Electron beam induced degradation of atrazine in aqueous solution

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HIGHLIGHTS

- Atrazine could be completely mineralized with electron beam irradiation.
- The radiolytic degradation of atrazine followed pseudo-first-order reaction kinetics.
- Hydroxyl radicals and hydrated electrons played vital roles in decomposition of atrazine.
- Some organic and inorganic intermediates were detected during the degradation processes.
- The potential degradation pathways of atrazine via electron beam were proposed.

ARTICLE INFO

ABSTRACT

Herein, the radiolytic degradations of atrazine and cyanuric acid were performed via electron beam irradiation. The results demonstrated atrazine could be completely mineralized without any residue of cyanuric acid in aqueous solution. The degradation of atrazine followed the pseudo-first-order reaction kinetics. The studies in the presence of different radical scavengers (O_2 and *tert*-butanol) indicated hydroxyl radicals were the main species for the decomposition of atrazine into cyanuric acid, while e_{aq}^- played vital role in the degradation of cyanuric acid. During the radiolysis processes of atrazine and cyanuric acid, some organic and inorganic intermediates were detected, implying dechlorination, dealkylation, and deamination occurred. On the basis of the effects of radicals and detected products, the potential radiolytic degradation pathways of atrazine via electron beam were proposed.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), one of the most widely used herbicides, has been widely utilized in agricultural and forestry fields [1]. As estimated, it was the most widely used herbicide in the word with between 70,000 and 90,000 tons applied per year [2]. However, due to the relatively high aqueous solubility and high mobility, atrazine can be transferred to surface waters by runoff or into groundwater through infiltration. As such, it was detected ubiquitously in surface and ground water in many countries [3–6]. The USEPA has classified atrazine as a Priority A chemical for potential groundwater contamination and of the 83 pesticides assessed in Agriculture Canada's priority scheme for potential groundwater contaminants, this herbicide ranked highest. The European Commission has labeled atrazine as one of the 33 priority substances of major

concern in European waters to be monitored under the Water Framework Directive [7]. Recently, atrazine has been implicated as a putative endocrine disruptor with extensive studies in experimental animals and humans [8–10].

With such background, there is an urgent need for decontamination processes aiming to the herbicide. Some researchers have attempted to employ conventional physical methods, such as flocculation, filtration, sterilization, reverse osmosis and adsorption for the removal of atrazine from drinking water. However, the facts manifested those approaches are ineffective and high costs [7]. Nowadays, advanced oxidation technologies (AOTs) are proved as fast and efficient methods for elimination of refractory organics in aqueous medium [11]. These processes involve the generation of a highly reactive oxidizing agent, the hydroxyl radical (·OH), in relatively high steady state concentration, which can react non-selectively with most of the organic compounds [12]. To deal with the ubiquitous herbicide, several AOTs have been applied for the removal of atrazine in water, including sonolysis [13], ozonation [14], Fenton reagent [15], UV [16], TiO_2-supported UV photolysis [17], and photocatalytic decomposition in the presence of polyoxometalates [18]. To sum up, most researchers seemed to

agree that decomposition of atrazine via AOTs involves dealkylation, deamination, and dechlorination to a lesser extent, mainly through the attack of ·OH radicals; whereas, with unexpectedness, cyanuric acid was reported to be the ultimate degradation product via majorities of those processes [19,20]. Unfortunately, cyanuric acid exhibited high potential toxicity to living organisms, especially with the coexistence of melamine [21]. Therefore, an effective process that could completely mineralize not only atrazine but also cyanuric acid should be explored.

Among the various AOTs, electron beam irradiation has been proved as an effective approach for dealing with various refractory organics [22,23]. What is more, it is one of the radiation chemical methods that could be considered as a potential technique in understanding with the fundamental reactions leading to the ring-opening of aromatics [24–26]. Water radiolysis mainly results in the formation of both oxidative and reductive radicals (hydroxyl radicals and hydrated electrons) as Eq. (1). The values in parentheses represent the radiation chemical yields of these species (G values, $\mu mol\,J^{-1}$) [27,28]. As reported previously, the reaction of radiolytically produced hydrated electron (e_{aq}^-) with cyanuric acid has been found via pulse radiolysis techniques in aqueous medium [29]. Thus, degradation of cyanuric acid under electron beam radiation is possible reasonable:

$$H_2O \rightarrow (0.28)^{\cdot}OH + (0.27)e_{aq}^- + (0.06)H^{\cdot} + (0.07)H_2O_2$$
$$+ (0.27)H_3O^+ + (0.05)H_2 \qquad (1)$$
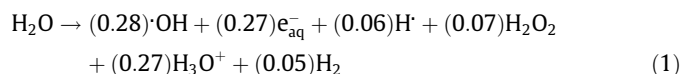
Herein, radiation induced degradation of atrazine and its recalcitrant photolytic product, cyanuric acid, was investigated. The chemical structures of these two target compounds are illustrated in Fig. 1. The degradation efficiency and mechanisms were both discussed in order to offer a proper approach for the efficient treatment of atrazine.

2. Methods and materials

2.1. Materials and reagents

Atrazine and cyanuric acid (both of 99.0% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) without any further purification before use. KH_2PO_4 and K_2HPO_4 (>99% purity) were purchased from Sinapharm Chemical Reagent (Shanghai) Co. Ltd. *tert*-Butanol, acetonitrile (chromatographic grade) and ionic standard liquids of $HCOO^-$, $C_2O_4^{2-}$, Cl^-, NO_3^- and NH_4^+ (99.99% purity) were purchased from Anpel Scientific Instrument (Shanghai) Co. Ltd. All the solutions in this research were prepared by deionized water produced through a Milli-Q-Plus ultra-pure water system (resistance >18.2 MΩ cm) from Millipore (Sartorius 611, Germany).

2.2. Radiolysis procedures

GJ-2-II electron accelerator (Shanghai Xianfeng electrical plant, China), providing a beam energy of 1.8 MeV and variable current (0–10 mA) was used as irradiation source. The current of electron beam was set as 1 mA in this experiment. The atrazine and cyanuric acid samples were placed with a distance of 30 cm from radiation window, and the solutions were irradiated with the dose range from 0.5 to 240 kGy ($J\,kg^{-1}$) at room temperature (20 ± 2 °C).
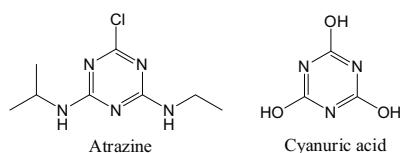

Fig. 1. Chemical structures of atrazine and cyanuric acid.

For comparison of the degradation capacity, a merry-go-round photochemical reactor (Sidongke Electric Plant, Nanjing, China) coupled with a max of 12 quartz tubes containing the reaction solution was used for the photodegradation experiments. The total volume of the tube was 100 mL and the liquid layer thickness was 35 mm. The light sources that UV irradiation simulated by a 300 W high-pressure mercury lamp immersed in the circulated-water cooled quartz well were employed in the UV-photolysis experiments. Testing cyanuric acid solutions were directly irradiated by UV lamp and samples were taken in regular time intervals of 15, 30, 50, 80, 100 and 120 h.

2.3. Chemical analyses

The concentrations of atrazine and cyanuric acid before and after the irradiation were determined by a high performance liquid chromatography (HPLC, Agilent 1200 series), coupled with a reversed phase column (C18 column, 150 × 4.6 mm) and an autosampler with the volume injection set to 10 μL. Based on previous researches [29,30], the determination methods of atrazine and cyanuric acid were proposed in this experiment. A UV–vis detector was employed with the determine wavelengths of 220 and 213 nm, respectively. The mobile phase for atrazine and cyanuric acid detection was a mixture of acetonitrile/water (50:50, v/v) at a flow rate of 0.8 mL min^{-1}, and acetonitrile/phosphate buffer (5:95, v/v) at a flow rate of 1 mL min^{-1}, respectively.

The measurement of organic and inorganic products released from electron beam degradation process was accomplished by ion chromatography (IC, Dionex) with an anionic and cationic exchange column. The mobile phases were a mixture of Na_2CO_3 (4.5 mM) and $NaHCO_3$ (1.4 mM) at a flow rate of 1.2 mL min^{-1}, and methanesulfonic acid aqueous solution (20 mM) with a flow rate of 1 mL min^{-1}, respectively. The injection volume was 20 μL.

3. Results and discussion

3.1. Kinetic studies of atrazine under electron beam radiolysis

Atrazine aqueous solutions with three different concentrations, 2, 4, and 6 mg L^{-1} were investigated at the irradiation dose ranging from 0 to 5 kGy. Unexpectedly, atrazine was decomposed rapidly with the electron beam radiolysis at a relatively low dose. The removal of this herbicide (6 mg L^{-1}) was nearly 85% with the irradiation dose of 0.5 kGy, and which reached 95% with 1 kGy, implying the electron beam approach was extremely effective for decomposition of atrazine.

Herein, when the natural logarithm (ln) of the atrazine concentration was plotted versus the irradiation dose, a straight line was given ($R^2 > 0.95$), suggesting the degradation of atrazine followed the pseudo-first-order reaction kinetics (Fig. 2).

In order to further determine the degradation rate, the following equations (Eqs. (2) and (3)) were used to calculate the doses required to degrade 50% ($D_{0.5}$) and 90% ($D_{0.9}$) of the initial atrazine concentration. Thus, $D_{0.5}$ and $D_{0.9}$ were used to analyze the contaminant removal:

$$D_{0.5} = \frac{\ln 2}{k} \qquad (2)$$

$$D_{0.9} = \frac{\ln 10}{k} \qquad (3)$$

As the calculated results, the required dose for removal of 50% and 90% atrazine via electron beam were 0.23 and 0.77 kGy, respectively. Apparently, radiolytic degradation of atrazine is efficient; an irradiation dose less than 1 kGy could remove more than 90% of the atrazine in aqueous solution.