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

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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): H₂O₂/UV (Gryglik et al., 2010; Ho & Bolton, 1998); O₃/UV (Esplugas et al., 1994; Machulek et al., 2009a); O₃-H₂O₂/UV (Yue, 1993); [TiO₂]/UV (Gaya & Abdullah, 2008; Henderson, 2011; Jenks, 2005; Matthews, 1992); Fe(III)/[TiO₂]/UV-Vis (Dominguez et al., 1998); direct photolysis of water with vacuum UV (Gonzalez et al., 2004); Fenton reaction or H₂O₂-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 H₂O₂ [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[•], or another species of similar reactivity such as the sulfate radical anion (SO₄^{•-}). 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[•] 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 generically represented as:



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

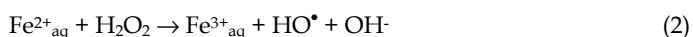
From an environmental standpoint, one must be sure that the degradation of the initial pollutant does not produce intermediate products that are as toxic as or more toxic than the initial pollutant that one wishes to degrade. Thus, it is absolutely essential that the progress of the degradation and the 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, CO₂, 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.

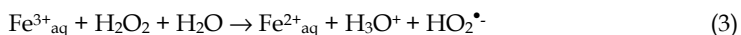
3. The Fenton reaction

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:



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:



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

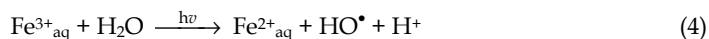
formation of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, a poisonous and persistent oxidation product of many degradation reactions. Since Fenton reactions are typically run at an initial pH of about 3 and oxalic acid is a relatively strong acid (with a first pK_a of 1.4), the accumulation of oxalic 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 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 to 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:



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 $\text{pH} < 2$, the dominant species is

hexaquoiron(III), $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ [or simply Fe^{3+} for convenience], which absorbs weakly in the ultraviolet above 300 nm. At $\text{pH} > 3$, freshly prepared solutions of Fe(III) are supersaturated with respect to formation of colloidal iron hydroxide, $\text{Fe}(\text{OH})_3$ and prone to precipitation of hydrated iron oxides upon standing for a prolonged period. At $\text{pH} 3$, however, the predominant Fe(III) species present in aqueous solution is $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ [or simply $\text{Fe}(\text{OH})^{2+}$], which absorbs throughout much of the ultraviolet spectral region (Martyanov et al., 1997).

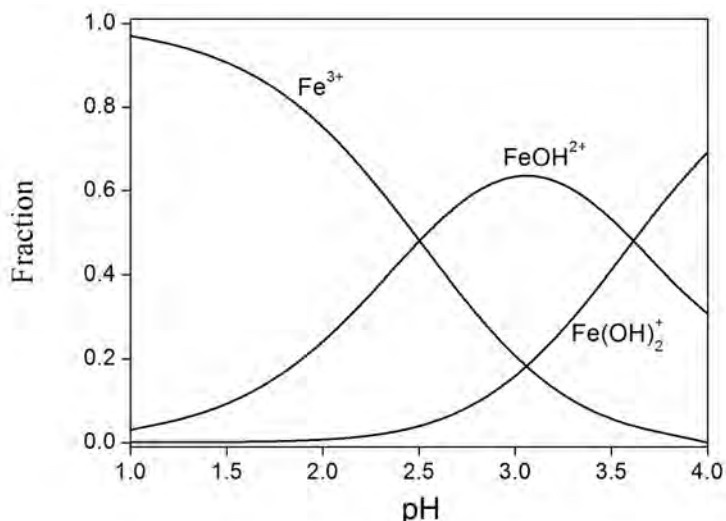


Fig. 1. Speciation of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.1. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with the program (excluding insoluble iron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

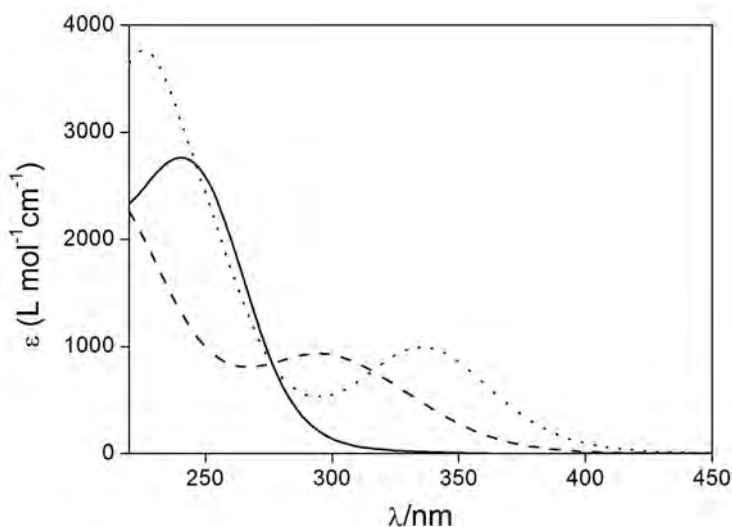
Studies of the photochemistry of $\text{Fe}(\text{OH})^{2+}$ have shown (Pozdnyakov et al., 2000) that $\text{Fe}(\text{OH})^{2+}$ undergoes a relatively efficient photoreaction to produce Fe(II) and the hydroxyl radical:



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% $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ or Fe^{3+} , see Figure 1;
(b) Dashed Curve: pH 2.5 with perchloric acid, ca. 50:50 $\text{FeOH}^{2+}:\text{Fe}^{3+}$, 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).

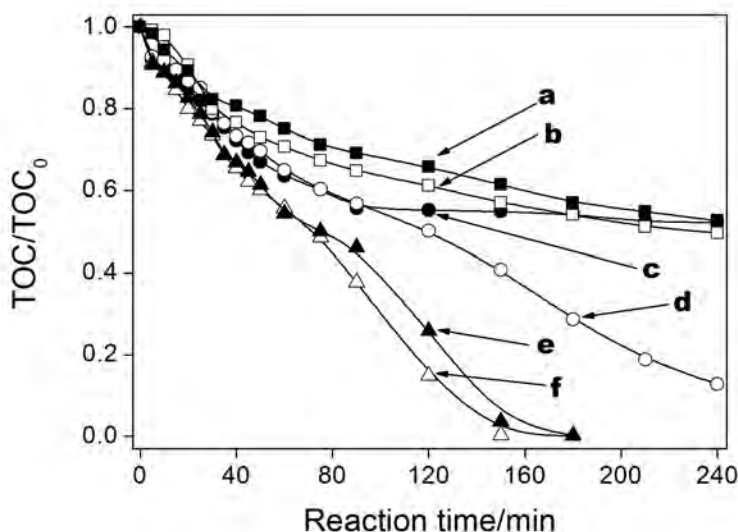


Fig. 3. Degradation of 12 mM phenol in the presence of 200 mM H_2O_2 and 0.5 mM Fe^{2+} . Fenton oxidation at $\text{pH}_{\text{initial}}$ 3.0 in the presence (curve a, \blacksquare) and absence (curve b, \square) of 0.5 M NaCl. Photo-Fenton degradation (400 W medium pressure Hg vapor lamp – incident photon intensities were 1.2×10^{-4} Ein/s) at $\text{pH}_{\text{initial}}$ 3.0 with no pH control in the absence (curve e, \blacktriangle) or presence (curve c, \bullet) of 0.5 M NaCl; or with pH 3.0 maintained throughout the reaction in the absence (curve f, \triangle) or presence of 0.5 M NaCl (curve d, \circ). 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 $\text{Cl}_2^{\bullet-}$ 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 $\text{Cl}_2^{\bullet-}$ radical anion, which absorbs at 340 nm ($\epsilon_{340\text{nm}} = 8000 \text{ M}^{-1}\text{cm}^{-1}$), 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 $\text{Cl}_2^{\bullet-}$ 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.

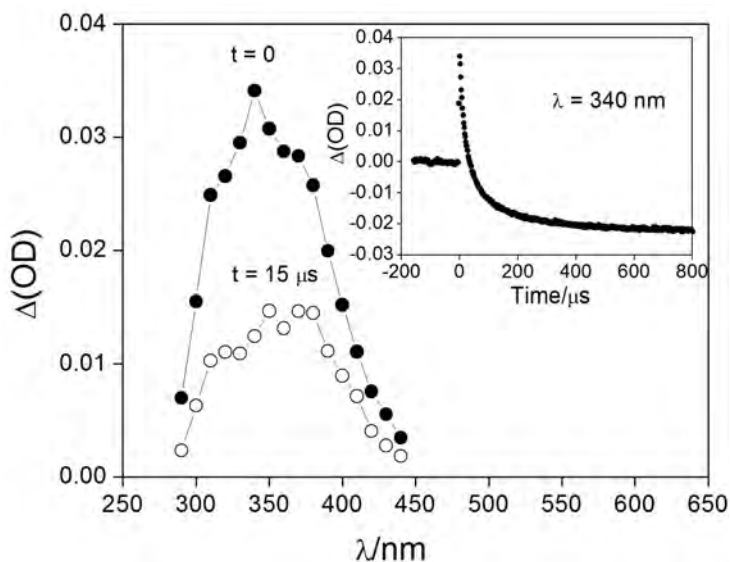


Fig. 4. Laser flash photolysis at 355 nm of 0.50 mM Fe(III) in the presence of 0.5 M NaCl at pH 1. Transient absorption spectra of Cl_2^* immediately (\bullet) and 15 μs (\circ) after the laser pulse. The insert shows the kinetics of Cl_2^* disappearance monitored at $\lambda = 340$ nm.

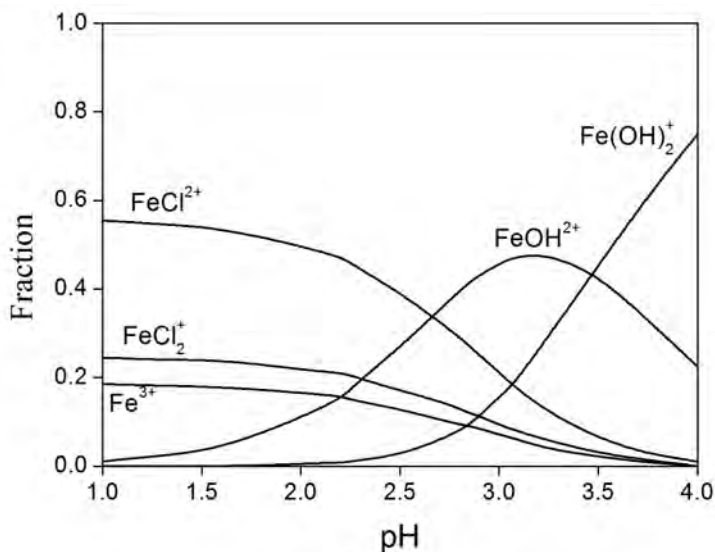


Fig. 5. Speciation of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.2 in the presence of 0.1 M NaCl. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with the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

Laser flash photolysis data for the production and decay of $\text{Cl}_2^{\bullet-}$ 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 $\text{pH} < 2.5$ 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 $\text{Fe}(\text{OH})^{2+}$ (Figure 2), but it also undergoes photolysis (equation 6) with a quantum yield higher than that of $\text{Fe}(\text{OH})^{2+}$ (equation 5).



The photoproducted chlorine atoms rapidly react with chloride ions to form $\text{Cl}_2^{\bullet-}$ (equation 7), the species actually detected in the laser flash photolysis experiments:



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



The model employed to fit the experimentally observed decay curves for $\text{Cl}_2^{\bullet-}$ took into account the initial photochemical formation of the hydroxyl radical from $\text{Fe}(\text{OH})^{2+}$ (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 $\text{mol}^{-1} \text{L s}^{-1}$)
<i>Speciation Equilibria ($I = 1$)</i>		
1	$\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{2+}$	$k_1 = 4.79 \times 10^{10}$, $k_{-1} = 1 \times 10^{10}$
2	$\text{Fe}^{3+} + 2 \text{Cl}^- \rightleftharpoons \text{FeCl}_2^+$	$k_2 = 6.31 \times 10^{10}$, $k_{-2} = 1 \times 10^{10}$
<i>Reactions of Iron Species</i>		
3	$\text{Fe}^{2+} + \text{Cl}^{\bullet} \rightarrow \text{Fe}^{3+} + \text{Cl}^-$	$k_3 = 5.9 \times 10^9$
4	$\text{Fe}^{2+} + \text{Cl}_2^{\bullet-} \rightarrow \text{Fe}^{3+} + 2\text{Cl}^-$	$k_4 = 5 \times 10^6$
<i>Reactions of Reactive Chlorine Species</i>		
5	$\text{Cl}^{\bullet} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^{\bullet-}$	$k_5 = 7.8 \times 10^9$, $k_{-5} = 5.7 \times 10^4$
6	$\text{Cl}^{\bullet} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^{\bullet} + \text{Cl}^- + \text{H}^+$	$k_6 = 1 \times 10^9$
7	$\text{Cl}_2^{\bullet-} + \text{Cl}_2^{\bullet-} \rightarrow 2\text{Cl}^- + \text{Cl}_2$	$k_7 = 2.8 \times 10^9$
8	$\text{Cl}_2^{\bullet-} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^{\bullet} + 2\text{Cl}^- + \text{H}^+$	$k_8 = 1.4 \times 10^5$
9	$\text{Cl}_2^{\bullet-} + \text{HO}_2^{\bullet} \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{O}_2$	$k_9 = 3.1 \times 10^9$
10	$\text{Cl}^- + \text{HO}^{\bullet} \rightleftharpoons \text{HOCl}^{\bullet-}$	$k_{10} = 4.2 \times 10^9$, $k_{-10} = 6.1 \times 10^9$
11	$\text{HOCl}^{\bullet-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{Cl}^{\bullet}$	$k_{11} = 2.4 \times 10^{10}$, $k_{-11} = 1.8 \times 10^5$
12	$\text{Cl}_2^{\bullet-} + \text{Cl}^{\bullet} \rightarrow \text{Cl}^- + \text{Cl}_2$	$k_{12} = 1.4 \times 10^9$

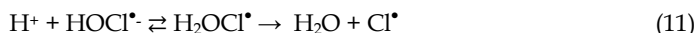
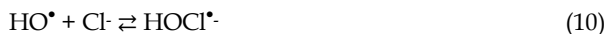
Table 1. Set of reactions required to simulate the kinetics for production and decay of $\text{Cl}_2^{\bullet-}$ upon laser flash photolysis of Fe^{3+} in the presence of chloride ion over a wide range of pH and Fe^{3+} and NaCl concentrations.

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

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

where $X = \text{OH}$ or Cl and $\Phi_{\text{HO}} = 0.21$ and $\Phi_{\text{Cl}} = 0.47$ are, respectively, the quantum yields for production of Fe(II) from $\text{Fe}(\text{OH})^{2+}$ or $\text{Fe}(\text{Cl})^{2+}$ at 355 nm. $A_{\text{Fe}(X)}$ is the absorbance of either $\text{Fe}(\text{OH})^{2+}$ or $\text{Fe}(\text{Cl})^{2+}$ 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 $A_{\text{Fe}(X)}/A_T$ was calculated from the initial concentrations of the species $\text{Fe}(\text{Cl})^{2+}$, $\text{Fe}(\text{Cl})_2^+$, Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and $[\text{Fe}_2(\text{H}_2\text{O})_4(\text{OH})_2]^{4+}$, together with molar absorption coefficients at 355 nm taken from the literature absorption spectra (Byrne & Kester, 1978, 1981). For each experimental condition (pH, $[\text{Cl}^-]$, $[\text{Fe}(\text{III})]$), 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 $\text{Cl}_2^{\bullet-}$ at time zero at pH 1.0 in the presence of 0.5 M NaCl, where competitive photolysis of $\text{Fe}(\text{OH})^{2+}$ 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 $\text{Fe}(\text{OH})^{2+}$ 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):



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 $\text{Fe}(\text{OH})^{2+}$ and where the chloride ion efficiently converts any HO• formed in the system into the intrinsically much less reactive $\text{Cl}_2^{\bullet-}$ 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 [$>0.03\text{ M NaCl}$ for aliphatic hydrocarbons (Moraes et al., 2004a); $>0.2\text{ M NaCl}$ 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 $\text{Cl}_2^{\bullet-}$ 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.

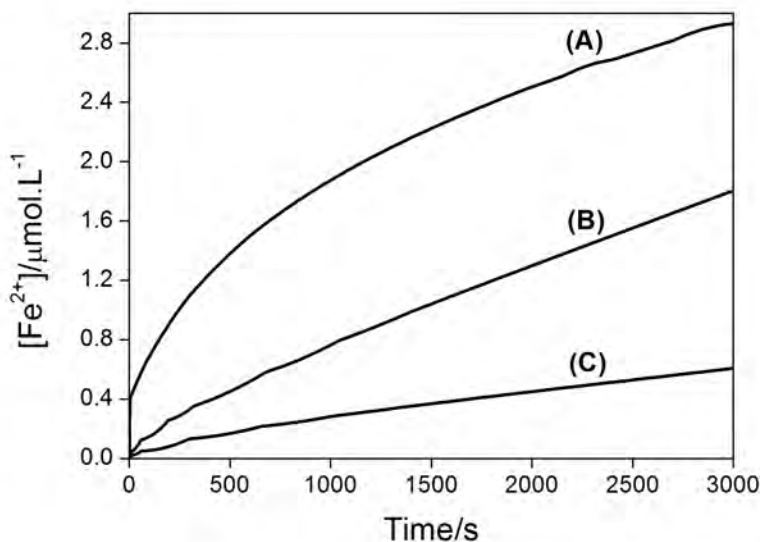


Fig. 6. The accumulation of ferrous ion during irradiation (350 nm) of 1.0 mM Fe(III) at: (A) pH 1.0 in the presence of 0.75 mol L^{-1} chloride ion; (B) at pH 3 in the absence of chloride ion; and (C) at pH 3 in the presence of 1.8 mmol L^{-1} sulfate ions.

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

Table 2. Set of additional ground state reactions required to fit the accumulation of Fe²⁺ during the steady-state irradiation of Fe³⁺ 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 Fe²⁺ 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 Laet & Le, 2005). Sulfate ion complexes strongly with Fe(III) over a wide pH range (Figure 7) and the quantum yield of production of Fe²⁺ plus a sulfate anion radical from photolysis of Fe(SO₄)⁺ 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 CO₂. 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 $mol^{-1} L s^{-1}$)
<i>Speciation Equilibria (I = 1)</i>		
1	$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$	$k_1 = 2.09 \times 10^{12}, k_{-1} = 1 \times 10^{10}$ (I=1)
2	$Fe^{3+} + 2SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$	$k_2 = 1.95 \times 10^{13}, k_{-2} = 1 \times 10^{10}$ (I=1)
3	$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4$	$k_3 = 1.55 \times 10^{11}, k_{-3} = 1 \times 10^{10}$ (I=1)
<i>Reactions of Sulfate Ions</i>		
4	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	$k_4 = 2.8 \times 10^{11}, k_{-4} = 1 \times 10^{10}$ (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	$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	$k_{10} = 2.7 \times 10^8$
<i>Reactions of Iron Species</i>		
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).

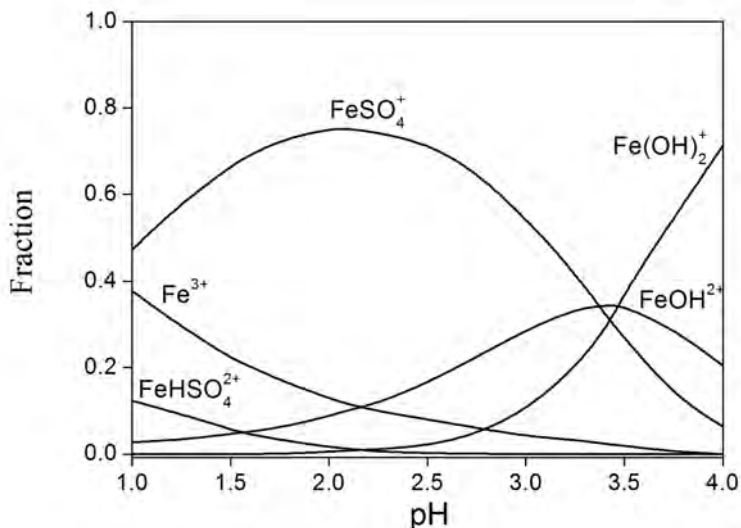


Fig. 7. Speciation of 1.0 mM Fe(III) between pH 1 and 4 at 25°C and an ionic strength of 0.2 in the presence of 1.8 mM sulfate. Mole fractions of each species were calculated with the public domain program Hydra (Puigdomenech, 2010), employing the equilibrium constants for complexation supplied with 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 $\text{Fe}(\text{OH})^{2+}$. 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.

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