The Use of Iron in Advanced Oxidation Processes

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Abstract: The oxidation of organic compounds by Fe(II)/H_2O_2 (known as Fenton's reagent) has been known for nearly a century. Recently, this reagent has been used in wastewater treatment technology. The scope and the range of applicability of Fenton and Fenton like [Fe(III)/H_2O_2] reagents in advanced oxidation technology is reviewed and selected examples of their application are presented. The rate of oxidation and the extent of mineralization of organic pollutants with these reagents is improved significantly by irradiation with UV-visible light. The usefulness of UV-visible/Fe(II)/H_2O_2 and UV-visible/Fe(III)/H_2O_2 processes are exemplified through specific applications. Still, much higher improvement in the rate of destruction of organic pollutants is achieved by replacement of Fe(II)/Fe(III) with ferrioxalate. Examples are provided indicating the superiority of the UV-visible/ferrioxalate/H_2O_2 process compared to the UV-visible/Fe(II)/H_2O_2 and UV-visible/Fe(III)/H_2O_2 processes. Finally, the ferrioxalate/H_2O_2 reagent is shown to be suitable for solar detoxification of contaminated water. Again, selected examples indicate the role that this reagent can play in the solar detoxification process.

Photochemical degradation processes [also called Advanced Oxidation Processes (AOP)] are gaining an increasingly important place in waste water remediation (1). AOP systems are based on oxidative reactions initiated by hydroxyl radicals (·OH), which are frequently generated by the photolysis of hydrogen peroxide. Since hydrogen peroxide does not absorb significantly beyond 300 nm and absorbs only weakly in the range 200-300 nm, the UV/H_2O_2 process is often not suitable for the treatment of polluted water with a high UV absorbance and/or a high background total organic carbon concentration. Thus an alternative oxidation process (or processes) is needed for the treatment of such highly contaminated waters. Photo-oxidation mediated by ferric ion and/or ferric chelates seems to provide a suitable treatment alternative.

Iron is the second most abundant metal and the fourth most abundant element found in the Earth's crust where it is found as ferrous [Fe(II)] or ferric [Fe(III)] ions. It is introduced into the atmosphere by wind and is found in aerosols, fogs, rain drops, ground waters and lakes. It plays a significant role in atmospheric photochemistry and its importance in the aquatic environment has long been recognized (2-7).

In solution at an acidic pH of about 0, ferric ion exists as $[Fe(H_2O)_6]^{3+}$. However, it hydrolyzes and forms hydroxo species at higher pH. The initial hydrolysis equilibria among various hydrolyzed Fe(III) species are (5):

$$Fe^{3+} + OH^- \rightleftarrows Fe(OH)^{2+} \qquad K_1 = 6.5 \times 10^{11} \quad (1)$$

$$Fe(OH)^{2+} + OH^- \rightleftarrows Fe(OH)_2^+ \qquad K_2 = 3.08 \times 10^{10} \quad (2)$$

As shown in Figure 1, the proportion of different species varies with the acidity of the solution. The hydroxylated species are yellow in color and exhibit a ligand-to-metal charge-transfer (LMCT) absorption band in the UV region which tails into the visible region. Figure 2 shows the absorption spectra of various Fe(III) species in solution. Irradiation of these species with UV and near-UV light (3) produces Fe(II) and the hydroxyl radical (·OH) according to:

$$Fe(III)(OH)^{2+} + h\nu \longrightarrow Fe(II) + \cdot OH \qquad (3)$$

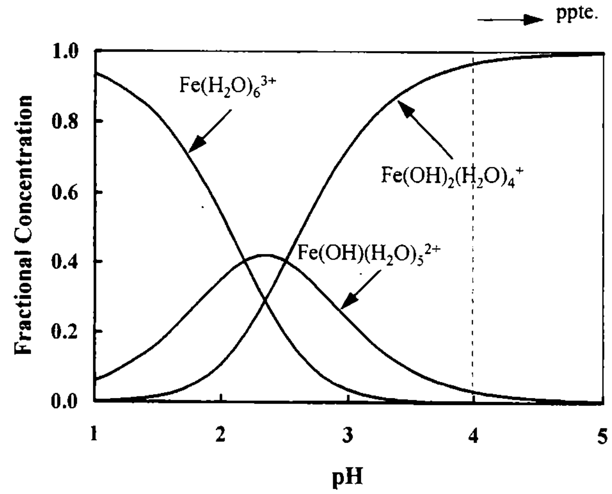

Figure 1. Variation of concentration of monomeric Fe(III) and Fe(III)-hydroxo species as a function of pH.

The hydroxyl radical is very reactive and reacts with most organic pollutants present in solution (8). The destruction of s-triazine by ·OH radicals released in reaction (*3*) was investigated by Larson et al. (9). Calculations (*5*) show that reaction (*3*) is the prime source of hydroxyl radicals and ferrous ions in

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atmospheric water during the day time. This conclusion is supported by the measured quantum yield of Fe(II) formation from various Fe(III) species (Table 1). The dark reduction of Fe(III) by chemical reductants present in solution is much slower than photoreduction.

Table 1. The quantum yield of Fe(II) formation for various species of Fe(III).

Fe(III) species	λ (nm)	$\phi_{Fe(II)}$	Ref.
$Fe(H_2O)_6^{3+}$	254	0.065	10
$Fe(OH)_2^{+}$	313	0.14	3
$Fe_2(OH)_2^{4+}$	350	0.007	10
$Fe(OH)^{2+}$	350	0.017	3

The ferrous ion formed in reaction (*3*) reacts with molecular oxygen (2) and generates hydrogen peroxide (H_2O_2) according to:

$$Fe(II) + O_2 \longrightarrow Fe(III) + O_2^{-}\cdot \qquad (4)$$

$$O_2^{-}\cdot + H^+ \longrightarrow HO_2\cdot \qquad (5)$$

$$HO_2\cdot + Fe(II) + H^+ \rightleftarrows H_2O_2 + Fe(III) \qquad (6)$$

This reaction is believed to be responsible for the formation of hydrogen peroxide in atmospheric and surface waters (2,3). However, this may not be a significant route for production of hydrogen peroxide, due to solubility limitations of Fe(III) species at natural pH.

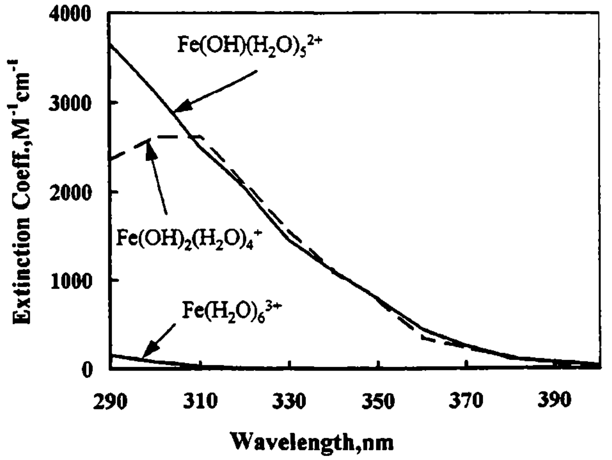

Figure 2. Absorption spectra of monomeric Fe(III) and Fe(III)-hydroxo species.

Atmospheric and surface waters are also rich in carboxylates ($RCOO^-$) and polycarboxylates, such as citrates, oxalates, etc. These species react with Fe(III) to form Fe(III)-carboxylate/polycarboxylate complexes and/or associated ion pairs. These complexes also exhibit a LMCT band in the UV-visible region. Excitation into this band results in transferring an electron from a ligand orbital to a metal orbital, thus generating Fe(II), CO_2, and organic radicals (11). It is assumed that solar irradiation of these complexes is responsible for: (a) the formation and destruction of hydrogen peroxide in natural aquatic environments; (b) the destruction and prevention of accumulation of organic pollutants in the environment; and (c) the recycling of carbon dioxide.

Fenton's and Fenton like Reagents

A hundred years ago, the oxidation of maleic acid by Fe(II)/H_2O_2 (known as the Fenton's reagent) was reported by Fenton (12). Subsequently, it was shown (13) that the hydroxyl radical is the oxidizing species in this system which is formed according to:

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + OH^- + \cdot OH \qquad (7)$$

$$k = 76.5\ M^{-1}\,s^{-1}$$

Although this reagent has been used in mechanistic investigations in organic chemistry, its potential in wastewater treatment has only begun in recent years (14-22). It has been demonstrated that Fenton's reagent is able to destroy phenols, chlorinated phenols and herbicides in water media, as well as reducing chemical oxygen demand (COD) in municipal wastewater. It is being employed for the treatment of wastewaters contaminated with phenolic pollutants. The usefulness of the Fe(II)/H_2O_2 process as a potential oxidant of soil contaminants has also been investigated (23-25). It has been shown that pentachlorophenol and trifluralin are extensively degraded (3), while hexadecane and dieldrin were partially transformed (25) in a soil suspension at an acidic pH.

The use of Fe(II)/H_2O_2 as an oxidant for wastewater treatment is attractive due to the fact that: (a) iron is a highly abundant and non-toxic element; and (b) hydrogen peroxide is easy to handle and is environmentally benign. However, it requires a stoichiometric amount of Fe(II), demanding a high concentration of Fe(II).

Hydrogen peroxide decomposes catalytically by Fe(III) and generates hydroxyl radicals in the process (13). Thus ferrous ion in Fenton's reagent can be replaced with ferric ion (21). The mechanism proposed for free ferric ion involves the hydroxyl ($\cdot OH$) and hydroperoxyl radicals ($HO_2\cdot$) according to:

$$Fe^{3+} + H_2O_2 \rightleftarrows H^+ + Fe(OOH)^{2+} \qquad (8)$$

$$k_8 = 2 \times 10^{-3}$$

$$Fe(OOH)^{2+} \longrightarrow HO_2\cdot + Fe^{2+} \qquad (9)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH \qquad (7)$$

$$Fe^{2+} + HO_2\cdot \longrightarrow Fe^{3+} + HO_2 \qquad (10)$$

$$k_{10} = 3 \text{ x } 10^6 \text{ M}^{-1} \text{s}^{-1}$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (11)$$

$$k_{11} = 2.7 \text{ x } 10^7 \text{ M}^{-1} \text{s}^{-1}$$

The rate constant for reaction of ferrous ion with hydrogen peroxide is high and Fe(II) oxidizes to Fe(III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. For this reason, it is believed that a majority of the waste destruction catalyzed by Fenton's reagent is simply Fe(III)-H_2O_2 catalyzed destruction process, and Fenton's reagent with an excess of hydrogen peroxide is essentially a Fe^{3+}/H_2O_2 process (known as a Fenton like reagent) (21).

The mineralization of the herbicide 2,4-D by Fenton and Fenton like reagents is shown in Figure 3. The data show that the extent and the overall rate of mineralization are independent of the oxidation state of iron employed (21). However, the initial rate of mineralization of organic pollutants is faster with Fe(II)/H_2O_2 than Fe(III)/H_2O_2. This is due to the surge of hydroxyl radicals which is produced by Fenton's reagent. The rate of production of hydroxyl radical is slow with Fenton like reagents. Thus, the use of Fenton's reagent is beneficial in cases where only the transformation of parent pollutants is desired.

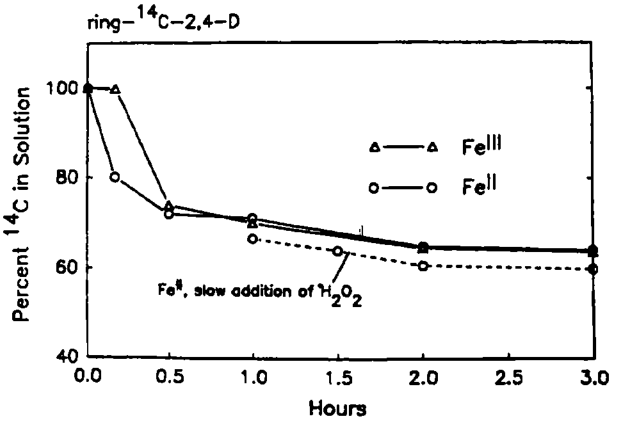

Figure 3. Comparison of Fe(II)/H_2O_2 with Fe(III)/H_2O_2 for mineralization of (ring-14C)-2,4D [from (21) with permission].

The Fe(II)/Fe(III)-H_2O_2 system has its maximum catalytic activity at a pH of about 2.8-3.0. An increase or decrease in the pH sharply reduces the catalytic activity of the metal ion. At high pH, the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of Fe(III) with H_2O_2 [reaction (*8*)] is inhibited. To overcome this problem, Sun and Pignatello (26) have employed Fe(III) chelates in place of Fe(II)/Fe(III). They have shown that a variety of herbicides and pesticides can be transformed and partially mineralized by Fe(III) chelates at neutral pH. The use of Fe(III) chelates for the destruction of organic pollutants in soil was also investigated by Pignatello and Baehr (27).

Fenton and Fenton like reagents can oxidize and transform, but do not completely mineralize, organic pollutants. Rather, the pollutants are partially oxidized and transformed to some intermediates which are resistant to further oxidation (20-22). At this point, hydrogen peroxide is consumed through Fenton's reaction and the following reactions:

$$Fe(III) + H_2O_2 \longrightarrow Fe(II) + HO_2\cdot + H^+ \qquad (12)$$

$$Fe(III) + HO_2\cdot \longrightarrow Fe(II) + O_2 + H^+ \qquad (13)$$

$$Fe(II) + \cdot OH \longrightarrow Fe(III) + OH^- \qquad (14)$$

$$k = 4.3 \text{ x } 10^8 \text{ M}^{-1} \text{s}^{-1}$$

and oxidation of Fe(II) by hydroxyl radical competes with the slow reaction of ·OH with some organic intermediates such as carboxylic acids. Normally, about 40-60% of the carbon is converted to CO_2, depending on the amount of Fe(II), peroxide and the solution temperature.

Photo-Fenton/Fenton like Processes

The rate of degradation of organic pollutants with Fenton/Fenton like reagents is accelerated strongly by irradiation with UV-visible light (19-22,28). An example is provided in Figure 4, where the destruction of ethylbenzene in tap water is compared using the Fenton's reagent or the photo-Fenton (*hv*/Fenton) process, demonstrating the greater efficiency of the latter process. If desired, organic pollutants can be mineralized completely with UV-visible irradiation. For example, Pignatello (21) and Sun and Pignatello (22) have shown that a number of herbicides and pesticides can be totally mineralized by the *hv*/Fe(III)/H_2O_2 process, and the mineralization of chlorophenol by the *hv*/Fenton process has been demonstrated by Rupert et al. (20).

The increased efficiency of Fenton/Fenton like reagents with UV-visible irradiation is attributed to:

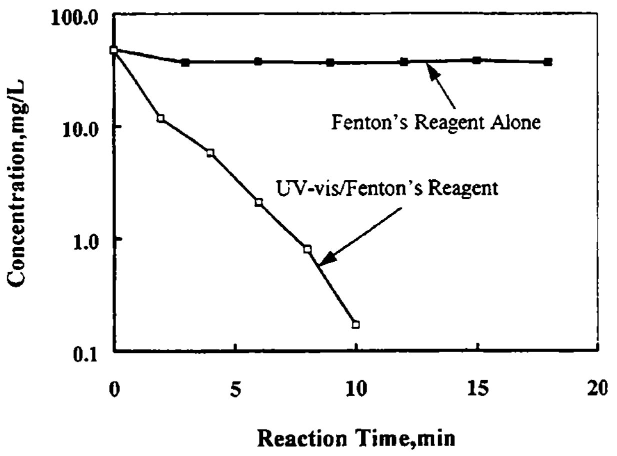

Figure 4. Comparison of Fenton and UV-visible Fenton's reagents for the destruction of ethylbenzene.

- *Photoreduction of ferric ion*: Irradiation of ferric ion (and/or ferric hydroxide) produces ferrous ion according to reaction (*3*). The formation of ferrous ion (20) during mineralization of phenol is shown in Figure 5. The ferrous ion produced reacts with hydrogen peroxide generating a second hydroxyl radical and ferric ion, and the cycle continues. Lunak et al. (29-32) observed the enhanced rate of photo-oxidation of salicylic and benzoic acid by hydrogen peroxide in the presence of Fe(III), as well as the increased rate of photodecomposition of hydrogen peroxide in the presence of transition metal ions. However, reaction (*3*) alone cannot account for the observed rate of disappearance and oxidation of organic pollutants.

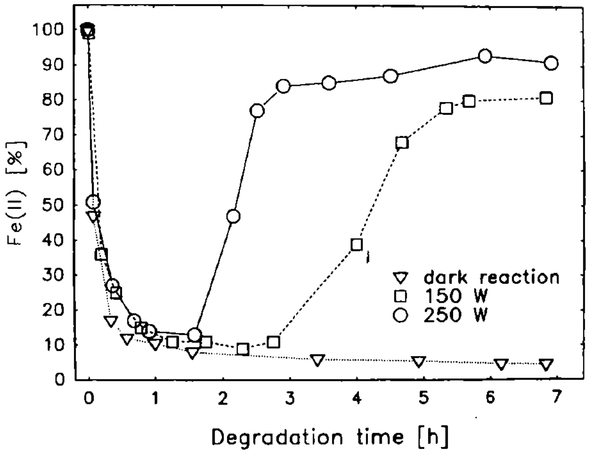

Figure 5. Effect of irradiation on the percentage of Fe(II) [from (21) with permission].

- *Efficient use of light quanta*: The absorption spectrum of hydrogen peroxide does not extend beyond 300 nm and has a low molar absorption coefficient beyond 250 nm. On the other hand, the absorption spectrum of ferric ion (and/or hydroxo ferric ions) extends to the near UV-visible region and has a relatively large molar absorption coefficient, thus making more efficient use of the lamp output when polychromatic light is employed. Consequently, photo-oxidation and mineralization can even proceed by irradiation with visible light (21,22).

- *Photolysis of Fe(III)-organic intermediate chelates*: The initial oxidation of organic pollutants generates oxygenated intermediates (i.e. intermediates with hydroxyl and/or carboxylic functional groups) which can react with Fe(III) and form complexes. These complexes are also photoactive and produce CO_2, organic radicals and ferrous ions on irradiation (11).

$$\mathrm{Fe(III)(RCO_2)} + h\nu \longrightarrow \mathrm{Fe(II)} + \mathrm{CO_2} + \mathrm{R\cdot} \qquad (15)$$

This results in an increased rate of destruction of organic pollutants as the reaction progresses. An example of this behavior is provided in Figure 6 for the destruction of toluene in tap water. Additional examples are provided by Sun and Pignatello (21). They have shown that mineralization of 2,4-D can be divided into two stages. The first stage is dominated by oxidation with hydroxyl radicals, where the light contributes to the production of ·OH, which is the primary oxidant at this stage of mineralization process. This was shown by quenching when known hydroxyl radical scavengers, such as methanol or *t*-butanol, were added. In contrast, the second stage of mineralization could not be quenched by hydroxyl radical scavengers. Thus it appears that the second stage (i.e. about 60% of mineralization) occurs without the participation of hydroxyl radicals and is likely entirely the result of the photochemistry of iron complexes [i.e. reaction (*15*)].

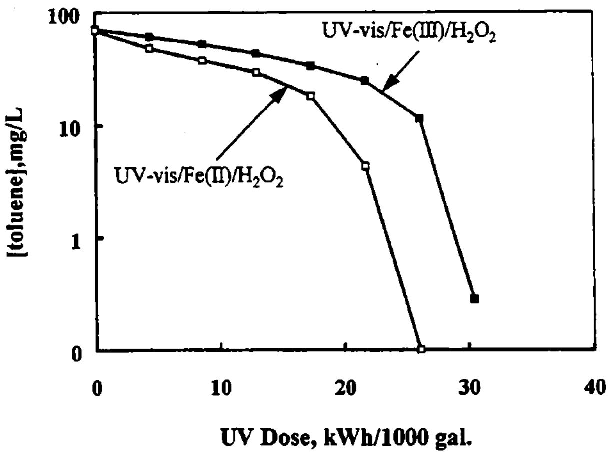

Figure 6. Destruction of toluene in tap water with UV-visible. irradiation in presence of Fe(II)/H_2O_2 and Fe(III)/H_2O_2.

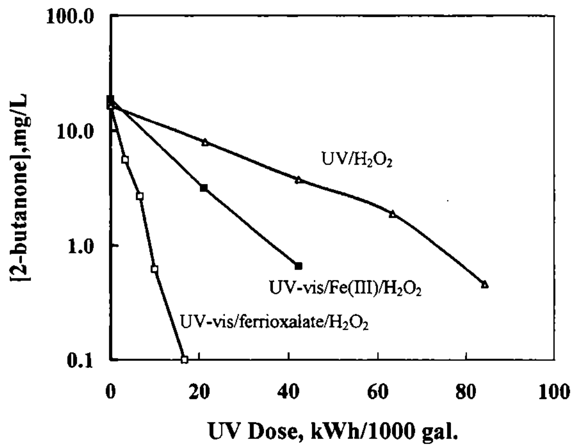

Figure 7. Destruction of 2-butanone in a contaminated ground water with different UV treatment processes.

unity and our preliminary results indicate that the quantum yield of hydroxyl radical formation is greater than one.

Any organic pollutant that has a reasonable rate of reaction with the hydroxyl radical can be oxidized and mineralized, if desired, with the *hv*/ferrioxalate/H_2O_2 process. Thus, aromatic and chloro-aromatic hydrocarbons, chlororinated ethylenes, ethers, alcohols, ketones, etc., can be treated efficiently with this new process. It can be used either for pollutant transformation or for the total mineralization of organic pollutants in contaminated waters. Mineralization is a slower process, as expected, and consumes a larger amount of oxidants and electrical power as compared to pollutant transformation. The rate of mineralization and transformation of 1,4-dioxane in process waste water with *hv*/ferrioxalate/H_2O_2 process is compared in Figure 8, indicating the slower rate of mineralization (38).

Table 2. The electrical energy per order (EE/O) for the destruction of a number of pollutants in a ground leachate water by various advanced oxidation processes.

Pollutant	Initial Conc. (mg/L)	EE/O, kWh/1000 US gallons[a]		
		UV/H_2O_2	UV-visible/ Fenton	UV-visible/ Ferrioxalate/H_2O_2
Toluene	12	20	9	1.6
Xylenes	5	23	10	2.5
MEK	18	54	29	5.7
Acetone	6	–[b]	108	58

a. The EE/O is defined as the amounts of electrical energy needed to reduce the concentration of a given pollutant by an order of magnitude in one thousand gallons of contaminated water.

b. Acetone was not treated at a measurable rate by this treatment procedure.

Table 3. The EE/O for the destruction of various pollutants in different contaminated waters.

Compound	Co-Contaminants	Water type	Conc. (mg/L)	COD (mg/L)	Absorbance	EE/O[a]
Benzene	Tol.,TCE,PCE	Ground	50	1250	Very High	8
Benzene	BTEX(100 mg/L)	Ground	26	350	Very High	7.9
1,4-Dioxane	Soap	Process	460	1480	Moderate	12

a. kWh/order/1000US gal.

Solar Detoxification of Polluted Waters

The use of the sun's free radiation energy for the treatment of contaminated water has attracted a lot of attention in recent years. However, almost all the solar radiation energy below 300 nm is absorbed by atmospheric ozone. Thus, any solar photo-oxidation process must rely on an absorber that is active above 300 nm. This effectively rules out ozone and hydrogen peroxide.

The best known catalyst for solar photo-oxidation is the anatase form of titanium dioxide, TiO_2 (39). It absorbs about 3% of solar spectrum (40) and has a low quantum yield (about 4%). Therefore, under ideal conditions, titanium dioxide can only utilize about 0.12% of the incident solar radiation energy. Transition metal ions and their complexes with organic molecules absorb in the near UV-visible region (*vide infra*) and are photoactive and thus should provide a suitable mediator for the capture and use of solar energy.

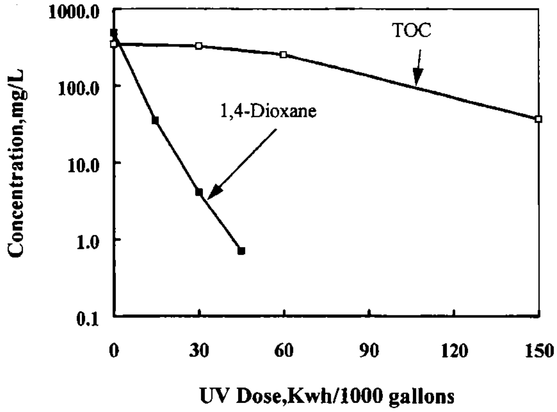

Figure 8. Transformation and mineralization of 1,4-dioxane in a process water by the UV-visible/ferrioxalate/H_2O_2 process.

The solar irradiation of hydroxo ferric ions and ferric-carboxylates/polycarboxylates is believed to play a crucial rule in the destruction of organic pollutants in clouds, lakes and oceans, and is responsible for the formation and destruction of hydrogen peroxide in natural waters. The concentration of dissolved iron species varies from 10^{-7} M to 10^{-4} M. This amount of iron could potentially destroy 0.027 g/L/day to 2.7 g/L/day of oxalic acid and/or similar amounts of other polycarboxylates in atmospheric water droplets (2c).

The use of sunlight for the destruction of organic pollutants was first demonstrated by Langford et al. (6). They have shown that solar irradiation of Fe(III)-nitrilotriacetate results in the destruction of nitrilotriacetic acid. From this work, they suggested that solar irradiation of Fe(III)-organic complexes could be responsible for the destruction of detergents (natural and synthetic) and hence prevents their accumulation in the environment. Miles et al. (7) in the early 1980's demonstrated that sunlight irradiation of Fe(III)-humic complexes consumes oxygen and the rate of oxygen consumption increases with increasing concentrations of Fe(III) and/or humic substances. This was attributed to the photoreduction of Fe(III) [i.e. reaction (*3*)] and the consumption of oxygen by the photolytic products [i.e. reactions (*4*-*6*)]. The consumption of oxygen was reduced by 50% with the esterification of humic substances. Thus, it was concluded that the sunlight driven photolysis of Fe(III)-humic complexes is responsible for the undersaturation of oxygen in colored lake surface waters. These observations indicate that Fe(III)-carboxylates/polycarboxylates are suitable candidates for capturing solar energy.

Ferrioxalate has been shown to be a highly suitable candidate for capturing solar energy. As indicated earlier, it absorbs strongly between 250-500 nm, has a quantum efficiency of ≥ 1 and can absorb and utilize about 18% of the incident solar radiation energy (40). Thus, the ferrioxalate/H_2O_2 system could theoretically be about 120 times more efficient than the TiO_2 photocatalyst in utilizing solar energy. Figure 9 compares the destruction of trichlorethylene (TCE) in tap water with ferrioxalate/H_2O_2 and TiO_2/H_2O_2 by solar irradiation, demonstrating the superiority of the former mediator compared to the latter one. As can be seen, sunlight photolysis of ferrioxalate/H_2O_2 is much more effective than titanium oxide/H_2O_2 in destroying TCE. The rate of destruction of TCE mediated by ferrioxalate/H_2O_2 is about fifty times faster than that catalyzed by titanium oxide. A second example of the use of sunlight for the clean-up of water (41) is provided in Figure 10. In this figure, the destruction of toluene in a contaminated ground water by sunlight photolysis of ferrioxalate/H_2O_2 and Fe(III)/H_2O_2 is compared, indicating the far greater efficiency of the former process as compared to the latter one.

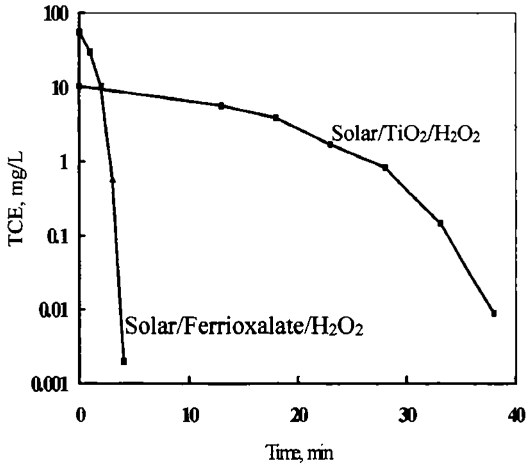

Figure 9. Comparison of TCE destruction by solar irradiation in presence of TiO_2/H_2O_2 and ferrioxalate/H_2O_2.

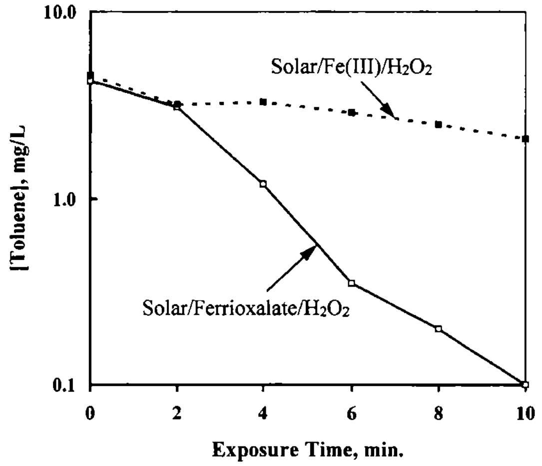

Figure 10. Comparison of toluene destruction in a polluted ground water by solar irradiation in presence of Ferrioxalate/H_2O_2 and Fe(III)/H_2O_2.

Conclusions

Although the UV/H_2O_2 oxidation process has the capacity of being able to virtually destroy most organic pollutants in water media and is being increasingly employed for the remediation of contaminated water, there are situations [high concentration and high chemical oxygen demand (COD)] where the UV/H_2O_2 process is too costly. The scope and range of applicability of photo-oxidation technology can be improved significantly by the use of ferric ion, hydroxylated ferric ion and Fe(III)-carboxylate/polycarboxylate complexes. These species exhibit LMCT bands in the UV-visible region and produce ferrous ion with excitation into this band. Thus, the

- *Participation of dissolved O_2*: Reaction of dissolved molecular oxygen with organoradicals produces oxygenated intermediates which can then react with ferric ion.

$$R\cdot + O_2 \longrightarrow ROO\cdot \longrightarrow \text{Oxygenated products} \qquad (16)$$

The oxygenated products react with Fe(III) and the resulting complexes are further photolyzed, producing more Fe(II) and thereafter hydroxyl radicals.

It is for these reasons that irradiation of Fenton/Fenton-like reagents with UV-visible light improves the rate of destruction and the extent of mineralization of organic pollutants. However, these reagents are only suitable for the remediation of polluted water with low to medium absorptivity in the UV, near-UV and visible region, and with low to moderate background chemical oxygen demand.

hv/Fe(III)-Oxalate/Hydrogen Peroxide

The photoreactivity of Fe(III)-carboxylate/polycarboxylates has long been recognized and photodecarboxylation of carboxylates (11) and deamination (33) of α-aminoacid complexes of Fe(III) has been known for some time. Ferrioxalate is the oldest and best known photoactive example of Fe(III)-polycarboxylate complexes. Its photoreactivity was first discovered in 1833 (34) and was later suggested as a chemical actinometer for light intensity measurements. Today, it is the actinometer of choice (11,35). Irradiation of ferrioxalate in acidic solution generates Fe(II) and carbon dioxide, according to:

$$[Fe(C_2O_4)_3]^{3-} + hv \longrightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{-}\cdot \qquad (17)$$

$$C_2O_4^{-}\cdot + [Fe(C_2O_4)_3]^{3-} \longrightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2\,CO_2 \qquad (18)$$

$$C_2O_4^{-}\cdot + O_2 \longrightarrow O_2^{-}\cdot + 2\,CO_2 \qquad (19)$$

The photochemistry of ferrioxalate has been studied extensively and the quantum yield of Fe(II) formation ($\phi_{Fe(II)}$) as a function of irradiation wavelength both in the absence and presence oxygen have been reported by numerous researchers. $\phi_{Fe(II)}$ is about 1.0-1.2 and independent of irradiation wavelength in the range of 250-480 nm and decreases with further increase of irradiation wavelength.

Although photochemistry of Fe(III)-carboxylate/polycarboxylates has been known for some time, its importance in the destruction of organic pollutants has only recently begun to emerge. The photolysis of ferrioxalate produces ferrous (free or complexed with oxalate) ion, which, in combination with hydrogen peroxide provides a continuous source of Fenton's reagent. The latter is, of course, a precursor to the hydroxyl radical. Lunak et al. (32) have shown that the rate of photolytic destruction of hydrogen peroxide is greatly accelerated in the presence of ferrioxalate and that hydrogen peroxide can be destroyed with irradiation in a region where only ferrioxalate absorbs radiation. This is not surprising in view of the photoreactivity of ferrioxalate [reactions (*13-15*)]. The formation of hydroxyl radicals in the photolysis of ferrioxalate/H_2O_2 mixtures was demonstrated recently by Zepp et al. (36). They showed that reaction with H_2O_2 is the preferred pathway for the oxidation of photogenerated Fe(II) and that the rate of formation of hydroxyl radicals is equal to the rate of formation of ferrous ions.

Until recently, the combination of ferrioxalate/H_2O_2 was not employed for the treatment of pollutants in contaminated water. Lunak et al. (29) observed that the rate of hydroxylation of salicylic acid with *hv*/H_2O_2 increases in the presence of Fe(III) or ferrioxalate. The increase in the rate of hydroxylation was partly attributed to reduction of ferric ion by photolysis [i.e. eq (*3*)] and partly to energy transfer from excited organic molecules to hydrogen peroxide and ferric ion. The latter is then reduced to ferrous ion. Their data, however, does not indicate that any advantages could be gained in employing ferrioxalate over ferric chloride, perhaps in part due to the use of monochromatic radiation in the near-UV region and to Fe(III)-salyclic acid/benzoic acid complex formation.

Safarzadeh-Amiri et al. (37,38) have shown that *hv*/ferrioxalate/H_2O_2 is a highly efficient and powerful oxidant for the destruction of organic pollutants in contaminated ground and waste waters. Figure 7 compares the destruction of 2-butanone (methylethylketone, MEK) in a ground leachate water with UV/H_2O_2, UV-visible/Fenton and UV-visible/ferrioxalate/H_2O_2, while Tables 2 and 3 provide a list of different pollutants in this and other contaminated waters that were treated by this new photo-oxidation process. Table 2 also provides data for the treatment of the same pollutants by other UV-visible/oxidation processes. The data clearly indicate that the UV-visible/ferrioxalate/H_2O_2 process is much more efficient (by a factor of 2-6, depending on the pollutant being treated) than other photo-oxidation processes.

The high efficiency of this process, as compared to other UV-driven processes, is attributed to: (a) ferrioxalate absorbs strongly in the UV-visible region, from 250-480 nm, resulting in more efficient use of the lamp output; and (b) the quantum yield of Fe^{2+} formation is high (about 1-1.2) and independent of irradiation wavelength in the range of 250-480 nm. Thus, the yield of hydroxyl radical formation is expected to be high (on the order of unity) in this process. Indeed, Zepp et al. (36) have shown that the quantum yield of hydroxyl radical formation is on the order of photolysis of these species in the presence of hydrogen peroxide provides a continuous source of hydroxyl radicals. The data and examples provided in this article clearly indicate the prominent role that ferric ion can play in AOP technology.

The photo-oxidation of organic pollutants in water mediated by iron and iron chelates, is initiated by the hydroxyl radical, which with dissolved oxygen eventually converts organic pollutants to CO_2, H_2O and mineral acids. However, the detailed mechanism of the complex reaction pathways have not been elucidated. Therefore, there is a need for further studies to understand these mechanisms and to expand the scope of *hv*-metal ion/H_2O_2 mediated remediation processes to include other transition metal ion(s).

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