ELSEVIER

Photodegradation of glyphosate in the ferrioxalate system

Yong Chen [a], Feng Wu [a,*], Yixin Lin [a], Nansheng Deng [a],
Nikolai Bazhin [b], Evgeni Glebov [b]

[a] *School of Resources and Environmental Science, Wuhan University, Wuhan 430079, PR China*
[b] *Institute of Chemical Kinetics and Combustion, 3 Institutskaya St., Novosibirsk 630090, Russia*

Abstract

The photoinduced degradation of glyphosate (GLP) in the ferrioxalate system was investigated under irradiation with a 250 W metal halide lamp ($\lambda \geq 365$ nm). The efficiency of orthophosphates release, representing the photodegradation efficiency of GLP, increased with decreasing the initial concentrations of GLP and Fe(III)/oxalate ratios. At acidic pH value in the range of 3.5–5.0, higher efficiency of orthophosphates release up to 60.6% was achieved, while the efficiency dropped to 42.1% at pH 6.0. The photochemical process mainly involved the predominant species of iron(III), namely $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$, which lead to the formation of hydroxyl radicals in the presence of dissolved oxygen under UV–vis irradiation. Also, the complexation of GLP with Fe(III) obviously increased the light absorption of GLP and facilitated its degradation by direct photolysis. The ninhydrin test for primary amines showed that the GLP was attacked by hydroxyl radicals with C−N cleavage to yield aminomethylphosphonic acid (AMPA) and C−P cleavage to yield sarcosine. The photodegradation may be enhanced by the decomposition of reactive radicals produced through ligand-to-metal charge transfer (LMCT) of ferric–GLP complexes.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Glyphosate; Ferrioxalate system; Photodegradation

1. Introduction

Glyphosate (*N*-(phosphonomethyl) glycine, glyphosate (GLP)), a postemergence nonselective broad spectrum herbicide, is extensively used in agriculture for the control of many annual and perennial weeds, which was introduced by Monsanto Company, US in the early 1970s [1]. Glyphosate is essentially nontoxic to mammals and birds, but fish and invertebrates are more sensitive to the herbicide [2]. Many researches showed that glyphosate could be degraded by microorganisms and plants to yield aminomethylphosphonic acid (AMPA) and sarcosine, which could be further degraded into water, carbon dioxide and phosphate, although the slower degradation of AMPA had been reported in some instances [3].

Abiotic degradation is also an important pathway for dissipation of glyphosate in the environment. Hydrolysis of glyphosate in sterile buffers is very slow. With respect to photodegradation of glyphosate, it was considered previously that no

direct photodegradation occurred [4]. Nevertheless, the experiments later showed that glyphosate could be photodegraded, but the extent of degradation was dependent on the light sources and composition of solution [5]. The glyphosate and aminomethylphosphonic acid also can be degraded by dilute aqueous suspensions of birnessete, a manganese oxide common in soils [6]. In most cases, glyphosate will dissipate rapidly from natural water bodies through adsorption to organic substances and inorganic clays, degradation, and dilution [7–10].

The degradation of glyphosate in natural environment affects not only the validity of herbicide but also the bioavailability of glyphosate since it could be photochemically transformed into orthophosphate, which is responsible for eutrophication in waters. It was suggested that the bioavailibility of organophosphorous compounds in freshwaters could be attributed to ferric ions but few researches proved the point of view [11]. The most relevant report just mentioned the photodegradation of glyphosate in Fe(III)/H_2O_2/UV system [12].

Our group has been engaged in the simulative researches on the photodegradation of organic compounds induced by different ferric species including Fe(III)–OH complexes, Fe(III)–polycarboxylate complexes, ferric oxides and Fe(III)

---

* Corresponding author. Tel.: +86 27 68778511; fax: +86 27 68778511.
  E-mail address: fengwu@whu.edu.cn (F. Wu).

–humic acid complexes and their applications to pollutant removal [13,14]. The photochemistry of Fe(III)–oxalate complexes had been studied since the 1950s [15]. However, till 1990s, much attention has been paid on the environmental chemistry research on Fe(III)–oxalate complexes and the photolysis of Fe(III)–oxalate complexes was a major pathway for the formation of H_2O_2 in atmospheric waters [16]. The H_2O_2 formed by the photolysis of Fe(III)–oxalate complexes can react with Fe^{2+}, according to a Fenton mechanism [17]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$
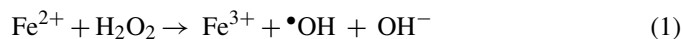
The production of ${}^{\bullet}OH$ radicals has considerable implications for the oxidation of a wide variety of natural and anthropogenic organic and inorganic substances [18,19]. For the extensive existence of ferric ions and oxalate ions in the natural waters, much concern was focused on the oxidation of pollutants mediated by the above ions or the photochemical cycling of iron since iron element was considered as a limiting factor in biological productivity [20,21].

In the present study, we focused our attention on the role of ferrioxalate system in the photodegradation of glyphosate to release orthophosphate. This work is aimed to understand the possible implications of glyphosate for the eutrophication in waters under irradiation. A possible photodegradation pathway of glyphosate in ferrioxalate system was proposed.

2. Materials and methods

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. 0.1 M HAc–NaAc buffer (pH 5.8) was prepared; 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 reactor of rotating type. The lamp was fixed in the center of a plate with large hole in the center and eight small holes around it. Eight identical 10 ml quartz test tubes (o.d. 1.5 cm, length 11.5 cm) were placed 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 equably distributed across the cells. During the photoreaction, a water-jacketed Pyrex was used to maintain a constant temperature at about 22 °C. Each run was performed by first switching on the lamp without test tubes in the cells. After the achievement of the stable irradiating power (10 min), the eight test tubes with 10 ml reaction solution were placed into the cells rapidly. The typical composition inside each test tube is $[GLP]_0 = 5.0$ mg L^{-1}, $[Fe^{3+}]_0/[C_2O_4{}^{2-}]_0 = 20/300$ (μmol L^{-1}) at pH 3.5.

2.3. Analysis

The UV absorbance spectra of GLP, $FeCl_3$, $Na_2C_2O_4$, and their mixed solutions were recorded with spectrophotometer UV-1601 (Shimadzu, Japan). Orthophosphate (PO$_4$-P) and total phosphorus (PO$_{4tot}$) were measured according to the standard methods with spectrophotometer at 700 nm, based on the formation of a blue molybdenum complex and after digestion using peroxodisulfate ($K_2S_2O_8$), respectively [22]. The detection limit is 0.01 mg L^{-1} PO$_4$-P. Each result was based on the measurement of triplicates. The measured PO$_{4tot}$ matched the expected values that were calculated according to the GLP specification. Ninhydrin colorimetric experiments were conducted to test qualitatively for the degradation of GLP to primary amine products in the HAc–NaAc buffer (pH 5.8) [6]. The samples were analyzed immediately after sampling to prevent further oxidation.

2.4. Calculation

The release of orthophosphates in the solution was calculated with Eq. (2). The phosphonate solutions initially contain orthophosphates (impurities in the solutions) that are not released from the irradiation of the phosphonates. To determine the actual release of orthophosphates from the phosphonates, the orthophosphate content of the solution without irradiation is subtracted from the total phosphorus and orthophosphate contents of the irradiated solution [23].

$$\%PO_4\text{-}P = ([PO_4\text{-}P]_t - [PO_4\text{-}P]_0)/([PO_{4tot}] - [PO_4\text{-}P]_0) \times 100$$
$$(2)$$

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

2.5. Equilibration calculation

All speciation in this study were performed with MEDUSA, a chemical equilibrium calculation program. The equilibrium constants were obtained from the literature and corrected for differences in ionic strength using the Davies equation.

3. Results and discussion

3.1. Control experiments

As shown in Fig. 1, GLP and $Na_2C_2O_4$ have no appreciable light absorption at $\lambda \geq 365$ nm. However, when they are mixed with ferric ions, the absorptions are noticeably strengthened. It was supposed that GLP, $Na_2C_2O_4$ and Fe(III) may form Fe(III)–GLP binary complex, Fe(III)–$C_2O_4{}^{2-}$ binary complexes and/or Fe(III)–$C_2O_4{}^{2-}$–GLP ternary complexes. Formation of ferric–glyphosate complex was confirmed by ATR–FTIR elsewhere [24]. Fig. 2 illustrates the importance of the strengthened absorption for the photodegradation by the fact
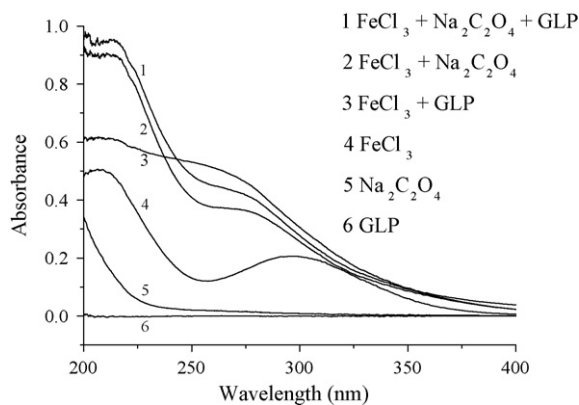
Fig. 1. The UV absorbance spectra of GLP, $FeCl_3$, $Na_2C_2O_4$, and their mixed solutions under the conditions: $[FeCl_3] = 20\,\mu mol\,L^{-1}$; $[Na_2C_2O_4] = 150\,\mu mol\,L^{-1}$; $[GLP] = 3.38\,mg\,L^{-1}$, pH 3.35.

that no obvious orthophosphate release was observed in the GLP aqueous solution after irradiation for 180 min. In contrast, the photodegradation is improved in the presence of $Na_2C_2O_4$ and Fe(III). The efficiency of orthophosphates release in ferrioxalate system is much higher than that in the Fe(III)-hydroxo system at pH 3.5, which is consistent with the fact that ferrioxalate complexes have higher photoreactivity than $Fe(OH)^{2+}$, as mentioned in previous studies [25].

3.2. Effect of initial concentrations

Fig. 3 shows that the efficiency of orthophosphates release is related to its initial concentrations. The orthophosphates release efficiency increases with decreasing the initial concentrations at the range of 1.0–4.0 mg L^{-1}. When the initial concentration of glyphosate is 1.0 mg L^{-1}, the Fe(III)/oxalate ratio 20/300 $\mu mol\,L^{-1}$, the initial pH value 3.0, 63.2% of glyphosate can be photochemically transformed into orthophosphate (PO_4-P) after a 180 min irradiation. As for the lower initial concentrations, it could be suggested that higher degradation will be obtained.
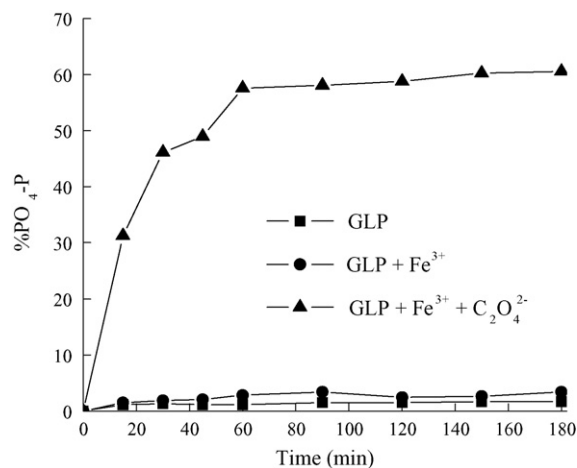

Fig. 2. Efficiency of orthophosphates release in control experiment under the conditions: $[GLP]_0 = 5.0\,mg\,L^{-1}$, $[Fe^{3+}]_0/[C_2O_4^{2-}]_0 = 20/300$ ($\mu mol\,L^{-1}$), pH 3.5.
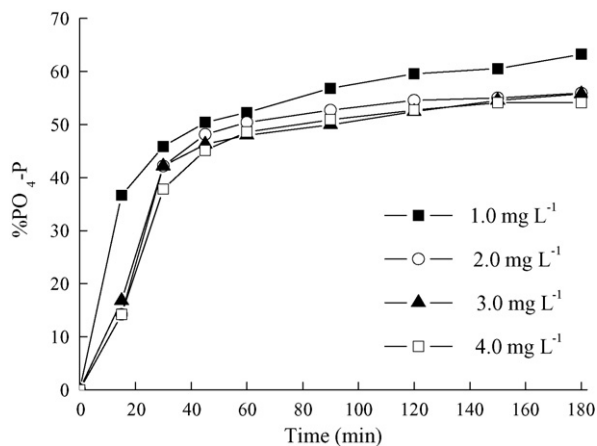

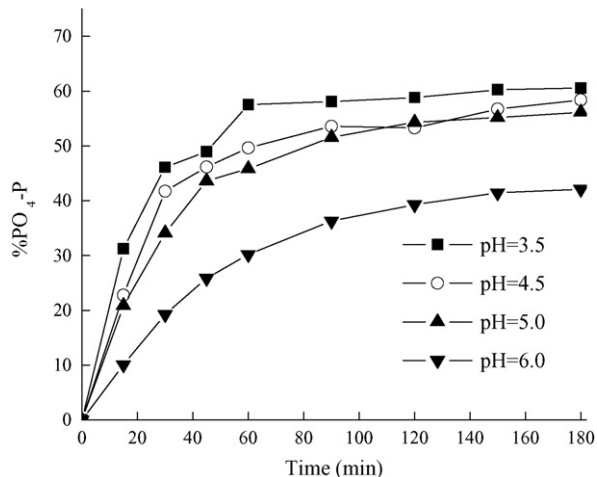Fig. 3. Effect of initial concentrations of GLP on photodegradation under the conditions: pH 3.0, $[Fe^{3+}]_0/[C_2O_4^{2-}]_0 = 20/300$ ($\mu mol\,L^{-1}$).

Fig. 4. Effect of initial pH values on photodegradation under the conditions: $[GLP]_0 = 5.0\,mg\,L^{-1}$, $[Fe^{3+}]_0/[C_2O_4^{2-}]_0 = 20/300$ ($\mu mol\,L^{-1}$).
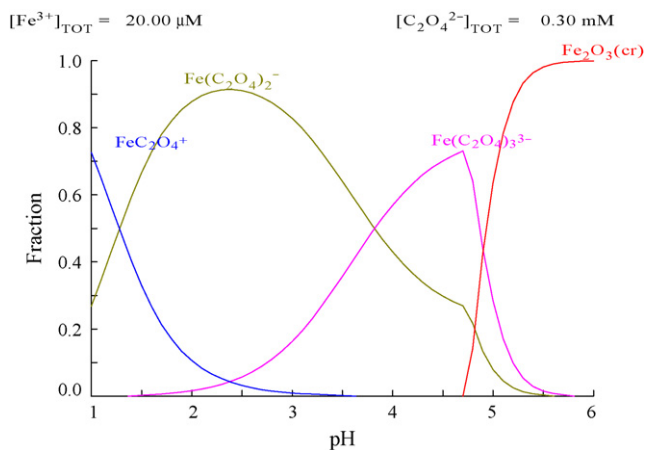

Fig. 5. Speciation fraction of Fe(III) calculated by MEDUSA at various pH from 1 to 6 under the conditions: $[Fe^{3+}]_{tot} = 20\,\mu mol\,L^{-1}$, $[C_2O_4^{2-}]_{tot} = 300\,\mu mol\,L^{-1}$.
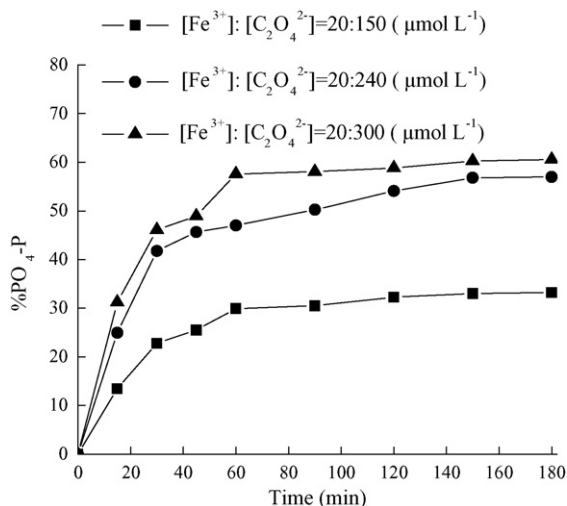
Fig. 6. Effect of Fe^{3+}/oxalate ratios on photodegradation under the conditions: $[GLP]_0 = 5.0 \, mg \, L^{-1}$, pH 3.5.

Fig. 7. Speciation fraction of Fe(III) calculated by MEDUSA at various oxalate concentration under the conditions: $[Fe^{3+}]_{tot} = 20 \, \mu mol \, L^{-1}$, pH 3.5.

3.3. Effect of initial pH values

Fig. 4 shows the photodegradation of GLP with the initial concentration $5.0 \, mg \, L^{-1}$ and Fe(III)/oxalate ratio 20/300 in the pH range of 3.5–6.0. GLP can be efficiently transformed into orthophosphate at pH 3.5–5.0. As shown in Fig. 5, the pH
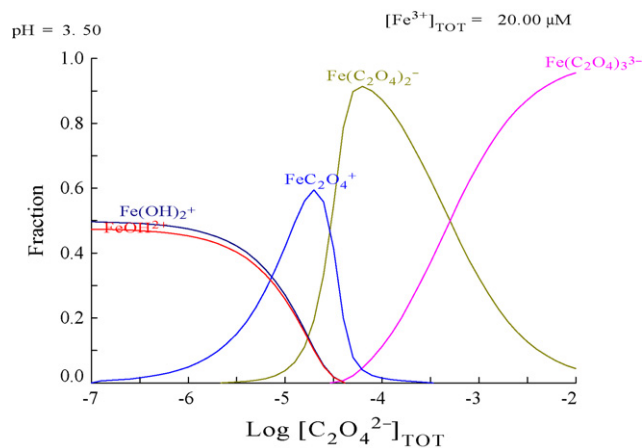
values determine the Fe(III) species contribution. The fraction of $Fe(OH)^{2+}$ is negligible and the ferrioxalate ions constitute the main Fe(III) species in ferrioxalate system. Ferrioxalate ions in the system are mainly present as $Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$. It was reported [26] that $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$ were much more efficiently photolyzed than $Fe(C_2O_4)^+$. Thus, the pH dependence of GLP degradation can be attributed to the speciation of ferrioxalate ions since they are
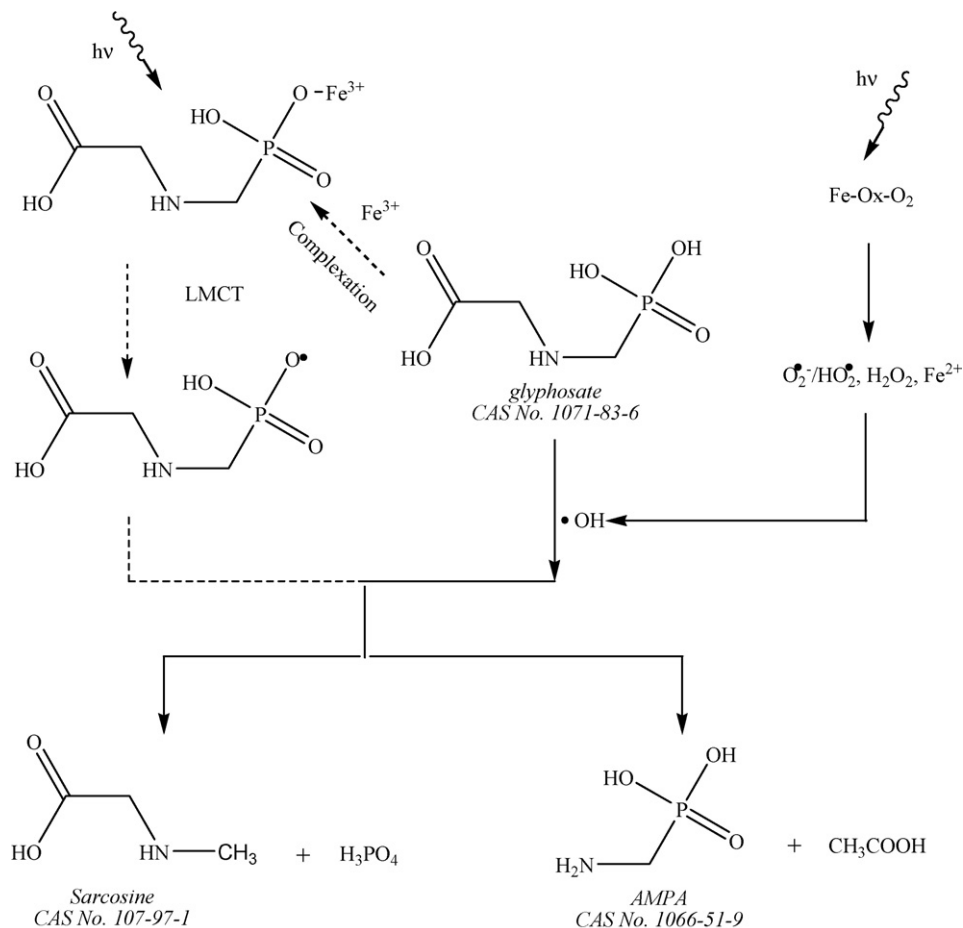

Fig. 8. The proposed reaction mechanism of GLP in ferrioxalate system. Solid line represents the major pathways and dashed line represents the possible pathways.

the 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. The 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 [27].

3.4. Effect of Fe(III)/oxalate ratios

Fig. 6 shows the photodegradation of GLP with its initial concentration 5.0 mg L^{-1} and pH 3.5 in different Fe(III)/oxalate ratios. The efficiency of orthophosphates release increases with the decrease of Fe(III)/oxalate ratios, but it becomes not as noticeable as the beginning when the ratios decrease. Oxalate ions play an important role in the photodegradation of GLP since the primary ligand-to-metal charge-transfer (LMCT) process in the photoexcited state of ferrioxalate ions is closely related to the oxalate ions. The reactive decay of the LMCT state via the pho-toinduced electron transfer (PET) by inner-sphere mechanism leads to the formation of $O_2^{\bullet-}$ and decomposition of oxalate to CO_2 [28]. As shown in Fig. 7, with the increase of logarithmic concentration of $C_2O_4^{2-}$, the ferrioxalate ions become dominant in the ferrioxalate system, which increases its photoreactivity. Accordingly, the increase of oxalate concentration is favorable to the photodegradation of GLP. Nevertheless, the superabun-dant ferrioxalate ions will oxidize the oxalate radicals and thus, prevent the reduction of O_2 and the formation of H_2O_2.

3.5. The proposed degradation pathway of GLP

As mentioned in the introduction section, GLP can be degraded by microorganisms and plants via C–N and C–P bonds cleavage. The ninhydrin test based on formation of the colored Ruhemann purple compound of primary amine showed that GLP possibly underwent C–N bonds breakage to yield aminomethylphosphonic acid. The C–P bond cleavage occurred under the irradiation, as evidenced by the formation of orthophosphate detected in this study. The cleavages of C–N and C–P bonds are believed to be attributed to hydroxyl radicals produced by the photolysis of ferric–oxalate complexes in the presence of dissolved oxygen. Additionally, the direct photoly-sis of ferric–GLP complex may also occur and the GLP radicals produced through ligand-to-metal charge transfer decompose to sarcosine (CAS No. 107-97-1) and AMPA (CAS No. 1066-51-9). Thus, the possible reaction pathway of GLP in the ferrioxalate system is proposed as in Fig. 8, which is similar to the proposed pathway by Barrett and McBride [6].

4. Conclusions

Glyphosate can be efficiently photodegraded in the ferriox-alate system. The efficiency of orthophosphates release increases with decreasing initial concentrations of GLP. The pH values and oxalate ions are the key factors for the photoreactivity in fer-rioxalate system since they govern the predominant speciation of ferrioxalate ions and affect the generation of $\bullet OH$ radicals. The efficiency of orthophosphates release of GLP increases

with the decrease of Fe(III)/oxalate ratios and GLP can be photodegradaded efficiently at the pH range of 3.5–5.0. The degradation of GLP in ferrioxalate system is mainly attributed to the attack of $\bullet OH$ radicals followed by C–N cleavage to yield aminomethylphosphonic acid and C–P cleavage to yield sarco-sine. The binary and ternary complexes of GLP with Fe(III) and $C_2O_4^{2-}$ may be partially responsible for the degradation of GLP via the reactive decay of LMCT excitation of GLP complexes, that is to say, the central Fe(III) ion undergoes reduction and GLP as the ligand or a sacrificial donor is a subject of oxidation.

References

[1] S.M. Carlisle, J.T. Trevors, Glyphosate in the environment, Water Air Soil Pollut. 39 (1988) 409–420.

[2] Weed Science Society of America, Herbicide Handbook, fifth ed., Weed Science Society of America, Champaign, IL, 1983.

[3] H.W. Talbot, L.M. Johnson, D.M. Munnecke, Glyphosate utilization by *Pseudomonas* sp. and *Alcaligenes* sp. isolated from environmental sources, Curr. Microb. 10 (1984) 255–260.

[4] M.L. Rueppel, B.B. Brightwell, J. Schaefer, J.T. Marvel, Metabolism and degradation of glyphosate in soil and water, J. Agric. Food Chem. 25 (1977) 517–528.

[5] K. Lund-Hoie, H.O. Friestad, Photodegradation of the herbicide glyphosate in water, Bull. Environ. Contam. Toxicol. 36 (1986) 723–729.

[6] K. Barrett, M.B. McBride, Oxidative degradation of glyphosate and aminomethyl-phosphonate by manganese oxide, Environ. Sci. Technol. 39 (2005) 9223–9228.

[7] J.C. Feng, D.G. Thompson, P.E. Reynolds, Fate of glyphosate in a Canadian forest watershed. 1. Aquatic residues and off target deposit assessment, J. Agric. Food Chem. 38 (1990) 1110–1118.

[8] M.F. Zaranyika, M.G. Nyandoro, Degradation of glyphosate in the aquatic environment: an enzymatic kinetic model that takes into account micro-bial degradation of both free and colloidal (or sediment) particle adsorbed glyphosate, J. Agric. Food Chem. 41 (1993) 838–842.

[9] F.L. Paveglio, K.M. Kilbride, C.E. Grue, C.A. Simenstad, Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: environmental fate, Environ. Toxicol. Chem. 15 (1996) 961–968.

[10] F. Li, Y. Wang, Q. Yang, D.G. Evans, C. Forano, X. Duan, Study on adsorption of glyphosate (*N*-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution, J. Hazard. Mater. 125 (2005) 89–95.

[11] O.C. Zafirou, R.G. Zepp, R.G. Zika, Photochemistry of natural waters, Environ. Sci. Technol. 18 (12) (1984) 358A–371A.

[12] P.L. Huston, J.J. Pignatello, Degradation of pesticide active ingredients and commercial formulationd in water by the photo-assisted Fenton reaction, Water Res. 33 (1999) 1238–1246.

[13] F. Wu, N. Deng, Photochemistry of hydrolytic iron(III) species and pho-toinduced degradation of organic compounds. A minireview, Chemosphere 41 (2000) 1137–1147.

[14] D. Zhou, F. Wu, N. Deng, W. Xiang, Photooxidation of bisphenol A (BPA) in water in the presenceof ferric and carboxylate salts, Water Res. 38 (2004) 4107–4116.

[15] C.A. Parker, Induced autoxidation of oxalate in relation to the photolysis of potassium ferrioxalate, Trans. Faraday Soc. 50 (1954) 1213–1221.

[16] Y. Zuo, J. Hoigné, Evidence for photochemical formation of H_2O_2 and oxidation of SO_2 in authentic fog water, Science 260 (1993) 71–73.

[17] R.G. Zepp, B.C. Faust, J. Hoigné, Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(III) with hydrogen peroxide: the photo-Fenton reaction, Environ. Sci. Technol. 26 (1992) 313–319.

[18] Y. Deng, H. Chen, T. Wu, M. Krzyaniak, A. Wellons, D. Bolla, K. Douglas, Y. Zuo, Iron-catalyzed photochemical transformation of benzoic acid in atmospheric liquids: product identification and reaction mechanisms, Atmos. Environ. 40 (2006) 3665–3676.

[19] Y. Zuo, J. Zhan, Effects of oxalate on Fe-catalyzed photooxidation of dissolved sulfur dioxide in atmospheric water, Atmos. Environ. 39 (2005) 27–37.

[20] J.H. Martin, S.E. Fitzwater, Iron deficiency limits photoplankton growth in the north-east Pacific subarctic, Nature 331 (1988) 341–343.

[21] F.M.M. Morel, Limitation of productivity by trace metals in the sea, Limnol. Oceanogr. 36 (1991) 1742–1755.

[22] State Environmental Protection Administration of China, Water and Waste Water Monitor and Analysis Method, Chinese Environmental Science Press, Beijing, 2002.

[23] C. Lesueur, M. Pfeffer, M. Fuerhacker, Photodegradation of phosphonates in water, Chemosphere 59 (2005) 685–691.

[24] B.C. Barja, M. dos Santos Afonso, An ATR-FTIR study of glyphosate and Its Fe(III) complex in aqueous solution, Environ. Sci. Technol. 32 (1998) 3331–3335.

[25] M.E. Balmer, B. Sulzberger, Atrazine degradation in irradiated iron/oxalate system: effects of pH and oxalate, Environ. Sci. Technol. 33 (1999) 2418–2424.

[26] L. Vincze, S. Papp, Individual quantum yields of $(Fe^{3+}OX_n^{2-}H_m)^{\bullet+}$ complexes in aqueous acidic solutions ($OX^{2-} \equiv C_2O_4^{2-}$, $n = 1$–3, $m = 0.1$), J. Photochem. 36 (1987) 289–296.

[27] J. Jeong, J. Yoon, pH effect on OH radical production in photo/ferrioxalate system, Water Res. 39 (2005) 2893–2900.

[28] P. Ciésla, P. Kocot, P. Mytych, Z. Stasicka, Homogeneous photocatalysis by transition metal complexes in the environment, J. Mol. Catal. A: Chem. 224 (2004) 17–33.