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Ascorbic acid induced atrazine degradation

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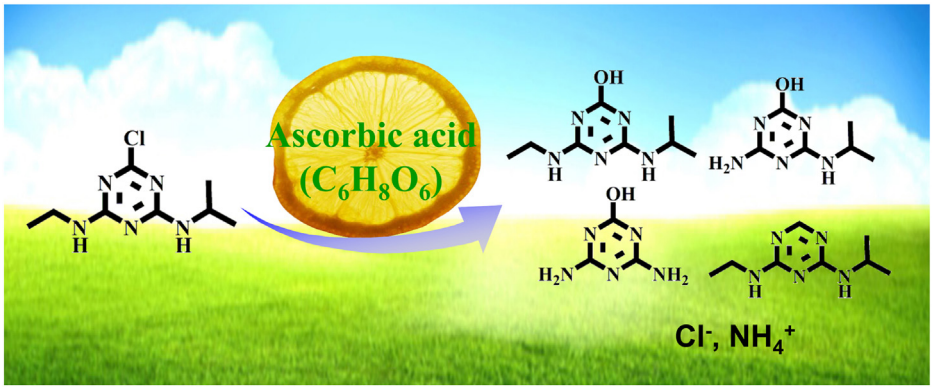
HIGHLIGHTS

- Atrazine could be degraded by AA in a wide range of pH from 4 to 12.
- The reductive ability of AA at different pH values was compared.
- The pH dependent reductive performance of AA was clarified.
- A kinetic model was proposed to discuss the atrazine degradation mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we systematically investigated the degradation efficiency and the degradation mechanism of atrazine in the presence of ascorbic acid at different pH values. Although atrazine could be degraded by ascorbic acid in a wide pH range from 4 to 12, its degradation under either acidic ($pH \leq 4$) or alkaline ($pH \geq 12$) condition was more efficient than under neutral condition ($pH = 7$). This pH dependent atrazine degradation was related to the reactive characteristic of atrazine and the reductive activity of ascorbic acid. The ascorbic acid induced atrazine degradation pathways at different pH were investigated by comparing the atrazine degradation intermediates with liquid chromatography-mass spectrometry, high performance liquid chromatography and ion chromatography. It was found that more products were detected in presence of ascorbic acid at alkaline condition. The appearance of chloride ions confirmed the dechlorination of atrazine by ascorbic acid in the absence of molecular oxygen, while its dechlorination efficiency reached highest at pH 12. These results can shed light on the application of AA for the organic pollutant remediation.

1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is widely used to kill pre- and postemergence broadleaf and grassy weeds, and gradually causes a worldwide environmental pollution [1–4], as well as exhibits identified reproductive and developmental abnormalities in rodent models [5–8]. Moreover, the high production (70 000–90 000 tons annually), moderate aqueous solu-

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bility, high persistence in water (the half-life of about 100 days), and high mobility of atrazine might further worsen its adverse health effects [9–12]. Unfortunately, the atrazine concentration in groundwater has been frequently found to be higher than the maximum permissible level (0.1 $\mu g\,L^{-1}$) for drinking water set by the European Community (EC) [13], while the United States Environmental Protection Agency (USEPA) set its drinking water limit at 3 $\mu g\,L^{-1}$ [14]. Therefore, it is obligatory to remove atrazine from water for the safety of human drinking.

Unfortunately, conventional water treatment processes such as coagulation/flocculation, filtration, and chlorination could not effectively remove atrazine from water [15–17]. Although physical treatments based on membrane technology, activated carbon adsorption, advanced oxidation processes (AOPs), biodegradation, and zerovalent metal reduction are efficient for the removal of atrazine from water [18–24], they are very expensive for the contaminated water remediation. Given that the widespread occurrence of atrazine pollution, it is of great importance to develop effective and inexpensive treatment technologies for the atrazine removal from contaminated water.

Ascorbic acid ($C_6H_8O_6$, H_2A), also known as vitamin C, is used as broadly as possible to include cosmetic, pharmaceutical and agricultural fields because of its biologic antioxidant property. It is a dibasic acid and can release protons in two steps in aqueous solution to form ascorbic anion ($C_6H_7O_6^-$, HA^-) with a pK_{a1} value of 4.25 (Eq. (1)) and dianionic ascorbic acid ($C_6H_6O_6^{2-}$, A^{2-}) with a pK_{a2} value of 11.79 (Eq. (2)) [25–27]. Meanwhile, AA (the general name for H_2A, HA^- and A^{2-}) can also serve as an ecofriendly reductant, being fully oxidized in two one-electron step or one two-electron step both in acid (Eqs. (3)–(6)) and alkaline aqueous solutions (Eqs. (7)–(9)) [28,29]. In addition, AA is ubiquitous in the plants and might thus be applied for environment pollution remediation. Moreover, the rate constants of AA oxidation via one-electron step under acid, neutral, and alkaline conditions are $2 \times 10^3\ M^{-1}\ s^{-1}$, $1 \times 10^5\ M^{-1}\ s^{-1}$, and $2 \times 10^5\ M^{-1}\ s^{-1}$, respectively, suggesting that the oxidation of AA is strongly dependent on the pH values and AA is more likely to be oxidized under alkaline condition than acid condition.

$$C_6H_8O_6 \rightarrow C_6H_7O_6^- + H^+ pK_{a1} = 4.25 \quad (1)$$

$$C_6H_7O_6^- \rightarrow C_6H_6O_6^{2-} + H^+ pK_{a2} = 11.79 \quad (2)$$

$$C_6H_8O_6 \rightarrow {}^\bullet C_6H_7O_6 + e^- + H^+ k_1 = 2 \times 10^3\ M^{-1}\ s^{-1} \quad (3)$$

$${}^\bullet C_6H_7O_6 \rightarrow C_6H_6O_6 + e^- + H^+ \quad (4)$$

$$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2e^- + 2H^+ \quad (5)$$

$$C_6H_7O_6^- \rightarrow {}^\bullet C_6H_6O_6 + e^- + H^+ k_2 = 1 \times 10^5\ M^{-1}\ s^{-1} \quad (6)$$

$$C_6H_6O_6^{2-} \rightarrow {}^\bullet C_6H_6O_6^- + e^- k_3 = 2 \times 10^5\ M^{-1}\ s^{-1} \quad (7)$$

$${}^\bullet C_6H_6O_6^- \rightarrow C_6H_6O_6 + e^- \quad (8)$$

$$C_6H_6O_6^{2-} \rightarrow C_6H_6O_6 + 2e^- \quad (9)$$

It is well known that the redox activity of AA is strongly dependent on the pH value. For example, Ogren and Saiprakash et al. demonstrated that methylene blue could be reduced by AA under strongly acidic conditions and also studied the kinetic process systematically [30,31]. Hsieh and his co-workers reported that Fe(III) could be stably reduced to Fe(II) by AA in the pH range of 4–6, but the Fe(III) reduction rate decreased markedly at pH > 6 [32]. Furthermore, some researchers suggested that dianionic ascorbic acid ($C_6H_6O_6^{2-}$) was the most important reductant for iron or iron complex under neutral pH values because the standard redox potential (0.019 V) of ${}^\bullet C_6H_6O_6^-/C_6H_6O_6^{2-}$ was lower than that (0.282 V) of ${}^\bullet C_6H_6O_6^-/C_6H_7O_6^-$ [33–35]. Recently, Liang's group reported that AA could reduce carbon tetrachloride at pH 13 [36], reduce *mer*-[$Ru^{III}(pic)_3$] complex (pic^- = picolinato) to produce a red ruthenium(II) species in a wide pH range of 1.0–7.4 [28]. In addition, they also confirmed that alkaline ascorbic acid exhibited more effective activity on reductive degradation of nitrobenzene [37]. In these previous studies, the AA concentrations were in the range of 1–50 mmol L^{-1}.

In this study, we demonstrate that ascorbic acid of relatively low concentration (1 mmol L^{-1}) can induce the degradation of atrazine in aqueous solution. Especially, we systematically investigate the degradation efficiency and degradation mechanism of atrazine in the presence of ascorbic acid at different pH values. Meanwhile, we analyze the atrazine degradation intermediates with different techniques and also propose a kinetic model to discuss the atrazine degradation mechanism.

2. Experimental section

2.1. Chemicals and materials

Atrazine was purchased from Sigma-Aldrich. Ascorbic acid, sulfuric acid and sodium hydroxide were all of analytical grade and purchased from National Medicines Corporation Ltd. China. Acetonitrile, acetone, and formic acid were of HPLC grade and obtained from Merk KGaA. All chemicals were used as received without further purification. Deionized water was used throughout the experiments. 1 mol L^{-1} of AA stock solution was prepared by directly dissolving AA in deoxygenized and deionized water. The atrazine solution (2 mg L^{-1}) was prepared by adding the required amount of pure atrazine in water and stirred for more than 24 h in a 1 L borosilicate reservoir at about 25 °C. NaOH and H_2SO_4 solutions were used to adjust the pH value of the solutions. All the stock solutions were freshly prepared before use.

2.2. Degradation procedures

All the experiments were performed in 100 mL conical flasks under Ar atmosphere at room temperature (25 ± 5 °C). Typically, the atrazine solutions were deoxygenized by pumping high-purity argon gas into for 30 min at a rate of 1.5 L min^{-1}. Different dosages of 1 mol L^{-1} AA solution were then added into 50 mL of the deoxygenized atrazine solutions (2 mg L^{-1}) at pH of 4, 7, and 12. Being sealed with the rubber stoppers, conical flasks were pumped with high-purity argon gas for another 30 min, along with needles being inserted in the rubber stoppers for gas escaping. All the reactions were carried out in darkness at 25 °C. Control experiments in the absence of AA were also carried out in parallel for comparison. All the experiments were conducted in triplicate and averaged data and error ranges with one standard deviation were presented.

2.3. Analytical methods

The concentration of atrazine was monitored by high performance liquid chromatography (HPLC, Ultimate 3000, Thermo, USA) with an Agilent TC-C18 reverse phase column (150 mm × 4.6 mm, 5 μm). The injection volume was 10 μL, the eluent was H_2O: acetonitrile = 50%:50%, the flow rate was 1 mL/min. The UV detector was set at 220 nm and the temperature of column was maintained at 30 °C.

AA concentration was measured by a modified previously described method [38]. The chlorine ions were detected by using an ion chromatograph (IC, Dionex ICS-900, Thermo, USA) equipped with an AS23 column. The possible degradation intermediates of atrazine and AA were identified by liquid chromatography-mass spectrometry (LC–MS, TSQ Quantum MAX, Thermo, USA) with a