



ADVANCED OXIDATION PROCESSES AND THEIR APPLICATION IN THE PETROLEUM INDUSTRY: A REVIEW

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Abstract. Advanced oxidation processes (AOP) are technologies based on the generation of highly reactive species, the hydroxyl radicals, used in oxidative degradation procedures for organic compounds dissolved or dispersed in aquatic media. These processes are promising alternatives for decontamination of media containing dissolved recalcitrant organic substances, which would not be efficiently removed by conventional methods. The present paper describes a series of AOP, analyzing the aspects related to each type of process, such as the interference of external agents and the ideal operating conditions, based on the analysis and comparison of different studies in the area. In addition, several applied AOP studies on treatment of oil wastewater and on remediation of soil contaminated with oil or its derivatives are presented.

Keywords: advanced oxidation processes; petrochemical wastewater; oil wastewater; hydrocarbons degradation; photocatalysis; Fenton's reagent; photo-Fenton; ozonation; wet air oxidation; electro-oxidation; wastewater treatment

1. INTRODUCTION

Despite the importance of oil in the world economy, the environmental question that surrounds its production must always be well assessed, owing to the composition of its residues and of the oil itself, which consists mainly of aromatic and aliphatic compounds (Mariano, 2005).

The toxicity of the aromatic fraction is higher than that of the aliphatic fraction. Aromatic compounds are known to be more recalcitrant, among which are benzene, toluene, ethylbenzene, xylene isomers (the so-called BTEX), and phenols (Stepnowski, 2002).

Contaminations from oil components can occur during the extraction process in

sedimentary basins and as a result of storage tank leaks, including gasoline stations and during marine transport (oil tankers) (Watts *et al.*, 2000). Moreover, during its processing a large volume of hydrocarbon-rich wastewater is generated, which, if left untreated, causes serious environmental impacts (Durell *et al.*, 2006). A large part of this wastewater is produced along with oil during gas and oil extraction processes in oil wells. The amount of wastewater produced can be 95% higher than the oil extracted in certain production wells.

The liquid wastes generated in refineries vary considerably in terms of amount and quality, as a function of the type of oil processed, the processing units of the refinery,

Table 1. Physical-chemical characteristics of oil refinery wastewaters.

Parameter	Limits	
	Minimum	Maximum
Temperature (°C)	22	41
pH	6.2	10.6
BOD (mg/L)	17	280
COD (mg/L)	140	3340
Sulfides (mg/L)	0	38
Hardness as CaCO ₃ (mg/L)	139	510
Alkalinity as CaCO ₃ (mg/L)	77	356
Oil (mg/L)	23	200
Phosphorus (mg/L)	0	97
NH ₃ (mg/L, as N)	0	120
Chlorides (mg/L)	19	1080
Sulfates (mg/L)	0	182

and the operation mode of these units. Refineries generally produce an amount of liquid waste that is relatively proportional to the amount of oil refined. Table 1 shows the general physical-chemical characteristics of refinery wastewaters (Mariano, 2005).

The conventional techniques applied in the treatment of these wastewaters are physical-chemical and mechanical, generally associated with biological treatment. The conventional treatments include gravitational separation, centrifugation, application of coagulants, flotation, filtration, and adsorption with activated coal, among others (Yavuz and Koparal, 2006; Saien and Nejati, 2007). These conventional techniques manage to remove free and emulsified oil and solids in suspension from the wastewater, in addition to reducing BOD when associated with biological treatment. However, applying the biological process is inadequate when the wastewater contains highly toxic recalcitrant compounds, such as the aromatic fraction from the dissolved organic compounds. In this case, more advanced techniques must be used to degrade these compounds (Yavuz and Koparal, 2006;

Saien and Nejati, 2007).

One of the processes for treating water containing toxic organic pollutants that has been increasingly used in recent years is the advanced oxidation process (AOP), a powerful tool applied to degrade these pollutants (Bolton *et al.*, 2001; Safarzadeh-Amiri *et al.*, 1997; Ghaly *et al.*, 2001; Pera-Titus *et al.*, 2004; Pérez-Moya *et al.*, 2007; Durán *et al.*, 2008).

2. ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOP) are technologies characterized by the generation of hydroxyl radicals, which are highly reactive and non-selective substances used to degrade toxic organic compounds present in a medium (such as wastewater and soil).

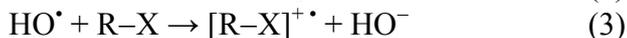
The hydroxyl radical has a high oxidation potential ($E^0 = 2.8$ V), as shown in Table 2 (Pera-Titus *et al.*, 2004), and is able to react with practically all classes of organic compounds, resulting in complete mineralization of these compounds, that is, the formation of carbon dioxide, water and inorganic salts, or their conversion into less

Table 2. Standard reduction potentials of some oxidants in volts (V) compared with the normal hydrogen electrode (NHE, $E^0 = 0$ V). Adapted from Legrini and coworkers (1993).

Oxidant	Standard reduction potential / V
Fluorine (F ₂)	3.03
Hydroxyl radical (\cdot OH)	2.80
Ozone (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.77
Potassium permanganate (KMnO ₄)	1.67
Chlorine dioxide (ClO ₂)	1.50
Chlorine (Cl ₂)	1.36
Bromine (Br ₂)	1.09

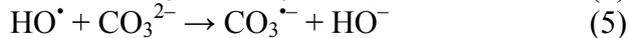
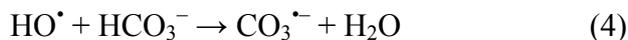
aggressive products (Andreozzi *et al.*, 1999; Bolton *et al.*, 2001; Pignatello, 1992). Pollutant destruction and consequent inhibition of generation of toxic residues are some of the main advantages of AOP, given that conventional water treatment methods such as flotation, filtration and adsorption with active coal are non-destructive physical separation processes, that is, they only remove the pollutants, transferring them to other phases, thereby generating concentrated deposits, as reported by Crittenden and coworkers (1997a).

The possible reaction pathways involving the attack of hydroxyl radicals onto organic compounds are: the electrophilic addition of a hydroxyl radical to organic compounds (unsaturated or aromatic) that contain a π bond leading to the formation of organic radicals (Equation 1), the hydrogen abstraction by reacting the hydroxyl radical with a saturated aliphatic compound (Equation 2) and electron transfer with reduction of the hydroxyl radical into a hydroxyl anion by an organic substrate (Equation 3) (Bossmann *et al.*, 1998; Tang, 2004).



The hydroxyl radical attack on organic substrates may be influenced by the presence of a number of chemical species in water (or originating in the mineralization process), such as carbonate and bicarbonate ions (Andreozzi

et al., 1999). These ions can react with the hydroxyl radicals (Equations 4 and 5), hence competing with the organic substrates through the hydroxyl radicals.



Hydroxyl radicals can be generated from several AOP, enabling the application of a better process for each specific treatment condition. According to Huang and coworkers (1993), the AOP can be classified as homogeneous and heterogeneous. Domènech and coworkers (2001) presented this classification in terms of whether light is used in the process. Table 3 shows a classification of AOP according to these authors.

The AOP are expensive processes owing to the high cost of reagents such as H_2O_2 and O_3 and electric energy when UV radiation is applied. For this reason they are considered in alternative treatment of wastewater that cannot be biologically treated.

Another significant aspect is the load of pollutants present in the wastewater, regularly expressed in terms of chemical oxygen demand (COD). The use of these processes is indicated only for wastewaters with COD below 5 g L⁻¹, given that a higher COD index would require very high consumption of reagents, precluding the treatment (Andreozzi *et al.*, 1999).

For wastewaters with high organic load, pretreatment operations, like dilution, coagulation and flocculation, are required in order to reduce the initial load (Rivas *et al.*,

Table 3. Types and classification of advanced oxidation processes.

Non-photochemical		Photochemical	
Homogeneous processes			
<ul style="list-style-type: none"> Ozonation in alkaline media (O_3/HO^-) Ozonation with hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$) Fenton ($\text{Fe}^{2+}$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$) Electro-oxidation Electrohydraulic discharge - ultrasound Wet air oxidation (WAO) Supercritical water oxidation (SCWO) 	<ul style="list-style-type: none"> Photolysis of water in vacuum ultraviolet (VUV) UV/H_2O_2 UV/O_3 UV/$\text{O}_3/\text{H}_2\text{O}_2$ Photo-Fenton (Fe^{2+} or $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$) 		
Heterogeneous processes			
<ul style="list-style-type: none"> Catalytic wet air oxidation (CWAO) 	<ul style="list-style-type: none"> Heterogeneous photocatalysis: ZnO/UV, SnO_2/UV, TiO_2/UV, $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ 		

2004). In contrast, AOP can be applied in the treatment of contaminated waters with very low organic loads (in ppb) and which contain dissolved organic compounds which are difficult to remove.

One way of reducing the costs of AOP is to use them as preliminary treatment operations to reduce toxicity, followed by biological treatment. This option has proven to be quite interesting from an economic point of view and has been studied by several authors (Martín *et al.*, 2008; Chamarro *et al.*, 2001; García-Montaña *et al.*, 2008; Lucas *et al.*, 2007; Malato *et al.*, 2007; Pérez-Moya *et al.*, 2007).

2.1. H₂O₂/UV

Hydrogen peroxide (H₂O₂) is a strong oxidant (see Table 2) applied, among other purposes, to reduce the low levels of pollutants present in wastewaters, as reported by Neyens and Baeyens (2003). However, the individual use of H₂O₂ is not efficient in oxidizing more complex and recalcitrant materials with a low reaction rate. The use of H₂O₂ becomes more effective when it acts in conjunction with other reagents or energy sources capable of dissociating it to generate hydroxyl radicals, which will act as oxidizing agents. With UV irradiation in wavelengths shorter than 300 nm, H₂O₂ can decompose and generate hydroxyl radicals, as shown in Equation 6.



Hydrogen peroxide can also react with hydroxyl radicals and the intermediary products formed thereby, according to the reaction mechanism described in a simplified way by Equations 7 to 11 (Alfano *et al.*, 2001).



The attack on organic compounds occur due to the hydroxyl (HO[•]) and hydroperoxyl (HO₂[•]) radicals formed. However, the hydroperoxyl radicals have a lower reduction potential

(1.7 V) than that of hydroxyl radicals (2.8 V); therefore, their generation is not interesting to the process. Several studies have shown that the rise in the initial concentration of H₂O₂ increases the degradation rate of contaminants up to a maximum value, after which they begin to decline when they reach very high H₂O₂ levels (López *et al.*, 2000; Cisneros *et al.*, 2002; Lunar *et al.*, 2000; Tang and Chen, 1996; Zhao *et al.*, 2004). López and coworkers (2000) attribute this decrease in the H₂O₂/UV process yield to hydroxyl radicals reacting with excess H₂O₂ (Equation 7), instead of reacting with the organic substrates, leading to the formation of the hydroperoxyl radical HO[•].

The photolysis of H₂O₂ is normally obtained with low or medium pressure mercury vapor lamps, both with high intensity, in order to reduce the amount of H₂O₂ needed. Nearly 50% of the energy consumed is lost in the form of heat or in emissions of wavelengths shorter than 185 nm, which are observed by the quartz jacket (Litter, 2005). The germicide lamp is a widely used cheaper alternative; however, the efficiency is lower because it emits in the 210 to 240 nm range and H₂O₂ absorption reaches a maximum of 220 nm.

The advantages of using the H₂O₂/UV process can be attributed to the fact that the reagent (H₂O₂) is totally soluble in water, there is no mass transfer limitation, it is an effective source of HO[•], and there is no need for a separation process after treatment (Gogate and Pandit, 2004b; Litter, 2005).

The operational pH must be low (pH < 4) to nullify the effect of sequestering radical species, specifically ionic species such as carbonate and bicarbonate ions, leading to a better degradation rate.

2.1.1. Application

Stepnowski and coworkers (2002) assessed the use of H₂O₂ in the presence and in the absence of UV radiation, in degrading an oil refinery wastewater pretreated with flotation and coagulation, analyzing total petroleum hydrocarbons (TPH), dichloromethane (DCM), 1,2-dichloroethane (DCE) and methyl *tert*-butyl ether (MTBE). It was observed that UV radiation did not significantly influence

compound degradation, with the exception of DCM, which was the most stable of all. In total 83% was removed with 11.76 nM of H₂O₂ in the presence of UV radiation. The authors observed slow degradation of the TPH, which removed 69% of the total initial concentration in 8 days of the experiment. The MTBE degradation was similar to that of DCE and after 24 hours there was total degradation.

The application of the H₂O₂/UV process to purify oily wastewater from a lubricant-producing unit belonging to an oil company was studied by Philippopoulos and Pouloupoulos (2003). Chromatographic analyses show that most of the compounds identified in the wastewater were removed by the end of the treatment, using a high concentration of H₂O₂. Nevertheless, a reduction of only 40% of the initial COD of the wastewater was obtained (around 9000 mg/L⁻¹). The authors attribute this to the formation of organic acids, resulting from the decomposition of organic compounds present in the wastewater, which are more resistant to photo-degradation with H₂O₂. The effect of pH on the process was also analyzed and it was found that in acid pH (3.5), there was enhanced reduction in the COD of the wastewater, when compared to neutral and basic pH's.

Hu and coworkers (2008) studied the degradation of MTBE, a gasoline additive and one of the most common contaminants in contaminated underground waters in the USA, owing to leakages in gasoline station storage tanks. The H₂O₂/UV process was assessed, which, under specific conditions, removed up to 98% of the MTBE. An increase in the removal percentage was found with a rise in H₂O₂ concentration, but up to a maximum value, after which this percentage started to fall. The authors attribute this effect to the competitive reactions of H₂O₂ and hydroxyl radicals shown in Equations 7 to 11.

2.2. Fenton and photo-Fenton

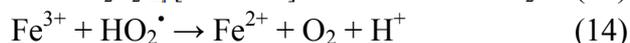
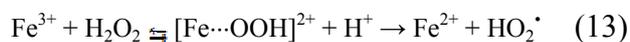
Fenton's reagent is a solution of hydrogen peroxide and ferrous ions and was discovered by the chemical engineer Henry John Horstman Fenton (1854-1929), reporting in 1894 that this solution in acid medium had high oxidizing

power (Machulek Jr., 2007; Fenton, H. J. H., 1894). However, Huang and coworkers (1993), cited by Neyens and Baeyens (2003), mentioned that the application of Fenton's reagent in oxidation processes to destroy toxic organic compounds was only attempted in the 1960s. There is considerable controversy about the reaction mechanism involving Fenton's reaction. The classic Fenton reaction interpreted by Haber and Weiss (1934), as cited by Bossmann and coworkers (1998), consists of an aqueous combination of hydrogen peroxide (H₂O₂) and ferrous ions (Fe²⁺), in acid medium, leading to the decomposition of H₂O₂ into a hydroxyl ion and a hydroxyl radical, and the oxidation of Fe²⁺ to Fe³⁺, as represented by Equation 12.



The Fe²⁺ and Fe³⁺ species, shown in a simplified form, correspond to the [Fe(OH)(H₂O)₅]⁺ aqueous complexes, which, together with H₂O₂, form the [Fe(OH)(H₂O₂)(H₂O)₄]⁺ and [Fe(OH)(H₂O)₅]²⁺ complexes, respectively, as reported by Bossmann and coworkers (1998).

As shown by Walling and Weill (1974), the Fe³⁺ formed in Equation 12 can react with the H₂O₂ present in the medium and be reduced to Fe²⁺ again, forming the hydroperoxyl radical, according to Equation 13. This reaction, referred to by Neyens and Baeyens (2003) as Fenton-like, occurs more slowly than reaction 12, as reported by Pignatello (1992). The Fe³⁺ ions also react with the HO₂[•] and are reduced to Fe²⁺, as shown by Equation 14.



The initial degradation rate using Fe⁺³ is much lower than that using Fe⁺², as pointed out by Safarzadeh-Amiri and coworkers (1997) and shown by Wang (2008).

The ideal pH in Fenton's reaction found in a number of studies is 3 (Benitez *et al.*, 2001; Gallard *et al.*, 1998; Guedes *et al.*, 2003; Lin and Lo, 1997; Pignatello, 1992), considered therefore to be the operating pH. At very low

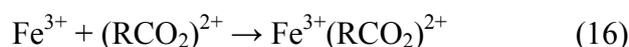
pH (< 2.5), the formation of complexes, such as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, occurs. These react more slowly with H_2O_2 than does $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{+}$, producing a lower amount of hydroxyl radicals, thus decreasing the system efficiency (Gallard *et al.*, 1998). At basic pH, iron reacts with the hydroxide ions (HO^-), precipitating the iron hydroxide ($\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$), which does not react with H_2O_2 , consequently precluding the Fenton reaction. Therefore, an adjustment in pH is required in the wastewater to be treated before adding the Fenton reagents.

It is important to previously establish the optimal relationship between ferrous and hydrogen peroxide ions. When higher concentrations of ferrous ions than hydrogen peroxide ions are used, the hydroxyl radicals generated by Equation 12 may react with excess ferrous ions, according to Equation 15, decreasing the attack of hydroxyl radicals on organic substrates (Neyens and Baeyens, 2003).



Guedes and coworkers (2003) observed that, although a $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio of 1:2 has a higher degradation rate, it is usually recommended to use the 1:5 ratio, which yields similar results and requires fewer reagents.

In most cases, the Fenton's reaction alone is not capable of degrading organic compounds and mineralizing them efficiently. The Fenton's reaction is effective up to the moment at which all the Fe^{2+} present in the medium is oxidized to Fe^{3+} , thus interrupting the generation of hydroxyl radicals and, consequently, the degradation of organic compounds. According to Balanosky and coworkers (2000), cited by Maciel and coworkers (2004), one of the factors that contribute to the interruption of the Fenton's reaction is that Fe^{3+} ions can form stable organic compounds (under normal conditions) with the degradation products (mainly the organic acids) present in the medium, as shown by Equation 16, impairing the regeneration of Fe^{2+} .

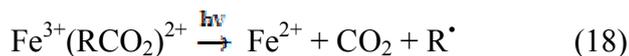


Although it has been widely studied and provided good wastewater treatment results, the Fenton's reaction was recognized as a powerful tool to degrade organic compounds when ultraviolet radiation is added to the system. This was achieved when Pignatello (1992) applied it in the treatment of wastewaters containing toxic organic pollutants in the early 1990s. It has served as a starting point for a number of studies related to the application of the photo-Fenton process (Bolton *et al.*, 2001; Celin *et al.*, 2003; Derbalah *et al.*, 2004; Durán *et al.*, 2008; Emilio *et al.*, 2002; Fallmann *et al.*, 1999; Gernjak *et al.*, 2003; Kavitha e Palanivelu, 2004; Maletzky and Bauer, 1998; Moraes *et al.*, 2004; Oliveros *et al.*, 1997; Pérez-Moya *et al.*, 2007; Rodríguez *et al.*, 2005; Sýkora *et al.*, 1997; Xu *et al.*, 2007).

According to Pignatello (1992), UV irradiation strongly accelerates the degradation rate of organic pollutants from Fenton's reagent, which has the advantage of being sensitive to UV-Vis radiation for wavelengths above 300 nm. Under these conditions, the photolysis of Fe^{3+} complexes enables regeneration of Fe^{2+} and the occurrence of Fenton's reaction, if H_2O_2 is available. Faust and Hoigné (1990) reported that the dominant species (between pH 2.5-5) in the photo-Fenton process is the ferric complex $\text{Fe}(\text{OH})^{2+}$, a simplified form of representing the aqueous complex $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, and the photolysis of this complex (wavelengths < 410 nm) is the largest source of hydroxyl radicals (Equation 17). Other photoreactive species are also present in the reaction medium, such as $\text{Fe}_2(\text{OH})_2^{4+}$ and $\text{Fe}(\text{OH})_2^+$, possibly leading to the formation of hydroxyl radicals (Faust and Hoigné, 1990).



Safarzadeh-Amiri and coworkers (1997) reported that Fe^{2+} regeneration can also occur with the photolysis of the complexes formed (Equation 16) from Fe^{3+} and the organic products generated in the degradation process, as shown by Equation 18.



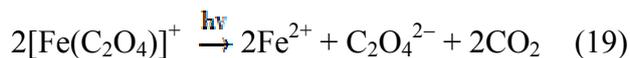
Thus, the ferrous ions regenerated by Equations 17 and 18 can react again with the H_2O_2 in solution (Equation 12) to generate more hydroxyl radicals, creating a photocatalytic cycle in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system. The use of radiation reduces significantly the concentration of ferrous ions required, compared with the dark Fenton reaction (in the absence of light). The concentration of ferrous ions must not be very high, as in the Fenton's reaction, in order to achieve good efficiency, since the addition of ferrous ions increases solution opacity, hindering radiation penetration and compromising Fe^{2+} regeneration when oxidized to Fe^{3+} . As a consequence, the degradation rate is diminished, as reported by Bhatkhande and coworkers (2004).

Malato and coworkers (2002) also cite the high depth of light penetration and the intense contact between the pollutant and the oxidizing agent as advantages of the photo-Fenton process, since it is a homogeneous process.

The disadvantages of the photo-Fenton process are associated with the low pH values required (normally below 4) and the need to remove iron after the reaction. However, as reported by Mota (2005), iron removal may not be needed if is used at concentrations below the discard limit established by law. It is important to have prior knowledge of the physical-chemical characteristics of the wastewater to be treated by this process because some substances or inorganic ions, such as Cl^- , SO_4^{2-} , H_2PO_4^- / HPO_4^{2-} present in the wastewater or added as reagents (FeSO_4 , FeCl_3 , HCl , H_2SO_4) may interfere in the reaction mechanism of the Fenton and photo-Fenton system, inhibiting the degradation process, as reported by De Laat and coworkers (2004) and Nadtochenko and Kiwi (1998). De Laat and coworkers (2004) suggest that the possible causes of these effects are the complexation reactions of the inorganic ion with Fe^{2+} or Fe^{3+} ions and the reactions with hydroxyl radicals that lead to the formation of less reactive inorganic radicals ($\text{Cl}^{\bullet-}$, $\text{Cl}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$).

Machulek Jr and coworkers (2007) found that the formation of $\text{Cl}_2^{\bullet-}$ radical anions, due to the presence of chloride ions in the reaction medium, can be avoided by controlling pH at 3 during the reaction period, given that the degradation process of an organic substrate by the photo-Fenton process leads to the formation of acids and thus pH reduction. It occurs due to pH decrease lower than 2.5 in the presence of chlorides ions, leading to more intense formation of ferric chloride complexes (FeCl^{2+} and FeCl_2^+). These complexes also undergo photolysis, thereby decreasing the amount of $\text{Fe}(\text{OH})^{+2}$, which is the main source of hydroxyl radicals in the photo-Fenton process, in addition to the formation of the $\text{Cl}_2^{\bullet-}$ radical anion, which can react with Fe^{2+} (oxidizing to Fe^{3+} without the formation of hydroxyl radicals) and the organic substrate.

One of the main advantages of using the photo-Fenton process compared with the other oxidation processes consists on using solar radiation in its reaction process. In this case, according to Machulek Jr. (2007), in the presence of oxalate ions ($\text{C}_2\text{O}_4^{2-}$), the Fe^{3+} present in the aqueous medium may form the $[\text{Fe}(\text{C}_2\text{O}_4)]^+$ complex (Equation 19), which absorbs light at wavelengths below 570 nm (the larger part of the visible UV solar spectrum).



The possibility of using solar radiation represents an enormous saving from the energetic point of view, given that there will be no need to use lamps. The development of pilot wastewater treatment plants that use solar reactors applied to the advanced oxidation processes has been one of the main focuses of research in the area (Blanco *et al.*, 1999; Dillert *et al.*, 1999; Gernjak *et al.*, 2006; Kositzi *et al.*, 2004; Malato *et al.*, 2002; Malato *et al.*, 2003; Momani *et al.*, 2007; Xu *et al.*, 2007).

2.2.1. Application

Safarzadeh-Amiri and coworkers (1997) used ferrioxalate as a source of iron in degrading different wastewaters containing BTEX, 1,4-dioxane and methyl *tert*-butyl ether,

using the photo-Fenton process and compared it with other photodegradation processes. Based on the use of energy, the results showed that, in some cases, the process was up to 30 times more efficient than the UV/H₂O₂ and UV-Vis/Fe²⁺/H₂O₂ processes. Thus, the authors concluded that the process using ferrioxalate requires less electric energy than the UV/H₂O₂ process, resulting in lower treatment costs.

Moraes and coworkers (2004) used the photo-Fenton process to degrade the hydrocarbons present in saline synthetic wastewater prepared with gasoline to simulate the water produced in oil production fields that contain high concentrations of dissolved salts. It was found that, in the presence of salt (NaCl), total pollutant degradation did not occur. This was achieved in tests without adding salt to the synthetic wastewater. The authors attributed this effect to Fe³⁺ ions that reacted with Cl⁻ ions, forming FeCl²⁺ complexes, which, in the presence of UV radiation, may give rise to Cl₂^{•-} radicals (lower oxidation potential than the HO[•] radicals), hence reducing the efficiency of the process.

Tiburtius and coworkers (2005) investigated the oxidation potential of the Fenton and photo-Fenton processes to degrade a solution containing benzene, toluene and xylenes (BTX) and water contaminated with gasoline (containing 25% ethanol). Rapid degradation of the BTX compounds was observed as well as the formation of intermediate phenolic compounds in the initial reaction periods that were completely degraded after 30 minutes of reaction. A level of 75% in degradation of total hydrocarbons present in gasoline-contaminated water was achieved, and the BTX compounds were removed in the first minutes of the reaction (when phenolic compounds were formed), after which they degraded slowly.

Mota and coworkers (2005) studied the photo-Fenton process in degrading phenol, a very common pollutant in the petrochemical industry, using black light fluorescent lamps as an UV-A radiation source. These are much cheaper and more economical (from the energy consumption point of view) compared with medium pressure mercury vapor lamps. The efficiency of black light fluorescent lamps was

confirmed when the dark Fenton and photo-Fenton processes to degrade phenol were compared. Degradation was twice as high when the photo-Fenton process was applied. The phenol degradation rate increased with the rise in intensity of the radiation emission source, owing to increased Fe²⁺ ion regeneration (Equation 17), and consequent elevation in the hydroxyl radicals generated. The authors report that the study of this variable is important because it enables the construction of reactors that use lamps as the UV emission source, which are important in companies that require continuous treatment of their wastewater. This cannot be done with solar reactors alone, given that they only operate in periods in which there is sunlight.

The photo-Fenton process for treating water-containing diesel oil was studied by Galvão and coworkers (2006). They conducted a study to optimize the amount of reagents used, in order to achieve high levels of degradation with a smaller amount of reagents. With Fe²⁺ ion concentrations of 0.1 mM, an amount below the maximum discard limit permitted by Brazilian law (0.27 mM), there was 99% degradation of the organic compounds originally present in the wastewater, expressed as total organic carbon (TOC). It is important for the photo-Fenton process to be effective, from the economic point of view, under these operational conditions, since it does not require subsequent treatment to remove residual iron.

Coelho and coworkers (2006) assessed the degradation of acid water effluents from oil refineries, which contained emulsified oil and a series of low-biodegradability micropollutants (such as phenols, sulphides, mercaptanes, ammonias, cyanides), through the application of different AOP. Among the processes analyzed, the Fenton and photo-Fenton obtained the best results. The dark Fenton reaction was used until reaction stagnation (with the removal of only 27% of initial dissolved organic carbon – DOC), followed by the photo-Fenton process, with the use of UV radiation. The combination of these two processes, applied continuously, reduced the initial DOC by 94%. The BTEX pollutants present in the original wastewater were

removed to non-detectable levels. The authors report that the Fenton and photo-Fenton processes were efficient in removing pollutants from the wastewater; however, high concentrations of reagents were used. They assert that an optimization study is needed to reduce the amount of reagents, making the process more effective.

Mater and coworkers (2007) investigated the efficiency of Fenton's reagent in the mineralization of organic compounds present in water contaminated with crude petroleum. The process was assessed by monitoring the H_2O_2 (with spectrophotometric measurements) and by the titrimetric quantification of CO_2 , which enabled the authors to calculate the rate of mineralized total organic carbon (TOC). These analyses showed a 75% reduction in the initial TOC of water contaminated with crude oil.

2.2.2. Soil treatment application

In addition to contaminating water, oil and its derivatives can also contaminate the soil, requiring an effective remediation process.

Soil remediation is one of the greatest challenges to technicians and researchers. Studies applying advanced oxidation processes have proven to be effective in treating and recovering soil, mainly because they are faster than the biological processes and are able to degrade toxic recalcitrant matter.

Fenton's reaction has been the most widely used process in the remediation of soils contaminated with toxic organic pollutants. In the reaction, the sources of iron are varied, and include the minerals found naturally in the soil.

Watts and Dilly (1996) analyzed different species of iron used as catalyst in the Fenton-like reaction to remediate diesel-contaminated soil. It was shown that the reaction of H_2O_2 catalyzed by iron (III) ions (Fenton-like) was more effective than that catalyzed by iron (II) ions (Fenton). Among the iron salts analyzed, iron (III) perchlorate and iron (III) nitrate were those that yielded the best percentages of diesel oxidation. However, the authors underscore that the large-scale use of iron (III) perchlorate is limited, since this reagent is not commercially available.

The remediation of diesel-contaminated soil was also studied by Kong and coworkers (1998). They used iron species in their mineral form (geotite and magnetite) and in their soluble salt form ($FeSO_4$) as catalyst and reagent for the Fenton's reaction. It was found that, although the use of mineral iron takes more time to reach the indices of diesel degradation (around 50%) obtained with the $FeSO_4$ solution, it requires a lower concentration of H_2O_2 , which makes its application more economically effective than that using $FeSO_4$.

Watts and coworkers (2000) studied the decontamination of soil containing gasoline, using Fenton's reagent, individually analyzing the degradation of aliphatic and aromatic compounds present therein. It was observed that, despite being more recalcitrant and toxic, the aromatics need fewer reagents (iron and hydrogen peroxide) for oxidation than do the aliphatic components. The authors emphasize the rapid action of the Fenton's reagent, which can effectively treat oil-contaminated soils in hours or days, whereas the bioremediation or natural attenuation of soil can take months or years.

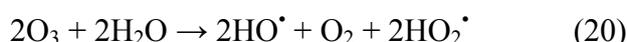
Mater and coworkers (2007), in addition to assessing the efficiency of Fenton's reagent in mineralizing the organic compounds in oil-contaminated water, investigated the mineralization of organic pollutants in soils contaminated with crude oil, calculating the rate of mineralized TOC by monitoring CO_2 and H_2O_2 . Under certain operational conditions, a 70% reduction in the initial TOC was obtained in soil contaminated with crude oil.

2.3. Ozone (O_3)

One of the uses of ozonation that has grown considerably in recent years is the treatment of drinking water, given that its action mechanism does not produce chlorinated compounds that may originate in the chlorine disinfection process (Augugliaro *et al.*, 2006). In addition, the ozone itself has the advantage of not being harmful to most organisms. However, its use in wastewater treatment is limited, owing to the high demand of energy to generate ozone (Pera-Titus *et al.*, 2004). Furthermore, the

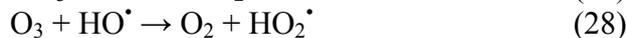
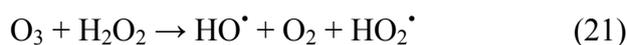
efficiency of ozone is extremely dependent on gas-liquid mass transfer, which is impeded by the low solubility of ozone in aqueous solution, as reported by Gogate and Pandit (2004a).

Ozone has a high reduction potential (2.07V), and can react slowly and directly with an organic substrate (Augugliaro *et al.*, 2006). However, the use of ozone is only characterized as an AOP when it decomposes to generate hydroxyl radicals (Equation 20), and can be catalyzed by hydroxyl ions (HO^-) in alkaline medium or by transition metal cations (Augugliaro *et al.*, 2006; Pera-Titus *et al.*, 2004; Strahelin and Hoigné, 1985).



The efficiency of ozone in degrading organic compounds is improved when combined with H_2O_2 , UV radiation or ultrasound.

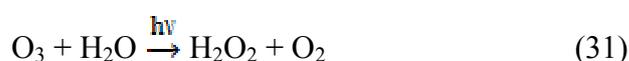
According to Huang and coworkers (1993), cited by Augugliaro and coworkers (2006), H_2O_2 induces the decomposition of O_3 by electron transfer through a reaction that can be understood as H_2O_2 activation by O_3 (Equation 21), by means of a mechanism shown in a simplified form in the following equations (22 through 29).



Wang and coworkers (2002) reported that hydrogen peroxide can simultaneously react with the superoxide radical anion ($\text{O}_2^{\bullet -}$) to produce another hydroxyl radical, as shown by Equation 30.



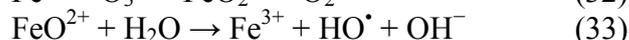
The O_3/UV process consists in UV irradiation (254 nm) on an aqueous system saturated with ozone producing H_2O_2 (Equation 31), which will also be exposed to the action of UV light, producing hydroxyl radicals (Andreozzi *et al.*, 1999), as shown by Equation 6. In this process, with the formation of hydrogen peroxide, there is a new reaction pathway to generate other hydroxyl radicals (Equations 21-29), creating a synergistic effect that comprises direct ozonation, direct photolysis and the decomposition of hydroxyl radicals (Agustina *et al.*, 2005; Wang *et al.*, 2002).



Combined with other techniques, the use of ultrasound and ozone may also strengthen the generation of hydroxyl radicals, since the turbulence created by the acoustic current induced by ultrasound reduces the limitations of mass transfer (Gogate and Pandit, 2004a).

2.3.1. Application

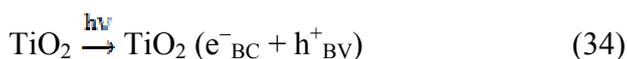
Garoma and coworkers (2008) studied the use of the ozone/UV process in removing components from gasoline, such as BTX, MTBE, *tert*-butyl alcohol and total petroleum hydrocarbons such as gasoline, present in contaminated groundwater samples. After treatment under previously established experimental conditions, removal indices higher than 99% of pollutants initially present in all contaminated water samples were obtained. In natural samples containing iron, lower degradation rates were obtained than in iron-free samples or in those with lower concentrations. The authors report that, although iron can act by degrading organic pollutants from the ferrous ion reactions with the ozone itself to generate hydroxyl radicals (reactions 17, 32-33), the presence of iron renders all samples progressively more turbid, reducing radiation absorption by the solution.



2.4. Heterogeneous photocatalysis

The first studies developed on the use of photocatalysis in the presence of a semiconductor to degrade an organic pollutant were conducted in the early 1980s by Pruden and Ollis (1983), among others, as cited by Alfano and coworkers (2000). Since then this process has been one of the main study focuses among the advanced oxidation processes (Alfano *et al.*, 1997; Bhatkhande *et al.*, 2003; Bockelmann *et al.*, 1995; Crittenden *et al.*, 1997b; Curcó *et al.*, 1996; Fujishima *et al.*, 2000; Fujishima *et al.*, 2007; Goslich *et al.*, 1997; Kositzi *et al.*, 2004; Ljubas, 2005; McLoughlin *et al.*, 2004; Malato *et al.*, 2002; Rodríguez *et al.*, 1996; Romero *et al.*, 1999; Salah *et al.*, 2004; Serpone, 1997; Sichel *et al.*, 2007).

The principle of heterogeneous photocatalysis is based on the activation of a semiconductor particulate material (CdS, TiO₂, ZnO, WO₃ *etc.*) by the action of radiation with an appropriate wavelength. This activation is achieved with the absorption of photons by the semiconductor particle possessing enough energy to promote the conduction of an electron (e⁻) from its valence band (VB) to the conduction band (CB) (a transition called bandgap energy), creating holes in the valence band (h⁺) that will act as oxidizing sites (Serpone, 1997). According to Alfano and coworkers (1997), titanium dioxide (TiO₂) in the anatase form is the most indicated material for use in photocatalytic water treatment processes, considering toxicity, resistance to photocorrosion, availability, catalytic efficiency and cost. TiO₂ absorbs radiation at wavelengths below 400 nm (which enables the use of sunlight), capable of forming e⁻-h⁺ pairs (Equation 34) that can recombine (Goslich *et al.*, 1997).



After the formation of these e⁻-h⁺ pairs, a recombination occurs in the catalyst, generating heat and adsorbing water molecules and hydroxyl ions present in the medium. These will act as electron donors, generating hydroxyl

radicals in the hole (h⁺) of the catalyst (Minero *et al.*, 1996; Alfano *et al.*, 1997), as shown by Equations 35 and 36.



The dissolved oxygen present or added to the medium, can act as an electron acceptor, generating the superoxide radical (Equation 37) and triggering a series of reactions that may lead to the formation of hydroxyl radicals (Quina *et al.*, 2004; Valente *et al.*, 2005). According to Bockelmann and coworkers (1995), the addition of hydrogen peroxide may also favor the process, given that, like oxygen, it may act as the acceptor of electrons available in the system, generating hydroxyl radicals, according to Equation 38.



Figure 1 shows the reaction mechanism involving the electrons and holes produced by UV light that can migrate to the surface of the anatase particle, where they react with adsorbed oxygen, water, hydroxide ions or organic species via electron transfer reactions (Quina *et al.*, 2004).

2.4.1. Application

Bessa and coworkers (2001) studied the treatment of water produced from oil fields via a photocatalytic process using TiO₂/UV, with

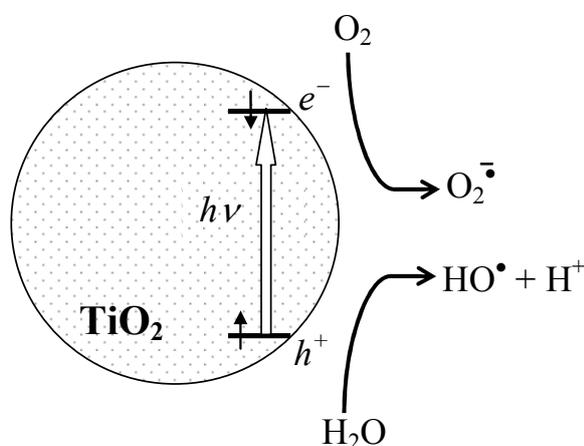


Figure 1. Schematic representation of the basic mechanism of TiO₂ photocatalysis. Adapted from Quina and coworkers (2004).

the addition of H_2O_2 . Chromatographic analyses showed the complexity of the wastewater, and most of the compounds present in the medium, remained unidentified. However, a considerable reduction in chromatogram peaks can be observed, showing pollutant degradation and the presence of a number of alkanes (considered non-toxic) in the treated wastewater. The addition of H_2O_2 in the photocatalytic process was unnecessary and even undesirable, owing to the corrosive and damaging effects of this substance on the catalysts (TiO_2).

As previously mentioned, Hu and coworkers (2008) studied the degradation of a gasoline additive (methyl tert-butyl ether – MTBE). In addition to the use of the $\text{H}_2\text{O}_2/\text{UV}$ process, the use of TiO_2/UV was compared with a modified catalyst ($\text{Ag}/\text{TiO}_2/\text{UV}$). The use of $\text{Ag}/\text{TiO}_2/\text{UV}$ achieved a higher degradation rate than that obtained with TiO_2/UV , reaching higher MTBE removal indices (around 80%) more rapidly. The authors suggested that this difference was due to the formation of micro-batteries on the surface of TiO_2 , where Ag acts as an electrode in coupling with TiO_2 , receiving the electron from the activation reaction of TiO_2 (Equation 34) and reducing the compound to its oxidized state.

Saien and Nejati (2007) used the TiO_2/UV process to degrade the organic pollutants of a refinery wastewater pretreated by physical-chemical processes. They studied the effect of TiO_2 concentration, finding an optimal condition (of maximum degradation, reaching 90%), in which increased TiO_2 concentration caused a decrease in the degradation rate, probably due to the increase in solution turbidity and consequent reduced light transmission in the medium. An assessment of pH obtained an optimal pH of around 3. The authors reported that this was due to the fact that the formation of $e^- - h^+$ pairs (Equation 34) is favored under conditions of lower pH than the point of zero charge of TiO_2 (pH = 6.25), and for pH values below 3, the absorption of anions formed from the dissociation of added sulfuric acid reduces the possibility of organic matter absorption on the surface of the catalyst, decreasing the degradation rate. The same

study also verified the influence of temperature and found that its increase leads to increased pollutant degradation, relating this effect to electron transfers in valence band to higher energy levels and, therefore, facilitating the production of $e^- - h^+$ pairs.

2.5. Electrochemical oxidation

According to Brillas and coworkers (1998), electrochemical processes can produce hydroxyl radicals by two means: anodic oxidation (direct form) and mediated electro-oxidation (indirect form). In anodic oxidation, the hydroxyl radical is generated in the anode (Pt, PbO_2 , doped with SnO_2 etc.) of an electrochemical cell from water oxidation (Equation 39). In mediated electro-oxidation, chemical species, such as H_2O_2 , are continuously generated in the cathode by the reduction of two electrons of dissolved oxygen, as shown by Equation 40 (Brillas and Casado, 2002).



The hydrogen peroxide generated can act as a reagent for Fenton's system, with the addition of iron, leading to the formation of hydroxyl radicals (Equation 12). This process, whereby the hydrogen peroxide from Fenton's reaction is electrochemically generated, is called the electro-Fenton process (Brillas and Casado, 2002). Oturan and Brillas (2007) reported that the Fe^{3+} obtained with Fenton's reaction (Equation 12) or added to the solution can be continuously reduced to Fe^{2+} , creating an electrochemical catalysis process, as shown by Equation 41.



The oxidation power of the system can also be increased with the introduction of ultraviolet radiation to help reduce Fe^{3+} to Fe^{2+} , as shown by Wang and coworkers (2008), consisting of a combination of techniques known as the photoelectron-Fenton process.

According to Saltmiras and Lemley (2002), the Fenton's electrochemical treatment can also

be used by means of an electrochemical cell with iron electrodes (cathode and anode), in which the anode has the function of transferring iron to the solution and the cathode functions as an inert electrode for water reduction, as shown in Equations 42 and 43. The Fe^{2+} transferred by the cathode acts in the Fenton's reaction (Equation 12), with the addition of hydrogen peroxide to the system.



One of the disadvantages of this process is that, owing to the formation of hydroxide ions in the cathode, the medium in which this process is applied is close to neutral pH, which is not suitable for Fenton's reaction. In addition, solids are formed in the solution, owing to iron hydroxide precipitation (Saltmiras and Lemley, 2002).

2.5.1. Application

Yavuz and Koparal (2006) studied the degradation of phenol present in a refinery wastewater via electrochemical oxidation, using a titanium electrode coated with titanium oxide and ruthenium oxide. The initial phenol concentration was 192.2 mg/L and the chemical oxygen demand (COD) was 590 mg/L. After treatment, a 94.5% removal of phenol and 70.1% of chemical oxygen demand (COD) was obtained, the latter because the wastewater still contained other organic and inorganic contaminants.

Santos and coworkers (2006) used dimensionally stable anodes (or DSA, a metallic base of titanium coated with titanium and ruthenium oxides) in the electro-remediation of oily wastewater produced during petroleum extraction and refining. The authors managed to remove up to 57% of initial COD from the wastewater and attributed this reduction to the consequence of the electro-degradation of organic compounds, through the anodic oxidation of components in the DSA electrode and the electro-flotation of oil droplets in suspension that aggregate on the surface owing to the gas formed in the cathode

(H_2) and in the anode (O_2 and Cl_2). The authors also found that the increased temperature favors the removal of COD by the electrochemical process.

2.6. Wet air oxidation and supercritical water oxidation

Wet air oxidation (WAO) is an ecologically safe technology for treating water containing organic pollutants (Zerva *et al.*, 2003). This technique enables the oxidation of pollutants from oxygen dissolved in water, under high pressure conditions (10-220 bar) and high temperatures (150-370°C), leading to the formation of hydroxyl radicals (Domènech *et al.*, 2001; Rivas *et al.*, 1998). Supercritical water oxidation (SCWO) consists of submitting water to higher temperature and pressure conditions than their critical point (above 374°C and 221 bar, respectively). This technique obtains rapid results, but requires high energetic demand and, consequently, high operational costs.

Wet air oxidation may have its efficiency improved with the presence of homogeneous catalysts (such as Cu^{2+} salts) and heterogeneous catalysts (MnO_2 , CuO , Fe_2O_3 *etc.*) in the reaction, as cited by Domènech and coworkers (2001), and known as catalytic wet air oxidation (CWAO).

2.6.1. Application

Sun and coworkers (2008) applied microwave assisted catalytic wet air oxidation in the treatment of petrochemical wastewater. It was observed that the use of microwaves helps in heating and heat conduction, accelerating the pollutant degradation rate. A positive effect on the pollutant degradation rate was also found with an increase in temperature and dissolved oxygen in the medium, as well as with a rise in microwave power levels. The authors concluded that microwave assisted catalytic wet air oxidation was efficient in removing non-biodegradable organic pollutants and demonstrated that this method, as a pretreatment process, made the wastewater adequate (with the increased biochemical demand of oxygen) for biological treatment.

3. CONCLUSIONS

Advanced oxidation processes provide an efficient alternative for treating wastewater contaminated with toxic organic compounds. With high oxidation power, the hydroxyl radicals are capable of totally or partially degrading practically all classes of organic compounds present in aqueous medium or in soils, resulting in the complete mineralization of these compounds or in their conversion to more biodegradable products.

The studies conducted in the petrochemical area presented in this study showed promising results, reducing the organic pollution load of wastewaters, in many of the investigations, to negligible levels. Even when not completely degraded, there is a large reduction in wastewater toxicity, which enables subsequent biological treatment. This capacity of AOP to completely degrade the organic load or to convert it into products that enable biological treatment is extremely important in the oil industry, since they allow the reuse of water for more productive purposes, such as irrigation, or in the production process itself, reducing the environmental impact caused by discarding or lowering the water consumption costs present in practically all oil production stages.

Reagent concentrations can be optimized by prior experimental studies with the wastewater to be treated, since each one has its peculiarities. The variables and the interference of external agents in the system are innumerable, varying from case to case. This optimization is fundamental to minimize the costs of reagents used in the AOP, which are the most costly elements of the process. Another possibility for reducing operational costs, in the case of photochemical processes, is the use of processes that enable the employment of solar radiation, such as TiO₂/UV and photo-Fenton processes.

The use of Fenton's reagent in the remediation of soils contaminated with oil and its derivatives yielded excellent results, with a significant reduction in the organic load present in the medium. These results are important for substituting the conventional techniques used to remediation of soils contaminated with oil and derivatives, when a bio-remediation is

unfeasible. These conventional techniques consists of simply removing the contaminated area, a process that has an environmental and physical impact on the affected site, followed by the storage or extraction of contaminants, which is a costly method that does not resolve the pollutant problem, but rather transfers the polluting load from one location to another.

One of the requirements to ensure the good use of AOP is to conduct large scale studies and scale-enlargement projects that more faithfully represent industrial applications (which have large flows), given that most studies in the area are still carried out at laboratory scale.

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