Treatment of winery wastewater by ozone-based advanced oxidation processes (O$_3$, O$_3$/UV and O$_3$/UV/H$_2$O$_2$) in a pilot-scale bubble column reactor and process economics

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ARTICLE INFO

ABSTRACT

The effectiveness of different ozone-based advanced oxidation processes (O$_3$, O$_3$/UV and O$_3$/UV/H$_2$O$_2$) on the treatment of winery wastewater was investigated in a pilot-scale, bubble column reactor. At the natural pH of the wastewater (pH 4) the effectiveness of each AOP followed the sequence: O$_3$/UV/H$_2$O$_2$ > O$_3$/UV > O$_3$ > UV-C. The rate of chemical oxygen demand (COD) and total organic carbon (TOC) removal were enhanced by operation at neutral (pH 7) and at alkaline pH (pH 10). The underlying chemistry involved in each of the AOPs is discussed and correlated with the observed reactivity. The rate of ozone consumption in the reactor with the O$_3$/UV and O$_3$/UV/H$_2$O$_2$ processes was in the range of 70–95% during the experiments, suggesting an effective use of the ozone supplied to the system. In all the experiments the disappearance of the winery wastewater organic load was described by pseudo-first-order apparent reaction kinetics. The fastest rate constant (6.5×10^{-3} min^{-1}), at the natural pH of the wastewater, was observed with the O$_3$/UV/H$_2$O$_2$ process under optimised oxidant dose (COD/H$_2$O$_2$ = 2). An economic analysis of the operating costs of the AOPs processes investigated revealed the O$_3$/UV/H$_2$O$_2$ to be the most economical process (1.31 Euro m^{-3} g^{-1} of TOC mineralised under optimised conditions) to treat the winery wastewater.

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1. Introduction

Wine is an alcoholic beverage made of fermented grape juice. Producing wine requires the implementation of several unit operations (grape reception, must production, fermentation, decanting, maturation-stabilization, filtration and transportation-disposal) [1,2]. In the unit operations performed in wineries, distilleries and other grape processing industries, large volumes of waste streams are generated annually. These include organic waste (solids, skins, pips, etc.), wastewater, greenhouse gases (CO$_2$, volatile organic compounds, etc.) and inorganic wastes (diatomaceous earth, bentonite clay and perlite). It is estimated that a winery produces between 1.3 and 1.5 kg of residues per litre of wine produced, 75% of which is winery wastewater [3].

The organic content of winery wastewater consists of highly soluble sugars, alcohols, acids and recalcitrant high-molecular-weight compounds (e.g., polyphenols, tannins and lignins) not easily removable by physical or chemical means.

Advanced oxidation processes (AOPs) are known for the ability to mineralise a wide range of organic compounds. AOPs involve the generation of highly reactive radical species, predominantly the hydroxyl radical ($^{\bullet}$OH) [4,5]. Ozone is a strong oxidizer having high reactivity and selectivity towards organic compounds such as polyphenols. Among AOPs, ozonation and ozonation in combination with UV-C radiation and/or peroxidation have been shown to be effective in the treatment of wastewater with polyphenol content such as that found in the cork manufacturing industry [6,7], the olive oil industry [8–11] and the wine distillery industry [12–17]. One major advantage of the application of ozone (undecomposed, pH < 6) in the treatment of wastewater with a complex matrix, of polyphenols and other species, rests in the higher selectivity of molecular ozone towards polyphenols when compared to the reaction of these with radical species (e.g., the hydroxyl radical). The differences in the selectivity of molecular ozone and radicals for polyphenols are associated with the different mechanism of oxidation by these species, with ozone following electrophilic attack of electron rich sites of the target molecule [18] and reactive radicals reacting non-selectively with all species in solution (e.g., the $^{\bullet}$OH radical reacts by either hydrogen abstraction, OH addition or substitution, or by electron transfer). On the other hand, the

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Nomenclature

a	interfacial area, m^2/m^3
COD	chemical oxygen demand, $g\,L^{-1}$
H_g	gas-hold up, %
k'	pseudo-first-order rate constant, min^{-1}
k_L	individual volumetric mass transfer coefficient, $m\,s^{-1}$
$k_L a$	volumetric mass transfer coefficient, s^{-1}
m_{O_3}	ozone mass flow rate, $g\,s^{-1}$
$[O_3^*]$	ozone interfacial concentration, $g\,L^{-1}$
P_{O_3}	ozone partial pressure in gas phase, kPa
Q_g	volumetric flow rate of gas phase, $L\,s^{-1}$
TOC	total organic carbon, $g\,L^{-1}$
t	ozonation time, s
U_g	superficial gas velocity, $m\,s^{-1}$

standard oxidation potential of the hydroxyl radical ($E_0 = 2.80\,V$) is much higher than that of ozone ($E_0 = 2.07\,V$), therefore, the combination of ozone with UV and/or H_2O_2 which yields hydroxyl, peroxyl and superoxide radicals should synergistically accelerate the removal of organic matter from complex wastewater matrices.

The treatment of winery wastewater by ozonation and ozone related AOPs have been demonstrated in small and a pilot-scale studies. Gimeno et al. [19] reported the photocatalytic ozonation of winery wastewater in a 1 L reactor and the total mineralisation of the COD removed in the presence of UV-A, ozone and titanium dioxide. Navarro et al. [20] investigated the degradation of wine industry wastewater by photocatalytic oxidation, UV-peroxidation and Fenton reaction over iron rich clays in 100 mL glass vials. In our previous work [21], we have investigated the kinetics of ozonation of winery wastewater in detail in a pilot-scale (9 L), semi-

batch bubble column reactor under alkaline, neutral and acidic conditions. We concluded that ozonation prior to biological treatment could be beneficial to remove the toxicity (polyphenols) from the wastewater. The degradation of aromatics and polyphenols was found to be significantly faster than the decrease in COD.

In this work, we investigate the effectiveness of different ozone-based AOPs (O_3, O_3/UV and $O_3/UV/H_2O_2$) on the treatment of winery wastewater, in a pilot-plant scale reactor, with the objective of suggesting the most efficient process which could be implemented by the industry. The effect of initial pH, organic load of winery wastewater and hydrogen peroxide concentration were investigated in the same pilot-scale reactor. The effect of each AOP on the reduction of chemical oxygen demand (COD) and total organic carbon (TOC) were evaluated and operating costs were estimated. The underlying chemistry involved in each of the AOPs is discussed and correlated with the observed reactivity.

2. Materials and methods

2.1. Winery wastewater

The winery wastewater was collected from a wine production unit located in the Douro region in the north of Portugal. The pH, the absorbance at 254 nm, the total carbon (TC), inorganic carbon (IC), the COD and polyphenols content measured as equivalent gallic acid content are presented in Table 1.

2.2. Ozonation

The ozonation and the experiments with ozone-based AOPs (O_3/UV and $O_3/UV/H_2O_2$) were conducted in a bubble-column, semi-batch reactor (internal diameter 0.1 m, height 1 m) made of QVF borosilicate glass equipped with a quartz UV-lamp tube (external diameter 40 mm) mounted in the axial position which houses

Table 1
Characterisation of the winery wastewater [21].

pH	$Abs_{254\,nm}$ (cm^{-1})	TC ($mg\,L^{-1}$)	IC ($mg\,L^{-1}$)	COD ($mg\,O_2\,L^{-1}$)	Polyphenols ($mg_{gallic\ acid}\,L^{-1}$)
4.0	1.562	1255	1.11	4650	103

Fig. 1. Schematic representation of the pilot plant used in this study: [1] oxygen cylinder; [2] silica filter; [3] ozone generator; [4] flowmeter; [5] Drechsel bottle (In); [6] ozonation reactor; [7] UV-C lamp; [8] variable power transformer; [9] recirculation pump; [10] ozone monitor; [11] Dreschel bottle (out); [12] ozone destructor; [13] extractor; [14] ozone detector.

Table 2
Hydrodynamic and operational conditions of the ozonation reactor.

Q_g (L min^{-1})	U_g (m s^{-1})	H_g (%)	a (m^{-1})	P_{O_3} (kPa)	$[O_3^*]^a$	m_{O_3} (mg min^{-1})	$k_L a^b \times 10^{-3}$ (s^{-1})
3.6	6.8×10^{-3}	3.5	65.1	1.31	7.5	100.1	11.2

[a] Based on Henry's constant 8400 kPa L mol^{-1} [22].
[b] Calculated from the results on ozone physical sorption by pure water [23] and confirmed by the correlation of Akita and Yoshida [24].

the lamp (Fig. 1). The UV-C lamp used (Philips TUV36W, 36 W nominal power, bulb dimensions: 1.156 m long, 28 mm in diameter) emits predominantly monochromatic radiation at 253.7 nm (15 W UV-C output).

The reactor was equipped with a liquid stream outlet at the bottom and an inlet at the top, connected to a peristaltic pump (Masterflex 77200-62, Cole-Parmer, USA) to assist water recirculation in the reactor. An in-line redox potential (ORP) sensor was installed in the water recirculation tube. The gas stream enriched with ozone entered the reactor via a sintered stainless steel porous disk S20 (Porvair Ltd., UK, mean pore size 15 μm) at the bottom of the reactor. A gas stream outlet at the top of the reactor led to a thermal ozone decomposition unit. Liquid samples were collected with a syringe through a sealed port in the reactor. The ozone concentration at the gas inlet and outlet of the reactor were measured by redirecting the flows to a series of Drechsel flasks containing a 2% potassium iodide solution.

High purity oxygen (99.999%, BOC gases, UK) was fed to a silica drier to remove trace water prior to entering the ozone generator (OZOMAX 8Vtt, Ozomax, Canada) which was capable of producing up to 0.68 g ozone per minute. The hydrodynamic and operational conditions used in this study are summarised in Table 2 with the symbols presented in Nomenclature.

Nine litres of winery wastewater were loaded into the reactor and the degradation experiments were performed with continuous ozone supply for various time periods. The water was re-circulated at a flow rate of 1 L min^{-1} in order to improve the mixing of the liquid in the reactor, in addition to the mixing provided by the gas bubbles.

In the O$_3$/UV/H$_2$O$_2$ process, the required amount of H$_2$O$_2$ was added to the reactor as a single dose at time zero, at COD/H$_2$O$_2$ ratios of 1, 1.3, 2 and 4. All samples collected from the experiments involving H$_2$O$_2$ were treated with a saturated solution of NaOH to quench the reaction of residual H$_2$O$_2$.

Water samples were withdrawn regularly and analysed. The pH was monitored at regular intervals through the ozonation process and, if required, it was controlled using 0.1 M NaOH or 0.1 M H$_2$SO$_4$ solutions. All solutions and reagents were prepared in ultra-pure water, supplied by a NANOpure Diamond UV water purification system that provides bacteria free water with resistivity of 18.2 MΩ cm^{-1} or higher and TOC < 1 ppb. The oxidation experiments were performed in duplicate and the observed standard deviation was always less than 6% of the reported value.

2.3. Analytical methods

The organic matter in the samples was characterised in terms of COD (HACH, model 45600 coupled with a colorimeter HACH, ODYSSEY) and TOC (Shimadzu TOC-VCPH). The absorbance of samples was determined by a UV/Vis Spectrophotometer, UV mini 1240 Shimadzu. The Folin-Ciocalteau method, using gallic acid as a standard, was followed to evaluate the total polyphenols content in the samples [25]. Hydrogen peroxide concentration in the samples was measured by means of Merckoquant Peroxide Test strips (0–25 mg H$_2$O$_2$ L^{-1}). If required, the samples were diluted several times in order to achieve an accurate measurement of the H$_2$O$_2$ concentration.

3. Results and discussion

3.1. AOPs comparison

Experiments were carried out with UV radiation, ozone only, O$_3$/UV and O$_3$/UV/H$_2$O$_2$ at the natural pH of the winery wastewater (pH = 4), in order to investigate the influence of each process on the rate of COD removal. The pH was not controlled by buffer during these oxidation experiments. Fig. 2 presents the removal of COD of the winery wastewater and a comparison of the four treatment processes. The direct photolytic action of UV-C radiation on the compounds dissolved in the winery wastewater was insignificant. Ozonation reduced the initial COD by 12% and the combination of UV-C radiation and ozonation removed 21% of COD, after 180 min of reaction. An enhancement of the COD removal was achieved by adding hydrogen peroxide to the solution in the O$_3$/UV/H$_2$O$_2$ process. With a COD/H$_2$O$_2$ (w/w) ratio equal to 4, the COD removal was 35% after 180 min. The UV light intensity and ozone dose were kept constant in the above experiments. At pH 4, ozone does not decompose to more reactive radical species, therefore the COD removal was limited. However, both the O$_3$/UV and O$_3$/UV/H$_2$O$_2$ processes were capable of oxidizing winery wastewater faster than ozone on its own showing a photochemical enhancement oxidation effect. This is principally due to the photolysis of ozone, the enhanced mass transfer of ozone and the generation of hydroxyl radicals that react rapidly with the organic matter in the winery wastewater [26].

The underlying chemistry of ozonation in the presence of UV-C and H$_2$O$_2$ is summarised below [4,5,27]. The photodecomposition of ozone by UV-C radiation leads to formation of H$_2$O$_2$ and hydroxyl radicals as shown by the following reactions:
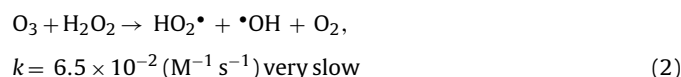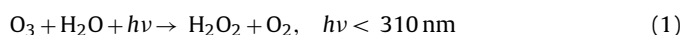
$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2, \quad h\nu < 310\,\text{nm} \tag{1}$$

$$O_3 + H_2O_2 \rightarrow HO_2^\bullet + {}^\bullet OH + O_2,$$
$$k = 6.5 \times 10^{-2}\,(\text{M}^{-1}\,\text{s}^{-1})\,\text{very slow} \tag{2}$$

Fig. 2. COD profile during the UV, O$_3$, O$_3$/UV and O$_3$/UV/H$_2$O$_2$ treatment of winery wastewater. Experimental conditions from Tables 1 and 2. Liquid volume 9 L; COD/H$_2$O$_2$ (w/w) = 4, initial pH 4.
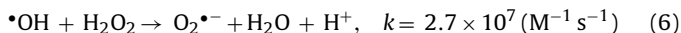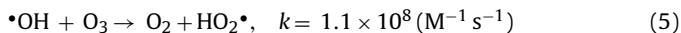
In addition, the photolysis of H_2O_2 by UV-C radiation yields two hydroxyl radicals from each molecule of hydrogen peroxide:
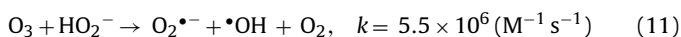
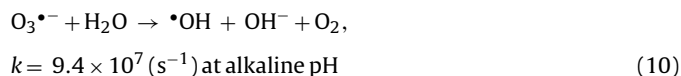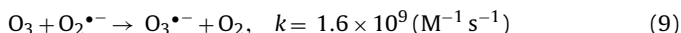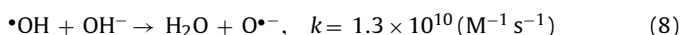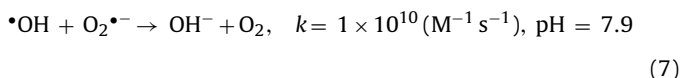$$H_2O_2 + h\nu \rightarrow 2\,^{\bullet}OH \quad (\phi_{OH^{\bullet}} = 1) \tag{3}$$
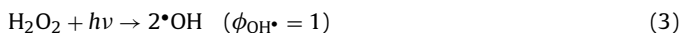
In the presence of H_2O_2, in addition to photolysis (3), the following equilibrium occurs:

$$H_2O_2 + H_2O \leftrightarrow H_3O^+ + HO_2^-, \quad pK = 11.65 \tag{4}$$
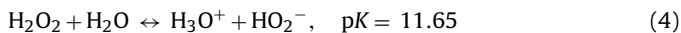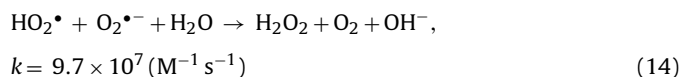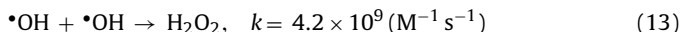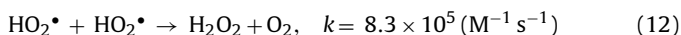
Both ozone and hydrogen peroxide react with the hydroxyl radicals to form the peroxyl and the superoxide radical (5) and (6):

$$^{\bullet}OH + O_3 \rightarrow O_2 + HO_2^{\bullet}, \quad k = 1.1 \times 10^8\,(M^{-1}\,s^{-1}) \tag{5}$$

$$^{\bullet}OH + H_2O_2 \rightarrow O_2^{\bullet-} + H_2O + H^+, \quad k = 2.7 \times 10^7\,(M^{-1}\,s^{-1}) \tag{6}$$

which in turn they react further with the hydroxyl radical and ozone in a propagation reaction scheme to yield hydroxyl radicals:

$$^{\bullet}OH + O_2^{\bullet-} \rightarrow OH^- + O_2, \quad k = 1 \times 10^{10}\,(M^{-1}\,s^{-1}),\ pH = 7.9 \tag{7}$$

$$^{\bullet}OH + OH^- \rightarrow H_2O + O^{\bullet-}, \quad k = 1.3 \times 10^{10}\,(M^{-1}\,s^{-1}) \tag{8}$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2, \quad k = 1.6 \times 10^9\,(M^{-1}\,s^{-1}) \tag{9}$$

$$O_3^{\bullet-} + H_2O \rightarrow\ ^{\bullet}OH + OH^- + O_2,$$
$$k = 9.4 \times 10^7\,(s^{-1})\ \text{at alkaline pH} \tag{10}$$

$$O_3 + HO_2^- \rightarrow O_2^{\bullet-} + \,^{\bullet}OH + O_2, \quad k = 5.5 \times 10^6\,(M^{-1}\,s^{-1}) \tag{11}$$

Hydroxyl, peroxyl and superoxide radical recombination ((12) and (13)) produce hydrogen peroxide which can be photolyzed again (3).

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2, \quad k = 8.3 \times 10^5\,(M^{-1}\,s^{-1}) \tag{12}$$

$$^{\bullet}OH + \,^{\bullet}OH \rightarrow H_2O_2, \quad k = 4.2 \times 10^9\,(M^{-1}\,s^{-1}) \tag{13}$$

$$HO_2^{\bullet} + O_2^{\bullet-} + H_2O \rightarrow H_2O_2 + O_2 + OH^-,$$
$$k = 9.7 \times 10^7\,(M^{-1}\,s^{-1}) \tag{14}$$

Under an excess of H_2O_2 the scavenging reaction (6) may become predominant followed by:

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2, \quad k = 8.0 \times 10^9\,(M^{-1}\,s^{-1}) \tag{15}$$
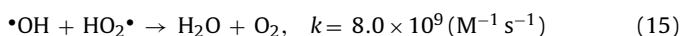
As the highest degradation capacity was showed by the O_3/UV and $O_3/UV/H_2O_2$ processes, the effects of the operational conditions, such as, pH, initial organic load (TOC) and COD/H_2O_2 (w/w) ratio, were studied in the treatment of the wastewater.

3.2. O_3/UV

O_3/UV experiments were carried out at the natural pH of the winery wastewater (pH = 4) and at two other initial pH, 7 and 10, in order to investigate the effect of radical formation on the rate of COD removal. Fig. 3 presents results of COD removal and pH profile. The fastest COD removal was observed at pH 10 as a result of the fast reaction of the organic matter with the radical species (i.e., $^{\bullet}OH$, $HO_2^{\bullet}$, $O_2^{\bullet-}$ and $O_3^{\bullet-}$). At alkaline pH, ozone self-decomposition to radicals occurs as a result of the initiation reaction [28]:

$$O_3 + OH^- \rightarrow HO_2^- + O_2, \quad k = 40\,(M^{-1}\,s^{-1}),\ pH = 10 \tag{16}$$
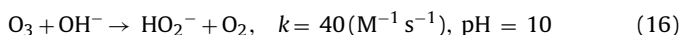
with a half life reported to be 20 s [29] (Fig. 3a). In addition, the H_2O_2 is deprotonated preferentially to water to give the hydroperoxide anion HO_2^- (reaction (4)) which then reacts in a chain mechanism (reactions (7)–(11)). However, after a few minutes once the pH reached values close to neutral and below (Fig. 3b) the COD removal rates were identical in the three experiments. During this stage the

Fig. 3. (a) COD profile during the O_3/UV treatment of winery wastewater. (b) Profile of pH. Experimental conditions from Tables 1 and 2. Liquid volume 9 L; initial pH 4 (■), 7 (●) and 10 (▲).

removal of COD was controlled by the generation of radical species by the reaction scheme presented above (in which reactions (4), (10), (11) and (15) become less important).

Fig. 3b shows the profile of pH for the above experiments. A slight decrease in pH from 4 to 3.7 was observed in the experiments performed at the natural pH. A sharp decrease in the pH of wastewater was observed in the experiments with initial pH of 7 and 10, and the final pH was 3.8 and 4.0, respectively, which indicates that a strong oxidation took place. The reduction in pH is attributed to the formation of dicarboxylic acids and small molecule organic acids, as well as CO_2 and carbonic acids from total mineralisation of the organic matter.

3.3. $O_3/UV/H_2O_2$

Experiments in the presence of ozone, UV radiation and hydrogen peroxide ($O_3/UV/H_2O_2$ process) were found to enhance the degradation of the organic matter in the winery wastewater. Fig. 4 shows the effect of pH in the removal of COD as a function of reaction time and the pH profile during the experiments. The removal efficiency is slightly higher at pH 10 (57%) than pH 4 (49%) and pH 7 (40%) after 300 min. In the $O_3/UV/H_2O_2$ process the production of hydroxyl radicals by reaction (3) becomes highly significant due to the supplementary H_2O_2 added to the solution, as well as reaction (6) under an excess of peroxide. In addition, the reaction of ozone with H_2O_2 (2) also produce hydroxyl radicals although at a slower rate.

The profile of pH in these experiments followed the same trends as in the experiments carried out in the absence of H_2O_2, although the experiments at pH 10 showed a slower rate of pH decay, which also explain partially the faster rates observed with the $O_3/UV/H_2O_2$ in comparison to the other AOPs.

Fig. 5. Profile of the ozone mass flow rate at different initial pH for the treatment of winery wastewater with O_3/UV (open symbols) and $O_3/UV/H_2O_2$ (filled symbols). The ozone mass rate at the reactor inlet is constant and equal to 100.1 mg O_3 min^{-1} ($\bigcirc$) in all cases. Experimental conditions from Tables 1 and 2. Liquid volume 9 L; COD/H_2O_2 (w/w) = 4.

3.5. Reaction kinetics

Due to the presence of a complex matrix and unknown multiple reactions, COD and TOC were used to describe the global kinetics of organic matter removal and to derive the essential kinetic parameters needed for reactor design and optimisation. The removal of COD from the winery wastewater by the different AOPs was fitted by an apparent first-order rate equation to compare all processes, although the results in Fig. 3 appear to suggest zero-order kinetics for ozonation. Table 3 shows the pseudo-first-order rate constants at pH 4, 7 and 10 and the %TOC removed after 300 min. The removal of TOC was found to follow the trend of COD removal. The COD rate constants and TOC removal with the $O_3/UV/H_2O_2$ process were the highest, and significantly higher at pH 4 (the natural pH of winery wastewater) compared to the other AOPs. The COD rate constants of the $O_3/UV/H_2O_2$ process were double the constants of the O_3 process alone and the TOC removal was 8 to 11 fold higher.

3.6. Effect of hydrogen peroxide concentration and organic load

Fig. 6 shows the influence of hydrogen peroxide concentration on the treatment of winery wastewater by the $O_3/UV/H_2O_2$ process at pH 4, the natural pH of the winery wastewater (Table 1) conveniently chosen to minimise expensive pH adjustment in an industrial process. The COD/H_2O_2 (w/w) ratio was varied: 1; 1.3; 2 and 4. It shows that in the pilot plant almost complete mineralisation can be achieved (88% TOC removal) under optimised oxidant dose ($COD/H_2O_2 = 2$). At $COD/H_2O_2 = 4$ there is insufficient supplementary peroxide, at $COD/H_2O_2 = 1.3$ the TOC removal is slightly lower than at the optimum COD/H_2O_2 ratio, and at $COD/H_2O_2 = 1$ there is excess peroxide which scavenges hydroxyl radicals (reactions (6)

Fig. 4. (a) COD profile during the $O_3/UV/H_2O_2$ treatment of winery wastewater. (b) Profile of pH. Experimental conditions from Tables 1 and 2. Liquid volume 9 L; COD/H_2O_2 (w/w) = 4; initial pH 4 (■), 7 (●) and 10 (▲).

3.4. Ozone consumption

The rate of ozone consumption was monitored through the measurement of the ozone mass flow rate at the inlet and at the outlet of the reactor. The mass flow rate at the reactor inlet was kept constant throughout each experiment. The difference between the values at the inlet and outlet of the reactor defines the rate of ozone consumed within the reactor. This includes the contribution from the reaction of molecular ozone with the organic matter, and can also include the contribution from ozone decomposition at alkaline pH and ozone consumption by the hydrogen peroxide formed or added to the reactor.

The profile of the ozone mass flow rate at the reactor outlet of the bubble column reactor with the O_3/UV and $O_3/UV/H_2O_2$ processes at different pH is shown in Fig. 5. In contrast with the results for ozonation alone presented in Lucas et al. [21] a much higher rate of ozone consumption, in the region from 70% to 95% was observed in these experiments, suggesting a more effective use of the ozone supplied to the system. At pH 4, a lower rate was observed with O_3/UV compared to the $O_3/UV/H_2O_2$ process as a result of lower contribution of reactions (2)–(4) since H_2O_2 can only be produced by reaction (1) in the first instance and by radical recombination reactions (12)–(14). Conversely, at pH 7 and 10 ozone consumption was found to be very similar (>85%) in both the O_3/UV and the $O_3/UV/H_2O_2$ processes. However, in the experiment at pH 10 with $O_3/UV/H_2O_2$ a significant reduction of the rate of ozone uptake was observed after 120 min, possibly due to the lower level of COD reached (Fig. 4a) and the decomposition of H_2O_2 (reaction (4)) at alkaline conditions, which in turns reduces the amount of hydroxyl radicals formed by H_2O_2 photolysis (reaction (3)).

Table 3
Initial pseudo-first-order rate constants (k') obtained from COD removal, R^2 and %TOC removed after a reaction time of 300 min with ozone and ozone related AOPs at different initial pH.

Process	k' (min^{-1})	R^2	%TOC removed after 300 min
O_3 (pH 4)	1.1×10^{-3}	0.994	4.4
O_3 (pH 7)	1.1×10^{-3}	0.986	5.4
O_3 (pH 10)	1.4×10^{-3}	0.989	7.9
O_3/UV (pH 4)	1.5×10^{-3}	0.997	8.5
O_3/UV (pH 7)	1.8×10^{-3}	0.986	13
O_3/UV (pH 10)	1.9×10^{-3}	0.966	26
$O_3/UV/H_2O_2$ (pH 4)	2.2×10^{-3}	0.983	49
$O_3/UV/H_2O_2$ (pH 7)	2.2×10^{-3}	0.969	49
$O_3/UV/H_2O_2$ (pH 10)	2.9×10^{-3}	0.979	64

Table 4
Operating costs for the 9 L pilot-scale bubble column reactor operated for 5 h under the hydrodynamic conditions in Table 2.

	Operating costs	Euro
1	Cost of oxygen supply[a]	0.03536
2	Cost of electricity for ozone generation[b]	0.03942
3	Cost of electricity for UV-lamp operation[c]	0.01971
4	Cost of UV-lamp replacement[d]	0.01250
5	Cost of H_2O_2 added (COD/H_2O_2 = 4)[e]	0.00837
	Pilot plant operating cost for each AOPs	**Euro/m^3**
	O_3 (1 + 2) Euro/9 L × 1000 L	8.31
	O_3/UV (1 + 2 + 3 + 4) Euro/9 L × 1000 L	11.89
	O_3/UV/H_2O_2 (1 + 2 + 3 + 4 + 5) Euro/9 L × 1000 L	12.82[f]

[a] @ 0.025 Euro/kg O_2.
[b] @ 0.1095 Euro/KWh, ozonator consumes 12 Wh/g ozone when fed with oxygen.
[c] 36 W nominal power.
[d] @ 20 Euro/lamp, 8000 h lifetime.
[e] @ 0.24 Euro/kg.
[f] 12.83 (COD/H_2O_2 = 2), 12.84 (COD/H_2O_2 = 1.3), 12.85 (COD/H_2O_2 = 1).

Fig. 6. Influence of initial hydrogen peroxide dosage in the mineralisation of winery wastewater with the O_3/UV/H_2O_2 process. Inset shows the apparent first-order rate constant of TOC removal. Experimental conditions from Tables 1 and 2. Liquid volume 9 L; initial pH 4, COD/H_2O_2 (w/w) = 1, 1.3, 2 and 4.

Fig. 7. Effect of initial TOC on the treatment of winery wastewater by the O_3/UV/H_2O_2 process. Experimental conditions from Table 2. Liquid volume 9 L; COD/H_2O_2 (w/w) = 2; initial pH = 4.

the original wastewater by 1:2 and 1:10. Although the apparent rate constant (slope) increases as the wastewater is diluted, the overall effect is a reduction of the overall TOC removal rates ($mg\,L^{-1}\,min^{-1}$), at lower initial TOC concentrations. In consequence, dilution of winery wastewater is not recommended.

3.7. Operating costs

The adoption of the optimal treatment process in the industrial environment ultimately would depend on favourable process economics. This aspect is most often neglected in the literature which compares treatment options of industrial or simulated wastewater. However, when the experiments are carried out in a pilot-scale reactor, a preliminary economic evaluation of the treatment processes can be attempted. In the case of the AOPs studied, the process economics are primarily dependent on the costs of electricity (for ozone generation and to power the UV-lamp), in situ oxygen generation to feed the ozone generator, UV-lamp replacement, and added chemicals. An estimation of the operating costs of the, O_3, O_3/UV and O_3/UV/H_2O_2 processes based on the experiments carried out in the pilot-scale reactor was performed. The analysis excludes capital, maintenance, labour and depreciation costs since these will be common to all AOPs investigated. Table 4 shows the costs for electricity, oxygen production, lamp replacement and H_2O_2 to operate the pilot plant. Table 5 shows the operating costs (Euro m^{-3} g^{-1} of TOC mineralised) for the conditions in each of the experiments. The lowest operating cost was found to be 1.31 Euro m^{-3} g^{-1} of TOC mineralised for the experiment carried

and (15)). Fig. 6 (inset) shows the apparent first-order rate constant of TOC removal to be significantly affected by the COD/H_2O_2 ratio. The highest rate constant (6.5×10^{-3} min^{-1} with COD/H_2O_2 = 2) is six-fold higher than the rate constant with O_3 process alone clearly showing the superiority of the O_3/UV/H_2O_2 process compared to the O_3 process alone, studied also in other work [21].

Fig. 7 shows the results of experiments at COD/H_2O_2 (w/w) = 2 (fastest TOC removal), pH = 4 (natural pH of the winery wastewater), and varying the initial TOC of the water by dilution of

Table 5
Operating costs (Euro m^{-3} g^{-1} of TOC mineralised) for each experiment.

Experiment	TOC$_0$ (mg L^{-1})	COD/H_2O_2 (w/w)	TOC removed in pilot plant (9 L) after 300 min (g)	Operating costs (Euro m^{-3} g^{-1} of TOC mineralised)
O_3 (pH 4)	1254	4	0.50	16.73
O_3 (pH 7)	1254	4	0.61	13.63
O_3 (pH 10)	1254	4	0.89	9.32
O_3/UV (pH 4)	1254	4	0.95	12.39
O_3/UV (pH 7)	1254	4	1.47	8.10
O_3/UV (pH 10)	1254	4	2.93	4.05
O_3/UV/H_2O_2 (pH 4)	1254	4	5.53	2.32
O_3/UV/H_2O_2 (pH 7)	1254	4	5.53	2.32
O_3/UV/H_2O_2 (pH 10)	1254	4	7.22	1.77
O_3/UV/H_2O_2 (pH 4)	1254	2	9.82	1.31
O_3/UV/H_2O_2 (pH 4)	1254	1.3	9.14	1.40
O_3/UV/H_2O_2 (pH 4)	1254	1	7.11	1.81
O_3/UV/H_2O_2 (pH 4)	628	2	5.54	2.31
O_3/UV/H_2O_2 (pH 4)	125	2	1.10[a]	4.93

[a] After 150 min.

out with the $O_3/UV/H_2O_2$ process at pH 4 and COD/H_2O_2 ratio of 2. Taking as a basis the operating costs of ozonation alone, a significant reduction of 25–56% and 80–86% in the treatment costs were obtained with the O_3/UV and $O_3/UV/H_2O_2$ processes, respectively. Fine tuning of the operating conditions could change the absolute costs obtained under each treatment process, however, this preliminary cost analysis and the kinetic data give an indication that the $O_3/UV/H_2O_2$ process is not only the most efficient but also the most economical process among those studied for the treatment of the present winery wastewater. Dilution of the wastewater should not be carried out since it increases treatment costs.

4. Conclusions

The overall results of this study carried out in a pilot-scale bubble column reactor indicate that the O_3/UV and $O_3/UV/H_2O_2$ processes are feasible methods for the treatment of winery wastewaters. These processes, comparatively to UV radiation and ozonation alone at natural pH (pH 4), involve the formation of highly reactive radicals in solutions resulting in faster degradation rates. O_3/UV and $O_3/UV/H_2O_2$ allowed significant COD and TOC removal and are shown to be highly dependent on the initial pH of the wastewater.

The rate of ozone consumption in the reactor was in the range of 70–95% during the experiments, suggesting an effective use of the ozone supplied to the system. In all the experiments the disappearance of the winery wastewater organic load was described by pseudo-first-order apparent reaction kinetics useful for the design of industrial reactors operating under similar conditions to this work. The fastest rate constant (6.5×10^{-3} min^{-1}), at the natural pH of the wastewater, was observed with the $O_3/UV/H_2O_2$ under optimised oxidant dose ($COD/H_2O_2 = 2$). Water dilution resulted in lower TOC removal rates. An economic analysis of the operating costs of the AOPs processes investigated revealed the $O_3/UV/H_2O_2$ to be the most economical process (1.31 Euro m^{-3} g^{-1} of TOC mineralised under optimised conditions).

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