Multi-criteria analysis of sustainable environmental clean technologies for the treatment of winery’s wastewater

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Abstract: The current study deals with the application advanced oxidation process (AOP), as a clean technology for the treatment of winery’s wastewater. In order to find out the best available technique (BAT) amongst several AOP, a multi criteria analysis was used. As key evaluation criteria the categories of costs, benefits, opportunities and risks, were applied, each one of them included a range of economic, environmental, technical and social sub-criteria. The final results indicated that the methods of homogeneous and heterogeneous photocatalysis can be applied satisfactorily to the treatment of wineries wastewater, resulting in reduction of total organic carbon in the range of 30% to 80%. The multi-criteria analysis indicated that, the homogeneous photocatalysis photo Fenton, predominates over other photocatalytic techniques due to the high rates of degradation of the organic load (80%). The application of a hybrid system combining homogeneous photocatalysis photo Fenton as a pre-treatment step followed by biological treatment is found to be relatively the optimal solution to resolve the problem of winery’s wastewater treatment, resulting in more than 90% reduction of total organic load.

Keywords: winery wastewater; advanced oxidation process; AOP; chemical oxidation; multi-criteria analysis.


Biographical notes: Antonis A. Zorpas studied chemical engineering and holds a PhD focuses on Environmental Management and Engineering. He has a rich academic record having more than 200 publications in academic journals, international conferences and is editor of three scientific books. His research background includes solid-liquid waste management-treatment, composting, chemical oxidation, sustainable development programs and strategic plans, environmental impact and environmental/risk assessment analysis, and waste to energy (>15 years). He is (2013–2017) the President of Cyprus Environmental Engineers Council. He is also in the advisory committee of the Office of the Cyprus Commissioner for the Environment.
1 Introduction

Throughout the last decades, wineries have rapidly increased in rural areas and particularly in insular areas. Wineries’ wastewater treatment is considered to be a high challenge because of their seasonal production and the great variability in composition, with values of chemical oxygen demand varying from 320 to 296,119 mg COD/L (Navarro et al., 2005; Mosse et al., 2011). The wine industry generates large volumes of wastewaters originating from various washing steps during the crushing and pressing of grapes as well as the rinsing of fermentation tanks, barrels and other items of equipment. According to Vlyssides et al. (1997), the total production of wastewater from a winery is about 1.2 times greater than the production of wine. Winery wastewater is characterised by high organic content, seasonal production, unpleasant odours and variable composition, which is associated with the winemaking technologies employed (i.e., for red, white or special wines) and the working period (i.e., peak wastewater generation occurs during the ‘crush’, in other words, when grapes are actively being processed into juice for fermentation); all these make winery effluents difficult to treat fully by conventional biological methods. Furthermore, its treatment by conventional treatment processes is problematic due to the fact that these methods do not provide a comprehensive solution because of the need to dispose of sludge or other by-products derived from such processes (Anastasiou et al., 2009).

Winery’s wastewater, can be characterised as hazardous because of their high organic load, consisting of sugars, alcohols, acids, aldehydes, durable high-molecular compounds, such as polyphenols, tannins and lignin’s, which affect the application of conventional biological methods for their treatment as well soaps and detergents from clean-up operations (Strong and Burgess, 2008; Mosse et al., 2011; Oller et al., 2011).

Winery wastewater normally is low in pH because of organic acids produced in the fermentation process. Generally, it has sufficient amount of phosphorus but the nitrogen is considered to be very low and some other trace minerals, which are essential for the biological treatment. Variability in wastewater composition depends mainly on the season and the particular operations being conducted at any given time. Winery wastewater is generated by the different activities carried out during the wine production, mainly from washing and rinsing operations of fermentation tanks, barrels, and other items (Mosteo et al., 2008). Volumes and pollution loads vary greatly in relation to the working period (vintage, racking, bottling) and to the winemaking technologies used (e.g., in the production of red, white and special wines) (Artiga et al., 2005; Lucas et al., 2010). The high amount of waste produced (usually 1–2 L water, 1 L wine), and the seasonal nature of this industry raise specific problems for the treatment process in terms of volume and composition of the influent (Eusebio et al., 2004).
Wineries’ wastewater treatment is considered to be a high challenge because of their seasonal production as long as their great variability in composition, with values of chemical oxygen demand varying from 320 to 296,119 mg COD/L (Navarro et al., 2005; Agustina et al., 2008; Mosse et al., 2011).

Although the application of biological processes, such as aerobic treatment and anaerobic digestion, is effective (mostly economically) for the treatment of wastewater of high organic load, the high content of polyphenols, aldehydes, tannins etc., make the processes ineffective and difficult to achieve complete degradation of the organic load. Furthermore, the acidic nature of the waste, usually pH ranges from 3–4 (Oller et al., 2011) combined with the low values of phosphorus and nitrogen makes the application of anaerobic digestion insufficient due to the fact that affect the growing up of microorganism which are useful and necessary for the process (Malandra et al., 2003; Strong and Burgess, 2008). Aerobic treatment systems are effectual in the treatment of wastewater from wineries, since they ensure sufficient ventilation, but the large fixed cost as well as the operational cost, makes their implementation difficultly (Strong and Burgess, 2008).

The most common type of biological treatment system is an aerated lagoon or ponds which are considered being traditional treatment processes and mainly for small wineries. Activated sludge, sequencing batch reactors (SBRs), and artificial wetlands are also used. Each of these processes is capable of producing an effluent that is suitable for spray irrigation of vineyards, woodland, or other suitable land. Some wineries have leach-fields, which are biological systems in that they depend on microbial treatment within a soil column.

2 Oxidation using Fenton reactions

Fenton’s reagent was discovered about 100 years ago, but its application as an oxidising process for destroying toxic organics was not applied until the late 1960s (ZorpaS and Costa, 2010). Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g., CO₂, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants. Recently, advanced oxidation processes (AOPs) have been proposed to treat relatively low-strength industrial wastewaters containing non-biodegradable substances toxic to microorganisms. Among them, the Fenton method is cost-effective, easy to apply and effective with relatively low-strength wastewater containing organic compounds and has been applied to the decolourisation of textile wastewater (Swaminathan et al., 2003; Kim et al., 2004; Meric et al., 2004, 2005; Zorpas and Inglezakis, 2011). The Fenton method consists of four stages. First, pH is adjusted to low acidity. Then, main oxidation reaction takes place at pH value of 3–5. The wastewater is then neutralised at pH of 7–8
and finally precipitation occurs (Zorpas and Costa, 2010). The oxidation mechanism in the Fenton process involves the reactive hydroxyl radical generated under acidic conditions by the catalytic decomposition of hydrogen peroxide, which reacts unselectively within 1 ms with organic substances (RH), which are based on carbon chains or rings and also contain hydrogen, oxygen, nitrogen, or other elements. The reaction mechanism is as follows (Xu et al., 2004; Zorpas and Costa, 2010; Zorpas and Inglezakis, 2011):

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \\
\text{RH} + \cdot\text{OH} & \rightarrow \text{R}^- + \text{H}_2\text{O} \\
\text{R}^- + \text{Fe}^{3+} & \rightarrow \text{product} + \text{Fe}^{2+} \\
\text{Fe}^{2+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^-
\end{align*}
\]

Only a few applications of Fenton oxidation to high-strength wastewater such as effluent from a baker’s yeast industry effluent or olive oil mill wastewater have been reported (Altinbas et al., 2003; Khoufi et al., 2006; Zorpas and Costa, 2010; Vlyssides et al., 2012). The Fenton oxidative process is a method of chemical oxidation and coagulation of organic compounds. It is performed by the implementation of hydrogen peroxide (H$_2$O$_2$) and a ferrous salt (Fenton’s reagent) (Zorpas and Costa, 2010; Zorpas and Inglezakis, 2011). With the addition of Fenton’s reagent, first soluble organics are successfully oxidised, and then, with the coagulation procedure, insoluble organics are successfully removed. The Fenton’s process combines oxidation and aggregation, increasing the concentration of dissolved oxygen. For a satisfactory oxidation degree of soluble organics, the pH should be below 4 (Gau and Chang, 1996). Fenton’s reagent is suitable to process a wide variety of effluents regardless of their contaminant concentrations and nature. It is an economical system characterised by its simple application and possibility of using perfectly mixed tank reactors. The system can also be adapted to different volumes and conditions (Bidga, 1995; Zorpas and Inglezakis, 2011).

The proposed of a new technology to improve the treatment of heavy polluted wastewaters like winery’s is a continuous process with a view to developing and implementing technologies that combine increased performance degradation of waste, low fixed and operational costs and low energy demand (which is very important as those systems could characterised as ‘on-off’ process). For this reason the implementation of AOP’s, such as photocatalysis, is considered to be a well promising technology for the complete resolution of the environmental pollution. In current years, AOP have gained considerable attention for the treatment of industrial effluents, including, amongst others, agro-industrial wastes. Of the various processes involved, Fenton oxidation provides a simple and effective method of generating hydroxyl radicals which can subsequently oxidise a wide array of organic pollutants. Additionally, process efficiency may be enhanced in the presence of light irradiation (hn) (i.e., photo-Fenton reactions) through the following redox cycle:
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Fe$^{3+}$ + H$_2$O + hv $\rightarrow$ Fe$^{2+}$ + H$^+$ + 'OH  

Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{2+}$ + OH$^-$ + 'OH  

Numerous researches (Mosse et al., 2011; Navarro et al., 2005; Agustina et al., 2008; Mosteo et al., 2007; Anastasiou et al., 2009; Ioannou et al., 2012), have shown very encouraging results in terms of the applicability of photocatalytic oxidation for the treatment of wineries wastewater (Table 1). It is noted that the application of these techniques, may constitute a definitive solution for the complete degradation of wineries effluents since it is based on the combined use of chemical oxidants and light source to break down complex organic molecules. The paper deals with the evaluation of the AOP through a multi-criteria analysis of the best available techniques (BATs) for the treatment of winery’s waste waters.

Table 1 Implementation of photocatalyst for wineries wastewater treatment

<table>
<thead>
<tr>
<th>Process</th>
<th>Mechanism</th>
<th>Critical parameters</th>
<th>Degradation of TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous photo – Fenton</td>
<td>Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + HO$^-$ + HO.</td>
<td>[Fe$^{2+}$]</td>
<td>pH $\leq$ 3</td>
</tr>
<tr>
<td></td>
<td>R-H + HO. $\rightarrow$ HOO. $\rightarrow$ CO$_2$ + Inorganic salts</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$ + H$_2$O + hv $\rightarrow$ Fe$^{2+}$ + H$^+$ + HO.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(55–250 g/m$^3$)</td>
<td></td>
</tr>
<tr>
<td>Homogeneous photocatalysis</td>
<td>H$_2$O + O$_3$ + UV $\rightarrow$ 2 HO$^-$ + O$_2$</td>
<td>Flow of O$_3$</td>
<td>pH = 10</td>
</tr>
<tr>
<td>with ozone O$_3$/H$_2$O$_2$/UV</td>
<td></td>
<td>(0.1 g/min)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 HO$^-$ $\rightarrow$ H$_2$O$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 O$_3$ + H$_2$O$_2$ + hv $\rightarrow$ 2 HO$^-$ + 3 O$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterogeneous photocatalysis</td>
<td>TiO$_2$ $\rightarrow$ e$^-$ + h$^+$</td>
<td>[TiO$_2$]</td>
<td>[H$_2$O$_2$]</td>
</tr>
<tr>
<td>with TiO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO$_2$(h$^+$) + H$<em>2$O$</em>{ad}$ $\rightarrow$ TiO$_2$ + HO$^-$ + h$^+$</td>
<td>(200–1,000 g/m$^3$)</td>
<td>[H$_2$O$_2$]</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$ + TiO$_2$(e$^-$) $\rightarrow$ TiO$_2$ + HO$^-$ + HO.</td>
<td>TiO$_2$; 80%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HO$^-$ + S$_{ad}$ $\rightarrow$ Intermediates</td>
<td>Anatase – 20% Routile</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wastewater $\rightarrow$ Intermediates $\rightarrow$ CO$_2$ + H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogeneous photocatalysis</td>
<td>H$_2$O$_2$ + hv $\rightarrow$ 2OH</td>
<td>-----</td>
<td>[H$_2$O$_2$]</td>
</tr>
<tr>
<td>H$_2$O$_2$/hv</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$ + OH $\rightarrow$ H$_2$O + HO$_2$</td>
<td></td>
<td>2.5 l/m$^3$</td>
</tr>
<tr>
<td></td>
<td>2HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Lucas et al. (2010), Mosteo et al. (2007) and Navarro et al. (2005)
3 Materials and methods

For the determination of the optimal technology for wineries wastewater treatment, the multi-criteria model of analytic hierarchy process (AHP) was applied, for the pair wise comparison of the candidate technologies. The objectives served by the application of AHP model, include the determination of the most viable treatment technology in terms of low operating costs combined with the high rate of degradation, thereby making it attractive for implementation in industrial scale and simultaneously satisfy regulatory requirements for wastewater management. Furthermore, it serves the identification of technology with lower environmental footprint, ensuring the protection of the environment and to achieve social acceptance. The application of the methodology of AHP is performed by using the software Make It Rational Professional, which was issued at 28/04/2012, by the company Make It Rational and it is available on line (Make It Rational Professional, 2012).

To determine the BAT for wineries wastewater, alternative scenarios considered were:

a photolysis with oxidant H₂O₂ (H₂O₂/hν)
b homogeneous photocatalysis photo Fenton, under the influence of sunlight (Fe²⁺/H₂O₂/hν)
c homogeneous photocatalyst is with ozone O₃/H₂O₂/UV
d heterogeneous photocatalyst is with catalyst TiO₂, under the influence of sunlight (TiO₂/H₂O₂/hν)
e the hybrid system by applying the homogeneous photo Fenton, as a pre-treatment step followed by biological treatment (Fe²⁺/H₂O₂/hν-Bio. Treat.).

The AHP analysis is based on three fundamental principles:

a the breakdown of the problem into sub-problems
b pair wise comparison of criteria and the various alternative scenarios
c the composition of preferences.

The analysis is completed through four steps as follows:

1 the degradation of the problem into sub-problems and the formation of an hierarchical structure
2 the pair wise comparison of decision elements used to derive normalised absolute scales of numbers whose elements are then used as priorities
3 the calculation of the priorities for the data of the problem
4 the composition of preferences for alternative scenarios to solve the problem.

The key element, of the method, is the pair wise comparison of the components at each level of the hierarchical structure, namely the criteria and sub-criteria of the alternative scenarios, which affect the problem. For this purpose comparison matrices are structured for the comparison of the elements of a level of the hierarchy with the elements of the next higher level and so. The data input in comparison matrices, which represent the
expression of preferences of the decision makers, resulting from the fundamental scale of Saaty, which is a qualitative scale that includes values from 1 to 9.

These values are used by the decision makers for the purpose of benchmarking as equal (1), moderately strong (3) strong (5), very strong (7) and very strong (9) importance. Based on the scale preferences Saaty, all possible gradations of preference is \[ P = \{1, 2, 3, 4, 5, 6, 7, 8, 9, 1/2, 1/3, 1/4, 1/5, 1/6, 1/7, 1/8, 1/9\} \]. Consequently, the scale proposed by Saaty, is a mathematical approximation of preferences and the importance of the criteria and alternative scenarios, attributed the decision makers. Nevertheless, in case that there is a precise measurement with respect to the preference of a criterion or alternative scenario over another, it is possible to use the exact measurement (Saaty, 1987, 1990; Karimi et al., 2011; Bottero et al., 2011).

To ensure consistency in the pair wise comparisons, during AHP analysis, the calculation of the consistency ratio (CR) is essential to take place in order to evaluate any discrepancies in matrices of pair wise comparisons that should lead the decision makers to revise their initial estimates. According to the literature, any pair wise comparison matrix is considered to be consistent and hence acceptable when CR is less than 10% (Ozdemir, 2005). In addition to that, a sensitivity analysis on the AHP weights is unfolded to show the impact of varying weights to the final outcome (Georgiou et al., 2012).

The criteria to be used in AHP analysis for the evaluation of alternative scenarios arising from the components of sustainable development and are classified into four main categories:

1. benefits
2. opportunities
3. costs
4. risks.

Each basic category is consisted by a number of environmental, economic and technical sub criteria (Table 2). For the comparative evaluation of alternative scenarios the processes included in the test system, involving the pair wise evaluation of alternative techniques have to do with the raw materials used by each technology, such as catalysts and key reagents, as long as the energy sources that each technology consumes, that may be produced either by renewable sources or generated by the local grid. Additional processes that fall within the limits of the system relating to the biological treatment of the effluent stream from photo Fenton process and the sludge production processes. Regarding the equipment required for the implementation of the under evaluation technologies, within the system falls equipment for collecting solar radiation (i.e., a compound parabolic collector) and an ozone generator. This equipment is taken into account as an important input for the investment cost of the technologies. From the test system is excluded any additional infrastructure needed to implement a full-scale photocatalyst is, since the host of available data in literature concerning laboratory applications. In addition to that from the test system is excluded any treatment processes for the sludge produced by both photocatalyst is and biological processes taking place during wineries wastewater treatment.
## Table 2  Criteria and sub criteria for AHP analysis of the alternative scenarios

<table>
<thead>
<tr>
<th>Main goal</th>
<th>Determination of the optimum technology for wineries wastewater treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criteria</strong></td>
<td><strong>Costs</strong></td>
</tr>
<tr>
<td>Sub criteria</td>
<td>Environmental</td>
</tr>
<tr>
<td></td>
<td>Non-renewable energy sources, land use</td>
</tr>
<tr>
<td></td>
<td>Economic</td>
</tr>
<tr>
<td></td>
<td>Capital investment, maintenance cost, operational cost</td>
</tr>
<tr>
<td></td>
<td>Technical</td>
</tr>
<tr>
<td></td>
<td>New infrastructure, need for qualified personnel, system complexity</td>
</tr>
</tbody>
</table>

### 4 Results and discussions

The first step in applying the AHP model was the calibration of the criteria and sub-criteria. Subsequently, pair wise comparison was performed in order to determine the relative weights for each criterion and the data entered into the software Make It Rational Professional, for the hierarchical classification of the alternatives. Figure 1 illustrates the weights of the core evaluation criteria is 28.12% for the criteria and sub-criteria that are included in the categories of benefits and costs and 21.88% on the criteria and sub-criteria that are included in the categories of opportunities and subheadings. The final ranking of the alternatives is given in the form of bar chart, which lists the technologies under evaluation (axis-y) in conjunction with the overall alternative utility of each technology (axis-x). Total utility represents the total score that occupies each scenario with respect to the satisfaction of the criteria and sub-criteria. The scenario with the highest total utility is considered to be the optimal one. From the application of AHP model is determined that the photocatalyst is technology that better accomplish the criteria and sub-criteria is homogeneous photocatalyst is photo Fenton. According to these results (Figure 2) the homogeneous photo Fenton, satisfies all the criteria in addition to the rate of 90%, with the other technologies run between 70 and 80%.
Photocatalyst is with ozone seems to be the technology that meet sat minor extent the criteria since it presents high operating cost, as long as high environmental risk according to data of life cycle assessment concerning the specific technology. A clear predominance of homogeneous photo Fenton over other technologies of photocatalyst is noticed in the category of benefits (Figure 3). Noteworthy is the fact that the homogeneous photocatalyst is with ozone have high satisfaction rate of technical sub-criteria benefit (high degree of degradation of the organic load up to 64%) did not meet the sub-economic and environmental benefits given the use of non-renewable energy unlike other technologies based on the use of solar energy sources. The adjacent chart gives the results of the sensitivity analysis (Figure 3 which is gradient sensitivity analysis diagram). On the x-axis shows the values attributed to the weighting factor being studied (e.g., benefits-28%) and the y-axis shows the values corresponding to the score of each alternative technology. Ratings by each scenario are shown as lines in ascending or descending slope by varying the weighting factor. The line x = y represents the equation...
weighting attributed to the criterion being studied. According to the results, the final ranking is not sensitive to the specific category of criteria.

Figure 3  Final ranking of alternative photocatalysis technologies in the category of benefits and sensitivity analysis (see online version for colours)

The homogeneous photo Fenton seems to be preferred in the sub categories of technical benefits and environmental risks (Figure 4). As environmental sub-criterion, in the category of risks, from life cycle assessment, were used for each photocatalytic technique under which the technologies were evaluated in comparison with the indices of global warming, ozone depletion potential, photochemical formation of ozone, and contribution to acidification, eutrophication, human toxicity and eco-toxicity (Munoz et al., 2006, 2007).
AHP results showed that in the category of criteria representing the Cost, the technologies of homogeneous photo Fenton, homogeneous and heterogeneous photocatalyst is in the presence of hydrogen peroxide and solar energy, exhibit similar results regarding the maintenance cost unlike homogeneous photocatalyst is with ozone has little satisfaction criterion in maintenance costs, given the high cost needed for replacement of lamps UV (Figure 5). The operating cost of this technology is also high due to the electricity consumption for ozone production and operation of UV. Heterogeneous photocatalyst is with TiO₂ was the technology that even though was considered to be based on the usage of renewable energy sources, satisfied at lesser extent the criterion of operating costs, due to the catalyst cost price. The results of the sensitivity analysis shows that this classification is not changed to any other value given to the importance of this criterion (Figure 5). For the determination of the optimum technology for wineries wastewater treatment, according to the basic groups of criteria (cost, benefit, opportunities and threats) along with technologies of photo catalysis was evaluated and compared the hybrid processing system which in the final ranking was
A.A. Zorpas and A. Saranti found to satisfy at a rate of 80% on all criteria and sub-criteria of the basic categories (Figure 6).

**Figure 5** Final ranking of alternative photocatalysis technologies in the category of costs and sensitivity analysis (see online version for colours)

Consistent with the results of sensitivity analysis, the final ranking of the technologies is not sensitive in the criteria and sub-criteria evaluation for the categories of the benefits and risks [Figures 7(a) and 7(c)]. The final ranking of the technologies is found to be sensitive to the criterion of cost, which is an expected finding given that the hybrid system is including the homogeneous photo Fenton as a pre-treatment step [Figure 7(d)]. This is also an indication that an optimisation of the hybrid system technology is important to be applied prior its implementation in real scale in order to determine the optimum concentrations of catalyst and hydrogen peroxide for the hybrid system. Regarding the sensitivity analysis in the category of opportunities the out coming result is considered satisfactory if the category of opportunities is expected to increase the weighting factor and not reduced so the dominance of the hybrid system over the others will continue to exist [Figure 7(b)].
Both the findings of the literature review and the results of applying multi-criteria analysis model, answer the key research questions, regarding whether there is an optimal technology for wastewater treatment impaired. Specifically, the findings of the literature research showed that the methods of homogeneous (Oller et al., 2007; Anastasiou et al., 2008) and heterogeneous photocatalysis (Mosteo et al., 2007; Oller et al., 2007; Ahmed et al., 2011) are effectively applied for the degradation of a substantial proportion of the high organic load of the wastewater from wineries. Accordingly, the methods of the
photolysis ($\text{H}_2\text{O}_2/\text{hv}$) (Pera-Titus et al., 2004; Agustina et al., 2008), photo Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{hv}$) (Primo et al., 2008; Monteagudo et al., 2012) and photocatalysis with ozone ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$) (Lucas et al., 2010; Cortez et al., 2011), cause a reduction of TOC at 30%, 80% and 64% respectively, while the application of heterogeneous photocatalysis (Agustina et al., 2008; Mosse et al., 2011) with catalyst TiO$_2$ ($\text{TiO}_2/\text{H}_2\text{O}_2/\text{hv}$) cause a reduction in TOC by 30%. Additionally, the results of applying multi-criteria AHP indicated that the implementation of homogeneous photocatalyst is photo Fenton, as a pre-treatment step prior to biological treatment SBR, is an optimal solution for achieving the complete mineralisation of the waste, achieving a total reduction of TOC than 90%. AHP evaluation revealed that the hybrid system presents the highest overall utility in the criteria and sub criteria for the categories of costs, benefits, opportunities and risks, followed by homogeneous photocatalyst is photo-Fenton, homogeneous photocatalyst is with ozone in the presence of ultraviolet light, homogeneous photolysis and finally heterogeneous photocatalyst is with catalyst TiO$_2$.

The homogeneous process of photo Fenton, dominates over the other techniques of homogeneous and heterogeneous photocatalyst is for the treatment of wineries wastewater, since beyond high rates of degradation of the organic load is found to be an economically sustainable photocatalyst is technology on the basis of cost-effectiveness, given the use solar energy to cover the technology’s energy requirements. Nevertheless, homogeneous photo Fenton is the most environmentally friendly technology based on life cycle assessment results (Munoz et al., 2006; Chong Nan et al., 2010). The largest economic cost for the implementation of photo Fenton technology, in industrial scale, is the capital investment cost, due to the installation of solar compound parabolic collector (Jordá et al., 2011). The critical operating parameters that affect the application of the method is the pH of the reaction of photocatalytic oxidation which must be less than 3, the concentration of oxidant [H$_2$O$_2$] as long as the concentration of iron (Zorpas and Inglezakis, 2011; Molinos-Senante et al., 2012). In comparison to the technologies of homogeneous photocatalyst and heterogeneous photocatalyst is with catalyst TiO$_2$ is considered to be the least effective technology for the degradation of TOC in wineries wastewater. In this case the critical operational parameters are the pH value of the process, the flow rate of the oxidising agent, which may be oxygen or air and the concentration of the catalyst, which harmfully affects both increases the speed of degradation of the waste. It is noted that by increasing the concentration of TiO$_2$, reduces the average rate of reaction of degradation due to the phenomenon of ‘shading’, from the catalyst particles which inhibit the effect of radiation directly to the effluent. The system of homogeneous photocatalyst is with ozone ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$) is the technology that meets at lesser extent the criteria and sub-criteria of economic costs due to the high maintenance costs which is due to periodic change the lamps UV (Peres et al., 2009; Lucas et al., 2010). The pH value and the concentration of H$_2$O$_2$, are critical parameters that affect the performance of the specific system, with the largest reduction percentage in COD and TOC observed in alkaline conditions pH value of 10 and optimum concentration of oxidant is given by COD/H$_2$O$_2$ = 2.

In contrast with the above, the results of multi-criteria AHP showed that the use of hybrid photocatalyst is photo Fenton, as a pre-treatment step, followed by biological treatment is comparatively optimal solution to finally resolve the problem of impaired processing wastewater since photocatalytic oxidation contributes to enhance the biodegradability of waste due to the rapid degradation of polyphenols, while the increase of carboxylic molecules of low molecular weight and therefore the increase in the ratio
BOD₅/COD. These results are consistent with the findings from the review of the wider literature, according to which the application of hybrid systems is the solution to achieve complete mineralisation of both industrial and municipal wastewater impaired (Klamert et al., 2009, 2010; Zapata et al., 2010; Oller et al., 2011; Ahmed et al., 2011; Molinos-Senante et al., 2012).

5 Conclusions

The methods of the photolysis (H₂O₂/hν), photo Fenton (Fe²⁺/H₂O₂/hν) and photocatalyst with ozone (O₃/H₂O₂/UV), cause a reduction of TOC at 30%, 80% and 64% respectively, while the application of heterogeneous photocatalyst with catalyst TiO₂ (TiO₂/H₂O₂/hν) cause a reduction in TOC by 30%. Similarly, the results of applying multi-criteria AHP showed that the implementation of homogeneous photocatalyst is photo Fenton, as a pre-treatment step prior to biological treatment, is an optimal solution for achieving the complete mineralisation of the waste, attaining a total reduction of TOC than 90%. AHP evaluation revealed that the hybrid system presents the highest general utility in the criteria and sub criteria for the categories of costs, benefits, opportunities and risks, followed by homogeneous photocatalyst is photo-Fenton, homogeneous photocatalyst is with ozone in the presence of ultraviolet light, homogeneous photolysis and lastly heterogeneous photocatalyst is with catalyst TiO₂.

References


