ADVANCED OXIDATION PROCESSES FOR FOOD INDUSTRIAL WASTEWATER DECONTAMINATION

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ABSTRACT

High organic matter content is a basic problem in food industry wastewaters. Typically, the amount and composition of the effluent varies considerably. In the article four groups of advanced processes and their combination of food industry wastewater treatment have been reviewed: electrochemical oxidation (EC), Fenton's process, ozonation of water and photocatalytic processes. All advanced oxidation processes (AOP`s) are characterized by a common chemical feature: the capability of exploiting high reactivity of HO• radicals in driving oxidation processes which are suitable for achieving decolonization and odour reduction, and the complete mineralization or increase of bioavailability of recalcitrant organic pollutants.

Keywords: advanced oxidation process, wastewater, food industry.

INTRODUCTION

Industrial wastewater characteristics vary not only between the industries that generate them, but also within each industry. These characteristics are also much more diverse than domestic wastewater, which is usually qualitatively and quantitatively similar in its composition. On the contrary, industry produces large quantities of highly polluted wastewater containing toxic substances, organic and inorganic compounds such as: heavy metals, pesticides, phenols and derivatives thereof, aromatic and aliphatic hydrocarbons, halogenated compounds, etc., which are generally resistant to destruction by biological treatment methods [Meriç et al. 2005, Shu 2006, Ledakowicz et al. 2001, Gogate & Pandit 2004].

Compared to other industrial sectors, food industry requires great amounts of water, since it is used throughout most of plant operations, such as production, cleaning, sanitizing, cooling and materials transport, among others [Mavrov & Be1ieres 2000, Cicek 2003, Álvarez et al. 2011].

As a result, meat, poultry, dairy, olive mill etc. processing plants are the facilities producing "difficult" wastewater with large total load of organic pollutants like proteins or fats and chemicals used for cleaning and sanitizing processing equipment [Álvarez et al. 2011, Zhukova et al. 2011].

The wastewater streams with different levels of pollution load (low, medium and high contamination) are collected and treated in an on-site installation or in a municipal sewage treatment plant. Increasing food production will increase the volume of sewage and the cost of disposal for food processing plants and present difficult challenges for municipal wastewater treatment plant operators [Mavrov & Be1ieres 2000, Cicek 2003]. Currently, in accordance with the legislation of the European Union introduced more stringent controls and rules concerning pollution of industrial wastewater [Marcucci et al. 2002, Mason 2000]. Due to the adverse impact of even small quantities of these compounds on the organoleptic characteristics of the discharge of waste waters such as colour, odour, taste, etc., as well as a threat to living organisms began to

look for effective, efficient and economically viable methods to remove them.

In order to achieve these aims the potential and promising methods need to include advanced oxidation methods (AOP's), which include the Fenton reaction, UV photolysis, sonication, ozonation, electrochemical oxidation, etc. These processes involve the generation of highly free radicals, mainly hydroxyl radical (HO·) via chemical, photochemical and photocatalytic reactions. Their application is unavoidable for the treatment of refractory organic pollutants. Numerous researches have evaluated on the treatment of refractory compounds by different AOP`s [Ledakowicz et al. 2001, Oller et al. 2011, Tarek et al. 2011, Pera-Titus et al. 2004].

The application of AOP`s in wastewater treatment leads to the degradation of the pollutant rather than transferring it to another phase, making the relevant technologies effective in the removal of organic pollutants in solution. In recent years, one of the main objectives of these processes mainly with highly polluted effluents has been not to mineralise the pollutant totally (AOP`s for complete mineralization are very expensive), but to improve the biodegradability for a possible coupling of the AOP`s with a conventional biological treatment process [Sanz et al. 2003, Muñoz et al. 2005].

PROCESSES FOR FOOD INDUSTRY WASTEWATER TREATMENT

The AOP`s has been used to reduce the organic load or toxicity of wastewaters from different industries. They are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential (Table 1). The generation of hydroxyl radicals involves the combination of classical oxidants, such as H_2O_2 or O_3 with UV radiation or a catalyst. The formed radicals react with organic materials breaking them down gradually in a stepwise process. The generation of hydroxyl radicals can be achieved by a variety of reactions, such as O_3/UV, H_2O_2/UV, Fenton reaction, photo-Fenton, TiO_2/ H_2O_2/UV etc. Such integrated solutions can lead to more efficient use of chemical oxidants while reducing the effect of toxic or inhibitory compounds in bioreactors, leading to more robust and stable biological treatment [Gogate & Pandit 2004, Pera-Titus et al. 2004, Turhan & Turgut 2009].

Table 1. Oxidizing potential for several chemical oxidizers [Pera-Titus et al. 2004, Turhan & Turgut 2009]

Oxidant	Electrochemical oxidation potential [V]
Fluorine (F_2)	3.03
Hydroxyl radical (HO·)	2.80
Atomic oxygen	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Hypobromous acid ($H_{br}O$)	1.59
Chlorine dioxide (ClO_2)	1.50
Chlorine (Cl_2)	1.36
Oxygen (molecular)	1.23
Bromine (Br_2)	1.09

Elektrochemical oxidation

It was observed that electrochemical oxidation (EC) has the potential to be a distinct economic and environmental choice for treatment of wastewater and due to strict environmental regulations [Kobya & Delipinar 2008, Gengec et al. 2012]. EC involves the formation of hydroxyl radicals at the active sites of anode and has been used for the decontamination of various inorganic and organic pollutants [Rizzo 2011]. One of the major advantages of electrochemistry is that on the surface of the electrodes only electrons are produced and consumed, thereby "pure reagents" and do not contribute to a further increase in the number of chemical compounds in the environment, which often takes place in other processes [Zaleska & Grabowska 2008]. Moreover, advantages of the EC compared to conventional chemical coagulation include reduced wastewater acidification and salinity, low dosage of coagulant, superior coagulant dispersion and intrinsic electroflotation separation capability [Gengec et al. 2012].

The efficiency of electrochemical process depends on electrode and supporting electrolyte types, applied current, solution pH, nature of target contaminant/water matrix and initial concentration of the pollutants [Rizzo 2011]. In the EC process different anodes have been investigated: graphite, Pt, TiO_2, IrO_2, PbO_2, several Ti-based alloys and boron-doped diamond electrodes but the most generally employed as a electrode material is iron (Fe) or aluminium (Al) [Gengec et al. 2012, Rizzo 2011].

Generally, six main processes occur during EC: (1) migration to an oppositely charged electrode (electrophoresis) and aggregation due to

charge neutralization; (2) the cation or hydroxyl ion (OH) forms a precipitate with the pollutant; (3) the metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation); (4) the hydroxides form larger lattice-like structures and sweeps through the water (sweep coagulation); (5) oxidation of pollutants to less toxic species; (6) removal by electroflotation or sedimentation and adhesion to bubbles [Kobya & Delipinar 2008, Roa-Morales et al. 2007].

Details of some food industry wastewater studies with EC performed in recent years are provided in Table 2. EC has been proved to be an efficient method for the treatment of food process wastewater such as distillery and fermentation wastewater [Kannan et al. 2006], yeast wastewater [Kobya & Delipinar 2008], potato chips manufacturing wastewater [Kobya et al. 2006], restaurant wastewater [Chen et al. 2000], egg process wastewater [Xu et al. 2002], oily wastewater [Calvo et al. 2003], poultry slaughterhouse wastewater [Bayramoglu et al. 2006] and olive oil wastewater [Rodrigo et al. 2010].

Fenton process

Many AOPs use hydrogen peroxide as the main oxidizing agent, which is a more efficient reagent than gaseous oxygen concerning the contaminants mineralization. Fenton's process has its origin in the discovery reported in 1894 that ferrous ion strongly promotes the oxidation of tartaric acid by hydrogen peroxide. However, only much later the oxidation activity has been ascribed to the hydroxyl radical [Herney-Ramirez et al. 2010].

Oxidation with Fenton's reagent is accomplished with a mixture of ferrous ions and hydrogen peroxide, and it takes advantage of the reactivity of the free hydroxyl radicals produced in acidic solution by the catalytic decomposition of hydrogen peroxide and of the coagulation produced by the ferric hydroxide precipitates [Gogate

**Table 2.** A brief summary of research studies in which EC were used for treating food industry wastewater

Biological and chemical treatment	Target wastewater	Concluding remarks	References
Aluminium electrocoagulation /H_2O_2	Pasta and cookie processing industrial wastewater	Under optimal conditions of pH 4 and 18.2 mA/m² current density, Treatment reduced chemical oxygen demand (COD) by 90%, biochemical oxygen demand (BOD_5) by 96%, total solids by 95% and fecal coliforms by 99.9%.	[Roa-Morales et al. 2007]
Electrocoagulation (electrode material Fe and Al)	Cattle-slaughterhouse wastewater	In the case of aluminium electrode, polyaluminum chloride (PAC) was used as the coagulant aid for the aforesaid purpose. COD removal of 94.4% was obtained by adding 0.75 g L/PAC. In the case of iron electrode, EC was conducted concurrent with the Fenton process. As a result, 81.1% COD removal was achieved by adding 9% H_2O_2.	[Ün et al. 2009]
Anaerobic electrocoagulation (AE) and (AAE) anaerobic-aerobic electrocoagulation	Baker's yeast wastewater	The maximum color, COD and TOC were 88%, 48% and 49% at 80 A/m², pH 4 and 30 min for AE and 86%, 49% and 43% at 12.5 A/m², pH 5 and 30 min for AAE, respectively.	[Gengec et al. 2012]
Conductive-diamond electrochemical oxidation	Synthetic melanoidins	The electrolysis was carried out the in lack of additional electrolyte (except for carbonates) and in the presence of NaCl (ranging from 17.5 to 85 mM). As it can be observed, the electrolysis without addition of NaCl (it remains around 20% of initial COD) while electrolyses with NaCl electrolyte obtain the complete removal of COD.	[Canizares et al. 2009]
Electrocoagulation (electrode material Fe and Al)	Baker's yeast wastewater	The maximum removal efficiencies of COD, TOC and turbidity under optimal operating conditions, i.e., pH 6.5 for (Al) and pH 7 for (Fe), current density of 70 A/m² and operating time of 50 min were 71, 53 and 90% for (Al) and 69, 52 and 56% for (Fe), respectively.	[Kobya & Delipinar 2008]
Aluminium electrocoagulation	Moroccan olive mill wastewater	Electrolysis time 15 min, NaCl concentration 2 g/L, initial pH 4.2 and current density 250 A/m²,the discoloration of the effluent, the reduction of the COD and the reduction of polyphenols exceeded 70%, the electrodes consumption was 0.085 kg Al/kg $COD_{removed}$.	[Hanafi et al. 2010]
Electrochemical oxidation (boron-doped diamond (BDD) as anode)	Sinapinic acid (representative polyphenolic type compounds present in olive oil mill wastewater)	Under optimal experimental conditions of flow rates (i.e. 300 L/h), temperature (T=50 °C) and current density (i.e. 10 mA/cm²), 97% of COD was removed in 3h electrolysis, with 17 kWh/m³energy consumption.	[Elaoud et al. 2011]

& Pandit 2004, Pera-Titus et al. 2004, Canizares et al. 2009].

The mechanism of the Fenton's process is quite complex, and some papers can be found in the literature where tens of equations are used for its description (Eq. 1) [Mert et al. 2010].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$
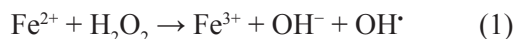
As iron(II) acts as a catalyst, it has to be regenerated, which seems to occur through the following scheme [Pérez et al. 2002, Rivas et al. 2003]:

$$Fe^3 + H_2O_2 \rightarrow Fe^{2+} + HO^{2\bullet} + H^+ \qquad (2)$$

$$Fe^3 + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad (3)$$
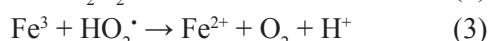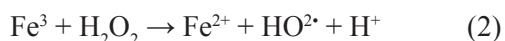
The photo-Fenton process, as its name suggests, is rather similar to the Fenton one, but employing also radiation [Tokumura et al. 2006].

$$Fe(OH)_2^+ + h\upsilon \rightarrow Fe^{2+} + HO^\bullet \qquad (4)$$
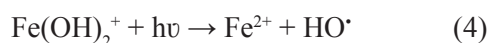
Its effectiveness is attributed to the photolysis of Fe(III) cations in acidic media yielding Fe(II) cations (Eq. 4). In this process, the regeneration of Fe^{2+} by photo-reduction of Fe^{3+} is accelerated, this photo-reduction being an additional source of highly oxidative hydroxyl radicals, as compared with the "simple" Fenton's process [Herney-Ramirez et al. 2010, Stasinakis 2008].

The major parameters affecting Fenton process are solution's pH, amount of ferrous ions, concentration of H_2O_2, initial concentration of the pollutant and presence of other ions [Mert et al. 2010, Stasinakis 2008, de Sena et al. 2009].

The main advantage of the process is degradation organic as well as inorganic pollutants that will leading to high mineralization levels [Sanz et al. 2003, Canizares et al. 2009, Stasinakis 2008, de Sena et al. 2009, Martins et al. 2011]. Among the advanced oxidation processes, the easy-to-handle Fenton's reaction has proven to be more effective in terms of removal rate as well as operating expenses for the treatment of toxic and/or refractory food industrial wastewater (Table 3) such as baker's yeast industry effluents [Altinbas 2003], juice wastewater [Amora et al. 2012], meat industry wastewater [de Sena et al. 2009], coffee effluent [Tokumura et al. 2008], winery and distillery wastewater [Oller et al. 2011], olive mill wastewater [Zorpas & Costa 2010] etc.

Table 3. A brief summary of research studies in which Fenton process were used for treating food industry wastewater

Biological and chemical treatment	Target wastewater	Concluding remarks	References
Fenton's oxidation	Baker's yeast industry effluents	The best dosage was 1200 mg/L Fe^{2+}/800 mg/L H_2O_2 at pH 4 and in reaction time of 20 min for mineralization of DOC and COD. For these conditions, The maximum color, DOC and COD were 99%, 90% and 88%.	[Pala & Erden 2005]
Photo-Fenton oxidation	Synthetic apple-juice wastewater	At the selected operation conditions (5800 ppm H_2O_2,40 ppm Fe^{2+}, pH 4.2 and 26 °C), 91% mineralization was achieved in 40 min when treating a synthetic wastewater with 700 ppm of the total organic carbon (TOC).	[Durán et al. 2011]
Fenton's oxidation	Livestock wastewater	The optimum ratio of H_2O_2 (mg/L) to the initial COD_{cr} was 1.05. The optimum initial pH were 3.5–4, H_2O_2/ Fe^{2+} was 2 and the optimum reaction time 30 min. The removal ratios of COD_{cr} and color of the supernatant after static precipitation of the produced sludge were 88 and 95.4%, respectively.	[Lee & Shoda 2003]
Photo-Fenton oxidation	Coffee effluent	The results suggest that the $UV/H_2O_2/ Fe^{2+}$ system is very efficient for the treatment of coffee effluents. The mineralization of 250 mg/L model coffee effluent was not complete but about 90% mineralization was found after 200 min of UV irradiation.	[Tokumura et al. 2006]
Solar photo-Fenton oxidation	Winery wastewaters	Under optimal conditions, 61% TOC was achieved in 360 min. Temperature and initial concentrations of H_2O_2 and oxalic acid were the most significant factors affecting the wastewater mineralization. The addition of H_2O_2 can be used to control the mineralization degree of this type of wastewater.	[Monteagudo et al. 2012]
Fenton's oxidation	Synthetic melanoidins	These high concentrations of refractory carbonis is not able to achieve the complete mineralization of the waste, and a high TOC remains at the end of the treatment (>40%).	[Canizares et al. 2009]
Fenton, Fenton-like process	Olive oil mill wastewater	Processes showed high COD (>80%) and total-phenol (>85%) removal performance on evaluated effluents	[Mert et al. 2010]
Electro-Fenton	Olive mill wastewater	Considered as a pre-treatment (COD removal 53%) before anaerobic digestion and ultrafiltration resulting in a complete detoxify of effluent.	[Khoufi et al. 2009]

Ozonation

Ozonation of water is a well-known technology and the strong oxidative properties of O_3 and its ability to effectively oxidize many organic compounds in aqueous solution have been well documented. Unlike other oxidizing agents such as Cl_2, oxidation with O_3 leaves no toxic residues that have to be removed or disposed [Sarayu et al. 2007, Ulson de Souza et al. 2010]. Ozonation is one of the AOP processes used to food wastewater treatment, which is versatile and environmentally sound [Sarayu et al. 2007]. Although, the cost of ozone production still is high interest in the use of ozone in wastewater treatment has increased considerably in last few years due to the numerous advantages of this process [Meriç et al. 2005, Ulson de Souza et al. 2010]. Ozonation can eliminate toxic substances, increase the biodegradability of organic pollutants and has high potential in decolourization [Zayas et al. 2007].

Ozone is very reactive towards compounds incorporating conjugated double bonds (such as C=C, C=N, N=N), often associated with colour [Gogate & Pandit 2004, Rizzo 2011, Coca et al. 2007]. Ozone can react with solutes either by direct oxidation between organic contaminants and molecular ozone (Eq. 5) or by indirect reactions with hydroxyl radicals resulting from ozone decomposition (Eq. 6, 7) [Meriç et al. 2005, Rizzo 2011, Coca et al. 2007].

$$O_3 + R \rightarrow RO + O_2 \qquad (5)$$

$$O_3 \leftrightarrow O + O_2 \qquad (6)$$

$$O + H_2O \rightarrow 2\ HO^\bullet \qquad (7)$$
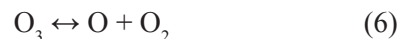
This arises from the fact that pH affects the double action of ozone on the organic matter which may be a direct or an indirect (free radical) oxidation pathway. At low pH, ozone exclusively reacts with compounds with specific functional groups through selective reactions, such as electrophilic, nucleophilic or dipolar addition reactions (i.e. direct pathway). At basic pH, ozone decomposes yielding hydroxyl radicals, a highly oxidizing species which reacts nonselectively with a wide range of organic and inorganic com-

Table 4. A brief summary of research studies in which ozonation were used for treating food industry wastewater

Biological and chemical treatment	Target wastewater	Concluding remarks	References
Ozonation and aerobic biological degradation	Table olive wastewater	In this combined process, the ozonation of the biologically pretreated table black-olive wastewater yielded a conversion of 62%, considerably higher than the 52% attained in the ozonation process.	[Beltran-Heredia et al. 2000]
Ozonation	Six phenolic acids typically found in olive mill wastewater	(O_3 production was varied 10 g/L, flow rate was 30 l/h). Process were effective in degradation of phenolic compounds 91%. The COD abatement (42%) proves that ozonation pathways at those conditions are mainly through partial oxidation rather than directly to end products (CO_2, H_2O).	[Martins & Quinta-Ferreira 2011]
Ozonation	Red-meat-processing wastewater	The decrease in COD and BOD of the wastewater were 10.7% and 23.6%, respectively, decolorization of the wastewater after ozonation.	[Wu & Doan 2005]
Ozonation	Olive mill wastewater	The ozonation of OMW carried out at three different times (60, 90 and 120 min) The highest efficiencies were achieved at 120 min). Polyphenols and COD reductions were about 82,4% and 59,8%.	[Andreozzi et al. 2008]
Ozonation	Winery wastewaters	The ozone dose rate 0.68 g/h/L, pH 4. Ozonation reduced the initial COD by 12% At pH 4, ozone does not decompose to more reactive radical species, therefore the COD removal was limited.	[Lucas et al. 2010]
Ozonation with conventional aerobic oxidation	Distillery wastewater	Ozone was found to be effective in bringing down the COD (up to 27%) during the pretreatment step itself. The integrated process achieved ~79% COD reduction along with decoloration of the effluent sample as compared to 34.9% COD reduction for non-ozonated sample, over a similar treatment period.	[Sangave et al. 2007]
Ozonation	Synthetic melanoidins	As it can be observed, it achieves very significant removals of COD and TOC (>80% and >70%, respectively) and the almost complete disappearance of the color (ozone production: 1 g/h, 25°C, pH 12, time change)	[Canizares et al. 2006]
Ozonation	Molasses fermentation wastewater	The highest efficiencies were achieved at 40 °C (the ozone dose rate constants = 2.3 g/h/L). Color and COD reductions were about 90% and 37%, respectively. In no case, the percentage of TOC removed was higher than 10–15%.	[Coca et al. 2005]

pounds in water (i.e., indirect ozonation pathway) [Meriç et al. 2005, Pera-Titus et al. 2004, Turhan & Turgut 2009].

Ozone has many properties desirable for the treatment of the wastewater [Gogate & Pandit 2004, Rizzo 2011]:
- no sludge remains,
- danger is minimal,
- decolorization and degradation occur in one step,
- it is easily performed,
- little space is required,
- all residual ozone can be easily decomposed to oxygen and water.

Ozonation has been successfully applied to the treatment of winery and distillery wastewater [Zaleska & Grabowska 2008], olive mile wastewater [Oller et al. 2011], meat industry wastewater [Millamena 1992], molasses wastewater [Coca et al. 2007] etc.
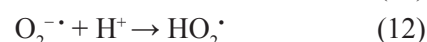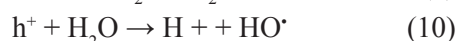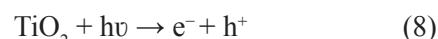
Photocatalytic process

The photocatalytic or photochemical degradation processes are gaining importance in the area of wastewater treatment, since these processes result in complete mineralization with operation at mild conditions of temperature and pressure [Tarek et al. 2011, Ugurlu & Karaoglu 2011]. In the process, semiconductor material is excited by electromagnetic radiation possessing energy of sufficient magnitude, to produce conduction band electrons and valence band holes [Gogate & Pandit 2004, Stasinakis 2008, Żmudziński 2010].

The selection of the adequate catalyst must consider the following properties: chemical activity, stability, availability and handiness, cost and lack of toxicity [Navarro et al. 2005]. The surface area and the number of active sites offered by the catalyst (thus nature of catalyst, i.e. crystalline or amorphous is important) for the adsorption of pollutants plays an important role in deciding [Gogate & Pandit 2004]. Several catalytic materials have been studied in photocatalysis (various oxides such as TiO_2, ZnO, SnO_2, WO_3, ZrO_2, CeO etc. or sulfides such as CdS, ZnS etc.) [Gogate & Pandit 2004, Sakthivel et al. 2003, Habibi et al. 2001]. Among the semiconductors reported so far, outstanding stability and oxidative power makes TiO_2 the best semiconductor photocatalyst for environmental remediation and energy conversion processes [Gogate & Pandit 2004, Ugurlu & Karaoglu 2011, Navarro et al. 2005, Chatzi-

symeon et al. 2008, Banu et al. 2008]. However, there are two potential drawbacks associated with the use of TiO_2, namely: (a) its possible toxic effects on human health and (b) reduced activity due to the complexity of water matrix (i.e., presence of solids or inorganic ions) [Chatzisymeon et al. 2008].

TiO_2 in its anatase form has an energy bandgap of 3.2 eV and can be activated by UV radiation with a wavelength up to 387.5 nm. It only requires 1 W/m^2 of light [Navarro et al. 2005, Navgire 2012]. Photocatalytic degradation occurs through a multistep process that involves the formation of reactive species on the surface of the photocatalyst and the subsequent generation of hydroxyl radicals that result in the mineralization of most organic compounds [Navarro et al. 2005, Chatzisymeon et al. 2008, Banu et al. 2008, Navgire et al. 2012]. The photocatalysis can be explained by the following simplified reaction (with TiO_2) [Stasinakis 2008, Navarro et al. 2005]:

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \qquad (8)$$

$$e^- + O_2 \rightarrow O_2^{-\bullet} \qquad (9)$$

$$h^+ + H_2O \rightarrow H + + HO^\bullet \qquad (10)$$

$$h^+ + OH^- \rightarrow HO^\bullet \qquad (11)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \qquad (12)$$

The UV radiation required for the photocatalytic processes can be obtained from artificial sources or the sun. There is a significant economic incentive for solar light based photocatalytic degradations [Banu et al. 2008].

The major factors affecting TiO_2/UV light process are: initial organic load, amount of catalyst, reactor's design, UV irradiation time, temperature, solution's pH, light intensity and the presence of ionic species. The use of excessive amounts of catalyst may reduce the amount of energy being transferred into the medium due to the opacity offered by the catalyst particles [Stasinakis 2008]. Organic compounds can then undergo both oxidative degradation through their reactions with valence band holes, hydroxyl and peroxide radicals and reductive cleavage through their reactions with electrons yielding various by-products and eventually mineral end-products [Gogate & Pandit 2004, Ugurlu & Karaoglu 2011, Chatzisymeon et al. 2008]. In several studies, photocatalytic process has been used to the treatment of winery and distillery wastewater [Lucas et al. 2009], olive mile wastewater [Chatzisymeon et al. 2008], dairy industry wastewater [Banu et al. 2008], molasses wastewater [Satyawali &

Table 5. A brief summary of research studies in which photocatalytic process were used for treating food industry wastewater

Biological and chemical treatment	Target wastewater	Concluding remarks	References
UV/H_2O_2/TiO_2/Sep	Olive mill wastewater	Optimum values of catalyst dose, temperature and H_2O_2 were found to be 318 K and 0.25 and 0.50 g/L, 30 ml/L H_2O_2, respectively. The degradation of lignin and phenol was favourable at pH 9–11.0 and natural sunlight. All pollutants could be removed under 24 h in 80–100% rates.	[Ugurlu & Karaoglu 2011]
Calcined $InYO_3$	Molasses fermentation wastewater	Specifically, $InYO_3$ calcined at 700 °C had a considerably larger surface area and lower reflectance intensity and showed higher photocatalytic activity. After 150-min reaction, the decolorization and COD removal were 98.23% and 92.98%, respectively.	[Qin et al. 2011]
Vacuum ultraviolet/TiO_2	Oily wastewater from the restaurant	Under the optimum conditions of irradiation 10 min, initial COD 3981 mg/L, TiO_2 150 mg/L, pH 7.0 and flow rate of air 40 L/h, the process TiO_2/VUV achieved removal efficiencies of COD, BOD_5 and oil about 63%, 43%, 70%.	[Kang et al. 2011]
TiO_2/H_2O_2	Black table olive processing wastewater	TiO_2 and H_2O_2 concentrations in the range 0.25–2 g/L and 0.025–0.15 g/L. Depending on the conditions employed, nearly complete decoloration (>90%) could be achieved, while mineralization never exceeded 50%.	[Chatzisymeon et al. 2008]
TiO_2/H_2O_2	Winery wastewater	The maximum COD removal were achieved at zero catalyst loading with COD removal of about 84%. Lower rates of chemical reaction in photocatalysis compared to photolysis were possibly because of the shielding of UV light by titania particles.	[Agustina et al. 2008]
TiO_2/H_2O_2, TiO_2/Fe-clays	Winery wastewater	The TiO_2/H_2O_2 treatment produces the highest efficiency, reaching to 52–58% of COD. The optimum dosage is: 2.5 mL/L H_2O_2 and 1.0 g/L TiO_2. Secondly, although the H_2O_2/clays system produces lower COD removal 34–45%, it requires a H_2O_2 dosage between three and six times lower than the TiO_2/H_2O_2 treatment.	[Navarro et al. 2005]
TiO_2/UV	Fresh-Cut Vegetable Industry wastewater	Photocatalysis was an effective disinfection method, reducing counts of bacteria, molds, and yeasts. Most of the treated wash waters had total bacteria reductions of 4.1±1.3 to 4.8±0.4 log CFU/ml after 10 min of treatment when compared with untreated water. That implementation of TiO_2/UV in the wash waters could allow the reuse of wash water.	[[Selma et al. 2008]
MoO_3/TiO_2/UV	Molasses wastewater	The color of the molasses solution decreases to around 70%, The maximum decreases in COD, BOD, and TDS about 90%, 90%, 50%, respectively. This system rate increases with an increase in temperature from 40 to 80 °C.	[Navgire et al. 2012]

Balakrishnan 2008], candy and sugar industry wastewater [Żmudziński 2010], fresh-cut vegetable industry wastewater [Selma et al. 2007] etc. Several applications are presented below (Table 5).

THE COMBINATION OF AOP`S FOR WASTEWATER TREATMENT

Differently combined AOP's have been developed and investigated by several research groups as alternatives for treating food industrial wastewater containing organic pollutants. This may commonly cause a reduction of toxicity or elimination of a specific pollutant or reduce the reaction time and economic cost [Oller et al. 2011, Stasinakis 2008, de Sena et al. 2009, Zayas et al. 2007].

Determining the target is an essential step in combination studies since it helps define process efficiency and provides a basis for comparing different operating conditions and optimizing the process [Oller et al. 2011, Stasinakis 2008].

CONCLUSION

Food industry uses large amounts of water for many different purposes including cooling and cleaning, as a raw material, as sanitary water for food processing, for transportation, cooking and dissolving, as auxiliary water etc. In principle, the water used in the food industry may be used as process and cooling water or boiler feed water. As a consequence of diverse consumption, the amount and composition of

Table 6. A brief summary of research studies in which combining various AOP's were used for treating food industry wastewater

Biological and chemical treatment	Target wastewater	Concluding remarks	References
Diamond electrochemical oxidation Fenton-ozonation	Synthetic melanoidins solution	Operation conditions – CDEO: natural pH; T: 25 °C; j: 300 A·cm^{-2}. Ozone production: 1 g/h, T: 25 °C; pH 12. Fenton process: pH 3; T: 25°C; Fe^{2+}: 667 mg/dm^{-3}. Complete mineralization of the waste is obtained and no refractory compounds remain at the end of the process in both cases.	[Canizares et al. 2009]
sonication/ anaerobic fermentation	Cassava wastewater	Hydrogen yield for cassava wastewater pretreated at pH 7.0 with sonication for 45 min using anaerobic seed sludge was 0.913 mol H_2/g COD. In wastewater COD removal was 40%.	[Leaño et al. 2012]
UD,ozonation	Thermally pretreated distillery wastewater	The study clearly shows the suitability of ozone and ultrasound as a pre-treatment step for the thermally pretreated wastewater for aerobic treatment by increasing the COD removal efficiency. Ozone was more efficient in COD removal with a 25-times increase in the rate of biodegradation of ozonated sample along with discoloration of the effluent sample.	[Sangave et al. 2007]
UV/H_2O_2/O_3	Coffee wastewater	The UV/H_2O_2/O_3 process is capable of reducing the COD content of the wastewater by 87% in 35 min at pH 2.0. By comparison, the UV/H_2O_2 and UV/O_3 treatments under the same conditions reduced the COD by approximately 84%.	[Zayas et al. 2007]
UV/H_2O_2/O_3	Winery wastewater	The COD removal efficiency is slightly higher at pH10 (57%), than pH4 (49%) and pH7 (40%) after 300 min.	[Lucas et al. 2010]
Dissolved air flotation (DAF) with UV/H_2O_2 or photo-Fenton	Meat industry wastewater	DAF/UV/H_2O_2 results for BOD$_5$ and COD reduction was 82.9% and 91.1% respectively. For TS and VS, reductions of up to 72.5% and 77.0% were achieved, respectively. DAF/photo-Fenton results for BOD$_5$ and COD reduction was 95.7% and 97.6\% respectively. For TS and VS, reductions of up to 61.5% and 90.8% were achieved, respectively.	[de Sena et al. 2009]
UV/H_2O_2	Synthetic melanoidin	The oxidation process was much more capable of removing color 99%, dissolved organic carbon (DOC) 50% and dissolved organic nitrogen (DON) 25% at the optimal applied dose of H_2O_2 for the system (3.3 g/L)	[Dwyer et al. 2008]
UV/O_3	Olive mill wastewater	In particular, biodegradation of UV/O_3 pretreated OMW found to have the highest removal levels; the percent of COD removal reaches about 91%.	[Lafi et al. 2009]
Modified photo-Fenton /ozonation	Olive mill wastewater	For Fe(III)/air/solar light and ozonation the highest efficiencies Polyphenols and COD reductions were about 87.9% and 64.9%.	[Andreozzi et al. 2008]

food industry wastewaters varies considerably. Characteristics of the effluent consist of large amounts of suspended solids, nitrogen in several chemical forms, fats and oils, phosphorus, chlorides and organic matter.

AOP's constitute a promising technology for the treatment of food industry wastewaters containing difficult to biodegradable organic contaminants. It involves the generation of free hydroxyl radical (HO$^•$), a powerful, nonselective chemical oxidant to change organic compounds to a more biodegradable form or of carbon dioxide and water. These processes can reduce a broad spectrum of chemical and biological contaminants which are otherwise difficult to remove with conventional treatment processes of food industry wastewater.

Acknowledgments

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