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► **To cite this version:**

Yinghao Wen, Eric Lichtfouse, Virender K Sharma, Xingmao Ma. Overlooked involvement of phosphate radicals in the degradation of the atrazine herbicide by sulfate radical-based advanced oxidation. *Environmental Chemistry Letters*, 2023, 21, pp.15-20. 10.1007/s10311-022-01523-9 . hal-03807028

**HAL Id: hal-03807028**

**<https://hal.science/hal-03807028>**

Submitted on 8 Oct 2022

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# Overlooked involvement of phosphate radicals in the degradation of the atrazine herbicide by sulfate radical-based advanced oxidation

Yinghao Wen<sup>1</sup> · Eric Lichtfouse<sup>2,3</sup>  · Virender K. Sharma<sup>3</sup>  · Xingmao Ma<sup>1</sup>

## Abstract

The persistence of recalcitrant pollutants in water is a major health issue calling for advanced and green techniques to clean polluted waters. For instance, direct activation of peroxydisulfate by visible light without any catalyst displays a remarkable potential to degrade recalcitrant pollutants in water, and the involved reactive species in pure conditions with deionized water have been elucidated recently. However, the impact of phosphates, which are commonly abundant in real waters, on the performance of this reaction is still unclear, and possible formation of secondary phosphate radicals has yet to be clarified. Here we studied the effect of phosphate on the degradation of atrazine by peroxydisulfate under visible light. Radicals were studied by electron paramagnetic resonance. Results show that 10 mM of phosphate as  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  decreased the pseudo-first-order rate constant of atrazine degradation by 47.6% in the peroxydisulfate/visible light system at pH 7.0. The degradation kinetics of atrazine correlated linearly with the concentration of phosphate and was pH dependent. Optimal degradation efficiency was achieved at pH 7.0, while higher pH significantly impeded atrazine degradation. These results suggest that the inhibitory effect of phosphate is due to the formation of less reactive phosphate radicals. This hypothesis is supported by the effect of pH on atrazine degradation and the reduced peak intensities of reactive species in electron paramagnetic resonance. Our findings imply that the presence of phosphates could highly decrease the efficiency of pollutant removal in real situations.

**Keywords** Sulfate radical · Peroxydisulfate · Phosphate · Secondary radicals · Micropollutants

## Introduction

In situ chemical oxidation that involves hydrogen peroxide is commonly used for soil and groundwater remediation; however, the applicability of this reaction is restricted by the poor yield of the hydroxyl radical,  $\text{OH}^\cdot$  (Liu et al. 2014;

Morin-Crini et al. 2022). To overcome these limitations, sulfate radical  $\text{SO}_4^{\cdot-}$ -based advanced oxidation was introduced as a promising alternative (Liu et al. 2014; Ji et al. 2019; Lee et al. 2020).  $\text{SO}_4^{\cdot-}$  has a higher redox potential, of +2.5–3.1  $V_{\text{NHE}}$ , than  $\text{OH}^\cdot$ , of +1.8–2.7  $V_{\text{NHE}}$ , and could oxidize a variety of organic pollutants with diffusion-limited kinetics (Neta et al. 1988; Armstrong et al. 2015; Chen et al. 2018; Zhou et al. 2019). An important advantage of  $\text{SO}_4^{\cdot-}$  over  $\text{OH}^\cdot$  is the easy generation of  $\text{SO}_4^{\cdot-}$  from diverse activation methods of persulfates (Luo et al. 2015; Ahn et al. 2016; Che et al. 2021). For example, we found that peroxydisulfate can be directly activated by visible light without any catalysts to produce  $\text{SO}_4^{\cdot-}$  and  $^1\text{O}_2$ , both of which contributed to the degradation of atrazine (Wen et al. 2022a). The production of  $^1\text{O}_2$  relies on the formation of an atrazine peroxy adduct, release of superoxide radical,  $\text{O}_2^{\cdot-}$ , and then oxidation of  $\text{O}_2^{\cdot-}$  by  $\text{SO}_4^{\cdot-}$ . To evaluate the applicability of this system in real applications, it is critical to elucidate the impact of common inorganic oxyanions in water and their interactions

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with  $\text{SO}_4^{\cdot-}$ -based advanced oxidation processes, especially phosphate,  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ , which has rarely been studied.

Phosphate is commonly present in surface waters in the range of 0.1–4.5  $\mu\text{M}$  and has been widely used as a buffer in many persulfate-based studies (Prashantha Kumar et al. 2018; Yang et al. 2018; Velusamy et al. 2021). However, the possible impact of phosphate on  $\text{SO}_4^{\cdot-}$ -based advanced oxidation processes has been largely ignored. Over four decades ago, Maruthamuthu and Neta reported that phosphate can be oxidized by  $\text{SO}_4^{\cdot-}$  to produce the phosphate radicals  $\text{H}_2\text{PO}_4^{\cdot-}/\text{HPO}_4^{\cdot-}$  (Maruthamuthu and Neta 1978). Nonetheless, the chemistry of these radicals and associated implications in water treatment remain unclear to date, which can be attributed to the difficulty in directly probing of these radicals and lack of research attention. With the recent elucidation of the direct interaction between phosphate and persulfates (Wen et al. 2022b), the possible role of phosphate in  $\text{SO}_4^{\cdot-}$ -based advanced oxidation processes should not be further ignored. Noteworthy, since the reactivities of phosphate radicals often depend on pH, determining the effect of pH in phosphate-present  $\text{SO}_4^{\cdot-}$ -based advanced oxidation processes can shed significant light on the possible involvement of these radicals.

Here we studied the effect of phosphate on the  $\text{SO}_4^{\cdot-}$ -based advanced oxidation by peroxydisulfate under visible light. We aimed to determine the impact of phosphate on the degradation efficiency of atrazine by the peroxydisulfate/vis system at different pH and to confirm the possible formation of phosphate radicals using electron paramagnetic resonance.

## Materials and methods

### Chemicals and materials

Potassium peroxydisulfate,  $\geq 99.0\%$  (purity), was purchased from Sigma-Aldrich, St. Louis, USA. Atrazine,  $\geq 97.0\%$ , was acquired from TCI America, Portland, USA. Sodium phosphate dibasic anhydrous,  $\geq 98.0\%$ , sodium thiosulfate, sulfuric acid, 98.0%, and 5,5-dimethyl-1-pyrroline N-oxide,  $\geq 98.0\%$ , were obtained from Fisher Scientific, Waltham, USA. 2,2,6,6-tetramethyl-4-piperidine, 99%, was purchased from ACROS Organics, Waltham, USA. All chemicals were used as received. Thin wall quartz sample tubes, of 4 and 2 mm, were purchased from Wilmad Labglass, Vineland, USA. A simulated sunlight lamp, with GLBULBM1000 metal halide bulb, 1000 W, 92,000 lm, was purchased from iPower and used as the light source. Ultrapure deionized water ( $> 18.2 \text{ M}\Omega\text{-cm}$ ) produced by a Millipore Milli-Q Direct 8 system was used for the preparation of all solutions.

### Effect of phosphate on the degradation of atrazine by peroxydisulfate/visible

The reactions were carried out in 40-mL glass tubes with constant stirring at 300 rpm at  $25.0 \pm 0.5$  °C. The solution in each tube contained 10.0  $\mu\text{M}$  of atrazine and 5.0 mM of peroxydisulfate. The effect of phosphate on the degradation of atrazine by peroxydisulfate in dark and under light was evaluated by varying its concentration at 0, 1.0, 5.0, and 10.0 mM. The selected phosphate concentrations were higher than its typical range found in natural water for better experimental observation. The initial pH of the reaction solutions was controlled at 7.0 using 0.1 M NaOH and 0.1 M  $\text{H}_2\text{SO}_4$ . The initial pH of each reaction solution was measured using an Accumet AE150 pH meter, Westford, USA. A GLBULBM1000 simulated sunlight lamp (1000 W, 92,000 lm) was used as the light source (iPower), and a UV filter film was used to block the UV irradiation. The irradiation fluxes received by the reaction solutions contain predominantly visible light, as were specified previously (Wen et al. 2022a). Treatment without irradiation, named peroxydisulfate/dark, was performed in dark by covering the tubes with aluminum foil. 1.0 mL of sample was withdrawn from each tube at different time intervals of 1.0, 2.0, 3.0, 4.0, 5.0, 10, 20, 30, 60, 90, 120, 240 min, and the reaction was immediately quenched by 20.0  $\mu\text{L}$  of 5.0 M sodium thiosulfate. The concentrations of atrazine in collected samples were measured with a Dionex UltiMate 3000 high-performance liquid chromatograph (HPLC, Sunnyvale, USA). A Restek 4.6  $\times$  250 mm, 5  $\mu\text{m}$  C18 column was used as the stationary phase, and the column temperature was set at 30 °C. The mobile phase consists of 60/40 v/v methanol and water at a flow rate of 1.0 mL/min.

### Effect of pH on the degradation of atrazine by peroxydisulfate/vis

The effect of pH on the degradation efficiency of atrazine by peroxydisulfate/vis was studied in the presence of 10.0 mM of phosphate. The initial solution pH was controlled at 5.0, 6.0, 7.0, 8.0, and 9.0 using 0.1 M NaOH or 0.1 M  $\text{H}_2\text{SO}_4$ . The concentration of atrazine in each sample (time = 0, 5, 10, 20, 30, 60, 90, 120, and 240 min) was measured by HPLC.

### Electron paramagnetic resonance

*Electron paramagnetic resonance* (EPR) was employed to detect the signals of reactive species produced in the PDS light system in the presence of phosphate. 5,5-Dimethyl-1-pyrroline N-oxide and 2,2,6,6-tetramethyl-4-piperidine were used as the spin trapping agents for  $\text{SO}_4^{\cdot-}$  and  $^1\text{O}_2$ ,

respectively. EPR measurements were performed using a Bruker Elexsys E500 EPR instrument with a standard resonator and CoolEdge cryo system, Billerica, USA. The instrument settings were: 20.0 mW microwave power, 9.8 GHz microwave frequency, 100 kHz modulation frequency, 1.00 G modulation amplitude, 3515 G center field, 150 G sweep width, and 40.0 s sweep time.

## Data analysis

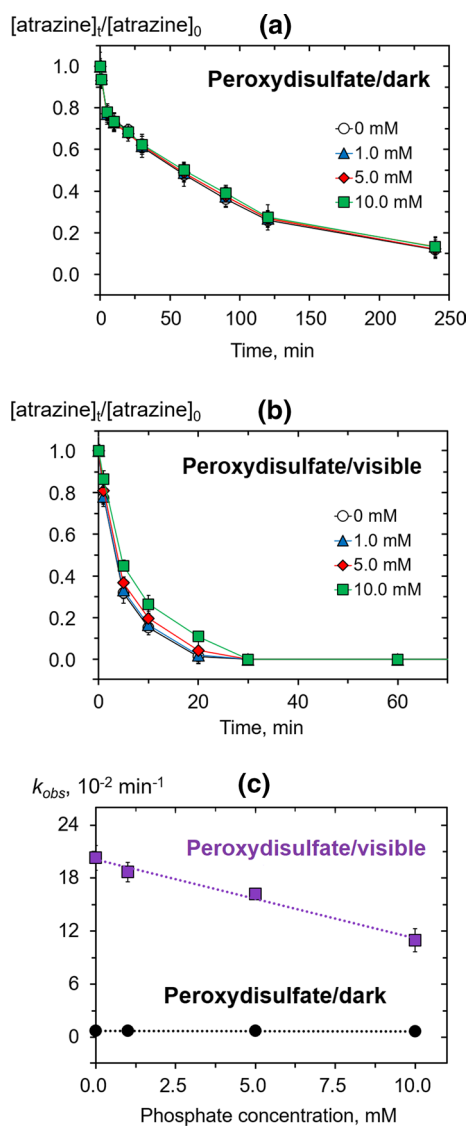
In order to determine the data variability, all experiments were performed in triplicate. One-way analysis of variance (ANOVA) followed by Tukey's test was used to determine the statistical differences among the pseudo-first-order rate constants of atrazine degradation by peroxydisulfate/dark with varying phosphate concentrations and peroxydisulfate/vis at different pH.

## Results and discussion

### Effect of phosphate on the degradation of atrazine by peroxydisulfate under visible light

Overall, phosphate displayed little effect on the degradation of atrazine by peroxydisulfate/dark at pH 7.0 (Fig. 1a), as indicated by one-way ANOVA (Fig. S1). This is possibly due to the absence of reactive radical species, e.g.,  $\text{SO}_4^{\cdot-}$ , in the dark and the lack of direct interaction between peroxydisulfate and phosphate (Wen et al. 2022a). In the case of peroxydisulfate under visible light, however, the presence of phosphate hindered the degradation efficiency of atrazine remarkably (Fig. 1b). The observed rate constants of atrazine degradation ( $k_{\text{obs}}$ ,  $\text{min}^{-1}$ ) fit well with pseudo-first-order kinetics and are presented in Table S1.

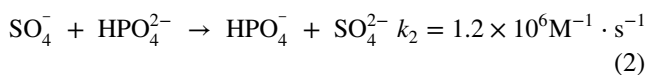
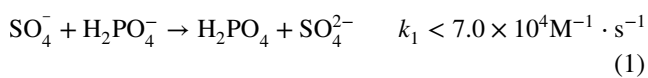
Phosphate ions mainly exist as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  at pH 7.0 ( $pK_{a2}=7.2$ ) and could react with  $\text{SO}_4^{\cdot-}$  to form phosphate radicals (1) and (2) (Maruthamuthu and Neta 1978). Phosphate radicals exist in three forms:  $\text{H}_2\text{PO}_4^{\cdot}$ ,  $\text{HPO}_4^{\cdot-}$ , and  $\text{PO}_4^{\cdot 2-}$ , with  $pK_a$  values of 5.7 and 8.9, respectively (Maruthamuthu and Neta 1978).  $\text{H}_2\text{PO}_4^{\cdot}$  is a strong but highly selective oxidant, with a redox potential ( $E^0(\text{H}_2\text{PO}_4^{\cdot}/\text{H}_2\text{PO}_4^-) = 2.75$  V) comparable to that of  $\text{SO}_4^{\cdot-}$  (Armstrong et al. 2015). However,  $\text{H}_2\text{PO}_4^{\cdot}$  reactivity decreases as it deprotonates, i.e.,  $\text{H}_2\text{PO}_4^{\cdot}$  is a stronger oxidant than  $\text{HPO}_4^{\cdot-}$  and  $\text{PO}_4^{\cdot 2-}$ . For example,  $\text{HPO}_4^{\cdot-}$  and  $\text{PO}_4^{\cdot 2-}$  can only oxidize  $\text{Br}^-$  and  $\text{I}^-$ , whereas  $\text{H}_2\text{PO}_4^{\cdot}$  can even oxidize  $\text{Cl}^-$ . In addition, the second-order rate constant of H-abstraction of 2-propanol by  $\text{H}_2\text{PO}_4^{\cdot}$  is more than five and seven times higher than that by  $\text{HPO}_4^{\cdot-}$  and  $\text{PO}_4^{\cdot 2-}$ , respectively (Neta et al. 1988). Since the rate constant of (2) is substantially higher than that of (1),  $\text{HPO}_4^{\cdot-}$  is likely the dominant species of phosphate radical at neutral pH, which



**Fig. 1** The effect of varying phosphate concentration on the degradation of atrazine by peroxydisulfate (a) in dark and (b) under visible light. Conditions:  $[\text{atrazine}]_0 = 10.0 \mu\text{M}$ ,  $[\text{peroxydisulfate}]_0 = 5.0 \text{ mM}$ ,  $[\text{phosphate}]_0 = 0, 1.0, 5.0, \text{ and } 10.0 \text{ mM}$ ,  $\text{pH}_0 = 7.0$ ,  $T = 25^\circ\text{C}$ . For peroxydisulfate under visible light, only data before  $t = 60$  min is presented for better comparison of the degradation efficiency at different phosphate concentrations. Varying phosphate concentration displayed negligible effect on the atrazine degradation by peroxydisulfate under dark, whereas higher phosphate concentration hindered the atrazine degradation by peroxydisulfate under visible light. (c) The linear dependency of the pseudo-first-order rate constant ( $k_{\text{obs}}$ ,  $\text{min}^{-1}$ ) of atrazine degradation on phosphate concentration. The  $k_{\text{obs}}$  was decreased linearly as the phosphate concentration increased

is a weaker oxidant than  $\text{SO}_4^{\cdot-}$ . Overall, the quenching of  $\text{SO}_4^{\cdot-}$  by phosphate species could compromise the degradation efficiency of atrazine, agreeing well with our results (Fig. 1b). The  $k_{\text{obs}}$  of atrazine degradation was reduced from  $2.1 \pm 0.4 \times 10^{-1} \text{ min}^{-1}$  to  $1.1 \pm 0.2 \times 10^{-1} \text{ min}^{-1}$  as

the phosphate concentration increased from 0 to 10.0 mM (Table S1).



In order to explore the dependency of  $k_{\text{obs}}$  on the phosphate concentration, their relationship at pH 7.0 is plotted in Fig. 1c. The  $k_{\text{obs}}$  showed a strong negative linear correlation with the phosphate concentration ( $r^2=0.99$ ), which suggested that the inhibitory effect was due to the scavenging of  $\text{SO}_4^{\cdot-}$  through a single reaction (2) to form less reactive  $\text{HPO}_4^{\cdot-}$ .

### Effect of pH on the degradation of atrazine by peroxydisulfate/visible in the presence of phosphate

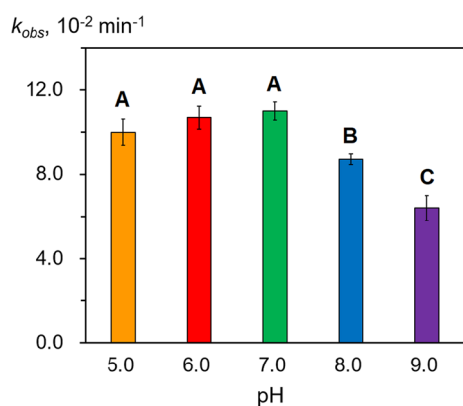
To further substantiate the involvement of phosphate radicals, the degradation efficiency of atrazine by peroxydisulfate/vis was determined from pH 5.0 to 9.0 (Fig. S2), and the corresponding  $k_{\text{obs}}$  is presented in Fig. 2 and Table S2. The maximum degradation efficiency was achieved at pH 7.0. While the  $k_{\text{obs}}$  was only slightly lowered as acidic pH, it was reduced dramatically from  $1.1 \pm 0.2 \times 10^{-1} \text{min}^{-1}$  to  $7.7 \pm 0.6 \times 10^{-2} \text{min}^{-1}$  and  $4.4 \pm 0.2 \times 10^{-2} \text{min}^{-1}$  when the pH was raised from 7.0 to 8.0 and 9.0, respectively. Note that atrazine has a  $pK_a$  of 1.60, so it remains predominantly

in its deprotonated form from pH 5.0 to 9.0 and is unlikely to have any significant impact on its degradation efficiency.

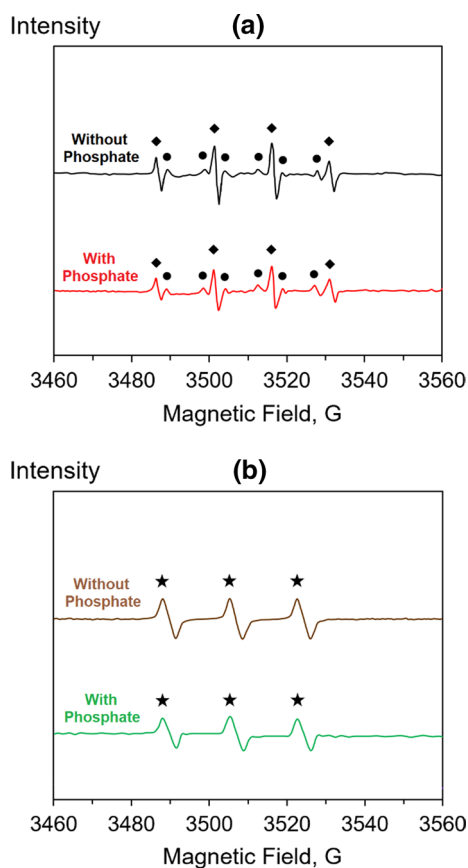
At pH 5.0 and 6.0,  $\text{H}_2\text{PO}_4^-$  is the dominant phosphate species, and  $\text{H}_2\text{PO}_4^{\cdot-}$  can be slowly produced via (1). According to the one-way ANOVA, the  $k_{\text{obs}}$  at pH 5.0 and 6.0 was not statistically different from pH 7.0 despite the slight reduction. This corroborates with the literature that the reactivities of  $\text{H}_2\text{PO}_4^{\cdot-}$  with various inorganic anions and organic compounds and the reaction mechanisms are similar to those of  $\text{SO}_4^{\cdot-}$  (Maruthamuthu and Neta 1978; Neta et al. 1977). For instance, both  $\text{H}_2\text{PO}_4^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$  react with aliphatic alcohols and carboxylic acids with second-order rate constants in the order of  $10^6$  to  $10^7$  (Maruthamuthu and Neta 1977), and their rate constants with aromatic carboxylic acids such as *p*-chlorobenzoic acid and *p*-hydroxybenzoic acid are all in the order of  $10^8$  to  $10^9$  (Maruthamuthu and Neta 1977; Neta et al. 1977). Furthermore, both  $\text{H}_2\text{PO}_4^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$  preferably initiate one-electron transfer and H-abstraction on the substrates (Maruthamuthu and Neta 1977). Therefore, although the reactivity of  $\text{H}_2\text{PO}_4^{\cdot-}$  toward atrazine is unknown, we postulate that it is comparable to that of  $\text{SO}_4^{\cdot-}$ . At pH 8.0 and 9.0,  $\text{HPO}_4^{2-}$  becomes the main phosphate species and can react with  $\text{SO}_4^{\cdot-}$  to form  $\text{HPO}_4^{\cdot-}$  via (2), a weaker oxidant than  $\text{SO}_4^{\cdot-}$  and  $\text{H}_2\text{PO}_4^{\cdot-}$  that might have led to the notably lower degradation efficiency of atrazine at higher pH. Our results are supported by the rate constants between  $\text{HPO}_4^{\cdot-}$  and aromatic carboxylic acids such as benzoic acid, which are generally at least one order of magnitude lower than  $\text{H}_2\text{PO}_4^{\cdot-}$  (Maruthamuthu and Neta 1977).

### Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) spectroscopy was employed to confirm the interaction between  $\text{SO}_4^{\cdot-}$  and phosphate by monitoring the changes in signal intensity of  $\text{SO}_4^{\cdot-}$  and  $^1\text{O}_2$  because direct probing of phosphate radicals remains challenging. The formation of  $\text{SO}_4^{\cdot-}$  and  $^1\text{O}_2$  in the peroxydisulfate/vis system was illustrated in our previous work (Wen et al. 2022a). Without adding any phosphate, the formation of 5,5-dimethyl-1-pyrroline N-oxide- $\text{SO}_4^{\cdot-}$  adduct and 5,5-dimethyl-1-pyrroline N-oxide-OH $^{\cdot}$  as a hydrolyzed product was clearly observed in the peroxydisulfate/vis system (Fig. 3a). The same signals were also captured when 10 mM phosphate was added, however, the peak intensities were about 33.4% lower, which agreed well with the reaction between  $\text{SO}_4^{\cdot-}$  and phosphate as discussed earlier. Moreover, the peak intensities of 2,2,6,6-tetramethyl-4-piperidine- $^1\text{O}_2$  adduct were decreased by approximately 36.5% in the presence of phosphate (Fig. 3b). Overall, the EPR measurements provided further evidence of the formation of phosphate radicals via the scavenging of  $\text{SO}_4^{\cdot-}$ .



**Fig. 2** The corresponding pseudo-first-order rate constants ( $k_{\text{obs}}, \text{min}^{-1}$ ) of atrazine degradation by peroxydisulfate/vis in the presence of 10.0 mM phosphate from pH 5.0 to 9.0. Conditions:  $[\text{atrazine}]_0 = 10.0 \mu\text{M}$ ,  $[\text{peroxydisulfate}]_0 = 5.0 \text{mM}$ ,  $[\text{phosphate}]_0 = 10.0 \text{mM}$ ,  $\text{pH}_0 = 5.0, 6.0, 7.0, 8.0, \text{ and } 9.0$ ,  $T = 25 \text{ }^\circ\text{C}$ . Different letters indicate statistical differences with  $p$  lower than 0.05 among  $k_{\text{obs}}$  according to one-way ANOVA followed by Tukey's test. The  $k_{\text{obs}}$  reached maximum at pH 7.0 and was markedly reduced as pH increased to 8.0 and 9.0. Although the  $k_{\text{obs}}$  at pH 5.0 and 6.0 was slightly lower than pH 7.0, the difference was not statistically significant



**Fig. 3** Electron paramagnetic resonance (EPR) spectra of (a) 5,5-dimethyl-1-pyrroline N-oxide- $\text{SO}_4^{\bullet-}$  adduct, labeled as black circle, and 5,5-dimethyl-1-pyrroline N-oxide- $\text{OH}^{\bullet}$  adduct, labeled as black diamond, and (b) 2,2,6,6-tetramethyl-4-piperidine- $^1\text{O}_2$  adduct, labeled as black star, in the peroxydisulfate/visible system in the presence and absence of phosphate. Conditions:  $[\text{peroxydisulfate}]_0 = 5.0 \text{ mM}$ ,  $[\text{atrazine}]_0 = 10.0 \text{ }\mu\text{M}$ ,  $[\text{5,5-dimethyl-1-pyrroline N-oxide}]_0 = [\text{2,2,6,6-tetramethyl-4-piperidine}]_0 = 50.0 \text{ mM}$ ,  $[\text{phosphate}]_0 = 0 \text{ or } 10.0 \text{ mM}$ ,  $\text{pH}_0 = 7.0$ ,  $T = 25 \text{ }^\circ\text{C}$ . The signal intensities of all three adducts were decreased when  $10.0 \text{ mM}$  phosphate was present, confirming the quenching effect of phosphate

## Conclusion

This study revealed the impeding effect of phosphate on the degradation of atrazine by a visible light-activated peroxydisulfate system. The reaction kinetics decreased linearly with the increase in phosphate concentration. The greater inhibitive effect of phosphate at alkaline pH suggested the formation of  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{\bullet-}$  through scavenging of  $\text{SO}_4^{\bullet-}$  and their involvements in the atrazine degradation. The decreased signal intensities of 5,5-dimethyl-1-pyrroline N-oxide- $\text{SO}_4^{\bullet-}$  and 2,2,6,6-tetramethyl-4-piperidine- $^1\text{O}_2$  adducts in EPR in the presence of phosphate further supported our postulation. Overall, our results underscored the potential formation of secondary phosphate radicals and their impact on the performance of  $\text{SO}_4^{\bullet-}$ -based advanced

oxidation processes, which have been generally overlooked. A deeper understanding on phosphate radicals could contribute to improving the applicability of  $\text{SO}_4^{\bullet-}$ -based advanced oxidation processes in treating contaminated water containing inorganic ions like phosphate.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10311-022-01523-9>.

**Funding** This study is financially supported by the Development of Water Programs of Excellence by Texas Water Resources Institute.

**Declaration**

**Conflict of interest** The authors declare no competing financial interests.

## References

- Ahn YY, Yun ET, Seo JW et al (2016) Activation of peroxymonosulfate by surface-loaded noble metal nanoparticles for oxidative degradation of organic compounds. *Environ Sci Technol* 50:10187–10197. <https://doi.org/10.1021/acs.est.6b02841>
- Armstrong DA, Huie RE, Koppenol WH et al (2015) Standard electrode potentials involving radicals in aqueous solution: inorganic radicals (IUPAC technical report). *Pure Appl Chem* 87:1139–1150. <https://doi.org/10.1515/pac-2014-0502>
- Che M, Chen Z, Qiu S et al (2021) High chloroform removal using tannic acid to promote the activation of persulfate with Fe/Ni nanoparticles. *Environ Chem Lett* 19:4015–4020. <https://doi.org/10.1007/s10311-021-01293-w>
- Chen L, Huang X, Tang M et al (2018) Rapid dephosphorylation of glyphosate by Cu-catalyzed sulfite oxidation involving sulfate and hydroxyl radicals. *Environ Chem Lett* 16:1507–1511. <https://doi.org/10.1007/s10311-018-0767-y>
- Ji Y, Yang Y, Wang L et al (2019) Sulfate radical-induced incorporation of  $\text{NO}_2$  group into chlorophenols. *Environ Chem Lett* 17:1111–1116. <https://doi.org/10.1007/s10311-018-00836-y>
- Lee J, Von Gunten U, Kim JH (2020) Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. *Environ Sci Technol* 54:3064–3081. <https://doi.org/10.1021/acs.est.9b07082>
- Liu H, Bruton TA, Doyle FM, Sedlak DL (2014) In situ chemical oxidation of contaminated groundwater by persulfate: decomposition by Fe(III)- and Mn(IV)-containing oxides and aquifer materials. *Environ Sci Technol* 48:10330–10336. <https://doi.org/10.1021/es502056d>
- Luo C, Ma J, Jiang J et al (2015) Simulation and comparative study on the oxidation kinetics of atrazine by  $\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{HSO}_5^-$  and  $\text{UV}/\text{S}_2\text{O}_8^{2-}$ . *Water Res* 80:99–108. <https://doi.org/10.1016/j.watres.2015.05.019>
- Maruthamuthu P, Neta P (1977) Reactions of phosphate radicals with organic compounds. *J Phys Chem* 81:1622–1625. <https://doi.org/10.1021/j100532a004>
- Maruthamuthu P, Neta P (1978) Phosphate radicals. Spectra, acid-base equilibria, and reactions with inorganic compounds. *J Phys Chem* 82:710–713. <https://doi.org/10.1021/j100495a019>
- Morin-Crini N, Lichtfouse E, Fourmentin M et al (2022) Removal of emerging contaminants from wastewater using advanced

- treatments. *Rev Environ Chem Lett* 20:1–43. <https://doi.org/10.1007/s10311-021-01379-5>
- Neta P, Madhavan V, Zemel H, Fessenden RW (1977) Rate constants and mechanism of reaction of  $\text{SO}_4^{\bullet-}$  with aromatic compounds. *J Am Chem Soc* 99:163–164. <https://doi.org/10.1021/ja00443a030>
- Neta P, Huie RE, Ross AB (1988) Rate constants for reactions of inorganic radicals in aqueous solution. *J Phys Chem Ref Data* 17:1027–1284. <https://doi.org/10.1063/1.555808>
- Prashantha Kumar TKM, Mandlimath TR, Sangeetha P et al (2018) Nanoscale materials as sorbents for nitrate and phosphate removal from water. *Environ Chem Lett* 16:389–400. <https://doi.org/10.1007/s10311-017-0682-7>
- Velusamy K, Periyasamy S, Kumar PS et al (2021) Advanced techniques to remove phosphates and nitrates from waters: a review. *Environ Chem Lett* 19:3165–3180. <https://doi.org/10.1007/s10311-021-01239-2>
- Wen Y, Huang C-H, Ashley DC et al (2022a) Visible light-induced catalyst-free activation of peroxydisulfate: pollutant-dependent production of reactive species. *Environ Sci Technol* 56:2626–2636. <https://doi.org/10.1021/acs.est.1c06696>
- Wen Y, Sharma KV, Ma X (2022b) Activation of peroxymonosulfate by phosphate and carbonate for the abatement of atrazine: roles of radical and nonradical species. *ACS ES&T Water* 2:635–643. <https://doi.org/10.1021/acsestwater.1c00482>
- Yang Y, Banerjee G, Brudvig GW et al (2018) Oxidation of organic compounds in water by unactivated peroxymonosulfate. *Environ Sci Technol* 52:5911–5919. <https://doi.org/10.1021/acs.est.8b00735>
- Zhou Z, Liu X, Sun K et al (2019) Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: a review. *Chem Eng J* 372:836–851. <https://doi.org/10.1016/j.cej.2019.04.213>

**Overlooked involvement of phosphate radicals in the degradation of the atrazine herbicide by sulfate radical-based advanced oxidation**

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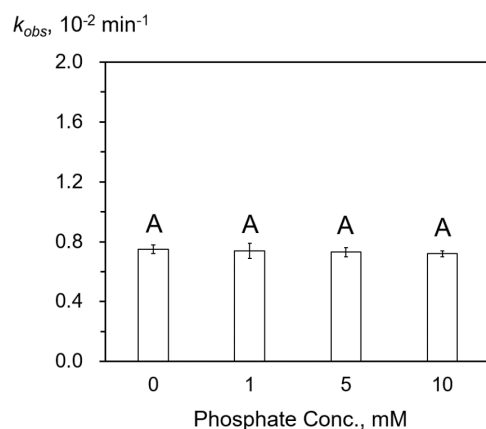
**Table S1.** Pseudo-first-order rate constants of atrazine degradation by PDS Dark and PDS Light with the presence of phosphate

Conc. (mM)	Parameters	PDS Dark	PDS Light
0	$k_{obs}$ (min <sup>-1</sup> )	$7.5 \pm 0.6 \times 10^{-3}$	$2.1 \pm 0.4 \times 10^{-1}$
	$r^2$	0.99	0.98
1.0	$k_{obs}$ (min <sup>-1</sup> )	$7.4 \pm 0.3 \times 10^{-3}$	$1.9 \pm 0.4 \times 10^{-1}$
	$r^2$	0.99	0.97
5.0	$k_{obs}$ (min <sup>-1</sup> )	$7.3 \pm 0.3 \times 10^{-3}$	$1.6 \pm 0.3 \times 10^{-1}$
	$r^2$	0.99	0.98
10.0	$k_{obs}$ (min <sup>-1</sup> )	$7.2 \pm 0.9 \times 10^{-3}$	$1.1 \pm 0.2 \times 10^{-1}$
	$r^2$	0.98	0.97

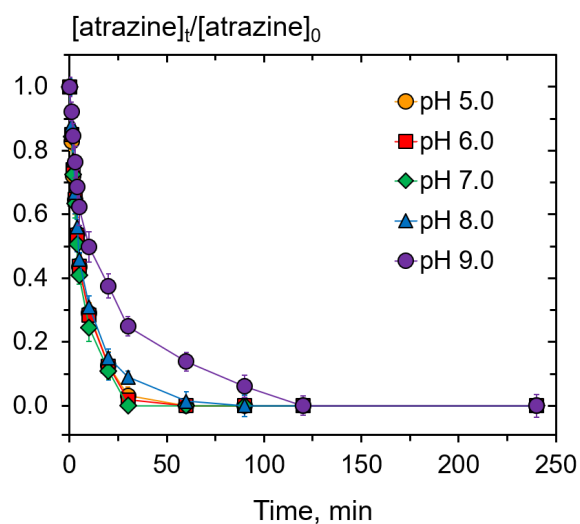
**Table S2.** The pseudo-first-order rate constants of atrazine degradation by PDS Light in the presence of 10.0 mM phosphate at different pH.

pH	Parameters	
5.0	$k_{obs}$ (min <sup>-1</sup> )	$1.0 \pm 0.3 \times 10^{-1}$
	$r^2$	0.93
6.0	$k_{obs}$ (min <sup>-1</sup> )	$1.1 \pm 0.3 \times 10^{-1}$
	$r^2$	0.96
7.0	$k_{obs}$ (min <sup>-1</sup> )	$1.1 \pm 0.2 \times 10^{-1}$
	$r^2$	0.97
8.0	$k_{obs}$ (min <sup>-1</sup> )	$8.7 \pm 0.6 \times 10^{-2}$
	$r^2$	0.99
9.0	$k_{obs}$ (min <sup>-1</sup> )	$6.4 \pm 0.2 \times 10^{-2}$
	$r^2$	0.95





**Figure S1.** Pseudo-first-order rate constants ( $k_{obs}$ ,  $\text{min}^{-1}$ ) of atrazine degradation by peroxydisulfate/vis in the presence of varying phosphate concentrations ( $[\text{atrazine}]_0 = 10.0 \text{ }\mu\text{M}$ ,  $[\text{peroxydisulfate}]_0 = 5.0 \text{ mM}$ ,  $[\text{phosphate}]_0 = 0, 1.0, 5.0, \text{ and } 10.0 \text{ mM}$ ,  $\text{pH}_0 = 7.0$ ,  $T = 25 \text{ }^\circ\text{C}$ ). No statistical differences ( $p \leq 0.05$ ) were detected among  $k_{obs}$  according to one-way ANOVA followed by Tukey's test, suggesting minimal effect of phosphate on  $k_{obs}$ .



**Figure S2.** Degradation efficiency of atrazine by the peroxydisulfate/vis system in the presence of 10.0 mM phosphate at varying pH ( $[\text{atrazine}]_0 = 10.0 \text{ }\mu\text{M}$ ,  $[\text{peroxydisulfate}]_0 = 5.0 \text{ mM}$ ,  $[\text{phosphate}]_0 = 10.0 \text{ mM}$ ,  $\text{pH}_0 = 5.0, 6.0, 7.0, 8.0, \text{ and } 9.0$ ,  $T = 25 \text{ }^\circ\text{C}$ ).