Oxidation of atrazine in aqueous media by solar- enhanced Fenton-like process involving persulfate and ferrous ion

Marina Khandarkhaeva, Agniya Batoeva*, Denis Aseev, Marina Sizykh, Oyuna Tsydenova

Baikal Institute of Nature Management of Siberian Branch of the Russian Academy of Sciences, 6, Sakhyanova str., Ulan-Ude 670047, Russia

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ABSTRACT

The oxidation of s-triazines (using atrazine (ATZ) as a model compound) by a solar-enhanced Fenton-like process involving persulfate and ferrous ion was studied. A flow-through tubular photoreactor was employed for the experiments. The solar-enhanced oxidative system involving ferrous ion and persulfate (Solar/$S_2O_8^{2-}$/Fe^{2+}) showed the highest ATZ degradation efficiency when compared with other treatments (unactivated $S_2O_8^{2-}$, Solar - sunlight only, $S_2O_8^{2-}$/Fe^{2+}, Solar/$S_2O_8^{2-}$). Complete degradation of ATZ and 20% reduction in total organic carbon (TOC) content were observed after 30 min of the treatment. The in situ generated $^\bullet$OH and $SO_4^{-\bullet}$ radicals were shown to be involved in ATZ oxidation using the radical scavengers methanol and *tert*-butyl alcohol. Furthermore, iron compounds were shown to act not only as catalysts but also as photo-sensitizers, as the introduction of ferrous ion into the reaction mixture led to an increased absorbance of the solution and expansion of the absorption spectrum into the longer wavelength spectral region.

1. Introduction

S-triazines are a group of chemical compounds used in a number of applications, e.g., manufacture of dyes (Klančnik and Gorenšek, 1997), explosives (Halasz et al., 2002), melamine thermoplastic resins (Fink, 2013; Kazenas, 1967), antituberculosis drugs (Patel et al., 2012) and herbicides (LeBaron et al., 2011). S-triazine herbicides were first discovered and introduced by the Swiss company "Ciba-Geigy" in the 1950s. Since then triazines (atrazine, simazine, propazine, prometryn, ametryn, etc.) have been widely used to provide broad-spectrum weed control in a variety of crops and noncrop sites (LeBaron et al., 2011).

Atrazine (ATZ) was and, in some countries, still is by far the most widely used of the s-triazines, mainly as an herbicide on corn. Consequently, large quantities of ATZ are used in the major corn-growing countries - the USA, China, Brazil, Mexico and Argentina (LeBaron et al., 2011). In the European Union, ATZ is banned and listed among 45 priority pollutants in the field of water policy with the maximum allowable concentration (MAC) of 2 µg/L for surface waters (EU, 2013). In Russia, ATZ is classified as a compound of the 3rd class of danger with MAC for natural waters equal to 5 µg/L (Medyankina and Sokolova, 2011). The long-term use of this persistent and relatively mobile substance led to its frequent detection in ground- and surface waters (Benotti et al., 2008; Gilliom et al., 2006) and may pose a long-term threat after cessation (Jablonowski et al., 2011). The toxic effects of ATZ, particularly endocrine disruption, are relatively well studied in

laboratory animals and wildlife (Fan et al., 2007; Jin et al., 2014; Kucka et al., 2012; Rohr and McCoy, 2010). Less information is available on human health effects of ATZ. In several human cancer cell lines ATZ was shown to induce activity of aromatase - an enzyme that carries out the conversion of androgens to estrogens (Gammon et al., 2005; Sanderson et al., 2001). The International Agency for Research on Cancer stated that "there is sufficient evidence in experimental animals for the carcinogenicity of ATZ", although such evidence is "inadequate" in humans (IARC, 1999). Despite the paucity of data on human health impacts, concerns have been raised over potential endocrine and carcinogenic activity of ATZ due to its long-term/continuing use, persistence and a number of adverse effects observed in laboratory studies (Jablonowski et al., 2011).

The so-called Advanced Oxidation Processes (AOPs) have been suggested as efficient methods for removal of recalcitrant compounds like atrazine (Comninellis et al., 2008; Ribeiro et al., 2015) The AOPs employ reactive oxygen species (ROS), such as hydroxyl radical $^\bullet$OH ($E^o = 2.7$ V) and sulfate anion radical $SO_4^{-\bullet}$ ($E^o = 2.6$ V), formed through activation of precursor compounds. Persulfate ($S_2O_8^{2-}$) is one of such precursors, which could be activated through reactions with transition metals (Liu et al., 2012), exposure to elevated temperatures (T > 50 °C) (Ji et al., 2015), ultrasound (Wang and Zhou, 2016), or UV (Luo et al., 2016). Among the AOPs, photo-activated processes have been drawing increasing attention (Comninellis et al., 2008; Malato et al., 2009; Ribeiro et al., 2015). The following photo-activated processes have

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been proposed for degradation of ATZ and other s-triazines: photo-Fenton and Fenton-like processes (Bandala et al., 2007; Bu et al., 2016; Khan et al., 2013), heterogeneous photocatalysis (Chong et al., 2010; Parra et al., 2004), combinations of UV with various oxidizing agents - O_3, H_2O_2, HSO_5^-, or $S_2O_8^{2-}$ (Beltrán et al., 1993; Gerrity et al., 2016; Lekkerkerker-Teunissen et al., 2012) and combinations of different AOPs (Bianchi et al., 2006; Pérez et al., 2006; Pineda Arellano et al., 2013; Yang et al., 2014). Furthermore, it is generally agreed that the use of natural sunlight as in such processes is environmentally and economically beneficial (Malato et al., 2009; Muñoz et al., 2005).

Despite the growing interest in AOPs and promises the processes hold in water/wastewater treatment, there are very few large-scale applications of solar-activated AOPs (Comninellis et al., 2008) highlighting the need for further research on the process fundamentals and mechanisms in order to facilitate scaling-up. The aim of this work was to study the oxidation of s-triazines (using ATZ as a model compound) by a solar-enhanced Fenton-like process involving persulfate and ferrous ion.

2. Materials and methods

2.1. Materials

Potassium persulfate $K_2S_2O_8$, iron (II) sulfate $Fe_2SO_4 \cdot 7H_2O$, methyl and tert-butyl alcohols ("Khimreaktivsnab", Russia) were used in the experiments. Solutions of ATZ, 6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine (98%, "Sigma Aldrich"), at a concentration of 5.18 μM were used in the experiments and were prepared using deionized water (Simplicity®UV, Millipore).

2.2. Experimental procedure

The model compound ATZ was subjected to different treatments, including $S_2O_8^{2-}$ alone (dark experiment), exposure to sunlight only (Solar), dark Fenton-like process ($S_2O_8^{2-}/Fe^{2+}$), combined $S_2O_8^{2-}$ and sunlight exposure (Solar/$S_2O_8^{2-}$), and a combination of a Fenton-like process and sunlight exposure (Solar/$S_2O_8^{2-}/Fe^{2+}$). Besides the above listed treatments, the exposure to sunlight and Fe^{2+} (Solar/Fe^{2+}) was also tested but no noticeable degradation of ATZ and no difference between the treatment and exposure to sunlight only (Solar) were observed. Therefore Solar/Fe^{2+} treatment was excluded from the discussion. The experiments were carried out under natural sunlight during summer in Ulan-Ude city, Russia (51°48'47.747"N 107°7'19.536"E). The intensity of solar irradiation in the ultraviolet and visible range was measured using the UV-radiometer "TKA-PKM" and the lux meter and UV-radiometer "TKA-PKM-6" ("TKA Scientific Instruments", Russia).

The experimental unit included a flow-through tubular photoreactor, a peristaltic pump and a mixing tank (Fig. 1). The photoreactor
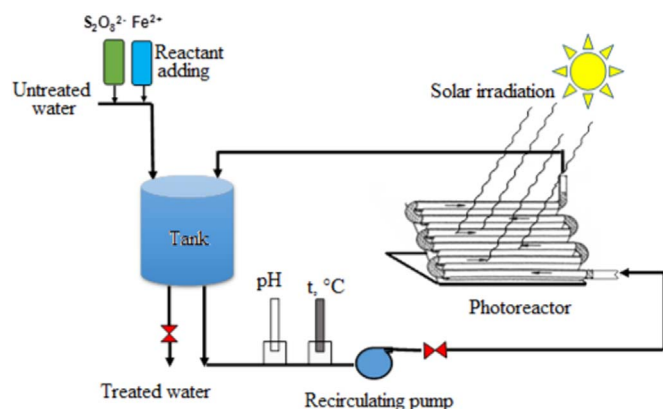

Fig. 1. A schematic representation of the solar experimental unit.

consisted of 5 quartz tubes connected in a sequence and placed into focus of the compound parabolic reflector surface. The flow rate and the total volume of the treated solution were 1 L min^{-1} and 1 L, respectively. To compare the results obtained on different days, i.e. under different solar irradiation conditions, the "normalized illumination time" $t_{30W,n}$ was used in calculations of kinetic parameters. The "normalized time" refers to a solar UV irradiance of 30 W/m^2 (typical solar UV irradiance on a sunny day) (Hincapié et al., 2005; Malato et al., 2009):

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \times \frac{UV}{30} \frac{V_i}{V_t} , \ \ \Delta t_n = t_n - t_{n-1}$$

where t_n – experimental time for each sample (min)

V_i – the illuminated volume (0.416 L).

V_t – the total volume of the photoreactor (1 L).

UV – the average solar UV irradiation measured during Δt_n (W m^{-2}).

2.3. Analytical methods

Changes in ATZ concentration during treatment were monitored by HPLC using the Agilent 1260 Infinity chromatograph with a diode-array UV detector. Chromatographic separation in an isocratic elution mode was performed using Zorbax SB-C18 4.6×150 mm column with 5 μm particle size. The mobile phase used was a mixture of acetonitrile and 75 mM acetic acid (60:40), flow rate was 0.5 mL/min, sample volume was 100 μL, and temperature was set at 35 °C. The degree of ATZ degradation/conversion was calculated according to the equation:

$$Conversion\,(\%) \ \ = \left(1 - \frac{C_\tau}{C_0}\right) \times 100,$$

where C_O and C_τ are the initial concentration of ATZ and that after treatment time τ (min), respectively.

The degree of ATZ mineralization was assessed by changes in total organic carbon (TOC) content measured by Shimadzu TOC-L CSN (detection limit 50 μg L^{-1}). Absorption spectra of the solutions were recorded using UV spectrophotometer UV–Vis Agilent 8453 using a quartz cuvette with 1 cm path length (l=1 cm). The toxicity of the treated solutions was assessed using the toxicity assessment kit "Biotox 10 M" based on measuring the luminescence of the recombinant strain of *Escherichia coli* K12 TG1 carrying lux operons of the luminescent bacteria *Photobacterium leiognathi* (Kuznetsov et al., 2002) (*for more details see Supplementary Material*). The pH was monitored using Pocket Meter MultiLine 3410 (WTW, Germany).

3. Results and discussion

3.1. Direct photolysis (Solar)

In order to assess the extent of direct photolysis, ATZ was first subjected to sunlight exposure only. The direct photolysis of ATZ under natural sunlight was observed to be a slow process. The initial oxidation rate W_0 was 0.037 μM min^{-1}. From the linear dependence of ln (C/C$_0$) against the normalized time t_{30W} and the rate equation for a pseudo first order reaction, the rate constant of ATZ degradation k and half-life $\tau_{1/2}$ of ATZ were determined to be 2·10^{-3} min^{-1} и 330 min, respectively. The slow transformation of chlorinated s-triazines by direct photolysis under natural or simulated solar light was reported previously (Konstantinou et al., 2001; Torrents et al., 1997). A study on kinetic aspects of direct photolysis of ATZ (λ=253.7 nm) revealed that the key step in the photolysis is the reaction of the nucleophilic substitution of chlorine atom yielding toxic hydroxylated ATZ, the photolysis of which was significantly slower than that of the original compound (Khan and Schnitzer, 1978). In the natural environment, the accumulation of this ATZ derivative takes place as a result of chemical, photochemical and