■) $pH_0=2.2$ (□) $pH_0=3.8$ (■) $pH_0=7$.

Figure 6. TOC and COD evolution and hydrogen peroxide decomposition in CWPO at different initial organic loads ($T=100$ °C, $pH_0=3.8$, $P=0.7$ MPa, $C_{CAT}=5$ g/L and $H_2O_2:COD=stoichiometric$). (■) $COD_0=35$ g/L (■) $COD_0=17.5$ g/L (□) $COD_0=3.5$ g/L.

Figure 7. Results of CWPO (4 h) at 125 °C with different hydrogen peroxide doses ($pH_0=3.8$, $P=0.7$ MPa and $C_{CAT}=5$ g/L). ■ TOC □ COD ▨ H_2O_2 (○) H_2O_2 efficiency.

Figure 8. Ecotoxicity of the CWPO (4 h) effluents at different hydrogen peroxide doses. Operating conditions: $T=125$ °C, $pH_0=3.8$, $P=0.7$ MPa and $C_{CAT}=5$ g/L.

Figure 9. Results of CWPO with graphite under stepwise (solid symbols) and once-

through (open symbols) feeding of the stoichiometric amount of H_2O_2 (COD: circles, TOC: squares; H_2O_2 concentration: triangles and hydrogen peroxide efficiency: rhombus. Operating conditions: $T=125\text{ }^\circ\text{C}$, $\text{pH}_0=3.8$, $P=0.7\text{ MPa}$ and $C_{\text{CAT}}=5\text{ g/L}$.

Table 1. Characterization of the carbon materials used as catalysts (analyses in % weight, dry basis)

Sample	S_{BET} (m ² /g)	A_{ext} (m ² /g)	$V_{micropore}$ (m ² /g)	C (%)	Ashes (%)	Fe (%)
Activated Carbon (AC)	931	472	0.161	93.7	1.0	< 0.01
Carbon Black (CB)	75	75	-	≈99	0	0
Graphite (G)	12	12	-	97.2	0.50	0.40

Figure 9

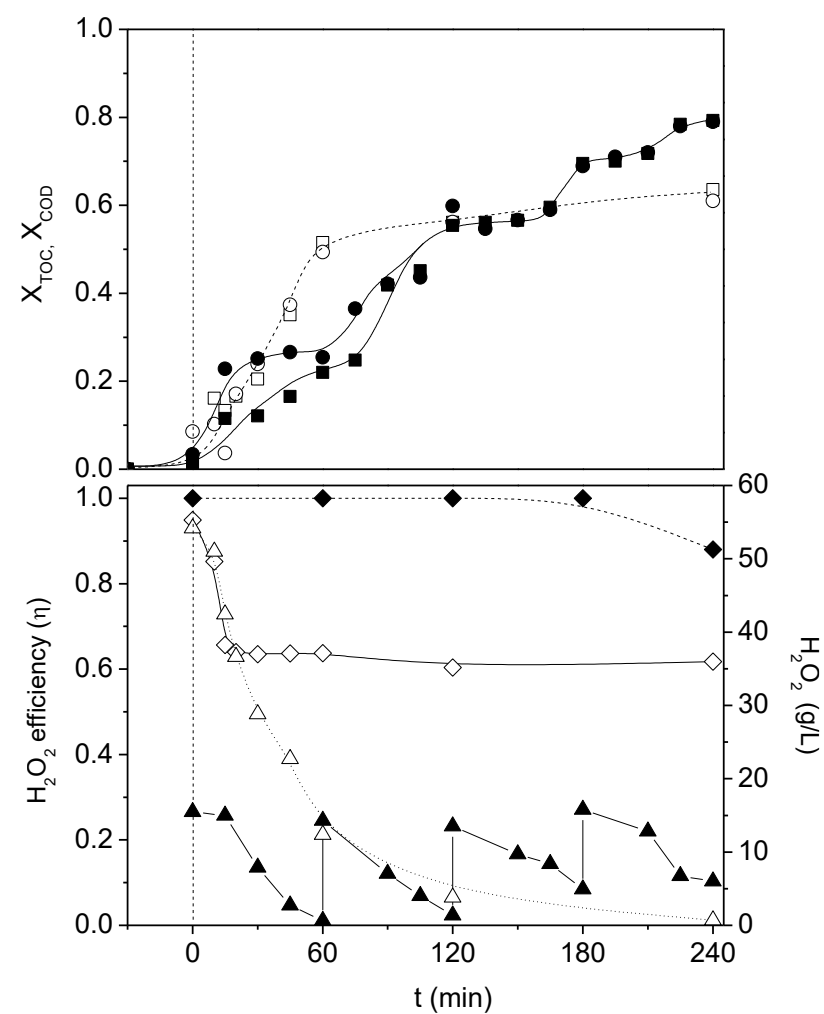


Figure 1

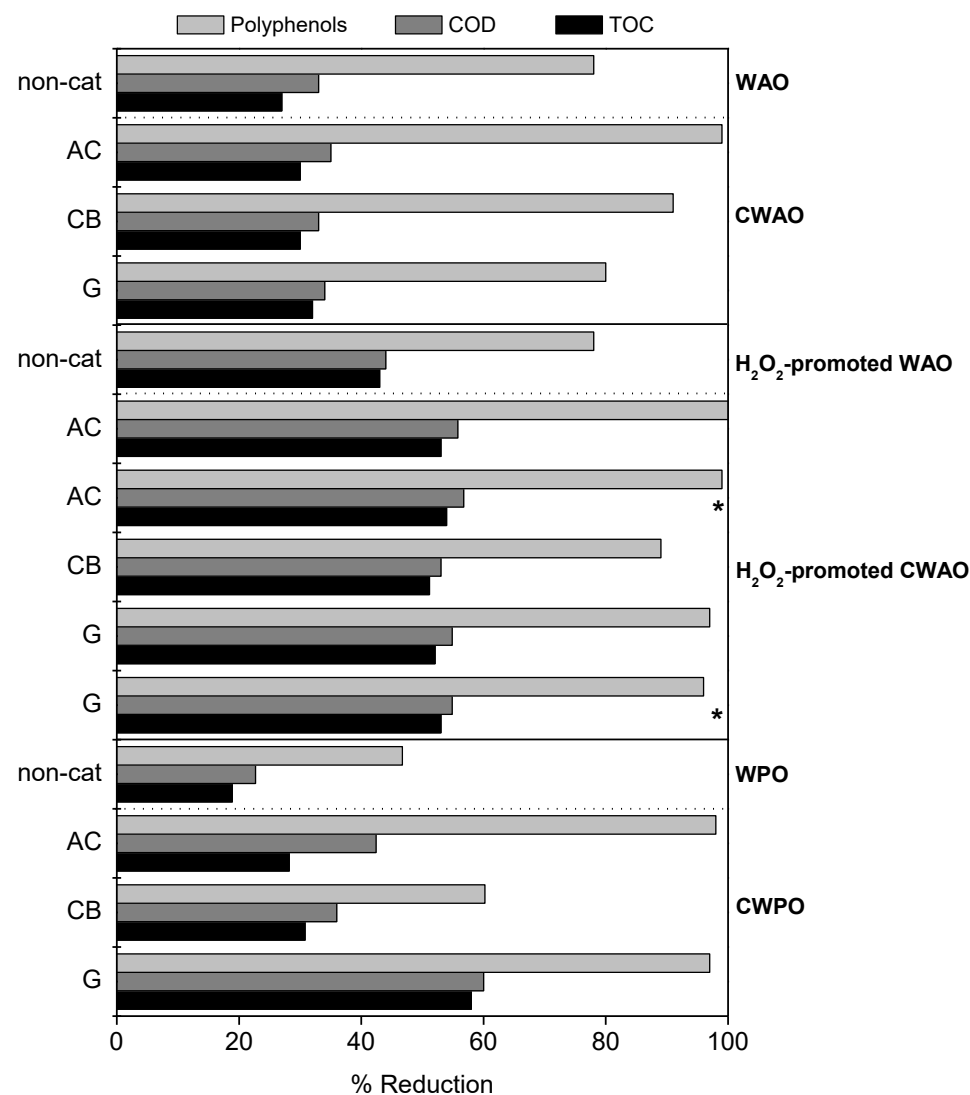


Figure 2

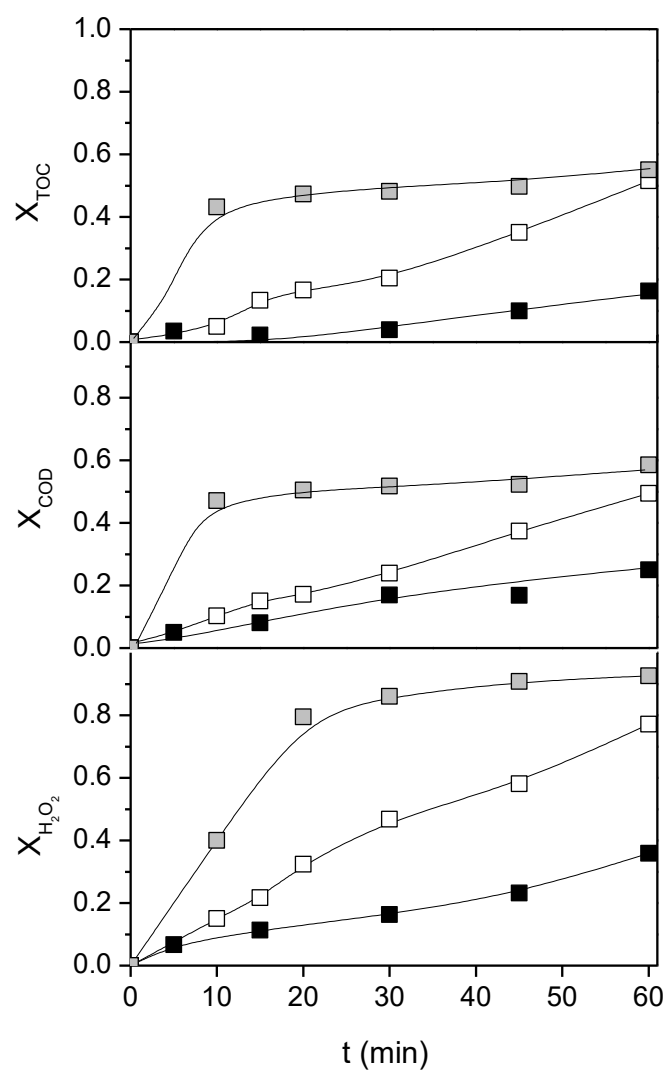


Figure 3

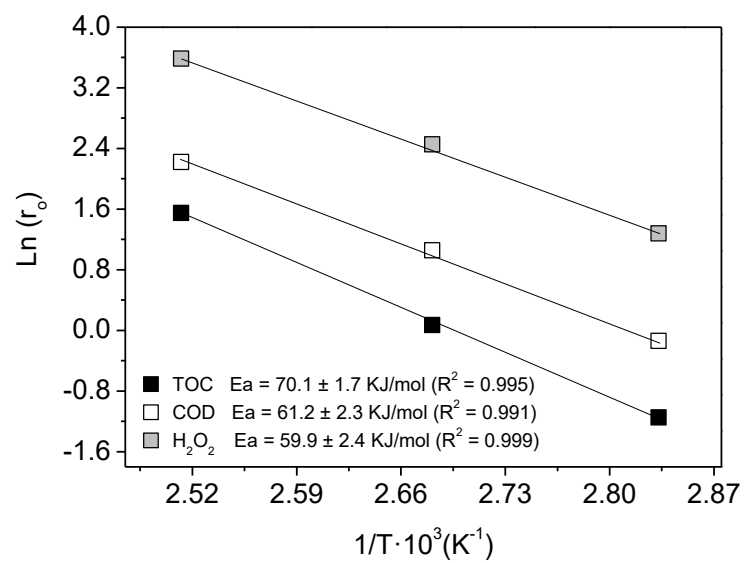


Figure 4

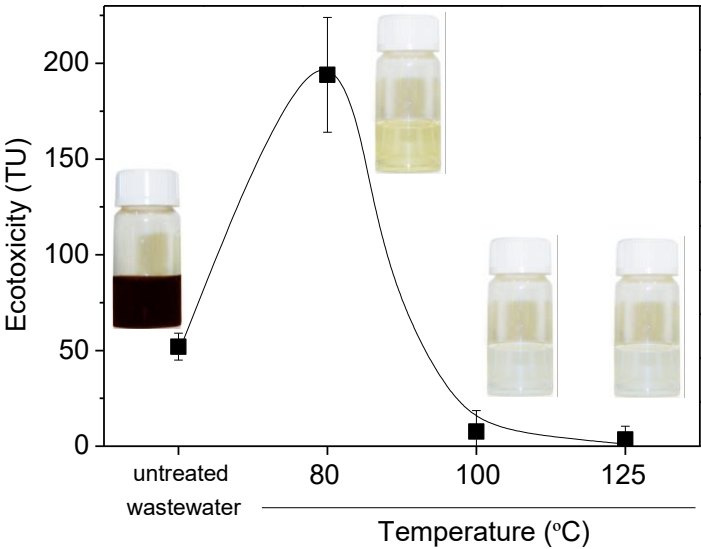


Figure 5

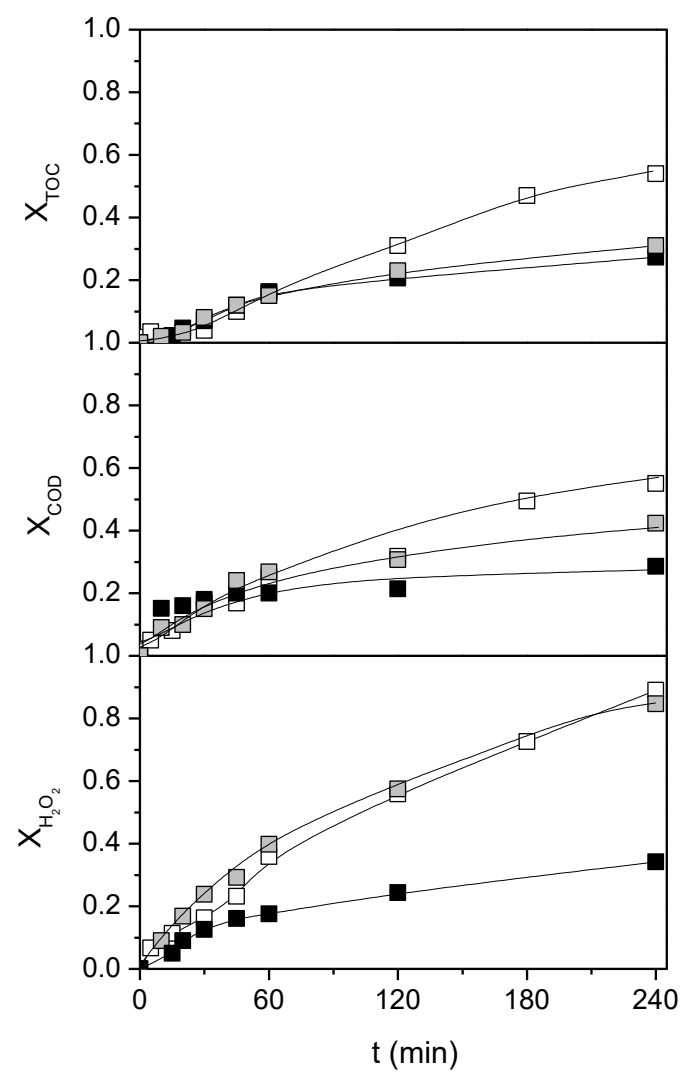


Figure 6

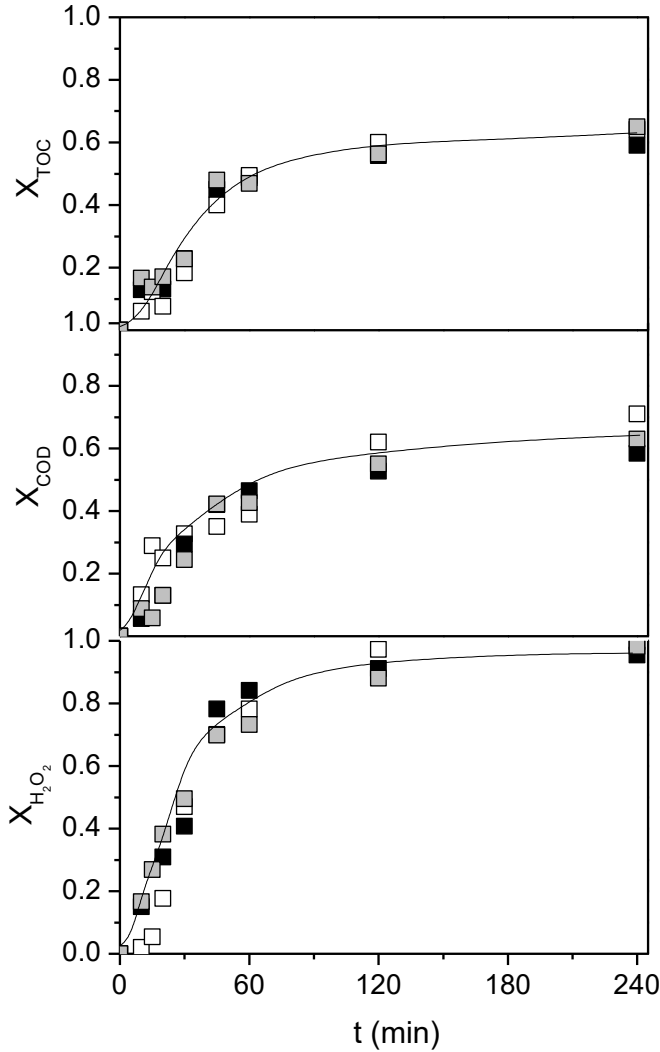


Figure 7

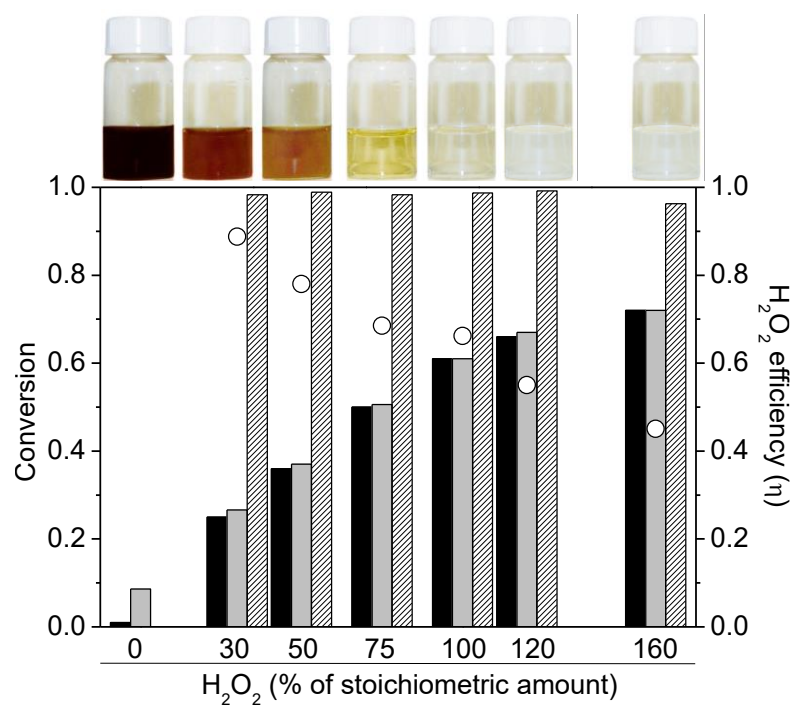


Figure 8

