



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 ($\text{COD}_0 \approx 35 \text{ g/L}$, $\text{TOC}_0 \approx 11 \text{ g/L}$) 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 analyzed 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 colorless effluents of very low Microtox ecotoxicity.

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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 (800–25,000 mg/L COD), high salinity (3000–4000 $\mu\text{S/cm}$) 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 wine-making 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 ($\approx 4000 \text{ mg/L}$) [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].

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Wastewaters with a low initial COD (600–1500 mg/L) have been treated by this way leading to COD reductions within a fairly wide range (60–90%) depending on the dose of hydrogen peroxide, the $[H_2O_2]/Fe$ 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 ($T = 120\text{--}300\text{ }^\circ\text{C}$, $P = 0.8\text{--}20\text{ MPa}$) are required [22] while WPO works under relatively milder operating conditions ($T = 50\text{--}125\text{ }^\circ\text{C}$, $P = 0.1\text{--}0.5\text{ MPa}$) 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 $N = 0.32\text{ g/L}$, $K = 2.5\text{ g/L}$ and $P = 0.28\text{ g/L}$, $S = 0.12\text{ g/L}$ and $Ca = 0.16\text{ g/L}$), COD = $35 \pm 2.2\text{ g/L}$ and TOC = $11.3 \pm 0.9\text{ g/L}$. 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 (propionic, 2-hydroxypropionic, ethyl ester 2-hydroxypropionic, butanoic, succinic, pentanoic, hexanoic, methyl phenylglyoxylate) and alcohols (ethanol, benzyl alcohol, phenylethyl alcohol, 2-ethylphenol, 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 N mL/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 pH = 3.8, 160 $^\circ\text{C}$ and 1 MPa with a pure oxygen flow of 92 N mL/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 pH = 3.8, 80 $^\circ\text{C}$, 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: $pH_0 = 2.2\text{--}7$, $T = 80\text{--}125\text{ }^\circ\text{C}$, $P = 0.1\text{--}0.7\text{ MPa}$, $[COD]_0 = 3.5\text{--}35\text{ g/L}$ and $[H_2O_2]_0 = 0\text{--}1.6$ 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 ($COD_{corrected} = COD_{measured} - 0.4635 \cdot C_{H_2O_2}$, 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

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