Advanced Oxidation Processes in Food Industry Wastewater Treatment – A Review

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1. Introduction

The 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 (EC, 2006). In 2008, for example, the total industrial water consumption in Finland was 7600 million m$^3$ of which 34.5 million m$^3$ was used by the food processing industry (Finnish Food and Drink Industries’ Federation, 2010).

As a consequence of diverse consumption, the amount and composition of 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 (Finnish Food and Drink Industries’ Federation, 2005). Generally, the BOD (biochemical oxygen demand) and COD (chemical oxygen demand) of food industry wastewater is 10 or even 100 times higher than those of domestic wastewater (EC, 2006). Unpleasant odours are also a typical problem in food industry wastewaters. These odours are usually the result of gases (hydrogen sulphide, indole) produced by the anaerobic decomposition of organic matter (Metcalf & Eddy, 2003).

2. Characteristics of food industry wastewaters

Considering the legislation of wastewater purification, total suspended solids (TSS), organic matter, total nitrogen ($N_{tot}$) and phosphorus ($P_{tot}$) must be removed from both municipal and industrial wastewaters before being released into the watercourse (Metcalf & Eddy, 2003). In 2008 in Finland, the amount of food processing industry wastewater was 4.1 million m$^3$ and the total amount of industrial wastewaters was 1130 million m$^3$ (Table 1) (Finnish Environment Institute, 2009).

In 2008, the amount of total suspended solids was 83 tonnes, $P_{tot}$ 4 tonnes, $N_{tot}$ 87 tonnes whilst the proportion of food industry wastewater of the total industry wastewaters was around 0.4 %. However, the volume of organic matter in food industry wastewater was notable: 0.024 kg m$^{-3}$ when for example, compared to BOD7 in the pulp and paper industry (0.015 kg m$^{-3}$) (Finnish Environment Institute, 2009).
<table>
<thead>
<tr>
<th>Industry</th>
<th>1000 m³ Wastewater</th>
<th>TSS</th>
<th>P_{tot}</th>
<th>N_{tot}</th>
<th>BOD₇</th>
<th>COD_{Cr}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp and paper industry</td>
<td>677058</td>
<td>14787</td>
<td>161</td>
<td>2347</td>
<td>10148</td>
<td>160813</td>
</tr>
<tr>
<td>Metal industry</td>
<td>208613</td>
<td>493</td>
<td>2</td>
<td>224</td>
<td>4</td>
<td>70</td>
</tr>
<tr>
<td>Chemical industry</td>
<td>115192</td>
<td>1193</td>
<td>14</td>
<td>435</td>
<td>217</td>
<td>2174</td>
</tr>
<tr>
<td>Mining and quarry industry</td>
<td>20449</td>
<td>431</td>
<td>1</td>
<td>69</td>
<td>7</td>
<td>686</td>
</tr>
<tr>
<td>Food industry</td>
<td>4067</td>
<td>83</td>
<td>4</td>
<td>87</td>
<td>99</td>
<td>290</td>
</tr>
<tr>
<td>Others</td>
<td>104981</td>
<td>628</td>
<td>9</td>
<td>42</td>
<td>272</td>
<td>1819</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1130360</strong></td>
<td><strong>17615</strong></td>
<td><strong>191</strong></td>
<td><strong>3204</strong></td>
<td><strong>10747</strong></td>
<td><strong>165852</strong></td>
</tr>
</tbody>
</table>

Table 1. Industrial discharge into the watercourse in 2008 in Finland (Finnish Environment Institute, 2009).

2.1 Total suspended solids
The most important physical factor of wastewater is its total solid content which is comprised of floating, settleable and colloidal matter, and matter in a solution. In the characterisation of various solids in wastewater, samples can be classified in ten different fractions. The most important fraction of these is total suspended solids (TSS) which is one of the two universally used effluent standards (along with BOD) to follow the performance of wastewater treatment plants (Metcalf & Eddy, 2003). The TSS of wastewater is determined according to APHA standard 2540 D. “Total Suspended Solids Dried at 103-105 °C” (APHA, 1998).

The solid matter of food industry wastewater can also vary considerably. For example in the slaughterhouse and meat industry wastewaters, the solid matter is composed of hairs, feathers, bowels and piece of tissues (Hiisvirta, 1976) compared to potato and vegetable industry wastewaters whose suspended solids are soil, peels and other vegetable parts (Lehto et al., 2007). Typically, food industry wastewaters contain lots of floating suspended solids which have to be removed since releasing it directly to the watercourse increases sediment (Metcalf & Eddy, 2003).

2.2 Organic matter
Organic compounds consist mainly of carbon, hydrogen and oxygen. The organic matter in wastewaters is typically a mixture of proteins and carbohydrates as well as oils and fats. In the slaughterhouse and meat industry wastewaters, for example, the organic content is mainly composed of grease which can be solid, suspended or emulsified (Hiisvirta, 1976). The low solubility of fats and oils reduces the rate of their biological decomposition and in the wastewater treatment plant, fats can block up the treatment devices of wastewaters. If grease is not removed before the discharge of treated wastewater, it can interfere with the biological life in surface waters. Wastewater also contains urea and small quantities of very large number of simple and extremely complex synthetic organic molecules (Metcalf & Eddy, 2003).

There are a number of different analyses to determine the organic content of wastewater. The analyses can be divided into those used to measure aggregate organic matter content of wastewater and those analyses used to quantify individual organic compounds (APHA, 1998). Typically, only aggregate organic matter content is measured. Those are: biochemical...
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oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) (Metcalf & Eddy, 2003).

2.2.1 Biochemical oxygen demand
The most widely used parameter for the determination of organic matter in wastewater is BOD. In this method, the biodegradable organic matter of wastewater is measured. The biochemical oxygen demand is the amount of oxygen which organic matter (solid or dissolved) in the water is consumed when biodegradation occurs in biological oxygen containing states (SFS-EN 1899-1). There are numerous standards for the determination of BOD such as SFS-EN 1899-1 (SFS-EN 1899-1), APHA standard 5210 B (APHA, 1998) and OECD 301 F-guide (OECD, 1992). For wastewater samples, the standard measuring time is five days (BOD5) at 20 °C, but other lengths of time and temperatures can also be used. In Finland, for example, the typical measuring time is seven days (BOD7) (Karttunen, 2003).

Although there is a high content of organic matter in food industry wastewaters, the organic compounds, such as fats and proteins, are usually easily biodegradable. Furthermore, the large amount of micro-organisms, for example in the slaughterhouse and meat processing industry wastewaters, facilitates the decomposition of organic compounds (Hiisvirta, 1976). However, there are also some exceptions such as food industry wastewaters containing salts, disinfectants and cleaning agents (Finnish Food and Drink Industries’ Federation, 2005).

2.2.2 Chemical oxygen demand
Chemical oxygen demand describes the number of chemically oxidising organic compounds of wastewater (SFS 3020). The COD value can be determined according to APHA standard 5220 “Chemical oxygen demand (COD)”. For wastewaters, the oxidising agent is dichromate in an acid solution (APHA, 1998). The ratio of the BOD and COD can provide more information about the wastewater sample. Usually, for industrial wastewaters, COD is higher than BOD because many organic substances which are difficult to oxidise biologically can be oxidised chemically. If the COD value is much bigger than the BOD value, the organic compounds in wastewater are slowly biodegradable (Hiisvirta, 1976). In food industry wastewaters, the COD and BOD values are often closely matched to each other due to the easily biodegradable organic compounds of the effluent (Finnish Food and Drink Industries’ Federation, 2005).

2.2.3 Total organic carbon
Total organic carbon (TOC) describes the amount of organic compounds in wastewater and is used as a more convenient and direct expression of the total organic content than either BOD or COD. TOC analysis provides different information to BOD or COD because the unit of the TOC value is [mg C L–1] while measuring BOD and COD uses the unit of mg O2 L–1. TOC is also independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganic compounds that can contribute to the oxygen demand measured by BOD and COD (APHA, 1998). The analysing methods for TOC utilise heat and oxygen, UV radiation, chemical oxidants, or a combination of these to decompose the organic compounds of the sample to
carbon dioxide which is measured with an infrared analyser, conductivity or by some other method (Metcalf & Eddy, 2003). The inorganic carbon content of the wastewater sample can be many times greater than the TOC fraction. Therefore, the inorganic carbon (CO₂, carbonates) must first be eliminated by acidifying samples to pH 2 or less to convert inorganic carbon species to CO₂. Alternatively, the inorganic carbon interference may be compensated for by separately measuring total carbon (TC) and inorganic carbon (IC). The TOC can be calculated from the difference between TC and IC. There are different methods available for the determination of TOC such as APHA standard 5310 (APHA, 1998) and SFS-EN 1484 (SFS-EN 1484, 1997). Nowadays, the TOC analysis is more favourable since its measuring time is quite short (5 to 30 minutes) compared to BOD determination which takes several days before the results are known (Metcalf & Eddy, 2003). For food industry wastewaters, TOC measurement provides practical information about the water sample because the organic matter content is usually quite high.

2.3 Nitrogen

Nitrogen is an important nutrient for microbes and other biological organisms. The chemistry of nitrogen is complex, because of the existence of several oxidation states in the element. The most common and important forms of nitrogen in wastewater are ammonia (NH₃), ammonium (NH₄⁺), nitrogen gas (N₂), nitrite ion (NO₂⁻) and nitrate ion (NO₃⁻). Overall, total nitrogen N_{tot} in wastewater is composed of organic nitrogen, ammonia, nitrite and nitrate. Organic nitrogen is determined using the Kjeldahl method (APHA, 1998) where the aqueous sample is first boiled to remove any ammonia, and then wet combusted. During wet combustion, the organic nitrogen is converted to ammonium. In aqueous solution, ammonia nitrogen exists as either ammonia gas or ammonium ion, depending on the pH of the solution according to the equilibrium reaction:

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \] (1)

At pH 7, over 98% of the ammonia nitrogen is ammonium ion and when the pH is increased, the equilibrium is displaced to the left. Ammonia is determined by raising the pH, distilling off the ammonia with the steam produced during sample boiling, and condensing the steam which absorbs the gaseous ammonia. The measurement can be made colourimetrically, titrimetrically or with specific ion electrodes (APHA, 1998).

Nitrite nitrogen is determined colourimetrically (APHA, 1998). It is relatively unstable and is easily oxidised to the nitrate. The amount of nitrite in wastewaters is seldom above 1 mg L⁻¹. Although present in low concentration, it is important to determine the amount of nitrite because of its extreme toxicity to most fish and other aquatic species (Metcalf & Eddy, 2003). Nitrate nitrogen, which can also be determined colourimetrically (APHA, 1998), is the most oxidised form of nitrogen found in wastewaters. The typical range (as nitrogen) detected in wastewaters is from 15 to 20 mg L⁻¹ (Metcalf & Eddy, 2003).

Ammonium nitrogen, also found in wastewater, can oxidise microbiologically in to a nitrate form (nitrification) and consumes vital oxygen in water systems. The nitrification consumes a relative high amount of oxygen: 1 g ammonium nitrogen needs 4.3 g oxygen for the oxidation process, a reason why ammonium nitrogen has to be converted to nitrate and for the removal of total nitrogen from wastewaters before discharging in to the watercourse (Metcalf & Eddy, 2003).
In food industry wastewaters, the amount of nitrogen is typically bigger than the amount of phosphorus whilst the total nitrogen content can be even ten folds compared with municipal wastewater (Finnish Food and Drink Industries’ Federation, 2005). In slaughterhouse and meat industry wastewaters, for example the decomposition of proteins raises the amount of nitrogen in the effluent (Hiisvirta, 1976).

2.4 Phosphorus
Phosphorus is also an essential nutrient to the growth of biological organisms. Due to noxious algal blooms occurring in surface waters, domestic and industrial waste discharges may contain 1 – 2 mg L\(^{-1}\) of phosphorus (P) (Metcalf & Eddy, 2003). The usual forms of phosphorus found in aqueous solutions include orthophosphate (e.g. PO\(_4^{3-}\), HPO\(_4^{2-}\), H\(_2\)PO\(_4^{-}\), and H\(_3\)PO\(_4\)), condensed phosphates (pyro-, meta-, and other polyphosphates) and organic phosphate. Phosphorus analyses include the conversion of a phosphorus form to dissolved orthophosphate and the colourimetric determination of this dissolved orthophosphate. Orthophosphate can be determined directly by adding an ammonium molybdate (forming a coloured complex), while condensed and organic phosphates must first be converted to orthophosphates by digestion before being determined as an orthophosphate (APHA, 1998).

In food industry wastewaters, phosphorus occurs as an organic phosphate that originates from proteins and some detergents used by machine washing which may contain phosphorus. However, the nitrogen content of food industry wastewaters is more significant than phosphorus (Hiisvirta, 1976).

2.5 Odours
Unpleasant odours in food industry wastewater are usually caused by gases produced by anaerobic decomposition of organic matter. The most common odour causing compound is hydrogen sulphide whose characteristic odour is that of rotten eggs (Metcalf & Eddy, 2003).

Sulphur is required in the synthesis of proteins and is released in to the degradation process. Under anaerobic conditions, sulphate is reduced biologically to sulphide which can further combine with hydrogen forming hydrogen sulphide (H\(_2\)S). This gas is readily soluble in water, colourless and inflammable, but also toxic. Although hydrogen sulphide is the most common gas formed during the anaerobic decomposition of organic matter when considering odours, other volatile compounds, such as indole, skatole and mercaptans, may cause odours far more unpleasant than H\(_2\)S (Metcalf & Eddy, 2003).

In recent years, the control of odours has become more important in the designing and operating of wastewater collection, treatment and disposal plants. Odours are the foremost concern of the public in wastewater treatment processes. Quite often, the psychological stress causing by odours is far more important rather than the harm they do to the health of humans (Droste, 1997).

Unpleasant odours are detected by the olfactory system, but which the precise mechanism is not well known. One of the difficulties in developing a global theory has been the insufficient explanation of why compounds with different molecular structures may have similar odours. Nowadays, some agreement has been achieved that the odour of a molecule has to be related to the molecule as a whole. Malodorous compounds in untreated...
wastewater are listed in Table 2. All these compounds can be found or may be developing in wastewaters, depending on ambient conditions (Metcalf & Eddy, 2003).

<table>
<thead>
<tr>
<th>Odorous compound</th>
<th>Chemical formula</th>
<th>Odour quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amines</td>
<td>CH$_3$NH$_2$, (CH$_3$)$_3$NH</td>
<td>Fishy</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Diamines</td>
<td>NH$_2$(CH$_2$)$_4$NH$_2$</td>
<td>Dead body</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>H$_2$S</td>
<td>Rotten eggs</td>
</tr>
<tr>
<td>Mercaptans (1-2 carbon)</td>
<td>CH$_3$SH, CH$_3$(CH$_2$)SH</td>
<td>Decayed cabbage</td>
</tr>
<tr>
<td>Mercaptans (over 2 carbon)</td>
<td>(CH$_3$)$_3$CSH, CH$_3$(CH$_2$)$_3$SH</td>
<td>Skunk</td>
</tr>
<tr>
<td>Organic sulphides</td>
<td>(CH$_3$)$_2$S, (C$_6$H$_5$)$_2$S</td>
<td>Rotten cabbage</td>
</tr>
<tr>
<td>Skatole</td>
<td>C$_9$H$_9$N</td>
<td>Faecal matter</td>
</tr>
</tbody>
</table>

Table 2. Malodorous compounds in untreated wastewater (Metcalf & Eddy, 2003).

In the complete characterisation of odour, four independent factors can be classified: intensity, character, hedonics and detectability. Odours can be measured by sensory methods and a specific odorant concentration can be measure by instrumental methods, such as GC-MS analysis (Metcalf & Eddy, 2003). In the sensory method, a panel of human subjects is exposed to odour-free air diluted odours and the minimum detectable threshold odour concentration (MDTOC) is noted. This procedure can be performed according to the Standard Method 2150B Threshold Odour Test (APHA, 1998).

3. Advanced oxidation processes

When selecting the most suitable wastewater treatment method for the specific effluent, both the feasibility of the treatment as well as the economics of the process need to be considered. There are multiplicities of different kinds of techniques available such as physical, chemical and biological wastewater treatments and their combinations.

Advanced oxidation processes (AOPs) belong to the chemical treatment category and are used to oxidise organic compounds found in wastewater which are difficult to handle biologically into simpler end products. Advanced oxidation processes involve the generation of free hydroxyl radical (HO$^\cdot$), a powerful, non-selective chemical oxidant (Table 3) (Munter, 2001).

<table>
<thead>
<tr>
<th>Oxidising agent</th>
<th>Relative oxidation activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positively charged hole on titanium dioxide, TiO$_2^+$</td>
<td>2.35</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.05</td>
</tr>
<tr>
<td>Atomic oxygen</td>
<td>1.78</td>
</tr>
<tr>
<td>Ozone</td>
<td>1.52</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.31</td>
</tr>
<tr>
<td>Permanganate</td>
<td>1.24</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>1.10</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3. Relative oxidation activity of some oxidising agents (Munter, 2001).
Hydroxyl radical is one of the most active oxidising agents known. It acts very rapidly with most organic molecules with rate constants in the order of $10^8 - 10^{11}$ M$^{-1}$ s$^{-1}$ (Table 4) (Munter, 2001). Depending upon the nature of the organic species, generated hydroxyl radical can attack organic radicals by radical addition, hydrogen abstraction, electron transfer and radical combination.

**Radical addition.** Reaction of the hydroxyl radical and unsaturated or aliphatic organic compound produces organic radical which can further oxidise by oxygen or ferrous iron to form stable oxidised end products.

$$\text{R} + \text{HO}^- \rightarrow \text{ROH} \quad (2)$$

**Hydrogen abstraction.** Generated hydroxyl radical can be used to remove hydrogen from an organic compound forming an organic radical and initiating a chain reaction where the organic radical reacts with oxygen. This produces a peroxyl radical, which can react with another organic compound, and so on.

$$\text{R} + \text{HO} \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \quad (3)$$

**Electron transfer.** Electron transfer results in the formation of ions with a higher valence. Oxidation of a monoatomic negative ion will result in the formation of an atom or a free radical.

$$\text{R}^{n+} + \text{HO}^- \rightarrow \text{R}^{n-1} + \text{HO}^- \quad (4)$$

**Radical combination.** Two radicals form a stable product.

$$\text{HO}^\cdot + \text{HO}^- \rightarrow \text{H}_2\text{O}_2 \quad (5)$$

Generally, the reaction of hydroxyl radicals and organic compounds will produce water, carbon dioxide and salts (SES, 1994). However, the attack of the HO$^\cdot$ radical, in the presence of oxygen, generates a complex series of oxidation reactions in which the exact routes of these reactions to complete mineralisation of the organics are still not quite clear. Chlorine containing organic compounds, for example, are oxidised first to intermediates, such as aldehydes and carboxylic acids, and finally to carbon dioxide and water, and to chlorine ions (Munter, 2001).

A very important point, which has to be considered in the case of natural waters, is the presence of carbonates. Efficient trapping of HO$^\cdot$ radicals by bicarbonate (equation 6) and
carbonate (equation 7), radical scavengers, can significantly reduce the efficiency of the abatement of pollutants.

\[ \text{HO} + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^- \]  
\[ \text{HO} + \text{CO}_3^{2-} \rightarrow \text{HO}^- + \text{CO}_3^- \]  

However, the generated carbonate radical anion is also an oxidant itself, but its oxidation power is less positive compared to a HO· radical (Legrini et al, 1993).

The destruction rate of contaminants is approximately proportional to a constant rate for the pollutant with a HO· radical. As we can see from Table 4, chlorinated alkenes decompose fastest because the double bond is very prone to a hydroxyl attack. Saturated molecules, such as alkanes, are more difficult to oxidise because of a slower reaction rate (Table 4). The powerfulness of the hydroxyl radical gives advanced oxidation processes the ability to achieve oxidative destruction of compounds refractory to conventional hydrogen peroxide or ozone oxidation. AOPs have been used successfully for example, destroying pesticides by photochemical degradation (UV/O₃ and UV/H₂O₂) (Andreozzi et al., 2003), photocatalysis (TiO₂/UV, Fenton and photo-Fenton process) (Legrini et al., 1993; Fallman et al., 1999) and chemical oxidation processes (O₃, O₃/H₂O₂ and H₂O₂/Fe²⁺) (Masten & Davies, 1994; Benitez et al., 2002), decomposing of organics from textile wastewater, such as surfactants and dyes, by photo-Fenton and H₂O₂/UV-C treatment (García-Montaño et al., 2006), photocatalysis with immobilised TiO₂ (Harrelkas et al., 2008) and also for the destruction of organics in different kind of effluents, such as paper mill wastewaters by photocatalysis (Pérez et al., 2001), landfill leachates by the Fenton process (Lopez et al, 2004; Gotvajn et al., 2009), olives mill wastewaters by wet air oxidation (Gomes et al., 2007) etc.

Advanced oxidation methods can be split into “cold” and “hot” oxidation. Cold oxidation methods work near to ambient temperature and pressure compared to hot oxidation at elevated temperatures and pressure (Verenich, 2003). Suitable applications of cold oxidation methods include effluents containing relatively small amount of COD (≤ 5.0 g L⁻¹). Higher COD contents would require the consumption of large amounts of expensive reactants, such as O₃ and H₂O₂ (Andreozzi et al., 1999). For wastewaters with higher COD values (≥ 5.0 g L⁻¹), hot oxidation techniques are more convenient (Mishra et al., 1995).

### 3.1 Ozone water processes

**Ozonation at elevated values of pH.** Ozone is an effective oxidising agent (Table 3) which reacts with most compounds containing multiple bonds, such as C=C, C=N, N=N, but not with species containing single bonds (C-C, C-O, O-H) at high rates (Gogate & Pandit, 2004a). At higher pH values, ozone reacts almost unselectively with all inorganic and organic compounds present in the solution (Staehelin & Hoigne, 1982). Rising the pH of the aqueous solution increases the decomposition rate of the ozone that generates the super-oxide anion radical O₂⁻ and hydroperoxyl radical HO₂⁻. For example, the ozonide anion O₃⁻ is formed by the reaction between O₃ and O₂⁻. The ozonide anion further decomposes to a HO⁻ radical, such that, three ozone molecules will produce two HO⁻ radicals (equation 8) (Munter, 2001):  

\[ 3\text{O}_3 + \text{HO}^- + \text{H}^+ \rightarrow 2\text{HO}^- + 4\text{O}_2 \]  

(Munter, 2001).
The rate constants of the hydroxyl radicals are typically \(10^6 - 10^9\) times higher than the corresponding reaction rate constants of molecular ozone (Table 4). The oxidation of organic compounds may also occur due to the combination of reactions with molecular ozone and reactions with hydroxyl radicals (Munter, 2001).

**Ozone with hydrogen peroxide.** The addition of hydrogen peroxide to the aqueous solution of ozone enhances the decomposition of \(O_3\) with the formation of hydroxyl radicals. To summarise: two ozone molecules will produce two hydroxyl radicals (equation 9) (Munter, 2001):

\[
2O_3 + H_2O_2 \rightarrow 2HO + 3O_2
\]  

(9)

The action of both ozone molecules and the generated hydroxyl radicals results in a significant improvement in the rates of decomposition of pollutants in aqueous solutions.

**Ozone and catalyst.** Catalytic ozonation is another opportunity to accelerate ozonation with compounds which are weakly reactive with ozone, such as atrazine. Several homogeneous catalysts, such as zinc and copper sulfates, silver nitrate, chromium trioxide (Abdo et al., 1988) and also heterogeneous catalysts, Ru/\(\text{CeO}_2\) (Delanoë et al., 2001), \(\text{MnO}_2\) (Ma & Graham, 1997), TiO\(_2\)/Al\(_2\)O\(_3\) (Beltrán et al., 2004) and Pt/Al\(_2\)O\(_3\) (Chang et al., 2009) have been studied. According to these studies, both homogeneous and heterogeneous catalysts are able to improve the efficiency of ozone for the removal of different organic compounds in an aqueous solution.

### 3.2 Photolysis

In a photo-oxidation reaction, UV radiation (photon) excites an electron of an organic molecule (C) from the ground state to the excited state (C\(^*\)) (equation 10). The excited organic molecule excites further molecular oxygen (equation 11) with a subsequent recombination of the radical ions or hydrolysis of the radical cation, or homolysis (equation 12) to form radicals which can react with oxygen (equation 13) (Legrini et al., 1993).

\[
C \xrightarrow{hv} C^* \\
C^* + O_2 \rightarrow C^+ O_2^- \\
R-X \xrightarrow{hv} R^- + X^* \\
R^- + O_2 \rightarrow RO_2
\]  

(10-13)

The rate of the photo-oxidation reaction depends on the adsorption cross section of the medium, the quantum yield of the process, the photon rate at the wavelength of excitation and the concentration of dissolved molecular oxygen (Legrini et al, 1993). However, to achieve the complete mineralisation of the treated effluent, photolysis is usually combined with oxidising compounds (hydrogen peroxide, ozone) or semiconductors (such as titanium dioxide).

#### 3.2.1 UV/ozone, UV/H\(_2\)O\(_2\) and UV/O\(_3\)/H\(_2\)O\(_2\) processes

The combination of UV light and ozone/hydrogen peroxide or both significantly enhances the rate of generating free radicals. Ozone adsorbs UV radiation at a wavelength of 254 nm
(equation 14) producing hydrogen peroxide as an intermediate, which decomposes further to hydrogen peroxide radicals (equation 15) (Munter, 2001):

\[
O_3 + hv \rightarrow O_2 + O(1D) \tag{14}
\]

\[
O(1D) + H_2O \rightarrow H_2O_2 \rightarrow 2HO \tag{15}
\]

The mechanism for the photolysis of hydrogen peroxide is the cleavage of the molecule into two hydroxyl radicals (equation 16) (Munter, 2001):

\[
H_2O_2 \xrightarrow{hv} 2HO \tag{16}
\]

Depending on the pH value of the aqueous H$_2$O$_2$ solution, HO$_2^-$ also absorbs UV radiation at 254 nm to form a hydroxyl radical (equations 17, 18):

\[
H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{17}
\]

\[
HO_2^- \xrightarrow{hv} + HO^- + O^- \tag{18}
\]

The combination of UV photolysis and ozone/hydrogen peroxide will be beneficial only for contaminants which require a relatively higher level of oxidation conditions (higher activation energy) (Gogate & Pandit, 2004b).

### 3.2.2 Photocatalysis

In the photocatalytic process, semiconductor material (often TiO$_2$) is excited by electromagnetic radiation possessing energy of sufficient magnitude, to produce conduction band electrons and valence band holes (equation 19) (Andreozzi et al, 1999):

\[
\text{TiO}_2 \xrightarrow{hv} e^- + h^+ \tag{19}
\]

Formed electrons can reduce some metals and dissolved oxygen to produce a superoxide radical ion O$_2^-$ (equations 20, 21):

\[
M + e^- \rightarrow O_2^- \tag{20}
\]

\[
O_2 + e^- \rightarrow O_2^- \tag{21}
\]

Remaining holes then oxidise and adsorbed H$_2$O or HO$^-$ to reactive hydroxyl radicals (equations 22, 23):

\[
\text{TiO}_2(h^+) + H_2O_{ad} \rightarrow \text{TiO}_2 + H_2O + H^+ \tag{22}
\]

\[
\text{TiO}_2(h^+) + HO^-_{ad} \rightarrow \text{TiO}_2 + HO + HO^+ \tag{23}
\]

Formed hydroxyl radicals may also react with organic compounds in water as described in the equations (2)-(5).

Several catalytic materials have been studied in photocatalysis although TiO$_2$ in the anatase form seems to possess the best photocatalytic performance (Andreozzi et al, 1999). 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. Therefore, many researchers have focused on examining the use of sunlight in photocatalytic processes. Unfortunately, only a few percent of solar energy reaches the surface of the earth that could in principle be utilised as a direct exciter to TiO$_2$ (Munter, 2001).

Degussa P-25 TiO$_2$ catalyst is probably the most active catalyst in photocatalytic reactions however its optimum effective will always be strongly dependent on the type and concentration of the treated pollutant (Gogate & Pandit, 2004a). In several studies, the doping of TiO$_2$ with metals, such as, platinum (Hufschmidt et al, 2002), silver, zirconium and iron (Kment et al, 2010) as well as, sulphur, carbon and nitrogen (Menendez-Flores et al, 2011; Wang et al, 2011) has been proven to enhance the activity of the catalyst.

### 3.3 Fenton processes

Fenton’s reagent consists of H$_2$O$_2$ and ferrous iron, which generates hydroxyl radicals (equation 24) (Munter, 2001):

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^+ \quad (24)$$

The generated ferric ion decomposes H$_2$O$_2$ forming hydroxyl radicals (equations 25, 26):

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Fe-OOH}^{2+} \quad (25)$$

$$\text{Fe-OOH}^{2+} \rightarrow \text{HO}^2^- + \text{Fe}^{2+} \quad (26)$$

After the reaction (26), the formed ferrous iron again decomposes H$_2$O$_2$ (24) etc. The hydrogen peroxide decomposition is an iron salt catalyzed reaction and in reactions (25, 26) iron is regenerated again to iron(II).

The most important operating parameter in the Fenton process is the pH of the solution. According to the majority of researchers, the optimum operating pH to be observed is 3. However, the Fenton process effectively generates hydroxyl radicals, it consumes one molecule of Fe$^{2+}$ for each HO· radical produced, which results in a high concentration of Fe(II) (Munter, 2001).

#### 3.3.1 Photoassisted Fenton processes

In photoassisted Fenton process, Fe$^{3+}$ ions are added to the H$_2$O$_2$/UV process. In acidic pH, a Fe(OH)$^{2+}$ complex is formed (equation 27) (Munter, 2001):

$$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad (27)$$

The photolysis of Fe$^{3+}$ complexes allows Fe$^{2+}$ regeneration and formation of hydroxyl radicals (equation 28) (Munter, 2001):

$$\text{Fe(OH)}^{2+} \xrightarrow{hv} \text{Fe}^{2+} + \text{HO}^- \quad (28)$$

The combination of H$_2$O$_2$/UV and iron salt produces more hydroxyl radicals compared with a conventional Fenton process or photolysis, thus the technique enhances the degradation of treated pollutants (Gogate and Pandit, 2004b).
3.3.2 Electro-Fenton processes
In the Electro-Fenton process, $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ are generated electrochemically, either separately or concurrently. Hydrogen peroxide can be electrogenerated by the reduction of dissolved oxygen (equation 29), and ferrous iron by the reduction of ferric iron (equation 30) or by oxidation of a sacrificial Fe anode (equation 31) (Szpyrkowicz et al., 2001):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (29)$$

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (30)$$

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (31)$$

The reaction between $H_2O_2$ and $\text{Fe}^{2+}$ produces hydroxyl radicals (equation 24).

3.4 Wet oxidation processes
The main differences in wet oxidation processes compared with “cold” oxidation techniques described earlier are the operating temperature and pressure. Typically, wet oxidation processes are operating at temperatures from 90 °C (wet peroxide oxidation) to even over 600 °C (supercritical wet air oxidation). The operating conditions of different wet oxidation techniques are described in Table 5.

<table>
<thead>
<tr>
<th>Operating parameter</th>
<th>Wet peroxide oxidation (WPO)</th>
<th>Catalytic wet air oxidation (CWAO)</th>
<th>Wet air oxidation (WAO)</th>
<th>Supercritical wet air oxidation (SCWO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>100-140</td>
<td>130-250</td>
<td>125-320</td>
<td>&gt; 374</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>3-5</td>
<td>20-50</td>
<td>5-200</td>
<td>&gt; 221</td>
</tr>
</tbody>
</table>

Table 5. Operating conditions of different wet oxidation techniques (Debellefontaine et al., 1996; Mishra et al., 1995).

The wet oxidation processes are suitable for wastewaters and sludges which are both too diluted to incinerate and too concentrated for biological treatment. The COD level of the wastes appropriate to be treated by WAO techniques is typically between 5 and 200 g L$^{-1}$ (Kolaczkowski et al., 1999).

3.4.1 Wet peroxide oxidation
WPO process is adapted from the Fenton process (Section 3.3) but it operates at temperatures above 100 °C. The oxidation mechanism is the same as for the Fenton’s reaction (equations 24-26), but as a consequence of a higher operating temperature more efficient TOC removal can be obtained (Debellefontaine et al., 1996). A typical catalyst in the WPO is iron but other catalytic materials have also been used successfully in the process such as copper (Caudo et al, 2008), activated carbon (Gomes et al., 2010), ruthenium (Rokhina et al., 2010) etc.

3.4.2 Wet air oxidation
In the WAO process organic and oxidisable inorganic compounds of the liquid phase are oxidised at elevated temperatures and pressures (Table 5) using oxygen containing gas (air,
molecular oxygen) to intermediates (short-chain organic molecules), CO₂ and water. The degree of oxidation is dependent on temperature, oxygen partial pressure, operating time and, of course, the oxidisability of the compounds under consideration. To summarise, it can be said that, the higher the operating temperature the higher is the extent of oxidation achieved (Mishra et al. 1995).

According to Lixiong et al. (1991) the WAO reaction starts with the reaction of oxygen and the weakest C-H bonds of the oxidised organic compound (R denotes the organic functional group) forming free radicals:

\[ \text{RH} + \text{O}_2 \rightarrow \text{R} + \text{HO}_2 \] (32)

More organic radicals are formed with the reaction of HO₂ and organic molecule:

\[ \text{RH} + \text{HO}_2 \rightarrow \text{R} + \text{H}_2\text{O}_2 \] (33)

At the high operating temperature of WAO, H₂O₂ decomposes rapidly in the homogeneous or heterogeneous species (term M) to hydroxyl radicals:

\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{HO} + \text{M} \] (34)

The chain reaction continues with the oxidation of organic compounds by hydroxyl radicals following a hydrogen abstraction mechanism described earlier (equation 3).

### 3.4.3 Catalytic wet air oxidation

Compared with conventional WAO, catalytic wet air oxidation (CWAO) has lower energy requirements. Due to the presence of homogeneous or heterogeneous catalysts, lower operating conditions (air/oxygen pressure and temperature) can be used to achieve much higher oxidation rates. Various heterogeneous catalysts have been synthesised and tested in CWAO reactions, based either on metal oxides or supported noble metals (Levec & Pintar, 2007). Mixtures of metal oxides such as Cu, Zn, Co and Al, are reported to exhibit good activity, but leaching of these metals has been detected (Mantzavinos et al., 1996a). Supported noble metal catalysts, such as Pt, Pd, Rh, Re, Ru on Al₂O₃ (Mantzavinos et al., 1996b) and ceria including doped-ceria supported Pt and Ru (Keav et al., 2010) are less prone to leaching and are also more effective for oxidising organic compounds than metal oxide catalysts. CWAO processes have also been commercialised. In Japan, several companies have developed catalytic wet air oxidation technologies relying on heterogeneous supported noble metal catalysts (Harada et al., 1987; Ishii et al., 1994). In Europe, homogeneous CWAO processes such as Ciba-Geigy, LOPROX, ORCAN and ATHOS have already been developed in the 1990s (Luck, 1999).

### 3.4.4 Supercritical wet air oxidation

In a supercritical water oxidation process the reaction temperature is above 374 °C and the oxygen containing gas is at a pressure of 221 bar, which is the critical point of water. Above this critical point, water is an excellent solvent for both organic compounds and gases; therefore oxidisable compounds and oxygen can be mixed in a single homogeneous phase. This is the great advantage of supercritical water oxidation and in general, the destruction efficiencies of pollutants are in the order of 99-99.9% at 400-500 °C for a residence time interval of 1-5 minutes (Mishra et al., 1995).
4. AOP applications in food industry wastewater treatment

Food industry wastewaters can generally be treated biologically, in both aerobic and anaerobic reactors. However, as a consequence of diverse consumption, the forming effluents may contain compounds which are poisonous to the micro-organisms in the biological treatment plant. The pre-treatment of the effluent by chemical oxidation, especially with AOPs, can oxidise biorefractory pollutants into a more easily biodegradably form. In the following Sections, there are several examples of AOP applications in different sectors of food industry wastewater treatment.

4.1 Winery and distillery wastewater

The winery industry generates strong organic wastewater whose quality is highly dependent on the production activities. A typical COD value of the effluent containing sugars, ethanol, organic acids, aldehydes, other microbial fermentation products, soaps and detergents, is between 800 and 1200 mg L\(^{-1}\) but can easily increase to over 25000 mg L\(^{-1}\). Winery wastewater is quite acidic (pH 3-4) and it usually contains large amounts of phosphorus, but not nitrogen and other trace minerals, which are important for biological treatment (Oller et al., 2010).

There are some studies that have considered the ozonation of winery wastewaters. Lucas et al. (2009a) for example, have treated winery wastewaters by ozonation in a bubble column reactor. During a three hour reaction period the degradation of aromatic and polyphenol content was found to be significant, thus the biodegradability of the wastewater was improved and therefore the ozonation may be considered as pre-treatment to further biological treatment. In addition, Beltrán et al. (1999) have noticed the same BOD/COD enhancement in winery effluent after ozonation whereas Lucas et al. (2010) have combined UV and UV/H\(_2\)O\(_2\) with ozone. According to the results, O\(_3\)/UV/H\(_2\)O\(_2\) combination was identified as the most economical process compared with O\(_3\) and O\(_3\)/UV to the treated winery wastewater.

Winery wastewaters were also treated by solar photo-Fenton integrated with activated sludge treatment in a pilot-plant scale (Mosteo et. al., 2008) and by UV and UV/TiO\(_2\) at lab-scale (Agustina et. al., 2008). With both techniques the efficient removal of organics was successfully achieved whereas photo-Fenton combined with biological treatment showed higher mineralisation rates and a significant toxicity decrease of the treated effluent.

Sources of distillery wastewater, much in common with winery wastewater, are stillage, fermenter and condenser cooling water, and fermenter wastewater. These effluents contain high concentrations of organic material (COD 100-150 g L\(^{-1}\) and BOD 40-200 g L\(^{-1}\)) and fertilisers such as potassium, phosphorus and nitrogen. In addition, the molasses wastewater from ethanol fermentation has a typical brown colour which is difficult to remove by traditional biological treatment (Oller et al., 2010).

Several AOP methods have been studied in the treatment of distillery wastewaters. Beltrán et al. (1997b), Benitez et al. (1999; 2003), Sangave et al. (2007) and Sreethawong & Chavadej (2008) have all used ozonation and its combination with UV, H\(_2\)O\(_2\) or Fe-catalyst in the degradation of organics from distillery wastewaters. All these researchers agree that the removal of organic matter improved with the simultaneous presence of UV radiation, hydrogen peroxide or Fe-catalyst in addition to ozone, due to the contribution of hydroxyl radicals generated in these combined processes. In addition, the combined process of ozone
pre-treatment followed by an activated sludge step provides enhancement in the removal of substrate obtained in relation to that obtained in the single aerobic treatment without ozonation, i.e. from 28% to 39% (Benítez et al., 1999; 2003). The integrated process (ozone pre-treatment-aerobic biological oxidation-ozone post-treatment) achieved almost 80% COD reduction in the treatment of distillery wastewater along with the decolouration of the effluent compared with 35% COD removal for non-ozonated samples (Sangave et al., 2007). UV/H$_2$O$_2$ (Beltrán et al., 1997a) and electro-Fenton (Yavuz, 2007) processes have also been used for the treatment of distillery wastewaters. The EF process (Yavuz, 2007) seems to be a promising technique with the COD removal over 90% compared with a UV radiation and hydrogen peroxide combination whose COD reduction is only 38% (Beltrán et al., 1997a).

Belkacemi et al. (1999; 2000) investigated wet oxidation and catalytic wet oxidation for the removal of organics from distillery liquors. The initial TOC of the effluent was 22500 mg L$^{-1}$ while in the AOPs described earlier the total organic carbon was 10 or even 100 times lower. In the temperature and oxygen partial ranges of 180-250 °C and 5-25 bar respectively, the highest TOC removal (around 60%) was achieved with Mn/Ce oxides and Cu(II)NaY catalysts. These catalysts were found to be very effective for short contact times, while for prolonged exposures catalysts deactivation by fouling carbonaceous deposit was shown to be the prime factor responsible for the loss of catalysts activity (Belkacemi et al., 2000). In the supercritical water oxidation of alcohol distillery wastewater (Goto et al., 1998) almost complete colour, odour and TOC removal was attained when more than stoichiometric amount (over 100%) of oxidant (H$_2$O$_2$) was used in temperatures between 200-600 °C.

### 4.2 Olive industry wastewater

Wastewaters from olive oil extraction plants, also called olive mill wastewaters, and wastewaters generated by table olive production, contain high concentration of phenolic compounds. In olive oil production, an oily juice is extracted from the fruit through milling or centrifugation. Table olive production requires the same treatment in order to eliminate the bitterness of the fruit, due to the presence of polyphenolic compounds (Bautista et al., 2008). Olive mill wastewater contains polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids, oil etc. and therefore, the COD of the effluent may be as high as 220 g L$^{-1}$ and even 190 g L$^{-1}$ for the amount of suspended solids (Oller et al., 2010).

For several years, olive mill wastewater has been the most polluting and troublesome waste produced by olive mills in all the countries surrounding the Mediterranean. Thus, the management of this liquid residue has been investigated extensively and the efficiency of AOPs for treating olive mill effluents has been studied widely (Mantzavinos & Kalogerakis, 2005). Many researchers have also investigated Fenton processes in the treatment of olive mill effluents (Table 6).

Olive mill wastewater has also been treated by several other AOPs such as ozonation or ozone/UV (Lafi et al., 2009) which have increased the biodegradability of the effluent. Minh et al. (2008) and Gomes et al. (2007) have been successful in decreasing the TOC and phenolic content of olive mill wastewater by CWAo. At reaction conditions of 190 °C and 70 bar of air using Pt and Ru supported on titania and zirconia carriers, the toxicity and phytotoxicity of the effluent decreased to a suitable level for anaerobic treatment (Minh et al., 2008). Gomes et al. (2007) reported that with the carbon supported Pt catalyst TOC and the colour of olive mill wastewater were completely removed after 8 h of reaction at 200 °C.
at 6.9 bar of O$_2$. Caudo et al. (2008) have also tested copper-pillared clays as catalysts in wet hydrogen peroxide catalytic oxidation (WHPCO) of olive mill wastewater. According to the research, copper pillared clays are effective and stable catalysts for WHPCO of wastes in water whilst this treatment decreases the toxicity of the olive mill wastewater.

<table>
<thead>
<tr>
<th>Fenton process</th>
<th>Conclusions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>COD removal 80-90%, followed by biological treatment</td>
<td>Bressan et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>COD and aromatics removal 40%</td>
<td>Ahmadi et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>Considered as a pre-treatment (COD removal 40-50%)</td>
<td>Dogruel et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>COD removal 70%</td>
<td>Lucas &amp; Peres (2009b)</td>
</tr>
<tr>
<td>Coagulation and</td>
<td>COD removal 85% by F and 95% by PF</td>
<td>Rizzo et al. (2008)</td>
</tr>
<tr>
<td>Fenton/photo-Fenton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulation-flocculation-Fenton</td>
<td>COD removal 60% and decrease of phytotoxicity</td>
<td>Ginos et al. (2006)</td>
</tr>
<tr>
<td>Fenton with zero-valent iron</td>
<td>Considered as a pre-treatment (COD removal 75-20%) before classical biological process</td>
<td>Kallel et al. (2009)</td>
</tr>
<tr>
<td>Solar photo-Fenton</td>
<td>COD removal 85%, phenolic compounds degradation even 100%</td>
<td>Gernjak et al. (2004)</td>
</tr>
<tr>
<td>Electro-Fenton</td>
<td>Considered as a pre-treatment (COD removal 66%) before anaerobic digestion</td>
<td>Khoufi et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>Considered as a pre-treatment (COD removal 53%) before anaerobic digestion and ultrafiltration resulting in a complete detoxify of effluent. Pilot plant.</td>
<td>Khoufi et al. (2009)</td>
</tr>
</tbody>
</table>

Table 6. Fenton processes for the treatment of olive mill wastewater.

The organic content of wastewater from a table olive process is quite similar to olive mill wastewater containing phenols, polyphenols, sugars, acids, tannins, pectins and oil residues, with a COD of several grams per litre. The inorganic fraction consists of high concentrations of NaCl and NaOH which are used for debittering and fermentation, as well as trace amounts of various metals. As a consequence of the complexity of these effluents, they are unsuitable for conventional aerobic and anaerobic processes (Öller et al., 2010). Recently, it has been possible to enhance the biodegradability of the table olive processing wastewater by different AOPs. Kyriacou et al. (2005) have scaled this treatment method up from a lab-scale to a pilot-scale for green table olive processing wastewater, which combines biological treatment with an electro-Fenton system. In the pilot plant, 75% COD removal was achieved and the post-treatment by coagulation finally gave an overall 98% COD removal for the treated effluent. Photocatalytic treatment and WAO alone (Chatzisymeon et al., 2008; Katsoni et al., 2008) as well as O$_3$, O$_3$/H$_2$O$_2$, O$_3$/UV, UV, UV/H$_2$O$_2$, Fenton, photo-Fenton and WAO processes combined with aerobic biological treatment have been studied for
organic matter removal from table olive processing wastewaters (Beltran-Heredia et al., 2000; Benitez et al., 2001a, b; Rivas et al., 2000, 2001).

4.3 Meat processing industry wastewater
Meat processing industry wastewaters constitute one of the greatest concerns of the agro-industrial sector, as approximately 62 Mm$^3$/year of water is used worldwide. However, only a small amount of this becomes a component of the final product. Meat processing industry wastewater contains high concentrations of fat, dry waste, sediments and total suspended matter as well as nitrogen and chlorides whilst possessing high biological and chemical oxygen demand (Sroka et al., 2004). Traditionally, meat processing industry wastewaters are treated by anaerobic or aerobic biological systems (Johns, 1995) but recently few studies concerning AOPs have been published. In the publication of Sena et al (2009), dissolved air flotation (DAF) followed by photo-peroxidation (UV/H$_2$O$_2$) and photo-Fenton reactions were evaluated in the treatment of meat processing industry wastewater. According to the results, DAF connected with photo-Fenton treatment achieved the best removals of COD, colour, turbidity and total solids of the treated effluent. WAO have also been used for the removal of organic compounds from meat processing industry wastewater (Heponiemi et al., 2009). After catalytic wet air oxidation treatment, the biodegradability of the wastewater sample has improved.

4.4 Vegetable and fruit processing wastewater
Various factors, such as seasonal and source variations, unit operations etc. affect the composition of vegetable and fruit processing industry wastewater. Typically, this effluent contains high organic loads, e.g. from peeling and blanching, cleaning agents and suspended solids such as fibres, dissolved solids, salts, nutrients etc. Furthermore, residual pesticides, which are difficult to degrade during wastewater treatment, may be a concern (EC, 2006). In some studies, AOPs have been used for the removal of organics from fruit and vegetable processing industry wastewaters. In the research of Beltran et al. (1997a, b), wastewater from a tomato processing plant was treated by UV, UV/H$_2$O$_2$, O$_3$, O$_3$/H$_2$O$_2$ and O$_3$/UV. According to results, an ozone-UV radiation system achieved the highest degradation rates (90% removal of COD). Due to the improved biodegradability of the treated effluent, Beltran et al. (1997a, b) recommended the combination of this process with biological oxidation. Caudo et al. (2008) have studied copper-pillared clays catalysed wet peroxide oxidation of citrus juice production wastewater. This effluent contains various phenolic compounds with a chemical oxygen demand of over 4000 mg L$^{-1}$. After 4 h of oxidation reaction, the TOC had decreased 50% and the biodegradability of the effluent ($BOD_5/COD$ index) had increased from 0.05 to 0.4.

4.5 Miscellaneous wastewater
Coffee industry wastewater is another example of a highly polluted food industry wastewater. The coffee industry uses large amounts (around 40-45 L per kilogram of coffee) of water during the various stages of the production process. The forming effluent contains e.g. caffeine, fat and peptic substances, as well as many different macromolecules such as lignins, tannins and humic acids, which are difficult to handle by conventional biological treatment processes. Recently, Zayas et al. (2007) studied the combination of the chemical
coagulation-flocculation process with various advanced oxidation processes (UV/H₂O₂, UV/O₃, UV/H₂O₂/O₃) for the treatment of coffee industry wastewater. Among the AOPs tested, UV/H₂O₂/O₃ process was the most effective in the reduction of COD, colour and turbidity of the treated effluent.

Baker’s yeast is a commercial product of molasses (the end product of sugar manufacture) which constitutes a solution of sugar, organic and inorganic material in water. Baker’s yeast industry wastewater has a high BOD and COD values which contains significant amount of nitrogen and non-biodegradable organic pollutants. In addition, the effluent has a typical dark colour and, therefore the possible decolourisation of the effluent has been investigated by the Fenton process (Pala & Erden, 2005). Fenton oxidation was applied to the biologically pre-treated baker’s yeast industry wastewater. In the optimum operating conditions, 99% colour removal and 88% COD reduction was achieved. Photo-Fenton and UV/H₂O₂ processes have also been studied in the removal of colour and organics from baker’s yeast effluents (Çatalkaya & Şengül, 2006).

Palm oil effluent is a colloidal dispersion of biological origin which has a typical unpleasant odour. The total solids content of the effluent is 5-7% and it constitutes of dissolved, organic and inorganic solids, a reason why it is extremely difficult to treat by conventional wastewater treatment methods (Zinatizadeh et al., 2006). In the study of Babu et al. (2010) a palm oil effluent was treated by a combined electro-Fenton-biological oxidation process. After 2 h of EF and 5 d of biological treatment 86% COD removal was achieved. The treated water can be reused for general purpose in an industrial application.

Dairy industry wastewater has a typical white colour and a high nutrient level as well as organic matter content. It is usually treated by biological methods such as the activated sludge process and anaerobic filters although aerobic biological processes have high energy requirements whilst anaerobic biological methods require additional treatment (Kushwaha et al., 2010). Recently, solar photocatalytic oxidation has been used after anaerobic sludge blanket reactor for the removal of COD from dairy industry wastewater (Banu et al., 2008). The combination of anaerobic process and solar photocatalytic oxidation using TiO₂ as a catalyst resulted in 95% removal of COD from dairy industry wastewater. This integrated system may be a promising alternative for the treatment of dairy industry effluents. In addition, Inamdar & Singh (2008) have applied photocatalysis in the treatment of dairy industry effluent.

5. Conclusion

The characteristics and treatment of food industry wastewaters by different advanced oxidation processes were considered. Typically, the amount and composition of the effluent varies considerably. The high organic matter content is a basic problem in food industry wastewaters but the organic compounds are usually easily biodegradable and the effluents can be treated by conventional anaerobic or aerobic biological methods. However, as a consequence of diverse consumption, the forming effluents may contain compounds which are poisonous to micro-organisms in the biological treatment plant. The pre-treatment of the effluent by chemical oxidation, especially with AOPs, can oxidise biorefractory pollutants to a more easily biodegradable form. Thus, the combination of AOP and biological treatment may be a possible solution for the treatment of variable food industry wastewaters.
6. Acknowledgements

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The global food industry has the largest number of demanding and knowledgeable consumers: the world population of seven billion inhabitants, since every person eats! This population requires food products that fulfill the high quality standards established by the food industry organizations. Food shortages threaten human health and are aggravated by the disastrous, extreme climatic events such as floods, droughts, fires, storms connected to climate change, global warming and greenhouse gas emissions that modify the environment and, consequently, the production of foods in the agriculture and husbandry sectors. This collection of articles is a timely contribution to issues relating to the food industry. They were selected for use as a primer, an investigation guide and documentation based on modern, scientific and technical references. This volume is therefore appropriate for use by university researchers and practicing food developers and producers. The control of food processing and production is not only discussed in scientific terms; engineering, economic and financial aspects are also considered for the advantage of food industry managers.

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