Photo-Degradation of Atrazine in Water Using UV and investigating its by-Products

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Abstract

Background: Atrazine is one of the most widely used chlorinated herbicides with properties, such as sustainability in soil and ability to penetrate into water sources. This study aimed to investigate the photo-degradation of atrazine using ultraviolet ray and to identify its by-products.

Methods: The efficiency of atrazine removal under UV irradiation with a power of 6-125 watts was investigated and some effective parameters, such as initial concentration (10-100 mg/l) and pH (3-5), were studied during the radiation period (5-90 minutes). In all experiments, the volume of the solution used in 250-ml Erlenmeyer flask was 100 ml. After all, the final and by-products produced during this process were identified by mass gas chromatography.

Results: The results showed that the removal efficiency did not change significantly by increasing pH. With increasing lamp power from 6 to 125 watts at one hour, the degradation efficiency increased by 24.5%, 23.5%, and 29.7% at concentrations of 10, 30, and 50 mg/l, respectively. Also, by increasing time from 5 to 15 minutes under the 125-watt radiation, the removal efficiency increased from 45.6 to 96.8%. Examining the results of mass gas chromatography revealed that atrazine photolysis process progressed towards the mineralization of atrazine. Accordingly, organic chlorine transformed to chlorine ion and organic nitrogen involved in ammonium and nitrate molecules.

Conclusion: Overall, the results indicated that photolysis at the wavelength of 254 nm could be used along with other purification methods to completely remove atrazine and simultaneously disinfect contaminated water sources.

Introduction

Atrazine (2-chloro-4- (ethylamino) -6-isopropylamino-s-triazine) is widely used to increase production on farms and agricultural lands. It is a Triazine herbicide and is used to combat weeds and broadleaves in corn, sorghum, and sugar cane cultivation.[1, 2] Low vapor pressure, high soil stability, low hydrolysis, high leakage potential, resistance to microbial decomposition and degradation, bioaccumulation property, moderate water solubility, and proper adsorption by organic matter and clay, have converted this substance into a groundwater and surface contaminant.[3-5] The potential effects of atrazine on human health include DNA destruction, sperm motility, and endocrine hormones disorders.[6] Considering the potential of contaminants such as toxins or drugs to penetrate into water resources or discharge of wastewater to recipient resources, the most important way of exposing humans to these substances is to use contaminated water resources. So far, various methods have been used to remove atrazine from water. One of these methods is the removal of atrazine by adsorption process using carbon adsorbent followed by chemical reduction process,[7] iron oxide saturated activated carbon

adsorbent,[3] Nano-filtration,[8] microwave radiation,[9] biological absorption,[10] photocatalysis process,[11] etc. Each of these methods has some disadvantages, such as high cost of the process, low efficiency, membrane and filters fouling, and high commissioning costs. In photo-degradation method, no chemicals are added to the sample and no sludge is produced. Therefore, it can be said that photo-degradation and photolysis are among green and environmentally friendly methods. Many organic species are susceptible to photolysis under UV radiation and they exhibit photolysis even under high sunlight. Differences in test conditions and changes in parameters, such as wavelength, light intensity, and pH, can affect the removal of contaminants.[12] One of the most important parameters is wavelength, which determines the energy level of photon packages. The process of photochemical degradation of a molecule occurs at suitable wavelengths and energy levels. During this process, the energetic photon packages collide with and absorbed by the molecules of the contaminants. Energy absorption excites the molecules. An excited molecule that tends to achieve sustainability may eliminate excess energy from various inactivation pathways. During the liberation of energy, physical or chemical changes occur. These events may occur in a completely separate molecule or in a molecule present in a complex compound.[13] Among different methods for removing atrazine, studies have been done on the use of UV rays. Studies in this field have often used oxidants, such as H_2O_2, HSO_5^-, $S_2O_8^{2-}$, and chlorine with UV radiation, in which atrazine degradation would occur through advanced oxidation reactions.[1, 14] Indeed, by-products produced by photo-degradation using UV alone have been less investigated in these studies. Hence, the present study aims to investigate the photo-degradation of atrazine under UV radiation with a wavelength of 254 nm and to assess the impact of effective parameters (pH, initial concentration, volume, time, and lamp power) on the removal efficiency. Considering the importance of the produced products, the compounds created as the ultimate products of the photo-degradation process are going to be identified and investigated, as well.

Materials and Methods

Chemicals

A standard solution of atrazine with a purity of 99.9% was purchased from Sigma Company. Acetonitrile, methanol, and special High Performance Liquid Chromatography (HPLC) water were purchased from Merck Company. All solutions were prepared on a daily basis. Deionized water was used to prepare the solutions.

Sample Preparation

In order to prepare atrazine solutions to increase the water solubility of atrazine, atrazine was first dissolved in methanol and then, water was added to it. Based on the one factor at a time method, sample size was 40 samples. All experiments were carried out on 100 ml of atrazine solution and in a discontinuous Pyrex photo-reactor with a volume of 250 ml and a cross-section of 50.24 cm² at ambient temperature. HCl, NaOH (1N), and pH meters (Metrohm, 827 pHlab, Swiss mode) were used to adjust pH. The prepared specimens were directly exposed to 6 (WT8/UVC, Narva), 15, 30, and 125-watt lamps to prevent UV absorption by the Pyrex container.

Examining the Effective Parameters in Atrazine Removal

In order to assess the effect of the initial concentration of the contaminants, atrazine solutions (100 cc) were prepared at 10, 30, 50, and 100 mg/l concentrations. After adjusting the pH at 7, the solutions were exposed to 6, 15, 30, and 125-watt lamps for an hour. In all experiments, the volume of the solution used in 250-ml Erlenmeyer flask was 100 ml. The effect of pH (3, 5, 7, and 9) on the degradation efficiency was investigated by keeping the initial concentration constant (50 mg/l) in a volume of 100 cc under the irradiation of 6- and 125-watt lamps for an hour. The effect of solution volume (100, 200, and 500 cc) was investigated by considering the initial concentration of 50 mg/l, pH=7, and time of 60 minutes under the radiation of 6- and 125-watt lamps. In order to investigate the effect of time on the degradation of atrazine, samples were taken from the solutions at pH=7, initial concentration of 30 mg/l, and irradiation of 6 and 125 watts with 5, 15, 30, 45, 60, and 90-minute intervals. The volume of each sample taken for injection into the HPLC machine was 2 ml. To investigate the effects of different parameters on the removal efficiency, at each stage, one of the parameters was changed and the others were kept constant and the removal efficiency was calculated.

Analysis Method

HPLC method was used for quantitative analysis of the remaining atrazine in the solution after the photolysis process. In doing so, the samples were filtered through a 0.22 μm pore size filter before injection into the HPLC. The specimens were then injected into the HPLC (Azura) equipped with a Diode Array Detector (DAD) to measure atrazine values. Column C18 (KNAUER) (250×4.6 mm) was used as the constant phase. Besides, acetonitrile and pure water at a 55:45 ratio and a flow rate of 1 ml/min was used as the mobile phase. All specimens were injected under the same conditions at a volume of 20 μl, 40 °C, and a 254 nm wavelength.

Examining the by-Products of Photolysis

In order to identify the by-products produced

during the photolysis process, a sample was extracted after an hour of irradiation under a 125-watt lamp and was injected into a Gas Chromatography/ Mass Spectrometry (GC-MS) (Agilent Technology) equipped with an Agilent Technology 59777B model from MSD series Mass Detector and an HP-5 ms column (3.0 m×0.25 mm×0.25 μm particle size). Extraction was carried out via Dispersive Liquid-Liquid Method (DLLME) using chlorobenzene organic solvent.[15] The detected compounds by GC-MS analysis were looked up in original Pest, NIST 14, and Wiley libraries.

Results

The initial concentration of atrazine, as a target contaminant and lamp power as the degradation factor, are among the most important parameters in the removal of atrazine. The effect of UV lamp (6, 15, 30, and 125 watts) on atrazine removal at three concentrations of 10, 50, and 100 mg/l at 1 hour has been shown in Figure 1. Based on the results, the degradation efficiency was 92% using a 6-watt lamp at the concentration of 10 mg/l. By increasing the concentration to 100 mg/l, the removal percentage was reduced to 32.9%.

In photolysis with higher-power lamps radiation also, the difference in efficiency reduced at different concentrations. The difference in the efficiency of 6- and 125-watt lamps was 59% and 11.5% at 10 mg/l and 100 mg/l concentrations, respectively. According to Figure 1, at the initial concentrations of 10, 50, and 100 mg/l, the removal of atrazine was 100%, 98.3%, and 88.5%, respectively using a 125-watt lamp. However, the degradation efficiency at similar initial concentrations was 92%, 61.6%, and 32.9%, respectively using a 6-watt lamp.

Atrazine reduction rate is a function of radiation time. The efficiency of atrazine removal at various times has been expressed in Figure 2. Accordingly,

atrazine removal rate reached 45.6% at 30 mg/l under the irradiation produced by a 125-watt lamp during 5 minutes. After about 15 minutes, atrazine removal rate reached 100%. By increasing time from 5 to 15 minutes, atrazine degradation efficiency increased from 8.3% to 27.5% under irradiation produced by a 6-watt lamp.

One of the most important parameters related to atrazine solution properties is its initial pH. The efficiency of atrazine removal at pH levels of 3, 5, 7, and 9 at the initial concentration of 50 mg/l has been shown in Figure 3. Accordingly, the highest degradation efficiency at pH=5 was 63.7% and 84.7% using 6- and 125-watt lamps, respectively. The removal process at different pH levels showed that pH had no significant effects on the process of atrazine degradation via a UV lamp.

The main factor in the photolysis process is the collision of UV rays and high-energy packages with contaminants molecules and their degradation. In order to investigate the effect of the solution volume, the removal efficiency was investigated at volumes of 100-500 cc. According to Figure 4, increase in the solution volume, despite continuous mixing during the radiation, led to a reduction in the degradation efficiency. By increasing the volume of the solution from 100 to 500 cc, the efficiency of atrazine photolysis decreased by 40.7% and 5.5%, using 6- and 125-watt lamps, respectively.

In addition to examining the removal efficiency and the impacts of effective parameters, monitoring and studying the final products and by-products produced during the removal process is important. Thus, the lateral and intermediate products produced during the photo-degradation of atrazine were investigated in the present study.

Chromatograms of the HPLC before and after 6- and 125-watt radiations at the 30 mg/l concentration
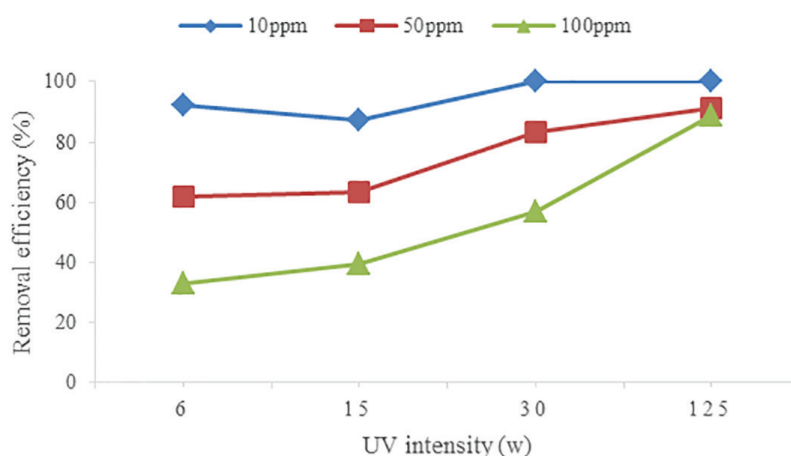
Figure 1: The effect of lamp power on atrazine removal (time=60 min, pH=7, volume=100 cc, concentration=10, 50, 100 mg/l)
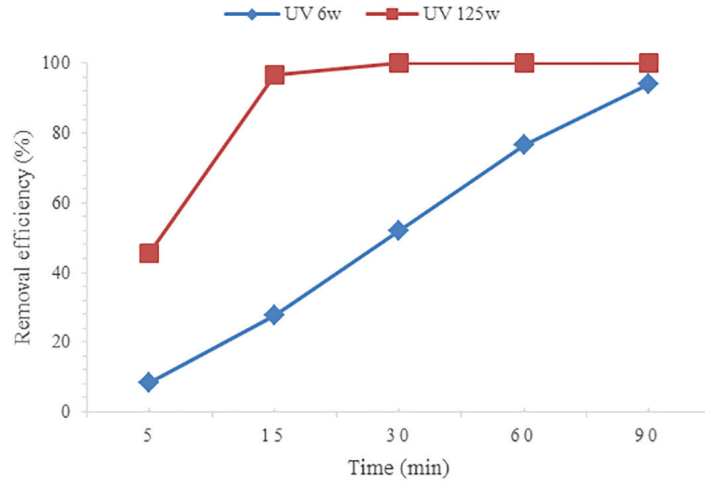
Figure 2: The effect of time on the efficiency of atrazine removal (concentration=30 mg/l, pH=7, volume=100 cc)
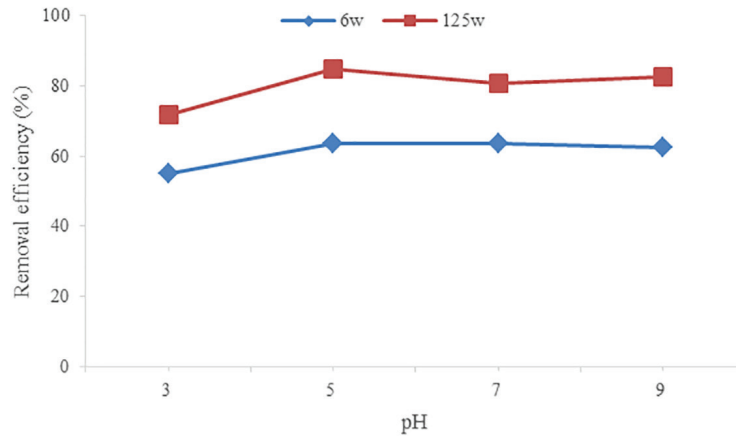

Figure 3: The effect of pH on the efficiency of atrazine removal (time=60 min, concentration=50 mg/l, volume=100 cc)
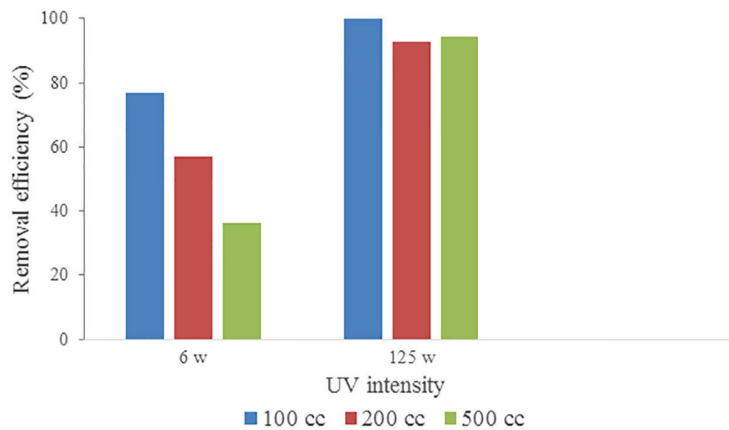

Figure 4: The effect of solution volume on the efficiency of atrazine removal (time=60 min, concentration=30 mg/l, pH=7)

have been shown in Figure 5. A characteristic peak can be observed at 6.8 min, which is attributed to atrazine. Chromatograms obtained from injection of the same specimens after radiation of 125 watts to the GC-MS device have been presented in Figure 6. The detected compounds were identified after investigating GC-MS output peaks and searching in specialized libraries. Names and retention times of these compound have been shown in Table 1. Atrazine peak was observed at 19.8 min. For more certainty, all observed peaks during the study time were investigated to determine the
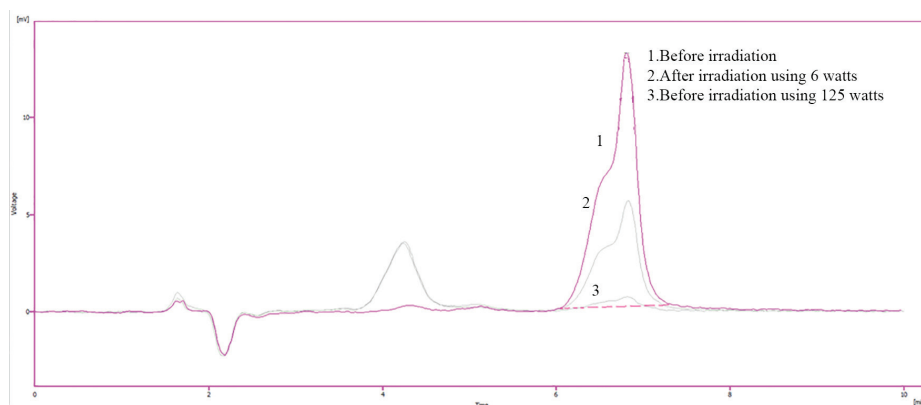
Figure 5: The chromatogram of the HPLC before and after radiation (time=60 min, concentration=30 mg/l, pH=7, volume=100 cc)
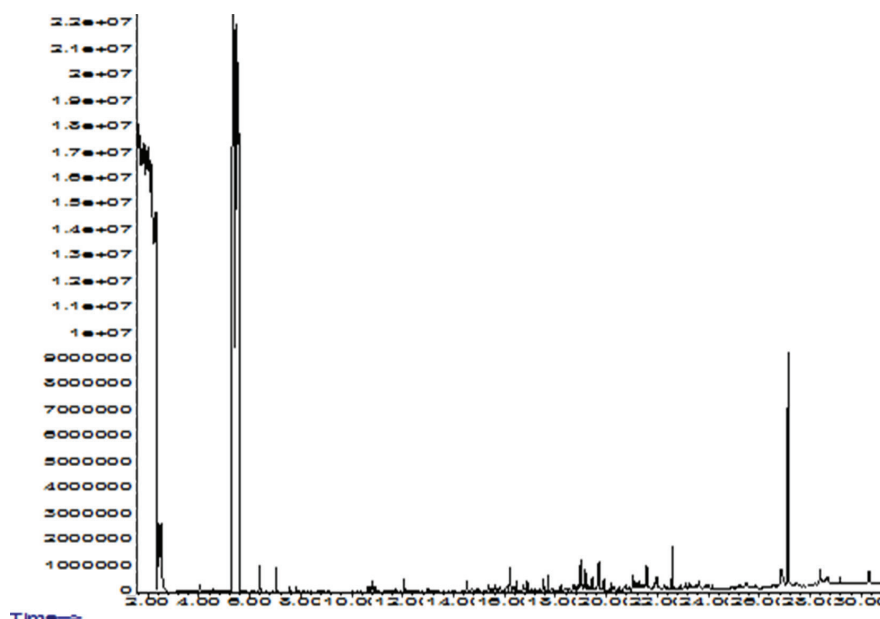

Figure 6: The chromatogram of atrazine photolysis under 125-watt radiation (time=60 min, concentration=30 mg/l, pH=7, volume=100 cc)

Table 1: By-products of atrazine photolysis under 125- and 6-watt UV

Peak NO.	Chemical name	Molecular formula	Retention time
1	Hexadecane	$C_{16}H_{34}$	17.77
2	Atrazine	$C_8H_{14}ClN_5$	19.8
3	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	21.96
4	Ethanone,1-(9-anthracenyl)	$C_{16}H_{12}O$	22.58
5	Diisooctyl phthalate	$C_{24}H_{38}O_4$	27.13

by-products or similar structures containing triazine ring, but none of them was found. The structural form of the atrazine molecule has been depicted in Figure 7. In the present study, the appeared peak at 5.99 minutes was attributed to chlorobenzene, an organic solvent used in DLLME process. A few shorter peaks at 6-8 minutes were related to some chlorobenzene impurities, such as Ortho Dichloro Benzene. Indeed, the observed peaks at 17.7, 21.9, 22.58, and 27.13 minutes might be related to Hexadecane, n-Hexadecanoic acid, Ethanone,1-(9-anthracenyl), and Diisooctyl phthalate, respectively.
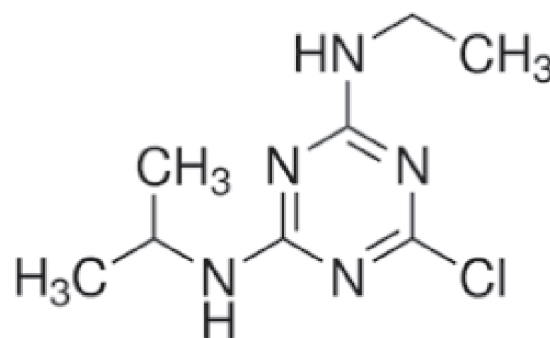

Figure7 : The molecular structure of atrazine

Discussion

Efficiency reducing by increasing the initial concentration might be attributed to the probable increase in the concentration of by-products and intermediate active species. Increase in the concentration of active species in the solution leads to competition in the absorption of photon packages, which reduces photon interactions with atrazine molecules and reduces their degradation.[16, 17] Chen et al. used photolysis to remove glabridin. They found that by increasing the initial concentration of the contaminant from 5 mg/l to 60 mg/l, the fixed rate of degradation was reduced to 0.33 per hour.[18]

The relationship between power of the lamp and efficiency may be due to increasing photons or energy packages by increasing the power of the lamp. Thus the total radiated energy is increased, eventually leading to higher photo-degradation. Another process that is likely to occur in addition to photolysis in the solution is the oxidation process by the free radicals generated during the radiation. Decomposition of water molecules due to the increase in the radiated energy results in production of more hydroxyl radicals, which causes more oxidation. Modirshahla et al. examined the effective parameters in malachite green photo-degradation by increasing the lamp power. They observed an increase in removal efficiency.[19] Kong et al. also compared the effect of increased UV radiation intensity in two states of photolysis of atrazine using UV radiation alone and in combination with chlorine. They found that increasing the radiation intensity from zero to 1000 mJ/cm^2 reduced the ratio of final concentration to the initial concentration of atrazine by about 0.7 and 0.9 in photolysis with UV alone and UV with chlorine, respectively. They stated that the difference in the rate of efficiency was related to different processes of removal in photolysis using UV alone and UV with chlorine. In the atrazine removal using UV with chlorine, the dominant process is oxidation. Accordingly, by increasing the intensity of irradiation and radiated energy, more hydroxyls are formed.[1]

According to the results, the optimum time for 6- and 125-watt lamps was 90 and 15 minutes, respectively. Imoberdorf et al. conducted a kinetic study on modelling of 2, 4-D photo-degradation and concluded that increase in radiation time resulted in a decrease in the rate of contaminant degradation. This could be due to the increased concentrations of by-products and competition in the reaction with hydroxyls.[20] Since UV lamps often have a certain lifetime, decreasing the time and increasing the lamp power determines the optimal application conditions of the lamp.[21]

Degradation of atrazine under UV light irradiation without the presence of oxidants acted independently of the pH effect. Lack of dependence on pH in the photolysis process can be mainly consistent with quantum yield and molar absorption coefficient, which is comparable to atrazine produced under different pH conditions. Kong et al. confirmed the independence of atrazine removal efficiency from pH.[1]

Results showed that efficiency and volume have a relationship inversely. Increasing the contact duration, using a high power lamp, and more mixing would compensate for the reduction of efficiency. Ye et al. also increased the solution volume from 1 to 3.5 liters and found that the fixed removal rate and the volume were reversely related to the coefficient of determination (0.9).[22] The necessary condition for photo-degradation is the absorption of UV rays by atrazine molecules. There is a direct relationship between radiation penetration in the solution and the ability to transfer water. Some parameters, such as solution heights, have an effect on the ability to transfer radiation in solution. In another study, Ye et al. investigated some of these parameters, such as reactor heights, impurities, and solution concentrations. They found that increasing these parameters was accompanied with a decrease in the rate of UV quanta emission to the contaminant molecules that were far away from the lamp.[23]

It should be noted that MS spectrum of by-products of atrazine photolysis process in other studies, such as atrazine-2-hydroxy (HAT),[24] desisopropylatrazine (DEA), deethylatrazine (DIA),[21] and hydroxyatrazine (OIET),[25] was expected to appear near the atrazine peak. Despite searching in all main libraries, no matched peaks with the above-mentioned compounds' structures or with similar structures were found. Due to the lack of common organic by-products, the appropriate efficiency of the employed direct photolysis process was confirmed. This process might progress to mineralization, resulting in conversion of organic compounds to mineral products. It can be mineralized to carbon dioxide, water, and inorganic mineral ions.[2] Although there are chlorine and nitrogen atoms in the molecular formula of atrazine, GC-MS analysis in the current study revealed no organic compounds containing nitrogen and chlorine atoms. This difference in the chemical formula of the reactants and products might indicate the transformation and conversion of these atoms to other compounds during photolysis. The final proposed form for chlorine atom is chlorine ion and the final form for nitrogen atom is involvement in ammonium and nitrate molecules. Xu et al. induced electron beam to remove atrazine. They found that atrazine was mineralized completely without any by-products.[26]

Mentioned appeared peaks are related to compounds resulted from commercial atrazine impurities. In order to prove this point, an atrazine sample at the concentration of 30 mg/l, as the reactor

input, was analyzed using GC-MS before treatment. Observing the aforementioned peaks before and after treating the samples confirmed the presence of impurities in commercial atrazine.

In similar studies, seven different mechanisms, namely de-alkylation, dechlorination-hydroxylation, alkylic-hydroxylation, alkylic-oxidation, olefination, deamination-hydroxylation, and dechlorination-hydrogenation, have been considered for the degradation of atrazine.[2] Jain et al. reported that among these mechanisms, dechlorination processes were the dominant mechanisms in photolysis using UV rays.[27] Khan et al. also studied the mechanisms and by-products of photochemical processes of atrazine. They reported that chlorine-containing by-products were the major factor in the toxicity of chlorine compounds due to the similar function with biochemical processes and the disruption of target tissues.[28] Due to the fact that the chlorine atom is removed from the combination in the dominant mechanism of dechlorination and the final products also lack the chlorine atom, it can be said that the toxicity of the atrazine molecule decreases via photo-degradation.

Conclusion

The photolysis of atrazine was investigated under UV irradiation with a wavelength of 254 nm in different powers. The final products were evaluated, as well. The results revealed that the initial concentration of atrazine was significantly reduced by UV radiation. The results also showed that photo-degradation of atrazine with UV radiation alone was independent of pH. The degradation efficiency was 92% using a 6-watt lamp at the concentration of 10 mg/l. Atrazine concentration at the initial concentration of 30 mg/l decreased by about 97% after 125 watts of radiation for 15 minutes. Investigation of the final products of direct photolysis reactions showed the re-combination of molecules and active intermediate products and the formation of long-chain hydrocarbons. Moreover, the absence of chlorine and nitrogen in the final products expressed the mineralization of a part of atrazine molecules. As a result, photolysis could be used along with other purification methods to remove atrazine.

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Conflict of Interest: None declared.

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