TRANSFORMATION OF ATRAZIN BY DIFFERENT ADVANCED OXIDATION PROCESSES

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Abstract

In this work ultraviolet photolysis (UV) and three advanced oxidation processes (AOPs), vacuum ultraviolet (VUV) photolysis, ultraviolet photolysis combined with vacuum ultraviolet photolysis (UV/VUV) and gamma (γ) radiolysis were used for the generation of reactive primary free radicals (hydroxyl radical ($^•$OH), hydrated electron ($e_{aq}^−$), hydrogen radical ($^•$H)) to induce the transformation of atrazine in aqueous solution. We examined different reaction conditions (solutions of atrazine saturated with dissolved oxygen or nitrogen). The aim of this work is the comparison of the oxidative transformation of atrazine during UV (254 nm), UV/VUV (254/185 nm) and VUV (172 nm) photolysis, as well as γ radiolysis. The efficiency of the photolytic methods increased in the following order: UV< VUV< UV/VUV photolysis. The economic efficiency of the used processes was compared based on Electric Energy per Order (E_{EO}). γ radiolysis was found to be the economically most feasible method compared to UV/VUV, VUV and UV photolysis.
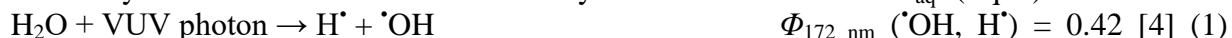
Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) (Figure 1.) is an s-triazine derivative and belongs to the group of Endocrine Disruptor Chemicals (EDCs). It is a widely used herbicide in crop production to control broadleaf and annual grasses. It is commonly detected in groundwater and soil in many countries, due to its high mobility and moderate solubility in water (34.7 mg L^{-1} at 26 °C) [1]. S-triazine derivatives are characterized by strong aromaticity and high stability against biological degradation [2]. Chemical degradation of atrazine is environmentally more important than biodegradation. Its elimination using AOPs, based on generation of reactive radicals ($^•$OH, $e_{aq}^−$, and $^•$H), is widely investigated.
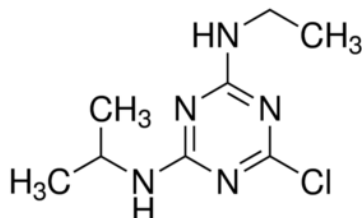
Figure 1. Chemical structure of atrazine

VUV radiation induces homolytic dissociation of water molecules, resulting in the formation of $^\bullet$OH and H$^\bullet$ (Eq. 1, 2) [3, 4]. With low yield, ionization also takes place. The so-called dry electron released in ionization may stabilize in the form of e_{aq}^- (Eq. 3):

$$H_2O + VUV\ photon \rightarrow H^\bullet + {}^\bullet OH \qquad\qquad \Phi_{172\ nm}\ ({}^\bullet OH,\ H^\bullet) = 0.42\ [4]\ (1)$$

$$\Phi_{185\ nm}\ ({}^\bullet OH,\ H^\bullet) = 0.33\ [4]\ (2)$$

$$H_2O + VUV\ photon \rightarrow H^+ + e_{aq}^- + {}^\bullet OH \qquad \Phi_{172\ nm}\ (e_{aq}^-) = \Phi_{185\ nm}\ (e_{aq}^-) < 0.05\ [5]\ (3)$$

The efficiency of VUV photolysis can be increased, in some cases, *e.g.* by the combination of this method with other techniques, like UV photolysis. The synergistic effect reported during some of the combinations underlines the relevancy of the combined techniques [6].

During γ radiolysis of aqueous solutions, the decomposition of water molecules results in $^\bullet$OH, e_{aq}^- and, in lower yield, $^\bullet$H as primary species. These reactive species are surrounded by water molecules in a small volume part, called Spur [7]. The primary radicals are generated (Eq. 4) with yields (G-values) of 0.280, 0.280 and 0.062 μmol J^{-1}, respectively [8, 9].

$$H_2O + \gamma\ photon \rightarrow {}^\bullet OH + e_{aq}^- + {}^\bullet H \qquad\qquad\qquad\qquad\qquad\qquad (4)$$
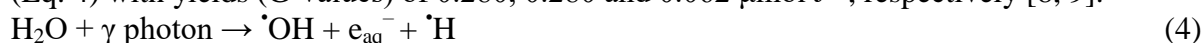
Using various dissolved gasses the radical set formed in solutions can be affected and therefore the effect of different species on the transformation of atrazine can be investigated.

In the presence of dissolved oxygen (DO) the reductive primary species ($^\bullet$H/e_{aq}^-) transform to less reactive $HO_2^\bullet/O_2^{\bullet -}$ [10]. The reaction of atrazine with e_{aq}^- can be examined in the presence of nitrogen (N$_2$).

Experimental

Materials and equipment

During all photolytic methods 250 mL and during γ radiolysis 5 mL atrazine (Sigma-Aldrich, 99.9%) solutions ($c_0 = 1.0\times10^{-4}$ mol L^{-1}) were irradiated. For UV (254 nm) and UV/VUV (254/185 nm) degradation a 15 W low pressure mercury vapour lamp (LightTech) was applied. A Radium Xeradex^{TM} 20 W Xe$_2$* excimer lamp emitting at 172±14 nm was used for VUV photolysis. Atrazine solutions were circulated by a peristaltic pump between the reactor and reservoir tanks (both thermostated at 25 ± 0.5 °C) at 375 ml min^{-1} flow rate. To investigate the influence of DO, O$_2$ or N$_2$ gas (Messer, > 99.5% purity) were bubbled through the solutions, starting 15 or 30 minutes before the measurement and continued until the end of the irradiation.

In γ radiolysis experiments the 5 mL ampoules with atrazine solution were placed to equal distance from the ^{60}Co-γ source of an SSL-01 panoramic type irradiator, to have a dose rate of 0.7 kGy h^{-1} (700 J kg^{-1} h^{-1}). The solutions were irradiated in open ampoules or in sealed ampoules saturated with N$_2$.

Analytical methods

The concentration of atrazine was followed by high performance liquid chromatography (Agilent 1100 HPLC equipment using a LiChroCART® C18 reverse-phase column) with diode array detector (DAD). Mixture of methanol (70%) and water (30%) was used as eluent, at a flow rate of 1.0 ml min^{-1}.

3. Results and discussion

The kinetic curves of atrazine ($c_0 = 1.0\times10^{-4}$ mol L^{-1}) were compared in presence and absence of DO during UV photolysis, VUV photolysis, UV/VUV photolysis and γ radiolysis. The results show that both in presence (Fig.2a) and absence (Fig.2b) of DO the degradation of

atrazine was faster with VUV and UV/VUV photolysis, than using only UV photolysis. This suggests that both $^•$OH and e_{aq}^- can have a significant role in the degradation of atrazine. The important role of the e_{aq}^- is also supported by the results observed during γ radiolysis (1 kGy), where again no significant effect of the DO (Fig.2c) on the transformation rates of atrazine could be observed. During the combined UV/VUV photolysis, atrazine and water molecules are excited by the UV and VUV photons, respectively. Although the 185 nm photons induce the generation of $^•$OH less effectively, than 172 nm light, used by VUV photolysis, the combined photolysis is more efficient than the simple UV or VUV photolysis, due to the presence of both radical and photoionization degradation mechanisms. The UV transformation of the target molecule was faster (30 min) in presence, than in the absence of DO (40 min). In this case the target molecule absorbs the UV light, and the presence of DO inhibits the recombination of the species formed by photoionization, increasing slightly the transformation rate.
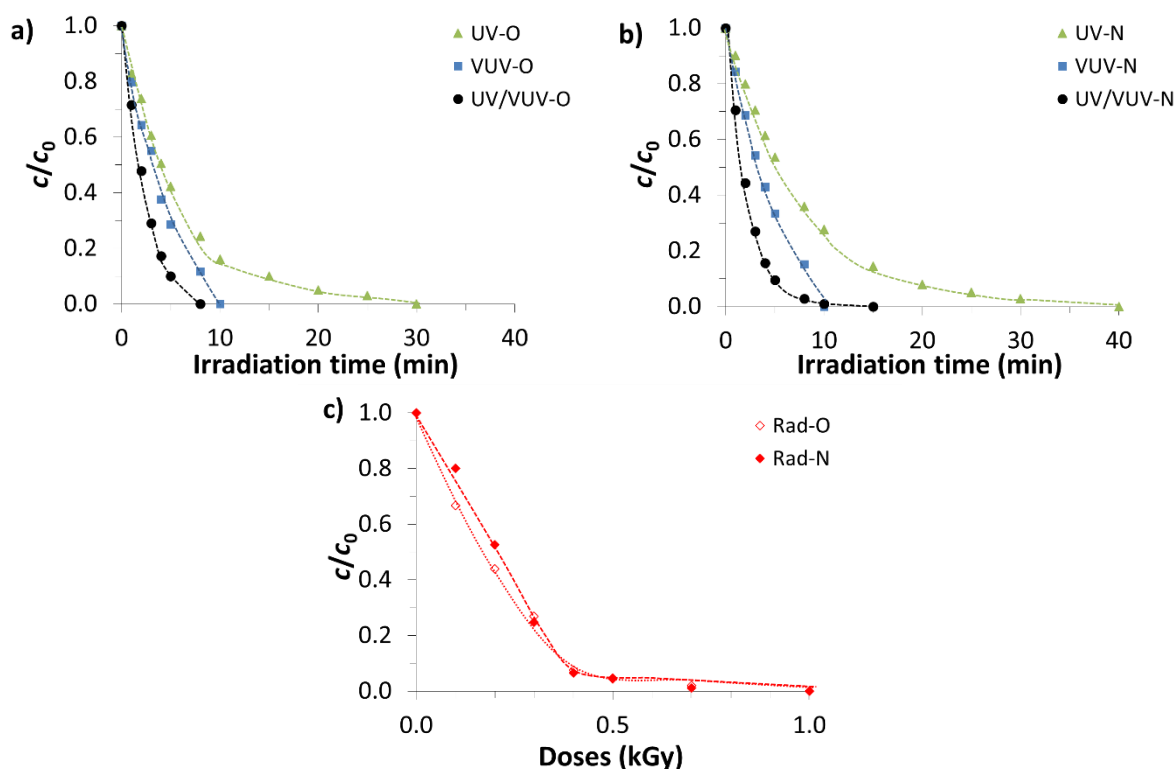
Figure 2. Kinetic curves of atrazine ($c_0 = 1.0 \times 10^{-4}$ mol L^{-1}) degradation during UV photolysis, VUV photolysis, UV/VUV photolysis and γ radiolysis in the presence (a, c) and absence (b, c) of dissolved O$_2$

The complete transformation of atrazine was reached by 30 and 40 min of UV, 15 and 15 min of VUV, 8 and 15 min of UV/VUV photolysis, and by 1.0 and 1.0 kGy of γ radiolysis for the initial concentration in the presence and absence of DO, respectively, showing that all investigated methods are suitable for the elimination of atrazine from aqueous solution.

Table 1. The electric energy per order (E_{EO}) calculated in case of various initial atrazine concentrations and methods

	UV photolysis	VUV photolysis γ radiolysis		UV/VUV photolysis
	E_{EO} (kW m^{-3} order^{-1})			
E_{EO1} (10^{-4} - 10^{-5})	**50.0**	**40.0**	**15.0**	**0.13**
E_{EO2} (10^{-5} - 10^{-6})	40.0	5.33	3.00	0.03
E_{EO2}/E_{EO1}	1.25	7.50	5.00	4.33

Calculated E_{EO} data are presented in Table 1 and show that γ radiolysis is the economically most feasible method, followed by UV/VUV, VUV and UV photolysis. Another observation can be made from the ratio of the E_{EO} calculated at different initial concentrations, namely, that in case of all methods it decreases strongly with the decrease of the initial concentration. This shows that the economic feasibility can be tuned with the initial concentration of the treated solution.

Conclusion

- Hydroxyl radicals and hydrated electrons both play vital role in the transformation of atrazine.
- The results showed that atrazine can be eliminated by all photolytic methods and γ radiolysis, as well.
- The combination of 185 nm VUV and 254 nm UV irradiation is the most effective method for the fast transformation of atrazine.
- Based on E_{EO} values γ radiolysis was the economically most feasible method for atrazine degradation.

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