



Aquatic photooxidation of phosphite in the presence of ferric and oxalate ions



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HIGHLIGHTS

- The indirect photooxidation of phosphite follows pseudo-first-order kinetics.
- Ferric/oxalate concentration, pH and light intensity affect the photooxidation.
- The decrease of phosphite coincides with the increase of phosphate.

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ABSTRACT

Phosphite is an important intermediate of the phosphorus cycle. Its life in environment is related to its oxidation rate. This paper investigated the photooxidation of phosphite in aqueous solution in the presence of ferric and oxalate ions under a Xe lamp. The photooxidation of phosphite followed pseudo-first-order reaction kinetics. The kinetics constant of $100 \mu\text{mol L}^{-1}$ phosphite was 0.0039 min^{-1} at pH 3 and Fe(III)/Ox $10.0/100.0 \mu\text{mol L}^{-1}$. The photooxidation was dependent upon the pH value, phosphite/ferric/oxalate concentration, and light intensity. The decrease of phosphite coincided with the increase of phosphate. The addition of 2-propanol, NaN_3 or furfuryl alcohol inhibited the photooxidation of phosphite, which indicated that the yielded reactive oxygen species played an important role in the oxidation of phosphite. The results contribute not only to predict the longevity of phosphite in the aqueous solutions, but also to understand the transfer of phosphite in P cycle.

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1. Introduction

Phosphite (HPO_3^{2-} , H_2PO_3^- , +3 valence), a reduced form of phosphorus (P), is widely used as fungicide or fertilizer in agriculture and intermediate in industry [1]. Limited to its determination and the traditional thoughts that only phosphate (HPO_4^{2-} , H_2PO_4^- , +5 valence) is involved in the biological P cycle, phosphite is usually excluded out of the hotspot in the P cycle study [2,3]. In recent years, phosphite has been widely determined in aquatic environments. Pech et al. [4] detected $0.06 \pm 0.02 \mu\text{M}$ of phosphite in a geothermal pool. Han et al. [5] determined 0.01 ± 0.01 to $0.17 \pm 0.01 \mu\text{M}$ of phosphite in Lake Taihu, accounting for 1–10% of the phosphate therein. The wastewater of metal plating also contains high concentration of phosphite [6]. Morton et al. detected high concentration (g L^{-1} level) of phosphite in process water samples from the thermal P plant [7].

Phosphite in environments may have dual effects as a P source or pesticide. In agriculture, phosphite is widely marked as a fungicide [2,8,9], and it also decreases the phosphate absorption of the intact komatsuna plants [10]. While some researchers believe that phosphite could also be used as a fertilizer [2]. 10–67% bacteria in natural aquatic and terrestrial environments can oxidize phosphite and used it as a sole P source [11]. Zhang et al. found that even though phosphite could not be utilized by *Microcystis aeruginosa* (one of the predominant species involved in algal blooms) as a sole P source, it could boost cell numbers and chlorophyll *a* content as long as phosphate was provided simultaneously in freshwater lake [12]. That means phosphite has a potential contribution to eutrophication.

P is the limiting nutrient in many ecosystems, for most phosphate minerals are poorly soluble and slow to dissolve at neutral pH and at room temperature [13]. Phosphite is more soluble than phosphate, which gives it greater mobility in aquatic environments [14]. Moreover, as a reduced form with relative thermodynamic instability [14], phosphite can be oxidized to phosphate or reduced to gaseous phosphine (PH_3 , -3) [8,13,15,16]. As reduction from phosphate is energetically unfeasible, unless phosphite or

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hypophosphite is present in the environment, other common reducing agent cannot produce phosphine at the concentration observed in nature [13]. As a result, the transformation of phosphite can be an important replenishment of PH_3 or phosphate, and the latter is considered with more bioactivity. The migration and transformation of phosphite should be an important part of the P biogeochemical circle in aquatic environments.

Although the oxidation of phosphite is very slow in practice, catalysis or strong oxidizing agents such as active radicals can accelerate its oxidation [1,2,14]. As Fenton oxidation mechanism implicates $\cdot\text{OH}$ radicals, some researcher have explored the oxidation of phosphite through a Fenton reactor and determined the yield of phosphate and condensed phosphates [17]. Phosphite could be oxidized through a radical exchange reaction such as the reaction of phosphite with an $\cdot\text{OH}$ radical to form H_2O and $\cdot\text{PO}_3^{2-}$. The longevity of phosphite in solution is directly proportional to the amount of oxidizing radicals in that solution [14,17]. Ferric ions and dissolved organic compounds are the extensive existence kinds of ions in natural water and their photolysis was a major pathway for the formation of hydrogen peroxide (H_2O_2) in atmospheric waters [18,19]. Oxalate is one of the ubiquitous organic ions which have been proved to contribute to the photochemical activity. In sunlit surface waters, photochemical reactions of oxalate complexes with Fe(III) were potentially important sources of Fe(II), H_2O_2 , $\cdot\text{OH}$ and other radicals [18,20]. The resulting production of $\cdot\text{OH}$ radicals are very significant as they can oxidize a wide variety of natural and anthropogenic organic and inorganic substances [20,21]. According to our knowledge, few studies have focused on the photooxidation of phosphite and the possible orthophosphate release to natural environment is ignored.

This study investigated aquatic photooxidation of phosphite in the presence of ferric and oxalate ions. The results allowed the development of a reference for predicting the longevity of phosphite in aqueous solutions and understanding the transfer of phosphite in the P cycle.

2. Materials and methods

2.1. Chemicals and materials

Phosphite ($\text{Na}_2(\text{HPO}_3) \cdot 5\text{H}_2\text{O}$) was purchased from the Sigma Aldrich Company (America). Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), potassium sodium tartrate ($\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$), and sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), analytical reagents, were purchased from Nanjing Chemical Reagent Co., Ltd, China. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2-propanol and NaN_3 , analytical reagents, were obtained from Xilong Chemical Co., Ltd, China. Furfuryl alcohol (FFA) was obtained from Shanghai Lingfeng Chemical Co., Ltd, China. Nanopure water (18.2 $\text{M}\Omega$ cm) was produced by a Milli-Q Plus system (Millipore, Bedford, MA, USA). All the stock solutions were prepared by dissolving the reagents directly in the water without further purification, stored at 4 °C in the dark and used within one month. Solutions for the photooxidation experiments were prepared immediately prior to irradiation. 1 mol L^{-1} HCl or NaOH solution was used to adjust the pH values of the solutions.

2.2. Photochemical experiments

Steady-irradiation experiments were performed in the XPA-7 photochemical reactor (Nanjing Xujiang Motor Factory, China) (Fig. 1). A 250/500 W xenon arc lamp used as the simulated sunlight source was placed inside a quartz cooling well. 290 nm cut-off glass filters were employed around the lamp. The average irradiation intensity were 43 $\mu\text{W cm}^{-2}$ (500 W) and 3.5 $\mu\text{W cm}^{-2}$ (250 W), respectively. The light intensity was measured by a

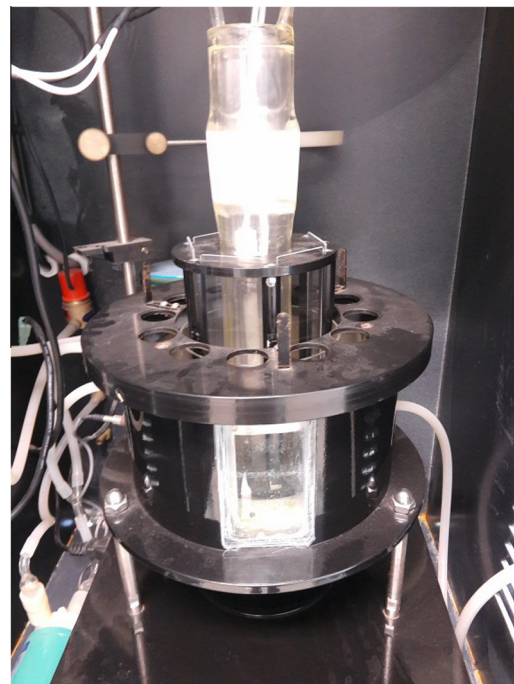


Fig. 1. XPA-7 photochemical reactor employed in the experiment.

radiometer (Model FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China). Capped quartz tubes containing 50 mL of reaction solution were placed in a rotating unit at a fixed distance. During the photoreaction, a steady flow of cooling water was used to maintain a constant temperature of about 25 °C. Before the experiment, the lamp was switched on 20 min early to guarantee that the irradiating intensity was stable during the experiment period. Unless otherwise stated, the typical composition inside each test tube was $C_0 = [\text{phosphite}]_0 = 100.0 \mu\text{mol L}^{-1}$, $[\text{Fe}^{3+}]_0 = 10.0 \mu\text{mol L}^{-1}$, $[\text{oxalate}]_0 = 100.0 \mu\text{mol L}^{-1}$ at pH 3.0, and the Xe lamp was 500 W.

2.3. Analyses

During the photolysis reaction, samples were collected at selected time intervals. After pretreatment by passing through a 0.22 μm filter membrane and OnGuard II H Cartridges (1 cc, Dionex), samples were analyzed by ICS 5000 ion chromatography (Thermo Fisher, America) equipped with an IonPac AS11-HC column (250 mm \times 2 mm) and a suppressed conductivity detector, to determine the concentrations of phosphite, phosphate and carboxylic acid. The configuration of the IC 5000 system can be seen in our earlier study [22]. In this study, only the analytical system (Dimension 1) of the IC 5000 was used. The injection volume was 25 μL by an AS-AP autosampler, and the detector cell temperature was held at 30 °C. The effluent flow rate was 0.38 mL min^{-1} with KOH gradient elution. The gradient program for separating and determined phosphite, phosphate and carboxylic ions is given in Table 1. The speciation in this study was performed with MEDUSA, a chemical equilibrium calculation program developed by Royal Institute of Technology (Sweden).

The photooxidation efficiency (%) is calculated as $(C_0 - C)/C_0 \times 100\%$ and the apparent first-order kinetics constant (k) is evaluated according to $\ln(C_0/C) = k \times t$, where C ($\mu\text{mol L}^{-1}$) represents the phosphite concentration at time t (min) and C_0 ($\mu\text{mol L}^{-1}$) is the initial concentration.

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