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Review

Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review

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ABSTRACT

Nowadays there is a continuously increasing worldwide concern for development of alternative water reuse technologies, mainly focused on agriculture and industry. In this context, Advanced Oxidation Processes (AOPs) are considered a highly competitive water treatment technology for the removal of those organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability. Although chemical oxidation for complete mineralization is usually expensive, its combination with a biological treatment is widely reported to reduce operating costs. This paper reviews recent research combining AOPs (as a pre-treatment or post-treatment stage) and bioremediation technologies for the decontamination of a wide range of synthetic and real industrial wastewater. Special emphasis is also placed on recent studies and large-scale combination schemes developed in Mediterranean countries for non-biodegradable wastewater treatment and reuse. The main conclusions arrived at from the overall assessment of the literature are that more work needs to be done on degradation kinetics and reactor modeling of the combined process, and also dynamics of the initial attack on primary contaminants and intermediate species generation. Furthermore, better economic models must be developed to estimate how the cost of this combined process varies with specific industrial wastewater characteristics, the overall decontamination efficiency and the relative cost of the AOP versus biological treatment.

Contents

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1. Introduction

One of the major threats to water quality is chemical pollution from heavy metals, solvents, dyes, pesticides, etc. Chemicals enter the aquatic medium in several different ways, either dumped directly, such as industrial effluents, or from wastewater treatment plants (WWTP) that do not fulfil their obligations. They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture. In general, very water-soluble substances can be transported and distributed more easily in the water cycle. Discharge resulting from lax enforcement of the rules, illegal use and inappropriate application of substances may be considerable.

In the past, the focus was on detecting the severe, direct effects of individual pollutants and the short-term negative impact on ecosystems. But as scientific understanding has advanced, and the more concentrated emissions have been lowered, environmental evaluation reveals a considerable number of chronic effects that can usually only be detected after a long period of time. Furthermore, larger and larger quantities of persistent substances are being found at long distances from their sources of discharge (Vare, 2006; Schindler and Smol, 2006; Meyer and Wania, 2007). Evaluation also used to concentrate mostly on the effect of individual substances, whereas we are now beginning to study and understand interactions in mixtures of these substances (Hildebrant et al., 2006; Eljarrat and Barceló, 2003; Barceló and Petrovic, 2007).

The main routes for destroying toxic compounds in natural water are biodegradation and photodegradation. Photodegradation, which is an important mechanism for degrading aromatic hydrocarbons, chlorinated aromatic hydrocarbons, chlorinated phenols, and many pesticides, may be by direct or indirect photolysis. In photolysis, a photosensitizer absorbs the light and transfers the energy to the pollutants, which otherwise would not react photochemically, since they do not absorb light in the wavelength interval of the solar photons that arrive on the Earth's surface. The most important photosensitizers in natural water are nitrate and a type of compound known generically as humic acids. Biological degradation of a chemical refers to the elimination of the pollutant by the metabolic activity of living organisms, usually microorganisms and in particular bacteria and fungi that live in natural water and soil (EUR 20418 EN/2). In this context, conventional biological processes do not always provide satisfactory results, especially for industrial wastewater treatment, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment (Steber and Wierich, 1986; Bowers et al., 1989; Adams et al., 1996; Pulgarín and Kiwi, 1996; García et al., 2001; Muñoz and Guieysee, 2006; Lapertot et al., 2006). Therefore, the only feasible option for such biologically persistent wastewater is the use of advanced technologies based on chemical oxidation, such as the Advanced Oxidation Processes (AOPs), widely recognized as highly efficient treatments for recalcitrant wastewater. These processes degrade organic pollutants by forming hydroxyl radicals (Balcioglu et al., 2001; Bhatkhande et al., 2002; Neyens and Baeyens, 2003; Gonze et al., 2003; Sarria et al., 2004; García-Montaño et al., 2006a), which are highly reactive and non-selective as stated in some key revision works (Gogate and Pandit, 2004a,b; Pera-Titus et al., 2004; Devipriyas and Yesodharan, 2005; Pignatello et al., 2006; Comninellis et al., 2008; Shannon et al., 2008).

Chemical oxidation for complete mineralization is generally expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation, and furthermore, they all consume energy (radiation, ozone, etc.) and chemical reagents (catalysts and oxidizers) which increase with treatment time (Muñoz et al., 2005). One attractive potential alternative is to apply these chemical oxidation processes in a pre-treatment to convert the initially persistent organic compounds into more biodegradable intermediates, which would then be treated in a biological oxidation process with a considerably lower cost (Kearney et al., 1988; Haberl et al., 1991; Heinzle et al., 1992; Hu and Yu, 1994; Kiwi et al., 1994; Reyes et al., 1998; Mantzavinos et al., 1999; Pulgarín et al., 1999; Parra et al., 2000; Beltrán-Heredia et al., 2001; Sarria et al., 2003a). Studies have long shown that the biodegradability of a waste stream changes when subjected to prior chemical oxidation (Randall and Knopp, 1980; Gilbert, 1983; Watt et al., 1985; Mohammed and Smith, 1992). Therefore, the main role of the chemical pre-treatment is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of mineralization should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. This is important because electricity represents about 60% of the total operating cost of photocatalytic reactors (Bandara et al., 1997). However, if the pre-treatment time is too short, the reaction intermediates generated could still be structurally very similar to the original non-biodegradable and/or toxic components.

Experimental examples of sequential chemical and biological oxidation treatment have been previously reviewed by Scott and Ollis (1995, 1997), Jeworski and Henzle (2000), Sarria et al. (2002), Mantzavinos and Psillakis (2004), Tabrizi and Mehrvar (2005), Augugliaro et al. (2006), Ikehata and Gamal El-Din (2006) and Gaya and Abdullah (2008). This review reports on the most recent experimental studies and developments (2000–2009) specifically combining AOPs and biological treatments (aerobic or anaerobic) for industrial wastewater decontamination. It highlights not only efforts in applying AOPs as a pre-treatment, but also real cases in which the combination strategy is in the opposite direction, first eliminating the highly biodegradable part of the wastewater and then degrading the recalcitrant contaminants (non-toxic) by a post-treatment AOP.

2. Bench-scale testing procedure

Selection of the best treatment option for remediation of a specific industrial wastewater is a highly complex task. The choice of one or more processes to be combined in a certain situation depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost. Therefore, the main factors which must be considered in the decision on the wastewater treatment technologies to be applied are:

- The quality of the original wastewater.
- Removal of parent contaminants.
- Conventional treatment options.
- Treatment flexibility.
- The facility decontamination capacity.
- Final wastewater treatment system efficiency.
- Economic studies.
- Life Cycle Assessment to determine environmental compatibility of the wastewater treatment technology.
- Potential use of treated water.

In general, the possibilities and capabilities of the conventional treatments available are widely known. However, information on the efficiency of the new technologies (AOPs) for eliminating certain specific pollutants present in wastewater compared to conventional options is necessary. For this reason, bench-scale and pilot-plant studies are required to develop the technologies and generate information on new industrial wastewater treatment processes. Such scaled studies are even more decisive when combining several technologies for decontamination or reuse of a specific industrial wastewater.

When preliminary chemical oxidation is applied in a combination treatment line, sometimes its effect is insignificant or even harmful to the properties of the original effluent, even though it is conceptually

advantageous. There are several reasons for this, the most common of which are:

- Formation of stable intermediates which are less biodegradable than the original molecules.
- Lack of selectivity for preferential attack on the more bioresistant fractions of the wastewater during chemical pre-treatment.
- Poor selection of treatment conditions. For example, excessive pre-oxidation can lead to generation of an effluent with too little metabolic value for the microorganisms.
- Too much oxidant and/or catalyst used for oxidation. Compounds such as ozone and hydrogen peroxide (both known as biocides), metals, metal oxides and metal salts (catalysts in many processes), are normally toxic to microorganisms.

These limitations underline the need to establish a step-by-step research methodology which takes these effects into account, because operating conditions effect on the original properties of the pre-treatment stream (contact time, oxidant and/or catalyst type, dose and toxicity, temperature, etc.) must be known. Such studies must employ analytical tools to infer the reaction mechanisms, pathway and kinetics, evaluate the effect of the chemical pre-treatment on toxicity and biodegradability, the effect of cations and anions in the wastewater matrix, and the application of various techniques for determining biodegradability and toxicity (Amat et al., 2003, 2007; Sirtori et al., 2009a; Radjenovic et al., 2009).

Fig. 1 summarizes the different steps necessary to evaluate the feasibility of applying a combined AOP/biological treatment strategy for industrial wastewater (toxic and/or non-biodegradable) treatment.

This general diagram depicts not only the necessary chemical and biological analyses that must be performed in a certain industrial wastewater treatment line, but also the different situations which could appear depending on the special characteristics of the particular wastewater.

As observed in this figure, the variables commonly used to describe chemical oxidation are the dissolved organic carbon concentration (DOC) and the chemical oxygen demand (COD). Apart from these measurements, another series of parameters related to the process conditions should be monitored during the AOP selected for each treatment, which, in general, include the catalyst concentration (Fe(II), Fe(III), TiO_2, etc.), the hydrogen peroxide or ozone concentration, the radiation intensity, pH and temperature. This is explained in more detail in the following section.

2.1. Design factors for the combined system

Appropriate techniques must be combined to provide technically and economically feasible options. The performance of an AOP treatment could be enhanced in several ways (Augugliaro et al., 2006). The first possibility is to position the AOP in a sequence of physical, chemical and biological treatments. Such a treatment approach often involves at least one AOP step and one biological treatment step. Whether the AOP or the biological process is first in the treatment line, the overall purpose of reducing costs will be nearly the same as minimizing AOP treatment and maximizing the biological stage, because of the wide difference in the cost of the two treatments. The key issue is to design the process for the best overall economic and ecological performance.

In combined chemical and biological wastewater treatment, it is very important to keep in mind how the characteristics of each individual treatment, such as the chemical oxidant to be used

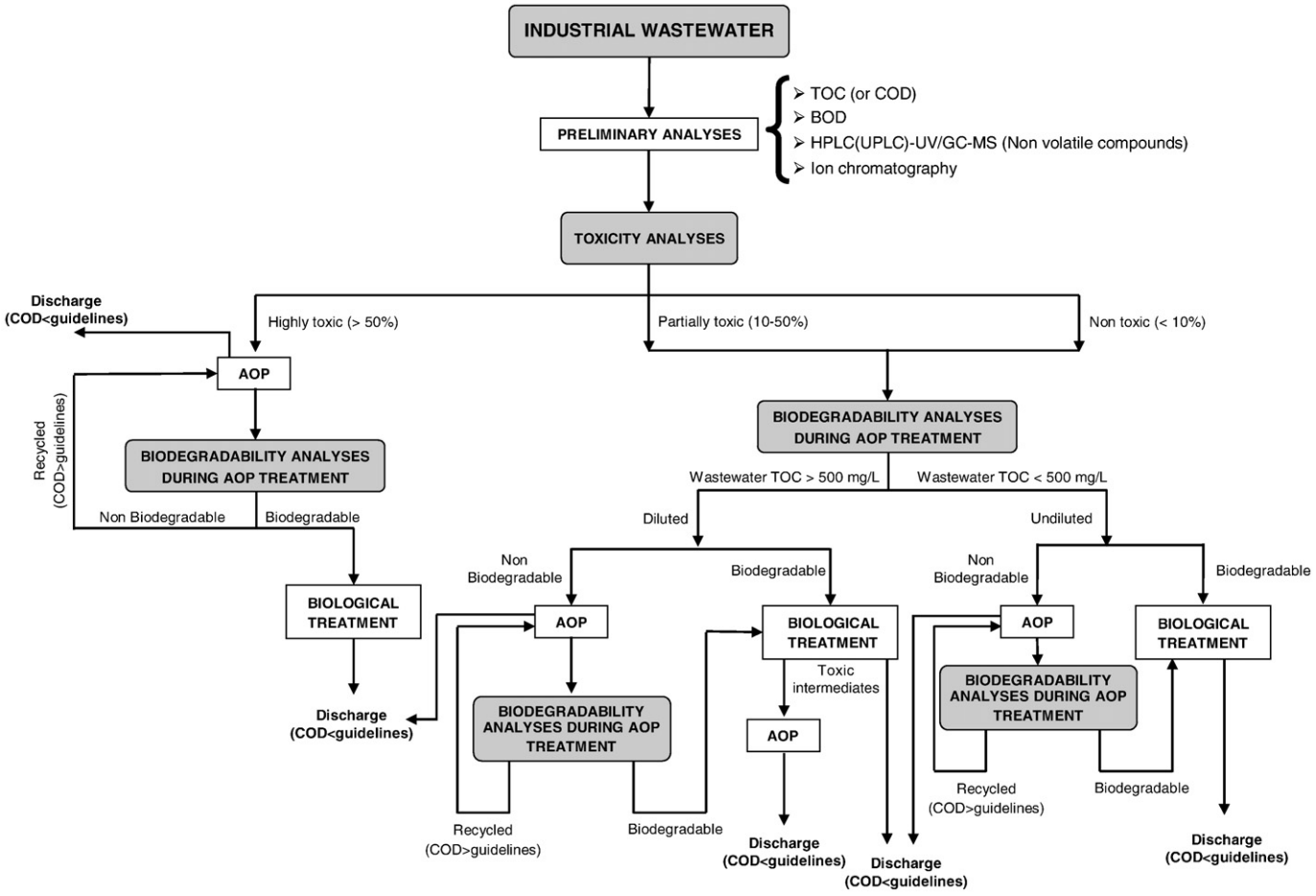

Fig. 1. Strategy for the selection of the best treatment option for a specific toxic and/or non-biodegradable industrial wastewater.

(photo-Fenton or Fenton reagent, O_3/H_2O_2, O_3/UV, H_2O_2/UV, TiO_2/UV, etc.) can improve the destruction of a persistent contaminant (Liu et al., 2007; Comninellis et al., 2008; Klavarioti et al., 2009). The rest of the aspects to be considered are also widely known: the chemical oxidation capacity (Jones et al., 1985; Lee and Carberry, 1992), its potential for forming toxic intermediates (Trgovcich et al., 1983; Bowers et al., 1991; Wang, 1992), change in pollutant behavior (Miller et al., 1988; Eckstein, 1994), choice of biological agent, comparison of different cultures (Lee and Carberry, 1992), comparison of acclimated and non-acclimated cultures (Bowers et al., 1989; Hu and Yu, 1994), and use of monospecific cultures and anaerobic cultures (Koyama et al., 1994; Adams et al., 1994).

Measurement of the combined process efficiency depends on the purpose of the treatment, but normally requires the independent optimization of each chemical and biological step. For example, the extent of mineralization of the organic compounds may be a measure of efficiency if highly pure water is needed or an effluent with a specific dissolved organic carbon limit. The main purpose of other treatments may be reduction of toxicity or elimination of a specific pollutant. Determining the target is an essential step in combination studies since it helps define process efficiency and provides a basis for comparing the different operating conditions and optimizing the process.

Calculation of the individual biological and chemical oxidation efficiencies is important for finding the optimal operating conditions for the combined process (Scott and Ollis, 1997). This task involves profound knowledge of both biological and chemical processes. Therefore, several analytical parameters must be monitored during each step of the treatment line. Chemical parameters normally measured are the total organic carbon (and/or chemical oxygen demand), the concentration of specific pollutants which could be present in the target wastewater (by chromatographic methods, such as HPLC-UV), and complete oxidation of heteroatoms released (Cl, N, P…) as inorganic species (Cl^-, NO_3^-, PO_4^{3-}…) into the media from contaminants completely degraded during the AOP treatment (by ion chromatography or commercial tests designed for each specific ion). Regarding biological assays, it is very important to perform toxicity analyses (with organisms like *Vibrio fischeri*, *Daphnia magna*, activated sludge by respirometric assays, etc.) and biodegradability tests (using activated sludge) to ensure the conditions of the AOP effluent to be subsequently treated by a conventional biodegradation process. In the biological system itself, and apart from daily control analyses such us total suspended solids and volatile solids, total organic carbon and chemical oxygen demand, pH and dissolved oxygen in the system, etc., the measurement of anions and cations present in the biological media is also essential since, on one hand, nutrients are vital to the microorganism populations in the activated sludge, and on the other hand, monitoring the nitrogen species provides much information related to nitrification and denitrification. This series of analytical parameters satisfies the engineering needs for designing the coupling strategy. If further understanding of the underlying processes is sought, additional analytical methods may have to be applied, which allow the identification of unknown intermediate degradation products. Such studies involve a considerable effort, dedication, and sophisticated analytical equipment (based on chromatography and mass spectrometry), but this is sometimes the only way to explain why acute toxicity arises during treatment, for example, by pinpointing a single intermediate degradation product that is more toxic than the original pollutant (Malato et al., 2009).

2.2. Toxicity tests

The problem of toxic pollutants present in the environment must be tackled not only by determining pollutants using analytical tools, total organic carbon and chemical oxygen demand measurements, etc., but also by biological assays. The combination of an AOP and a conventional biological wastewater treatment for toxic or non-biodegradable substances requires application of toxicological and biological methods evaluating effluent toxicity and biodegradability before it can be transferred to a biological treatment for its complete oxidation.

Toxicity analysis of the wastewater during different stages of its AOP treatment is done by acute toxicity testing (with 96 h of maximum exposure time) using different microorganisms. There are many procedures for toxicity bioassays available (U.S. EPA-821-R-02-012, 2002), nevertheless, as toxicity is a biological response, there is no universal monitoring system and therefore, to increase the reliability of toxicity assays, different organisms representative of taxonomic groups from the typical local environment must be employed.

Severe toxicity has usually been determined in freshwater microorganisms by *D. magna* and *Selenastrum capricornutum*, and in marine microorganisms like *V. fischeri* (Fernández-Alba et al., 2002; Emery et al., 2005; Calza et al., 2006; Chacón et al., 2006; Fotiadis et al., 2007; Sakkas et al., 2007; Trovó et al., 2009). Nevertheless, some authors have also employed other organisms for toxicity assessment, *Pseudomonas* (*fluorescens or putida*) (Farré et al., 2002; Lange et al., 2006; De la Rochebochard d'Auzay et al., 2007), *Staphylococcus aureus* (Hirose et al., 2005; Reyes et al., 2006), *Escherichia coli* (Chatzitakis et al., 2008) marine algae like *Phaeodactylum tricornutum* (Germirli Babuna et al., 2009) different microalgal strains (Andreozzi et al., 2006) and *Pseudokirchneriella subcapitata* (De Schepper et al., 2009), and plants like *Lepidium sativum* (Rizzo et al., 2009).

In some cases, it has been found that the toxicity of the original effluent grows during early pre-treatment up to a maximum due to the formation of toxic intermediates (Lu and Chen, 1997; Lizama et al., 2002; Parra et al., 2002; Shang et al., 2002; Gonze et al., 2003; Wang et al., 2003; Hincapié et al., 2005; Pérez-Estrada et al., 2007; Kim et al., 2007). It is important to keep in mind that such reaction intermediates formed during chemical oxidation could be more toxic to the biological systems than the original compound, and that different oxidation processes can lead to different intermediates.

On the other hand, the oxygen demand obtained in respirometric assays has recently turned into an excellent control parameter as it represents a direct measure of the correct activity and viability of microorganisms present in aerobic activated sludge. Furthermore, as this test represents a direct assessment of the primary function in a process based on activated sludge, it can be used as an efficient tool for the measurement of acute toxicity that could provoke different industrial wastewater inlets on the activated sludge of a Municipal Wastewater Treatment Plant (MWWTP) (Arslan-Alaton et al., 2005; Arslan-Alaton and Caglayan, 2006; García et al., 2006; Arslan-Alaton and Teksoy, 2007; Vilar et al., 2009).

In general, toxicity assays do not require a strong investment in equipment or excessively specialized training in their handling. But, it is also very important to mention that previous to the application of these toxicity analyses, any toxic substance which could be present during the chemical pre-treatment (ozone, hydrogen peroxide, high amounts of catalysts, etc.) must be eliminated from the media and the pH of the water must be kept between 6.5 and 7.5. Most AOPs lower the pH due to the generation of inorganic acids, or they theoretically need to operate at a certain pH in order to maximize their treatment efficiency (e.g., pH around 3 for Fenton or pH around 9 for ozone), which is why prior neutralization is required for toxicity and biodegradability tests, and for a final biological treatment step.

Toxicity analyses during AOP treatment of wastewater provide valuable information on samples in which the percentage of inhibition has changed enough to make performing biodegradability tests worthwhile, because a significant change in toxicity would usually be related to a substantial change in biodegradability.

Moreover, toxicity studies can also demonstrate how the application of AOPs reduces wastewater toxicity permitting its safe disposal.

However, further biodegradability tests must be always performed to ensure that the following biological treatment is successful.

2.3. Biodegradability tests

The most significant biodegradation systems are based on bacteria or fungi (Howard et al., 1975; Alexander, 1994). The relative concentration of these species, their enzyme induction and ability to acclimatize once they have been exposed to a certain chemical compound, make them very sensitive to changes in certain environmental parameters such as temperature, salinity, pH, oxygen concentration, redox potential, the concentration and nature of various substrates and nutrients, and the presence of toxic substances. Therefore, how biodegradable a wastewater is depends on the environment in which it has been discharged.

When considering combined chemical oxidation and biological processes for treating recalcitrant contaminants, biodegradability assessment is required not only of the raw wastewater, but also during the AOP pre-treatment. In this sense, enhancement of biodegradability by an AOP application can be monitored by means of (Sarria et al., 2003b):

(i). Analysis of general parameters, such as the biological oxygen demand (BODx), chemical oxygen demand (COD), and dissolved organic carbon (DOC),

(ii). Calculation of the BOD_5/COD ratio or the average oxidation state (AOS) (Pulgarín et al., 1999). These ratios provide an approximate index of the proportion of organic substances present in the wastewater that are biodegradable under aerobic conditions for a predetermined period of time (for example 5 days for BOD_5).

(iii). Long activated-sludge biodegradability assays, such as the Zahn–Wellens test, which is used to evaluate the biodegradability of water-soluble, non-volatile organic contaminants when exposed to a relatively high concentration of microorganisms. It takes 28 days kept at 20–25 °C under diffuse illumination. The ratio of DOC eliminated after each interval to the original DOC is expressed as the percentage of biodegradation. Samples analyzed are considered biodegradable when the biodegradation percentage is over 70% (Lapertot et al., 2006, 2008).

(iv). Oxygen uptake rate by respirometric measurements (short analysis). Respirometry equipment measures the oxygen used by bacteria during growth, which is interrelated to reduction in BOD. In this biological assay, the oxygen uptake rate from a mixture of raw or pre-treated wastewater and activated sludge (in endogenous phase with autotrophic bacteria activity inhibited) is measured for a contact period of around 20 min. At the end of the test, the readily biodegradable fraction of the COD is obtained (based on total oxygen consumption and biomass growth rate, and denoted as COD_{rb}). The COD_{rb}/COD ratio shows the sample biodegradability. A ratio over 0.1 means that it is biodegradable, and under 0.05 that it is not biodegradable (values between 0.05 and 0.1 are considered with low biodegradability) (Orupold et al., 2001). In this sense, the different wastewater COD fractions (biodegradable, non-biodegradable, non-soluble, etc.), can also be determined by respirometric assays (Mathieu and Etienne, 2000; Lagarde et al., 2005).

Recently, some authors have also used other microorganism cultures for determining biodegradability of synthetic wastewater partially treated by AOPs. *P. putida*, for instance, is a reliable and reproducible method for assessing both toxicity and biodegradability of a commercial pesticide solution partially treated by photo-Fenton and TiO_2 photocatalysis (Ballesteros-Martín et al., 2008a,b, 2010; García-Ripoll et al., 2009).

In general, the majority of studies in this field employ conventional bioassays, such as biological oxygen demand (BOD_x/COD rate) to determine enhancement of the biodegradation rate after pre-treatment of a biorecalcitrant wastewater by AOPs (Chamarro et al., 2001; Ho Suh and Mohseni, 2004; Bacardit et al., 2006; Méndez-Arriaga et al., 2008). Some authors have focused on pharmaceutical wastewater, evaluating how partial treatment by O_3 and O_3/H_2O_2, photo-Fenton or catalytic wet peroxide oxidation increases the effluent biodegradability to BOD_5/COD over 0.3 (Arslan-Alaton and Balcioglu, 2002; González et al., 2007; Melero et al., 2009). On the other hand, ozonation and ozonation/UV radiation have been applied to enhance biodegradability of wood pulping and bleaching wastewater from paper industry (Ledakowicz et al., 2006; Balcioglu and Moral, 2009). Finally, biodegradability as expressed by the BOD_5/COD ratio, has also been used to evaluate ozonation pre-treatment of textile wastewater, photo-Fenton and homogeneous photocatalysis (UV/semi-conductor catalyst such as TiO_2, ZrO_2) for partial oxidation of olive mills wastewater until being biocompatible with a subsequent aerobic biological treatment (Somensi et al., 2010; Badawy et al., 2009).

Long biodegradability analyses such as the Zahn–Wellens test (28 days) are also widely employed when it is desirable to study any biomass acclimation effect or highly reliable results are required, for example, to find the increase in biodegradability of wastewater containing hazardous water-soluble pesticides by solar photocatalysis (Oller et al., 2006; García-Ripoll et al., 2007; Zapata et al., 2009a; Amat et al., 2009). Other authors have also evaluated the biocompatibility of biorecalcitrant compounds used as synthesis intermediates in the pharmaceutical industry, finding only a slight enhancement of their biodegradability during the mixture pre-treatment by solar photo-Fenton (Zapata et al., 2008). In this case, complete wastewater treatment by AOPs was the only possible choice despite the high operating costs.

Finally, respirometry is the biodegradability analysis least used to evaluate the efficiency of partial wastewater oxidation. Only a few authors have studied biodegradation parameters, such as maximum oxygen uptake rate and dissolved oxygen consumption found by respirometry to evaluate textile wastewater, landfill leachate wastewater, phenolic wastewater, etc., treated by AOPs (TiO_2/UVA, Fenton, etc.), (Arslan-Alaton et al., 2005; Rubalcaba et al., 2007; Goi et al., 2009).

Anaerobic biodegradability analyses are less common and normally measure the biogas production rate (e.g., the biochemical methane potential assay) (Owen et al., 1979; Takeuchi et al., 2000). Today, this assay is mainly applied to solid wastes (Rodriguez et al., 2005; Bilgili et al., 2009).

Although toxicity and biodegradability tests provide useful information concerning the effect of chemical pre-treatment on subsequent biological degradation of wastewater, experiments integrating chemical and biological degradation are usually necessary for an additional, more realistic viewpoint of the combined process. The biodegradability of the original effluent, combined reactor operating mode, chemical and biological characteristics of the treated solutions by AOPs, optimal conditions for both processes, and efficiency of the combined reactor should be taken into consideration for the design of this combined system (Parra et al., 2002). Various authors (Jeworski and Henzle, 2000; Mantzavinos and Psillakis, 2004) emphasize that this strategy is not a universal solution and each effluent must be considered and evaluated separately.

3. Industrial wastewater treatment by combined AOPs/biotreatment technology

Industrial wastewater characteristics vary not only with the industry that generates them, but also within the industry. These characteristics are also much more diverse than domestic wastewater, which is usually qualitatively and quantitatively similar in its composition. On the contrary, treatment of industrial wastewater

is a complex problem due to the wide variety of compounds and concentrations it may contain.

It is clear that the study of real wastewater is inevitably compromised by the amount and quality of information available. If the exact composition of the original effluent is hard to find, the identification of all the reaction intermediates of any applied treatment is impracticable, and therefore, the kinetics must be based on dissolved organic carbon or chemical oxygen demand measurements, as mentioned above. Although studies with model effluents provide useful information for optimizing the chemical pre-treatment, this information cannot be applied directly to real wastewater. The combination of these two extremes requires a chain of experimental studies beginning with model wastewaters before undertaking the more complex real effluents. Such laborious studies have recently being done by several researchers (Maldonado et al., 2006; Kajitvichyanukul and Suntronvipart, 2006; Dantas et al., 2007; Gonzalez et al., 2007; Gotvajn et al., 2007; Zapata et al., 2009a).

In this context, it must also be considered that the real wastewater might contain substances that could compete with the target pollutant for the oxidizing agent (•OH), such as other organic and inorganic compounds and natural organic matter. This usually causes a decrease in process efficiency (Lipczynska-Kochany et al., 1995; Maciel et al., 2004; Moraes et al., 2004; Le Truong et al., 2004; De Laat et al., 2004; Lu et al., 2005; Bacardit et al., 2007; Zapata et al., 2009a). Even in effluents in which the target pollutants are predominant, oxidation may lead to the quick formation of a multitude of intermediates that could lower overall process efficiency, since these species could be less reactive with the hydroxyl radicals (Buxton and Greenstock, 1988; Kiwi et al., 2000).

In this sense, Scott and Ollis (1995) have identified four types of wastewater as potentially treatable by combined AOPs/biological degradation: wastewater containing biorecalcitrant compounds such as large macromolecules like soluble polymers that are not easily biodegradable due to their large size and lack of active centers (Steber and Wierich, 1986; Kearney et al., 1988; Somich et al., 1990; Kiwi et al., 1993); highly biodegradable industrial wastewater which still requires chemical post-treatment as it contains a large amount of biodegradable organic compounds in addition to small concentrations of recalcitrant compounds (Haberl et al., 1991; Adams et al., 1994; Berge et al., 1994; Sierka and Bryant, 1994); wastewater containing inhibiting compounds which are somewhat toxic to a certain percentage of some biological cultures (Gilbert, 1983; Manilal et al., 1992); wastewater containing inert intermediates such as specific metabolites which must be effectively degraded or, they would accumulate in the medium and inhibit growth of the microorganisms (Kearney et al., 1986; Hapeman et al., 1994).

In recent years, research in combined AOPs/biological technologies for the treatment of certain industrial wastewaters difficult (or impossible) to treat by conventional physical–chemical/biological processes has greatly increased (Gogate and Pandit, 2004b; Mantzavinos and Psillakis, 2004). Interest in this topic has grown due to the real possibility of reusing industrial wastewater as a safe water resource under adequate sanitary conditions (for example, as stipulated by Spanish legislation on the reuse of treated water, Royal Decree 1620/2007).

3.1. Wastewater containing pesticides and/or herbicides

Among the priority substances polluting water are soluble pesticides, which are a serious threat to surface and groundwater, since their high solubility makes their propagation in the environment extremely easy. Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions (Grover and Cessna, 1991). Among the possible chronic effects of these compounds are carcinogenesis (Blair et al., 1993), neurotoxicity (Tanner and Laangston, 1990), and effects on reproduction (Hileman, 1994) and cell development (Gray et al., 1994), particularly in the early stages of life.

Monitoring programmes in many European countries demonstrate the presence of pesticides in surface waters ranging from streams and ditches directly adjacent to agricultural fields (Liess and Von der Ohe, 2005) up to large rivers, lakes and reservoirs (Environment Agency, 2007). Part of the larger-scale contamination is known to result from non-agricultural uses of pesticides (Skark et al., 2004) or from point sources, including discharge from farmyards following filling and washing activities (Neumann et al., 2002). Nevertheless, diffuse contributions of pesticides to water are also important. These are predominantly from pesticides applications including spray drift, surface runoff and leaching to field drains. Less significant routes to surface water include groundwater seepage, sub-surface lateral flow and wet or dry deposition following longer range transport in air. Movement via field drains has been shown to be important in a number of countries and rapid transport of pesticide residues in drain flow has been demonstrated in a large number of field experiments (Brown and Van Beinum, 2009). Field studies undertaken in the US to investigate pesticide transport to sub-surface drains were comprehensively reviewed by Kladivko et al. (2001).

Pesticide contamination in wastewater from these sources may be as high as 500 mg/L. Nevertheless, whatever the concentration detected, pesticides have to be removed either to protect our water resources or to achieve drinking water quality. As often mentioned in this review, biological processing is usually the preferred method for the treatment of effluents containing organic substances, in particular pesticides. However, as biological methods are normally susceptible to such toxic compounds, which inactivate waste-degrading microorganisms, a potentially useful approach is to partially pre-treat the toxic waste by oxidation technologies, producing intermediates that are more readily biodegradable. Many oxidation treatments have traditionally been studied for this purpose, including photochemical degradation processes (UV/O_3 and UV/H_2O_2) (Zepp et al., 1994; Andreozzi et al., 2003b; Chelme-Ayala et al., 2010), photocatalysis (TiO_2/UV, Fenton and photo-Fenton process) (Legrini et al., 1993; Fallmann et al., 1999; Kitsiou et al., 2009), and chemical oxidation processes (O_3, O_3/H_2O_2, and H_2O_2/Fe^{2+}) (Masten and Davies, 1994; Benitez et al., 2002a).

Initially, titanium dioxide was the most widely accepted photocatalyst for pesticide destruction in water (Tinucci et al., 1993). Electrochemically assisted photocatalysis using TiO_2 electrodes has also been exhaustively described (Vinodgopal et al., 1994). However, in recent years, homogeneous photocatalysis for detoxifying wastewater polluted with pesticides has been the focus of growing interest (Malato et al., 2001, 2003; Oller et al., 2005; Sanches et al., 2010). Ozone application for pesticide degradation has also recently been investigated (Qiang et al., 2010). On the other hand, data on the efficiency of new advanced treatment methods such as ultrasonic processes, which have been successfully used for decomposing atrazine and alachlor (Kotronarou et al., 1992) and carbofuran (Ying-Shih et al., 2010) are scarce. Vacuum UV oxidation of atrazine has also been reported (Gonzalez et al., 1994). Nevertheless, there are still difficulties with application of those methods in practical disposal situations.

In any case, the efficiency of these methodologies has hardly been assessed under real conditions, i.e., in the presence of a mixture of several pesticides and their formulating agents at concentrations over 100 mg/L (Oller et al., 2006; Zapata et al., 2009b).

Reports on pesticide photodegradation products in the literature are relatively abundant. However, little information is available on the reaction mechanisms involved in the photolysis of pesticides under typical environmental conditions. It is important to distinguish reactions that occur over a common pathway, the hydroxyl radical mechanism, from other steps that are due to other oxidants such as ozone, direct hole attacks or even direct photolysis, as different oxidants generally lead to different intermediates and different final products (Chiron et al., 2000; Burrows et al., 2002).

Because a treatment is usually not considered finished until compound mineralization is nearly complete, AOPs need to be combined with biodegradation to completely eliminate the organic content of a given wastewater. In this sense several research studies have also been carried out in recent years, focusing on the decontamination of both synthetic and real wastewater containing pesticides by combining different AOPs and biological treatment technologies. Heterogeneous photocatalysis using TiO_2 supported on glass rings was used to completely eliminate isoproturon, leaving about 80% dissolved organic carbon which was finally treated in a biological reactor containing bacteria supported on biolite (Parra et al., 2002). In this combined system, 100% of the initial isoproturon concentration and 95% DOC were removed. The experiments in the photocatalytic part of the combined treatment were carried out using sunlight.

TiO_2 in slurry has also been employed combined with an aerobic biological treatment for photocatalytic degradation of 4-chlorophenol at an initial concentration of 400 mg/L (96 h for complete mineralization) (Goel et al., 2010). The use of slurry-form Degussa P25 TiO_2 and TiO_2 coated on a support in a novel photocatalytic circulating-bed biofilm reactor is also worth mentioning. This system, which makes use of macro-porous carriers to protect the biofilm from toxic reactants and UV light, was successfully used for the treatment of 2, 4, 5-trichlorophenol (Marsolek et al., 2008).

Few studies have been published reporting on ozonation and O_3/UV combined with aerobic biological treatment for the removal of pesticides such as Destamethrin, attaining 95% elimination of initial COD (Lafi and Al-Qodah, 2006). Christensen et al. (2009) have compared AOPs like ozonation, Fenton reagent and UV/H_2O_2 to find the most efficient pre-treatment for preceding an activated-sludge sequential batch reactor for complete treatment of persistent organic compounds such as dichlorodiethyl ether.

However, the most recent studies combining AOPs with aerobic biological treatment to fully treat wastewater containing pesticides widely employ homogeneous photocatalysis by Fenton and photo-Fenton. For example, Fenton reagent has been studied as a pre-treatment followed by an aerobic biodegradation process to completely eliminate 4-chlorophenol (Kastaned et al., 2007). The herbicides diuron and linuron were removed by photo-Fenton until suitable non-toxic and biodegradable intermediates were obtained and treated in a biological system composed of a sequencing batch reactor (Farré et al., 2006). The same photocatalytic pre-treatment was also employed for the decontamination of a mixture of five pesticides (alachlor, atrazine, chlorfenvinphos, diuron and isoproturon) although, in this case, a packed-bed bioreactor was used to reduce the total carbon conversion of the pesticides mixture by 50% (Lapertot et al., 2007).

In the last two decades, interest is growing in replacing UV lamps with solar energy for partial oxidation of pesticides by photo-Fenton to lower operating costs. For instance, a 12-L bubble column bioreactor inoculated with *P. putida* has been combined with a solar photo-Fenton pre-treatment in a compound parabolic collectors (CPCs) photo-reactor to successfully degrade synthetic water containing alachlor and pyrimethanil, and a mixture of four commercial pesticides (laition, metasystox, sevnol and ultracid) commonly used in citric orchards in eastern Spain (Ballesteros-Martín et al., 2008a,b). Activated sludge has also been employed in an immobilised biomass reactor combined with a solar photo-Fenton CPC pilot plant for the degradation of a mixture of five pesticides (methomyl, dimethoate, oxamyl, cymoxanil and pyrimethanil) (Oller et al., 2007b). The same solar CPC photo-Fenton system was also used in combination with a conventional sequencing batch bioreactor for complete mineralization of diuron and linuron (Farré et al., 2008).

Finally, assessment of this combined technology should take into account higher pesticide concentrations and how this factor affects both the AOP and subsequent biological oxidation efficiencies. Therefore, studies with higher organic content (200 to 500 mg/L DOC) in wastewater polluted by commercial pesticides are being carried out (Ballesteros-Martín et al., 2009a,b; Zapata et al., 2010b) integrating CPC photo-reactors and sequencing batch bioreactors or immobilised biomass reactors.

3.2. Wastewater containing pharmaceuticals and emerging contaminants

ECs (Emerging Contaminants) have been defined in several ways, but essentially they are either naturally occurring or synthetic substances that interfere with the functioning of endocrine systems resulting in unnatural responses. These contaminants are mostly unregulated compounds that may be candidates for future regulation depending on research on their potential effects on health, and monitoring data regarding their occurrence. Particularly relevant examples of such emerging compounds are those which do not need to persist in the environment to cause a detrimental effect, because their high transformation/removal rates are compensated by their continuous introduction into the environment (Petrovic et al., 2003). Pharmaceuticals, personal-care products, steroid sex hormones, illicit drugs, flame retardants and perfluorinated compounds are considered environmental emerging contaminants of particular concern because of their endocrine-disrupting properties. These ECs enter the wastewater network after use in households and industry (Hirsch et al., 1999; Kuster et al., 2005). Estrogenic hormones have been detected not only in sewage treatment plant influents and effluents in many countries (Baronti, et al., 2000; Jeannot et al., 2002), but also in surface water (Liu et al., 2004; Zhou et al., 2007), and in drinking water (Kuch and Ballschmiter, 2001). In view of the widespread occurrence and potential impact of ECs, they must be removed before discharge or reuse (Heberer, 2002; Zhang and Zhou, 2008).

Pharmaceutical residues are another group of compounds of particular interest and unknown fate. For instance, during monitoring in Italy, France, Greece and Sweden, carbamazepine, clofibrate, phenazone and aminopyrine, clofibric acid, diclofenac, fenofibrate, fenoprofen, flurbiprofen, gemfibrozil, ibuprofen, ketoprofen and naproxen, all belonging to different therapeutic pharmaceuticals classes, were found in the effluents of sewage treatment plants (Andreozzi et al., 2003a).

There are four generally recognized main removal pathways for organic compounds during conventional wastewater treatment: adsorption onto suspended solids or association with fats and oils, aerobic and anaerobic degradation, and chemical (abiotic) degradation by processes such as hydrolysis and volatilization (Belgiorno et al., 2007).

Granular activated carbon (GAC) adsorption, for example, is a versatile technology particularly suited to removing ECs from water and wastewater. However, GAC only transports ECs from one medium (water) to another (GAC). In addition, the relatively high cost of activated carbon has prevented its wide application, particularly in developing countries.

In general, the presence of residual pharmaceuticals in the environment and in aquatic systems in particular constitutes a serious problem as they are extremely resistant to biological degradation and usually escape intact from conventional treatment plants. They may have serious toxic and other effects on humans and other living organisms, and they are present at minute concentrations, thus requiring more sophisticated and laborious analytical tools for their accurate determination. Therefore, the ability to increase biodegradability and detoxify effluent streams containing polar and hydrophilic chemicals by alternative treatment with AOPs, such as photocatalysis (Arana et al., 2002; Ohko et al., 2002; Arslan-Alaton and Gurses, 2004; Al-Bastaki, 2004; Chiang et al., 2004; Coleman et al., 2005; Andreozzi et al., 2006; Achilleos et al., 2010; Hapeshi et al., 2010; Méndez-Arriaga et al., 2010; Xekoukoulotakis et al., 2010), ozonation (Ternes et al., 2003; Andreozzi et al., 2005; Deborde et al., 2005; Dantas et al., 2008), and ultrasound

oxidation (Stavarache et al., 2002; Abu-Hassan et al., 2006; Jiang et al., 2006; Naddeo et al., 2010) has been studied (Cokgor et al., 2004).

Although the application of AOPs to wastewater containing pharmaceuticals or ECs has been widely studied, not many cost-effective chemical and biological treatment combinations are available. In this sense, ozonation is one of the AOPs most employed as a pre-oxidation step in a combined treatment line. Effluent from the formulation of penicillin was subjected to ozonation at varied pH (2.5–12.0) and perozonation ($O_3 + H_2O_2$) with different initial H_2O_2 concentrations (2–40 mM) and pH 10.5. Afterwards, raw, ozonated and perozonated penicillin formulation effluent in a synthetic domestic wastewater was subjected to biological activated-sludge treatment using a consortium of acclimated microorganisms. Experimental results showed that pre-ozonation at least partially removed the non-biodegradable COD fraction from the effluent (Arslan-Alaton et al., 2004). Ozonation combined with a moving-bed biofilm reactor applied to the removal of micro-contaminants, including estrogenic substances, from the effluent of a conventional activated-sludge treatment (Gunnarsson et al., 2009) provided valuable data to the assessment of advanced treatment technologies for removing estrogenic substances. Finally, ozonation has also been used for sludge pre-treatment to improve its stabilisation by anaerobic digestion of wastewater containing pharmaceutical and personal-care products (Carballa et al., 2007). The use of this process leads to improved COD solubilization of 60%, thus increasing the biogas production and the soluble organic matter removal efficiency during anaerobic digestion. However, no mineralization was observed during the ozonation pre-treatment.

Solar photo-Fenton is another AOP widely used in combination with an aerobic biological system for the treatment of pharmaceutical wastewater. For example, a combined solar photocatalytic–biological pilot-plant system was employed to enhance the biodegradability and complete mineralization of a biorecalcitrant industrial compound (α-methylphenylglycine, a common pharmaceuticals precursor), dissolved in distilled water and simulated seawater at 500 mg/L (Oller et al., 2007a). Evaluation of the combined AOP/biological system developed demonstrated that in batch mode operation, photo-Fenton pre-treatment completely removed the pollutant and enhanced its biodegradability, producing a biocompatible effluent which was completely mineralized by the biological system in an immobilised biomass reactor. The combined system was able to mineralize 95% of initial TOC. This recently developed combined technology has also been employed for the treatment of a real pharmaceutical wastewater (TOC = 775 mg/L) containing a non-biodegradable antibiotic pertaining to the quinolone group called nalidixic acid (45 mg/L) (Sirtori et al., 2009a). This compound completely disappeared after 190 minutes of solar photo-Fenton treatment and 66 mM of H_2O_2 consumed. Biodegradability and toxicity bioassays showed that photo-Fenton should be performed until total degradation of nalidixic acid before following with a biological treatment. An immobilised biomass reactor operated in batch mode was then able to reduce the remaining TOC to less than 35 mg/L. Overall TOC degradation efficiency of this combined system was over 95%, of which 33% corresponded to the solar photochemical process and 62% to the biological treatment.

3.3. Textile wastewater

The textile industry is very water intensive. Water is used for cleaning the raw material and for many flushing steps throughout production. Textile wastewater includes additions of a wide variety of dyes and chemicals that make the chemical composition of textile industry effluents an environmental challenge. Most pollution in textile wastewater comes from dyeing and finishing processes (Al-Kdasi et al., 2004). Textile finishing includes bleaching, dyeing, printing and stiffening during processing of textile products (fibre, yarn, fabric, knits, and finished items). The textile industry's impact on the environment, both in terms of the discharge of pollutants and of the consumption of water and energy, has been recognized for some time (Lacasse and Baumann, 2006).

Major pollutants specifically found in textile wastewater are suspended solids, highly recalcitrant chemical oxygen demand, dyes giving intense colour and other soluble substances (Venceslau et al., 1994; Dae-Hee et al., 1999; World Bank, 2007). The removal of colour from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern. Its strongest impact on the environment is related to primary water consumption (80–100 m^3/ton of finished textile) and wastewater discharge (115–175 kg of COD/ton of finished textile, a large range of organic chemicals, low biodegradability, colour, and salinity) (Savin and Butnaru, 2008). Therefore, reuse of the effluents represents an economical and ecological challenge for the entire sector (Li Rosi et al., 2007). Textile processing employs a variety of chemicals, depending on the nature of the raw material and product (Aslam et al., 2004). The effluents resulting from these processes differ greatly in composition, due to differences in processes, fabrics and machinery (Bisschops and Spanjers, 2003).

Typical textile industry wastewater characteristics can be summarized by a COD range from 150 to 12000 mg/L, total suspended solids between 2900 and 3100 mg/L, total Kjeldahl nitrogen from 70 to 80 mg/L, and BOD range from 80 to 6000 mg/L leading to a BOD/COD ratio of around 0.25, showing that it contains large amounts of non-biodegradable organic matter. An important group of auxiliary textile chemicals are non-ionic (ethoxylate) + anionic (aryl sulfonate) detergent mixtures that are frequently applied in the preparation (scouring, washing and mercerizing) stage to remove impurities from the fabric and prepare them for dyeing.

Research studies in this field have usually focused on the development of new treatment strategies for synthetic wastewater mainly containing azo-dyes, the largest class of dyes used in textile industry, and surfactants, which are responsible for foam formation on the surface of rivers, anomalies in the growth of algae (eutophization) and toxicity for some aquatic organisms. Furthermore, few studies have been carried out using synthetic textile wastewater or real wastewater coming from the different steps in textile manufacturing. In this sense, AOPs have been widely shown to have the greatest promise for treating textile wastewater as summarized in Table 1.

From all of these studies, it can be concluded that a single, universally applicable end-of-pipe solution is unrealistic, and combination of different techniques is required to devise a technically and economically feasible option. Hai et al. (2007) recently published a comprehensive review of potential hybrid technologies found in the literature for treatment of dye wastewater in general and textile wastewater in particular. Based on the array of potential hybrid technologies and the available cost information, it can be concluded that biological hybrid technologies appear to be the most promising. In these integrated processes, in contrast to the conventional pre- or post-treatment concepts, where process designs of different components are independent of each other, the effectiveness of combining biological and other treatments is specifically designed to be synergetic rather than additive.

As shown in Table 1, during recent years an enormous amount of studies dealing with partial pre-oxidation of dye wastewater involving all of the AOPs, have been reported without actually testing in a biological reactor. In fact, few investigations carried out in the last years actually include a biological system following the AOP pre-oxidation to complete the treatment of a real or synthetic textile wastewater. For example, applicability of AOPs (ozone, hydrogen peroxide, UV radiation and Fenton's reagent) combined with an aerobic biological treatment was studied in three industrial wastewater samples from the production of stilbene fluorescent whitening agents, used in the textile and paper industries and in household detergents. Results showed that processes producing hydroxyl

Table 1
A brief summary of research studies in which AOPs were used for treating textile or dyeing wastewater.

Advanced Oxidation Processes	References	Concluding remarks
Conventional chemical treatment methods: $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3$ and $FeSO_4$ compared to AOPs (O_3, O_3/UV, H_2O_2/UV, $O_3(H_2O_2$/UV, Fe^{2+}/H_2O_2)	Azbar et al. (2004b)	Superior performance of O_3/H_2O_2/UV system: 99% COD removal and 96% colour removal from a fibre dyeing effluent
O_3/H_2O_2/UV H_2O_2/UV	Ledakowicz and Gonera (1999) Lidia et al. (2001) Stanislaw et al. (2001) Cisneros et al. (2002) Ahmet et al. (2003)	Effectively decolourized dyes and synthetic textile wastewater (COD removed was not complete)
Ozonation	Wang et al. (2003) Babuna et al. (2009)	Formation of by-products which increased toxicity of the formulation
TiO_2-assisted photocatalysis Ozonation	Gomes de Moraes et al. (2000)	Complete decolourization and TOC reduction over 60% 60% decolourization and negligible TOC reduction
TiO_2 photocatalysis (solar light or UV) with or without H_2O_2	Liu and Chiou (2005) Reddy and Kotaiah (2005)	High removal efficiency for reactive dyes
Photocatalytic membrane reactor (PMR) integrating novel flat plate PTFE membrane module along with a TiO_2 slurry photo-reactor	Damodar and You (2010) You et al. (2010)	Nearly 99.99% colour removal and 75–85% TOC and COD removal. Faster than an anaerobic (aerobic membrane biological process for the mineralization of Reactive Black 5 dye
Fenton and photo-Fenton (solar light or UV)	Pérez et al. (2002a) Torrades et al. (2004) Amat et al. (2004) Liu et al. (2007) Ay et al. (2009)	Successful treatment of textile dyes and commercial surfactants
Electrochemical and electro-Fenton (Fe^{2+} in combination with electro-generated H_2O_2 on the polyacrylonitrile-based activated carbon fibre cloth cathode)	Raju et al. (2009) Wang et al. (2010) El-Desoky et al. (2010)	Successful treatment of textile effluents and real dyeing wastewater

radicals without UV irradiation were suited for the oxidation of all three wastewaters. Furthermore, the pre-oxidation applied did not always lead to a significant improvement in biological degradation (Hörsch et al., 2003). On the other hand, commercial homo-bireactive dye (125 mg/L) and a commercial grade non-ionic/anionic textile surfactant (initial COD of 500 mg/L), were successfully treated by an integrated photochemical (photo-Fenton and H_2O_2/UV-C) and a biological treatment in a conventional sequencing batch reactor (García-Montaño et al., 2006b; Arslan-Alaton et al., 2006). Other biological system configurations like biofilm reactors have also been combined with AOPs such as H_2O_2/UV, TiO_2/UV and photo-Fenton to treat reactive azo-dyes, achieving 99% removal efficiency (Sudarjanto et al., 2006; Kim and Park, 2008; García-Montaño et al., 2008a,b). Anaerobic biological treatment has also been combined with photocatalysis with immobilised TiO_2 (as a pre- or post-oxidation method) to treat raw solutions of azo, anthraquinone and phthalocyanine textile dyes (Harrelkas et al., 2008). Finally, membrane bioreactors implementing special dye-degrading microorganisms and involving simultaneous addition of adsorbent in MBR may surface as potential contenders among present-day dye wastewater treatment processes (Hai et al., 2006). The MBR technology may also be combined with advanced oxidation facilities. Case-specific selection of the appropriate hybrid technology is the key to a feasible system.

3.4. Paper mill wastewater

The pulp and paper making industry is a very water-intensive industry and ranks third in the world, after the primary metals and the chemical industries, in terms of freshwater withdrawal. This high water usage, between 75 and 227 m^3/ton of product results in large amounts of wastewater generation. However, the practice of recycling a certain amount of water is commonplace, as this recovers some of the fibres which have escaped in the wastewater. The effluents from this industry cause slime growth, thermal impact, scum formation, colouration, and loss of aesthetic beauty in the environment. They also increase the amount of toxic substances in the water, killing zooplankton and fish, and severely affecting the terrestrial ecosystem.

Wood pulping and manufacture of paper products generate a large number of pollutants characterized by BOD, COD (which can be as high as 11000 mg/L), suspended solids, toxicity, and colour when untreated or poorly treated effluents are discharged into natural water. The process stages which are the most significant sources of pollution are wood preparation, pulping, pulp washing, screening, washing, bleaching, and paper machine and coating operations. Pulp bleaching generates the most toxic substances, as chlorine is used for brightening. Depending upon the type of pulping process, various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, chlorinated resin acids, and others are generated in the pulp and paper making process (Pokhrel and Viraraghavan, 2004).

The characteristics of the wastewater generated from pulp and paper industry processes depend upon the type of process, type of wood, technology applied, management practices, internal recirculation of the recovery effluent, and the amount of water to be used in the particular process.

To date, many studies have been conducted in this sector on the impact and control of pollutants. Kahmark and Unwin (1999), and Bérubé and Kahmark (2001) have reviewed management and pollution control in the pulp and paper industry. Pokhrel and Viraraghavan (2004) recently reviewed treatability of pulp and paper mill wastewater and compare performance of available treatments.

Among the various treatments currently used for pulp and paper effluents, only a few are commonly adopted by this industry especially for tertiary treatments. Some of them, such as ozonation, Fenton's reagent, adsorption, and membrane technology are efficient, but expensive. Sedimentation is the process most commonly used in the pulp and paper industry to remove suspended solids (Chen and Horan, 1998; De Pinho et al., 2000). Coagulants are a preferred option for removing turbidity and colour from wastewater. Adsorption

Table 2
A brief summary of recent research studies in which AOPs were used for treating paper mill wastewater.

Advanced Oxidation Processes	References	Concluding remarks
TiO_2-photocatalysis	Pérez et al. (2001)	50% of mineralization and total removal of colour and phenols from a cellulose ECF effluent
Ozone/UVA or visible light/Fe(II)/Fe(III)	Pérez et al. (2002b)	High efficiency removal of TOC and COD of a Kraft pulp mill bleaching effluent
Ozone or ozone/UV	Amat et al. (2003b)	Real effluents COD decrease was dependent on the fatty acids/phenols ratio. Respirometric studies showed an increase in the BOD in effluents subjected to a mild oxidation, while under stronger conditions a BODst decrease was observed
Fenton and photo-Fenton (black-light fluorescent lamp, xenon lamp and solar light irradiation)	Pérez et al. (2002c) Torrades et al. (2003)	Successful degradation of the organic content of a Kraft pulp mill bleaching effluent and a conventional cellulose bleaching effluent
Different AOPs	Pérez et al. (2002d) Eskelinen et al. (2010)	Fenton and photo-Fenton achieved better degradation than photocatalysis with lower costs in the treatment of bleaching effluents from pulp and paper mills Ozonation is effective but expensive although the use of UVA increased its effectiveness with a significant decrease in operating costs

processes are useful to remove colour, COD and AOX. In Table 2 some of the most relevant and recent publications using AOPs for paper mill wastewater treatment are summarized.

It may be concluded from these studies that, although each individual treatment could improve the treatability of bleaching wastewater, neither of them could generate treated effluents that met the strict requirement of a COD limit below 200 mg/L, thus suggesting the need for integrating physico-chemical treatments and biological processes for the degradation of recalcitrant compounds.

In this sense, toxicity and biodegradability assays are being employed to evaluate the efficiency of AOPs as a pre-treatment step for the improvement of paper mill wastewater biodegradability (Pintar et al., 2004). For example, ultrasonic treatment has been studied as a pre- or post-oxidation option combined with biodegradation for real paper mill wastewater treatment, showing a final decrease in toxicity and a biodegradability enhancement (Gonze et al., 2003). The post-bleaching effluent from cellulose and paper, with a BOD/COD ratio of 0.11 (non-biodegradable), was subjected to a first coagulation–flocculation treatment followed by a UV/TiO_2/H_2O_2 system using mercury lamps, which raised the biodegradability index to 0.71 (Rodrigues et al., 2008a,b). Solar photocatalysis (photo-Fenton and TiO_2) to increase real paper mill wastewater biodegradability was studied by measuring the oxygen uptake rate of each photo-treated sample by means of an active sludge respirometer (Amat et al., 2005). Finally, electrochemical pre-treatment (using iron electrodes) of pulp and paper wastewater raised the biodegradability index from 0.11 to 0.46 (Soloman et al., 2009). This simple electrochemical pre-treatment could be expected to reduce the following biological reactor volume requirement.

In contrast, few research studies have been published showing the whole integrated treatment of pulp and paper mill effluents including the biological step. In this field, ozonation is the AOP most employed for combination with biological mineralization and COD reduction by activated sludge or specific organisms such as algae (Bijan and Mohseni, 2005; Balcioglu et al., 2006). Pre-ozonation enhanced the performance of following algal treatment in a sequential batch reactor and activated-sludge treatment.

3.5. Olive mill wastewater

Olive oil extraction is one of the most traditional agricultural industries in the Mediterranean region, and is still of primary importance to its economy. The extraction of olive oil generates huge quantities of highly phytotoxic waste that may impact on land and water environments. Several studies have proven the negative effects of such waste on aquatic ecosystems (DellaGreca et al., 2001). Therefore, integrated solutions using various clean technologies within the production process and the development of new wastewater treatment technologies in connection with by-product

Table 3
A brief summary of recent research studies in which AOPs were used for treating olive mill wastewater.

Advanced Oxidation Processes	References	Concluding remarks
UV/H_2O_2 combined with ultrafiltration	Drouiche et al. (2004)	Efficient to finish the treatment of the permeate
Fenton and photo-Fenton (with or without coagulation)	Ahmadi et al. (2005) Rizzo et al. (2008a) Lucas and Peres (2009) Dogruel et al. (2009)	Successfully used for removing organic pollutants and to evaluate their effect on the COD particle size distribution
Electrochemical oxidation, photocatalysis, Fenton oxidation, ozonation	El Hajjouji et al. (2008) Chatzisymeon et al. (2009)	They can only achieve partial decontamination even after prolonged treatment times
Zero-valent iron and H_2O_2	Kallel et al. (2009a,b)	Highly efficient in removal of pollutants. Possible combination with a classical biological process
Solar photo-Fenton	Gernjak et al. (2003, 2004)	Promising, cost-effective method for treating olive mill effluents
Ozonation	Beltrán-Heredia et al. (2001)	Not capable of completely treating highly concentrated olive mill effluents. COD removal not surpasses 20–30%
Wet-air oxidation	Mantzavinos and Kalogerakis (2005) Gomes et al. (2007)	Can achieve high COD removal in relatively short treatment times but it is usually expensive

utilization approaches can dramatically reduce these problems (Vlyssides et al., 2004).

For many years, olive mill wastewater has been the most polluting and troublesome waste produced by olive mills in all Mediterranean countries. Thus, the management of this liquid residue has been extensively investigated, and some extensive, detailed reviews, which focus mainly on its management, have been published (Niaounakis and Halvadakis, 2004; Azbar et al., 2004a).

It is estimated that the annual olive mill effluent production in the Mediterranean Region exceeds 30×10^6 m^3. COD in olive mill effluents may be as high as 220 g/L. Organic matter consists mainly of polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids and oil. Moreover, olive mill effluents contain considerable amounts of suspended solids that may be up to 190 g/L.

In recent years, the efficiency of AOPs for treating olive mill wastewater has been studied extensively. Typical examples are shown in the review by Mantzavinos and Kalogerakis (2005) and in Table 3.

As discussed previously, it is evident that olive mill wastewater treatment is a complex issue with no single optimum solution. In view of this, process integration may be a step in the right direction, bearing in mind the stringent discharge limits that need to be met. Such an integrated system could combine AOPs with conventional biological treatment. The majority of the research activities published in this field only study the decrease in toxicity and biodegradability enhancement from using an advanced oxidation process to partially treat olive mill wastewater. Some examples are comparison of TiO_2 photocatalysis and photo-Fenton for biodegradability enhancement of olive mill wastewater, where photo-Fenton was the more efficient of the two (Badawy et al., 2009); the elimination of phenolic compounds contained in olive mill wastewater by ozonation or ozone/UV increased effluent biodegradability (Amat et al., 2003; Lafi et al., 2009); and phytotoxicity decrease in olive mill wastewater was obtained by means of catalytic wet-air oxidation using platinum and ruthenium-supported titania or zirconia (Minh et al., 2008) and by using a coagulation–flocculation–hydrogen peroxide oxidation process (Ginos et al., 2006). However, some authors have also developed the whole integrated AOP/biological system for the treatment of olive mill wastewater. Fenton's reagent is frequently used as a pre-treatment step in combination with a selected microbial consortium for degrading residual volatile and non-volatile organic compounds into CO_2 and biomass (Bressan et al., 2004). This chemical oxidation process has also been compared to ozonation, followed by treatment with aerobic microorganisms in both cases (Beltrán-Heredia et al., 2000). Finally, an innovative process for the treatment of olive mill wastewater has recently been up-scaled from lab-scale to pilot-plant (Khoufi et al., 2006, 2009). This process combines the electro-Fenton reaction followed by anaerobic digestion and ultrafiltration as a post-treatment to completely detoxify the anaerobic effluent and remove its high-molecular-mass polyphenols. Working in semi-continuous mode, removal efficiencies are 50% for COD and 95% for monophenolic compounds.

3.6. Landfill leachate

A landfill site is a large area of ground, normally lined, that is used for dumping/disposing of waste material. As long as rainfall is higher than the water evaporation rate, the level of liquid (leachate) in the landfill will tend to rise. Environmental regulations require the leachate level to be controlled, which means that excess leachate must be removed and disposed of. The most economical way to dispose leachate is generally discharge into a local watercourse or sewer, although on-site treatment is invariably a prerequisite. This can be done in several ways, depending on the nature of the leachate (Robinson, 2005).

Leachates are defined as the aqueous effluent generated by rainwater percolation through wastes, biochemical processes in waste cells and the inherent water content of the waste itself. Leachates may contain large amounts of organic matter (biodegradable, but also refractory to biodegradation), where humic-type components comprise an important group, as well as ammonia–nitrogen, heavy metals, chlorinated organic and inorganic salts. The removal of ammonium and organic material verified by chemical oxygen demand (COD) and biological oxygen demand (BOD) from leachate is usually a prerequisite for discharging the leachates into natural water. Toxicity analyses using various test organisms have confirmed the potential dangers of landfill leachates (Marttinen et al., 2002) and the need to treat them to meet the standards for discharge into receiving water.

Conventional landfill leachate treatments can be classified in three major groups: (a) leachate transfer: recycling and combined treatment with domestic sewage, (b) biodegradation: aerobic and anaerobic processes and (c) chemical and physical methods: chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/flotation and air stripping (Renou et al., 2008).

For many years, conventional biological treatments and classical physico-chemical methods have been considered the most appropriate technologies for manipulation and management of high-strength effluents like landfill leachates. The biological method of nitrification/denitrification is probably the most efficient and cheapest process to eliminate nitrogen from leachate. However, biological treatment is hampered by specific toxic substances (such as PAHs—polyaromatic hydrocarbons, AOXs—adsorbable organic halogens, and PCBs—polychlorinated biphenyls) and/or by the presence of bio-refractory organics (such as humic acids or surfactants). The limited amount of biodegradable organics reduces the efficiency of denitrification, in particular in stabilised landfills. The integrated chemical–physical–biological process (whatever the order) ameliorates the drawbacks of individual processes, augmenting efficacy of the overall treatment.

Conventional leachate treatment methods, such as air stripping, coagulation, flocculation and settling, are often costly in terms of initial outlay of plant equipment, energy requirements and frequent use of additional chemicals. For instance, coagulation–flocculation has some disadvantages, such as the production of a consistent volume of sludge and an increase in the aluminium or iron concentrations in the liquid phase (Silva et al., 2004). Other methods, such as reverse osmosis or active carbon adsorption only transfer the pollution and do not solve the environmental problem (Wiszniowski et al., 2006).

In recent years, Advanced Oxidation Processes have been proposed as an effective alternative for mineralization of recalcitrant organics in landfill leachate (Table 4).

However, these treatments are not economically acceptable for application to large-scale effluents. A significant decrease in overall leachate treatment cost could be achieved by combining AOPs with a biological process, but their compatibility must first be proven. For instance, Koh et al. (2004) successfully combined biological nitrification/denitrification and UV/H_2O_2 followed by a biological oxidation stage. This solution decreased the BOD_5, COD and AOX concentrations below the legal threshold for direct discharge of wastewater. Recently, pre-treatment with coagulation and Fenton oxidation followed by a biological aerated filter reduced landfill leachate COD to 75 mg/L (Wang et al., 2009). The biological reactor most combined with AOPs at lab-scale for landfill leachate effluents treatment is the SBR. Electro-Fenton assisted by chemical coagulation was found to be highly efficient in removing a large amount of refractory organic and inorganic compounds in the leachate, before the SBR (Lin and Chang, 2000). Sonication under stationary conditions using the UD-20 disintegrator, 20 kHz field frequency and 20 μm amplitude, followed by an SBR operated for 24 h, showed a significant improvement in COD and nitrogen-compound removal rates

Table 4
A brief summary of recent research studies in which AOPs were used for treating landfill leachate.

Advanced Oxidation Processes	References	Concluding remarks
TiO_2 photocatalysis	Cho et al. (2002)	Study of the relationship between TiO_2 dose and reaction rate
Fenton process	Lopez et al. (2004) Kang and Hwang (2000) Surmacz-Gorska (2001) Gotvajn et al. (2009)	COD removal efficiency from 60% to 86% for mature, heavily polluted tannery landfill leachate and biologically pre-treated leachate
O_3, O_3/H_2O_2 and O_3/UV after $FeCl_3$ or $Fe_2(SO_4)_3$ coagulation step	Wu et al. (2004) Poznyak et al. (2008)	Landfill leachate biodegradability increased from a BOD_5/COD ratio of 0.06 to 0.5 with 1.2 g/L of O_3 Decomposing toxic compounds from Mexico City waste sanitary landfill leachate after 15 min of ozonation
O_3 alone or combined with granular activated carbon (GAC)	Kurniawan et al. (2006)	Treated raw leachate did not comply with the 200 mg/L of COD limit
H_2O_2 oxidation process followed by a GAC adsorption	Kurniawan and Lo (2009)	Raw leachate biodegradability improved from a BOD_5/COD ratio of 0.08 to 0.36
Electrochemical oxidation using an oxide-coated titanium anode	Moraes and Bertazzoli (2005)	Achieved 73% of COD elimination in a municipal landfill leachate
Electro-oxidation	Deng and Englehardt (2007)	Brief review related to the influence of pre-treatment methods, anode materials, pH, current density and chloride concentration.
Electro-Fenton	Atmaca (2009) Mohajeria et al. (2010)	Study of the effect of treatment time, DC current, initial pH, initial H_2O_2 concentration, H_2O_2/Fe^{2+} molar ratio and distance between electrodes
Photochemically-assisted electrochemical oxidation (UV lamps)	Tauchert et al. (2006) Zhao et al. (2010)	After previous chemical precipitation, 90% and 74% COD removal, respectively

compared to biological treatment of non-pre-oxidized leachate (Neczaj et al., 2007).

3.7. Winery and distillery wastewater

Wineries present a challenge for treatment of wastewater. This industry generates strong organic wastewater that is highly dependent on production activities. The bulk of wastewater (typically over 80%) is generated during production, which lasts for only 3 months a year. Dissolved wastewater components include sugars, ethanol, organic acids, aldehydes, other microbial fermentation products, and soaps and detergents from cleanup operations. Winery wastewater typically has a low pH (3–4) because of organic acids produced during fermentation, and it generally has quite a large amount of phosphorus although it is deficient in nitrogen and other trace minerals, which are necessary for efficient biological treatment. Winery wastewater COD is typically between 800 and 1200 mg/L, indeed it can increase to 25000 mg/L depending on the harvest load and processing activities. Biological systems evaluated, such as activated-sludge reactors (Petruccioli et al., 2000, 2002), are efficient for BOD removal, but require long retention times. Furthermore, capital and operating costs are high. Consequently, there is no general agreement on the most suitable treatment method for winery wastewater. Recently, AOPs have provided a promising potential alternative treatment method for this kind of wastewater. Among them, ozonation and ozonation in combination with UV-C radiation and/or peroxidation have been shown to be effective in the treatment and biodegradability enhancement of wastewater with polyphenol content such as winery wastewater (Beltrán et al., 1999, 2001a; Lucas et al., 2010). Remediation by heterogeneous photocatalysis with TiO_2 and homogeneous photocatalysis with photo-Fenton has also been studied using UV light at lab-scale (Agustina et al., 2008) and using solar light at pilot-plant scale (Mosteo et al., 2007; Lucas et al., 2009a,b). Although high mineralization rates were attained in both experimental configurations, photo-Fenton with solar radiation showed higher removal efficiencies and a significant toxicity decrease. Although a large number of studies related to AOPs applied to toxicity reduction or biodegradability enhancement of winery wastewater have been published, few contain a fully integrated AOP–biological system at lab-scale or at pilot-plant scale. Ozonation pre-treatment combined with activated-sludge aerobic processes was mainly used to enhance removal not only of organic carbon, but also of nitrogen in the following biological step and settling properties of the sludge (Beltrán et al., 2001b; Benitez et al., 2003a).

Apart from wastewater generated in the winery industry itself, other wastewater is generated during industrial processes directly related to the wine production market, such as cork boiling and bleaching wastewater. Cork boiling wastewater usually contains some corkwood extracts, such as phenolic acids (gallic, protocatechuic, vanillic, syringic, ferulic and ellagic), tannic fraction, 2,4,6-trichloroanisol and pentachlorophenol. Afterwards, during chemical bleaching, chlorophenols are formed from direct chlorination of the cork lignin (Vilar et al., 2009).

These effluents are highly toxic and lead to partial inhibition of biodegradation (Benitez et al., 2003b, 2008), requiring the application of a physico-chemical pre-treatment (some examples are shown in Table 5). Highly acute toxicity was detected in cork boiling effluents

Table 5
A brief summary of recent research studies in which AOPs were used for treating winery and distillery wastewater.

Advanced Oxidation Processes	References	Concluding remarks
Fenton process	Guedes et al. (2003) Beltrán-Heredia et al. (2004)	79% and 87% COD removal, respectively. Biodegradability ratio increased from 0.27 to 0.63
Integrated Fenton-coagulation/flocculation process	Peres et al. (2004)	Reduction of COD, total polyphenols and aromatic compounds by 74, 99% and 98%, respectively
Fenton pre-oxidation	Dias-Machado et al. (2006)	Cork boiling wastewater biodegradability increased
Solar heterogeneous and homogeneous photocatalytic pre-treatment	Vilar et al. (2009)	Determine the optimal energy dose to reduce real cork boiling wastewater toxicity

with EC_{50} ranging from 2.3% to 29.5% for the two species tested (*V. fischeri* and *D. magna*) (Mendonca et al., 2007).

Another wastewater having much in common with wineries is distillery wastewater. Sources of distillery wastewater are stillage, fermenter and condenser cooling water and fermenter wastewater. The liquid wastes produced during the industrial phase of the production of alcohol are liquor, sugar cane washing water, water from the condensers and from the cleaning of the equipment, apart from other residual water. This extract is extremely polluting as it contains approximately 5% organic material and fertilizers such as potassium, phosphorus and nitrogen. Furthermore, the molasses wastewater from alcoholic fermentation has a large amount of a brown pigment. The colour is hardly degraded by conventional treatments and can even increase during anaerobic treatments due to repolymerization of compounds (Pant and Adholeya, 2007). A recently published review of the existing status and advances in biological and physico-chemical methods applied to the treatment of molasses-based distillery wastewater (Satyawali and Balakrishnan, 2008) reports that anaerobic treatment, the most attractive primary treatment, removes over 80% BOD combined with energy recovery in the form of biogas. However, further treatment to reduce the residual organic load and colour includes biological methods employing different fungi, bacteria and algae, and physico-chemical methods such as adsorption, coagulation/precipitation, oxidation and membrane filtration.

Typical BOD and COD for used wash water from a batch distillery are 35–50 and 80–100 g/L, respectively, whereas for a continuous process, they are in the range of 60–100 and 160–200 g/L, respectively. Thermal methods, like thermal pre-treatment, thermo-chemical liquefaction, wet-air oxidation and especially anaerobic digestion are also employed. Each of these methods has some technical or techno-economic problems, and it appears that no single method can be suggested as a complete economical solution for the used distillery wash water disposal (Lele et al., 2000). Hybrid methods combining two or more oxidation processes are also becoming popular for distillery wastewater treatment. These processes generate complementary oxidation conditions and also help counteract the drawbacks associated with the individual methods. For instance, ultrasound is one of the AOPs most commonly applied as a pre-treatment followed by an aerobic activated-sludge reactor for distillery wastewater COD removal (Sangave and Pandit, 2004, 2006). Furthermore, the same authors have studied thermal pre-treatment with ultrasound and ozone, and were able to increase the aerobic biodegradation rate 25 times and obtain a maximum COD reduction of 45.6% (Sangave et al., 2007a). However, ozonation has also been applied as the main step in the treatment line for remediation of distillery wastewater. In this case an integrated ozonation–aerobic oxidation–ozonation process achieved around 79% of COD reduction along with decolouration of the effluent sample compared to 35% of COD reduction with an unozonated sample (Sangave et al., 2007b).

Table 6
A brief summary of recent research studies in which AOPs were used for treating tannery wastewater.

Advanced Oxidation Processes	References	Concluding remarks
H_2O_2/UV, UV, TiO_2/UV, TiO_2/H_2O_2/UV, O_3, O_3/UV and Fenton process	Schrank et al. (2004, 2005) Sauer et al. (2006)	Toxicity reduction monitored by *Daphnia magna*, *Vibrio fischeri* and *Artemia salina*
Electrochemical processes and electro-Fenton	Kurt et al. (2007) Rodrigues et al. (2008a,b) Costa and Olivi (2009)	Recovery and reuse of tannery wastewater. High capacity for toxicity reduction
Ozonation	Preethi et al. (2009)	Biodegradability ratio increased from 0.18 to 0.49

Table 7
A brief summary of recent research studies in which AOPs were used for treating petrochemical industry wastewater.

Advanced Oxidation Processes	References	Concluding remarks
TiO_2 photocatalysis (submerged mercury UV lamp)	Saien and Nejati (2007)	More than 90% reduction in COD
TiO_2 photocatalysis	Kuburovic et al. (2007)	Achieved 91% degradation of methyl tertiary butyl ether and the biodegradability improvement was verified with *Pseudomonas* strain CY
Fenton process	Millioli et al. (2003)	Removal and oxidation of oil spilled onto the beach in Guanabara Bay in Rio de Janeiro (Brazil).
Electrochemical process	Santos et al. (2006)	Successful in remediation of wastewater from oil extraction achieving a maximum COD reduction of 57%
Low-temperature, low-pressure microwave-assisted catalytic wet-air oxidation	Sun et al. (2008)	Oil refining wastewater biodegradability ratio improved from 0.04 to 0.47

3.8. Miscellaneous wastewater

Due to the wide diversity of contaminated industrial wastewater discharged into the environment, there are some well-known industrial waste streams which have scarcely been tackled by advanced treatment. This section presents a brief summary of application of AOPs combined with biological systems for the complete treatment of some of these highly polluted industrial effluents.

The leather industry is one of the most polluting in terms of the volume and complexity of the effluent discharge. The transformation of the raw hide into leather products involves several processing steps consuming considerable amounts of water. Tannery wastewater contains high concentrations of organic matter and chemicals, such as chlorides, bactericides, emulsifiers, ammonia, detergents, etc. These effluents cannot be released into the environment without pre-treatment, because of their toxicity (Vrcek and Bajza, 2001). In fact, after conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as COD, salinity, ammonia and surfactants (Schrank et al., 2004).

Table 8
A brief summary of recent research studies in which AOPs were used for treating table olive processing wastewater.

Advanced Oxidation Processes	References	Concluding remarks
TiO_2 photocatalysis	Chatzisymeon et al. (2008)	Degradation completed with aerobic non-acclimated activated sludge
Electrochemical oxidation	Deligiorgis et al. (2008)	73% of COD removal
Wet-air oxidation	Katsoni et al. (2008)	More than 90% of phenol degradation and decolourization and 70% mineralization

Table 9
Integrated AOP/biological systems for the treatment of different kinds of industrial wastewater.

References	Target wastewater (pollutant degraded)	AOP employed	Biological degradation	Analyses performed	Main results
Zeng et al. (2000)	Polycyclic aromatic hydrocarbons (benzo[a]pyrene)	Ozonation	BOD (after 5, 10 and 15 days of incubation)	BOD, COD, *E. coli* toxicity test Reaction products by GC–FID and GC–MS	Effluent non-toxic for *E. coli* Final $BOD_5/COD = 0.43$
Nadarajah et al. (2002)	Polycyclic aromatic hydrocarbons	Fenton process	A mixed bacterial culture (*Enterobacter agglomerans*, *Erwinia herbicola*, *Pseudomonas fluorescens*, *Pseudomonas syringae* and *Pseudomonas testosterona*)	Anthracene, benzo[a]pyrene concentrations (CG-14A)	Successful removal of 80–85% of polycyclic aromatic hydrocarbons
Rafin et al. (2009)	Polycyclic aromatic hydrocarbon benzo [a]pyrene	Fenton process	Biodegradation process with *Fusarium solani*	Benzo[a]pyrene concentration (HPLC) *F. solani* toxicity test	25% of benzo[a]pyrene degradation with the combined system
Park et al. (2001)	Dimethyl sulphoxide (widely used in manufacture of electronics, polymers, dyes, membranes, etc.)	Fenton process	Activated-Sludge biosystem	TOC, COD, BOD	BOD_5/COD ratio increased from 0.035 to 0.87 Only by activated sludge 90% removal of TOC Integrated system not efficient
Entezari and Pétrier (2003)	Substituted phenols	Sonolysis	Enzyme treatment	Contaminants concentration (HPLC)	Combined method more efficient for phenol and its halogenated derivatives
Wang et al. (2008)	Surfactant wastewater (with abundant sulfate)	Fenton process	Immobilised biomass reactor	COD and linear alkylbenzene sulfonate (LAS) concentration (HPLC)	20 h of HRT Removal efficiencies of COD and LAS over 94% and 99%, respectively
Chen et al. (2009)	Di-(2-ethylhexyl) phthalate (widely used in manufacturing and processing of plastic products)	Photo-Fenton process (mercury lamp)	Fixed bed biological reactor	TOC, COD, BOD_5, *Vibrio fischeri* toxicity test HPLC and GC–MS	Removal efficiency <80%
Lee et al. (2009)	Reverse osmosis brine from water reclamation facilities	Ozonation	Biological activated carbon system	TOC, BOD_5, colour, anions and cations concentration (ionic chromatography)	Combined system achieved 3 times higher TOC removal compared to using biological activated carbon process alone
Yan et al. (2010)	Trihalomethanes (THMs) precursor	Ozonation	Biological granular activated carbon filtration	TOC, turbidity, alkalinity, iodine, GC.	Integration process is superior to granular activated carbon system to THMs precursor removal.
Torres et al. (2003)	5-amino-6-methyl-2-benzimidazolone (AMBI)	Electrochemical oxidation	Fixed bed biological reactor	TOC, AMBI concentration (HPLC), chloride concentration. BOD, *Vibrio fischeri* toxicity test, Zahn–Wellens test	100% AMBI degradation. Solution pre-treated finally biocompatible
Sarria et al. (2001)	Real industrial wastewater containing AMBI	$H_2O_2/h\nu$, $TiO_2/H_2O_2/h\nu$, Fe^{3+}/H_2O_2 and $Fe^{3+}/H_2O_2/h\nu$	Fixed bed biological reactor	TOC, AMBI concentration (HPLC), BOD	100% AMBI degradation. 80.3% of TOC removed
Sarria et al. (2003a)	Real industrial wastewater containing AMBI	Fe(III)-photo-assisted process (suntest simulator/CPC reactor).	Fixed bed biological reactor	TOC, COD, AMBI concentration (HPLC), Zahn–Wellens test	80% of AMBI eliminated 90% of TOC removal in the combined system
Kastaned et al. (2007)	Chlorinated organic substances (4-chlorophenol).	Fenton process	Activated-sludge biotreatment	COD, BOD.	Biodegradation rate enhanced by two-fold by the application of the combined system
Gonze et al. (2003)	Raw Paper Mill wastewater (bleaching process)	Ultrasonic process	Activated-sludge biotreatment	COD, TOC, *Vibrio fischeri* toxicity test, BOD_5/COD	The combined treatment is inefficient for concentrated basic paper mill wastewater The acidification of the solution accelerates oxidation and mineralization Biodegradability rate improved at the end of the combined process
Bijan and Mohseni (2005)	Paper Mill wastewater (pulp mill alkaline bleach plant effluent)	Ozonation	Batch aerobic biological system	COD, TOC, BOD_5 and molecular weight distribution	20% organic compounds removal in ozonation pre-treatment. 30% TOC removal during biological process
Balcioglu et al. (2006)	Paper Mill wastewater (bleached Kraft pulp mill effluents)	Ozonation	Sequential batch reactor	AOX, COD, BOD_5/COD	BOD_5/COD ratio increased from 0.16 to 0.32 87% AOX removal rate
Bijan and Mohseni (2008)	Paper Mill wastewater (Kraft pulp mills)	Ozonation (membrane pre-treatment)	Activated-sludge biotreatment	COD, BOD_5, total carbon, colour and ozone	The biodegradability of the wastewater during the ozone oxidation increased significantly
Toor and Mohseni (2007)	Disinfection by-products (trihalomethanes and haloacetic acids)	$UV–H_2O_2$	Biological activated carbon treatment	Disinfection by-products concentrations TOC, absorbance at 254 nm (UV_{254})	The combined treatment showed reductions of 43%, 52% and 59% for disinfection by-products, TOC and UV_{254}, respectively

In Table 6 the most recent studies related to tannery wastewater treatment by AOPs are presented.

Due to the characteristics of raw tannery effluents, the majority of research on specific AOPs/biological systems for the treatment of this wastewater is focused on using the AOP as a post-treatment step after a previous biological treatment. These studies are presented in the following section.

In petroleum and petrochemical industries, there is strong interest in improving wastewater management by optimizing water use and introducing recycling technologies in production units. The traditional treatment of refinery wastewater is based on physico-chemical and mechanical methods and further biological treatment in the integrated activated-sludge treatment unit. However, there is still a need to develop advanced techniques to remove aliphatic and aromatic hydrocarbons present in the wastewater, among which the aromatic fraction is not readily biodegradable and is more toxic. In recent years, AOPs for the treatment of petrochemical industry wastewater and related effluents, such as those coming from oil extraction have been evaluated. In Table 7 some examples are shown.

The food industry is another important consumer of water and major contributor of loads discharged into water resources (Badawy and Ali, 2006). In this field, wastewater from processing table olives is a serious environmental concern, since they are either dumped untreated into natural receivers or sent to evaporation ponds where natural attenuation processes may cause foul odours or spread into surface and groundwater (Parinos et al., 2007). The organic fraction of wastewater from table olive processing contains phenols, polyphenols, sugars, acids, tannins, pectins and oil residues, with a chemical oxygen demand (COD) of several grams per liter depending on the variety of olive and manufacturing process employed. The inorganic fraction consists of high concentrations of sodium chloride and sodium hydroxide which are used for debittering and fermentation, as well as trace amounts of various metals. These effluents have antimicrobial, ecotoxic and phytotoxic properties, thus rendering them unsuitable for complete treatment by aerobic (Brenes et al., 2000) or anaerobic (Aggelis et al., 2001) processes. In recent years, in an attempt to improve the biodegradability of table olive processing wastewater, several studies have dealt with the use of AOPs as a suitable pre-treatment for reducing the effluent's COD and phenolic content (Table 8) (Benitez et al., 2001a, b; Beltrán-Heredia et al., 2000; Rivas et al., 2000, 2001).

Meat processing industry effluents are included as a part of food industry wastewaters, and they constitute one of the greatest concerns of the agro-industrial sector, as they use approximately 62 Mm^3/year of water worldwide. Nevertheless, only a small amount of this becomes a component of the final product. The remaining part has high biological and chemical oxygen demands, high fat content and high concentrations of dry waste, sediments and total suspended matter as well as nitrogen and chlorides (Sroka et al., 2004). AOP treatments have recently come into use for elimination and degradation, water reuse and pollution control issues. As an example, evaluation of the effectiveness of meat processing wastewater treatment by dissolved air flotation followed by AOPs using photo-peroxidation (H_2O_2/UV) or photo-Fenton reactions showed that photo-Fenton provided the best overall results (Sena et al., 2009).

Finally, coffee industry effluents are another example of highly polluted food industry wastewater. The coffee industry uses large amounts of water during the various stages of the production process, around 40–45 L per kilogram of coffee. Such wastewater contains compounds such as caffeine, fat, and peptic substances, as well as many different macromolecules such as lignins, tannins, and humic acids, which are difficult to degrade using conventional biological treatment processes. Therefore, a combination of chemical coagulation–flocculation and AOPs (UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3) was used for highly efficient removal of organic material, including recalcitrant organic compounds, reducing COD by a maximum of 87% (Zayas et al., 2007).

Apart from the studies summarized above, some integrated chemical/biological systems evaluated for the treatment of other industrial wastewater containing toxic and/or non-biodegradable pollutants are presented in Table 9.

3.9. AOPs as a post-treatment stage

As demonstrated in previous sections, further chemical oxidation in combined oxidation followed by biodegradation systems may not lead to any significant change in the molecular weight distribution. Hence, it is reasonable for pre-oxidation to be as short as possible and remove the biodegradable portion by cost-effective biological processes. Nonetheless, the amount of COD removable with this strategy may be limited, making use of longer oxidation necessary and the following biological process redundant (Poole, 2004.). Internal recycling between the oxidation and biological stage has been recommended for reducing the chemical dose in such circumstances (Libra and Sosath, 2003). For instance, Dogruel et al. (2002) have pointed out the selective preference of ozone for simpler readily biodegradable soluble COD fractions, leading to its unnecessary consumption. They suggest pre-ozonation of segregated recalcitrant streams from a dye house prior to biological treatment of the whole mixed effluent. If the original wastewater contains a considerable amount of biodegradable compounds, the pre-oxidation step obviously will not lead to a significant improvement of biodegradability; rather, it will only cause unnecessary consumption of chemicals.

In such cases, a biological pre-treatment (removing biodegradable compounds) followed by an AOP (converting the non-biodegradable portion into biodegradable compounds with less chemical consumption) and a biological polishing step may prove to be more useful (Hörsch et al., 2003; Vidal et al., 2004).

Such integrated systems are particularly favourable for effluents such as olive mill wastewater or landfill leachates, which initially contain some biodegradable fractions (i.e. sugars and proteins) which could easily be removed first and so, not compete for the chemical oxidant.

Table 10 presents a summary of several recent studies performed in the field of advanced integrated technologies, which apply an AOP as a post-oxidation step after a primary biological treatment, for effluents containing a rather large biodegradable COD fraction.

4. Large-scale industrial wastewater treatment

This review has compiled a large amount of research assessing integrated AOPs/biological treatment technologies for the remediation of a wide range of industrial wastewater. Nevertheless, the majority of these studies are bench-scale or pilot-plant treatment systems, but few references on demonstration or industrial applications of recently developed technologies are available.

It is important to take into account that combination of chemical and biological processes presents an additional difficulty for efficient operation of a large-scale plant, as the chemical oxidant and biological culture must not come in undue contact with each other. For example, high concentrations of hydrogen peroxide cause an adverse effect on the microorganisms, although relatively low concentrations are not a problem. Special stages to keep chemical oxidants from entering biological post-treatment have been developed for some time (Carberry and Benzing, 1991; Barton and Drake, 1994). The chemical oxidation reaction time must also be taken into account, because when a biological process receives a chemically overdegraded effluent, the highly oxidized products' metabolic value for the microorganisms is minimal. Furthermore, large doses of oxidant may be spent in the degradation of easily biodegradable intermediates, reducing overall system efficiency.

In 1997, a few large-scale experiments in the field of combined AOPs/biological plants for the treatment of landfill leachate had already been reported (Steensen, 1997). All used a combination of several individual

Table 10
Research studies in which AOPs were integrated in the treatment train as a post-treatment step after a biological process.

Reference	Target wastewater (pollutant degraded)	AOP employed	Biological degradation	Analyses performed	Main results
Di Iaconi et al. (2002)	Tannery wastewater	Ozonation	Sequencing batch biofilm reactor	COD, ammonium, total suspended solids	COD, ammonium and total suspended solids average removals were 97%, 98% and 99.9%, respectively
Benitez et al. (2003a,b)	Cork processing industry wastewater	Ozonation	Activated-sludge system	COD, total phenolics, absorbance at 254 nm BOD_5/COD	Ozonation-aerobic degradation sequence increased substrate removal efficiencies
Dogruel et al. (2006)	Tannery wastewater	Ozonation	Activated-sludge biological treatment	COD, total suspended solids, volatile suspended solids, oxygen uptake rate measurements, total Kjeldahl nitrogen	With post-ozonation the highest inert COD removal efficiencies together with an effluent quality meeting the discharge standards were obtained
García-Montaño et al. (2008b)	Dye wastewater (Cibacron Red FN-R reactive azo dye)	Ozonation	Anaerobic digestion	DOC, Biotox®, Zahn–Wellens	Ozonation as post-treatment at pH 10.5, allowed achieving a global 83% mineralization
Mänttäri et al. (2008)	Paper industry wastewater (discharge waters from an activated-sludge process)	Ozonation (after microfiltration and nanofiltration)	Activated-sludge process	DOC, COD, BOD_5, UV and visible light absorbance at various wavelengths Ions concentration by ionic chromatography	Ozone significantly decreased colour, UV absorbing materials (lignin) and turbidity of the NF concentrate. COD also decreased and simultaneously increased biodegradability
Assalin et al. (2009)	Paper industry wastewater (Kraft E_1 effluent)	Ozonation	Activated-sludge process	COD, DOC, total phenols concentration and colour	Ozonation post-treatment at pH 8.3 achieved COD, DOC, colour and total phenols removal of 75.5, 59.1, 77 and 52.3%, respectively
Artanto et al. (2009)	Non-evaporative removal of water from low-rank coals prior to combustion by mechanical thermal expression	Ozonation	Anaerobic digestion	COD, TOC, BOD, total suspended solids, electrical conductivity and turbidity Organic compounds determination by Py-GC–MS	Aliphatic and aromatic hydrocarbons were reduced by approximately 95% by anaerobic treatment. Overall COD removal of 97%
Schaar et al. (2009)	Pharmaceutical wastewater (bisphenol-A, 17α-ethinylestradiol, erythromycin and roxithromycin)	Ozonation	Aerobic biological process	Micropollutants concentration	Ozonation application increased the removal of most of the micropollutants, especially for compounds not degraded in the previous biological process
Mascolo et al. (2010)	Pharmaceutical wastewater (resulting from the production of acyclovir, an anti-viral drug)	Ozonation	Membrane bioreactor	COD, organic compounds concentration	MBR efficiency was improved from 20% to 60% as soon as ozonation was placed in the recirculation stream
Reungoat et al. (2010)	Pharmaceutical wastewater	Ozonation	Biological denitrification	DOC, non-purgeable organic carbon, micropollutants analysis by LC/MS–MS Six bioassays: *Vibrio fischeri*, estrogenic activity, arylhydrocarbon receptor response, neurotoxicity, phytotoxicity and genotoxicity	Overall concentration reductions were typically higher than 90% and most of the compounds were removed to levels lower than 0.01 mg/L
Rosal et al. (2010)	Emerging contaminants (25 compounds detected in μg/L range)	Ozonation	Activated-sludge process	Liquid chromatography-QTRAP–mass spectrometry and gas chromatography coupled to mass spectrometry. Inorganic anions and cations. DOC	Ozonation as post-treatment allowed the removal of many individual pollutants including some of those refractory to biological treatment
Treguer et al. (2009)	Drinking water (improvement of conventional processes)	Ozonation	Membrane bioreactor	DOC, particulate organic carbon, UV absorbance	Residual DOC after membrane bioreactor was the major part of the non-biodegradable fraction. Ozonation post-treatment increased the global efficiency and the biodegradability

Rizzo et al. (2008b)	Organic matter and bacteria released from a biological denitrification process	TiO_2-photocatalysis	Heterotrophic–autotrophic denitrification process	DOC, ammonium, nitrate, nitrite, UV absorbance at 254 nm Trihalomethanes by GC	Biological process proved high nitrate removal. Trihalomethanes concentrations were lower than 2.5 μg/L after photocatalytic treatment. Bacteria released also eliminated by TiO_2-photocatalysis
L'Amour et al. (2008)	Phenol in a high salinity medium	TiO_2-photocatalysis	Activated-sludge process	DOC, phenol and hydroxylated intermediates concentration by HPLC	Complete removal of phenol and a mineralization degree above 98% were achieved within 25 h of global treatment
Barreto-Rodrigues et al. (2009)	Nitrocellulose industry wastewater (delignification water results from alkaline treatment of cotton fibres)	TiO_2-photocatalysis	Fungus isolated from activated sludge (*Aspergillus* 2BNL1)	Colour, total phenol, TOC, toxicity tests with *Escherichia coli*	Fungus and photocatalysis in combination reduced colour, total phenol, toxicity and TOC by 94.2%, 92.6%, 4.9% and 62%, respectively
Banu et al. (2008)	Dairy wastewater	Solar TiO_2-photocatalysis	Anaerobic sludge blanket reactor (HUASB)	COD, BOD, volatile fatty acids, alkalinity, total suspended solids, volatile solids, total Kjeldhal nitrogen	Anaerobic reactor removed 84% of COD. Solar photocatalytic post-treatment removed 62% of the COD from primary anaerobic treatment. 95% of global COD removal
Gulyas et al. (2009)	Biologically pre-treated greywater	Solar TiO_2-photocatalysis in the presence of powdered activated carbon	Biological treatment in a wetland	TOC	TOC concentrations subsequent to photocatalytic oxidation were less than 2 mg/L even after reusing the TiO_2/powdered activated carbon mixture 10 times
Kotsou et al. (2004)	Food industry wastewater (green table olive processing wastewater)	Fenton's reagent	Aerobic biological treatment using *Aspergillus niger* strain in bubble column bioreactor	Total phenolics, COD, total solids, suspended solids, volatile solids, oxygen consumption rate	After 2 days of biological treatment COD was reduced by 70% and chemical oxidation step eliminated persistent phenolic compounds
Ben et al. (2009)	Swine wastewater (veterinary antibiotics)	Fenton's reagent	Sequencing batch reactor (SBR)	COD, TOC, free ammonia, total nitrogen (TN), total phosphorous (TP), suspended solids. Toxicity with *Daphnia magna* Concentration of antibiotics by LC–MS	SBR removed more than 95% COD, TN and suspended solids. Fenton's reagent effectively removed selected antibiotics and achieved 2.4 log of bacteria disinfection and 25% of toxicity reduction
Justino et al. (2009)	Olive Oil Mill wastewater	Photo-Fenton	Treatment with fungi (especially *Pleutrotus sajor caju*)	COD, toxicity tests by *Daphnia longispina* Organic compounds quantification by GC–MS	Fungi species were responsible for 72.9 and 77% reduction in COD and total phenolics and organic compounds contents. Photo-Fenton as a post-treatment seemed to be a solution for colour elimination although toxicity was not enough reduced
Sirtori et al. (2009b)	Pharmaceutical wastewater (containing nalidixic acid)	Solar photo-Fenton	Immobilised biomass reactor (IBR)	DOC, toxicity with *Vibrio fischeri* and *Daphnia magna*, and Zahn–Wellens test. Anions and cations by ionic chromatography. Nalidixic acid concentration by HPLC-UV. Intermediates by LC–TOF–MS	After IBR treatment 96% of DOC was removed and more than 50% of nalidixic acid adsorbed on biomass. Solar photo-Fenton post-treatment totally degraded nalidixic acid increasing the biodegradability
Kim et al. (2002)	Textile wastewater	Electrochemical oxidation (after chemical coagulation)	Fluidized biofilm process (isolated microbes used: *Aeromonas salmonicida* and *Pseudomonas vesicularis*)	COD, suspended solids, colour, dissolved oxygen	The fluidized biomass process showed 68.8% and 54.5% of COD and colour removal efficiency. COD and colour removals of 95.4% and 98.5% were achieved by overall combined process
Szpyrkowicz et al. (2005)	Tannery wastewater	Electrochemical oxidation	Activated-Sludge biological treatment	COD, BOD, TOC, anode potential, total Kjeldahl nitrogen, chloride, and conductivity	Electrochemical oxidation can be applied as a post-treatment after conventional biological process to remove residual ammonia with low energy consumption
Kyriacou et al. (2005)	Food industry wastewater (green table olive processing wastewater	Electrochemical oxidation	Biological treatment using *Aspergillus niger*	Electrical conductivity, COD, BOD, total suspended solids, volatile solids, NH_4^+, P, K, $Cl^-$and SO_4^{2-}. Phenolic compounds measured by GC/FID and GC/MS	In biological treatment step COD removal efficiency varied between 66–86% and the concentration of phenols was reduced by 65%. Electrochemical step at pilot plant removed 75% COD
Lei et al. (2007)	Landfill leachate.	Electrochemical oxidation	Two-stage aged-refuse biological reactor (ARB)	COD, BOD, TOC, AOX, total nitrogen (TN) and ammonia Organic pollutants measured by GC–MS	ARB removal efficiencies of COD, BOD, TOC, TN and ammonia were 98.5, 99.9, 98.0, 64.2 and 99.9%, respectively Electrolysis processes reduced colour although AOX increased greatly

processes. More than 60% of the plants were equipped with a biological stage which is the first stage of the treatment. In 15 plants, the chemical oxidation was chosen for further treatment.:

Nitrification/denitrification-O_3/UV-post-biological oxidation

The treatment plant in Singhöfen (Germany), in operation since 1994, is an example of combined biological and chemical processes for treating 107.4 m^3/day of landfill effluent. The system includes a pre-denitrification and nitrification reactor with sedimentation tank and sand filter in a first stage of treatment. This is followed by ozonation-UV and sand filter and by a post-biological aerated packed-bed stage. During the first operating period, it was observed that the effectiveness of ozone used alone was sufficient to fulfil treatment requirements without UV assistance. Moreover, ozone treatment increases the BOD fraction in leachate considerably. This fraction was successfully removed in the post-biological stage. It not only decreased overall treatment technology cost due to reduced ozone consumption, but also ensured the final discharge requirements.

Nitrification/denitrification–precipitation–ozonation

The landfill leachate treatment plants (LLTPs) in the Bord-Matin landfill, near Saint-Etienne (France) treat stabilised leachate from landfill effluent, and have been operated since 1972 (Poitel et al., 1999). The leachate amounts to 12.5 m^3/day, containing 1750 and 850 mg/L of COD and ammonia, respectively. The treatment plant system consists of a biological stage including nitrification and post-denitrification processes followed by chemical precipitation with lime in a lamellar settling tank. The process ends with ozonation, which meets the final discharge standard for refractory COD.

Biological pre-treatment—TiO_2/UV-post-biological oxidation

The first stage of biological treatment resulted in nitrification and removal of biodegradable organics from the leachate (Wiszniowski et al., 2003, 2004). At the end of photocatalytic treatment total decolouration was observed. COD and TOC significantly decreased to below the threshold for direct discharge of leachates. Photocatalysis converted refractory organics from the landfill leachates into readily biodegradable species (BOD). It was demonstrated that the BOD fraction formed in that way can be removed via aerobically biological oxidation. Similarly, the organic fraction (BOD) can be used by heterotrophs (denitrifiers) during the reduction of nitrite or nitrate to N_2. However, the amount of biodegradable species provided to denitrifying bacteria from the photocatalytic stage allows the standard for nitrogen concentration to be met.

In 2007, a new demonstration plant in a pharmaceutical factory was developed in the framework of a European project called CADOX (5th EU Framework Programme). Based on pilot-plant results (Malato et al., 2007), a pre-industrial plant with 100 m^2 of CPC collector surface (for photo-Fenton partial oxidation), combined with a biological treatment plant based on an immobilised biomass activated-sludge reactor (1 m^3 of total volume) was designed and constructed for the treatment of 4 m^3/day of saline industrial wastewater containing around 600 mg/L of a non-biodegradable compound (α-methylphenylglycine, a common precursor in pharmaceuticals) and from 400 to 600 mg/L of dissolved organic carbon (Oller et al., 2007c). The overall efficiency in this combined system was around 95% mineralization (50% of initial DOC was degraded in the photo-Fenton pre-treatment and 45% was removed in the aerobic biological treatment).

Furthermore, an aerobic biomass system (SBBGR—Sequencing Batch Biofilter Granular Reactor) integrated with ozonation for the efficient treatment of tannery wastewater has also been recently scaled up to a demonstrative plant (Di Iaconi et al., 2009). In this system, the SBBGR consisted of a cylindrical reactor (working volume: 1 m^3 and fixed bed volume: 0.38 m^3) partly filled with biomass support material integrated in an ozonation unit consisting of a pump, which extracted the biologically treated wastewater from the SBBGR (at a flow rate of 2 m^3/h) and pumped it through an ozone reactor (volume: 0.25 m^3) equipped with a residual ozone destroyer. The results showed that this technology was able to efficiently remove COD, TSS, TKN, surfactants and colour to residual concentrations much lower than the current discharge limits.

Finally, the technical feasibility of a large-scale combined solar photo-Fenton/aerobic biological process for the treatment of real industrial wastewater polluted with commercial pesticides has recently been evaluated (Zapata et al., 2010a). Partial photo-Fenton oxidation was carried out under sunlight in a 150-m^2 CPC-based plant (1.06 m^3 of total volume). Afterwards, complete wastewater treatment was performed in a biological system based on two 1.23-m^3 immobilised biomass reactors filled with Pall®Ring supports colonized by activated sludge from the municipal WWTP. The results showed that the combined system was able to efficiently eliminate the pesticides and reduce DOC and COD (more than 80% mineralization) in the wastewater.

5. Economic and degradation kinetic models

Process models suggest that each application of an integrated treatment system usually exhibits an optimal operating condition in economic terms. This means that each new technology designed for the treatment of a specific industrial wastewater usually requires kinetic models to be developed in order to determine the optimal operating conditions for low-cost high efficiencies, when changing the process parameters (Scott and Ollis, 1995).

Scott and Ollis already pointed out in 1997 that the general parameters such as BOD or TOC, widely employed to measure poorly characterized industrial and domestic wastewater, were included in kinetic models describing parts of the overall two-step systems (AOPs/biological treatment). These models do not provide a complete picture of wastewater degradation due to the lack of specificity of the parameters measured, although they can be very useful (Scott and Ollis, 1997).

Nevertheless, in the last few years, research has focused mainly on modeling only AOP remediation of wastewater, without considering strategies combining them with biological treatments. For example, computational fluid dynamic models simulating the performance of UV reactors were developed to simulate UV photo-reactors for chemical removal using oxidation triggered by UV-based hydroxyl radicals oxidation process (Elyasi and Taghipour, 2010). A one-dimensional, one-directional radiation field model was also proposed to compute photon absorption inside a TiO_2 slurry photocatalytic reactor (Satuf et al., 2007) employed for 4-chlorophenol elimination. However, the most common proposal is kinetic models (sometimes including mass and/or thermal balances) demonstrating the dependence of degradation or mineralization rate constants on the operating parameters, H_2O_2 concentration, initial organic content, light intensity, catalyst concentration, etc. (Li et al., 2008; Lan et al., 2008; Lucas et al., 2009a,b; Kusic et al., 2009; Farias et al., 2010; Kralik et al., 2010; Santos et al., 2010).

An overall kinetic model would be required to design combined processes (AOPs/biological treatment) and determine the most efficient or economical operating regions. Although, few recent research activities related to the development of kinetic models for combined chemical–biological processes can be found, the first publication dates from 1996. It reported on steady-state biological degradation models representative of situations found in the treatment of wastewater difficult to degrade, with chemical pre-treatment (Scott and Ollis, 1996). Multiple reactor configurations and inhibitory biological kinetics were used to study a reaction chain in which a non-biodegradable compound was chemically oxidized to

yield biodegradable intermediates. Simulations showed that the combined reactor system could achieve higher mineralization efficiencies than either reactor alone and demonstrated specific cases and operating regions where enhancement of mineralization occurred. Optimal operating regions were identified under given design constraints. Overall efficiency and achievement of treatment targets were dependent on waste characteristics, kinetics, and the reactor configurations used.

In general, overall engineering models were able to predict the effect of changing integrated system variables, such as flow rates, reactor volumes, organic load, etc., on total system efficiency, which is quite important (Eckenfelder et al., 1992; Esplugas et al., 2004). There are several other similar studies in the literature. For instance, a theoretical model applied to predict experimental data and to investigate the effects of dioxane concentration, pH and H_2O_2 concentration found a linear correlation between dioxane oxidation and BOD enhancement (Suh and Mohseni, 2004). The parameters of a proposed Grau model were estimated for degradation and COD removal of two pesticides in a combined O_3/UV and biological treatment (Lafi and Al-Qodah, 2006). Furthermore, industrial wastewater treatment with this combined technology has been also modeled. In this sense, treatment of synthetic wastewater simulating effluents from the Polish textile industry, using O_3, H_2O_2 and UV light combined with acclimated activated sludge was studied (Ledakowicz et al., 2001). The experimental evidence of the positive effect of chemical oxidation pre-treatment on the biodegradation of recalcitrant compounds was quantified by estimation of the Monod equation kinetic parameters. Due to partial oxidation by the AOPs, the Monod constant decreased and maximal specific growth rate increased. Real wastewater generated during different stages in the black table olive industry treated by ozone combined with UV radiation and aerobic microorganisms was also investigated and modeled (Benitez et al., 2002b). The evolution of substrate and biomass was monitored during aerobic degradation alone, and a kinetic study was performed by applying the Contois model to the experimental data, giving the specific biokinetic constant, the cell yield coefficient, and the rate constant for the microorganism death phase. Finally, a combined process, consisting of the aerobic degradation of pre-ozonated wastewaters was performed, and its effect on substrate removal and kinetic parameters of the following biological stage was discussed.

6. Conclusions

The large number of studies reviewed here is indicative of the extensive and intense research that has been carried out in the field of chemical oxidation, and more specifically, in the use of AOPs, mainly as a pre-treatment stage for industrial wastewater remediation. In recent years, many authors have also developed combined AOP and biological systems for the treatment of a diversity of industrial wastewater. These studies cover a wide spectrum of industrial pollutants, and discuss from model solutions with individual substances to real effluents containing a mixture of various persistent substances. Furthermore, there is growing interest in the development of biological reactor configurations (suspended biomass, fixed biomass, aerobic granular biomass systems, membrane bioreactors, etc.) to optimize this time consuming step in the treatment line to maximize efficiency and design specific biological systems for each target industrial wastewater.

Although a systematic procedure consisted on using model substances before studying the real wastewater, and evaluating toxicity and biodegradability during and after the degradation process, the assessment of chemical parameters (overall, such as COD and more accurate such as chromatography) is usually employed in these research studies, and more pilot-plant scale experiments with real industrial wastewater must be performed. From the application point of view, this new integrated technology requires assessing the complete wastewater treatment in order to be reused in the industry itself.

More studies on how system characteristics enhance or limit the individual and global efficiencies, and eventually, the overall treatment cost, must be performed than in the publications shown in this review. Furthermore, competition for the chemical oxidant by the contaminants and multiple substrate kinetics for biological mixed cultures must be studied.

Finally, it should also be taken into account that effluents from chemical pre-treatments will include many solutes with different biodegradabilities. Studies to date have modeled biological kinetics but have not considered multiple substrates. Neither have models been extended to circumstances where a fraction of the compounds present at high concentrations may inhibit biodegradation. Only a few studies have used kinetic or mechanistic models to represent substrate degradation, with the majority of the biological studies relying on general parameters.

In addition to the experimental and modeling work, the aspect most lacking in combined AOPs/biological systems for the treatment of hardly biodegradable specific industrial wastewater is the performance of complete economic studies which could present this innovative technology as a cost-competitive one.

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