



Photochemistry of hydrolytic iron (III) species and photoinduced degradation of organic compounds. A minireview

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Abstract

On the basis of the research literature of the last fifty years, we have reviewed the photochemical properties of different hydrolytic Fe(III) species and the photodegradation of organic compounds in aqueous solutions initiated by them (mainly including low-molecular-weight Fe(III)-OH complexes, Fe(III) oxides (Fe₂O₃) and Fe(III) hydroxides (FeOOH)). Furthermore, the feasibility and prospects of the novel photochemical methods of using Fe(III) salts and oxides in wastewater treatments are being discussed in this paper. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fe(III) salts; Hydrolysis; Species; Photochemical properties; Photodegradation; Organic compounds

1. Introduction

Water pollution treatment is a major task of environmental protection. Among the treatment techniques, photocatalytic oxidation processes have drawn much attention. At present, research has shown that it can degrade organic compounds at low or medium concentration with little secondary pollution, and a potential of utilizing solar energy. Iron is one of the most abundant elements on earth. Many classes of iron metal, compounds, and mixtures are extensively used in industrial production and daily life, especially in chemical engineering as catalysts. It is important to develop environment-friendly iron catalysts with high efficiency, less energy cost and low price, which is one of the essential goals of Green Chemistry.

Early in 1949 (Evans and Uri, 1949) photochemical redox reactions of acidic FeCl₃ solutions were studied. Bates and Uri (1953) indicated when irradiated with UV-light, ferric ion could oxidize organic compounds in acidic aqueous solutions. The reagent responsible for the reaction was believed to be the hydroxyl radical ($\cdot\text{OH}$), a common and important environmental oxidant. After nearly fifty years, a research system for degradation of organic compounds by homogeneous photochemical system of Fe(III)-OH complexes was developed.

Since the late 1970s, semiconductor photocatalytic oxidation process for organic wastewater treatments has been extensively investigated. Besides the most populous photocatalyst TiO₂, many species of Fe(III) oxides, oxyhydroxides, and hydroxides have also drawn scientists' attention. Oxides such as $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$ and $\gamma\text{-FeOOH}$ were used for their special photochemical properties of oxidizing organic compounds especially in natural waters and atmospheric and surface droplets (Leland and Bard, 1987).

In the last 50 years, there have been many studies dealing with the photochemical properties and applications of different Fe(III) species. In this paper, some

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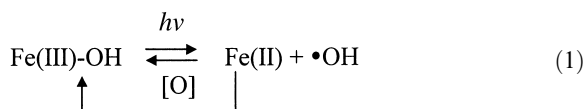
representative studies in this area are reviewed. The purpose of this work is not only to present some systematic and useful information on the progress in this area, but also to underline the importance of this research and promote its development.

2. Species produced from the hydrolysis in aqueous Fe(III) solutions

The hydrolysis of Fe(III) salts in aqueous solutions is a complicated time-dependent process, usually simply defined as hydrolysis-polymerization-precipitation. A popular mechanism (Flynn, 1984) divided the hydrolysis process into the following steps: (a) primary hydrolysis giving rise to low-molecular-weight complexes (mono- and dimer); (b) formation and aging of polynuclear polymers; (c) precipitation of ferric oxides and hydroxides. During these steps, about three classes of products of different species are involved, i.e., low-molecular-weight complexes ($\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, etc.), hydrolytic polymer ($\text{Fe}_n(\text{OH})_m(\text{H}_2\text{O})_x^{(3n-m)+}$, or $\text{Fe}_m\text{O}_n(\text{OH})_x^{(3m-2n-x)+}$), and precipitated oxides (amorphous(am)- $\text{Fe}(\text{OH})_3$, FeOOH , and Fe_2O_3).

3. Photochemical properties of low-molecular-weight Fe(III)-hydroxy complexes

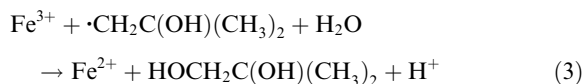
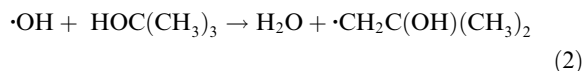
In aqueous solutions, low-molecular-weight Fe(III)-hydroxy complexes undergo photochemical reduction to Fe(II) irradiated with UV light (Baxendale and Magee, 1955; Langford and Carey, 1975), consequently, Fe(III) is reoxidized by oxidants (e.g., dissolved oxygen) to Fe(III) again. Thus the basic redox circle of Fe(III)/Fe(II) is completed. In the meantime, hydroxyl radical ($\cdot\text{OH}$) forms. The general reaction can be expressed as:



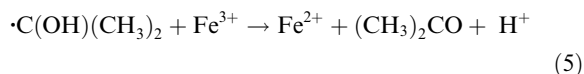
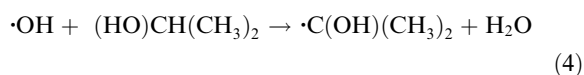
Some of the previous investigations were focused on the quantum yields of Fe(II) and $\cdot\text{OH}$ in the photochemical redox reactions in aqueous solutions containing Fe(III) ions, and the influence factors (e.g., irradiation wavelength, pH of the solutions etc.). Most previous studies (some examples are shown in Table 1) were carried out in acidic solutions with μM – mM Fe(III) and 1 mM –0.1 M scavengers for $\cdot\text{OH}$ radicals.

Measurement of quantum yield for $\cdot\text{OH}$ radicals by adding scavengers is an important method to investigate the photolysis of Fe(III) species. Langford and Carey

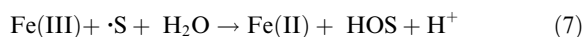
(1975) used tert-butyl alcohol as a scavenger to detect the photoformation of $\cdot\text{OH}$ in the photolysis of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$, the reactions are:



When 2-propanol was used as the scavenger for $\cdot\text{OH}$, acetone formed as the oxidized product (Carey and Langford, 1975; Benkelberg and Warneck, 1995):



More generally, the scavenging reactions for $\cdot\text{OH}$ can be expressed as:



where HS represents scavengers for hydroxyl radicals, $\cdot\text{S}$ activated states or radicals of the scavengers, HOS oxidized products of the scavengers. Different results were gained on $\cdot\text{OH}$ quantum yield or Fe(II) quantum yield when using different radical scavengers.

In fact, as we know, in the pH range ≤ 5 at least four different Fe(III) ions, which are well characterized, coexist in aqueous solution: Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and the dimer $\text{Fe}_2(\text{OH})_2^{4+}$. The species distribution is governed by the hydrolysis equilibria shown as reactions (8)–(10) (Flynn, 1984; Faust and Hoigné, 1990). Fig. 1 displays species distribution of three simple low-molecular-weight Fe(III)-hydroxy complexes.

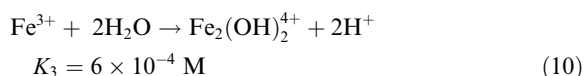
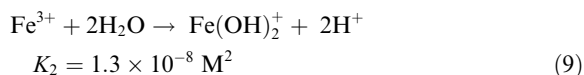
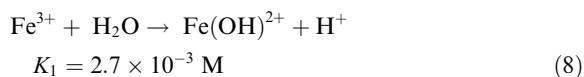


Table 1
Some research results reported on the photochemical properties of Fe(III)-OH complexes

Fe(III) salts solution	Light source	Quantum yield of $\cdot\text{OH}$	Quantum yield of Fe^{2+}	Reference
$[\text{Fe}^{3+}]_0 = 0.01 \text{ M}$ [Benzoic acid] = 2 mM [HClO ₄] = 0.02 M	125 W medium pressure mercury vapor lamp $\lambda = 365 \text{ nm}$	–	0.067	Bates and Uri (1953)
$[\text{Fe}^{3+}]_0 = 0.0346 \text{ mM}$ [HClO ₄] = 0.010 M In the absence of benzene In the presence of benzene	Mercury lamp $\lambda = 313 \text{ nm}$	– –	0.0114 0.113	Baxendale and Magee (1955)
$[\text{Fe}^{3+}]_0 = 2.07 \text{ mM}$ [HClO ₄] = 0.010 M [Methyl alcohol] = 0.07 M	Mercury lamp $\lambda = 313 \text{ nm}$	–	0.286	Baxendale and Magee (1955)
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$ Tert-butyl alcohol	Medium pressure mercury lamp $\lambda = 253.7 \text{ nm}$	0.065	0.130	Langford and Carey (1975)
$[\text{Fe}^{3+}]_0 = 10.0 \mu\text{M}$ pH = 4.0 [Tert-butyl alcohol] = 200 μM	Medium pressure mercury lamp $\lambda = 313 \text{ nm}$ $\lambda = 360 \text{ nm}$	0.14 ± 0.04 0.017 ± 0.003	–	Faust and Hoigné (1990)
$[\text{Fe}^{3+}]_0 = 0.2 \text{ mM}$ [Isopropanol] = 2 mM pH = 2 ~ 3	150 W xenon arc lamp $\lambda = 370 \text{ nm}$ $\lambda = 280 \text{ nm}$	0.07 0.31	–	Benkelberg and Warneck (1995)

Different species have their photochemical properties, respectively.

3.1. $\text{Fe}(\text{OH})^{2+}$

Shown in Fig. 1, $\text{Fe}(\text{OH})^{2+}$ is the dominant Fe(III)-hydroxy complex in aqueous solution from pH ≈ 2.5 –5. Its charge transfer band strongly overlaps the solar UV

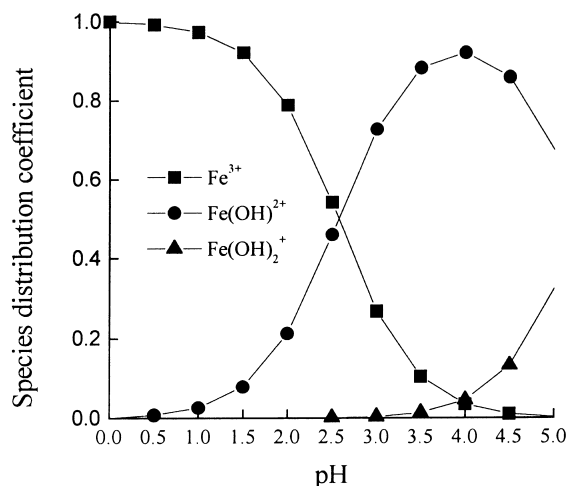


Fig. 1. Low-molecular-weight species distribution of hydrolytic Fe(III) salts in aqueous solutions at pH ≤ 5 . (Calculated according to the hydrolysis equilibria in reaction (8)–(10).)

spectrum (290–400 nm) (Weschler et al., 1986; Faust and Hoigné, 1990), and it photolyzes efficiently to produce $\cdot\text{OH}$ radicals (Baxendale and Magee, 1955; Faust and Hoigné, 1990):

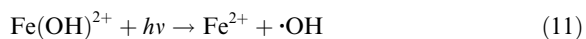
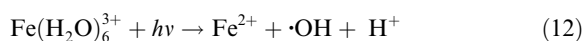


Table 2 shows the comparison of spectra and photochemical properties of low-molecular-weight Fe(III)-OH complexes. It can be seen that the quantum yield of $\cdot\text{OH}$ produced from the photolysis of $\text{Fe}(\text{OH})^{2+}$ is much higher than that of the other two species $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$. So, in the solution at pH 2.5 to 5, $\text{Fe}(\text{OH})^{2+}$ is the dominant photoreactive species.

3.2. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$

It was reported (Langford and Carey, 1975; Benkelberg and Warneck, 1995) that the photochemical reaction of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ can be expressed as



At low pH (<2.5), $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is the dominant species (Fig. 1). In spite of its low quantum yield of $\cdot\text{OH}$, it might be the important contributor for photoformation of $\cdot\text{OH}$ in the system. With increasing pH value, the contribution of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ to the photoformation of $\cdot\text{OH}$ decreased. Especially, in the solutions above pH ≈ 3 , its contribution can be completely ignored (Faust and Hoigné, 1990).

Table 2

Spectra and photochemical properties of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})^{2+}$, and $\text{Fe}_2(\text{OH})_2^{4+}$

Species	λ_{max} (nm)	Molar absorption coefficient ϵ ($\text{M}^{-1} \text{cm}^{-1}$) ^a	Quantum yield of $\cdot\text{OH}$ (Φ_{OH})	
			Radiation wavelength	(Φ_{OH})
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	240	4250	$\lambda = 254 \text{ nm}$ $\lambda \leq 300 \text{ nm}$	0.065 ^b 0.05 ^c
$\text{Fe}(\text{OH})^{2+}$	297	2030	Average value	0.14 ~ 0.19 ^d
	205	4640	Max: $\lambda = 280 \text{ nm}$	0.31 ^d
$\text{Fe}_2(\text{OH})_2^{4+}$	335	5000	$\lambda = 350 \text{ nm}$	0.007 ^b

^a Knight and Sylva (1975).^b Langford and Carey (1975).^c Benkelberg and Warneck (1995).^d Baxendale and Magee (1955).

3.3. $\text{Fe}_2(\text{OH})_2^{4+}$

The Fe(III) dimer, $\text{Fe}_2(\text{OH})_2^{4+}$, absorbs strongly in the solar UV region (290–350 nm) (Knight and Sylva, 1975). It photolyzes to produce free $\cdot\text{OH}$ radical. However, because of its small molar-fraction over pH range <3, its contribution to photoformation of $\cdot\text{OH}$ can also be ignored (Faust and Hoigné, 1990). Besides pH value, molar-fraction of $\text{Fe}_2(\text{OH})_2^{4+}$ depends also on the total concentration of Fe(III) species in the solution, so does its contribution to $\cdot\text{OH}$ formation.

3.4. $\text{Fe}(\text{OH})_2^+$

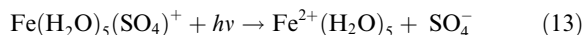
Either the concentration of $\text{Fe}(\text{OH})_2^+$ is too small to make an impact on the spectrum or its spectrum is indistinguishable from that of $\text{Fe}(\text{OH})^{2+}$, the photochemical properties of $\text{Fe}(\text{OH})_2^+$ have not been previously reported (Benkelberg and Warneck, 1995). It is likely that $\text{Fe}(\text{OH})_2^+$ may also photolyze to produce $\cdot\text{OH}$ radicals, since its precursors, Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$, and the further hydrolytic dimerization product, $\text{Fe}_2(\text{OH})_2^{4+}$, are all photoreactive. However, this idea should be tested in the future.

3.5. Influences of inorganic anions

Different inorganic anionic ligands show different tendencies to form complexes with iron(III) ions (Perrin, 1958; David and David, 1976). In aqueous solutions containing weak anionic ligands, such as NO_3^- and ClO_4^- , the principal ion pair is $\text{Fe}^{3+}\text{OH}^-$ formed by hydrolysis (Rabinowitch and Stockmayer, 1942), while in the presence of Cl^- or SO_4^{2-} , the ion pairs $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ or $\text{Fe}^{3+}\text{SO}_4^{2-}$ coexist, which has an influence on the photoreduction of Fe^{3+} to form $\cdot\text{OH}$ radicals and the oxidant capability of the system.

The photoreactivities of the two species, $\text{Fe}^{3+}\text{Cl}^-$ and $\text{Fe}^{3+}\text{SO}_4^{2-}$, were both reported by some authors (Uri,

1952; Benkelberg and Warneck, 1995). David and David (1976) conducted a comparative study on the photoredox chemistry of FeCl_3 and $\text{Fe}(\text{ClO}_4)_3$ in aqueous media, they thought that the primary photoprocess was the photodissociation of $\text{Fe}(\text{OH})^{2+}$ in aqueous solutions of FeCl_3 as well as $\text{Fe}(\text{ClO}_4)_3$, and the photodissociation of $\text{Fe}^{3+}\text{Cl}^-$ to produce $\cdot\text{Cl}$ radicals ($\text{Fe}^{3+}\text{Cl}^- + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{Cl}$) was not supported. Weschler et al. (1986) indicated that under the typical rain and fog water conditions, $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{SO}_4)^+$ are major ionic Fe(III) species, and both of their ultraviolet charge transfer spectra overlap with solar radiation in the 290–400 nm wavelength region. The associated photochemical process of $\text{Fe}(\text{SO}_4)^+$ was confirmed to be



Photodecomposition of the NO_3^- ion irradiated by UV light at the wavelength near 200 and 300 nm has been studied by many authors since the 1970s. Some authors (Treinin and Hayon, 1970; Strehlow and Wagner, 1982; Warneck and Wurzinger, 1988) indicated that the photolysis of NO_3^- in aqueous solution resulted in a convenient formation of $\cdot\text{OH}$ radicals. So, when irradiated, NO_3^- coexisting with $\text{Fe}^{3+}\text{OH}^-$ complexes may have an influence on the oxidation of organic compounds in aqueous solutions (Zepp et al., 1987).

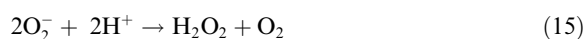
In the recent study (Zhou et al., 2000) on photodegradation of dyes in aqueous solutions containing Fe(III)-hydroxy complexes, Zhou et al., found that the anion's influence on photodegradation rate of the dyes is in the order of increasing photoreactivity as follows: $\text{NO}_3^- > \text{Cl}^- \approx \text{ClO}_4^- > \text{SO}_4^{2-}$.

4. Degradation of organic compounds in aqueous solutions induced by photolysis of Fe(III)-hydroxy complexes

Early in the 1950s, the photo-oxidation of organic compounds in aqueous acidic solutions containing

Fe(III)-hydroxy complexes with UV-light radiation was investigated (Bates and Uri, 1953; Baxendale and Magee, 1955). The oxidant was believed to be hydroxyl radicals produced from the photolysis of Fe(III)-OH complexes, typically, $\text{Fe}(\text{OH})^{2+}$ (reaction (11)). Now, the basic conclusions have been made as follows: in aqueous Fe(III) solutions at pH 3 ~ 5, $\text{Fe}(\text{OH})^{2+}$ is the dominant species; it photolyzes to produce hydroxyl radicals, which is an extremely strong ($E_0 = +2.80$ V) nonselective oxidant that can attack organic compounds and degrade them.

Besides reaction (11), hydroxyl radicals can also be formed in several other reactions:



Since the 1990s, with the flourishing of Advanced Oxidation Processes, many researchers have stressed the photochemical degradation system containing Fe(III)-OH complexes. Both man-made UV-light and the natural sunlight have been used in their studies on the photo-oxidation and degradation of organic compounds of many classes such as benzene, phenols and its derivatives (Kochay, 1992; Hideki and Atushi, 1993; 1994; Brand et al., 1998), chloro-organic carboxylates compounds (Maruthamuthu and Huie, 1995), as well as triazines (Larson et al., 1991). Kinetics, influence factors, and mechanisms of the photodegradation have been involved in these studies.

For different organic compounds, the photodegradation rates are not identical, which reflects their photodegradabilities. An important idea should be emphasized that there must be several steps in the whole reaction of the photodegradation of organic compounds in aqueous solutions. At least, one was the photoformation of $\cdot\text{OH}$ radicals; another was $\cdot\text{OH}$ radicals' attacking target groups or bonds in organic compounds, and the latter might be a rate-controlling step in the photodegradation system, which mainly caused the difference of photodegradation rates among organic compounds. That was why the authors got different $\cdot\text{OH}$ quantum yields or Fe(II) quantum yields when using different radical scavengers.

5. Photochemistry of Fe(III) oxides, oxyhydroxides, and hydroxides

There are many naturally occurring and synthetic iron oxides. Transformation of one structure to another is possible by hydration-dehydration and/or partial ox-

idation-reduction (Blesa and Matijevic, 1989). There are differences in physical, chemical, photochemical, and photoelectrochemical properties of Fe(III) oxides (Leland and Bard, 1987). All these properties can be associated with the photocatalytic semiconductors, typically TiO_2 with a band gap of 3.2 eV, and the activity of photoproducing e^- - h^+ couple.

Leland and Bard (1987) studied the photoelectrochemical properties of colloids and particles of different iron oxides. They believed α - Fe_2O_3 was the most effective catalyst for the photo-oxidation of sulfite. Frank and Bard (1977) investigated the photocatalytic oxidation of cyanide and sulfite by several semiconductor powders. They found that TiO_2 rather than α - Fe_2O_3 was an active photocatalyst for cyanide oxidation. Cunningham et al. (1988) presented evidence for the photocatalytic formation of $\cdot\text{OH}$ radicals in illuminated suspensions of α - FeOOH .

Wells et al. (1991) investigated the photolysis of colloidal iron in the oceans, and found that the photoreductive dissolution/rapid reoxidation/precipitation involving organic chromophores and yielded amorphous, highly labile Fe(III) precipitation. Fe^{2+} was also a transient species in oxic seawater of pH 8. From above, we can primarily see that the mechanism of photochemical reaction of Fe(III) oxides might differ from that of photocatalytic semiconductors.

5.1. Fe_2O_3

Iron oxide, a possible n-type semiconductor with a band gap of 2.2 eV, is a potentially interesting semiconductor for interfacial electron transfer (Baumgartner et al., 1983). Faust and Hoffmann (1986) proposed the mechanism of photoinduced reductive dissolution of α - Fe_2O_3 in bisulfite. They interpreted their results in terms of a photoinduced ligand-to-metal charge transfer from adsorbed organic reductant to a Fe(III) center on the metal oxide surface. This idea was accepted by most authors (Stramel and Thomas, 1986; Cunningham et al., 1988; Litter et al., 1991; Litter and Blesa, 1992; Goldberg et al., 1993; Pehkonen et al., 1995; Pulgarin and Kiwi, 1995). Goldberg et al. (1993) also proposed that, in many cases, the electron transfer step is rate-limiting, and the rate constant for this step has been shown to depend on the surface properties of the metal oxide and the nature of the complexing ligand.

Kormann and his coworkers (Kormann et al., 1989) examined the photocatalytic activity of α - Fe_2O_3 colloids and compared them to the colloids and suspensions of ZnO and TiO_2 . The formation of H_2O_2 and the oxidation of organic molecules were studied. ZnO and TiO_2 were found to be quite active photocatalysts in

producing hydrogen peroxide and in the degrading chlorinated hydrocarbon molecules, while only negligible photocatalytic activity was found for α -Fe₂O₃.

Another exploration of photochemical properties of Fe(III) oxides has focused on utilizing solar energy to photodecomposition of water to produce hydrogen. Khader et al. (1987a,b) reported the preparation and photochemical behavior of an iron oxide catalyst with much improved activity, which was undoped and produced hydrogen when illuminated with light. In the presence of N₂, dissociation of H₂O and reduction of N₂ to NH₃ occurred concomitantly. The reactions are shown as below:



These explorations have shown great potential for sunlight-driven production for clean hydrogen energy. But further work is needed.

5.2. FeOOH

Goldberg et al. (1993) reported the photoreductive dissolution of colloidal goethite (α -FeOOH) in the presence of different mono-carboxylate and polycarboxylate species. They pointed out that the photoreduction rate depended strongly on the structure of the adsorbed acid. Their results helped to explain the role of photolysis in the dissolution of iron from a goethite lattice when an organic acid was adsorbed as a ligand complex and radiated with sunlight. Photo-dissolution is one of the environmental behaviors of goethite and other iron(III) oxides, which is important for iron cycle in the environment.

Waite and Morel (1984) proposed a model of photoreductive dissolution of γ -FeOOH in natural waters (see Fig. 2). This model basically presented the photochemical redox cycle of Fe(III)/Fe(II) between solid

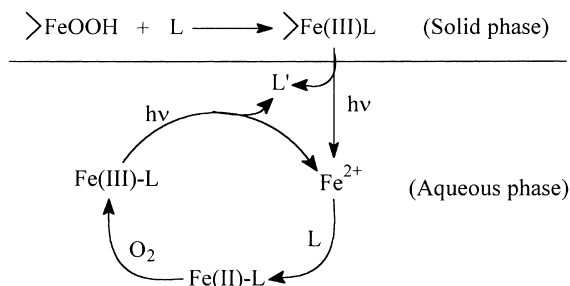
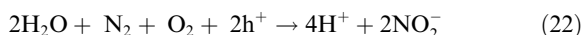
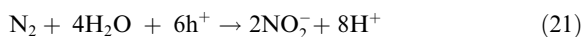
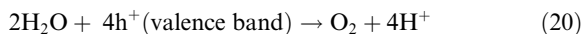
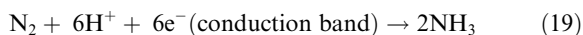


Fig. 2. Model on photoreductive dissolution of FeOOH in the system containing organic ligand L where >FeOOH represents Fe(III) oxides; L organic ligands; L' oxidized product of L .

phase and aqueous phase, i.e., the photolysis of Fe(III)-organic ligand complexes at the colloid surface and the concomitant release of reduced Fe(II) to solution, which was subsequently oxidized to Fe(III).

In fact, as we can see, there is no absolutely significant difference between Fe₂O₃ and FeOOH in the mechanism of photoinduced reductive dissolution.

Additionally, there have been some studies dealing with other applications of iron(III) hydroxides as photocatalysts to produce hydrogen or fix nitrogen, which are thought to be important for solving some problems related with energy shortage and nitrogenous fertilizer production. Tennakone et al. (1987) reported a simple system for practical photofixation of N₂ to NH₃. They had found that hydrous iron(III) oxides loaded Nafion films in aerated water at alkaline pH yields both NH₃ and NO₂⁻/NO₃⁻ upon UV irradiation (Tennakone et al., 1991). The reactions are shown as follows:



5.3. Amorphous Fe(OH)₃

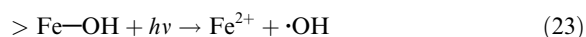
In acidic solutions, amorphous Fe(OH)₃ can easily dissolve to produce Fe³⁺ and Fe(III)-hydroxy complexes, which undergo further photolysis. That is proposed to be the predominant mechanism of photoformation of reduced Fe²⁺ and hydroxyl radicals in the system. The transition from the solid phase to aqueous phase is faster in the solution containing am-Fe(OH)₃ than other polymorphous Fe(III) oxides. So, It is believed that aqueous photochemical reactions play an important role in reductive dissolution of am-Fe(OH)₃ in natural waters.

6. Photodegradation of organic compounds on the surface of Fe(III) oxides in aqueous solutions

Pekkonen et al. (1995) investigated the photo-oxidation of halogenated acetic acids on the surface of iron oxides. The fastest rate of photoreduction of Fe(III) to Fe(II) was achieved with iron oxide as an electron acceptor and fluoroacetic acid as an electron donor. The relative rates of photo-oxidation of the monohalogenated acetic acids with iron oxide were in order: $\text{FCH}_2\text{CO}_2\text{H} > \text{ClCH}_2\text{CO}_2\text{H} > \text{BrCH}_2\text{CO}_2\text{H} >$

ICH₂CO₂H; for multiple substituents: FCH₂CO₂H > F₂CHCO₂H > F₃CCO₂H. With respect to the iron oxide electron acceptors, the relative order of reactivity toward monohaloacetate oxidation was am-Fe₂O₃·3H₂O > γ-Fe₂O₃ > γ-FeOOH ≳ α-Fe₂O₃ ≳ Fe_{aerosol} > α-FeOOH.

Pulgarin and Kiwi (1995) indicated the photo-oxidation of 2-aminophenol in an aerated iron oxide suspension could be due to three mechanisms, i.e., (i) a ligand-to-metal charge transfer process as shown in Fig. 2; (ii) photoproduction of e⁻-h⁺ couple, the holes are scavenged by 2-aminophenol and the electrons by the surface iron(III) ion, and (iii) the OH radicals resulting from the oxidation of surface OH groups (reaction (23)).



But, after comparison of photo-oxidation of phenol, nitrophenol, and chlorophenol, Pulgarin and Kiwi (1995) suggested that the photocatalytic degradation of 2-aminophenol was more related to a surface complex in mechanism (i) other than to a semiconductor-assisted photodegradation in mechanism (ii).

Although till now, no one has confirmed that Fe(III) oxides or oxyhydroxides are high efficient photocatalysts, most of the researchers believe that, with a narrow band gap, Fe(III) oxides would show better photoelectrochemical response at longer wavelengths in the visible region than TiO₂. They have the potential of utilizing solar energy, perhaps in wastewater treatment in the future.

Studies on photodegradation of organic compounds on the surface of Fe(III) oxides included the degradation reaction kinetics, influence factors, and mechanisms. It has been found that the reaction kinetics of the degradation of adsorbed organic compounds was generally in accordance with the Langmuir–Hinshelwood (L–H) equation (Fox and Dulay, 1993)

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{(k+K) \cdot C}$$

where r represents photodegradation rate of the substrate, k the rate constant of pseudo-first-order reaction, K the adsorption constant, C the concentration of the substrate.

7. Hydrolytic polymers and their photochemical properties

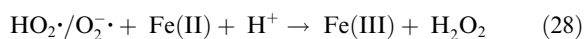
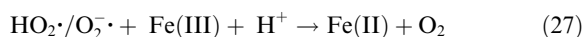
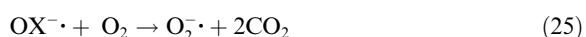
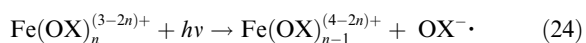
Polymeric products of hydrolyzed ferric salts are the mediate products between primary hydrolysis products of low-molecular-weight and precipitated products. In spite of their complicated structures and large quantity of species, they are thought to be photoreactive since their precursor and advanced hydrolytic products are all

photochemical reactive species. This idea is about to be confirmed.

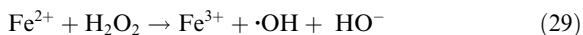
8. Fe(III)-organic ligand complexes and their photochemical properties

The photo-oxidation of carboxylic acids has long been known to be sensitized by Fe(III), but only till 1960s has attention been paid to what coordination species might be involved (Balzani and Carassiti, 1970). The carboxylate group [RC(O)O⁻] is one of the most common functional groups of the dissolved organic compounds present in natural waters (Thurman, 1985; Perdue and Gjessing, 1990). Polycarboxylates (e.g., oxalate, malonate, and citrate) form strong complexes with Fe³⁺ that undergo rapid photochemical reactions in sunlight (Zuo and Hoigné, 1992; Faust and Zepp, 1993).

Since the 1950s, numerous investigations have found that Fe(III)-oxalato complexes photolyze with high efficiency (Parker, 1954; Parker and Hatchard, 1959; Cooper and DeGraff, 1971; 1972; Miles and Brezonik, 1981). Zuo and Hoigné (1992; 1994) have shown that the photolysis of Fe(III)-oxalato complexes is a major pathway for the formation of H₂O₂ in atmospheric waters. The possible photochemical reactions in the Fe(III)-oxalato-oxygen system are shown as (Zuo and Hoigné, 1992):

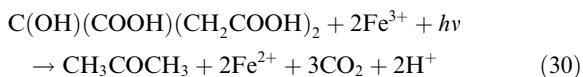


If the C₂O₄²⁻· radicals react with Fe(II), additional Fe(III) formed; however, if they react with O₂, then a sequence of oxidants (·O₂⁻/HO₂·, H₂O₂, and ·OH) is formed (Faust and Zepp, 1993). Zuo and Hoigné (1992) detected the H₂O₂ formation in the solutions containing 10 μM Fe(III) and 120 μM oxalate at pH 4, they found the observed rate of formation of H₂O₂ in September noon sunlight was 80 nMs⁻¹. The formation rate of H₂O₂ is related to pH, irradiation intensity and the concentrations of oxalate and dissolved iron. The H₂O₂ formed in the Fe(III)-oxalato system can react with Fe²⁺ according to a Fenton mechanism (Zepp et al., 1992)



Zuo and Hoigné (1992) indicated that the production of $\cdot\text{OH}$ radicals in atmospheric water droplets has considerable significance as they can oxidize a wide variety of natural and anthropogenic organic and inorganic substances.

Since the 1910s, some studies have shown that the photochemical dissociation of Fe(III) citrate complexes in aqueous solutions involved reduction of Fe(III) to Fe(II) and concomitant oxidation of the carboxylic acid, resulting in the formation of acetone and carbon dioxide as the final products (Frahn, 1958; Buchanan, 1970). The general reaction can simply be represented as



where the coordination structure was not given. The efficiency of the photoreduction reaction in aqueous solutions depends much on two factors: the pH and the initial citrate to metal ratio (Abrahamson et al., 1994). It is thought that Fe(III)-citrate complex can photolyze to produce hydrogen peroxide and hydroxyl radicals through the similar pathway as that of Fe(III)-oxalato complex (Deng et al., 1998a).

Additionally, members from EAWAG at ETH (Institute for Water Resources and Water Pollution Control at Swiss Federal Institute of Technology), especially W. Stumm, J. Hoigné, L. Sigg, Y. Zuo, and their co-workers R.G. Zepp, B.C. Faust etc., have done outstanding work on photochemical redox cycle of Fe(III)/Fe(II) in natural waters and their chemical and ecological effects (Behra and Sigg, 1990; Zuo, 1992; Zuo and Hoigné, 1993). This research indicated the importance of dissolved organic compounds and iron ions involved in the photochemical formation of hydrogen peroxide and other photooxidants in natural surface waters.

9. Application of different Fe(III) species to photochemical process of wastewater containing organic compounds

The photocatalytic oxidation method, one of the Advanced Oxidation Processes, is based on utilizing hydroxyl radicals formed in the system. Since 1993, Deng and Wu et al. (Deng et al., 1996, 1997a,b, 1998a; Luo et al., 1999; Wu et al., 1999) have paid much attention to applying Fe(III) salts and oxides as photosensitizer or photocatalysts to promote the degradation and decolorization of dyes in aqueous solutions both under UV-light and sunlight. The results have shown that photodegradation rates of dyes were not identical

when using different Fe(III) species. Among those Fe(III) complexes used, Fe(III)-organic ligand complexes (Ferric-oxalato (Deng et al., 1997a) and Ferric citrate (Deng et al., 1998b)) are more efficient than Fe(III)-hydroxy complexes (Deng et al., 1996, 1997b) in accelerating the photodegradation of the dyes, especially under sunlight (Wu et al., 1999).

At present, there has been no report about the practical use of Fe(III) oxides in photochemical process for wastewater treatment. The feasibility of this application needs to be shown. In the photodegradation of dyes, some forms of Fe(III) oxides were used as catalysts (Deng et al., 1998a), amorphous Fe(OH)₃ presented most photochemically reactive, probably for its dissolution to produce Fe(III)-OH complexes in acidic solutions. Additionally, multi-techniques combination for wastewater treatment is a practicable routine for industrial wastewater of high pollutant concentration. In a preliminary investigation, Wu et al. (1998) designed a flocculation-photo-oxidation combination to treat the dye Reactive Red 2 solution at a concentration of 300 mg/l. A decolorization efficiency of 82.5% was obtained.

This research is basic and simple, and needs to be improved in many aspects such as developing new photochemical reactors and catalysts carriers, involving typical pollutants for treatment, their photodegradation mechanisms, and so on.

10. Conclusion

Hydrolytic Fe(III) species have their respective photochemical properties, which shows not only in absorption spectra, photochemical reaction mechanisms and products, but in their effects on the formation, transfer, transformation, and sinks of environmental chemicals. The pH, Fe(III) concentration, wavelength and energy of irradiation source, and the nature of organic compounds coexisting have strong influence on their photochemical properties. All the products of low-molecular-weight of hydrolytic iron(III) species can photolyze to produce hydroxyl radicals, among them Fe(OH)²⁺ is the most photochemically active species. It can be presumed that hydrolytic Fe(III) polymers also have photoactivity. Fe(III) oxides, oxyhydroxides, and hydroxides photodissolve in aqueous acidic solutions and initiate the degradation of organic compounds. Their mechanisms of photochemical reactions are not identical to that of the semiconductors such as TiO₂.

The photochemical properties of hydrolytic Fe(III) species can be applied to wastewater treatment either for its photoformation of hydroxyl radicals, or for the charge transfer from adsorbed organic compounds to

the metal. These applications realize the transformation from fundamental theories of environmental chemistry to applied technologies for pollution control.

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