

A Discussion Paper on Challenges and Proposals for Advanced Treatments for Potabilization of Wastewater in the Food Industry

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1. Introduction

The World Commission on Environment and Development (WCED, 1987, apud Burkhard et al., 2000) defines sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. Sustainable production is a realistic dilemma in food industries, especially in slaughterhouses and the meat processing industry due to the many types of processes involved (Oliver et al., 2008; Casani et al., 2005).

Unfortunately, in many cases the implementation of environmental actions for industrial purposes depends on large-scale economic incentives (Cornel et al., 2011). Concomitantly, the increased costs of fresh water, wastewater treatment and waste disposal are important economic incentives for wastewater reuse and biomass-to-energy actions in industries. Hence, environmental, financial and social sustainability must be achieved together. Since pollution is predominantly due to human behavior, social sustainability requires the commitment of managers, workers and consumers (Burkhard et al., 2000).

Water scarcity is a reality in many world regions. Water pollution and overexploitation, climate change, urbanization, industrialization and increases in the world population and, consequently, food consumption and production are the main factors aggravating the global fresh water crisis (EPA, 2004; Clevelario et al., 2005; Khan et al., 2009; Luiz et al., 2009, 2011). Hence, sustainability in water and wastewater management is a current requirement of industries in order to promote the minimization of fresh water consumption and reduction of wastewater production preserving high-quality groundwaters (Cornel et al., 2011).

Concerning the water consumption in food industries, this input is mostly used for cleaning and disinfection, cooling and heating (Oliver et al., 2008), and also for processing food for human consumption and for sanitary uses. International organizations (e.g. Codex Alimentarius, 2001, 2007) have recognized and stimulated the implementation of direct and indirect wastewater reuse and indirect potable reuse with techniques that take into account hygienic concerns (Casani et al., 2005) to avoid risking adverse effects on the product

integrity, the environment and the health of workers and customers. However, these procedures will be universal in the near future.

Currently, conventional wastewater techniques are not satisfactory to produce reuse wastewater with drinking water quality, further procedures being necessary. Advanced oxidation processes (AOPs) are the most suitable tertiary treatment. AOPs are based on chemical oxidation and can degraded any kind of organic matter with highly reactive and non-selective radicals, mainly hydroxyl radicals ($\bullet\text{OH}$) (Oller et al., 2010; Luiz et al., 2010). AOPs can involve a combination of strong oxidants (e.g. O_3 and H_2O_2), ultraviolet (UV), semiconductor catalysts (e.g. TiO_2 and ZnO) and ultrasound (15 kHz to 1 MHz), and the most common examples are: $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$, O_3/UV , TiO_2/UV , $\text{H}_2\text{O}_2/\text{catalyst}$, Fenton (Matilainen and Sillanpää, 2010).

There are many studies and reviews on advanced processes to treat secondary wastewater from industries which also address the challenges and limitations to water reuse and the hygienic concerns especially in food industries. However, the challenges associated with treating a secondary wastewater to provide drinking water quality become clear when real wastewater is treated in batch and in pilot scale. The limitations are several, particularly in food industries. Hence, this review aims to present an overview and a discussion regarding the challenges and proposals related to the advanced treatment of food industry wastewater to provide drinking water quality, elucidating some experimental and theoretical questions surrounding such processes. Valuable experimental advice which is not usually found in research papers will be provided, for instance, which oxidation treatment should be chosen, which initial experiments should be carried, and which methodology should be followed to evaluate the kinetics constants in different situations will be provided, along with methodology issues. Some previous papers by the authors will be discussed and also some unpublished data on experiences in slaughterhouses and the meat processing industry. The oxidation treatments discussed are ozonation and many AOPs; ultraviolet treatment will also be addressed.

Due to the wide variety of processes and food products, food-processing wastewater can be a complex mixture, and this must be taken into account when considering the recycling, reuse, reconditioning for recycling or reuse, treatment or disposal of water. It is known that the segregation of wastewater streams in at an industrial plant – separating the effluent of each process – or at least the combining of the most similar streams in terms of physical-chemical and microbiological characteristics, enables an optimal treatment for each type of wastewater, energy savings, greater efficiency and lower cost of disposal and reuse. Nevertheless, in most plants the wastewater from all process – including from the toilets – are collected together, making the treatment difficult and costly. Hence, ascertaining the basic nature of food industry wastewater and its variability is the first challenge. This information is important to selecting the best combination of processes through which to treat the effluent.

Besides the need to remove minerals (by filtration) and organic matter, it is also necessary eliminate nitrogen compounds, especially in the dairy and meat industries. Advanced oxidation processes can remove simultaneously organic matter and nitrate; however, there are many parameters that should be taken into account, e.g., concentration of organic compounds and oxygen-free media. Some industrial plants also need to remove a specific recalcitrant organic compound which can be oxidized by advanced treatments; however, the

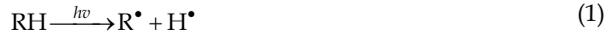
effectiveness of the treatment is mainly dependent on whether the oxidant is selective or non-selective, the presence of oxidant scavengers and the dosage of oxidant.

Given that the growing demand for water, limited access to water in some regions and increased concern regarding the environmental impact of industrial activities on the environment are aspects driving the research on and implementation of water reuse in industrial plants, the theme discussed in this review will be of interest to several fields of chemistry, as well as food, chemical and environmental engineering.

2. UV radiation

UV radiation can degrade organic compounds via two routes: direct photolysis and photo-oxidation via radical generation. In the first route, direct photolysis or photodegradation, the efficiency is directly related to the ability of the target organic compound to absorb UV radiation at the wavelength used (λ) (Beltran et al., 1993). The UV absorption leads to direct excitation and the breakdown of organic pollutants (Rincón; Pulgarin, 2006). Lau et al. (2007) leading to the formation of excited radicals (R^*) by UV excitation of organic compounds (RH). These radicals can be converted into stable molecules (dimers) via a dimerization process (Equations 1-6) which is favored by the presence of O_2 in water. If the free radical chain is interfered with (termination reactions, Equations 4-6), UV treatment may be less effective (Lau et al., 2007).

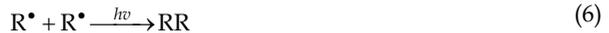
Initiation:



Propagation:



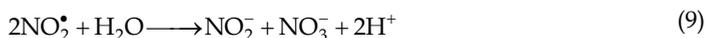
Termination:



According to Beltran-Heredia et al. (2001), for $pH < 7.0$, the rate of photodecomposition increases with increasing pH , which may be due to an increase in the generation of free radicals (R^*) (Equations 1-3).

The second route is photo-oxidation via oxidative processes by radical generation. When natural water matrices are used, the presence of nitrate, iron (III) and/or organic matter can provide $\bullet OH$ due to photo-oxidation of these compounds by UV or other AOP in combination with UV, such as UV/ H_2O_2 , UV/ O_3 , UV/ H_2O_2/O_3 .

Nitrate ions absorb UV radiation by acting as an internal filter to UV light and, in parallel, can form $\bullet\text{OH}$ through the mechanism detailed below (Equations 7-11) (Neamtu and Frimmel, 2006).



For wavelengths longer than 300 nm, complex aqueous ferric iron $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_4^-$, $\text{Fe}(\text{OH})_2^{2+}$, Fe^{3+} , $\text{Fe}_2(\text{OH})_2^{4+}$) can generate ferrous ions and $\bullet\text{OH}$ radicals by photolysis through the internal transfer of electrons (Equation 12) (Espinoza et al., 2007).



Dissolved organic matter absorbs UV light and can generate reactive radicals such as singlet oxygen, superoxide anions ($\bullet\text{O}_2^-$), $\bullet\text{OH}$ radicals and peroxy radicals ($\text{ROO}\bullet$). These reactive transients can degrade organic pollutants following different paths, and consequently they are not degraded only by direct photolysis (Chin et al. 2004; Neamtu and Frimmel, 2006).

The UV radiation is also used for disinfection, especially of reuse water. Ultraviolet radiation is bactericidal because it causes damage to the nucleic acids (DNA and RNA) of microorganisms (bacteria and viruses), inactivating them. Consequently, UV radiation prevents micro-organisms from multiplying because the photoproducts formed from nucleic acids (e.g., pyrimidine dimers) inhibit replication and transcription (Achilleos et al., 2005). The peak absorbance of nucleic acid is around 260 nm, but below 230 nm absorbance is also high. UV lamps, most of which emitted light at 254 nm (low pressure mercury lamps) are commonly used in studies on the disinfection of aqueous matrices, but polychromatic UV lamps can also be effective in inactivating certain microorganisms (Hijnen et al., 2006).

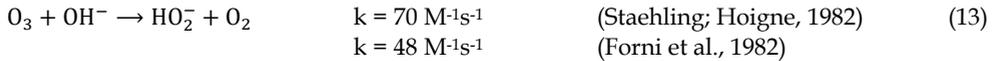
The use of UV disinfection is increasing mainly due to the fact that it is less expensive than chlorine disinfection, safer than chlorine gas, does not form organochlorine and is effective against *Cryptosporidium* and *Giardia*, while chlorine is not. Additionally, UV disinfection does not form by-products or residual toxicity, and has a low regrowth of bacteria. However, UV radiation requires water with low turbidity to allow the radiation to be effective (Achilleos et al., 2005).

As solar radiation is composed of approximately 4% of UVA/UVB (295-400 nm), besides visible light (400-800 nm) and infrared radiation, this natural radiation has been used for disinfection, color reduction and dissolved organic matter removal in surface waters (Kulovaara et al., 1995, Martín-Domínguez et al., 2005, Davies et al., 2009).

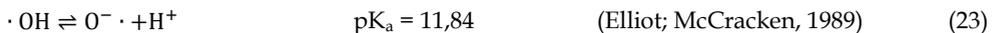
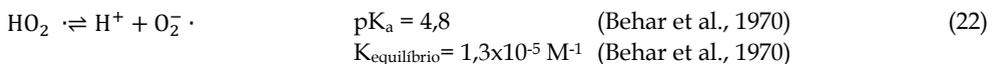
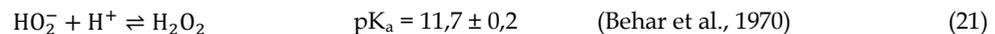
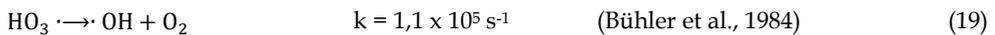
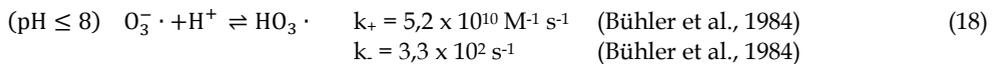
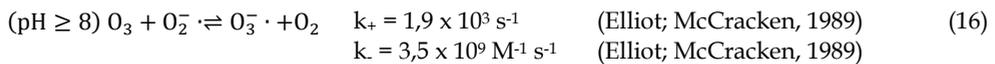
3. Ozonation

Ozone decomposes to oxygen after generation, so it cannot be stored and must be generated on-site. As this oxidant is a gas with low solubility in water (1.05 g L⁻¹), the efficiency of the gas-liquid transfer of ozone is the main variable affecting the effectiveness of organic compound oxidation by ozone in water matrices (Sievers, 2011). The main decomposition reactions of ozone in pure water at ambient temperature (around 20°C) are Equations 13-23.

Initiation:



Propagation:



Where pK_a is the acid dissociation constant. The termination reactions are any reactions between •O₂⁻, •O₃⁻, HO₂⁻, HO₂• and •OH (Bühler et al. 1984; Nadezhdin, 1988).

Analyzing the mechanism described above (Equations 13-23), it appears that the decomposition of ozone can be accelerated by increasing the pH, since hydroxyl ions (OH⁻) (Equation 13) start this process and the HO₂⁻ concentration is pH-dependent (Equation 21) (Andreozzi et al., 1999). As the decomposition of ozone leads to the formation of H₂O₂ (Equation 21), the addition of hydrogen peroxide will promote the decomposition of ozone and increase the formation of •OH. Therefore, the combination O₃+H₂O₂ provides the advanced oxidation process (AOP) O₃/H₂O₂.

In the decomposition reactions (organic matter oxidation reactions), there are two mechanisms: direct attack of ozone and free radical attack. The direct attack of ozone is selective and usually occurs in the case of unsaturated compounds (carbon-carbon double or triple bonds - π bonds), aromatic rings, amines and sulfides (von Gunten, 2003a). The primary reaction of ozone with a certain compound (C) occurs through the generation of an electrophilic additional intermediate compound ($C-O_3$) which decomposes via consecutive reactions until the formation of stable compounds (von Gunten, 2003a).

The direct attack of ozone on tertiary amine occurs by hydrolysis and demethylation, generating the corresponding aldehyde and secondary amine, which is the most stable compound containing the nitrogen atom. Similarly, the same reactions occur with the secondary and primary amine until the formation of the most stable organic compound (Muñoz and von Sonntag, 2000, Lange et al., 2006, Luiz et al., 2010). The oxidation of ammonia through direct attack by ozone is very slow, but it generates the same product as the radical attack: NO_3^- . The replacement of hydrogen atoms by alkyl groups (C_nH_{2n+1}) in the amine nitrogen increases the rate constant of oxidation via ozone (k). The k value for oxidation via ozonation of ammonia (NH_3) is $20 M^{-1} s^{-1}$, of diethylamine is $9.1 \times 10^5 M^{-1} s^{-1}$ and of triethylamine is $4.1 \times 10^6 M^{-1} s^{-1}$ (von Gunten, 2003a).

In the radical attack, radical ions are formed during the oxidative degradation of ozone in water, the main ones being: oxygen free radical ($O\cdot$), superoxide radical ($\cdot O_2$) and hydroxyl radical ($\cdot OH$) (Hoigné; Bader, 1983, Luiz et al., 2010).

The free radical attack is usually faster than the direct attack of ozone. However, in an ozonation process, the concentration of ozone is higher than that of its degradation radicals and hence the oxidation is mainly due to molecular attack. There are molecules that are slowly degraded by ozone treatments (because the molecular attack is selective) and rapidly degraded in advanced oxidation processes in which the attack by $\cdot OH$ radicals predominates (non-selective, higher removal efficiency and the mineralization of organic compounds) (Lau et al., 2007). Therefore, in tertiary wastewater treatment, it is necessary to know which organic contaminants are present in the wastewater in order to verify whether they can be oxidized by simple ozonation or if an AOP would be more effective.

Ozone is a powerful disinfectant, causing cell inactivation through direct damage to the membrane and cell wall, disruption of enzymatic reactions and DNA damage, including in the case of highly resistant pathogens such as protozoan *Cryptosporidium parvum* (EPA, 2004; von Gunten, 2003b). Compared with chlorination, disinfection with ozone is a better option for water bodies which are not organochlorine receivers and its excess can be easily dissipated (Achilleos et al. 2005; EPA, 2004). However, since the concentration required to inactivate the most resistant organisms is very high, there may be the formation of non-desirable disinfection by-products, especially bromates which have carcinogenic potential (von Gunten, 2003b).

4. Advanced oxidation processes (AOP)

Advanced oxidation processes (AOPs) degrade organic contaminants into carbon dioxide, water and inorganic anions through the action of transient oxidizing species, especially hydroxyl radicals ($\cdot OH$). AOPs are clean processes because they do not generally require post-treatment or the final disposal of potential waste.

The $\bullet\text{OH}$ radicals are not selective, thus they have the ability to degrade all organic substances present in a liquid or gas to be treated. The abstraction of H for the reaction of $\bullet\text{OH}$ and organic compounds in the presence of saturated oxygen is the main route for the shortening of the chains of ketones, aldehydes and carboxylic acids (Mellouk et al., 2003).

4.1 UV/H₂O₂

Ultraviolet (UV) treatment promotes photolysis (or photo-oxidation) of organic compounds. To achieve a greater degradation, there are processes that combine UV radiation with other chemical agents such as O₃ and H₂O₂ (Parkinson et al., 2001). Among the variety of AOPs available and their combinations, the reagent H₂O₂ is frequently used due to its stability during transport and storage, almost infinite solubility in water, and low installation and operation costs compared to other processes, such as the application of O₃ (Alfano et al., 2001). In UV/H₂O₂ treatment, radiation with a wavelength shorter than 300 nm (UV-C irradiation) breaks H₂O₂ into $\bullet\text{OH}$ radicals (Equation 24) which oxidize the pollutant compounds. However, for the organic compound degradation to be effective, and mineralization of the compounds to occur (into CO₂ and H₂O), the H₂O₂ concentration must be above the stoichiometric demand and the reaction time under UV radiation must be sufficient, as previously determined experimentally (Alfano et al., 2001).

The photolysis of water yields dissolved oxygen (Equation 24) which can favour the photodegradation of organic compounds (Equation 2). Nevertheless the photolysis of hydrogen peroxide by UV radiation promotes the formation of stronger oxidants: hydroxyl radicals ($\bullet\text{OH}$) (Equation 25). The mechanism of AOP UV/H₂O₂ treatment includes initiation, propagation and termination reactions, and degradation reactions of the organic compounds (RH) (Equations 25-32) (Alfano *et al.*, 2001).



Initiation:



Propagation:

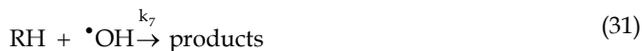


Termination:





Decomposition:



The propagation (Equations 26-27) and termination (Equations 28-30) reactions indicate that when there is H_2O_2 in excess and, subsequently, an excess of $\bullet\text{OH}$ radicals, the recombination of these radicals is favored (Equation 28) reversing the initiation reaction (Equation 25) and inhibiting the oxidation reactions of organic compounds (Equations 31-32).

Yang et al. (2005) found that there is no significant effect of pH on the degradation efficiency if the treatment is only via photodegradation by UV radiation. However, in a UV/ H_2O_2 reaction the generation of hydroxyl radicals ($\bullet\text{OH}$) may be affected by the presence of high concentrations of H^+ and OH^- . Many authors have observed higher rates of decomposition of organic contaminants at low pH (Song et al., 2008). However, Yang et al. (2005) found the efficiency of mineralization of the complex sodium ethylenediamine tetraacetic acid (Na-EDTA) decreased from 98% (in ultra-pure water and without pH correction) to around 70% with initial pH values of 2.3 and 11.6, respectively.

The commercial and industrial applications of UV/ H_2O_2 processes require the determination of optimal oxidant and irradiation dosages. Therefore, the development of a mathematical model for these processes can help the determination of such variables (Crittenden et al., 1999). Usually, the kinetic model used for common pollutants in aqueous solutions is a pseudo-first-order model by photodegradation (UV radiation) and also by the AOP $\text{H}_2\text{O}_2/\text{UV}$ (Chen et al. 2007; Song et al. 2008; Luiz et al., 2009).

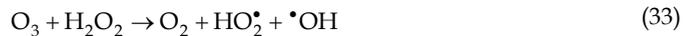
Dosages below 15 mg L^{-1} of hydrogen peroxide do not have a significant toxic effect on bacteria when the system is not exposed to light (in darkness) (Rincón; Pulgarin, 2006; Sciacca et al., 2010). However, hydrogen peroxide in the extracellular region weakens the cell walls, making the bacteria more sensitive to oxidative stress and this may explain the observed inactivation at lower concentrations. Therefore, although H_2O_2 is not directly toxic to the bacteria, the cleavage products, for instance, the hydroxyl ($\bullet\text{OH}$) and superoxide ($\text{HO}_2\bullet$ and $\bullet\text{O}_2^-$) radicals generated by the addition of another agent in the system, such as UV, O_3 , ferric or ferrous ions (Fenton reaction) (Sciacca et al., 2010) can be toxic. Such species can induce reactions in lipids, proteins and DNA, inactivating the cells.

4.2 $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$

The AOPs $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ have been developed to treat wastewater highly contaminated by both organic matter and microorganisms. The effectiveness of these treatments is due to synergistic interaction of the positive effects of three reactions: direct ozonation (molecular attack), photolysis and oxidation by hydroxyl radicals ($\bullet\text{OH}$) (Lau et al., 2007, Luiz et al., 2010). Some important factors, such as quantifying the speed of photons

absorbed in the heterogeneous medium (ozone gas in water matrices), and assessing the degree of ozone reactivity with unsaturated organic compounds, still need to be better understood (Legrini et al., 1993).

The mechanism of the AOPs O_3/H_2O_2 , O_3/UV and $O_3/H_2O_2/UV$ are very similar to each other, and all have the hydroxyl radical ($\bullet OH$) as the most important intermediate compound (Beltran et al. 1995; Legrini et al., 1993). In the AOP O_3/H_2O_2 , besides the initiation reaction of ozone decomposition, another initiation reaction is the decomposition of hydrogen peroxide by ozone into hydroxyl radicals (Equation 33). The decomposition of hydrogen peroxide by ozone (Equation 33) is very slow (Legrini et al., 1993), but it enhances the other ozone decomposition reactions which generate more $\bullet OH$ radicals (Equations 13-23). Therefore, the reaction rate can be increased with increasing the pH, because the ionic form of H_2O_2 (HO_2^-) reacts with O_3 (Staelin; Hoigné, 1982) (Equation 14) followed by other reactions of propagation, termination and decomposition.



The absorbance spectrum of ozone indicates that it has a greater absorption at 254 nm than H_2O_2 , 3300 and 18.6 $M^{-1} cm^{-1}$, respectively, and the influence of the internal effects of the system is lower in an O_3/UV system, due to the effect of suspended solids and aromatic compounds which can act as a UV filters. Nevertheless, the quantum yield of $\bullet OH$ radicals in the AOP O_3/UV (around 0.1) is lower than in H_2O_2/UV (Sievers, 2011). The quantum yield of a photochemical reaction is the number of events divided by the number of absorbed photons of a specific wavelength during the same period time (Khun *et al.*, 2004). The absorption of UV light by O_3 in water leads, firstly, to the generation of H_2O_2 (Equation 34) (Legrini et al., 1993). Therefore, the other reactions of propagation, termination and decomposition are all cited for O_3 treatments, and for O_3/H_2O_2 H_2O_2/UV (Equations 14-33).



The AOP $O_3/H_2O_2/UV$ should be used to enhance the generation of hydroxyl radicals, as its initiation reactions are the same as those of ozonation, H_2O_2/UV , O_3/H_2O_2 and O_3/UV (Equations 13, 25, 33 and 34). All other reactions are of the types propagation, termination and decomposition (Equations 14-32).

AOPs promote a higher degree of mineralization compared to other tertiary oxidative treatments (such as simple ozonation), ensuring decreased levels or the absence (if the mineralization is total) of oxidized intermediate products that, usually, reduce the initial toxicity (Rosal et al., 2008).

4.3 Homogeneous fenton and fenton-like process

A widespread AOP is the homogeneous Fenton process involving the reaction of hydrogen peroxide (H_2O_2) with the Fenton catalyst (ferrous ion - $Fe(II)$ - dissolved in acid aqueous media) generating hydroxyl radicals ($\bullet OH$) and ferric ions ($Fe(III)$). $Fe(III)$ ions undergo reduction to $Fe(II)$ mainly through the action of the oxidant H_2O_2 ensuring the continuation of the catalytic reaction. The main reactions of the Fenton process are represented by Equations 35 to 41 (Garrido-Ramirez et al. 2010; Herney-Ramirez et al. 2010; Navalon et al., 2010, Umar et al., 2010).

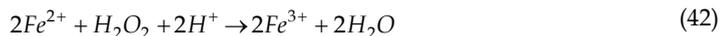


There are many variations of the Fenton process and the main ones are:

- Modified Fenton or Fenton-like reaction: ferric ion or another transition metal (such as copper) is used instead of ferrous ion (Herney-Ramirez *et al.*, 2010);
- Heterogeneous Fenton: supported catalyst is used in a solid matrix (heterogeneous system);
- Photo-Fenton: the regeneration of Fe(II) is accelerated due to photoreduction of Fe(III), and the generation of hydroxyl radicals is increased due to the photolysis of hydrogen peroxide (Equation 25) (Umar *et al.*, 2010);
- Electro-Fenton: continuous generation of H_2O_2 in acidic solution by reducing gaseous O_2 in carbon cathodes (Sirés *et al.*, 2007);

Other variations: heterogeneous Fenton-like, heterogeneous photo-Fenton, Photo-Fenton-like, and heterogeneous Photo-Fenton-like processes.

Equation 42 describes the Fenton reaction and its variations should occur at acid pH through the occurrence of hydrogen peroxide decomposition in the presence of a ferrous ion catalyst (Umar *et al.*, 2010).



The homogeneous Fenton process is carried out in four stages: (1) pH adjustment (optimal pH is around 2.8), (2) oxidation reaction through the action of oxidizing radicals (especially $\bullet\text{OH}$), (3) neutralization followed by coagulation (formation of ferric hydroxide complexes), and (4) precipitation (Umar *et al.*, 2010). Therefore, the organic substances are removed by oxidation and by coagulation. Thus, the homogeneous Fenton process has the great disadvantage of producing, at the end of the process, solid waste (sludge) with a high metal concentration, generating environmental risks and extra costs due to the post-treatment of sludge to recover

part of the catalyst (Herney-Ramirez et al., 2010, Umar et al., 2010). Hence, the heterogeneous Fenton process eliminates the step of catalyst precipitation and removal at the end of the process (Garrido-Ramirez et al. 2010; Herney-Ramirez et al. 2010 ; Navalon et al., 2010). Among the various factors that affect the efficiency of the Fenton process, pH and the $H_2O_2/Fe(II)$ ratio are the most important ones. In reactions with a low $H_2O_2/Fe(II)$ ratio, chemical coagulation is predominant in the removal of organic matter, whereas with high ratios the chemical oxidation is dominant (Umar et al., 2010).

4.4 Heterogeneous AOPs

The heterogeneous AOPs using a semiconductor as the catalyst and ultraviolet radiation have the advantage of not requiring the addition of a strong oxidant to produce hydroxyl radicals (photocatalysis process, e.g., the AOP TiO_2/UV). However, the addition of an oxidant can accelerate the production of oxidizing radicals and increase the speed of organic matter removal (e.g. the AOP $TiO_2/UV/H_2O_2$).

Photocatalysis is the catalysis of a photochemical reaction on the surface of a solid, usually a semiconductor, TiO_2 being the most used (Fujishima et al., 2008). In this reaction the oxidation of organic pollutants occurs in the presence of an oxidizing agent, followed by activation of a semiconductor with light energy (Ahmed et al., 2010) at wavelengths ≤ 400 nm (Malato et al., 2009).

The catalyst is activated when it absorbs photons with energies greater than the value of its "band gap" energy resulting in the excitation of electrons from the valence band to the conduction band forming a hole (h^+) in the valence band. This hole promotes the oxidation of pollutants (in the case of photo-catalytic oxidation of organic pollutants) or water, in the latter case producing hydroxyl radicals ($OH \bullet$). The electron (e^-) of the conduction band reduces the oxygen or other oxidative agent in the absence of O_2 (Ahmed et al., 2010). The oxidizing agent binds to the conduction band, where the reduction occurs through the gaining of electrons (e^-), while the organic compound to be degraded binds to the valence band, where oxidation occurs, donating e^- and receiving h^+ . Thus the organic compound is the reducing agent or electron donor (hole scavenger) (Malato et al., 2009).

Photocatalysis is an AOP because, during the photochemical reactions and the activation of the catalyst, hydroxyl radicals are formed (Malato et al., 2009, Hermann, 2010). Hence, these treatments may reduce the toxicity of wastewaters by total or partial mineralization of synthetic organic compounds transforming them into more biodegradable substances.

There are photocatalytic processes using solar energy, representing a Green Chemistry technology approach (Hermann, 2010), with the following benefits: 1) process carried out at ambient temperature and pressure, 2) the oxidizing agent can be oxygen obtained from the atmosphere, 3) many catalysts are low-cost, safe and reusable, and 4) use of solar energy as an energy source (Malato et al., 2009).

5. Water and wastewater management

Prior to the implementation of a tertiary process for wastewater treatment aiming at water reuse to reduce the consumption of fresh drinking water, it is essential to minimize and to optimize the water consumption in all processes of an industrial plant. Thus, it is essential to

understand the industrial process in detail, and to develop a methodology for water management, presenting alternatives for minimizing water consumption and effluent generation, obeying the specific laws of the industry sector.

The authors of this review carried out a water and wastewater management (W2M) study in a slaughterhouse based on water consumption and effluent generation in the various sectors. The W2M proposed was aimed at minimizing water consumption and the evaluation of possibilities for water and indirect potable reuse in food industries.

5.1 Case study in a meat processing plant

The case study was carried out in a meat processing plant located in the west of Santa Catarina State (southern Brazil) where water pollution and overexploitation, the uneven distribution of rainfall throughout the seasons and long periods of drought especially in summer, have become a problem. The industrial activities include the slaughter and processing of poultry and swine. The industry has its own drinking water treatment plant (DWTP) and wastewater treatment plant (WWTP). The major water resource of this industry is a river. Its DWTP produces around 8,600 m³/day of drinking water and the WWTP treats around 7,900 m³/day of wastewater. The first step of the wastewater treatment is equalization, followed by coagulation, flocculation, and flotation. The last step is the secondary treatment: activated sludge.

5.1.1 Water minimization

To evaluate the possibilities for water minimization, it was first necessary to analyze the current Brazilian laws concerning slaughterhouses for poultry and swine. These guidelines provide the technical standards required for the facilities and equipment used in the slaughter of animals and meat industrialization, including water quality and minimum water consumption in each process. As a further step, a water balance was carried out for all processes. The processes or equipment which have the greatest water demand are usually the most important and the easiest points for which to verify the possibilities to avoid the misuse and overexploitation of fresh water (drinking water from plant's DWTP). Hence, four high consumption points were identified with the potential for reducing the fresh water consumption in-line with the current Brazilian legislation: (1) pre-cooling of giblets, (2) washing of poultry carcasses before pre-chiller, (3) transportation of giblets, poultry necks and feet, and (4) washing of swine carcasses after buckling. It was found that in the first two processes the water consumption could be reduced; in the third process the devices could be substituted by others which do not need water to function properly; and in the last process there was an unnecessary step, according to the legislation. The minimization of the water demand achieved in these four process steps alone was approximately 806 m³/d.

5.1.2 Direct wastewater reuse

After the minimization of water use, the most important action is to prioritize direct recycling and reuse of wastewater, without the need for advanced reconditioning or treatment. Hence, following the water balance, the wastewater with the possibility for direct or indirect recycling or reuse was evaluated physically, chemically and microbiologically to verify if and where it could be recycled and reused. Four wastewaters were identified as having a real possibility of reuse after carrying out all of the characterization analysis: (1)

defrosting of refrigerating and freezing chambers, (2) purging of condensers, (3) cooling of smoke fumigator chimneys, and (4) sealing and cooling of vacuum pumps. These four wastewaters totaled approximately 1,383 m³/day of wastewater with the possibility for reuse in processes without direct contact with food products, that is, in non-potable uses (e.g., as cooling water, for flushing toilets or as irrigation around the plant), thus saving fresh potable water. These wastewaters had similar water quality parameters indicating that they could be mixed before undergoing the same reconditioning treatment. Hence, the mixed wastewater was also characterized and it was shown that it could be simply treated to remove total suspended solids and chlorinated/disinfected before reuse as, for example, cooling water.

The successful results achieved from the proposed W2M (*i.e.*, financial saving of 28.2% and 25.4% in the fresh water requirement - Table 4) prompted the managers of the pilot industrial plant to suggest and to develop other research projects related to water and wastewater reuse in partnership with Brazilian government funded research centers, to develop indirect wastewater technologies. These results are consistent with the work of Tokos et al. (2009) who presented several mixed-integer nonlinear programming models for the optimization of a water network in a brewery plant. The authors presented a theoretical reduction of around 27% in the fresh water demand and associated costs.

Condition	Water flow [m ³ /dia]	Water saving [%]	Annual Costs ¹ [\$]
Production in 2007	8,616.0	-	1,539,353
Theoretical production after water minimization	7,810.0	9.4	1,366,000
Theoretical production after wastewater reuse	7,216.8	16.0	1,256,996
Theoretical production after water minimization and wastewater reuse	6,410.0	25.4	1,104,731

¹Considering costs in 2007: \$0.10 and \$0.42 per m³ to treat water (DWTP) and wastewater (WWTP) respectively, in pilot industrial plant.

Table 1. Water and financial savings

5.1.3 Indirect wastewater reuse: indirect potable reuse

Additionally, to reduce even further the percentage of fresh water consumption, indirect wastewater reuse can be carried out after reconditioning of the secondary effluent (*i.e.*, after secondary activated-sludge treatment) by applying tertiary treatments such as advanced oxidation processes (AOPs). This tertiary treated water could be used in other processes without contact with food products, that is, non-potable uses (e.g. as cooling water, boiler feed water, toilet flushing water or for irrigation around the plant) (Cornel et al., 2011; Luiz et al., 2011).

Luiz and co-workers (2009, 2011) evaluated some AOPs in bench- and pilot-scale tests with the aim of providing reclaimed water with drinking water quality (according to Brazilian legislation) for industrial water reuse in processes without direct contact with food products. In the first study (Luiz et al., 2009) evaluated the kinetics of the photo-induced

degradation of color and UV₂₅₄ under UV radiation with and without the addition of H₂O₂ to treat secondary wastewater after ferric sulfate coagulation. The H₂O₂/UV treatment was 5.2 times faster than simple UV application in removing aromatic compounds.

In the second study (Luiz et al., 2011) four tertiary hybrid treatments using a pilot plant with a capacity of 500 L/h were evaluated. This pilot plant consisted of a pre-filtration system, an oxidation (H₂O₂) or second filtration system and a UV radiation device. The best combination was pre-filtration followed by H₂O₂ addition and UV radiation (AOP H₂O₂/UV). In addition to H₂O₂/UV treatment, the authors also carried out experiments in pilot scale with O₃, O₃/UV and O₃/H₂O₂. However, H₂O₂/UV was found to be a faster and more efficient option to treat slaughterhouse wastewater to the drinking water quality standard, with the exception of one quality parameter, that is, nitrate.

Hence, another treatment was evaluated by the authors to remove the nitrate content, allowing the reuse of the wastewater with drinking water quality in cases without direct contact with food products, reducing the fresh water consumption and conserving natural water resources. The p-n junction photocatalyst p-ZnO/n-TiO₂ was prepared by decomposition of zinc nitrate and photodeposition on TiO₂ and it was used to reduce nitrate ions in aqueous solution and in synthetic and real slaughterhouse wastewater.

Heterogeneous photocatalytic reduction of nitrate over semiconductor materials have also been developed as a promising method for controlling the concentration of nitrate in water. Metal doping (Pt, Pd, Rh, Pt-Cu, Cu, Fe, Bi) and addition of hole scavengers are essential for the reductive removal of nitrate (Rengaraj and Li, 2007; Sá et al., 2009; García-Serrano et al., 2009; Kim et al., 2008; Li et al., 2010). Hole scavengers are electron donors, such as methanol, benzene, oxalic acid, formic acid and humic acids which have been used to improve photocatalytic efficiency (Xu et al., 2010; Li and Wasgestian, 1998; Rengaraj and Li, 2007).

There were a number of studies related to the photocatalytic activity of TiO₂ or ZnO coupled with metals, and the results showed that these catalysts presented more efficient charge separation, and increased lifetime of the charge carriers, and an enhanced interfacial charge transfer to adsorb substrates (Shifu et al., 2008). Coupled photocatalyst ZnO/TiO₂ has showed higher photocatalytic activity than that of single one, since the p-n junction that is formed by the integration of p-type ZnO and n-type TiO₂ contributes to enhance the electrons/holes separation (Shifu et al., 2008).

The selectivity, conversion and activity data indicated ZnO-TiO₂ was a better catalyst than TiO₂ (Table 2). This indicates that Zn ion exerted its role as a doping ion, promoting the charge separation of the pairs of vacancy-electron photoproducted by acting as an electron sink, and consequently increase of electrons reaching the surface for reaction to take place (Sá et al., 2009; Ranjit and Viswanathan, 1997).

Catalyst	Selectivity [%]	Conversion [%]	Activity [$\mu\text{mol}_{\text{NO}_3^-} \cdot (\text{min } g_{\text{catalisador}})^{-1}$]
TiO ₂	70.71	87.46	0.92
ZnO-TiO ₂	95.45	91.67	14.24

Table 2. Selectivity (S_N) and conversion ($C\%$) within reaction time = 120 min and activity within reaction time = 20 min.

Prior to the photocatalytic reactions, the real wastewater (RSW) was filtered 50 micron cartridge filter, activated carbon filter and 10 micron cartridge filter to remove suspended

particles (RSW-F) simulating the microfiltration of the previous studies (Luiz et al., 2009, 2011). Due to low TOC concentration in RSW-F, formic acid was added as hole scavenger (Zhang et al., 2005; Rengaraj; Li, 2007; Sá et al., 2009; Malato et al., 2009; Wehbe et al., 2009). Formic acid was added in enough amount to satisfy the stoichiometric relationship nitrate:formic acid (Equation 43) without formation of intermediates (including nitrite and ammonia) (Zhang et al., 2005). Hence, the evaluated molar ratios were CHOOH:nitrate = 2.7, 1.6 and 1.0, respectively [HCOOH] = 1636, 1000 and 500 mg L⁻¹ or 427, 261 and 130 mg C L⁻¹, and catalyst 1 g L⁻¹.



Therefore, after the application of microfiltration for the removal of mainly suspended solids and the catalytic photoreduction of nitrate with the addition of a hole scavenger (carbon source), it was necessary to remove the excess of this carbon source. Hence, after nitrate was below the Brazilian legislation limit, (CHOOH_{initial (0 min)}:H₂O_{2, initial (120 min)} = 1:1 (M:M)) was added into the reaction to promote another advanced oxidative process (AOP): H₂O₂/TiO₂/UV (Figure 1). Hence, after all these steps, the wastewater achieved drinking water quality, being the main critical parameters shown in Table 3.

	RSW ²	RSW-F ²	A ¹	B ¹	C ¹	BRL ³
pH	6.8 ± 0.6	6.2 – 6.5	6.20	6.15	6.00	6.0 - 9.50
Turbidity, FTU	40 ± 33	22 – 25	2.00	2.00	1.00	5
Apparent color, Pt-Co unit	217 ± 177	11 – 13	3.00	3.00	10.00	15
Total coliforms, CFU/100 mL	> 10 ⁵	> 10 ⁵	0	0	0	0
Nitrate, mg N L ⁻¹	45.9 ± 17.7	39.8 – 41.9	1.20	4.50	4.00	10
Nitrite, mg N L ⁻¹	-	3.74 – 3.77	0.06	0.08	0.21	1
Ammonia, mg N L ⁻¹	-	0.4 – 1.0	0.30	0.90	0.30	1.24

¹ Composite samples (RSW). Composite samples after filtration (RSW-F)

²A: [CHOOH]_i = 1636 mg L⁻¹ / H₂O₂ = 1209 mg L⁻¹; B: [CHOOH]_i = 1000 mg L⁻¹ / H₂O₂ = 739 mg L⁻¹; C: [CHOOH]_i = 500 mg L⁻¹ / H₂O₂ = 370 mg L⁻¹. Zn-TiO₂ catalyst = 1 g L⁻¹. Reaction time: 300 min.

³BRL: Brazilian regulatory legislation (Brazilian drinking water standards: Brazilian Ministry of Health Administrative Ruling 518/2004).

Table 3. Average quality of the secondary effluent of the slaughterhouse and quality parameters of the wastewater after the treatments: filtration (RSW-F, Table 1) + TiO₂/UV/Argon (reaction time 120 min) + H₂O₂/TiO₂/UV (reaction time 300 min).

Table 3 shows the average characterization of three composite samples collected to characterize the secondary effluent from the slaughterhouse (RSW). The real effluent slaughterhouse wastewater used in those studies was collected after treatment (coagulation+floculation followed by aerobic biological treatment) from a Brazilian poultry slaughterhouse. The point to collect real treated effluent was the one located immediately outside the secondary sedimentation tank. A composite sample of 24h (1 L of sample collected per hour for 24 hours) was collected and characterized. All organic, inorganic and microbiological parameters of Brazilian drinking water standards (Brazilian Ministry of

Health Administrative Ruling 518/2004) were analyzed, and only nitrate, nitrite, color, turbidity and total coliform were above the limit. The proposal treatments were able to reduce those parameters and also remove micropollutants that are not removed by secondary treatment (e.g. activated sludge).

The influent of the slaughterhouse RSW contained the mixture of sewage from meat processing and sanitary sewage, the treated wastewater still contained persistent pollutants arising from animal and human use, e.g., drugs and personal care products. The target compounds nonyl- (NP) and octylphenol (OP), linear alkylbenzene sulfonates (LAS), triclosan and ibuprofen could be detected and confirmed applying a LTQ Orbitrap mass spectrometer (Thermo Electron, Bremen, Germany) to the SPE-extracts after HPLC-(HR)MS. Besides these pollutants octylphenol- (OPEO) and nonylphenol ethoxylates (NPEO), polyethylene glycols (PEG), erythromycin, sulfamethoxazole and sulfadimidine were also observed.

The AOPs evaluated were also very effective to remove the micropollutants present in the already treated slaughterhouse wastewater. Among all the compounds found by LC-MS in the samples only NP, NPEO and PEG were still observable in the samples after the tertiary treatments proposed, however, in lower amounts.

Figure 1 shows the suggested flowchart of the process suggested by the authors to treat secondary wastewater with high concentrations of nitrogen compounds and recalcitrant organic compounds as antibiotics, medicament and personal care products which are commonly found in sanitary, domestic and industrial wastewater.

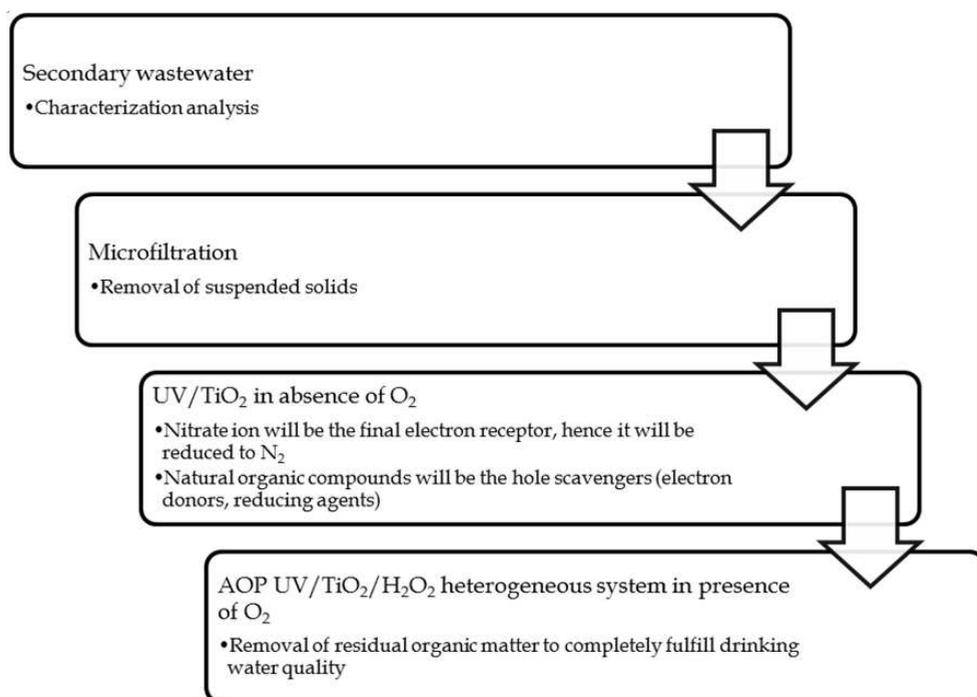


Fig. 1. Suggested process to treat secondary wastewaters with high concentration of nitrate and residual organic matter.

6. Selection of an AOP and alternatives for water reuse

As proposed in section 5.1 (Case Study in a Meat Processing Plant), experiments in bench and pilot scale should be carried out before the selection of an AOP for the tertiary treatment of the wastewater intended for reused (Sievers, 2011). This initial research would define: (i) the best treatment for each kind of industrial wastewater considering the reused water quality required and hence which improvements should be sought (e.g. color or turbidity removal, target recalcitrant organic compound removal, disinfection); (ii) the kind and quantity of radical scavengers present in the wastewater (e.g. humic substances); (iii) the dosage of oxidant (if used) and the impact of its residual concentration on the subsequent use or disposal of the tertiary treated wastewater, and (iv) the energy and investment costs (Sievers, 2011).

The tertiary treated water could be used in other processes without contact with food products (non-potable uses) where public health and product integrity would not be compromised. Therefore, "this major health concern makes it imperative for governments and the global community to implement proper reuse planning and practices, emphasizing public health and environmental protection" (EPA, 2004). Boiler feed water, cooling water, toilet flushing water or irrigation around the plant are some alternatives for the use of reclaimed water (Cornel et al., 2011; Luiz et al., 2011). Cooling water may be the most attractive option because it does not need to be of high quality, and usually a large amount is required (Cornel et al., 2011).

A sentence at EPA (2004) resume the past and the future of wastewater reuse (indirect potable reuse): "Notwithstanding the fact that some proposed, high profile, indirect potable reuse projects have been defeated in recent years due to public or political opposition to perceived health concerns, indirect potable reuse will likely increase in the future" (EPA, 2004).

7. References

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