



# The role of Fe(III) on phosphate released during the photo-decomposition of organic phosphorus in deionized and natural waters



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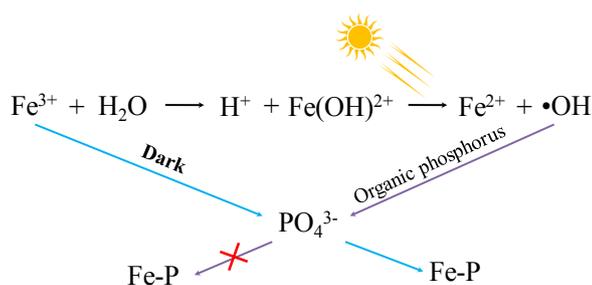
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## HIGHLIGHTS

- Glyphosate was efficiently photo-degraded in Fe<sup>3+</sup>/UV and Fe<sup>3+</sup>/sunlight systems.
- The release and immobilization of phosphate during the decomposition of glyphosate by Fe<sup>3+</sup> was found with and without light irradiation.
- The formation and steady-state concentration of ·OH in the Fe<sup>3+</sup>/UV and Fe<sup>3+</sup>/sunlight systems were determined.
- Fe<sup>3+</sup> plays an important role in phosphate that was released from the photo-decomposition of organic phosphorus in deionized and natural waters.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The photo-decomposition of organic phosphorus is an important route for the phosphorus cycle by which phosphate is regenerated in the aquatic environment. In this study, the role of Fe<sup>3+</sup> as a natural photosensitizer toward the decomposition of organic phosphorus to release phosphate was examined in deionized and natural waters under UV and sunlight irradiation using glyphosate as the organic phosphorus model. The results showed that the concentration of glyphosate decreased with irradiation time in the Fe<sup>3+</sup>/UV and Fe<sup>3+</sup>/sunlight systems and TOC gradually decreased, which confirmed that glyphosate was degraded by Fe<sup>3+</sup>. The amount of phosphate released from the photo-decomposition of glyphosate was higher in the presence of Fe<sup>3+</sup> than that of the control experiment under UV and sunlight irradiation conditions, and the generation rate of phosphate also increased with increasing Fe<sup>3+</sup> concentrations. The formation of hydroxyl radicals (·OH) in the Fe<sup>3+</sup>/UV and Fe<sup>3+</sup>/sunlight systems was identified according to the photoluminescence spectra (PL) using coumarin as the trapping molecule, and the steady-state concentrations of ·OH for the Fe<sup>3+</sup>/UV and Fe<sup>3+</sup>/sunlight systems were 1.06 × 10<sup>-14</sup> M and 0.09 × 10<sup>-14</sup> M, respectively. When natural water was spiked with glyphosate and Fe<sup>3+</sup>, the phosphate that was released in the Fe<sup>3+</sup> was higher than that of the control, and the phosphate that was released was inhibited when isopropanol was added to the reaction. All of these results demonstrate that the

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photochemical activity of  $\text{Fe}^{3+}$  has significantly impact in the release of phosphate from the photo-decomposition of organic phosphorus.

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## 1. Introduction

Phosphorus, an essential element for organisms in the aquatic environment, has been recognized as the most significant nutrient that influences the trophic status of a lake (Conley et al., 2009). The increase of phosphorus concentration in water has been considered to be the primary reason for eutrophication (Meinikmann et al., 2015). As a major component of phosphorus in the aquatic environment, organic phosphorus plays an important role in the phosphorus cycle (Qin et al., 2015; Zhu et al., 2004). Previous studies revealed that the decomposition of organic phosphorus into phosphate in the natural environment could be an important source of phosphorus in the water column and the dynamic mechanism may be involved in the decomposition of organic phosphorus (Gardolinski et al., 2004; Morin and Morse, 1999). However, little is known about this mechanism.

Some studies demonstrated that dissolved nutrients, such as  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  could be released when marine and estuarine resuspended sediments were irradiated by sunlight (Kieber et al., 2006; Southwell et al., 2010, 2011; Zhang et al., 2016). After irradiation for 6 h, the release rate for total dissolved nitrogen and phosphate were  $2.2 \pm 0.5 \mu\text{mol g}^{-1} \text{h}^{-1}$  and  $0.09 \pm 0.005 \mu\text{mol g}^{-1} \text{h}^{-1}$ , respectively. However no significant change was found in the dark controls. This study suggests that the photolysis process leads to a significant input of nutrients in overlying waters, extending its bio-availability (Southwell et al., 2011). The inorganic nutrients from photolysis could be utilized quickly, especially these release occurred in surface water (Zheng and Chen, 2013). These earlier studies have found that the photochemical processes play an important role in nutrient recycling in aquatic environment. However, the influence of environmental factors and mechanisms aspects of this phenomenon were not adequately addressed.

The reaction between iron and phosphorus at the sediment-water interface has been widely studied in the past decades (Wang et al., 2015; Han et al., 2015). Fe(II) in sediment would be oxidized to Fe(III) when anaerobic sediment is transferred to aerobic conditions during sediment suspension in the shallow lake (Morgan et al., 2012). A large quantity of phosphate would be fixed by Fe(III) by forming Fe(OOH)-P complexes or precipitates (Kleeberg et al., 2013), which inhibit the release of phosphorus. Meanwhile, the dissolved phosphate could be released from the phosphorus – humus - iron complex under UV irradiation (Francko and Heath, 1979, 1982; Jones et al., 1998; De Haan et al., 1990). The mechanisms were mainly concluded as following: (1) UV light can damage the phenol group of dissolved humus, which reduced affinity for dissolved iron, thereby promoting dissociation of phosphate; (2)  $\text{Fe}^{3+}$  of phosphorus – humus - iron complexes can obtain electronic from the dissolution of humus or other sources under UV light, resulting in the release of phosphorus. In fact, the dissolved Fe(III) is often present as  $\text{Fe}(\text{OH})^{2+}$  in aqueous solutions, which can absorb solar irradiation ( $\lambda > 290 \text{ nm}$ ) and yield  $\cdot\text{OH}$  and  $\text{Fe}^{2+}$  according to Eqs. (1) and (2) (Hammerschmidt and Fitzgerald, 2010; Calza et al., 2012).  $\cdot\text{OH}$  could initiate the oxidative degradation of organic phosphorus to release phosphorus as reported (Shah et al., 2015; Fisher et al., 2006). However, this possibility is unclear for the release and immobilization of phosphate generated from the photo-decomposition of organic phosphorus by  $\text{Fe}^{3+}$  under

light irradiation.



In this work, the role of  $\text{Fe}^{3+}$  as a natural photosensitizer toward the decomposition of organic phosphorus to release phosphate was examined in deionized and natural waters under UV and sunlight irradiation. Glyphosate, an organophosphate herbicide that is widely used around the world (Munira et al., 2016; Mamy et al., 2016), was employed as a model for organic phosphorus due to its wide distribution and stable chemical property, and a series of experiments were carried out to address the influence of the environmental parameters of water on the release of phosphorus from the decomposition of phosphonates by  $\text{Fe}^{3+}$ . This work is useful to understand the phosphorus cycle for eutrophication in water.

## 2. Materials and methods

### 2.1. Chemicals

The following reagents were used: glyphosate, coumarin and 7-hydroxycoumarin were purchased from Sigma-Aldrich (U.S.). NaOH, HCl and  $\text{FeCl}_3$  were supplied from Guoyao Chemical Co. (Shanghai, China). Humic acid (HA) was purchased from IHSS (International Humic Substances Society). All of the reagents were used as received. The solutions in the experiments were prepared with deionized water from a Millipore device (Milli-Q) or natural water. Natural water was sampled in April 2016 from Nanhu Lake, Wuhan, China. The experiments reported in Section 3.4 were performed just after the sampling.

### 2.2. Experimental setup and procedure

The irradiation experiments were carried out in a rotating photoreactor, which has been widely used for photochemical experiments (Xie et al., 2014). Water samples were placed in the sample quartz tubes and a 500 W xenon lamp was put in a quartz condenser, which was used to provide the sunlight source. The distance from the sample to the lamp was approximately 7.5 cm. 5 mL samples were collected at schedule time. The experiments were carried out by changing the following parameters: (i) initial  $\text{Fe}^{3+}$  concentrations, (ii) initial substrate concentration, (iii) initial pH, and (iv) initial HA concentrations. Most of the experiments were performed at an initial concentration of 5 mg P/L of glyphosate.

### 2.3. Analysis determinations

The concentrations of glyphosate was determined by high-performance liquid chromatography (HPLC, Agilent 1100) with a C18 column (4.6 mm  $\times$  250 mm, 5  $\mu\text{m}$ ). The mobile phase was constituted by a mixture of 10% acetonitrile and 90% water +0.1% TEA. The injection volume was 20  $\mu\text{L}$  and flow rate was at 1 mL  $\text{min}^{-1}$ . The temperature of the column was at 30  $^\circ\text{C}$ . Total

organic carbon (TOC) was determined by Shimadzu TOC-5000A. Orthophosphate ( $\text{PO}_4^{3-}$ ) was measured according to the molybdenum-blue method (Manassero et al., 2010), the limit of detection is  $0.01 \text{ mg L}^{-1}$ . The steady-state concentration of hydroxyl radicals ( $\cdot\text{OH}$ ) in the  $\text{Fe}^{3+}/\text{UV}$  and  $\text{Fe}^{3+}/\text{sunlight}$  systems was measured by employing coumarin as a selective trap. 7-hydroxycoumarin (7-HOC) was generated by the reaction between coumarin and  $\cdot\text{OH}$ , whose concentration is directly correlated with the steady-state concentration of  $\cdot\text{OH}$ . The concentration of 7-HOC was determined basing on a calibration curve by Shimadzu RF-5301 PC spectrometer due to its highly fluorescent. The experiments were carried out under the same conditions with glyphosate degradation as follows:  $[\text{Fe}^{3+}] = 3 \text{ mg L}^{-1}$  and  $[\text{coumarin}] = 0.1 \text{ mM}$ .

### 3. Results and discussion

#### 3.1. Photo-decomposition of glyphosate by $\text{Fe}^{3+}$ in deionized water

To examine the effect of the photochemical activity of  $\text{Fe}^{3+}$  on the behavior of organic phosphorus in the environment, experiments for the decomposition of glyphosate by  $\text{Fe}^{3+}$  were performed. Fig. 1a shows that glyphosate was degraded under UV light irradiation and the degradation rate reached 20%, which was similar to a previous report (Guo et al., 2011). However, the UV/ $\text{Fe}^{3+}$  system resulted in a reduction in the concentration of glyphosate of ~95% after 60 min under UV irradiation. To reveal the transformation of organic phosphorus compounds under a natural aquatic environment, transformation of glyphosate by  $\text{Fe}^{3+}$  was also performed under sunlight irradiation. For the sunlight control system, no obvious degradation of glyphosate was found under sunlight irradiation in deionized water, which indicated that glyphosate was stable under sunlight irradiation (Fig. 1b). When

$\text{Fe}^{3+}$  appeared in the system, the degradation rate of glyphosate by  $\text{Fe}^{3+}$  reached ~50% after 360 min under sunlight irradiation. Because  $\text{Fe}^{3+}$  light absorption occurs at wavelengths  $>200 \text{ nm}$ , the simulated sunlight conditions caused the absorption of photons at  $300 \text{ nm}$ , which produced active species (Chen et al., 2007, 2011). Reactions between glyphosate and the active species can occur and promote the transformation form.

The study of total organic carbon (TOC) is useful to understand the mass concentrations of organic matter in water bodies, which could provide the degree of glyphosate mineralization. Fig. 1c shows the results of TOC for glyphosate photo-decomposition in the  $\text{Fe}^{3+}/\text{UV}$  and  $\text{Fe}^{3+}/\text{sunlight}$  processes. The TOC decreased by 53% and 40% after UV irradiation for 60 min and sunlight irradiation for 360 min, respectively. These results indicate that the glyphosate could be decomposed by  $\text{Fe}^{3+}$  under UV and sunlight irradiation.

The objectives of this work were to reveal the photochemical activity of  $\text{Fe}^{3+}$  on the phosphate released from the decomposition of organic phosphorus and to understand the possible driving force for the nutrients released in the natural aquatic environment under sunlight irradiation. Hence, the phosphate that was released from the decomposition of glyphosate by  $\text{Fe}^{3+}$  under UV and sunlight irradiation was determined. The phosphate that was released during the decomposition of phosphonates by  $\text{Fe}^{3+}$  under UV and sunlight irradiation compared to the decomposition of glyphosate only is shown in Fig. 1d. The amount of phosphate that was released from the decomposition of phosphonates by  $\text{Fe}^{3+}$  under UV and sunlight irradiation was  $2.08 \text{ mg L}^{-1}$  and  $0.12 \text{ mg L}^{-1}$ , respectively. In comparison, trace amounts of phosphate were released under the control treatment. These results indicated that the photochemical activity of  $\text{Fe}^{3+}$  could affect the phosphate that was released from degrading organic phosphorus. Fig. 2 shows the release and immobilization of phosphate during the decomposition of glyphosate by  $\text{Fe}^{3+}$  under UV and dark conditions. The

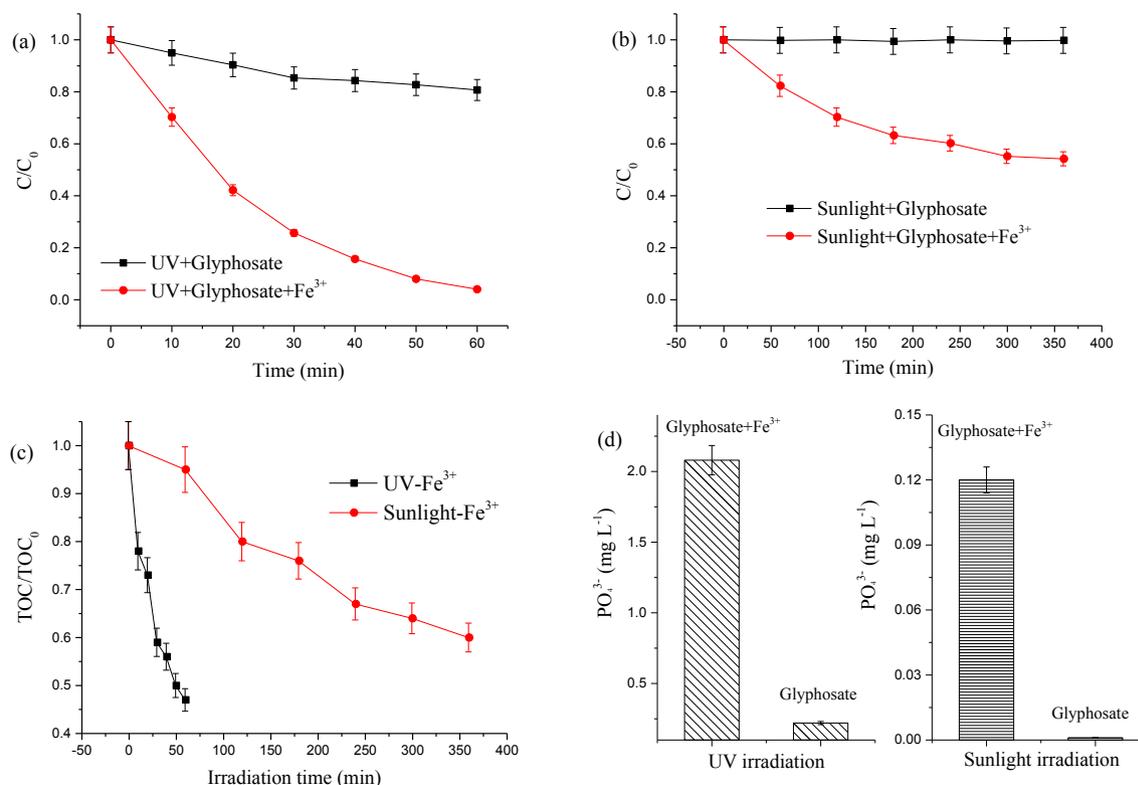
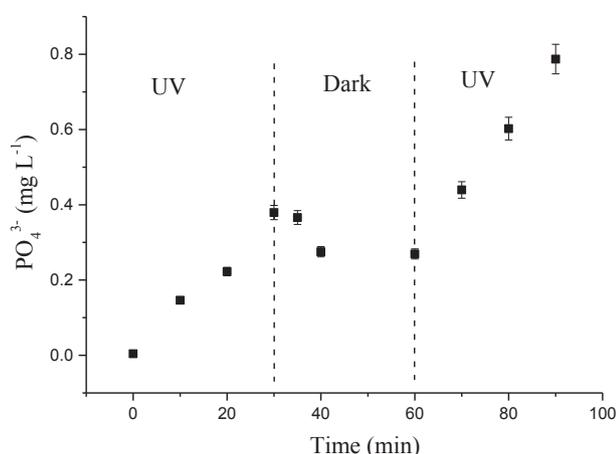


Fig. 1. The degradation of glyphosate by  $\text{Fe}^{3+}$  under UV (a) and sunlight (b) irradiation; (c) TOC concentration under UV and sunlight irradiation; (d) Phosphate released from glyphosate photo-decomposition by  $\text{Fe}^{3+}$  under UV and sunlight irradiation ( $[\text{Fe}^{3+}] = 3 \text{ mg/L}$ ,  $[\text{glyphosate}] = 5 \text{ mg P/L}$ ).



**Fig. 2.** The release and immobilization of phosphate during glyphosate decomposition by  $\text{Fe}^{3+}$  under UV and dark condition ( $[\text{Fe}^{3+}] = 3 \text{ mg/L}$ ,  $[\text{glyphosate}] = 5 \text{ mg P/L}$ ).

concentration of phosphate from the photo-decomposition of glyphosate by  $\text{Fe}^{3+}$  increased under UV irradiation for 30 min. However, when the xenon lamp was turned off, the concentration of phosphate was significantly reduced from  $0.38 \text{ mg L}^{-1}$  to  $0.28 \text{ mg L}^{-1}$  in 10 min. When the reactor was shifted to UV irradiation, the concentration of phosphate increased again. All of these results revealed that the phosphate could be fixed by  $\text{Fe}^{3+}$ , but could also be released from the photo-decomposition of organic phosphorus by  $\text{Fe}^{3+}$  under light irradiation.

### 3.2. The effects of the environmental parameters of water on phosphorus that is released from the decomposition of organic phosphorus by $\text{Fe}^{3+}$ in deionized water

The  $\text{Fe}^{3+}$  photochemical activity was clearly influenced by some of the environmental factors (Chen et al., 2007). Therefore, the initial concentrations of glyphosate,  $\text{Fe}^{3+}$ , and humic acid and the initial pH were chosen to determine the effects of the environmental parameters of the water on the phosphate release rate by  $\text{Fe}^{3+}$ . UV light covers 5% of the solar spectrum (Han et al., 2011) and the release amount of phosphate under UV irradiation was higher than that of sunlight. Therefore, we focused on the UV process to determine how the different environmental parameters of water affected phosphate that was released from the photo-decomposition of phosphonates by iron.

#### 3.2.1. Effect of glyphosate concentrations

The effect of the initial concentration of glyphosate on phosphate released was assessed based on its degradation by  $3 \text{ mg L}^{-1} \text{ Fe}^{3+}$  under UV light irradiation for 60 min, as shown in Fig. 3a. The amount of phosphate that was released from the decomposition of glyphosate by  $\text{Fe}^{3+}$  increased as the initial concentration of glyphosate increased from 1 to 10 mg P/L. Most likely, more glyphosate were exposed to radicals at a higher concentration, resulting in more phosphate being released. However, the increased initial concentration of glyphosate decreased the observed phosphate release rate constant. This observation was consistent with a previous study by Khan et al. (Khan et al., 2013), which should be attributed to the ratio of reactive radicals decreased to the target organic phosphorus. The high absorptivity for glyphosate at 254 nm with higher initial concentrations of glyphosate could affect its direct photolysis and the activation of  $\text{Fe}^{3+}$  for radical generation (Dutta et al., 2001). Moreover, the

competition for reactive radicals between glyphosate and its by-products became stronger when the initial concentrations of glyphosate increased, which inhibited the phosphate that was released from the decomposition of glyphosate by  $\text{Fe}^{3+}$  (Ghodbane and Hamdaoui, 2010). This result also indicated that low concentrations of organic phosphorus can quickly be photochemically transformed into phosphate by  $\text{Fe}^{3+}$  in the aquatic environment.

#### 3.2.2. Effect of $\text{Fe}^{3+}$ concentrations

The photoactivity of the  $\text{Fe}^{3+}$  under UV irradiation is influenced by chemical equilibrium. To reveal the effect of the  $\text{Fe}^{3+}$  concentrations on phosphate that was released from the decomposition of glyphosate, the phosphate release was carried out in the  $\text{Fe}^{3+}$ /UV system at different  $\text{Fe}^{3+}$  concentrations (Fig. 3b). The results showed that the phosphate release rate increased with increasing  $\text{Fe}^{3+}$  concentrations. The observed phosphate release was lowest in the absence of  $\text{Fe}^{3+}$ , and the phosphate release rate increased with increasing  $\text{Fe}^{3+}$  concentrations. These results are consistent with those of previous studies regarding the degradation of alkyl-phenol by the Fe-oxalated system. Higher  $\text{Fe}^{3+}$  concentrations could generate more reactive oxygen species (ROS) and lead to more phosphate being released. In addition, the pH in the reaction solution decreased with increasing  $\text{Fe}^{3+}$  ion concentration, which benefited the photochemical activity of  $\text{Fe}^{3+}$  (Hammerschmidt and Fitzgerald, 2010).

#### 3.2.3. Effect of humic acid

Humic acids (HA), one kinds of humic substances, was widely distributed in the aquatic environment formed from the transformations of plant and animal residual (Zeng et al., 2012). Humic acids are important natural photosensitizer because they contain many active functional groups, such as carboxyl groups, phenolic hydroxyl, and carbonyl-type chromophores. These active functional groups could absorb solar radiation between 300 and 500 nm to reach an excited state and generate free radicals (e.g., hydroxyl radicals, peroxy radicals and singlet oxygen), which result in the photooxidation degradation of organic contaminants (Kohn et al., 2007; Thirumavalavan et al., 2012). Iron ions have an important function in this photochemical process because HA is strong affinity with iron ions (Christoforidis et al., 2015; Martínez-Zapata et al., 2013). In our case, the disappearance rate of glyphosate was faster in the presence of  $\text{Fe}^{3+}$  alone than in the presence of both HA and  $\text{Fe}^{3+}$  ions (Fig. 3c). The phosphate release rate decreased with increasing HA concentrations. The inhibiting effect of humic acid on  $\text{Fe}^{3+}$  photolysis is due to a screen effect. The inhibition might have been partly due to the scavenging of hydroxyl radicals by HA (Christoforidis et al., 2015). In fact, the interactions between iron, phosphorus, light, and organic matter are very complex (Jones et al., 1998; De Haan et al., 1990). The glyphosate is one kind of stable organic phosphorus and the transformation of glyphosate to phosphate by  $\text{Fe}^{3+}$  was inhibited by HA. However, the photochemical activity of HA on the some labile organic phosphorus was unclear.

#### 3.2.4. Effect of pH

The solution pH can influence the photochemical activity of iron by changing the light adsorption properties of the Fe complex. In this study, the effect of pH on the phosphate that was released from the photo-decomposition of glyphosate was evaluated. The experiments were performed at pH values ranging from 4.0 to 10.0 and the glyphosate initial concentration of 5 mg P/L. The pH was adjusted by adding amount of 1 N NaOH. The results showed that the best condition for phosphate being released from the decomposition of glyphosate by  $\text{Fe}^{3+}$  took place under acidic conditions and the release rate decreased as the pH increased. However, the

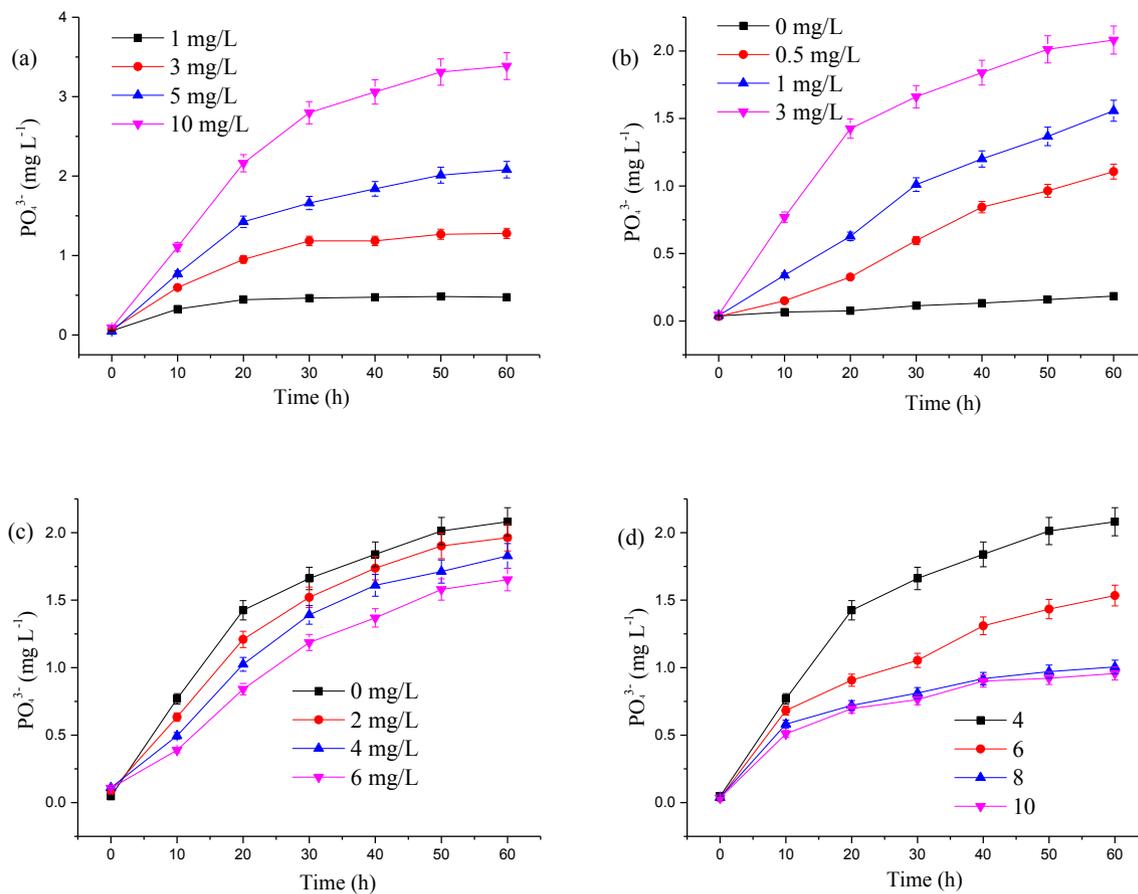


Fig. 3. The effect of initial concentration of glyphosate (a),  $\text{Fe}^{3+}$  (b), HA (c) and pH (d) on phosphate released by  $\text{Fe}^{3+}$  under UV irradiation.

photolysis degradation of glyphosate were more quickly under alkaline condition as previous reports (Manassero et al., 2010). When  $\text{Fe}^{3+}$  was added to the reaction system, the indirect photolysis was dominant reaction in the process of phosphate released from glyphosate degradation. There were no significant differences between pH values of 8 and 10 (Fig. 3d). This result could be attributed to the decreased photochemical activity of  $\text{FeOOH}$  when  $\text{Fe}^{3+}$  exists in the alkaline condition, resulting in fewer  $\cdot\text{OH}$  being produced by  $\text{FeOOH}$  (Garrido-Ramírez et al., 2010).

### 3.3. The steady-state concentration of $\cdot\text{OH}$ in $\text{Fe}^{3+}/\text{UV}$ and $\text{Fe}^{3+}/\text{sunlight}$ system

The steady-state concentration of  $\cdot\text{OH}$  is directly correlated to the phosphate released from glyphosate photo-decomposition by  $\text{Fe}^{3+}$  under UV and sunlight irradiation. To determine the steady-state concentration of  $\cdot\text{OH}$  in the photo-degradation of glyphosate in  $\text{UV}/\text{Fe}^{3+}$  and  $\text{sunlight}/\text{Fe}^{3+}$  systems, the coumarin was chose as a  $\cdot\text{OH}$  trap. Due to the direct correlation between  $\cdot\text{OH}$  and 7-HOC, monitoring the fluorescence of 7-HOC demonstrated the production of  $\cdot\text{OH}$  in the  $\text{Fe}^{3+}/\text{UV}$  and  $\text{Fe}^{3+}/\text{sunlight}$  systems.

The formation of 7-HOC in the  $\text{Fe}^{3+}/\text{UV}$ ,  $\text{Fe}^{3+}/\text{sunlight}$  systems and control without  $\text{Fe}^{3+}$  treatment as a function of irradiation time was shown in Fig. 4. The steady-state concentration of  $\cdot\text{OH}$  could be calculated by the concentration of 7-HOC as Zhao's report (Zhao et al., 2014). As shown in Fig. 4, the concentration of 7-HOC in the  $\text{Fe}^{3+}/\text{UV}$  and  $\text{Fe}^{3+}/\text{sunlight}$  systems is higher than that of control treatment, which means that more  $\cdot\text{OH}$  generated with

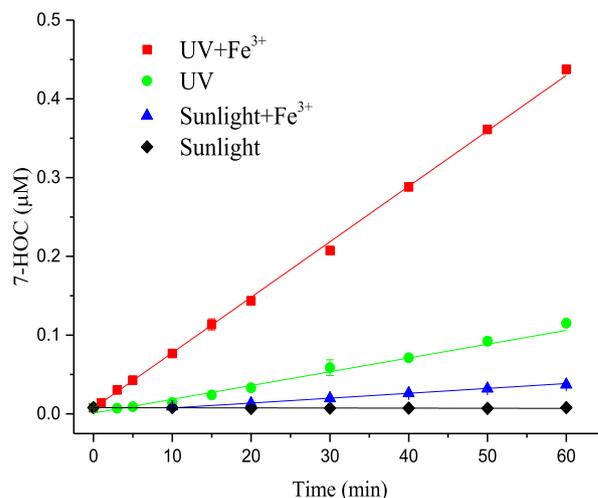


Fig. 4. The formation of 7-HOC in  $\text{Fe}^{3+}/\text{UV}$  (a) and  $\text{Fe}^{3+}/\text{sunlight}$  (b) system ( $[\text{Fe}^{3+}] = 3 \text{ mg L}^{-1}$ ,  $[\text{coumarin}] = 0.1 \text{ mM}$ ).

$\text{Fe}^{3+}$ . The steady-state concentration of  $\cdot\text{OH}$  was  $10.88 \pm 1.13 \times 10^{-14} \text{ M}$  and  $2.73 \pm 0.12 \times 10^{-14} \text{ M}$  with  $\text{Fe}^{3+}$  added under UV and sunlight irradiation, respectively. The production of  $\cdot\text{OH}$  is approximately ten times higher under UV irradiation compared to sunlight irradiation, which is the reason for the more phosphate generated in the  $\text{Fe}^{3+}/\text{UV}$  system than that of  $\text{Fe}^{3+}/\text{sunlight}$  system.

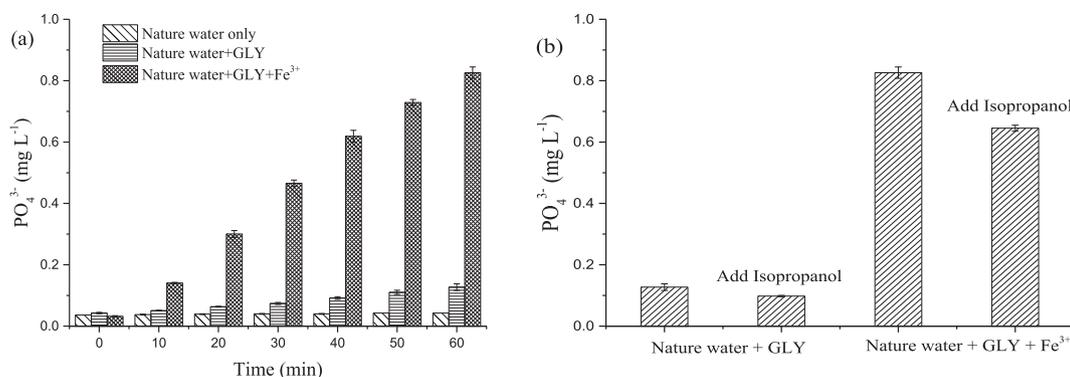


Fig. 5. The effect of  $\text{Fe}^{3+}$  (a) and isopropanol (b) on the phosphate released from glyphosate photo-decomposition in natural water ( $[\text{Fe}^{3+}] = 3 \text{ mg L}^{-1}$ , [glyphosate] = 5 mg P/L).

### 3.4. Phosphate photo-released in natural water with added glyphosate and $\text{Fe}^{3+}$

Natural water was spiked with glyphosate and  $\text{Fe}^{3+}$  and irradiated as described above. Fig. 5a shows the release of phosphate after exposure to light. It was found that the concentration of phosphate increased in natural water treated with UV light irradiation, which should be attributed to the direct photolysis or indirect photolysis of organic phosphorus by natural photosensitizers. With the glyphosate added to natural water, more phosphate was generated from light irradiation, which revealed that more phosphate will be photo-released when organic phosphorus was injected into the overlying water by resuspended sediment. When  $\text{Fe}^{3+}$  was added, the concentration of phosphate that was generated was higher than that of the control treatment. It should be noted that the concentration of phosphate in the natural water/glyphosate/ $\text{Fe}^{3+}$  system was  $1.77 \text{ mg L}^{-1}$ , which was lower than that in deionized water ( $2.08 \text{ mg L}^{-1}$ ). This could be due to the presence of scavengers, such as  $\text{HCO}_3^-$  and humic acids, as already described (Passananti et al., 2013).

To determine the role of  $\text{Fe}^{3+}$  as a natural photosensitizer toward the decomposition of organic phosphorus to release phosphate, the known  $\cdot\text{OH}$  scavenger isopropanol was added to the photolysis experiments (Jacobs et al., 2011). While isopropanol is not the ideal  $\cdot\text{OH}$  scavenger (due to its ability to react with other ROS), these data provide us with a rough estimate of the role of  $\text{Fe}^{3+}$  in phosphate released from the photo-decomposition of organic phosphorus in natural water. Fig. 5b shows the effect of isopropanol on the phosphate released from the photo-decomposition of glyphosate by  $\text{Fe}^{3+}$  in natural water with the concentration of isopropanol 0.05 M. It was observed that the concentration of phosphate in the natural water/glyphosate system with isopropanol added, inhibited the indirect photolysis of organic phosphorus which should be attributed to the fact that the ROS generated by the natural photosensitizer were scavenged by isopropanol. For the natural water/glyphosate/ $\text{Fe}^{3+}$  system, the concentration of phosphate decreased from 0.83 to  $0.65 \text{ mg L}^{-1}$ . All of these results revealed that  $\text{Fe}^{3+}$  has significant impact in phosphate released from organic phosphorus decomposition.

## 4. Conclusions

Determining the role of the  $\text{Fe}^{3+}$  photochemical activity on phosphorus that was released from the decomposition of glyphosate under UV and sunlight irradiation in deionized and natural water was carried out in this work. The glyphosate was degraded by  $\text{Fe}^{3+}$  under UV and sunlight irradiation, and the TOC results demonstrated that glyphosate in sunlight and  $\text{Fe}^{3+}$ /UV and

$\text{Fe}^{3+}$ /sunlight systems occur during oxidative degradation. Meanwhile, the results confirmed that the  $\text{Fe}^{3+}$  photochemical activity can lead to dissolved phosphate that was released from the organic phosphorus under light irradiation. The environmental factors of the water influenced phosphorus that was released from the decomposition of glyphosate in the  $\text{Fe}^{3+}$ /UV system. Low concentrations of glyphosate were easier to transform from organic phosphorus into inorganic phosphorus. Improving the system for the content of  $\text{Fe}^{3+}$  can significantly improve the efficiency of the release of phosphorus. Increasing the pH of the system and the concentration of humic acid inhibited phosphorus released from the decomposition of glyphosate. The formation and steady-state concentrations of  $\cdot\text{OH}$  in the  $\text{Fe}^{3+}$ /UV and  $\text{Fe}^{3+}$ /sunlight systems were determined. In natural water, the concentration of phosphate generated in the  $\text{Fe}^{3+}$  added treatment was higher than that of the control treatment. All of these results demonstrated that the  $\text{Fe}^{3+}$  photochemical system had promising effects on the release and fixation of phosphorus under light irradiation, which is useful to understand the phosphorus cycle in the natural aquatic environment.

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