

DEGRADATION OF ATRAZINE BY ADVANCED OXIDATION PROCESSES

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ABSTRACT

Advanced oxidation processes like ozonation (O_3) and ultrasonic irradiation (US) can be employed for the removal of recalcitrant compounds from water matrices. Atrazine is a pesticide which has been banned in the EU countries, since it is toxic and potentially carcinogenic even in very small concentrations. After their use in agricultural areas, the pesticides tend to leave residuals on the soil and in the surface waters or the groundwaters. The degradation of atrazine was studied by scientists before, but they could not get very high removal rates with the conventional wastewater treatment techniques. This study includes the investigation of the efficiency of O_3 and US and also of their combined application (US + O_3) for the degradation and potential mineralization of atrazine in water. Under the conditions applied, all three systems proved to be effective in inducing atrazine oxidation, leading to 95% removal for O_3 and 78% for US after 90 min of treatment. The synergy observed in the combined schemes, mainly due to the effects of US in enhancing the O_3 decomposition, led to higher removal (100%) for 20 min treatment. The synergy was so efficient that the results showed significantly higher removal level for shorter treatment duration.

Keywords: Atrazine, Advanced Oxidation, Ultrasound Irradiation, Ozonation

1. INTRODUCTION

The groups of artificially synthesized substances which are used to fight pests and improve agricultural production are called pesticides. These substances are generally toxic for living organisms and are difficult to degrade, being toxic agents with persistent bio-accumulative effects. Atrazine (2-chlorine-4-ethyl-6-isopropyl-1,3,5-triazine) (Figure 1) is a widely used herbicide mostly for corn, cotton and sugar-cane. It is frequently detected in natural waters [1] and has been known to affect the reproduction of aquatic flora and fauna [2]. The use of pesticides also constitutes a risk for water quality in agricultural areas due to the fact that these components may pass through the soil and subsoil and

pollute surface waters and groundwater. In Europe, pesticides are considered hazardous substances in accordance with current legislation regarding water [3,4].

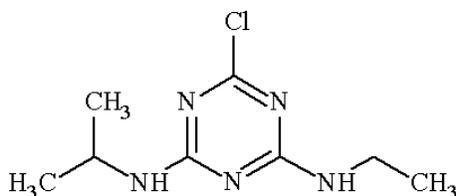


Figure 1. Structural formula of atrazine

In this study, the degradation of atrazine by ultrasonic irradiation, ozonation and their combination was investigated. Ultrasonic irradiation has been proposed as one of the techniques for the degradation of hazardous organic compounds [5]. Implosion of cavity bubbles in sonicated water containing dissolved gases result in hydrogen and hydroxyl radicals by fragmentation of water molecules. These in turn combine and generate other oxidative species such as peroxy and superoxide radicals as well as hydrogen peroxide [6,7].

Ozone (O₃) in water treatment is usually applied for multiple purposes (e.g., disinfection, taste and odor removal, and degradation of contaminants). Several studies have demonstrated that ozone-based advanced oxidation processes (AOPs) could be a potential approach for removal of atrazine [8,9].

When ozone is injected into water simultaneously with ultrasonic irradiation, an additional pathway of hydroxyl radical generation arises upon the decomposition of ozone in the gaseous bubbles during implosive collapse [10,11].

Since atrazine is a hydrophilic solute, the destruction pattern during combined ozonation and sonolysis is expected to be governed by •OH mediated oxidation in the bulk liquid, although it may also react directly with molecular ozone and hydrogen peroxide [12,13]. In any case, the rate-limiting step is the mass transfer of ozone in solution and the diffusion of •OH radicals into the bulk liquid.

2. MATERIALS AND METHODS

Atrazine (99.9%) was purchased from Labor Dr. Ehrenstorfer. Working solutions of 100 to 2.5 ppb were prepared after series of dilutions by using the ultra-pure water obtained from Sartorius 61316 and 611UV ultra ultrapure water system. The methanol (Merck), acetonitrile (Merck), ammonium formate (Fluka) were all Liquid Chromatograph grade and were used as received.

A multi-frequency medium-high frequency ultrasonic system (Meinhardt Ultraschalltechnik) composed of a generator, an amplifier and a titanium plate type transducer operating at three different frequencies (575, 861 and 1141 kHz) was used to perform all the reactions. The transducer was connected at the bottom of a double jacketed 500 mL cylindrical glass reactor.

Ozone was generated from air using OPAL OG 400 model ozone generator with a maximum production capacity of 40 mg/h O₃.

To measure the change of concentrations of atrazine in the degradation reactions, HPLC (Shimadzu 3200) which was coupled with MS/MS system (BioApplied Sciex Q-TRAP) was used. The column was Synergi 4 μ Fusion-RP 80A, 50 x 2.0 mm x 4 μ m and the mobile phase was methanol and ultra-pure water buffered with ammonium formate. The gradient program applied in atrazine measurements was: methanol rises to 95% (in volume) in 4 min., then hold at 95% for 1 min., decrease to 5% in 50 sec., hold at 5% for 10 sec. and stop the run. In the MS/MS detection system the m/z value of atrazine was 215.68 amu and the most intense fragment ions used for identification were 174.3 and 104.1 amu.

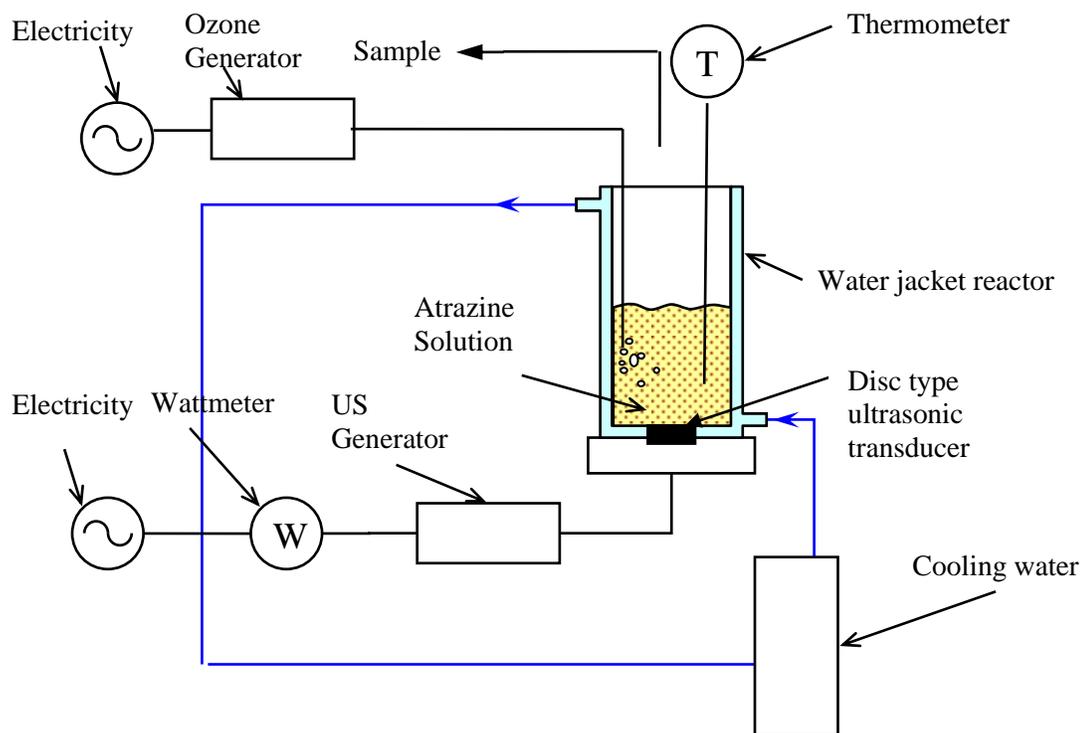


Figure 2. Schematic view of the Ultrasound / Ozone System

After having prepared 5 different concentrations of aqueous atrazine solutions, 250 mL of each solution has been irradiated at 3 different ultrasonic frequencies (575, 861, 1141 kHz). The water jacketed ultrasonic reactor was operated for 90 min degradation.

For the ozonation experiments, the same concentrations of solutions were subjected to ozone introduction for 90 min and samples were drawn at the same time intervals with the ultrasonic process.

To investigate the effect of ultrasound together with ozone, the two processes were applied together on the same solution.

Samples were drawn from the reactor on regular time basis to be analyzed for the concentration of atrazine by HPLC-MSMS. Each set of experiment was repeated at least twice to ensure the reproducibility of results.

3. RESULTS

The executed experiments have revealed that the degradation of atrazine follows first order reaction kinetics when either ultrasonic irradiation and/or ozone is applied to its aquatic solutions. The Figure 3 shows an example of atrazine degradation at 100 ppb aquatic solution and equation 1 below shows the mathematical expression for the calculation of the first order reaction rate, k.

$$\frac{dC}{dt} = -kC \quad , \quad C_i = C_o e^{-kt} \quad (1)$$

where;

C: the concentration of atrazine in aqueous solution

C_i : the concentration of atrazine in aqueous solution at time zero

C_o : the concentration of atrazine in aqueous solution at time t

k: the degradation rate constant of atrazine, min^{-1}

t: reaction time, min.

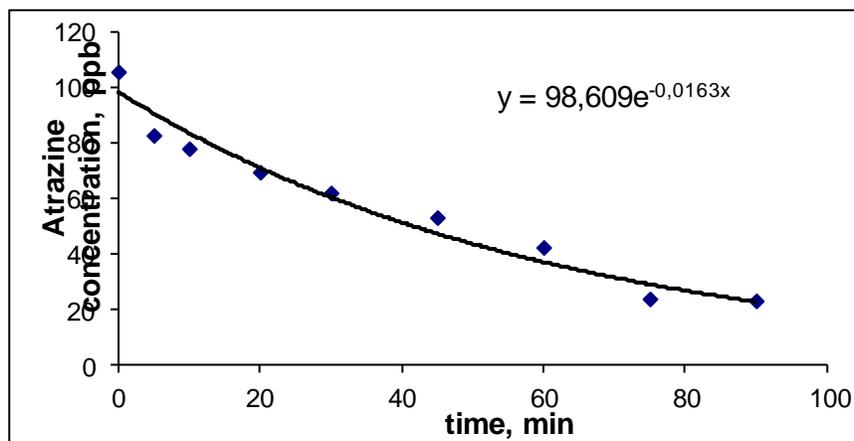


Figure 3. Degradation of 100 ppb atrazine solution at 575 kHz ultrasonic irradiation

3.1 Effect of Initial Atrazine Concentration in Ultrasonic Degradation

Having applied the same degradation procedure to all 5 different concentrations, we have found out that at elevated concentrations the degradation follows a faster route. The summary of all reaction rate constants is given in the Table 1 below:

Table1: Effect of the initial concentration of atrazine at 575 kHz US degradation on the reaction rate constant.

Initial concentration, ppb	Reaction rate, k, min ⁻¹
100	0,0163
50	0,0153
10	0,0113
5	0,0128
2,5	0,0118

The previous degradation studies by other researchers on atrazine were performed at higher concentrations, such as ppm level [14]. Examining the natural drinking water resources literally, the pesticides are found at very low concentrations like 50 or less ppb levels. As we have worked between 100 and 2.5 ppb concentrations, the results from this study exhibit realistic results if the treatment technique would be applied to real case studies.

In the processes at ppm levels, the limiting factor in the reaction is the number of cavitation bubbles, such that improving the cavitation efficiency would increase the removal rate and percentage. On the other hand at trace levels, there is very high probability of the atrazine compounds staying without encountering the cavitation bubbles in the aqueous medium. For this reason, keeping in mind that the number of cavitation bubbles would be constant under the same conditions, increase of atrazine concentration would statistically increase the encountering and degradation probability. This argument seems to explain the reason of detecting the highest degradation rate at the highest concentration of atrazine, which is 100 ppb. Studies with trace level pollutants have already demonstrated low degradation rates as the concentration decreases [15,16].

3.2 Effect of Applied Frequency in Ultrasonic Degradation

The 100 ppb atrazine solutions were subjected to degradation at the same physical conditions but different ultrasonic frequencies.

Examining Figure 4, the reaction rates for the three frequencies were observed as 0.0163 min⁻¹, 0.0156 min⁻¹ and 0.0101 min⁻¹ for 575, 861 and 1141 kHz, respectively. During the ultrasonic degradation at medium frequencies (300-1000 kHz), the main degradation mechanism is the oxidation reactions caused by the •OH radicals. According to its physical properties such as; low solubility (30 mg/L at 20 °C), low vapor pressure

(2.78×10^{-7} mmHg at 20 °C), Henry's constant (2.63×10^{-9} atm-m³/mole); Octanol-water partitioning coefficient ($\text{Log } K_{ow} = 2.75$) and its positive ionization, atrazine is best degraded at the cavitation bubble-water interface. This phenomenon was explained before in the previous studies [15,17]. The highest degradation rate which was observed at 575 kHz, makes sense depending on the foresighting above.

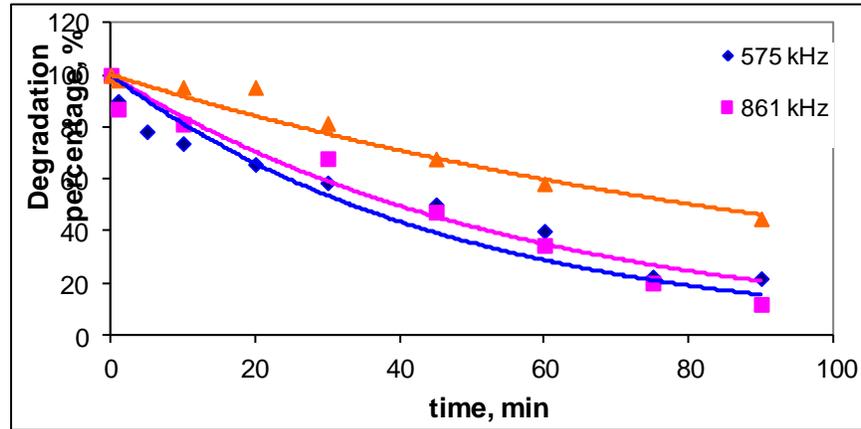


Figure 4. Degradation of 100 ppb atrazine solution at three different ultrasonic frequencies.

3.3 Effect of Ozonation on Atrazine Removal

The results of the ozonation processes in this study, show great resemblance to the results of the previous studies [18]. The degradation curve and the calculated degradation rate are given in Figure 5 below.

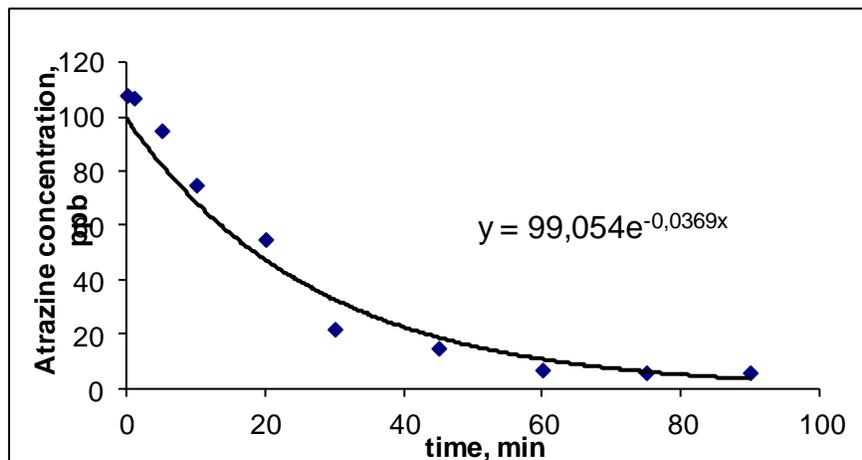


Figure 5. Degradation of 100 ppb atrazine solution under ozonation

The observed degradation rate of ozonation with 60 mg O₃/h flowrate is more than 2 folds greater than that of ultrasonic irradiation. This outcome shows that ozonation is a faster and stronger oxidizing agent than ultrasound, but sonication process is more user friendly for smaller volumes of solutions because there is no toxic gas produced in the

medium where the experiment is being conducted. Any process, which helps to improve the rate and the duration of the reaction would help to obtain better results for the removal of atrazine. For this purpose, ozonation and ultrasonic irradiation were coupled together to see their influence on the removal of atrazine.

3.4 Degradation of atrazine by Ozone / Ultrasound

Ultrasonic irradiation when catalyzed by ozonation has yielded a degradation rate constant of $k=0.2169 \text{ min}^{-1}$ (Figure 6), which is 13 and 7 times greater than k of ultrasonic irradiation alone and ozonation alone, respectively. This fact emerges from the catalyzation of ultrasonic irradiation by ozone and the improvement of the solubility of ozone by ultrasound. Ultrasonic waves provide homogeneity in the water medium by giving very high energy and vibration, so that the solubility of ozone is enormously increasing. The increased solubilized ozone molecules result in more radicals and more oxidative reactions in the medium.

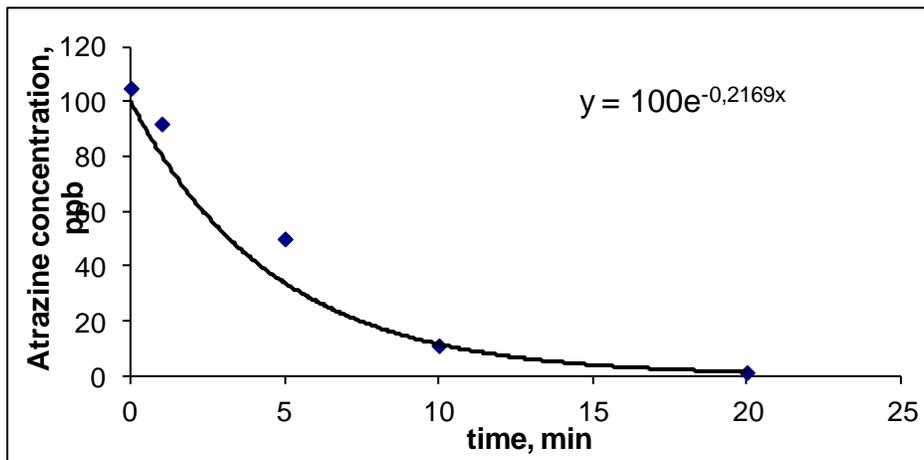


Figure 6. Degradation of 100 ppb atrazine solution under ozonation and 575 kHz ultrasonic irradiation

4. CONCLUSION

The use of ultrasound for destroying pesticides in water and wastewater is a promising approach as an environmental remediation technique, owing to the oxidative degradation. The medium frequency ultrasound (~575 kHz) provides more than 75% atrazine removal at aqueous solutions with concentrations around 100 ppb. Ozone, a compound known to be one of the most effective oxidants, provides 95% removal of atrazine. As shown in Table 2, integration of ultrasonic techniques with ozonation definitely enhances the efficiency of the process, leading to 100% removal of atrazine at shorter times and higher reaction rates compared to single processes. .

Table 2. Reaction rate constants resulting from three different process flows

Process Applied	Rate constant, min⁻¹
US (575 kHz)	0,0163
Ozonation (60 mg/h)	0,0369
US (575 kHz) + Ozonation (60 mg/h)	0,2169

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