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JournalKinetic and mechanism investigation on the photochemical degradation of atrazine with activated H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ and HSO_5^- Javed Ali Khan^{a,b}, Xuexiang He^b, Noor S. Shah^{a,b}, Hasan M. Khan^a, Evroula Hapeshi^c, Despo Fatta-Kassinos^c, Dionysios D. Dionysiou^{b,c,*}^a Radiation Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120, Pakistan^b Environmental Engineering and Science Program, University of Cincinnati, 705 Engineering Research Center, Cincinnati, OH 45221-0012, United States^c Nireas-International Water Research Centre, University of Cyprus, P.O. Box 20537, Nicosia 1678, Cyprus

HIGHLIGHTS

- Degradation of atrazine was investigated in UV, UV/ H_2O_2 , UV/ HSO_5^- and UV/ $\text{S}_2\text{O}_8^{2-}$ AOPs.
- UV/ $\text{S}_2\text{O}_8^{2-}$ process was found to be more efficient as well as more economical.
- The pH affected UV/ $\text{S}_2\text{O}_8^{2-}$ but had no significant influence on UV, UV/ H_2O_2 and UV/ HSO_5^- .
- Second order rate constants of atrazine with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ were found to be comparable.
- Degradation mechanism was investigated by GC–MS and LC–MS/MS analysis.

GRAPHICAL ABSTRACT

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ABSTRACT

Degradation of atrazine was investigated under UV-254 nm irradiation, alone or in combination with peroxides, i.e., hydrogen peroxide, persulfate (PS) or peroxymonosulfate (PMS). UV/PS was found to be the most efficient process in this study, which was probably due to its higher radical quantum yield under UV irradiation, considering atrazine's comparable second order rate constant of $2.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $2.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with sulfate radical and hydroxyl radical, respectively. The pH values showed no significant effect on direct photolysis of atrazine, with observed UV fluence based pseudo-first-order rate constant (k_{obs}) of 7.59×10^{-4} , 7.73×10^{-4} and $6.72 \times 10^{-4} \text{ cm}^2 \text{ mJ}^{-1}$ at pH 3.0, 5.7 and 11.0, respectively. Performance of UV/ H_2O_2 and UV/PMS were more independent of initial pH values while that of UV/PS appeared to be more efficient at neutral pH condition. UV/PS was observed as a less energy consumption process. Eight new degradation by-products were identified in this study, namely, 2-chloro-4-acetamido-6-(2-hydroxy-isopropylamino)-s-triazine (CDHT), 2-hydroxy-4-(2-hydroxy-ethylamino)-6-isopropylamino-s-triazine (ONIT), 2-chloro-4-vinylamino-6-isopropylamino-s-triazine (CVIT), 2-hydroxy-4-vinylamino-6-(2-hydroxy-isopropylamino)-s-triazine (OVHT), 2-hydroxy-4-acetamido-6-isopropenylamino-s-triazine (ODPT), 2-hydroxy-4-(2-hydroxy-ethylamino)-6-vinylamino-s-triazine (ONVT), 2-hydroxy-4-(2-hydroxy-ethylamino)-6-methylamino-s-triazine (ONMT) and 2-chloro-4-vinylamino-6-amino-s-triazine (CVAT). Potential degradation pathways were further proposed.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most widely used s-triazine herbicides for pre- and post-emergence control of broad leaf and grassy weeds in corn, cotton, sorghum and sugar-cane crop fields [1,2]. In USA, for obtaining high agricultural yield, more than 24 million kilograms of atrazine was applied annually between 1995 and 1997 [3]. US Environmental Protection Agency (USEPA) estimated that in United States, 71–76, 70–75 and 68–73 million pounds of atrazine has been applied in 1987, 1993 and 1995, respectively [4]. Due to its relatively high aqueous solubility (33 mg L^{-1}), widespread use in huge quantity, low ability to adsorb onto soil particles, high water mobility, relatively long half-life and non-biodegradable nature, atrazine has been frequently detected in surface and ground waters above its European Union recommended level of $0.1 \mu\text{g L}^{-1}$ in drinking water in European countries, and in USA [3,5]. The use of atrazine has been banned by many European countries yet some countries such as USA and China are still using it [5]. As a result, the investigation of efficient atrazine removal methods from aquatic environments is highly important.

Recently, advanced oxidation processes (AOPs) have received considerable attention for their effective destruction and mineralization of organic pollutants [6,7]. The conventional AOPs mainly rely on in situ formation of highly reactive and non-selective hydroxyl radicals ($\cdot\text{OH}$) to oxidize a wide range of organic contaminants rapidly [7,8]. For example, Sanches et al. [9] employed low pressure Hg lamp and found that the UV fluence based *pseudo-first-order* rate constant for degrading 1 mg L^{-1} atrazine was 7.56×10^{-4} , 7.43×10^{-4} and $9.15 \times 10^{-4} \text{ cm}^2 \text{ mJ}^{-1}$ by UV, UV/ H_2O_2 and UV/ TiO_2 , respectively, using $40 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ and $2.5 \text{ mg L}^{-1} \text{ TiO}_2$. In addition to hydroxyl radical-based AOPs (HR-AOPs), sulfate radical-based AOPs (SR-AOPs) are gradually gaining consideration as in situ chemical oxidation technologies for water and soil cleanup from hazardous materials [10]. Chan and Chu, for example, achieved a 95% atrazine removal within 1 h in PMS/ Co^{2+} system with various Co^{2+} ions sources from $\text{Co}(\text{NO}_3)_2$, CoSO_4 , and $\text{Co}(\text{CH}_3\text{COO})_2$ using a 0.1 mM initial concentration of atrazine, PMS and cobalt each at pH 5–6 (not buffered) [11].

In addition to kinetics, the degradation mechanism of atrazine has also been widely studied, by UV radiation, ozonation, $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV , photocatalysis, H_2O_2 photolysis, ultrasound radiation, H_2O_2 coupled microwave radiation, Fenton, electrochemical Fenton, as well as photo-Fenton AOPs [12–14]. In all these processes de-alkylation, de-amination and de-chlorination with subsequent hydroxylation were shown to be the main degradation pathways. Although much work has been carried out on the degradation of atrazine both kinetically and mechanistically yet no information is available on the degradation of atrazine by UV/persulfate and UV/peroxymonosulfate processes and their comparisons with traditionally applied UV/ H_2O_2 process with respect to kinetics as well as mechanism.

Hydrogen peroxide (H_2O_2) has been used in various chemical oxidation processes such as Fenton, photo-Fenton and UV/ H_2O_2 . It yields water as its final product under appropriate reaction conditions; therefore, H_2O_2 is considered as an environmentally friendly oxidizing agent and has received great interest in green chemistry and green engineering applications recently [15]. Persulfate ($\text{S}_2\text{O}_8^{2-}$, PS, and also known as peroxydisulfate or peroxodisulfate), on the other hand, has certain advantages such as high redox potential ($E^0 = 2.01 \text{ V}$), easy storage and transport due to its solid state at ambient temperature, moderate stability in the subsurface environment, high water solubility and relatively low cost [16,17]. Another merit of using PS as an oxidizing agent is that it reacts less with natural organic matters (NOMs), as a result, PS

appears to be more appropriate for the decontamination of aqueous solutions with high NOM contents [18]. Peroxymonosulfate (HSO_5^- , PMS) is the active ingredient of Oxone[®], which is the trade name of a triple potassium salt, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$. It has been widely launched as an environmentally friendly and adaptable oxidant additive in water treatment process in recent years [7].

The objective of the present study was to investigate the efficacy of atrazine degradation by UV, UV/ H_2O_2 , UV/PS and UV/PMS AOPs. The second order rate constants of atrazine with $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were determined through competition kinetics. The effect of various oxidant concentrations and different pH conditions on degradation efficiency was evaluated. Potential degradation mechanisms of atrazine were also accessed based on the identified degradation by-products.

2. Materials and methods

2.1. Chemicals

Atrazine (99.9%), sodium persulfate and potassium peroxy-monosulfate were obtained from Sigma Aldrich. Hydrogen peroxide (50%, v/v), hydrochloric acid, sodium hydroxide, ammonium acetate, monosodium phosphate, disodium phosphate, acetonitrile and methanol were purchased from Fisher Scientific. The chemicals were used without further purification.

2.2. Analytical methods

Quantification of atrazine was performed by HPLC (Agilent 1100 Series with quaternary pump) equipped with UV diode array detector. The details of the analytical method can be found elsewhere [19]. Identification of degradation by-products of atrazine was performed by liquid chromatography–mass spectrometry (LC–MS/MS) and gas chromatography–mass spectrometry (GC–MS). GC–MS can be applied efficiently for the identification of chlorinated by-products of atrazine but it is less suitable for those having low volatility such as hydroxylated by-products. LC–MS/MS is more universal due to its compatibility with most of atrazine by-products [20].

LC–MS/MS analysis was performed by a 1200 series liquid chromatography coupled with 6410 Triple Quad Mass Spectrometer (Agilent Technologies, USA) using a modified USEPA method [21]. A Zorbax Eclipse XDB-C18 ($2.1 \times 50 \text{ mm}$, $3.5 \mu\text{m}$) analytical column was used as stationary phase. The analysis was carried out under gradient eluent flow conditions with a mixture of A (5 mM ammonium acetate solution) and B (HPLC grade pure methanol) from 90% A in the first 3.0 min, to 10% A from 3.0 to 8.0 min and then back to 90% A from 8.0 to 15.0 min with corresponding adjustment by B to 100%. The flow rate was 0.5 mL min^{-1} and the injection volume was $20 \mu\text{L}$. Samples were analyzed by positive ion mode electro-spray-ionization (ESI), with MS scan from 50 to 250 m/z , detector temperature of 300°C and capillary voltage of 0.5 kV .

GC–MS (Agilent 7890 Series) used for by-product analysis was equipped with HP-5 capillary column ($30 \text{ m} \times 0.25 \text{ mm}$, $0.25 \mu\text{m}$ film thickness). The extraction was performed by solid phase micro-extraction (SPME) using polydimethylsiloxane (PDMS) fiber with a manual holder. The oven temperature was programmed as: 80°C (hold for 2 min) to 160°C at $10^\circ\text{C min}^{-1}$ (hold for 2 min) and then to 260°C at $20^\circ\text{C min}^{-1}$ (hold for 2 min) with a total run time of 19 min. The injector and MS detector temperatures were 250°C and 300°C , respectively. The analysis was performed under electron impact ionization mode with MS scan from 50 to 250 m/z and carrier gas (Helium) flow rate of 1.5 mL min^{-1} .

2.3. Experimental set up

A bench-scale photochemical apparatus was used for the illumination of atrazine solutions with a monochromatic emission at 254 nm [19]. The initial concentration of atrazine solution was 4.64 μM in the kinetic study, and 23.20 μM in the by-product analysis. Initial pH values were adjusted by HCl, NaOH or phosphate buffer as noted. Each experiment was performed in triplicate; the error bars in figures represent the standard error of the mean. In case of dark reaction, the samples were collected at the time interval corresponding to the same UV fluence of irradiated solutions. The solutions were prepared in Milli-Q water (resistivity of 18.2 $\text{M}\Omega\text{ cm}$).

3. Results and discussion

3.1. Direct photolysis of atrazine

Direct photolysis of water molecule to generate $\cdot\text{OH}$ and hydrated electron can only be achieved at wavelengths lower than 190 nm [22]. Therefore, any observed degradation of atrazine by UV-254 nm alone in this study was probably resulted from its absorption of UV photons with subsequent direct photolysis. It has been previously reported that an organic molecule can undergo direct photolysis if the following two conditions are fulfilled: (1) organic molecule absorbs photon at the specified wavelength(s) to produce an electronically excited state molecule (Eq. (1)), and (2) chemical decomposition of the excited state molecule is competitive with a physical deactivation process to non-excited state molecule (Eqs. (2) and (3)) [23]. It has been reported that 254 nm UV can excite the aromatic ring and, therefore, atrazine could be excited and degraded by UV-254 nm directly [24], as observed in the current study (Fig. 1).

Applying the *pseudo-first-order* kinetics to atrazine photolysis, the degradation rate can be written as:

$$-\frac{d[\text{ATZ}]}{dt} = k[\text{ATZ}] \quad (4)$$

Eq. (4) can be modified to the UV fluence based degradation rate as Eq. (5):

$$-\ln \frac{[\text{ATZ}]}{[\text{ATZ}]_0} = k_{\text{obs}} \cdot \text{UV fluence} \quad (5)$$

where $[\text{ATZ}]_0$ and $[\text{ATZ}]$ are the molar concentrations of atrazine before reaction and at given UV fluence, respectively.

The rate of pollutant degradation by direct photolysis is directly influenced by two fundamental parameters, i.e., molar absorption co-efficient (ϵ_{ATZ} , $\text{M}^{-1}\text{ cm}^{-1}$) and quantum yield (Φ_{ATZ}), according to Eq. (6) [25]:

$$\Phi_{\text{ATZ}} = \frac{10 \cdot U_{\lambda} \cdot k_{\text{obs}}}{\epsilon_{\text{ATZ}} \cdot \ln(10)} \quad (6)$$

where k_{obs} is in unit of $\text{m}^2\text{ J}^{-1}$ and U_{λ} is the energy of one mole of photon (J einstein^{-1}) at the wavelength of UV radiation, i.e., 471,528 J einstein^{-1} at 254 nm [25]. The k_{obs} was calculated from the slope of the plot of “ $-\ln ([\text{ATZ}]/[\text{ATZ}]_0)$ ” versus UV fluence using Eq. (5), whereas ϵ_{ATZ} was determined using Beer–Lambert law ($A = \epsilon lc$) by plotting absorbance versus concentration and using

Fig. 1. Effect of pH on direct photolysis of atrazine. Reaction solutions at pH 3.0 and 11.0 were adjusted with 0.1 N HCl and 0.1 N NaOH, respectively, while that at pH 5.7 was unadjusted.

the slope as ϵ_{ATZ} because the path length (l) was 1 cm. The Φ_{ATZ} and ϵ_{ATZ} values at pH 3.0, 5.7, and 11.0 were determined as 0.045 and 3504 $\text{M}^{-1}\text{ cm}^{-1}$, 0.044 and 3498 $\text{M}^{-1}\text{ cm}^{-1}$, and 0.038 and 3586 $\text{M}^{-1}\text{ cm}^{-1}$, respectively, which were consistent with previously reported values [25–27]. The comparable Φ_{ATZ} and ϵ_{ATZ} at different pH conditions clearly resulted in the no significant impact of initial pH on the direct photolysis of atrazine with the observed UV fluence based *pseudo-first-order* rate constant (k_{obs}) of 7.59×10^{-4} , 7.73×10^{-4} and $6.72 \times 10^{-4} \text{ cm}^2 \text{ mJ}^{-1}$, at pH 3.0, 5.7 and 11.0, respectively.

3.2. Degradation of atrazine by UV/oxidant processes

The low quantum yield values of atrazine by UV direct photolysis promoted a further investigation for more effective removal methods, e.g., through radical chemistry [19]. The degradation of atrazine was performed by three different AOPs in this study, i.e., UV/ H_2O_2 , UV/PS and UV/PMS, as shown in reactions (7)–(9) [28]. The resulted k_{obs} at different reaction conditions are presented in Figs. 2 and S9–S12 in Supporting information (SI).

In order to identify the contribution of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ in atrazine degradation, second order rate constant of these radicals with atrazine were determined by competition kinetics, according to Eq. (10) taking into consideration of the direct photolysis of atrazine at 254 nm [29]:

$$k_{\text{OH}(s)} = \frac{k_{\text{s-UV}/\text{H}_2\text{O}_2} - k_{\text{s-UV}}}{k_{\text{ref-UV}/\text{H}_2\text{O}_2} - k_{\text{ref-UV}}} \times k_{\text{OH}(ref)} \quad (10)$$

where k_{OH} , $k_{\text{UV}/\text{H}_2\text{O}_2}$ and k_{UV} represent the second order rate constant with hydroxyl radical, observed rate constant in UV/ H_2O_2 and that in UV only condition, respectively. The words “s” and “ref” were used to denote the substrate and reference compounds, respectively. The same equation was used for sulfate radical rate constant determination. The *para*-chlorobenzoic acid (*p*-CBA, $k_{\text{OH}/\text{p-CBA}} = 5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and meta-toluic acid (*m*-TA, $k_{\text{SO}_4^{\cdot-}/\text{m-TA}} = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) were used as a reference for $k_{\text{OH}(s)}$ and $k_{\text{SO}_4^{\cdot-}(s)}$ determination, respectively [30,31]. The experimental results obtained are shown in Fig. 3.

Fig. 2. Effect of initial oxidant concentration on k_{obs} . Reaction solution at pH 4.5, 5.3 and 5.7 were unadjusted whereas those at 3.0 and 7.4 were adjusted with 0.1 N HCl and 5 mM phosphate buffer, respectively.

The bimolecular rate constant of atrazine with $\cdot\text{OH}$ was calculated as $2.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is in good agreement with previously reported values, i.e., 1.7×10^9 , 2.4×10^9 and $(2.6 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [32–34]. The second order rate constant with $\text{SO}_4^{\cdot-}$ was determined to be at a comparable value of $2.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, the higher efficiency in UV/PS than that in UV/PMS and UV/ H_2O_2 could probably be attributed to other factors such as the properties of the peroxides for radical generation [35].

Due to its bulky size, $-\text{SO}_3$ influences the oxygen–oxygen bond length in PMS and PS. The peroxide bond (O–O bond) length in H_2O_2 , PMS and PS was calculated as 1.458, 1.463 and 1.497 Å, respectively, while the bond energies in H_2O_2 and PS were calculated as 213.3 and 140.0 kJ mol^{-1} , respectively [7,36]. There is currently no such a value available in literature for PMS, however, it was suggested that it could be between that for H_2O_2 and PS based on the O–O bond length [7]. The lower peroxide bond energy resulted in an easier activation of PS by UV radiation than PMS and H_2O_2 , which was also supported by their radical quantum yield of 1.8, 1.04, and 1.0 for UV-254 nm/PS, UV-254 nm/PMS and UV-254 nm/ H_2O_2 , respectively [37–39]. As shown in Fig. 2, UV/PS showed higher removal efficiency followed by UV/PMS and then UV/ H_2O_2 at all same initial oxidant molar concentration conditions.

It can be seen from Fig. 2 that the presence of reactive radicals led to a higher removal rate of atrazine in AOPs, with k_{obs} increased linearly with increasing initial oxidant concentration regardless of the oxidant species, which was consistent with previous studies [40]. This observation was probably resulted from the increased radical concentration by increasing initial oxidant concentration in illuminated solutions as shown in reactions (7)–(9) within current initial oxidant molar concentration ranges.

3.3. Influence of pH on UV/oxidant AOPs

The influence of pH on the AOPs was evaluated. As shown in Figs. 2 and S9–S12 that UV/ H_2O_2 and UV/PMS were not significantly affected by the change in pH while the impact on UV/PS was obvious. The radical quantum yield in UV/ H_2O_2 (reaction (7)) has been reported to be independent of pH, with H_2O_2 concentration in the range of 2×10^{-5} to 0.1 M and light intensities in the range of 4.5×10^{-6} to $5.0 \times 10^{-4} \text{ einstein L}^{-1} \text{ min}^{-1}$ [39,41]. As a result, non-significant influence of pH was observed in UV/ H_2O_2 process in this study. The small difference in k_{obs} , e.g., 1.77×10^{-3} and $1.61 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$ ($[\text{H}_2\text{O}_2]_0 = 92.80 \text{ μM}$) at pH 5.7 and 3.0, respectively, was likely due to the competitive reactions for hydroxyl radicals in the presence of chloride ions (from

Fig. 3. Determination of second order rate constant of atrazine with (a) $\cdot\text{OH}$ and (b) $\text{SO}_4^{\cdot-}$. For $k_{\text{OH/ATZ}}$ determination, the initial concentration of atrazine, *p*-CBA and H_2O_2 were 4.64 μM , 4.64 μM and 1 mM, respectively. For $k_{\text{SO}_4^{\cdot-}/\text{ATZ}}$ determination, the initial concentration of atrazine, *m*-TA, PS, *tert*-butanol and phosphate buffer (pH = 7.4) were 4.64 μM , 4.64 μM , 1 mM, 50 mM and 5 mM, respectively.

HCl) at pH 3.0 (reaction (11)). The $\text{ClOH}^{\cdot-}$ species could react fast with H^+ to generate $\text{Cl}^{\cdot}$ which subsequently led to the formation of $\text{Cl}_2^{\cdot-}$ (reactions (12)–(14)) [42] that had limited reactivity towards organic compounds compared to $\cdot\text{OH}$ [43].

Although the phosphate buffer used was at pH 7.4, the presence of monohydrogen phosphate ion (61% HPO_4^{2-}) and dihydrogen phosphate ion (39% H_2PO_4^-) which had a much lower reaction rate constant with hydroxyl and sulfate radicals [44] showed less significant influence on the performance of UV/PS or UV/PMS. Consequently, the unaffected efficiency of UV/PMS by changing the pH from 4.5 to 7.4 was probably resulted from the unchanged radical quantum yield [38]. It has been reported that PS has minimal activation energy at neutral pH [45,46], so that higher k_{obs} was observed for the degradation of trichloroethylene at pH 7.0 than at pH 4.0 or 9.0 in a thermally activated PS process. Similarly, Gao et al. [46] observed higher k_{obs} for sulfamethazine at pH 6.5 than at pH 3.0 or 11.0 by UV-254 nm/PS. The improved

degradation efficiency of UV/PS from pH 5.3 to 7.4, as suggested by an increase in k_{obs} from 3.46×10^{-3} to $5.10 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$ in this study could thus be explained.

3.4. Economic comparison of the UV/oxidant AOPs

The economic comparison of the UV-assisted AOPs in terms of pollutant degradation efficiency was made from the determination of electrical energy per order (EE/O). The electrical energy per order is defined as the electrical energy in kilowatt hours (kW h) required to carry out the degradation of a pollutant by one order of magnitude (90% removal) in a unit volume, i.e., 1 m^3 or 1000 L of contaminated water or air [47]. The kinetic results obtained in this work can be used to compare the EE/O of the studied AOPs by the following equation [47]:

$$\frac{\text{EE}}{\text{O}} = \frac{Pt}{V} \quad (15)$$

where P is the total electrical power or flux in kW entering the solution; t is the irradiation time in h; and V is the volume of the treated solution in m^3 .

Using $0.08 \text{ \$/kW h}$ as electricity cost and 45% of total electricity cost as maintenance cost, the EE/O can be used for the rapid determination of total electrical energy cost as well as total cost of the system [47,48].

$$\begin{aligned} \text{Electrical energy cost (\$ m}^{-3}\text{)} \\ = \text{EE/O (kW h m}^{-3}\text{)} \times \text{power cost (\$/kW h)} \end{aligned} \quad (16)$$

$$\begin{aligned} \text{Total system cost (\$ m}^{-3}\text{)} = 1.45 \times \text{electrical energy cost} \\ + \text{reagent cost} \end{aligned} \quad (17)$$

In the present work, the initial concentration of atrazine was $4.64 \text{ }\mu\text{M}$ ($1000 \text{ }\mu\text{g L}^{-1}$) and four-order removals brought atrazine to $0.00046 \text{ }\mu\text{M}$ ($0.1 \text{ }\mu\text{g L}^{-1}$), which is the maximum permissible

concentration of atrazine in drinking water in accordance with European Commission Directives [12]. Table 1 presents the electricity and total costs of the applied systems based on four-order removals, suggesting that UV/PS is the most effective as well as the most cost efficient process in degrading atrazine among the AOPs studied.

3.5. Degradation by-products and potential degradation mechanisms

The degradation by-products of atrazine formed in four different processes, i.e., UV only, UV/ H_2O_2 , UV/PS and UV/PMS, were monitored by LC–MS/MS and GC–MS. All the identified by-products with their molecular weight, retention time, abbreviation, name and structure are shown in Table S1 in SI. The nomenclature used in abbreviations for representing the compound names has been previously reported [14,20]: A amino, C chloro, D acetamido, E ethylamino, F formamido, I isopropylamino, M methylamino, N 2-hydroxy-ethylamino, O hydroxy, V vinylamino and T s-triazine ring. The characters H and P were used here for the first time to represent 2-hydroxy-isopropylamino and isopropenylamino, respectively.

In addition to electronic excitation in all cases, the intermediates formed in UV/ H_2O_2 could be attributed to the $\cdot\text{OH}$ attack, while in UV/PS and UV/PMS to both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ reactions. However, the reaction intermediates formed in UV/PS and UV/PMS cannot be distinguished with certainty to be resulted from either radical species due to the similarities in the reaction mechanisms of these two radical species, i.e., (i) addition to unsaturated carbon including aromatic ring, (ii) hydrogen abstraction (H-abstraction) from saturated carbon, and (iii) electron abstraction (e-abstraction) from aromatic ring, double bond or carboxylate [49–52]. In case of atrazine, the reactive radicals can attack the aromatic ring or the side chains (ethylamino and isopropylamino). Reaction of $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ with the aromatic ring results in the formation of short life-span radical adducts or aromatic cation radicals [49], which react with water forming hydroxylated atrazine radicals and finally lead to hydroxylated by-products (reaction (18)) [52].

Table 1

Economic comparison of various AOPs for the degradation of atrazine. The electricity and total costs were based on a four-order removal of atrazine. Experimental conditions: $[\text{ATZ}]_0 = 4.64 \text{ }\mu\text{M}$ and $[\text{H}_2\text{O}_2]_0 = [\text{PS}]_0 = [\text{PMS}]_0 = 92.80 \text{ }\mu\text{M}$. pH was unadjusted.

Oxidation technology	UV/ H_2O_2	UV/PS	UV/PMS
k_{obs} ($\text{cm}^2 \text{ mJ}^{-1}$)	1.77×10^{-3}	6.70×10^{-3}	3.60×10^{-3}
UV fluence required for one-order removal of atrazine (mJ cm^{-2})	1.30×10^3	3.44×10^2	6.40×10^2
EE/O ($\text{kW h m}^{-3}/\text{order}$)	7.09×10^{-1}	1.87×10^{-1}	3.48×10^{-1}
UV fluence required for four-order removal of atrazine (mJ cm^{-2})	5.20×10^3	1.38×10^3	2.56×10^3
EE/four-order ($\text{kW h m}^{-3}/\text{four-order}$)	2.83	0.75	1.39
Electricity cost ($\text{\$ m}^{-3}$) ^a	0.227	0.060	0.111
Reagent cost ($\text{\$ g}^{-1}$) [69]	0.00841	0.00636	0.07949
Total cost ($\text{\$ m}^{-3}$) ^a	0.3557	0.2275	2.4280

^a Per four-order removal.

The reactive radicals can also rapidly attack on the side ethyl-amino or iso-propylamino chains and may abstract a hydrogen atom followed by different reactions including addition of $\cdot\text{OH}$, oxygen or water molecules. Due to steric hindrance, the lateral chains of atrazine are more likely exposed to reactive radicals than s-triazine ring. With no carboxylate or double bond, atrazine mainly reacts with the radicals through H-abstraction at the lateral chains.

In the present study, thirty-five degradation by-products were identified, with eight of them being new degradation by-products [12,13,20,53–55]. Details of these new by-products are presented in SI. A potential degradation mechanism for atrazine was then evaluated exhibiting seven different degradation pathways including de-alkylation, dechlorination–hydroxylation, alkyl–hydroxylation, alkyl–oxidation, olefination, deamination–hydroxylation and dechlorination–hydrogenation.

regard to the bond strength, it has been reported to follow the order of $\text{F} > \text{C} > \text{B} > \text{E}$ (Scheme 1), showing that the removal of ethyl group is easier than isopropyl group [55]. Indeed, reactive radicals generated in AOPs are much more effective in removing the lateral alkyl groups of atrazine [12]. Torrents et al. [13] found that the $\cdot\text{OH}$ mediated degradation of atrazine mainly led to the removal of lateral alkyl groups resulting in the formation of 20% 2-chloro-4-amino-6-isopropylamino-s-triazine (CAIT) and 10% 2-chloro-4-ethylamino-6-amino-s-triazine (CEAT) at 87% atrazine degradation. The $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ undergoes H-abstraction from side chain of atrazine resulted in the formation of carbon centered radical. This radical is then attacked by oxygen generating peroxy radical intermediate which upon subsequent reactions leads to the removal of lateral alkyl group with the formation of acetaldehyde (reaction (19)) [57,58].

(1) De-alkylation reactions, illustrated by path 1 in Scheme 3, engaged in the removal of alkyl groups from the lateral chains of atrazine and may occur alone or in combination with other classes of reactions. The most acceptable mechanism of atrazine de-alkylation through direct photolysis is the Chugaev type elimination reaction (Scheme 2) [56]. The de-alkylation reactions could also arise from the homolytic or heterolytic cleavage of the B, C, E and F bonds of the excited atrazine molecules during UV irradiation. With

(2) Dechlorination–hydroxylation (path 2, Scheme 3) involved the replacement of chlorine with a hydroxyl group. During direct UV photolysis at 254 nm, atrazine followed either homolytic or heterolytic cleavage of C–Cl bond of the excited molecules. In case of homolytic cleavage, the process is followed by the transfer of an electron from carbon atom to chlorine radical resulting in carbocation formation, whereas heterolytic cleavage is favored by water molecules due to its polar nature and both of the cleavages are proceeded by carbocation reaction with water to form 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (OEIT) [59]. Chen et al. [53] reported that the bond length of C–Cl bond in atrazine is 1.734 Å and was considered to be the longest bond among all other bonds, whereas the polarity associated with this bond is relatively low and found to be 0.293. As a result, the cleavage of this bond is the easiest and the hydroxy-atrazine was obtained in maximum concentration compared to any other degradation by-products of atrazine in their study. Previous studies showed that this reaction of dechlorination–hydroxylation was mainly attributed to direct UV photolysis. Torrents et al. [13] observed that the rate of dechlorination is unaffected by $\cdot\text{OH}$ and singlet oxygen which strongly emphasizes that dechlorination–hydroxylation occurred as a result of direct UV photolysis only. The OH group during dechlorination–hydroxylation is probably provided by water molecules (reaction (20)) [60]. However, Angelini et al. [61] observed the formation of OEIT in gamma

Scheme 1. Chemical structure of atrazine.

Scheme 2. Chugaev type de-alkylation of atrazine by direct photolysis.

Scheme 3. Proposed degradation mechanism of atrazine: (1) de-alkylation, (2) dechlorination–hydroxylation, (3) alkylic-hydroxylation, (4) alkylic-oxidation, (5) olefination, (6) deamination–hydroxylation, and (7) dechlorination–hydrogenation. The by-products inside the brackets were not detected in this study but reported by other researchers [53] or proposed. Reaction conditions: $[ATZ]_0 = 23.20 \mu\text{M}$, $[H_2O_2]_0 = [PS]_0 = [PMS]_0 = 232.00 \mu\text{M}$.

Scheme 3 (continued)

radiolysis study, which suggests that dechlorination-hydroxylation can also be initiated by reactive radicals in UV/oxidant processes (reaction (18)).

(3) Alkyl-hydroxylation, represented by path 3 in Scheme 3, is a process when a hydrogen atom of the side chain is replaced by hydroxyl group. The H-abstraction by $\cdot\text{OH}/\text{SO}_4^{\cdot-}$ on the

lateral alkyl-amino chains resulted in a carbon centered radical which could be attacked by $\cdot\text{OH}$ to form alkyl-hydroxylation by-products (reaction (21)).

- (4) Alkyl-oxidation, shown by path 4 in Scheme 3, resulted from H-abstraction by $\cdot\text{OH}/\text{SO}_4^{\cdot-}$ leading to the formation of a carbon radical compound (reaction (22)).

- (5) Olefination by-products (path 5 in Scheme 3) can be resulted from the dehydration of alkyl-hydroxylation by-products (reaction (23)) [20]. The H-abstraction by reactive radicals from lateral chains of atrazine can also lead to the formation of olefination by-products in accordance of reaction (24). The conjugation of the formed double bond with the aromatic ring allows these by-products to be thermal dynamically stable.

- (6) Deamination–hydroxylation (path 6 in Scheme 3) is expected to take place after the removal of lateral alkyl chains and then a subsequent replacement of amino groups by hydroxyl groups [55]. If only alkyl groups are removed from lateral amino-alkyl chains then it might result in the formation of neutral alkenes or alkyl radicals as suggested by Ta et al. [55]. However, the determination of ethylamine and iso-propylamine as degradation by-products of atrazine suggests that deamination–hydroxylation can also take place before the removal of alkyl groups (path 6, Scheme 3) [61].
- (7) Dechlorination–hydrogenation (path 7 in Scheme 3) is similar to dechlorination–hydroxylation mechanism except that chlorine is replaced by hydrogen atom possibly from water molecules [62,63].

The chlorine group in atrazine has been considered to be essential for the toxicity of this compound, since the chlorinated

by-products could share a similar mode of biochemical action towards the target organ or tissue [64]. However, the mode of action for hydroxylated atrazine by-products was suggested to

be different; and the hydroxylated by-products were generally shown to be less toxic [64]. In fact, the overall toxicity of atrazine and its degradation by-products was shown to be closely related to the de-chlorination extent achieved in water treatments [65]. For example, Stratton [66] investigated the toxic effects of atrazine and its degradation by-products (i.e., 2-chloro-4-amino-6-isopropylamino-s-triazine (CAIT), 2-chloro-4-ethylamino-6-amino-s-triazine (CEAT), 2-chloro-4,6-diamino-s-triazine (CAAT) and hydroxy-atrazine (OEIT)). Atrazine was found to be significantly more toxic than these by-products towards photosynthetic microorganisms. The ammeline and ammelide (i.e., 2-hydroxy-4,6-diamino-s-triazine (OAAT) and 2,4-dihydroxy-6-amino-s-triazine (OOAT)) were reported to have a reduced toxicity, and the toxicity of cyanuric acid was found to be even less than these two compounds [67]. Through the replace of chlorine with hydroxyl group to be common radical reaction mechanisms in the AOPs, it can be expected that the toxicity of the reaction solution can be reduced. Nevertheless, more studies are needed for the evaluation of the toxicity of the reaction by-products.

4. Conclusions

This study explored the degradation of atrazine by four different processes, i.e., UV only, UV/H₂O₂, UV/PS and UV/PMS. The *pseudo-first-order* kinetics was followed in all studied cases. It was observed that atrazine could be removed from water by direct photolysis at 254 nm, however, the combination of oxidants especially PS with UV radiation significantly accelerated the degradation process. The second order rate constant of atrazine with $\text{SO}_4^{\cdot-}$ was determined to be $2.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, whereas that with $\cdot\text{OH}$ to be $2.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The easier activation and higher stability of persulfate suggested that SR-AOPs, e.g., UV/PS, were a good alternative to HR-AOPs, e.g., UV/H₂O₂. Considering both energy consumption and the chemical cost, UV/PS appeared to be a better economical choice.

Based on the LC-MS/MS and GC-MS techniques, thirty-five different atrazine degradation by-products were identified, of

Scheme 3 (continued)

which eight were proposed as newly identified. Potential degradation mechanisms for atrazine were evaluated exhibiting seven different degradation pathways including de-alkylation, dechlorination–hydroxylation, alkyl–hydroxylation, alkyl–oxidation, olefination, deamination–hydroxylation and dechlorination–hydrogenation. The by-products analysis showed that the reactions occurred more likely at C–Cl bond and lateral alkyl-amino chains rather than opening of the s-triazine ring with cyanuric acid (OOT) as the final by-product. It has been reported that atrazine by-products especially hydroxylated derivatives (e.g. cyanuric acid) have low toxicity than atrazine [64,68], therefore, UV-assisted HR- and SR-AOPs have a high potential for the detoxification of water contaminated with atrazine.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.04.104>.

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