Degradation of atrazine photoinduced by Fe(III)–pyruvate complexes in the aqueous solution

Changbo Zhang^{a,b}, Lei Wang^c, Gang Pan^c, Feng Wu^{a,*}, Nansheng Deng^a, Gilles Mailhot^b, Hana Mestankova^b, Michele Bolte^b

^a School of Resource and Environmental Science, Wuhan University, Wuhan 430079, PR China

^b Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR 6505 CNRS, Université Blaise Pascal de Clermont-Ferrand, F-63177 Aubière Cedex, France

^c State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

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ABSTRACT

The composition and photochemical properties of the Fe(III)–Pyr complexes in the aqueous solution was studied in this work. Fe(III) was complexed by Pyr in the ratio of 1:3. The photochemical processes occurred in the Fe(III)–Pyr system was studied in detail. Fe(II) was the main intermediate product. DMPO was used as scavenger to determine the active radicals, such as $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $\text{CO}_2^{\cdot-}$, $\text{H}\cdot$ and $\text{RCO}_2^{\cdot}$ by ESR. Photodegradation of atrazine induced by the photolysis of Fe(III)–Pyr was studied and the reaction kinetics fitted the first order reaction. Parameters such as pH, the initial concentrations of Fe(III), pyruvate (Pyr) and atrazine were all investigated. Photoproducts were detected by the LC–MS and the photodegradation scheme was proposed. $\cdot\text{OH}$ radical was the main pathway of atrazine degradation.

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1. Introduction

Carboxylic acids have received considerable attention as one of the most common dissolved organic compounds in natural environment [1,2]. They were also considered to be one of the dominant classes of organic compounds found in the atmosphere in a variety of phases [3–8]. They have been found in rainwater [9–12], snow and ice [13], on aerosol particles [14–17] and in the gas phase [18–20]. Pyruvic acid was one of the most abundant ketoacids presented in the atmosphere. Its presence has been reported in aerosols, rainwater and in the gas phase in urban atmosphere as well as in remote continental and marine areas. Andreae et al. [21] demonstrated that it was a product of the photochemical oxidation of natural organic compounds such as isoprene and cresols. It was expected to play a role in the precipitation acidity [22]. Available data indicated that pyruvic acid was lost in the gas phase mainly through photolysis. Mellouki and Mu [23] measured the reaction rate constant of $\cdot\text{OH}$ with pyruvic acid ($\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{OH}$) in the gas phase. The value was $k_{\text{PA}} = (1.2 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. They also detected $\cdot\text{OH}$ with a relative quantum yield of $5 \pm 3\%$ by the direct photolysis of pyruvic acid. However, the study of the ratio composition of the pyruvic acid complex with Fe(III) and

its detailed photolysis processes were unavailable from literature. In this work, we studied the ratio of Fe(III)–Pyr complexes and its photochemical properties.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was used as a model compound. It was a selective inside-absorbing herbicide which can be used in the fields of corn, sorghum, orchard and forest, controlling broad-leaf and grassy weeds [24]. It was not readily biodegradable and presented a relatively high persistence in soils and even reaches the groundwater. Its solubility in water was low ($1.61 \times 10^{-4} \text{ M}$) and did not depend on pH [25]. Atrazine, like other herbicides of the S-triazine group, was barely oxidized by ozone [26]. Many methods have been developed to remove atrazine, including adsorption on activated carbon and advanced oxidation processes. These comprised both homogeneous and heterogeneous systems, for example the UV photolysis of hydrogen peroxide [27,28], the reaction of hydrogen peroxide with ozone [29] or Fe(II) [30], ionizing radiation, ultrasound [31], photolysis by TiO_2 colloidal particles [32–35] and Fe(III)/oxalate systems [36]. There was no report that had been published with respect to the photodegradation of atrazine in the Fe(III)–Pyr systems.

The aims of this study were as follows: (1) characterizing the physicochemical and photochemical properties of Fe(III)–Pyr complex; (2) determining the active oxygen species and proposing the photochemical processes that happened in the Fe(III)–Pyr system; (3) studying the photochemical degradation of atrazine induced by

* Corresponding author. Tel.: +86 27 68778511; fax: +86 27 68778511.

E-mail address: fengwu@whu.edu.cn (F. Wu).

the Fe(III)–Pyr system and examining several factors that controlled the kinetics of atrazine degradation.

2. Experimental materials and methods

2.1. Chemicals and preparation of solutions

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CH}_3\text{COCOONa}$, atrazine, 1,10-phenanthroline, ammonium acetic acid, $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, FeSO_4 , H_2SO_4 , 5,5-dimethylpyrrolidine-*N*-oxide (DMPO), acetonitrile, HCl and NaOH were all analytical grade and used without further purification. Ferric chloride was used as Fe(III) sources. Sodium pyruvate was used as pyruvate source. All of the solutions were prepared by doubly distilled water.

Great care was taken to prepare stock solutions of Fe(III). In order to prevent precipitation of Fe(III), an appropriate weight of ferric chloride was dissolved in hydrochloric acid (1N, a few mL) and then added to an appropriate volume of doubly distilled water to get the desired concentration of Fe(III) and pH 3.0.

2.2. Determination of the composition of the Fe(III)–Pyr complex

Molar ratio method was used to determine the composition of Fe(III)–Pyr complexes. This method was based on the spectrophotometric analysis. The concentration of metal ions (C_M) in aqueous solution was kept constant and the concentration of the relative acid (C_L) was increased in the experiment. The absorbance of the aqueous solution increased with the increasing of the acid concentration until it became stable, which indicated that the metal ions were totally coordinated by the acids.

The stoichiometry of the complex corresponded to the ratio (C_L/C_M) where the absorbance began to be stable; no more increasing was measured with the supplementary addition of acids.

2.3. Measurement of Fe(II)

Under irradiation, Fe(II) was formed in aqueous solutions in the presence of Fe(III). The concentration of Fe(II) was determined by complexometry with 1,10-phenanthroline taking $\varepsilon_{510\text{ nm}} = 1.118 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ [37,38]. At different irradiation times intervals, 2 mL of the samples were added to 5 mL flask, followed by the addition of 0.5 mL of 1,10-phenanthroline (0.1% by mass) and 1 mL of ammonium acetate buffer (pH 4.5). After agitation, the solutions were kept in the dark for 1 h and then the UV–vis measurement was carried out at 510 nm by UV-120-02 spectrophotometer (Shimadzu).

Quantum yields of Fe(II) generation were determined by ferrioxalate potassium actinometer.

2.4. Photodegradation experiments

Irradiation experiments were carried out in a 250 mL homemade cylindrical reactor with a diameter of 10 cm. The metal halide lamp ($\lambda \geq 350 \text{ nm}$, 250 W) was used as the irradiation source, which was surrounded by a water jacket and cooling water was used to keep the reaction solutions at room temperature ($298 \pm 1 \text{ K}$). In order to get the complexed solutions, Fe(III)–Pyr were magnetically stirred for 1 h before adding atrazine solution. The pH of the aqueous solutions was adjusted to the desired value by HCl (1N) or NaOH (1N). All the reaction solutions were prepared and kept in the dark prior to irradiation. All of the experiments were carried out three times in this work and the error bar represented the standard error.

2.5. Analysis

At different time intervals during the irradiation, samples were collected and analyzed by HPLC. Atrazine was monitored at 240 nm by HPLC (Shimadzu LC-10AT) with a UV–vis detector (Shimadzu SPD-10A). The mobile phase was acetonitrile/water mixture (50/50, v/v) at a flow rate of 1.0 mL min^{-1} using Kromasil, KR100-5C18 column ($250\text{ mm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$). LC–MS studies were carried out with a Waters (Alliance 2695) HPLC system coupled to a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ionization source (ESI). Data acquisition and processing were performed by MassLynx NT 3.5 system.

2.6. Electron spin resonance (ESR) spectroscopy

ESR spectra were recorded at room temperature on a Bruker ER 200D, X BAND spectrometer operating at 9.6 GHz and a cavity equipped with a quartz flat cell designed for liquid samples. Typical spectrometer parameters were: scan range, 100 G; centre field set, 3440 G; time constant, 327 ms; scan time, 167 s; modulation amplitude, 1.5 G; modulation frequency, 100 kHz; receiver gain, 1.25×10^6 ; and microwave power, 25.2 mW, frequency, 9.64 GHz.

The 5,5-dimethylpyrrolidine-*N*-oxide (DMPO) was used as a scavenger in this study. The irradiation experiments were carried out under a Xe–Hg lamp with two different filters. Cooling water was used to maintain the reaction at room temperature.

3. Results and discussion

3.1. Study of the physicochemical properties of Fe(III)–Pyr complex

UV–vis spectra of different aqueous solutions were shown in Fig. 1(a). The absorption spectra of organic complex iron species were shifted toward the visible and its charge transfer band strongly

Fig. 1. Spectrophotometric evolution of the Fe(III)–Pyr complex as a function of Pyr concentration.

Fig. 2. UV-vis spectra of Fe(III)-Pyr complex as function of pH value.

overlapped with the solar UV spectrum (318–500 nm). Therefore, it could be easily photolyzed and the absorbance was higher than hydrated iron species or Pyr, which led the Fe(III)-Pyr system to use the light energy more efficiently.

The composition of the Fe(III)-Pyr complex was studied using molar ratio method. The concentration of Fe(III) ions was kept constant at 0.3 mM and then increased the Pyr from 0 to 1.0 mM. Experiments were carried out three times. Fig. 1(b) presented the evolution of the Fe(III)-Pyr complex as a function of Pyr concentration. The absorbance became stable when the concentration of the Pyr got above 0.8 mM. It indicated that the Fe(III) ions were complexed by Pyr with the molar ratio equal to 1:3. The stability of Fe(III)-Pyr complex was studied in the dark at room temperature. The complex was stable in the aqueous solutions under our experimental condition (pH 3.0). Results showed that the pH was an important parameter for the stability of the complex and its speciation (Fig. 2). At pH < 2.0, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ became the main species in the solutions while from pH 2.5 to 5.0 the Fe(III)-Pyr complex was the major species. From 5.0 to 6.0, $\text{Fe}(\text{OH})_2^+$ gradually became the main species but this species rapidly disappeared with time. When pH > 7.0, the precipitation of Fe(III) was observed. The absorbance of the solution was intervened by the precipitate.

3.2. Photochemical properties of Fe(III)-Pyr complex

3.2.1. Fe(II) formation in the Fe(III)-Pyr system under irradiation

Fe(II) was an important intermediate product generated by the photolysis of Fe(III)-Pyr complexes under irradiation. The concentration of Fe(II) was detected in the aqueous solutions containing Fe(III) or Fe(III)-Pyr complexes. Irradiation experiments were carried

Table 1

Quantum yields of Fe(II) in the aqueous solutions with 0.3 mM Fe(III), 0.3 mM Fe(III)-Pyr complexes and the initial pH value was 3.0. ($\lambda_{\text{irr}} = 365 \text{ nm}$).

Different reaction systems	$\Phi_{\text{Fe(II)}}$
$[\text{Fe(III)}] = 0.3 \text{ mM}$	0.027
$[\text{Fe(III)-Pyr}] = 0.3 \text{ mM}/0.9 \text{ mM}$	0.21

out under metal halide lamp. As it can be realized by comparing the results in Fig. 3(a) and (b), we got higher concentration of Fe(II) in the presence of Pyr than without Pyr. At different pH 3.0, 4.0 and 5.0, the same trend was noticed. Quantum yields of Fe(II) generation was also determined in this work, observing a $\Phi_{\text{Fe(II)}}$ seven times higher in the presence of Fe(III)-Pyr complex than Fe(III) (Table 1). It was demonstrated that Pyr could enhance the photoreduction process of Fe(III) and photocycling of Fe(III)/Fe(II).

The pH was a crucial parameter and it could affect the competition between the reaction of Fe(III)/Fe(II) and the distribution of Fe(III) species in the Fenton and photo-Fenton-type systems [39]. Fig. 3 also presented a decrease of the Fe(II) generation with the increase of pH value. At high pH, the precipitation of Fe(III) was happened. Thus Fe(III) was less available in the water. And high pH was also unfavorable for the photocycling of Fe(III)/Fe(II).

3.2.2. Photolysis of Fe(III)-Pyr complex

In order to understand the photochemical processes in the Fe(III)-Pyr system, experiments were carried out by ESR spin trapping techniques. DMPO (1 mg mL^{-1}) was used as scavenger for different radicals formed in the aqueous solution. The irradiations were carried out directly in the cavity ESR using a Xe-Hg lamp with two different filters. At short wavelength irradiation ($\lambda \geq 280 \text{ nm}$), the four-line ESR spectrum (1:2:2:1) of the DMPO-OH spin adduct was observed at the beginning of the irradiation in the Fe(III)-Pyr system (Fig. 4(a)). For longer irradiation time a more complicated signals were observed. The ESR signals were different as a function of irradiation wavelength. These signals were attributed to the combination of the classical 1:2:2:1 signal of $\cdot\text{OH}$ adduct and of the $\text{CO}_3^{\cdot-}$ adduct (Fig. 4(b)). At long irradiation wavelength ($\lambda \geq 350 \text{ nm}$), a nice dedoubled triplet signal was observed and this signal corresponded to a mixture of radical types $\text{CO}_2^{\cdot-}$ and $\text{RCO}_2^{\cdot}$ adducts trapped by the DMPO (Fig. 4(c)) [40]. $\text{H}^{\cdot}$ radical reacted very fast with oxygen to form $\text{HO}_2^{\cdot}$ radicals, which led to the formation of H_2O_2 . Moreover, this recombination was more efficient when involving the basic and the acid forms of the radicals $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ [41].

The photolysis mechanism of the Fe(III)-Pyr system was proposed in Fig. 5. In this process, Fe(III)-Pyr was excited under irradiation which led to the photolysis of iron complex with the formation of Fe(II) species and the excited state Pyr. In the presence

Fig. 3. Fe(II) photogeneration in the water with (a) $[\text{Fe(III)}] = 10 \mu\text{M}$ and (b) $[\text{Fe(III)/Pyr}] = 10 \mu\text{M}/10 \mu\text{M}$ as function of pH.

Fig. 4. ESR spectra of the aqueous solution with 1 mg mL^{-1} of DMPO and 0.3 mM of Fe(III)–Pyr complex at pH 3.0 under irradiation.

Fig. 5. Proposed photolysis processes of Fe(III)/Pyr.

of the dissolved oxygen, the excited state Pyr underwent a further decomposition with the formation of $\bullet\text{OH}$, $\bullet\text{COOH}$, $\text{CO}_3^{\bullet-}$, $\text{H}^\bullet$ and $\text{HO}_2^\bullet$ [40,42]. At the same time, Fe(II) was again oxidized into Fe(III). The photocycling process of Fe(III)/Fe(II) existed in the system. Fe(II) generation has been discussed above. In the water with $10.0 \mu\text{M}$ Fe(III) and $30.0 \mu\text{M}$ Pyr at pH 3.0, $\bullet\text{OH}$ was produced following a 160 min irradiation in the amount of $34.0 \mu\text{M}$. The generation rate constant of $\bullet\text{OH}$ was $0.21 \mu\text{M L}^{-1} \text{ min}^{-1}$ with a quantum yield of generation of 0.02 [43].

3.3. Photodegradation of atrazine in the aqueous solutions

The photodegradation of atrazine was studied in this work. The control experiments were carried out in the systems with $20.0 \mu\text{M}$ Fe(III), $20.0 \mu\text{M}$ Pyr and $20.0 \mu\text{M}/60 \mu\text{M}$ Fe(III)–Pyr complex. The initial concentration of atrazine was 10.0 mg L^{-1} . The dark reaction was carried out to keep the mixture of atrazine, Fe(III) and pyruvate in the dark. From the results in Fig. 6, no degradation of atrazine was observed in the 150 min dark control and light proved to be an essential element for the degradation of atrazine. Direct irradiation of 10.0 mg L^{-1} atrazine showed no degradation of atrazine. The

photodegradation efficiency of atrazine was higher in the aqueous solution with Fe(III)–Pyr complex than in the one only containing Pyr or Fe(III). Although $\bullet\text{OH}$ radicals could be produced by the direct photolysis of Fe(III) and Pyr, the amount of the radicals produced

Fig. 6. Photodegradation of atrazine under different conditions at pH 3.0.

Fig. 7. Photodegradation of atrazine in the Fe(III)–Pyr systems, (a) at different pH values; (b) with different Fe(III) concentrations; (c) with different Pyr concentrations; (d) with different atrazine concentrations.

Table 2

Kinetics analysis of the photodegradation of atrazine.

System	R	Initial Rate ($\text{mg L}^{-1} \text{min}^{-1}$)
Pyr (μM)	[Fe(III)] = 20.0 μM , [atrazine] = 10 mg L^{-1} , pH 3.0	
10	0.9761	0.025
20	0.9965	0.061
40	0.9887	0.088
60	0.9971	0.141
80	0.9906	0.168
Fe(III) (μM)	[Pyr] = 40.0 μM , [atrazine] = 10 mg L^{-1} , pH 3.0	
10	0.9704	0.021
20	0.9870	0.091
40	0.9972	0.314
60	0.9981	0.388
80	0.9881	0.637
pH	[Fe(III)–Pyr] = 20.0 μM /20.0 μM , [atrazine] = 10 mg L^{-1}	
3.0	0.9966	0.061
4.0	0.9695	0.029
6.0	0.9574	0.011
Atrazine (mg L^{-1})	[Fe(III)–Pyr] = 20.0 μM /20.0 μM , pH 3.0	
2.0	0.9997	0.069
4.0	0.9993	0.087
6.0	0.9942	0.097
8.0	0.9989	0.088

was less than in the Fe(III)–Pyr system given that the Fe(III)–Pyr complex overlapped with the solar UV spectrum (318 nm–500 nm), allowing the effective use of irradiation. After 150 min irradiation, nearly 85% atrazine had been degraded in the Fe(III)–Pyr system.

3.4. Effect of pH, initial Fe(III), Pyr and atrazine concentrations on the degradation of atrazine

The pH as an important parameter was studied in the solution with 20 μM Fe(III) and 20.0 μM Pyr and 10.0 mg L^{-1} atrazine under irradiation. Fig. 7(a) illustrates the experiment results. More than 55% of the atrazine degraded at pH 3.0 after 150 min of irradiation. The photodegradation efficiency was low at high pH. Only 20% of atrazine was degraded at pH 4.0 and 13% at pH 6.0 after 150 min of irradiation. It appeared that the pH played an important role in the photodegradation of atrazine. Acidic condition was favourable for the photocycling of Fe(III)/Fe(II) and the formation of active oxygen species, which was the main reason for the degradation of atrazine.

In this work, both Fe(III) and Pyr were the essential elements for the degradation of atrazine. It was necessary to study their effect on the reaction. Experiments were carried out to study the effect of different ratio of Fe(III)/Pyr on the photodegradation of atrazine. Fig. 7(b) presented results in the water with the following as the initial concentrations: 10.0 mg L^{-1} of atrazine, 40.0 μM

Fig. 8. Kinetics analysis of atrazine degradation and Fe(II) formation.

of Pyr and different Fe(III) concentrations under irradiation at pH 3.0. With an increase of the initial concentration of Fe(III) from 0.0 to 80.0 μM , the photodegradation efficiency increased from 30% to 80% after 150 min irradiation. As presented in Fig. 7(c), the photodegradation efficiency of atrazine was also increased from 35% to 84% with the increase of Pyr concentration from 0.0 to 80.0 μM .

The enhancement of atrazine degradation efficiency was attributed to the high concentration of Fe(II) generated at high concentration of Fe(III)–Pyr, producing more active oxygen radicals in the system. For high activity of $\bullet\text{OH}$ radicals, it was found that they were the most effective radicals for the pollutant degradation. From the photolysis processes of Fe(III)–Pyr, both reagents were found to be

Fig. 9. LC-MS spectra of the atrazine degradation in Fe(III)–Pyr systems after 4 h of irradiation: (a) total ions chromatogram from LC-MS; (b) mass spectra of the main products. [Atrazine] = 10 mg mL⁻¹, [Fe(III)]/Pyr = 10 μM /30 μM , pH 3.0.

essential to promote organic compounds degradation under this type of irradiation. Experiments were carried out under different atrazine initial concentrations in the Fe(III)–Pyr system at pH 3.0. Results are shown in Fig. 7(d). The photodegradation efficiency of atrazine decreased with the increase of atrazine concentration from 2.0 to 10.0 mg L⁻¹.

According to the time evolution of atrazine under different conditions, we analyzed the reaction kinetics. The photodegradation of atrazine fitted well with the first order reaction kinetics. Results were presented in Table 2. Through comparing the formation of Fe(II) and degradation of atrazine under the same reaction conditions, it was concluded that the initial rate $k_{\text{Fe(II)}}$ was higher than the k_{atrazine} as shown in Fig. 8.

3.5. Degradation products

Under irradiation, atrazine was attacked by the active radicals, especially •OH radicals, in the Fe(III)–Pyr system. LC–MS was used to identify the intermediate photoproducts. The mass spectra were presented in Fig. 9. As expected the most intense peak was observed at m/z 216 deriving from atrazine, corresponding to $[M+H]^+$. The four main fragments-ions m/z 174, 188, 197 and 146 clearly demonstrated the formation of the degradation products 2-chloro-4-ethylamino-6-amino-1,3,5-triazine (P1), 2-chloro-4-isopropylamino-6-amino-1,3,5-triazine (P2), 2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine (P3) and 2-chloro-4,6-diamino-1,3,5-triazine (P4).

4. Conclusions

In this work, the formation and composition of Fe(III)–Pyr complex was first studied and Fe(III) was complexed by Pyr in the ratio of 1:3. This kind of complex was stable in the aqueous solution. Under irradiation, the photolysis of Fe(III)–Pyr complexes could represent the source of active oxygen radicals, such as •OH, CO₃•⁻, CO₂•⁻, H• and RCO₂•. In the Fe(III)–Pyr system, free Fe(III) species could generate •OH radicals through the reaction $\text{Fe(III)} + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe(II)} + \bullet\text{OH} + \text{H}^+$. •OH radicals could also be generated by direct photolysis of pyruvic acid with a relative quantum yield of $5 \pm 3\%$ [23]. Oxygen was always involved in the formation of active oxygen species. Acidic condition was favourable for this photochemical reaction.

Fe(III)–Pyr complex could enhance the photodegradation of atrazine in the aqueous solution and under irradiation. High degradation efficiency was obtained at high concentrations of Fe(III)–Pyr and at low pH. However, the photodegradation efficiency was decreased with the increase of initial atrazine concentration. Four kinds of photoproducts were identified in this work. This type of complexes could be formed in the natural aquatic environment due to the presence of carboxylic acids and iron. Thus, such complexes could influence the fate of inorganic and organic pollutants existing in the natural environment. This work could help us to fully understand the photoreaction processes concerning Fe(III)–Pyr complex and its potential for the degradation of pollutants in the natural surface and atmosphere water environment under solar irradiation.

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