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Persulfate activation induced by ascorbic acid for efficient organic pollutants oxidation

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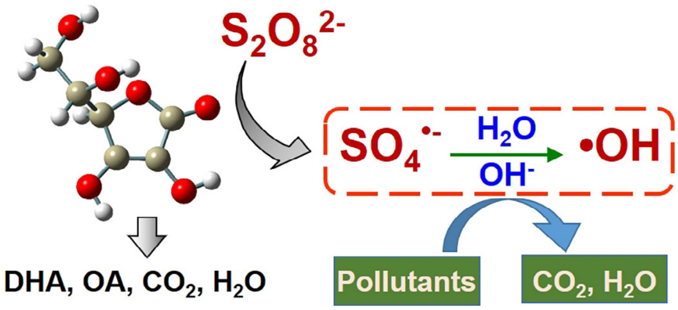
HIGHLIGHTS

- Ascorbic acid exhibited extremely high activity on persulfate activation to produce $SO_4^{\cdot -}$ and ·OH.
- Atrazine degradation rate constant during PS activation in presence of AA was 29 times that in absence of AA.
- Atrazine, pentachlorophenol, alachlor, tetracycline, and chloramphenicol were effectively degraded by AA/PS.
- Persulfate activation by ascorbic acid was attributed to the electron transfer from AA to PS.
- Atrazine in the real aquifer sediment system could be totally oxidized by AA/PS process.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we demonstrate that ascorbic acid (AA) exhibited extremely high activity on persulfate (PS) activation (AA/PS) to produce $SO_4^{\cdot -}$ and ·OH for the degradation of various organic pollutants, including atrazine, pentachlorophenol, alachlor, tetracycline, and chloramphenicol. Taken atrazine as a model natural organic micropollutants, we surprisingly found that the degradation rate constant of atrazine during PS activation in presence of AA was about 29 times larger than that in the absence of AA. The underlying mechanism of persulfate activation induced by AA was then systematically investigated by electron spin resonance (ESR) analysis, theoretical density functional theory (DFT) calculations, and kinetic experiments. The combination of ESR and DFT results confirmed that the persulfate activation induced by ascorbic acid was attributed to the electron transfer from AA to PS. In this process, AA undergoes a two-step oxidation by PS to generate $SO_4^{\cdot -}$ and dehydroascorbic acid with the formation of an intermediate ascorbate free radical. More interestingly, atrazine in the real aquifer sediment system could be totally oxidized in the presence of PS and AA. These findings offer a new economically feasible persulfate activation strategy for the in situ chemical oxidation of organic compounds in contaminated water and sediment systems.

1. Introduction

In recent years in situ chemical oxidation (ISCO) technologies based on persulfate activation have been received increasing attention for the remediation of contaminated soils, groundwater, and sediments, since persulfate could be decomposed to produce sulfate radical ($SO_4^{\cdot -}$).

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$SO_4^{\cdot -}$ is a strong oxidant with a redox potential of 2.5–3.1 eV [1,2], which can degrade a wide range of organic pollutants, including chlorophenols, trichlorobiphenyl, polycyclic aromatic hydrocarbons, methylene blue, methyl orange, and perfluorinated compounds [3–9]. In addition, $SO_4^{\cdot -}$ could react with water or hydroxyl to produce hydroxyl radical ($\cdot OH$) (Eqs. (1) and (2)) [10–12], another powerful oxidizing agent, which could oxidize and even mineralize a wide range of organic contaminants.

$$SO_4^{\cdot -} + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \tag{1}$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + \cdot OH \tag{2}$$

Generally, UV, heat, base, microwave or transition metals are frequently used for the activation of persulfate to yield $SO_4^{\cdot -}$ [13–17]. Unfortunately, high energy inputs required in radiation or heat activation, and the metal toxicity or risk constrain the further industrial application of these methods. Thus, it is of great significance to build low energy-input, metal-independent and environment friendly persulfate activation methods. Recently, Fang et al. found that persulfate could be efficiently activated by semiquinone radicals that were produced from the self-redox cycling process of widely distributed quinones in natural environment [5]. Watts et al. reported that phenols could also induce persulfate activation to form sulfate radicals, which was similar to the metal ions-mediated PS activation reaction (Eq. (3)) [18]. These persulfate activation methods illustrate that some organic species could be used for the activation of persulfate because of their reducibility.

$$S_2O_8^{2-} + Me^{n+} \rightarrow Me^{(n+1)+} + SO_4^{2-} + SO_4^{\cdot -} \tag{3}$$

Ascorbic acid ($C_6O_8H_6$, AA), a kind of ubiquitous water-soluble vitamin, is a common antioxidant and natural reducing agent [19]. Ascorbic acid has shown great potential in polluted water remediation. For example, Liang et al. reported that ascorbic acid could effectively reduce carbon tetrachloride over a wide pH range (2–13) with rate constants of $0.253 \pm 0.018\,M^{-1}\,s^{-1}$ [20,21]. Furthermore, ascorbic acid also exhibited effective activity on reductive degradation of nitrobenzene, 1,3-dinitrobenzene and atrazine [22–24]. Ascorbic acid could also enhance the H_2O_2 decomposition in heterogeneous Fenton (Fe^0/H_2O_2 and α-Fe_2O_3/H_2O_2) systems or persulfate decomposition in the Fe(III)/PS system by accelerating the Fe(III)/Fe(II) cycle [25–27].However, to the best of our knowledge, the study of organic pollutants degradation during the persulfate activation process only induced by AA has rare been reported.

In this study, we developed a chemical oxidation process by combining PS and AA (AA/PS) for the effective degradation of organic pollutants. As atrazine was a typical environment persistent organic pollutant in groundwater and soil [28], it was used as the target contaminant to evaluate the feasibility of the AA/PS process. The atrazine degradation efficiency, main factors affecting the degradation, and the mechanism of AA activated PS decomposition were investigated in detail. Furthermore, some other organic pollutants, including pentachlorophenol, alachlor, tetracycline, and chloramphenicol, were also used to assess the designed AA/PS process's universality for remediation of contaminant water and aquifer sediment systems.

2. Experimental section

2.1. Chemicals and materials

Sodium persulfate ($Na_2S_2O_8$, PS), NaOH (≥99%), H_2SO_4 (95–97%), ethanol, and isopropanol were all of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical grade ascorbic acid (AA) (99%), atrazine, pentachlorophenol, alachlor, tetracycline, and chloramphenicol were purchased from Sigma-Aldrich. Methyl cyclopentenolone (MCP) and sodium ascorbyl phosphate (SPA) were of analytical grade and purchased from Maya Regent Co., Ltd. Methanol, acetone, and dichloromethane were of HPLC grade and obtained from Merck KGaA. $10\,mmol\,L^{-1}$ AA stock solution was prepared by dissolving AA in oxygen-free deionized water. $400\,mmol\,L^{-1}$ PS stock solution was produced by dissolving 9.5242 g PS into 100 mL oxygen-free deionized water. All the concentrations of organic pollutants were $5\,mg\,L^{-1}$. The NaOH (0.5 mol/L) and H_2SO_4 (0.5 mol/L) solutions were utilized to adjust the pH value of the reaction solutions. All the stock solutions were freshly prepared with oxygen-free deionized water before use and fully covered with aluminum foil to avoid light.

The sediment materials used in the natural aquifer sediment system were sampled from an aquifer located within 5–6 m under the ground surface near Yangtze river in Wuhan city (113.678331°E, 30.175845°N), Central China with a pocket earth drill (Australia, CHRISITE, SD-1). The sediment was air dried, ground, sieved though a 60-mesh sieve before use. The particle size distribution of the sediment was measured with a laser particle analyzer (Mastersizer 3000). Main characters of the sediment were listed in Table S1 in the Supplementary material (SM).

2.2. Degradation procedures

The atrazine degradation experiments were carried out at ambient temperature (25 ± 2 °C) in 50 mL conical glass flask. Typically, 200 μL of $10\,mmol\,L^{-1}$ AA stock solution was mixed with 20 mL of $10\,mg\,L^{-1}$ atrazine stock solution, followed by adding 200 μL of $400\,mmol\,L^{-1}$ PS stock solution to initiate the atrazine degradation experiments. At predetermined time intervals, samples were taken and mixed with adequate ethanol (v 10%) to quench the reaction before analysis. The degradation of atrazine by PS in the presence of other activators were also conducted and kept the same as those in the presence of AA. The initial pH of AA/PS system was 4.2 without adjustment. The atrazine degradation experiments under different pH conditions were carried out with using NaOH to adjust the pH value of the reaction solutions. Typically, 200 μL of $10\,mmol\,L^{-1}$ AA stock solution was mixed with 20 mL of $10\,mg\,L^{-1}$ atrazine stock solution. Then we adjusted the pH of the mixed solution to 10 and 13 with using NaOH, followed by adding 200 μL of $400\,mmol\,L^{-1}$ PS stock solution to initiate the atrazine degradation experiments. Then the pH of the reaction systems after adding PS solution were 7.5 and 9.3, respectively. The anaerobic experiments were conducted with oxygen-free deionized water. Briefly, the deionized water in the conical flasks were first heated and then the conical flasks were sealed with the rubber stoppers and pumped with high purity Ar gas for 2 h with needles being inserted in the rubber stoppers for gas escaping.

The experiments of atrazine degradation by AA/PS system in the presence of natural aquifer sediment were also conducted. Typically, suspensions were prepared with aquifer sediment concentration of 5 g/20 mL with using anaerobic deionized atrazine stock solution. In this process, the aquifer sediment was air dried, ground, sieved though a 60-mesh sieve before use. Then, the experiments were initiated by adding 200 μL of $10\,mmol\,L^{-1}$ AA stock solution and 200 μL of $400\,mmol\,L^{-1}$ PS stock solution to initiate the atrazine degradation experiments. The initial reaction pH was 4.2. Besides atrazine, the degradation experiments of pentachlorophenol, alachlor, tetracycline, and chloramphenicol, were also conducted and kept the same as those of atrazine degradation.

2.3. Analytical methods

The concentrations of organic pollutants were determined by high pressure liquid chromatography (HPLC, Ultimate 3000, Thermo) with an Agilent TC-C18 column (150 mm × 4.6 mm, 5 μm). The composition of eluents for organic pollutants were acetonitrile/H_2O (50/50, v:v) for atrazine, acetonitrile/0.01 mol/L acetic acid (30/70, v:v) for pentachlorophenol, acetonitrile/H_2O (30/70, v:v) for alachlor, acetonitrile/0.01 $mol\,L^{-1}$ acetic acid (20/80, v:v) for tetracycline, and acetonitrile/