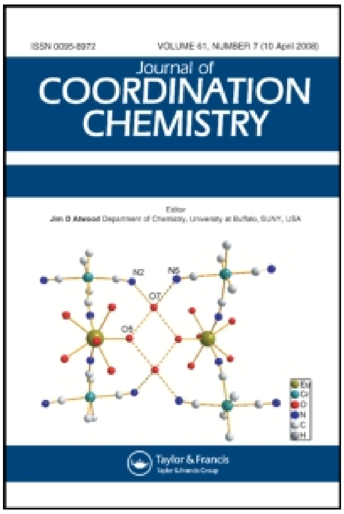

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Fe(III)-pyruvate and Fe(III)-citrate induced photodegradation of glyphosate in aqueous solutions

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The photolysis of Fe(III)-pyruvate and Fe(III)-citrate complexes in water produces hydroxyl radicals in the presence of dissolved oxygen, and can promote the oxidation of organic compounds. The photodegradation of glyphosate with Fe(III)-pyruvate and Fe(III)-citrate complexes was investigated under irradiation at $\lambda \geq 365$ nm. The effect of initial concentration of glyphosate, the initial pH value, and the Fe(III)/carboxylate ratio were examined. Upon irradiation of glyphosate aqueous solution with the complexes in the acidic range of natural waters, the bioavailable orthophosphate could be released from degradation of glyphosate. The amount of orthophosphate increased with increasing Fe(III)/carboxylate ratio.

Keywords: Fe(III)-pyruvate; Fe(III)-citrate; Glyphosate; Photodegradation

1. Introduction

Glyphosate (*N*-(phosphonomethyl)glycine) (GLY), is a widely used, broad-spectrum, foliar-applied herbicide for the control of many annual and perennial weeds, introduced by Monsanto Company, US in the early 1970s [1, 2]. Glyphosate is essentially nontoxic to mammals and birds, but fish and invertebrates are more sensitive to the herbicide [3]. Glyphosate shares a similar structure with amino acids and can be easily degraded by microorganisms and plants to yield aminomethylphosphonic acid (AMPA) and sarcosine, which could further degrade into water, carbon dioxide and phosphate, although slower degradation of AMPA has been reported in some instances [4–6]. The degradation of glyphosate in a natural environment affects the function of the herbicide, but also the bioavailability of glyphosate since it could be photochemically transformed into orthophosphate, responsible for eutrophication.

Due to the low Henry constant and UV absorption, glyphosate is difficult to dissipate via vaporization and direct photodegradation by sunlight [7]. Glyphosate is not readily hydrolyzed or oxidized in the field [8, 9]. However, the photodegradation becomes

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complicated in the aqueous environment due to the formation of coordination compounds, some of which have photoreactivity. Thus, abiotic degradation is also an important pathway for dissipation of glyphosate in the environment.

Many iron complexes have photoactivity [12]. Carboxylic acids (pyruvic acid and citric acid) and various iron species are abundant in natural waters, and can form Fe(III)-carboxylate coordination compounds with high photoreactivity [10, 11]. The coordination compounds can produce Fe(II) and $^{\bullet}$OH through ligand-to-metal charge transfer (LMCT) when they absorb light, equations 1–5 [13].

$$\mathrm{Fe(III)-carboxylate}+h\nu \xrightarrow{\mathrm{LMCT}} \mathrm{Fe(III)-carboxylate}^{*} \tag{1}$$

$$\mathrm{Fe(III)-carboxylate}^{*} \rightarrow \mathrm{Fe(II)}+\mathrm{carboxylate(ox)} \tag{2}$$

$$\mathrm{Carboxylate(ox)}+\mathrm{O_2} \rightarrow \mathrm{O_2^{\bullet -}}+\mathrm{product} \tag{3}$$

$$\mathrm{Fe(II)}+\mathrm{O_2^{\bullet -}}/\mathrm{HO_2^{\bullet -}} \rightarrow \mathrm{Fe(III)}+\mathrm{H_2O_2}+\mathrm{OH^-} \tag{4}$$

$$\mathrm{Fe(II)}+\mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)}+{}^{\bullet}\mathrm{OH}+\mathrm{OH^-} \tag{5}$$

The OH radical is a nonselective strong oxidant, responsible for the abatement of a wide variety of natural and anthropogenic organic substances in natural waters. Our group has been engaged in simulation of photodegradation of organic substances mediated by ferric complexes including Fe(III)–OH complexes, Fe(III)-carboxylate complexes, and Fe(III)-humic acid complexes [14–18]. Few reports exist for photodegradation in the presence of Fe(III)-pyruvate and Fe(III)-citrate system, especially for the potential implications to the ecosystem.

The objective of the present research was to investigate the effect of Fe(III)-pyruvate and Fe(III)-citrate coordination compounds (see figure 1) on the photodegradation of glyphosate in simulated natural waters. The bioavailable orthophosphate was detected to evaluate the possible effect of photodegradation on the aqueous ecosystem and the validity of glyphosate.

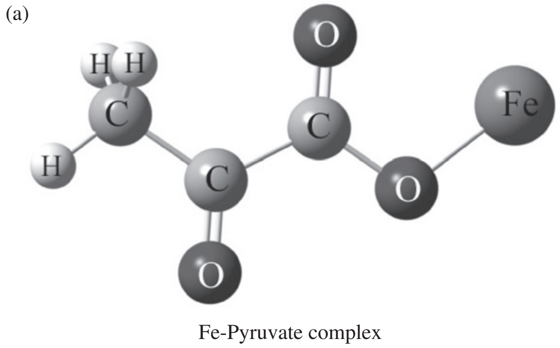
2. Experimental

2.1. *Material*

GLP (97% purity) was purchased from Damao Chemicals Co. (Tianjin, PRC). All other reagents are analytical reagent and used without purification. HCl and NaOH were used to adjust the pH values of the solutions. Water used was doubly distilled.

2.2. *Photochemical reactor*

Irradiation under UV light was performed with a 250 W metal halide lamp (Yaming illumination Instrument Co., Wujin, PRC), having a polychromatic spectrum with $\lambda \geq 365$ nm, in a centric photochemical rotating reactor. The lamp was fixed in the center of a plate with a large hole in the center and 8 small holes around it. Eight identical 10 mL quartz test tubes (o.d.1.5 cm, length 11.5 cm) were placed



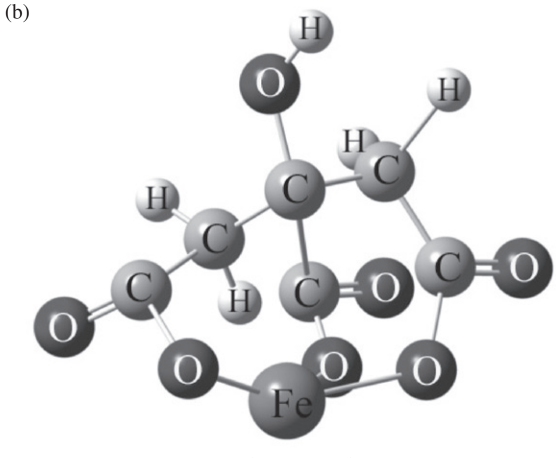


Figure 1. (a) Structure of Fe(III)-pyruvate complex; (b) structure of Fe(III)-citrate complex.

vertically in each hole as photochemical reaction cells, so that the light and the cells were kept parallel with a fixed distance of 7.0 cm. The tubes were rotated at 50 rpm. Irradiation influx was equally distributed across the cells. During the photoreaction, water-jacketed Pyrex was used to maintain a constant temperature about 22°C.

2.3. *Analysis*

The UV absorbance spectra of GLP, $FeCl_3$, pyruvate, citrate and their mixed solutions were recorded with a UV-1601 (Shimadzu, Japan) spectrophotometer. Orthophosphate (PO_4–P) and total phosphorus (P_{tot}) were measured according to the standard methods at 700 nm, based on the formation of a blue molybdenum complex and after digestion using peroxodisulfate ($K_2S_2O_8$), respectively [19]. The detection limit is $0.01\,mg\,L^{-1}$ PO_4–P. Each result was based on triplicate measurements. The measured P_{tot} matched the expected values that were calculated according to the GLP specification.

Each run was performed by first switching on the lamp without test tubes in the cells. After the achievement of the maximum irradiating power (10 min), the test tubes were placed into the cells rapidly. The samples were analyzed immediately after sampling to prevent further oxidation.

2.4. *Calculation*

The release of orthophosphates in the solution was calculated with equation (6). The glyphosate solutions initially contain orthophosphates (impurities in the solutions) that are not released from irradiation of glyphosate. To determine the actual release of orthophosphates from glyphosate, the orthophosphate content of the solution without irradiation is subtracted from the total phosphorus and orthophosphate contents of the irradiated solution [20].

$$\%\mathrm{PO_4{-}P} = ([\mathrm{PO_4{-}P}]_t - [\mathrm{PO_4{-}P}]_0)/([\mathrm{PO_{4tot}}] - [\mathrm{PO_4{-}P}]0) \times 100 \tag{6}$$

$\%PO_4$–P is the release of orthophosphates, $[PO_4–P]_t$ is the orthophosphate content at t irradiation time ($mg\,L^{-1}$), $[PO_4–P]_0$ is the orthophosphate content without irradiation and $[PO_{4tot}]$ is the total phosphorus content at irradiation time t ($mg\,L^{-1}$).

3. Results and discussion

3.1. *UV spectra analysis*

As shown in figure 2, GLP, pyruvate and citrate have no absorption at $\lambda \geq 365\,nm$. When mixed with Fe(III), the absorption spectrum changes showing that Fe(III), GLP, pyruvate, and citrate form Fe(III)-pyruvate, Fe(III)-citrate, and Fe(III)-pyruvate-GLP coordination compounds in aqueous solutions.

3.2. *Control experiments*

Figure 3(a, b) shows that no direct photodegradation of GLP occurs after irradiation for 180 min since GLP has no absorption at $\lambda \geq 365\,nm$ and is not readily hydrolyzed. The degradation efficiency of GLP in Fe(III)-pyruvate and Fe(III)-citrate systems is much higher than in the Fe(III)-hydroxo system. Thus, the Fe(III)-pyruvate, Fe(III)-citrate complexes have higher photoreactivity than $Fe(OH)^{2+}$.

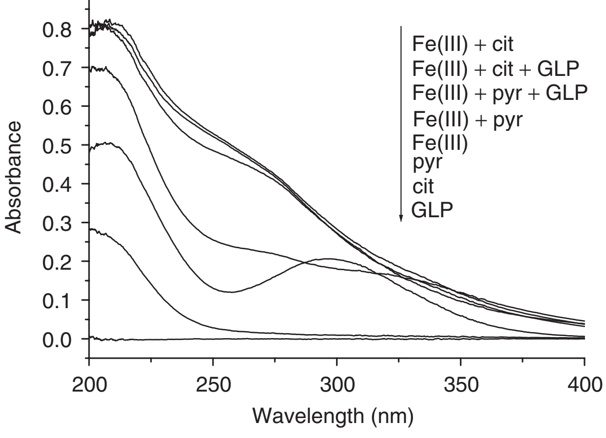


Figure 2. The UV absorbance spectra of GLP, pyruvate, citrate, Fe(III) and binary and ternary coordination compounds in aqueous solutions.

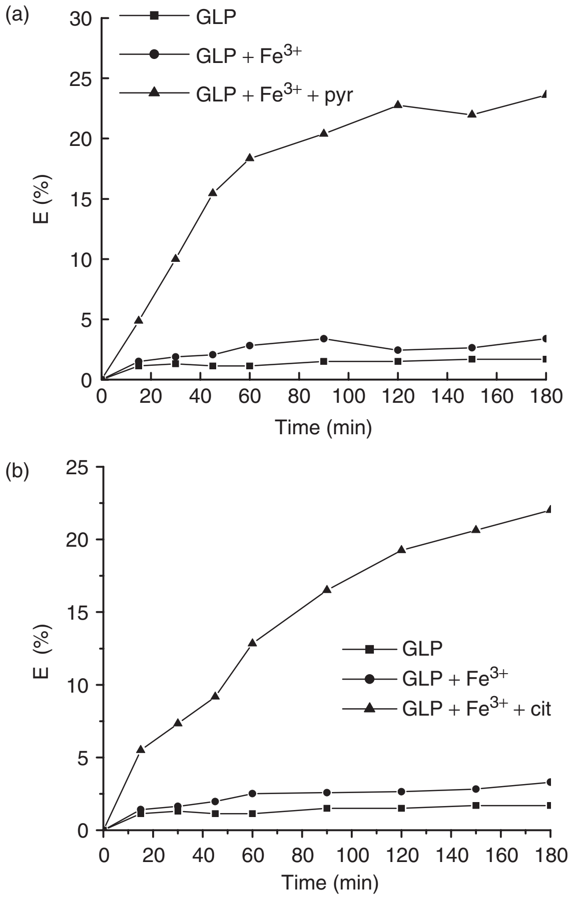


Figure 3. (a) Efficiency of photodegradation of GLP in the Fe(III)-pyruvate system in control experiment. $[\mathrm{GLP}]_0 = 5.0\,\mathrm{mg\,L^{-1}}$, $[\mathrm{Fe(III)}]_0/[\mathrm{pyr}]_0 = 20/300$ ($\mu\mathrm{mol\,L^{-1}}$), pH = 3.5; (b) efficiency of photodegradation of GLP in the Fe(III)-citrate system in control experiment. $[\mathrm{GLP}]_0 = 2.0\,\mathrm{mg\,L^{-1}}$, $[\mathrm{Fe(III)}]_0/[\mathrm{cit}]_0 = 20/300$ ($\mu\mathrm{mol\,L^{-1}}$), pH = 8.0.

3.3. *Effect of initial concentrations*

Figure 4(a, b) shows that the photodegradation efficiency of GLP is related to its initial concentrations, increasing with decreasing initial concentrations in the range 1.0–06.0 mg $\mathrm{L^{-1}}$. When the initial concentration of glyphosate is 1.0 mg $\mathrm{L^{-1}}$, an Fe(III)/carboxylate ratio of 20/300 µmol $\mathrm{L^{-1}}$ (initial pH value 3.5 for Fe(III)-pyruvate and 8.0 for Fe(III)-citrate aqueous solution) 38.5 and 24.8% of glyphosate can be photochemically transformed into orthophosphate ($\mathrm{PO_4}$–P), respectively. As for the lower initial concentrations, higher degradation will be obtained in natural acidic waters.

3.4. *Effect of initial pH values*

Figure 5(a, b) shows the photodegradation of GLP at initial concentration 5.0 mg $\mathrm{L^{-1}}$ and 2.0 mg $\mathrm{L^{-1}}$ in Fe(III)-pyruvate and Fe(III)-citrate solutions, respectively, with Fe(III)/carboxylate ratio 20/300 in different pH range. GLP can be efficiently

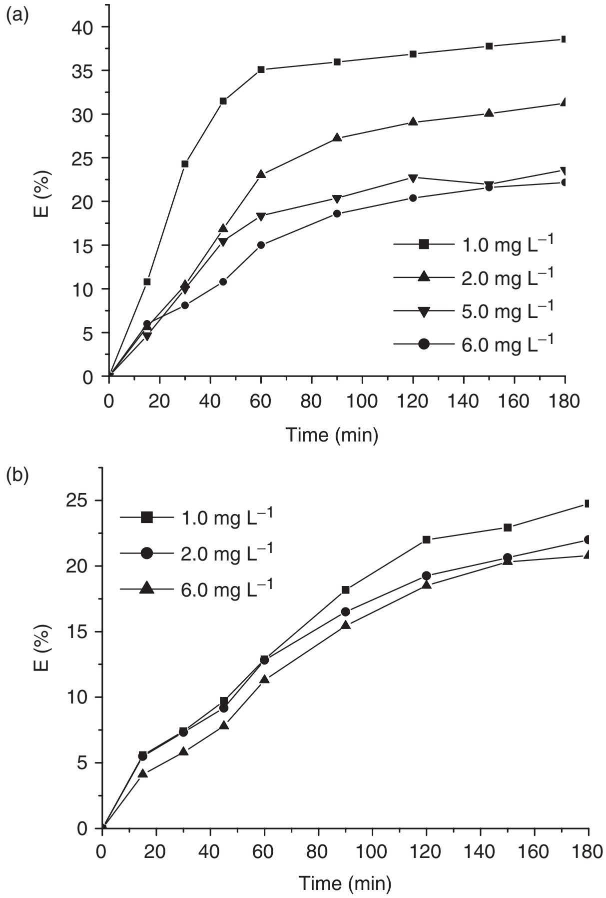


Figure 4. (a) Effect of initial concentrations on photodegradation of GLP in the Fe(III)-pyruvate system. pH = 3.5, $[Fe^{3+}]_0/[pyr]_0 = 20/300$ (μmol L^{-1}); (b) effect of initial concentrations on photodegradation of GLP in the Fe(III)-citrate system. pH = 8.0, $[Fe^{3+}]_0/[cit]_0 = 20/300$ (μmol L^{-1}).

transformed into orthophosphate in both systems. As shown in figure 5(a), in the Fe(III)-pyruvate system, the optimum pH values for the photodegradation of GLP was in the range 4.5–5.0. As shown in figure 5(b), in the Fe(III)-citrate system, the release efficiency of orthophosphate increases with increasing pH in the range 6.0–9.0. The pH dependence of GLP photodegradation could be attributed to the speciation of Fe(III)-carboxylate ions, a function of pH values. Furthermore, the pH values govern the relative amount of $O_2^{-\bullet}/HO_2^{-\bullet}$, which can react with Fe(II) to form H_2O_2. Faster reactions of Fe(II) with $O_2^{-\bullet}/HO_2^{-\bullet}$ in the higher pH range where $O_2^{-\bullet}$ becomes dominant, result in greater H_2O_2 formation, which in turn leads to more $^{\bullet}OH$ production [21]. For the Fe(III)-pyruvate system, in the high pH range (pH ≥ 6.0) the system becomes unstable due to ferric precipitation.

3.5. *Effect of Fe(III)/carboxylate ratios*

Figure 6(a, b) shows the photodegradation of GLP in both Fe(III)-pyruvate and Fe(III)-citrate systems with definite initial concentration and pH values. Although the

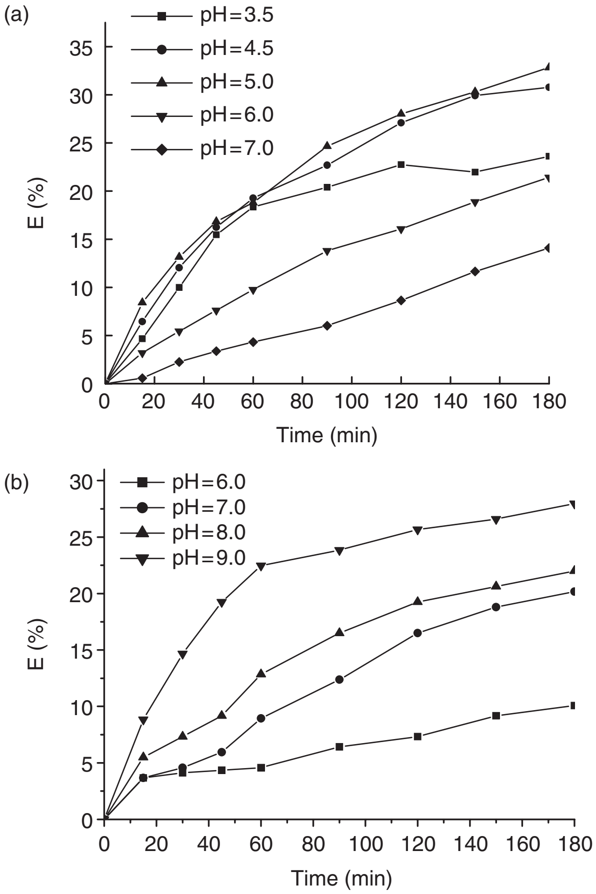


Figure 5. (a) Effect of initial pH values on photodegradation of GLP in the Fe(III)-pyruvate system. $[GLP]_0 = 5.0\,mg\,L^{-1}$, $[Fe^{3+}]_0/[pyr]_0 = 20/300$ ($\mu mol\,L^{-1}$); (b) effect of initial pH values on photodegradation of GLP in the Fe(III)-citrate system. $[GLP]_0 = 2.0\,mg\,L^{-1}$, $[Fe^{3+}]_0/[cit]_0 = 20/300$ ($\mu mol\,L^{-1}$).

individual conditions such as pH and initial concentration are different in both systems, the common trend for the generation of orthophosphate is the same. The release efficiency of orthophosphate increases with Fe(III)/carboxylate ratios in the range 20/150-20/300 and 20/60-20/300 for Fe(III)-pyruvate and Fe(III)-citrate systems, respectively.

4. Conclusions

The efficiency of photodegradation of GLP into orthophosphate increases with decreasing initial concentrations of GLP. The pH values and Fe(III)-carboxylate ions are key factors for the photoreactivity in both Fe(III)-pyruvate and Fe(III)-citrate systems. The pH values govern the speciation of Fe(III)-carboxylate ions and influence the generation of OH radicals. The degradation efficiency of GLP increases with Fe(III)/carboxylate ratios. GLP can be photochemically transformed into orthophosphate efficiently at the optimum pH range of 4.5–5.0

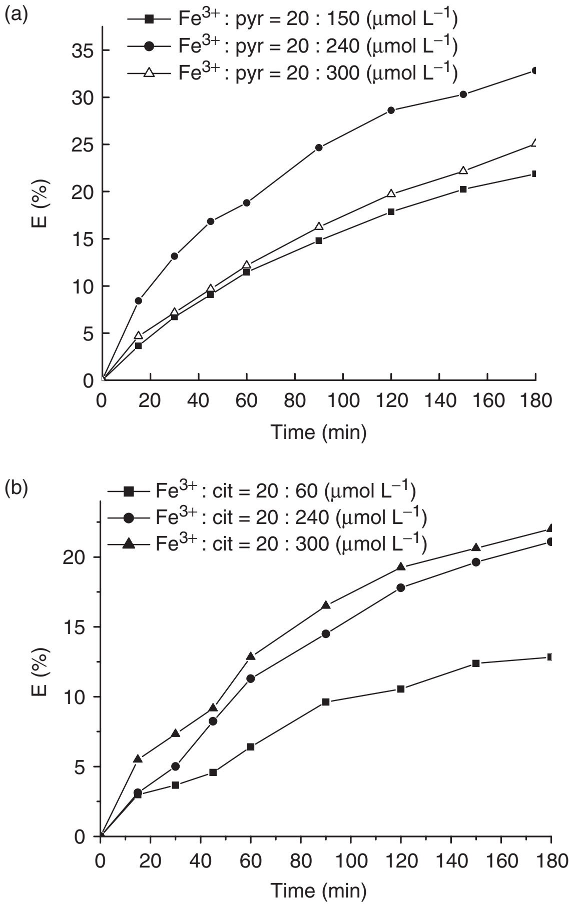


Figure 6. (a) Effect of Fe(III)/pyr ratios on photodegradation of GLP in the Fe(III)-pyruvate system. $[GLP]_0 = 5.0\,mg\,L^{-1}$, pH = 5.0; (b) effect of Fe(III)/cit ratios on photodegradation of GLP in the Fe(III)-citrate system. $[GLP]_0 = 2.0\,mg\,L^{-1}$, pH = 8.0.

in Fe(III)-pyruvate complexes system. In Fe(III)-citrate complexes system, the release efficiency of orthophosphate increases with increasing pH values in the pH range of 6.0–9.0.

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References

[1] M.F. Zaranyika, M.G. Nyandoro. *J. Agric. Food. Chem.*, **41**, 838 (1993).
[2] I.D. Merás, T.G. Díaz, M.A. Franco. *Talanta*, **65**, 7 (2005).

[3] Weed Science Society of America. *Herbicide Handbook*, Weed Science Society of America, Champaign, IL (1983).

[4] D.L. Shinabarger, H.D. Braymer. *J. Bacteriol.*, **168**, 702 (1986).

[5] H.W. Talbot, L.M. Johnson, D.M. Munnecke. *Current Microbial.*, **10**, 255 (1984).

[6] R.E. Hoagland. *Weed Sci.*, **28**, 393 (1980).

[7] M.L. Rueppel, B.B. Brightwell, J. Schaefer, J.T. Marvel. *J. Agric. Food Chem.*, **25**, 517 (1977).

[8] F.A. Anton, L.M. Cuadra, P. Gutierrez, E. Laborda, P. Laborda. *Bull. Environ. Contam. Toxicol.*, **51**, 881 (1993).

[9] M.F. Zaranyika, M.G. Nydandoro. *J. Agric. Food., Chem.*, **41**, 838 (1993).

[10] Y. Zuo, J. Hoigné. *Atmos. Envir.*, **28**, 1231 (1994).

[11] B.C. Faust, R.G. Zepp. *Environ. Sci. Technol.*, **27**(12), 2517 (1993).

[12] M. Izakovič, J. Šima, M. Žitňanský. *J. Coord. Chem.*, **58**, 1039 (2005).

[13] L. Wang, C. Zhang, F. Wu, N. Deng. *J. Coord. Chem.*, **59**, 803 (2006).

[14] N. Deng, T. Fang, S. Tian. *Chemosphere*, **33**, 547 (1996).

[15] N. Deng, F. Wu, F. Luo, Z. Liu. *Chemosphere*, **35**, 2697 (1997).

[16] N. Deng, F. Wu, S. Tian, F. Tao. *Chemosphere*, **34**, 2725 (1997).

[17] F. Wu, N. Deng, Y. Zuo. *Chemosphere*, **39**, 2079 (1999).

[18] D. Zhou, F. Wu, N. Deng, W. Xiang. *Water Res.*, **38**, 4107 (2004).

[19] State Environmental Protection Administration, *Handbook of Water and Wastewater Monitoring and Analysis Method*, China Environmental Press, Beijing, (2002).

[20] C. Lesueur, M. Pfeffer, M. Fuerhacker. *Chemosphere*, **59**, 685 (2005).

[21] J. Jeong, J. Yoon. *Water Res.*, **39**, 2893 (2005).