We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Fundamental Mechanistic Studies of the Photo-Fenton Reaction for the Degradation of Organic Pollutants

Amilcar Machulek Jr.[1], Frank H. Quina[2], Fabio Gozzi[1],
Volnir O. Silva[2], Leidi C. Friedrich[2] and José E. F. Moraes[3]
[1]Universidade Federal de Mato Grosso do Sul, Departamento de Química – UFMS,
[2]Universidade de São Paulo, Instituto de Química and NAP-PhotoTech – USP,
[3]Universidade Federal de São Paulo, Escola Paulista de Engenharia – UNIFESP,
Brazil

1. Introduction

Very few regions of the planet possess abundant fresh water and access to adequate fresh water resources can be expected to worsen as a result of population growth and industrial demands for water. Liquid effluents containing toxic substances are generated by a variety of chemistry-related industrial processes, as well as by a number of common household or agricultural applications. The inadequate management of these residues can cause contamination of the soil and of subterranean and surface water sources.

In general, the recovery of industrial effluents containing low levels of organic substances by conventional treatments is not economically viable. Thus, for example, removal of the pollutant by adsorption onto active charcoal, while often efficient, requires subsequent recovery or incineration of the charcoal and merely transfers the pollutant from one phase to another (Matthews, 1992). Substances that are biocides or that are non-biodegradable represent a particular threat to the environment and prevent the use of conventional biological treatments. Social and legal demands for environmental safety increasingly require that effluents discharged into the environment have minimal impact on human health, natural resources and the biosphere. These demands have fueled increasing research into the development of new, more effective and economically viable methods for pollution control and prevention. When applied to the degradation of pollutants, these reactions are usually grouped together under the designations of Advanced Oxidation Processes (AOP) or Advanced Oxidation Technologies (AOT).

2. The principal advanced oxidation processes (AOP)

Advanced Oxidation Processes typically employ chemical oxidizing agents in the presence of an appropriate catalyst and/or ultraviolet light (Legrini, et al., 1993; Sonntag, 2008; Matilainen & Sillanpää, 2010) to oxidize or degrade the pollutant of interest. AOPs have been employed for the degradation of a variety of organic pollutants, such as aliphatic and aromatic hydrocarbons, halocarbons, phenols, ethers, ketones, etc. Examples of the major

types of AOPs that have been proposed in the literature include (oxidant [catalyst, when present]/light): H_2O_2/UV (Gryglik et al., 2010; Ho & Bolton, 1998); O_3/UV (Esplugas et al., 1994; Machulek et al., 2009a); O_3-H_2O_2/UV (Yue, 1993); [TiO_2]/UV (Gaya & Abdullah, 2008; Henderson, 2011; Jenks, 2005; Matthews, 1992); Fe(III)/[TiO_2]/UV-Vis (Domínguez et al., 1998); direct photolysis of water with vacuum UV (Gonzalez et al., 2004); Fenton reaction or H_2O_2-Fe(II) (Dao & Laat, 2011; Haddou et al., 2010; Kwon et al., 1999; Pignatello et al., 2006; Pontes et al., 2010); and the photo-Fenton reaction or H_2O_2 [Fe(II)/Fe(III)]/UV (Benitez et al., 2011; Huston & Pignatello, 1999; Kim & Vogelpohl, 1998; Kiwi et al., 1994; Machulek et al., 2007; Martyanov et al., 1997; Nichela et al., 2010; Pignatello et al., 2006; Ruppert et al., 1993).

In most AOP, the objective is to use systems that produce the hydroxyl radical, $HO^{\bullet}$, or another species of similar reactivity such as the sulfate radical anion ($SO_4^{\bullet-}$). The hydroxyl radical is one of the most reactive species known in aqueous solution, surpassed only by fluorine atoms, and reacts with the majority of organic substances with little or no selectivity and at rates often approaching the diffusion-controlled limit (unit reaction efficiency per encounter). The principal modes of reaction of $HO^{\bullet}$ with organic compounds include hydrogen abstraction from aliphatic carbon, addition to double bonds and aromatic rings, and electron transfer (Bauer & Fallmann, 1997). These reactions generate organic radicals as transient intermediates, which then undergo further reactions, eventually resulting in final products (P_{oxid}) corresponding to the net oxidative degradation of the starting molecule (R). Overall, a typical AOP process can be can be generically represented as:

$$HO^{\bullet} + R \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow P_{oxid} \qquad (1)$$

Evidently, however, this representation belies the underlying complexity of the intermediate steps that occur on the pathway(s) from R to P_{oxid}.

From an environmental standpoint, one must be sure that the degradation of the initial pollutant does not produce intermediate products that are as toxic as or more toxic than the initial pollutant that one wishes to degrade. Thus, it is absolutely essential that the progress of the degradation and the final degradation products be adequately characterized. Since the degradation of organic pollutants by the hydroxyl radical is typically stepwise, even a relatively simple molecule like 4-chlorophenol can give rise to a plethora of intermediates, with from six to two carbon atoms, in various states oxidation (Li et al., 1999a, 1999b; Jenks, 2005) before converging to the final mineralization products, CO_2, water and HCl. Identification and quantification of all of the intermediates and determination of the kinetics and mechanisms of the individual reactions represent formidable tasks. For actual industrial effluents or wastewaters, which are often complex mixtures of pollutants, the intricacy of the degradation reactions can be enormous and one or more of the components or intermediates may be resistant to degradation and accumulate in the system. Not surprisingly, basic research into degradation pathways and mechanisms is still in its infancy for most of the AOP.

Photochemical and photocatalytic processes have enormous potential for becoming viable alternatives to conventional chemical AOP for the treatment of polluted waters and effluents. Currently available photochemical technology permits the conversion of organic pollutants having a wide range of chemical structures into substances that are less toxic and/or more readily biodegradable. In favorable cases, they can cause total decomposition of the organic constituents of the pollutant, generally referred to as "total mineralization" (complete oxidation to carbon dioxide and water, plus inorganic salts of all heteroatoms

other than oxygen). Light of wavelengths in the range of 250-400 nm, corresponding to the ultraviolet (UV) region of the spectrum, is most commonly used in photochemical degradation processes (Braslavsky et al., 2011). Since ultraviolet light is a natural component of solar radiation, the sun provides a low-cost, environmentally friendly, renewable source of ultraviolet photons in photochemical processes. Thus, the use of solar photochemical reactors is an extremely interesting, cost-effective option for treatment of effluents in many of the tropical and sub-tropical regions of the planet. In areas with marginal or inadequate solar radiation intensity, conventional photochemical reactors fitted with ultraviolet lamps or hybrid UV lamp/solar photoreactors can be employed. In addition to light, the common AOPs use low to moderate concentrations of environmentally compatible chemical reagents and are capable, in favorable cases, of complete mineralization of the organic constituents of aqueous effluents. Although the initial or primary photochemical steps of the reactions employed to treat effluents can be conceptually rather simple, a large number of subsequent quite complex chemical steps are often involved in the overall degradation process.

Of the AOPs that have been proposed thus far, the Fenton reaction and the light-accelerated Fenton reaction, commonly known as the photo-Fenton reaction, appear to be the most promising for practical industrial applications (Pignatello et al., 2006). In the remainder of this chapter, we shall focus our attention on fundamental mechanistic details of the Fenton and photo-Fenton reactions, information that is essential for the adequate design and control of photo-Fenton processes for the degradation of organic pollutants.
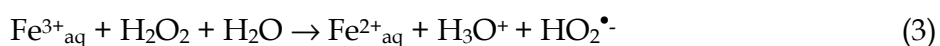
3. The Fenton reaction

Over a century ago, Fenton (Fenton, 1894) demonstrated that a mixture of H_2O_2 and Fe(II) in acidic medium had very powerful oxidizing properties. Although the precise mechanism of this reaction, now known as the Fenton reaction, is still the subject of some discussion (Bossmann et al., 1998; Pignatello et al., 1999, 2006), it is generally assumed to be an important chemical source of hydroxyl radicals. The classical mechanism is a simple redox reaction in which Fe(II) is oxidized to Fe(III) and H_2O_2 is reduced to hydroxide ion and the hydroxyl radical:

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + HO^{\bullet} + OH^- \tag{2}$$
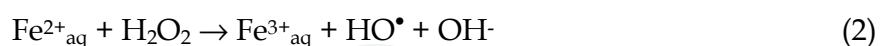
For the degradation of organic molecules, the optimum pH for the Fenton reaction is typically in the range of pH 3-4 and the optimum mass ratio of catalyst (as iron) to hydrogen peroxide is 1.5 (Bigda, 1995).

In the conventional Fenton reaction, carried out in the absence of light, the ferric ion produced in reaction (2) can be reduced back to ferrous ion by a second molecule of hydrogen peroxide:

$$Fe^{3+}_{aq} + H_2O_2 + H_2O \rightarrow Fe^{2+}_{aq} + H_3O^+ + HO_2^{\bullet-} \tag{3}$$

However, this thermal reduction (reaction 3) is much slower than the initial step (reaction 2). Thus, although chemically very efficient for the removal of organic pollutants, the Fenton reaction slows down appreciably after the initial conversion of Fe(II) to Fe(III) and may require the addition of relatively large amounts of Fe(II) in order to degrade the pollutant of interest. Another important limitation of the Fenton reaction is the formation of recalcitrant intermediates that inhibit the complete mineralization. Particularly noteworthy is the

formation of oxalic acid, $H_2C_2O_4$, a poisonous and persistent oxidation product of many degradation reactions. Since Fenton reactions are typically run at an initial pH of about 3 and oxalic acid is a relatively strong acid (with a first pK_a of 1.4), the accumulation of oxalic acid causes further acidification of the reaction mixture (to ca. pH 2) as the reaction proceeds. In addition, Fe(III) is very efficiently chelated by the oxalate anion. This prevents the reduction of Fe(III) back to Fe(II) and hence the complete mineralization of the organic matter. A still unresolved question in the mechanism of the Fenton degradation of organic material is the relative importance of other potential oxidizing species besides the hydroxyl radical. The stoichiometry of Fenton degradation reactions is complex and, in addition to Fe^{2+}/Fe^{3+} and hydrogen peroxide, can involve the participation of the hydroperoxyl radical, $HOO^{\bullet}$, iron(IV) or ferryl, FeO^{2+}, dissolved molecular oxygen, organic hydroperoxides, and other intermediates formed during the degradation. Despite these potential limitations, the conventional Fenton reaction has been widely used for the treatment of effluents (Benitez et al., 1999; Pignatello et al., 2006).

Any reaction or process that enhances the rate of conversion of Fe(III) back to Fe(II) will in principle accelerate the rate of the Fenton reaction. In the electro-Fenton reaction, this is accomplished electrochemically. Chemically, the Fenton reaction can be efficiently catalyzed by certain types of organic molecules, especially benzoquinones or dihydroxybenzene (DHB) derivatives. The catalytic influence of DHBs on the Fenton reaction was originally reported by Hamilton and coworkers (Hamilton et al., 1966a, 1966b). Because DHBs such as catechol or hydroquinone and their analogs are common initial intermediates in the degradation of aromatic molecules, their presence in the reaction medium can result in efficient DHB-catalyzed redox cycling of Fe^{3+} back o Fe^{2+} (Chen & Pignatello, 1997; Nogueira et al., 2005). Indeed, in several cases, it has been shown that the addition of catechol or catechol derivatives can enhance the rate and the overall mineralization efficiency of Fenton reactions (Aguiar et al., 2007; Zanta et al., 2010). In addition, DHB-catalyzed redox cycling of iron may be important in fungal degradation of lignin and several possible mechanisms have been suggested (Aguiar et al., 2007). The third method of accelerating the Fenton reaction is via irradiation with ultraviolet light, generally known as the photo-assisted Fenton or photo-Fenton reaction, which will be the primary focus of the remainder of this chapter.

4. The Photo-Fenton reaction

4.1 General features of the Photo-Fenton reaction

About two decades ago, it was found that the irradiation of Fenton reaction systems with UV/Visible light strongly accelerated the rate of degradation of a variety of pollutants (Huston & Pignatello, 1999; Ruppert et al., 1993). This behavior upon irradiation is due principally to the photochemical reduction of Fe(III) back to Fe(II), for which the net reaction can be written as:

$$Fe^{3+}_{aq} + H_2O \xrightarrow{h\nu} Fe^{2+}_{aq} + HO^{\bullet} + H^+ \qquad (4)$$

More detailed studies of the pH dependence of the photo-Fenton reaction have shown that the optimum pH range is ca. pH 3. The reason for this pH dependence becomes clear when one examines the speciation of Fe(III) as a function of pH (Figure 1) and the absorption spectra of the relevant Fe(III) species (Figure 2). At pH < 2, the dominant species is

hexaquoiron(III), $Fe(H_2O)_6{}^{3+}$ [or simply Fe^{3+} for convenience], which absorbs weakly in the ultraviolet above 300 nm. At pH > 3, freshly prepared solutions of Fe(III) are supersaturated with respect to formation of colloidal iron hydroxide, $Fe(OH)_3$ and prone to precipitation of hydrated iron oxides upon standing for a prolonged period. At pH 3, however, the predominant Fe(III) species present in aqueous solution is $Fe(H_2O)_5(OH)^{2+}$ [or simply $Fe(OH)^{2+}$], which absorbs throughout much of the ultraviolet spectral region (Martyanov et al., 1997).
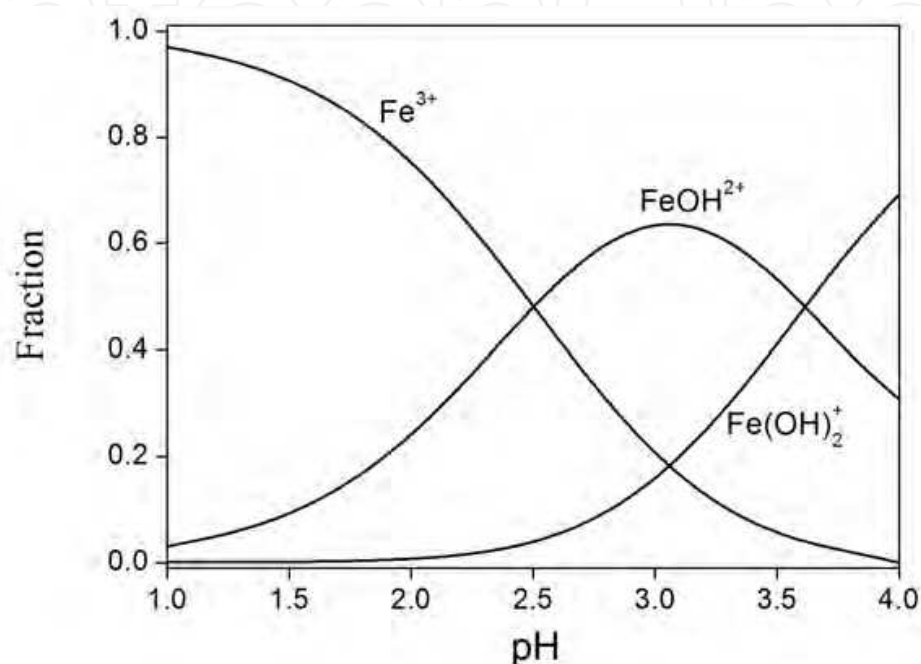

Fig. 1. Speciation of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.1. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with the program (excluding insoluble iron species).

Studies of the photochemistry of $Fe(OH)^{2+}$ have shown (Pozdnyakov et al., 2000) that $Fe(OH)^{2+}$ undergoes a relatively efficient photoreaction to produce Fe(II) and the hydroxyl radical:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^\bullet \tag{5}$$

Thus, irradiation of the Fenton reaction not only regenerates Fe(II), the crucial catalytic species in the Fenton reaction (reaction 2), but also produces an additional hydroxyl radical, the species responsible for the degradation of organic material. As a consequence of these two effects, the photo-Fenton process is faster than the conventional thermal Fenton process. Moreover, since Fe(II) is regenerated by light with decomposition of water (equations 4-5) rather than H_2O_2 (reaction 3), the photo-Fenton process consumes less H_2O_2 and requires only catalytic amounts of Fe(II).

The photo-Fenton reaction has several operational and environmental advantages. The classes of organic compounds that are susceptible to photodegradation via the Fenton reaction are rather well known (Bigda, 1995). The photo-Fenton process produces no new

pollutants and requires only small quantities of iron salt. At the end of the reaction, if necessary, the residual Fe(III) can be precipitated as iron hydroxide by increasing the pH. Any residual hydrogen peroxide that is not consumed in the process will spontaneously decompose into water and molecular oxygen and is thus a "clean" reagent in itself. These features make homogeneous photo-Fenton based AOPs the leading candidate for cost-efficient, environmental friendly treatment of industrial effluents on a small to moderate scale (Pignatello et al., 2006). An early example of an industrial-scale application of the photo-Fenton process was the decontamination of 500 L batches of an industrial effluent containing 2,4-dimethylaniline in a photochemical reactor fitted with a 10 kW medium pressure mercury lamp (Oliveros et al., 1997).
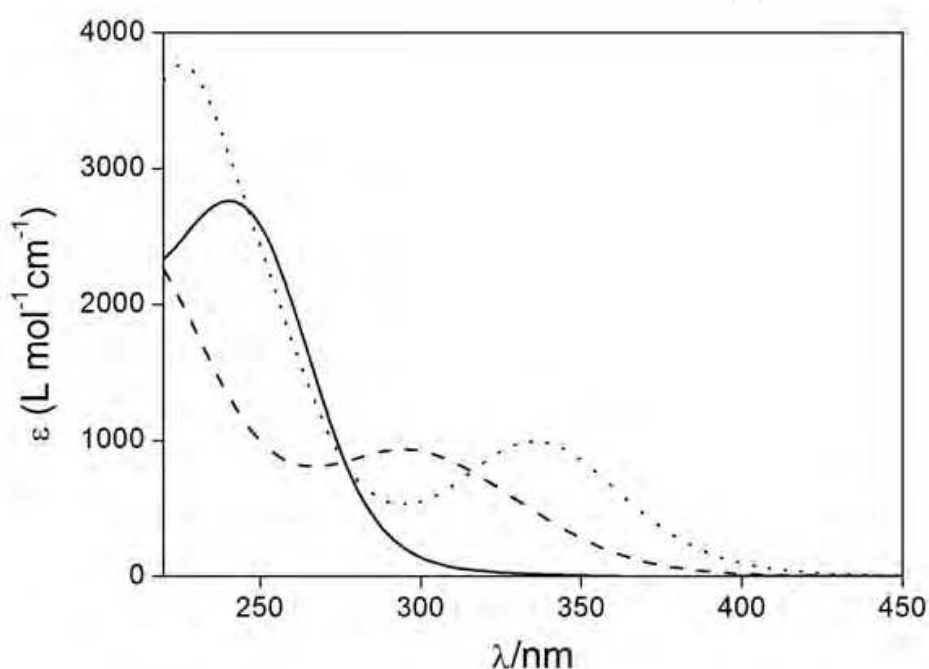
(a) Solid curve: pH 1.5 with perchloric acid, 90% Fe(H$_2$O)$_6$ $^{3+}$ or Fe^{3+}, see Figure 1;
(b) Dashed Curve: pH 2.5 with perchloric acid, ca. 50:50 FeOH^{2+}:Fe^{3+}, see Figure 1;
(c) Dotted Curve: pH 1.5 plus added 500 mmol L^{-1} NaCl, 30% FeCl^{2+} and 65% FeCl$_2$$^{+}$.

Fig. 2. Absorption spectra of 0.43 mM Fe(III) perchlorate under three typical conditions, expressed as the apparent extinction coefficient, ε, defined as the observed absorbance divided by the total Fe(III) concentration.

4.2 Inhibition of the Photo-Fenton reaction by chloride ion

Our interest in the fundamental mechanistic aspects of the photo-Fenton reaction arose from the necessity to optimize the degradation of organic material in effluents or wastewaters containing high concentrations of chloride ion. With such effluents, such as petroleum wastewaters from offshore marine environments or residues from organochloride pesticide production, the photo-Fenton reaction is strongly inhibited. Thus, although the photo-Fenton reaction results in essentially complete mineralization of phenol in the absence of chloride ion (Figure 3, curve e), in the presence of the chloride ion the mineralization process (indicated by the reduction in the amount of total organic carbon, TOC) stops after only partial decomposition of the organic material (Figure 3, curve c).
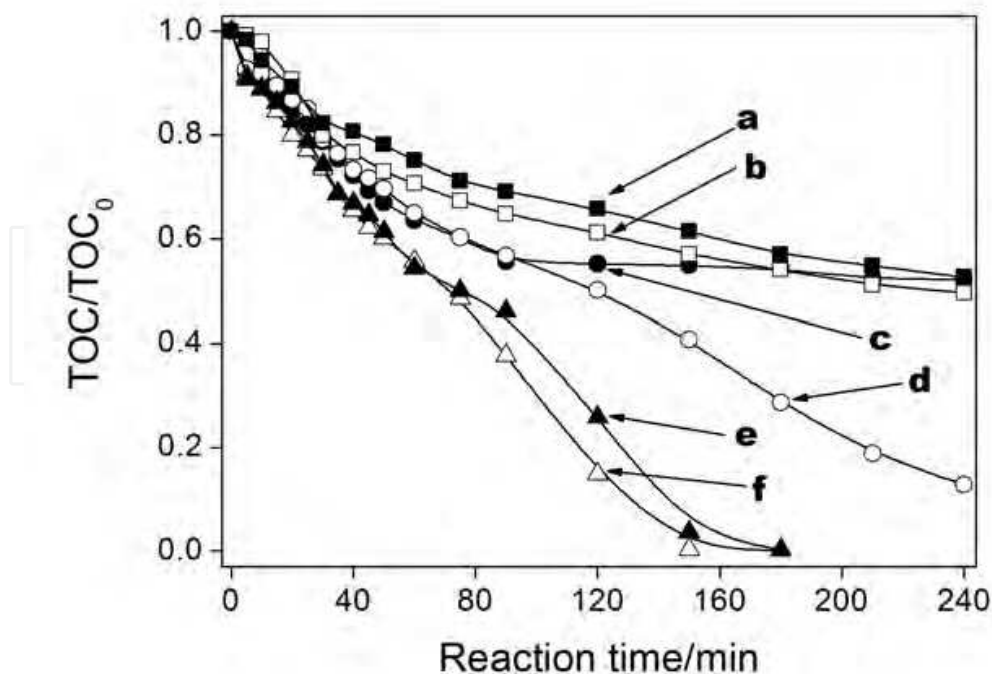
Fig. 3. Degradation of 12 mM phenol in the presence of 200 mM H_2O_2 and 0.5 mM Fe^{2+}. Fenton oxidation at $pH_{initial}$ 3.0 in the presence (curve a, ■) and absence (curve b, □) of 0.5 M NaCl. Photo-Fenton degradation (400 W medium pressure Hg vapor lamp – incident photon intensities were 1.2 x 10^{-4} Ein/s) at $pH_{initial}$ 3.0 with no pH control in the absence (curve e, ▲) or presence (curve c, ●) of 0.5 M NaCl; or with pH 3.0 maintained throughout the reaction in the absence (curve f, ∆) or presence of 0.5 M NaCl (curve d, ○). For details, see (Machulek et al., 2007).

In the presence of chloride ion, the extent of mineralization in the photo-Fenton reaction (Figure 3, curve c) is comparable to that observed in the analogous thermal Fenton reaction carried out in the dark in the presence or absence of chloride ion (Figure 3, curves a and b). Although we (Moraes et al., 2004a, 2004b) and others (De Laat & Le, 2006; Kiwi et al., 2000; Maciel et al., 2004; Pignatello, 1992) had ascribed this inhibition to the preferential formation of the less-reactive $Cl_2^{\bullet-}$ radical anion instead of the desired hydroxyl radical, optimization of photo-Fenton reactions required a fuller understanding of the mechanistic details of the inhibition. For this purpose, we (Machulek et al., 2006) used nanosecond laser flash photolysis to investigate the influence of added chloride ion on the photocatalytic step that converts Fe(III) back to Fe(II) (equation 5), deliberately omitting H_2O_2 from the reaction mixture to prevent the thermal Fenton reaction. Although direct spectroscopic detection of the hydroxyl radical has proved elusive (Marin et al., 2011), the $Cl_2^{\bullet-}$ radical anion, which absorbs at 340 nm (ε_{340nm} = 8000 $M^{-1}cm^{-1}$), can be readily detected upon excitation of aqueous solutions of iron(III) at acidic pH in the presence of added sodium chloride at 355 nm with the third harmonic of a Nd-YAG laser. Differential absorption spectra (Figure 4) and kinetic traces (insert, Figure 4) showed fast formation of the $Cl_2^{\bullet-}$ radical anion, within the lifetime of the laser pulse (5 ns), and its subsequent decay via mixed first and second order kinetics. The net decrease in absorption at longer times, relative to that prior to the laser pulse, reflects the conversion of Fe(III) to Fe(II), which does not absorb in this spectral region.
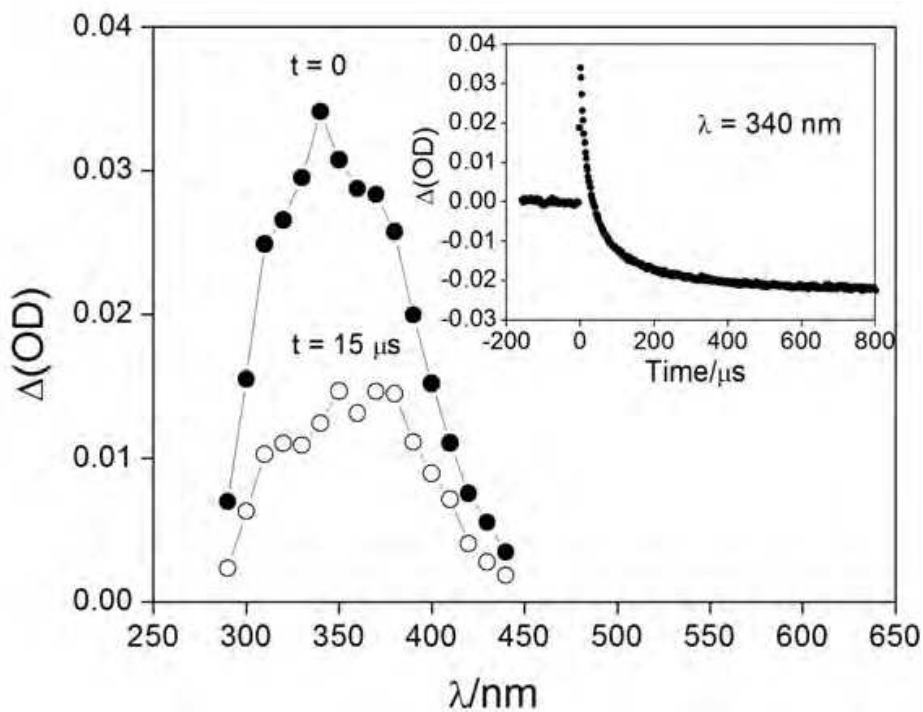
Fig. 4. Laser flash photolysis at 355 nm of 0.50 mM Fe(III) in the presence of 0.5 M NaCl at pH 1. Transient absorption spectra of $Cl_2^{\bullet-}$ immediately (●) and 15 μs (○) after the laser pulse. The insert shows the kinetics of $Cl_2^{\bullet-}$ disappearance monitored at λ= 340 nm.
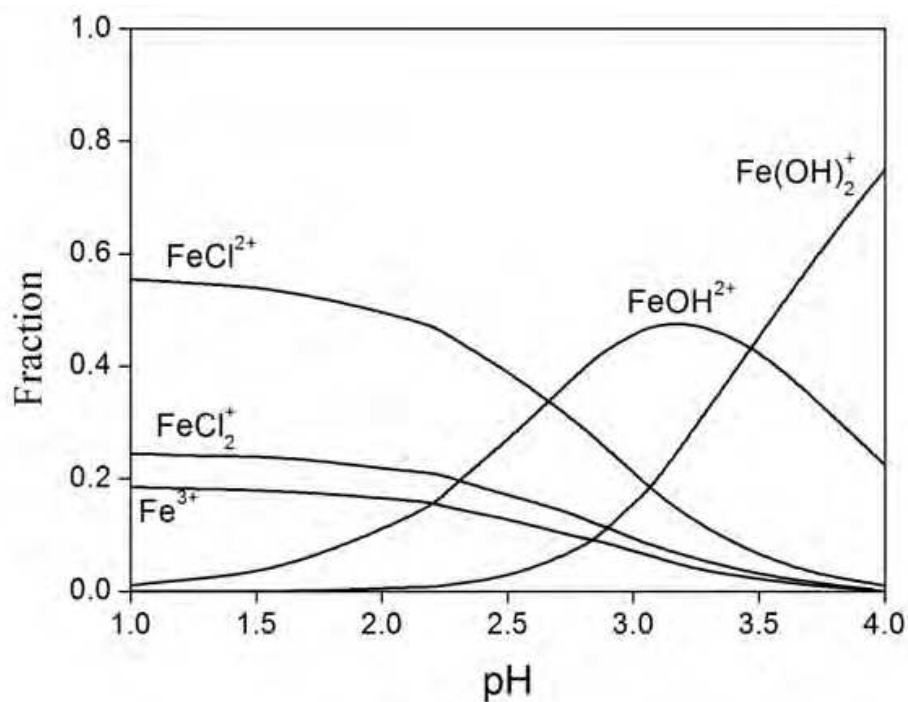

Fig. 5. Speciation of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.2 in the presence of 0.1 M NaCl. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with the program (excluding insoluble iron species).

Laser flash photolysis data for the production and decay of $Cl_2^{\bullet-}$ were then obtained over a wide range of pH and concentration of Fe(III) and chloride ion and these data used to develop an explicit mechanistic model for the initial photoinduced processes involved in the photo-Fenton reaction in the presence of chloride ion (Machulek et al., 2006). As indicated in Figure 5, in the presence of chloride ion, the dominant species present at pH < 2.5 is no longer Fe^{3+}, but rather $FeCl^{2+}$ and $FeCl_2^+$ (coordinated waters being omitted).

Moreover, $FeCl^{2+}$ not only absorbs further out in the ultraviolet than $Fe(OH)^{2+}$ (Figure 2), but it also undergoes photolysis (equation 6) with a quantum yield higher than that of $Fe(OH)^{2+}$ (equation 5).

$$Fe(Cl)^{2+} \xrightarrow{h\nu} Fe^{2+} + Cl^{\bullet} \tag{6}$$

The photoproduced chlorine atoms rapidly react with chloride ions to form $Cl_2^{\bullet-}$ (equation 7), the species actually detected in the laser flash photolysis experiments:

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} \tag{7}$$

and whose second order decay component is due to the disproportionation reaction:

$$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow 2\,Cl^- + Cl_2 \tag{8}$$

The model employed to fit the experimentally observed decay curves for $Cl_2^{\bullet-}$ took into account the initial photochemical formation of the hydroxyl radical from $Fe(OH)^{2+}$ (equation 5) and of chlorine atoms from $FeCl^{2+}$ (equation 6) and the subsequent reactions of these via the set of elementary steps outlined in Table 1 (Machulek et al., 2006).

| No.	Reaction	k (s^{-1} or mol^{-1} L s^{-1})
Speciation Equilibria (I = 1)		
1	$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$	$k_1 = 4.79 \times 10^{10}$, $k_{-1} = 1 \times 10^{10}$
2	$Fe^{3+} + 2\,Cl^- \rightleftarrows FeCl_2^+$	$k_2 = 6.31 \times 10^{10}$, $k_{-2} = 1 \times 10^{10}$
Reactions of Iron Species		
3	$Fe^{2+} + Cl^{\bullet} \rightarrow Fe^{3+} + Cl^-$	$k_3 = 5.9 \times 10^9$
4	$Fe^{2+} + Cl_2^{\bullet-} \rightarrow Fe^{3+} + 2Cl^-$	$k_4 = 5 \times 10^6$
Reactions of Reactive Chlorine Species		
5	$Cl^{\bullet} + Cl^- \rightleftarrows Cl_2^{\bullet-}$	$k_5 = 7.8 \times 10^9$, $k_{-5} = 5.7 \times 10^4$
6	$Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+$	$k_6 = 1 \times 10^9$
7	$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow 2Cl^- + Cl_2$	$k_7 = 2.8 \times 10^9$
8	$Cl_2^{\bullet-} + H_2O_2 \rightarrow HO_2^{\bullet} + 2Cl^- + H^+$	$k_8 = 1.4 \times 10^5$
9	$Cl_2^{\bullet-} + HO_2^{\bullet} \rightarrow 2Cl^- + H^+ + O_2$	$k_9 = 3.1 \times 10^9$
10	$Cl^- + HO^{\bullet} \rightleftarrows HOCl^{\bullet-}$	$k_{10} = 4.2 \times 10^9$, $k_{-10} = 6.1 \times 10^9$
11	$HOCl^{\bullet-} + H^+ \rightleftarrows H_2O + Cl^{\bullet}$	$k_{11} = 2.4 \times 10^{10}$, $k_{-11} = 1.8 \times 10^5$
12	$Cl_2^{\bullet-} + Cl^{\bullet} \rightarrow Cl^- + Cl_2$	$k_{12} = 1.4 \times 10^9$

Table 1. Set of reactions required to simulate the kinetics for production and decay of $Cl_2^{\bullet-}$ upon laser flash photolysis of Fe^{3+} in the presence of chloride ion over a wide range of pH and Fe^{3+} and NaCl concentrations.

The initial concentrations of $HO^•$ and $Cl^•$ produced at t = 0 by the laser pulse were calculated from the relationship (equation 9):

$$\left[X^• \right]_{t=0} = \left(I_{Laser} \right) \left(\frac{A_{Fe(X)}}{A_T} \right) \left(1 - 10^{A_T} \right) \left(\Phi_X \right) \tag{9}$$

where X = OH or Cl and $\Phi_{HO} = 0.21$ and $\Phi_{Cl} = 0.47$ are, respectively, the quantum yields for production of Fe(I1) from $Fe(OH)^{2+}$ or $Fe(Cl)^{2+}$ at 355 nm. $A_{Fe(X)}$ is the absorbance of either $Fe(OH)^{2+}$ or $Fe(Cl)^{2+}$ and A_T the total absorbance of the solution, both at the laser excitation wavelength of 355 nm (in an effective optical path length of 0.5 cm). The ratio $A_{Fe(X)}/A_T$ was calculated from the initial concentrations of the species $Fe(Cl)^{2+}$, $Fe(Cl)_2^+$, Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $[Fe_2(H_2O)_4(OH)_2]^{4+}$, together with molar absorption coefficients at 355 nm taken from the literature absorption spectra (Byrne & Kester, 1978, 1981). For each experimental condition (pH, [Cl⁻], [Fe(III)]), the relative concentrations of the iron(III) species were calculated with the public domain speciation program Hydra (Puigdomenech, 2010), employing the set of standard equilibrium constants for complexation supplied with the program. The incident laser intensity (I_{laser}) was estimated by fitting the transient absorbance of $Cl_2^{•-}$ at time zero at pH 1.0 in the presence of 0.5 M NaCl, where competitive photolysis of $Fe(OH)^{2+}$ is negligible. The concentrations of $HO^•$ and $Cl^•$ at t = 0 calculated from equation 9 served as the initial conditions for numerical solution of the set of reactions and rate constants listed in Table 1. This kinetic model provided a quantitative fit of the observed transient decay curves (like that shown in the inset of Figure 4) over the entire range of pH and concentrations of chloride ion and Fe(III) investigated.

Having established the basic mechanistic scheme for the photoinduced steps of the photo-Fenton reaction, one can then use it to infer the course of a typical photo-Fenton degradation in the presence of chloride ion. At the beginning of the photo-Fenton reaction, when the pH is still ca. 3.0, the concentration of $Fe(OH)^{2+}$ exceeds that of $FeCl^{2+}$ or $FeCl_2^+$, even in the presence of relatively high concentrations of chloride ion (Figure 5). The pH-dependent scavenging of $HO^•$ by chloride ion (equations 10-11):

$$HO^• + Cl^- \rightleftarrows HOCl^{•-} \tag{10}$$

$$H^+ + HOCl^{•-} \rightleftarrows H_2OCl^• \rightarrow H_2O + Cl^• \tag{11}$$
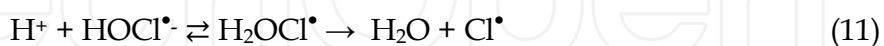
is also still a relatively inefficient process, so that the photochemical formation of $HO^•$ should predominate. However, as the photo-Fenton process proceeds, partial degradation of the organic material causes the pH of the medium to fall to ca. pH 2.0, where photolysis of $FeCl^{2+}$ dominates over photolysis of $Fe(OH)^{2+}$ and where the chloride ion efficiently converts any $HO^•$ formed in the system into the intrinsically much less reactive $Cl_2^{•-}$ radical anion (Bacardit et al., 2007; Buxton et al., 1999; De Laat et al., 2004; George & Chovelon, 2002; Kiwi et al., 2000; McElroy, 1990; Moraes, et al., 2004a; Nadtochenko & Kiwi, 1998; Pignatello, 1992; Soler et al., 2009; Truong et al., 2004; Yu, 2004; Yu et al., 2004; Yu & Barker, 2003a, 2003b; Zapata et al., 2009). As a result, virtually complete inhibition of the photo-Fenton degradation of typical organic substrates (Kiwi & Nadtochenko, 2000; Machulek et

al., 2007; Moraes et al., 2004a, 2004b; Pignatello, 1992) will occur at moderate chloride ion concentrations [>0.03 *M* NaCl for aliphatic hydrocarbons (Moraes et al., 2004a); >0.2 *M* NaCl for phenols] when the pH of the medium reaches pH 2.0 or below. On the other hand, this sequence of events clearly indicates that it should be possible to circumvent the inhibition by chloride ion by simply maintaining the pH at or slightly above pH 3 throughout the degradation process (see Figure 5). This is nicely illustrated by curve d in Figure 3, which shows that pH control does indeed permit nearly complete mineralization of phenol in the presence of chloride ion (Machulek et al., 2006, 2007). Although pH control also enhances the rate of the photo-Fenton reaction in the absence of chloride ion by optimizing the concentration of $Fe(OH)^{2+}$ (see Figure 1), the effect is much less dramatic (compare curves e and f in Figure 3).

Although the mechanism outlined in Table 1 nicely rationalizes the kinetics of formation and decay of $Cl_2^{\bullet-}$ on a fast time scale, it does not permit prediction of the accumulation of Fe(II) in the same system in the absence of H_2O_2 under steady-state irradiation. For this purpose, one must include additional kinetic steps that are too slow to be relevant on the time scale of the laser flash photolysis experiments. Experimentally (Machulek et al., 2009b) it is found that the concentration of Fe^{2+} eventually reaches a plateau value at long times, more quickly in the presence of chloride ion than in its absence (Figure 6). Simulation of this behavior required the inclusion of additional kinetic steps, in particular for the back reactions that result in reoxidation of Fe^{2+}. These additional kinetic steps are listed in Table 2.
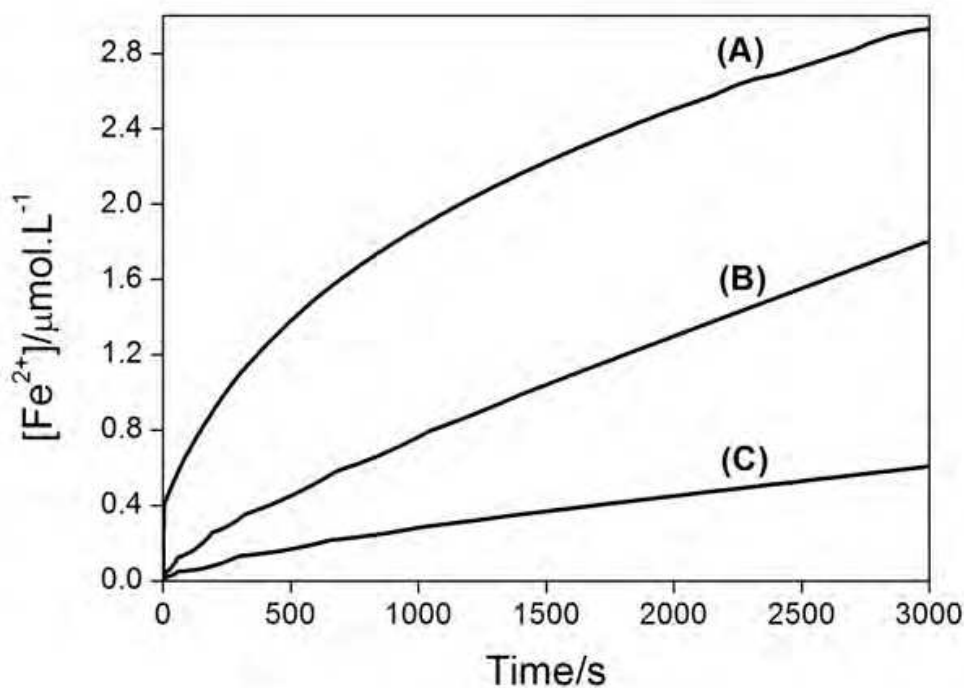

Fig. 6. The accumulation of ferrous ion during irradiation (350 nm) of 1.0 mM Fe(III) at: (A) pH 1.0 in the presence of 0.75 mol L^{-1} chloride ion; (B) at pH 3 in the absence of chloride ion; and (C) at pH 3 in the presence of 1.8 mmol L^{-1} sulfate ions.

No.	Reaction	k (s^{-1} or mol^{-1} L s^{-1})
Speciation Equilibria (I = 1)		
1	$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+$	$k_1 = 1.91 \times 10^7$, $k_{-1} = 1 \times 10^{10}$
2	$Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2^+ + 2H^+$	$k_2 = 3.39 \times 10^3$, $k_{-2} = 1 \times 10^{10}$
3	$2Fe^{3+} + 2H_2O \rightleftarrows [Fe_2(OH)_2]^{4+} + 2H^+$	$k_3 = 1.12 \times 10^7$, $k_{-3} = 1 \times 10^{10}$
Reactions of Reactive Oxygen Radicals		
4	$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	$k_4 = 6.0 \times 10^9$
5	$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$	$k_5 = 2.7 \times 10^7$
6	$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$	$k_6 = 8.3 \times 10^5$
7	$HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + O_2 + H_2O$	$k_7 = 0.5$
Reactions of Iron Species		
8	$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^-$	$k_8 = 4.3 \times 10^8$
9	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^-$	$k_9 = 63$
10	$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$	$k_{10} = 1 \times 10^6$
11	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$	$k_{11} = 0.01$

Table 2. Set of additional ground state reactions required to fit the accumulation of Fe^{2+} during the steady-state irradiation of Fe^{3+} in the presence and absence of chloride ion (Machulek et al., 2009b)

4.3 Inhibition of the Photo-Fenton reaction by sulfate ion

Also indicated in Figure 6 is the inhibition of the formation of Fe^{2+} in the presence of a relatively low concentration of added sulfate ions, based on the rate constants for complexation of Fe(III) by sulfate in Table 3. Sulfate ion is often present in photo-Fenton reactions as a result of the addition of iron in the form of readily available sulfate salts (De Laat & Le, 2005). Sulfate ion complexes strongly with Fe(III) over a wide pH range (Figure 7) and the quantum yield of production of Fe^{2+} plus a sulfate anion radical from photolysis of $Fe(SO_4)^+$ is only about 0.05 (Benkelberg & Warneck, 1995). Iron phosphate is even more photoinert than the iron sulfate complex (Benkelberg & Warneck, 1995; Lee et al., 2003) and should be an even more powerful inhibitor of the photo-Fenton reaction.

4.4 Catalysis of the Photo-Fenton reaction by complexation of Fe(III)

The efficiency of the photo-Fenton process can be further enhanced by using organic carboxylic acids to complex Fe(III) (Pignatello et al., 2006). A particularly important example is provided by oxalic acid. Thus, unlike the thermal Fenton reaction, in which oxalic acid is a recalcitrant intermediate, in the photo-Fenton reaction it can act as a catalyst. Thus, ferrioxalate complexes can absorb light as far out as 570 nm, i.e., well into the visible region of the spectrum. Moreover, upon irradiation, they decompose efficiently (quantum yields of the order of unity) to Fe(II) and CO_2. The net result is that, in the presence of oxalate, the photo-Fenton reaction is intrinsically more efficient, can be induced by a wider range of wavelengths of light, and results in the mineralization of the oxalate ion. Thus, for example, in a municipal water treatment system, Kim & Vogelpohl (1998) found that, with UV irradiation, the photo-Fenton process was at least 30% more energy efficient in the presence of oxalate than in its absence. Clearly, the sensitivity of the ferrioxalate-catalyzed photo-Fenton process to both UV and visible light makes it particularly attractive for applications in which the sun is employed as the radiation source (Silva et al., 2010; Trovó & Nogueira, 2011).

No.	Reaction	k (s^{-1} or mol^{-1} L s^{-1})
Speciation Equilibria (I = 1)		
1	$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4^+$	$k_1 = 2.09 \times 10^{12}$, $k_{-1} = 1 \times 10^{10}$ (I=1)
2	$Fe^{3+} + 2SO_4^{2-} \rightleftarrows Fe(SO_4)_2^-$	$k_2 = 1.95 \times 10^{13}$, $k_{-2} = 1 \times 10^{10}$ (I=1)
3	$Fe^{2+} + SO_4^{2-} \rightleftarrows FeSO_4$	$k_3 = 1.55 \times 10^{11}$, $k_{-3} = 1 \times 10^{10}$ (I=1)
Reactions of Sulfate Ions		
4	$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$	$k_4 = 2.8 \times 10^{11}$, $k_{-4} = 1 \times 10^{10}$ (I=1)
5	$HSO_4^- + HO^\bullet \rightarrow SO_4^{\bullet-} + H_2O$	$k_5 = 3.5 \times 10^5$
6	$SO_4^{\bullet-} + H_2O \rightarrow H^+ + SO_4^{2-} + HO^\bullet$	$k_6 = 6.6 \times 10^2$
7	$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^\bullet$	$k_7 = 1.4 \times 10^7$
8	$SO_4^{\bullet-} + H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2^\bullet$	$k_8 = 1.2 \times 10^7$
9	$SO_4^{\bullet-} + HO_2^\bullet \rightarrow SO_4^{2-} + H^+ + O_2$	$k_9 = 3.5 \times 10^9$
10	$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	$k_{10} = 2.7 \times 10^8$
Reactions of Iron Species		
11	$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2-}$	$k_{11} = 3.0 \times 10^8$

Table 3. Set of additional ground state reactions required to fit the accumulation of Fe^{2+} during the steady-state irradiation of Fe^{3+} in the presence of sulfate ion (Machulek et al., 2009b).
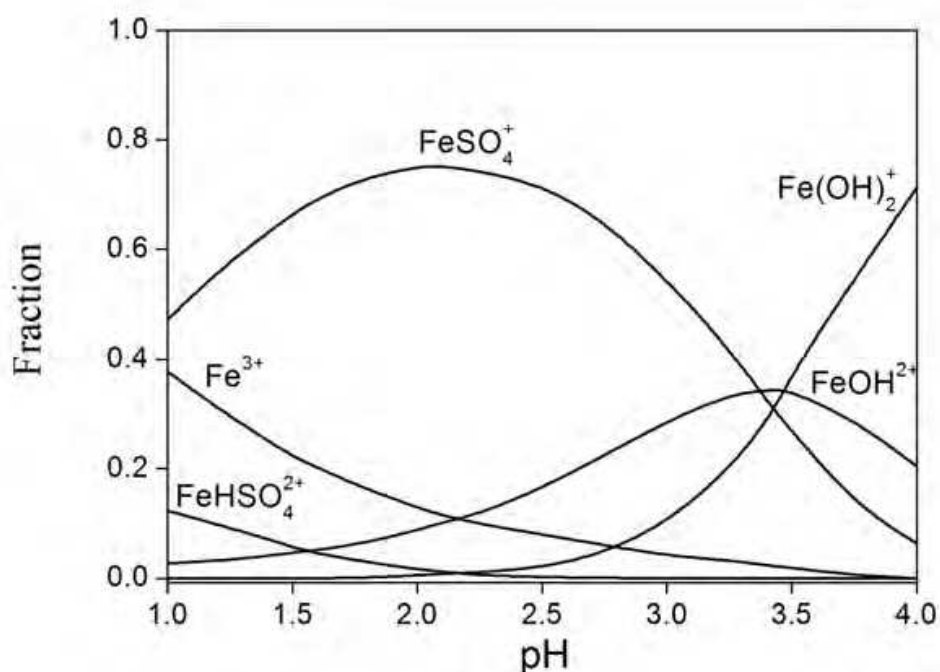

Fig. 7. Speciation of 1.0 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.2 in the presence of 1.8 mM sulfate. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with the program (excluding the insoluble iron species).

4.5 Concurrent Photo-Fenton and Fenton reactions

A final point that should be emphasized is that, under typical photo-Fenton reaction conditions, both the thermal Fenton reaction and the photo-Fenton reactions occur concurrently in the reaction mixture. Light is almost always the limiting reagent in photochemical reactions and photo-Fenton reactions are often conducted in reactors in which the solution is recirculated through the photoreactor from an external reservoir. Thus, at any given moment, the photo-Fenton reaction will be operative only in the portion of the total reaction mixture that is contained in the photoreactor *per se*, while the thermal Fenton reaction can proceed throughout the entire reaction volume. Indeed, comparison of the degradation of phenol under various conditions (Figure 3) strongly suggests that the initial phase of the reaction is dominated by the thermal reaction, with the inflection at about 80 min where the curves diverge indicating the point at which the photo-Fenton reaction becomes dominant.

Particularly interesting is the apparent insensitivity of the thermal Fenton degradation of phenol to the presence of added chloride ion, as indicated by the similarity of curves a and b of Figure 3. At the initial pH of 3 of the reaction mixture, the hydroxyl radical is inefficiently scavenged by chloride and produces, as the initial products of phenol degradation, the DHBs catechol and hydroquinone. Thus, unlike the photo-Fenton reaction, which depends on the intermediacy of the hydroxyl radical, the thermal degradation of phenol shifts to the DHB-catalyzed reaction mentioned above for the Fenton reaction until all of the DHBs have themselves been degraded (Chen and Pignatello, 1997). At that point, most of the iron(III) is rendered redox inert by complexation with oxalic acid and/or other recalcitrant aliphatic acids and the Fenton reaction ceases (Zanta et al., 2010).

5. Areas for future development

Despite significant advances in the last decade, the widespread successful application of photochemical technology for the treatment and decontamination of industrial residues and wastewaters is still not a reality. Research chemists and process engineers must work together to solve several important practical problems that limit the technological applications of the photo-Fenton reaction on a large scale (Braun et al., 1991). Since the overall effective quantum efficiency can be relatively low, long irradiation times must be employed in order to achieve total mineralization of the organic components of effluents. Electrical power consumption can then easily represent 60% of the total operating expense of a lamp-based photochemical reactor. Additional costs associated with non-solar photochemical reactors include cooling, maintenance and depreciation of the lamps and UV radiation shielding and protection for workers. One of the obvious economic benefits of the use of solar photochemical reactors is the elimination of costs associated with installation and maintenance of lamps and with electrical power consumption (Moraes et al., 2004b; Nascimento et al., 2007). In parallel with the development of solar reactors or hybrid lamp/solar reactors, an important area is the development of photocatalysts that operate effectively under visible or solar irradiation (Anpo, 2000).

Particularly in larger scale reactors, operational problems such as the formation of deposits on the reactor walls that block the incident radiation must be addressed. Optimization strategies (Braun et al., 1991, 1993; Cassano et al., 1995; Nascimento et al., 1994; Oliveros et al., 1998) must be applied to the design of reactors that homogenize the incidence of light on

the reactor walls and maximize the total amount of light absorbed by the system. Reactor design must also take into account the strong interdependence between light absorption, mass transport and reaction kinetics in solutions with high optical densities and optimize the balance between the concurrent photochemical and thermal contributions to the Fenton reaction. Although the relatively long irradiation times required for the complete mineralization of organic contaminants tend to compromise the economic viability of stand-alone photo-Fenton processes, they can be viable as a pre-treatment to reduce the toxicity of the effluent to levels compatible with other remediation technologies such as conventional biological treatment. Hence, the design of photo-Fenton reactors should also take into account the necessity of facile integration with other effluent decontamination technologies. A final point that has only recently been considered in a more systematic context is the intensification of Fenton processes by increasing the temperature (Zazo et al., 2011), particularly attractive in the case of photo-Fenton reactions where a substantial part of the absorbed light energy is dissipated as heat in the solution.

6. Conclusions

Of the currently known advanced oxidation processes, the Fenton reaction and the photo-Fenton reaction appear to be the most promising for practical industrial applications on a moderate scale. The fundamental photomechanistic aspects of the photo-Fenton reaction have been clarified by studies of the photochemistry of Fe(III) in the absence of hydrogen peroxide in order to avoid the complications due to the competing Fenton reaction. The Fe(III) species primarily responsible for the initial photochemical generation of Fe(II) plus a hydroxyl radical is $Fe(OH)^{2+}$. Inhibition of the photo-Fenton by ions such as chloride or sulfate can be understood by considering the competitive pH-dependent complexation of Fe(III) by these ions, the competitive absorption and photochemistry of these complexes and/or the subsequent chemical reactions that can convert the hydroxyl radical into less reactive species. Adequate mechanisms, together with the relevant rate constants, are now available for the inhibition of the net photoconversion of Fe(III) to Fe(II) by both chloride and sulfate, allowing quantitative or semi-quantitative simulation of the experimentally observed inhibitory effects. As predicted by the mechanistic models, the inhibitory effect of chloride ion on real photo-Fenton degradations can be readily circumvented by simply maintaining the medium pH at ca. pH 3 throughout the reaction. Areas where additional progress would be welcome include an understanding of the role of temperature effects on the Fenton and photo-Fenton reactions and new strategies for further enhancing the efficiency of the photo-Fenton reaction. Improvements in photoreactor design are necessary in order to optimize the contribution of the photoinduced processes relative to the concurrent thermal Fenton reaction.

7. Acknowledgment

8. References

Aguiar, A.; Ferraz, A.; Contreras, D. & Rodríguez, J. (2007). Mecanismo e aplicação da reação de Fenton assistida por compostos fenólicos redutores de ferro. *Química Nova*, Vol. 30, No. 3, pp. 623-628, ISSN 0100-4042

Anpo, M. (2000). Utilisation of TiO_2 photocatalysts in green chemistry. *Pure and Applied Chemistry*, Vol. 72, No. 7, pp. 1265-1270, ISSN 0033-4545

Bacardit, J.; Stötzner, J.; Chamarro, E. & Esplugas, S. (2007). Effect of salinity on the photo-Fenton process. *Industrial & Engineering Chemistry Research*, Vol. 46, No. 23, pp. 7615-7619, ISSN 0888-5885

Bauer, R. & Fallmann, H. (1997). The photo-Fenton oxidation - a cheap and efficient wastewater treatment method. *Research on Chemical Intermediates*, Vol. 23, No. 4, pp. 341-354, ISSN 0922-6168

Benitez, F.J.; Beltran-Heredia, J.; Acero, J.L. & Rubio, F.J. (1999). Chemical decomposition of 2,4,6-triclorophenol by ozone, Fenton's reagent, and UV radiation. *Industrial & Engineering Chemistry Research*, Vol. 38, No. 4, pp. 1341-1349, ISSN 0888-5885

Benitez, F.J.; Acero, J.L.; Real, F.J.; Roldan, G. & Casas, F. (2011). Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices. *Chemical Engineering Journal*, Vol. 168, No. 3, pp. 1149-1156, ISSN 1385-8947

Benkelberg, H. J. & Warneck, P. (1995). Photodecomposition of iron(III) hydroxo and sulfate complexes in aqueous solution: Wavelength dependence of OH and SO_4^- quantum yields. *Journal of Physical Chemistry*, Vol. 99, No. 14, pp. 5214-5221, ISSN 0022-3654

Bigda, R. (1995). Consider Fenton's chemistry for wastewater treatment. *Chemical Engineering Progress*, (Dec.), Vol. 91, No. 12, pp. 62-66, ISSN 03607275

Bolton, J. R. (1999). Light Compendium – Ultraviolet Principles and Applications. *Inter-American Photochemical Society Newsletter*, Vol. 22, No. 2, pp. 20-61

Bossmann, S.H.; Oliveros, E.; Göb, S.; Siegwart, S.; Dahlen, E.P.; Payawan, L.; Straub, M.; Wörner, M. & Braun, A.M. (1998). New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton Reactions. *Journal of Physical Chemistry A*, Vol. 102, No. 28, pp. 5542-5550, ISSN 1089-5639

Braslavsky, S.E.; Braun, A.M.; Cassano, A.E.; Emeline, A.V.; Litter, M.I.; Palmisano, L.; Parmon, V.N. & Serpone, N. (2011). Glossary of terms used in photocatalysis and radiation catalysis (IUPAC recommendations 2011). *Pure and Applied Chemistry*, Vol. 83, No. 4, pp. 931-1014, ISSN 0033-4545

Braun, A.M.; Maurette, M.T. & Oliveros, E. (1991). *Photochemical Technology*. John Wiley & Sons, ISBN-13 978-0471926528, New York, USA

Braun, A.M.; Jakob, L.; Oliveros, E. & Nascimento, C.A.O. (1993). Up-scaling photochemical reactions, *In: Advances in Photochemistry*, Volman, D.H.; Hammond, G.S. & Neckers, D.C., Vol. 18, pp. 235-313, ISBN 9780471591337, John Wiley & Sons, USA

Buxton, G.V., Bydder, M. & Salmon, G.A. (1999). The reactivity of chlorine atoms in aqueous solution—Part II. The equilibrium $SO_4^{\bullet-} + Cl^- \rightarrow Cl^{\bullet} + SO_4^{2-}$. *Physical Chemistry Chemical Physics*, Vol. 1, No. 2, pp. 269–273, ISSN 1463-9076

Byrne, R.H. & Kester, D.R. (1978). Ultraviolet spectroscopic study of ferric hydroxide complexation. *Journal of Solution Chemistry,* Vol. 7, No. 5, pp. 373–383, ISSN 0095-9782

Byrne, R.H. & Kester, D.R. (1981). Ultraviolet spectroscopic study of ferric equilibria at high chloride concentration. *Journal of Solution Chemistry,* Vol. 10, No. 1, pp. 51–67, ISSN 0095-9782

Cassano, A.; Martín, C.A.; Brandi, R.J. & Alfano, O.M. (1995). Photoreactor analysis and design: fundamentals and applications. *Industrial & Engineering Chemistry Research*, Vol. 34, No. 7, pp. 2155-2201, ISSN 0888-5885

Chen, R. & Pignatello, J.J. (1997). Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compouds. *Environmental Science & Technology,* Vol. 31, No. 8, pp. 2399-2406, ISSN 0013-936X

Dao, Y.H. & Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research*, Vol. 45, No. 11, pp. 3309-3317, ISSN 0043-1354

De Laat, J.; Le, G.T. & Legube, B. (2004). A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H_2O_2 and organic compounds by $Fe(II)/H_2O_2$ and $Fe(III)/H_2O_2$. *Chemosphere,* Vol. 55, No. 5, pp. 715-723, ISSN 0045-6535

De Laat, J. & Le, T. G. (2005). Kinetics and Modeling of the $Fe(III)/H_2O_2$ System in the Presence of Sulfate in Acidic Aqueous Solutions. *Environmental Science & Technology,* Vol. 39, No. 6, pp. 1811-1818, ISSN 0013-936X

De Laat, J. & Le, T. G. (2006). Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process. *Applied Catalysis, B: Environmetal,* Vol. 66, No. 1-2, pp. 137-146, ISSN 0926-3373

Domínguez, C.; García, J.; Pedraz, M.A.; Torres, A. & Galán, M.A. (1998). Photocatalytic oxidation of organic pollutants in water. *Catalysis Today*, Vol. 40, No. 1, pp. 85-101, ISSN 0920-5861

Esplugas, S.; Yue, P.L. & Pervez, M.I. (1994). Degradation of 4-chlorophenol by photolytic oxidation. *Water Research*, Vol. 28, No. 6, pp. 1323-1328, ISSN 0043-1354

Fenton, H.J.H. (1894). Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society,* Vol. 65, pp. 899-901, ISSN 0368-1769

Gaya, U.I. & Abdullah, A.H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 9, No. 1, pp. 1-12, ISSN 1389-5567

George, C. & Chovelon, J.M. (2002). A laser flash photolysis study of the decay of SO_4^- and Cl_2^- radical anions in the presence of Cl^- in aqueous solution. *Chemosphere,* Vol. 47, No. 4, pp. 385–393, ISSN 0045-6535

Gonzalez, M.C.; Oliveros, E.; Wörner, M. & Braun, A.M. (2004). Vacuum-ultraviolet photlolysis of aqueous reaction systems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* Vol. 5, No. 3, pp. 225-246, ISSN 1389-5567

Gryglik, D.; Olak, M. & Miller, J.S. (2010). Photodegradation kinetics of androgenic steroids boldenone and trenbolone in aqueous solutions. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 212, No. 1, pp. 14-19, ISSN 1010-6030

Haddou, M.; Benoit-Marquié, F.; Maurette, M.T. & Oliveros, E. (2010). Oxidative degradation of 2,4-dihydroxybenzoic acid by Fenton and photo-Fenton process: Kinetics, mechanisms, and evidence for the substitution of H_2O_2 by O_2. *Helvetica Chimica Acta*, Vol. 93, No. 6, pp. 1067-1080, ISSN 0018-019X

Hamilton, G.A.; Friedman, J.P. & Campbell, P.M. (1966a). The hydroxylation of anisole by hydrogen peroxide in the presence of catalytic amounts of ferric ion and catechol. Scope, requirements and kinetic studies. *Journal of the American Chemical Society*, Vol. 88, No. 22, pp. 5266–5268, ISSN 0002-7863

Hamilton, G.A.; Hanifin Jr., J.W. & Friedman, J.P. (1966b). The hydroxylation of anisole by hydrogen peroxide in the presence of catalytic amounts of ferric ion and catechol. Product studies, mechanism, and relation to some enzymic reactions. *Journal of the American Chemical Society*, Vol. 88, No. 22, pp. 5269–5272, ISSN 0002-7863

Henderson, M.A (2011). A surface science perspective on TiO_2 photocatalysis. *Surface Science Reports*, Vol. 66, No. 6-7, pp. 185-297, ISSN 0167-5729

Ho, T.L. & Bolton, J.R. (1998). Toxicity changes during the UV treatment of pentachlorophenol in dilute aqueous solution. *Water Research*, Vol. 32, No. 2, pp. 489-497, ISSN 0043-1354

Huston, P.L. & Pignatello, J.J. (1999). Degradation of selected pesticide active ingredientes and commercial formulations in water by the photoassisted Fenton reaction. *Water Research*, Vol. 33, No. 5, pp. 1238-1246, ISSN 0043-1354

Jenks, W.S. (2005). The Organic Chemistry of TiO_2 Photocatalysis of Aromatic Hydrocarbons, In: *Environmental Catalysis*, Vicki H. Grassian, 307-346, CRC, ISBN 1-57444-462-X, New York, USA

Kim, S.M. & Vogelpohl, A. (1998). Degradation of organic pollutants by the photo-Fenton process. *Chemical Engineering Technology*, Vol. 21, No. 2, pp. 187-191, ISSN 0930-7516

Kiwi, J.; Pulgarin, C. & Peringer, P. (1994). Effect of Fenton and photo-Fenton reactions on the degradation and biodegradability of 2-nitrophenols and 4-nitrophenols in water treatment. *Applied Catalysis, B: Environmetal*, Vol. 3, No. 4, pp. 335-350, ISSN 0926-3373

Kiwi, J., Lopez, A. & Nadtochenko, V. (2000). Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl^-). *Environmental Science & Technology*, Vol. 34, No. 11, pp. 2162-2168, ISSN 0013-936X

Kwon, B.G.; Lee, D.S.; Kang, N. & Yoon, J. (1999). Characteristics of *p*-chlorophenol oxidation by Fenton's reagent. *Water Research*, Vol. 33, No. 9, pp. 2110-2118, ISSN 0043-1354

Lee, Y., J. Jeong, C. Lee, S. Kim and J. Yoon (2003) Influence of various reaction parameters on 2,4-D removal in photo/ferrioxalate/H_2O_2 process. Chemosphere, Vol. 51, No. 9, pp. 901-912, ISSN 0045-6535

Legrini, O.; Oliveros, E. & Braun, A.M. (1993). Photochemical processes for water treatment. *Chemical Reviews*, Vol. 93, No. 2, pp. 671-698, ISSN 0009-2665

Li, X.; Cubbage, J. W. & Jenks, W. S. (1999a). Photocatalytic degradation of 4-chlorophenol. 1. The 4-chlorocatechol pathway. *Journal of Organic Chemistry*, Vol. 64, No. 23, pp. 8525-8536, ISSN 0022-3263

Li, X.; Cubbage, J. W.; Tetzlaff, T. A. & Jenks, W. S., (1999b). Photocatalytic degradation of 4-chlorophenol. 1. The hydroquinone pathway. *Journal of Organic Chemistry*, Vol. 64, No. 23, pp. 8509-8524, ISSN 0022-3263

Machulek Jr., A.; Vautier-Giongo, C.; Moraes, J. E. F.; Nascimento, C. A. O. & Quina, F.H. (2006). Laser flash photolysis study of the photocatalytic step of the photo-Fenton reaction in saline solution. *Photochemestry and Photobiology*, Vol. 82, No. 1, pp. 208-212, ISSN 0031-8655

Machulek Jr., A.; Moraes, J.E.; Vautier-Giongo, C.; Silverio, C.A.; Friedrich, L.C.; Nascimento, C.A.O.; Gonzalez, M.C. & Quina, F.H. (2007). Abatement of the inhibitory effect of chloride anions in the photo-Fenton process. *Environmental Science & Technology*, Vol. 41, No. 24, pp. 8459-8463, ISSN 0013-936X

Machulek Jr., A.; Gogritcchiani, E.; Moraes, J.E.F.; Quina, F.H.; Braun, A.M. & Oliveros, E. (2009a). Kinetic and mechanistic investigation of the ozonolysis of 2,4-xylidine (2,4-dimethyl-aniline) in acid aqueous solution. *Separation and Purification Technology*, Vol. 67, No. 2, pp. 141-148, ISSN 1383-5866

Machulek Jr., A.; Moraes, J.E.F.; Okano, L.T.; Silvério, C.A. & Quina, F.H. (2009b). Photolysis of ferric íon in the presence of sulfate or chloride íons: implications for the photo-Fenton process. *Photochemical & Photobiological Sciences*, Vol. 8, No. 7, pp. 985-991, ISSN 1474-905X

Maciel, R.; Sant'Anna Jr., G. L. & Dezotti, M. (2004). Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions. *Chemosphere*, Vol. 57, No. 7, pp. 711-719, ISSN 0045-6535

Marin, M.L.; Lhiaubet-Vallet, V., Santos-Juanes, L.; Soler, J.; Gomis, J.; Arques, A.; Amat, A. M. & Miranda, M.A. (2011). A photophysical approach to investigate the photooxidation mechanism of pesticides: Hydroxyl radical versus electron transfer. *Applied Catalysis, B: Environmetal*, Vol. 103, No. 1-2, pp. 48-53, ISSN 0926-3373

Martyanov, I.N.; Savinov, E.N. & Parmon, V.N. (1997). A comparative study of efficiency of photooxidation of organic contaminants in water solutions in various photochemical and photocatalytic systems. 1. Phenol photoxidation promoted by hydrogen peroxide in a flow reactor. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 107, No. 1-3, pp. 227-231, ISSN 1010-6030

Matilainen, A. & Sillanpää, M. (2010). Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere*, Vol. 80, No. 4, pp. 351-365, ISSN 0045-6535

Matthews, R.W. (1992). Photocatalytic oxidation of organic contaminants in water: An aid to environmental preservation. *Pure and Applied Chemistry*, Vol. 64, No. 9, pp. 1285-1290, ISSN 0033-4545

McElroy, W.J. (1990). A laser photolysis study of the reaction of $SO_4^{\bullet-}$ with Cl^- and subsequent decay of Cl_2^- in aqueous solution. *Journal of Physical Chemistry*, Vol. 94, No. 6, pp. 2435–2441, ISSN 0022-3654

Moraes, J.E.F.; Quina, F.H.; Nascimento, C.A.O.; Silva, D.N. & Chiavone-Filho, O. (2004a). Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process. *Environmental Science & Technology*, Vol. 38, No. 4, pp. 1183-1187, ISSN 0013-936X

Moraes, J.E.F.; Silva, D.N.; Quina, F.H.; Chiavone-Filho, O. & Nascimento, C.A.O. (2004b). Utilization of solar energy in the photodegradation of gasoline in water and of oil-field-produced water. *Environmental Science & Technology*, Vol. 38, No. 13, pp. 3746-3751, ISSN 0013-936X

Nadtochenko, V.A. & Kiwi, J. (1998). Photolysis of $Fe(OH)^{2+}$ and $Fe(Cl)^{2+}$ in aqueous solution. Photodissociation kinetics and quantum yields. *Inorganic Chemistry*, Vol. 37, No. 20, pp. 5233-5238, ISSN 0020-1669

Nascimento, C.A.O.; Teixeira, A.C.S.C.; Guardani, R.; Quina, F.H.; Chiavone-Filho, O. & Braun, A.M. (2007). Industrial wastewater treatment by photochemical processes based on solar energy. *Journal of Solar Energy Engineering*, Vol. 129, No. 1, pp. 45-52, ISSN 0199-6231

Nascimento, C.A.O.; Oliveros, E. & Braun, A.M. (1994). Neural-network modeling of photochemical processes. *Chemical Engineering Process*, Vol. 33, No. 5, pp. 319-324, ISSN 0255-2701

Nichela, D.; Haddou, M.; Benoit-Marquié, F.; Maurette, M.T.; Oliveros, E. & Einschlag, F.S.G. (2010). Degradation kinetics of hydroxy and hydroxynitro derivates of benzoic acid by Fenton-like and photo-Fenton techniques: A comparative study. *Applied Catalysis, B: Environmetal*, Vol. 98, No. 3-4, pp. 171-179, ISSN 0926-3373

Nogueira, R.F.P.; Silva, M.R.A. & Trovó, A.G. (2005). Influence of iron source on the solar photo-Fenton degradation of different classes of organic compounds. *Solar Energy*, Vol. 79, No. 4, pp. 384-392 , ISSN 0038-092X

Oliveros, E.; Benoit-Marquie, F.; Puech-Costes, E.; Maurette, M.T. & Nascimento, C.A.O. (1998). Neural network modeling of the photocatalytic degradation of 2,4-dihydroxybenzoic acid in aqueous solution. *Analusis*, Vol. 26, No. 8, pp. 326-332, ISSN 0365-4877

Oliveros, E.; Legrini, O.; Hohl, M.; Müller, T. & Braun, A.M. (1997). Industrial waste water treatment: Large scale development of a light-enhanced Fenton reaction. *Chemical Engineering and Processing*, Vol. 36, No. 5, pp. 397-405, ISSN 0255-2701

Pignatello, J.J. (1992). Dark and photoassisted Fe^{3+}- catalysed degradation of chlorophenoxy herbicides by hydrogen-peroxide. *Environmental Science & Technology*, Vol. 26, No. 5, pp. 944-951, ISSN 0013-936X

Pignatello, J.J.; Liu, D. & Huston, P. (1999). Evidence for an additional oxidant in photoassisted Fenton reaction. *Environmental Science & Technology*, Vol. 33, No. 11, pp. 1832-1839, ISSN 0013-936X

Pignatello, J.J; Oliveros, E. & Mackay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science & Technology*, Vol. 36, No. 1, pp. 1-84. Errata. (2007). *Critical Reviews in Environmental Science & Technology*, Vol. 37, No. 3, pp. 273-275, ISSN 1064-3389

Pontes, R.F.F.; Moraes, J.E.F; Machulek, A. & Pinto, J.M. (2010). A mechanistic kinetic model for phenol degradation by the Fenton process. *Journal of Hazardous Materials,* Vol. 176, No. 1-3, pp. 402-413, ISSN 0304-3894

Pozdnyakov. I. P.; Glebov, E. M.; Plyusnin, V. F.; Grivin, V. P.; Ivanov, Y. V.; Vorobyev, D. Y. & Bazhin, N. M. (2000). Mechanism of $Fe(OH)^{2+}_{(aq)}$ photolysis in aqueous solution. *Pure and Applied Chemistry*, Vol. 72, No. 11, pp. 2187-2197, ISSN 0033-4545

Puigdomenech, I. (April 2010). Chemical Equilibrium Diagrams, 14.07.2011, Available from http://www.kemi.kth.se/medusa

Ruppert, G.; Bauer, R. & Heisler, G. (1993). The photo-Fenton reaction - an effective photochemical wastewater treatment process. *Journal of Photochemistry and Photobiology A: Chemistry,* Vol. 73, No. 1, pp. 75-78, ISSN 1010-6030

Silva, M.R.A.; Vilegas, W.; Zanoni, M.V.B. & Nogueira, R.F.P. (2010). Photo-Fenton degradation of the herbicide tebuthiuron under solar irradiation: Iron complexation and initial intermediates. *Water Research*, Vol. 44, No. 12, pp. 3745-3753, ISSN 0043-1354

Soler, J.; García-Ripoll, A.; Hayek, N.; Miró, P.; Vicente, R.; Arques, A. & Amat, A.M. (2009). Effect of inorganic íons on the solar detoxification of water polluted with pesticides. *Water Research*, Vol. 43, No. 18, pp. 4441-4450, ISSN 0043-1354

Sonntag, C. von. (2008). Advanced oxidation processes: mechanistic aspects. *Water Science & Technology*, Vol. 58, No. 5, pp. 1015-1021, ISSN 0273-1223

Trovó, A.G. & Nogueira, R.F.P. (2011). Diclofenac abatement using modified solar photo-Fenton process with ammonium iron(III) citrate. *Journal of the Brazilian Chemical Society,* Vol. 22, No. 6, pp. 1033-1039, ISSN 0103-5053

Truong, G.L.; De Laat, J. & Legube, B. (2004). Effects of chloride and sulfate on the rate of oxidation of ferrous ion by H_2O_2. *Water Research,* Vol. 38, No. 9, pp. 2384-2394, ISSN 0043-1354

Yu, X.-Y. & Barker, J. R. (2003a). Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions Containing Chloride Ions. I.Chemical Mechanism. *Journal of Physical Chemistry A*, Vol. 107, No. 9, pp. 1313-1324, ISSN 1089-5639

Yu, X.-Y. & Barker, J. R. (2003b). Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions Containing Chloride Ions. II.Quantum Yield of $HO^{\bullet}$ (Aq) Radicals. *Journal of Physical Chemistry A*, Vol. 107, No. 9, pp. 1325-1332, ISSN 1089-5639

Yu, X.-Y. (2004). Critical Evolution of Rate Constants and Equilibrium Constants of Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions containing Chloride Ions. *Journal of Physical and Chemical Reference Data*, Vol. 33, No. 3, pp. 747-763, ISSN 0047-2689

Yu, X.Y., Bao, Z-C. & Barker, J.R. (2004). Free radical reactions involving $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $SO_4^{\bullet-}$ in the 248 nm photolysis of aqueous solutions containing $S_2O_8^{2-}$ and Cl^-. *Journal of Physical Chemistry A,* Vol. 108, No. 2, pp. 295–308, ISSN 1089-5639

Yue, P.L. (1993). Modelling of kinetics and reactor for water purification by photooxidation. *Chemical Engineering Science,* Vol. 48, No. 1, pp. 1-11, ISSN 0009-2509

Zanta, C.L.P.S., Friedrich, L.C., Machulek Jr., A, Higa, K.M. & Quina, F.H. (2010). Surfactant degradation by a catechol-driven Fenton reaction. *Journal of Hazardous Materials*, Vol. 178, No. 1-3, pp. 258-263, ISSN 0304-3894

Zapata, A.; Oller, I.; Bizani, E.; Sánches-Pérez, J.A.; Maldonado, M.I. & Malato, S. (2009). Evaluation of operational parameters involved in solar photo-Fenton degradation of a commercial pesticide mixture. *Catalysis Today*, Vol. 144, No. 1-2, pp. 94-99, ISSN 0920-5861

Zazo, J.A.; Pliego, G.; Blasco, S.; Casas, J.A. & Rodriguez, J.J (2011). Intensification of the Fenton process by increasing the temperature. *Industrial & Engineering Chemistry Research*, Vol. 50, No. 2, pp. 866-870, ISSN 0888-5885
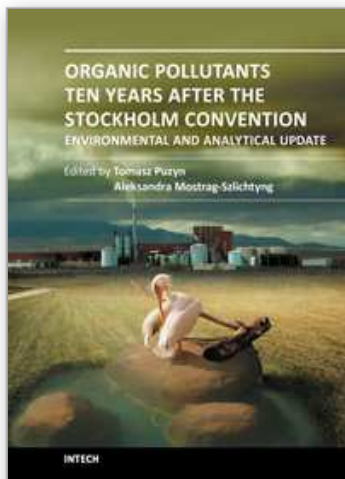
Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

Edited by Dr. Tomasz Puzyn

Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Amilcar Machulek Jr., Frank H. Quina, Fabio Gozzi, Volnir O. Silva, Leidi C. Friedrich and José E. F. Moraes (2012). Fundamental Mechanistic Studies of the Photo-Fenton Reaction for the Degradation of Organic Pollutants, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), ISBN: 978-953-307-917-2, InTech, Available from: http://www.intechopen.com/books/organic-pollutants-ten-years-after-the-stockholm-convention-environmental-and-analytical-update/fundamental-mechanistic-studies-of-the-photo-fenton-reaction-for-the-degradation-of-organic-pollutan

INTECH
open science | open minds