Photodegradation of Atrazine by Ultraviolet Radiation in Different Conditions

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Abstract

Background: Atrazine is one of the most widely used triazine herbicides which has been used for controlling broadleaf and grassy weeds for many years. Its widespread use in water has caused environmental concern because of frequent detection of atrazine in aquatic systems where this herbicide has been spilled. Therefore, the purpose of this study was to determine the herbicide removal efficiency at the optimal conditions.

Methods: The effect of different parameters including pH at three different levels (3-11), the initial concentration of atrazine at three different levels (0.1-10 mg/L), and reaction time at five different levels (0-120 min) on the removal of atrazine in the aqueous phase using ultraviolet radiation (1020 µw/cm^2) was investigated. Finally, the data were analyzed using SPSS software (version 16).

Results: The results demonstrated that atrazine removal rate increased by increasing pH, initial atrazine concentration, and reaction time. The maximum rate of atrazine removal (99.2%) at optimal condition occurred in pH=11, atrazine concentration=10 mg/L at 30 min.

Conclusion: According to the findings, it can be concluded that the UV-A process is an effective and commodious method for reducing atrazine in polluted water resources.

Introduction

The contamination of surface waters with atrazine herbicide is mainly caused by surface runoff from agricultural activities.[1] Atrazine is a triazine herbicide (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) mostly used in controlling many broad-leaf and grassy weeds in maize fields.[2,3] It is also applied as an agricultural herbicide on crops such as sorghum and horticultural and forests as well.[4] Atrazine enters plants through roots and leaves and inhibit photosynthesis via the blockage of electron transport.[4,5] It was the most widely used herbicide worldwide because of its low cost and effectiveness.[6,7]

Moreover, atrazine is persistent in different environmental media and is hardly biodegradable; it can remain in soil and aquifers for many years after its application.[8] The half-life of atrazine is between one to twelve months;[9] as a result, it may cause deleterious environmental impact.[10] Atrazine is one of the most common contaminants of waters resources.[11]

Atrazine with low volatility and moderate water solubility of 33 mg/L at 25 ºC has relative mobility and leaching properties in soil; therefore, it has a high potential to contaminant the groundwater resources.[12] Many reports showed that atrazine herbicide is frequently detected in many water resources due to its widespread application.[13,14]

Atrazine is reported to bean endocrine disruptor herbicide with the evidence of carcinogenicity in laboratory animals (Group 2B carcinogen).[11,15] The other toxicological effects of this herbicide are heart stroke, lungs claps, kidney disorder, low blood pressure, muscle spasm, weight loss, and damage to the adrenal gland.[10] The maximum contamination level (MCL) for atrazine in drinking water is suggested 3.0

µg/L by the USEPA.[11]

There are many different methods for the removal of atrazine and its related metabolite from the aqueous environment such as biodegradation,[10,16] adsorption,[17] oxidation by ozone, or Fenton reagents, direct and catalyzed photolysis, and sonication.[16]

The oxidation of atrazine or other pesticides breaks down the organic molecule into smaller compounds, or completely mineralizes them to CO_2 and H_2O. The most common oxidation processes are ozone (O_3), hydrogen peroxide (H_2O_2) and ultraviolet (UV) photo oxidation.[18-20] Ultraviolet treatments are mostly used for treatment of drinking water as disinfectant with the lowest potential for the formation of disinfectant by-products.[21] However, the UV source has to be carefully chosen in order to ensure that the spectrum emitted by the lamp is best suited for its application.[22] Bushnqe and colleagues showed that the atrazine removal rate at concentration of 5 mg/L, in the presence of UV-A radiation with the intensity of 1.25 mw is at 11% after 5 hours.[17] Fogarty and colleagues showed that photocatalytic oxidation of ciprofloxacin under UV-LED light was 98% after 60 min and the maximum degradation occurred in the first 20 min of reaction time.[21] Dehghani and colleagues demonstrated that the maximum removal rate (38%) of penicillin G using UV-A radiation with the intensity of 8 W occurred in pH=3 and antibiotic concentration of 10 mg/L.[23]

Since atrazine is persistent in the environmental media and is hardly biodegradable, the feasibility of atrazine pollution in water resources is extremely high. In addition, atrazine is an endocrine disruptor with the potential of carcinogenicity; there is much concern about its effect on human health. Fars province has the top rank in the production of wheat and corn in the country. According to the records, during the last few decades atrazine has been frequently used. Several studies were conducted in this respect, but no study was done on the efficiency of UV-A process for the removal of atrazine herbicide in the aqueous solution. Therefore, the main objective of this study was to determine atrazine removal efficiency at the optimal condition.

Materials and Methods

This study was done in 2015 in Shiraz. The experiment was replicated twice in batch mode. The study parameters were pH, initial atrazine concentration, and reaction time. One factor at the time of designing the study was used for analysis of the parameters and their interaction effects were studied as well. All data were presented based on the mean.

Chemicals and Analytical Method

Atrazine with 99.9% purity was purchased from Sigma Aldrich Company (USA). Other chemical products were purchased from Merck (Germany). UV lamp, 1020 µw/cm² was used as the radiation source.

For atrazine detection in the aqueous phase, a Waters Model high performance liquid chromatography (HPLC) (Waters YL9100HPLC SYSTEM, USA) system with C18 columns (CP-SIL 5 CB column model, 250*4.6 mm, 5 µm) was calibrated and tested prior to the injection of samples. The mobile phase included methanol and water (20/80 V/V) with a flow rate of 0.5 mL/min. A UV absorbance detector at 224 nanometer wave length was used to detect atrazine in the samples.

Reactor Specification

The specification of photochemical reactor is shown in Figure 1.The experiment was performed in a 1-liter volume reactor. The test was performed in a closed glass reactor with adjustable mixer. The source of radiation was a UV lamp which was protected by a Quartz tube. The UV radiation source was immersed
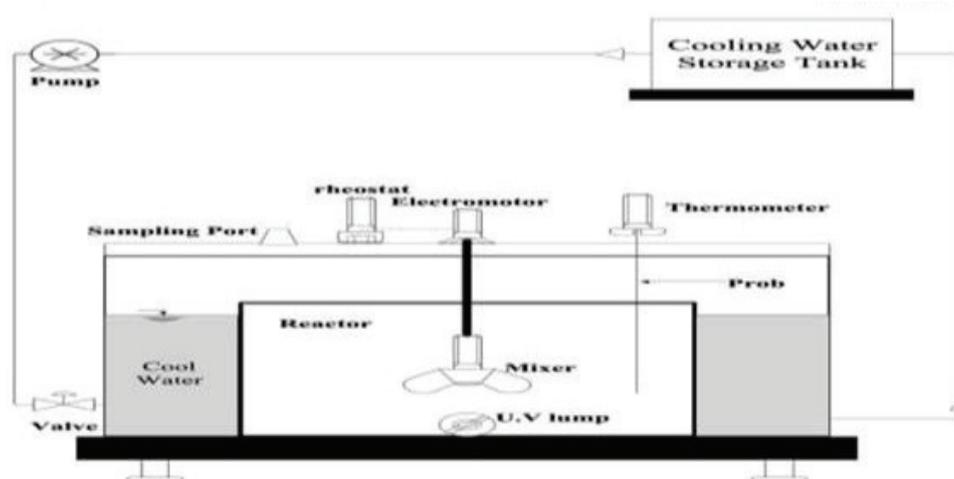

Figure 1: The specification of photochemical reactor

in the solution for better radiation. The whole system was wrapped in an aluminum foil in order to prevent reflection.

Effects of pH, Initial Atrazine Concentration and Reaction Time on the Removal Rate of Atrazine by UV-A Process

To measure the effect of different parameters on the removal rate of atrazine by UV-A process in the aqueous phase, different parameters such as pH)11–3 (, initial atrazine concentration (0.1, 1, and 10 mg/L) similar to another study,[24] and the contact times of 0, 30, 60, 90 and 120 min were studied. The samples were passed through a Whatman filter cellulose acetate membrane with 0.22 micron pore size (Germany). After that, the residual atrazine was determined by HPLC. All the experiments were performed in two replications in the presence of the control samples. Finally, SPSS software(version16) with repeated measures was used to analyze the data.

Results

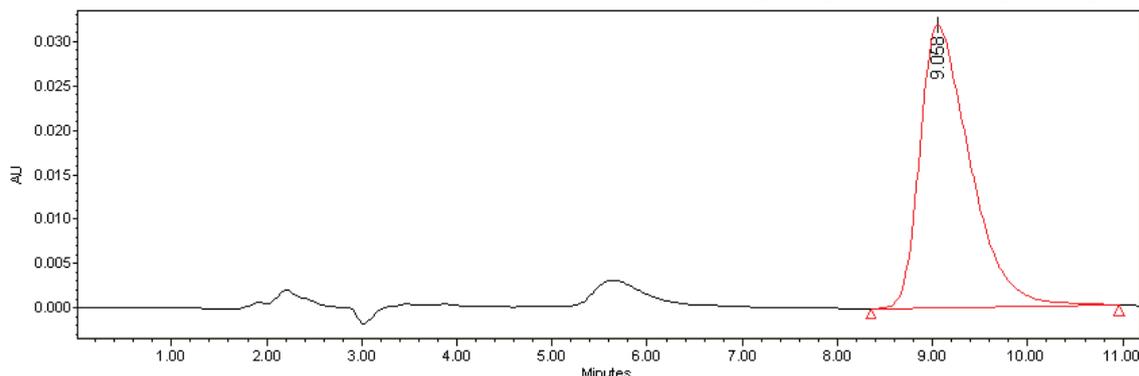The retention time for the atrazine was 9 minutes. The

detection limit for the sample was 0.001 mg/L. Atrazine chromatogram is presented in Figure 2.

The photodegradation of atrazine using UV-A is shown in Figures 3-5. In addition, the effect of pHon the removal efficiency is shown in Figure 3.

According to Figure 3, the maximum and minimum removal efficiency of atrazine occurred at pH of 11 and 7, respectively. Furthermore, the maximum removal efficiency (99.2%) occurred at pH=11, initial atrazine concentration of 10 mg/L and the reaction time 30 min. However, the results of regression analysis showed that there was no linear relationship and significant difference between the atrazine removal rates and pH ($P>0.05$).

According to Figure 4, the maximum removal rate of atrazine occurred at initial atrazine concentration of 10 mg/L (99.2%) and atrazine removal rate increased by increasing the initial atrazine concentration. However, the results of regression analysis showed that there was no linear relationship and significant difference between the atrazine removal rates and initial atrazine concentration ($P>0.05$).

According to Figure 5, at first the photodegradation
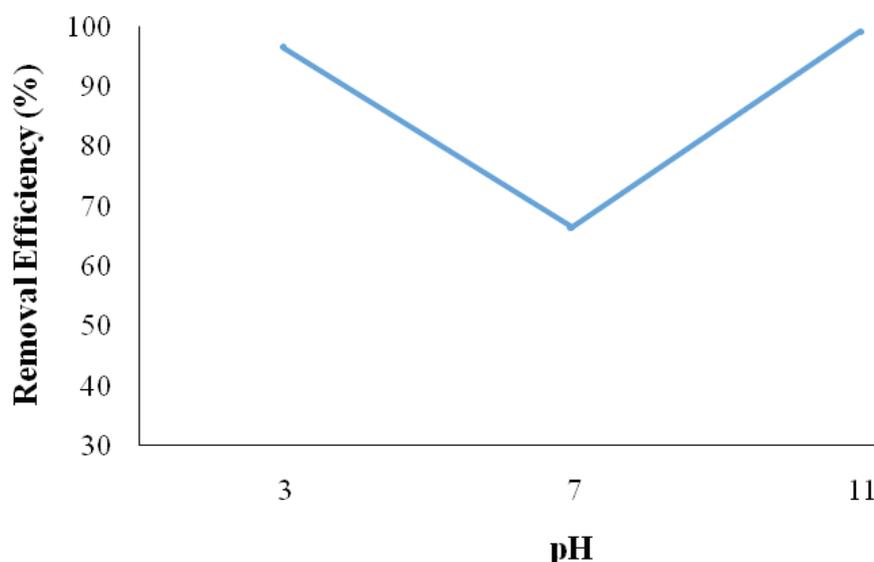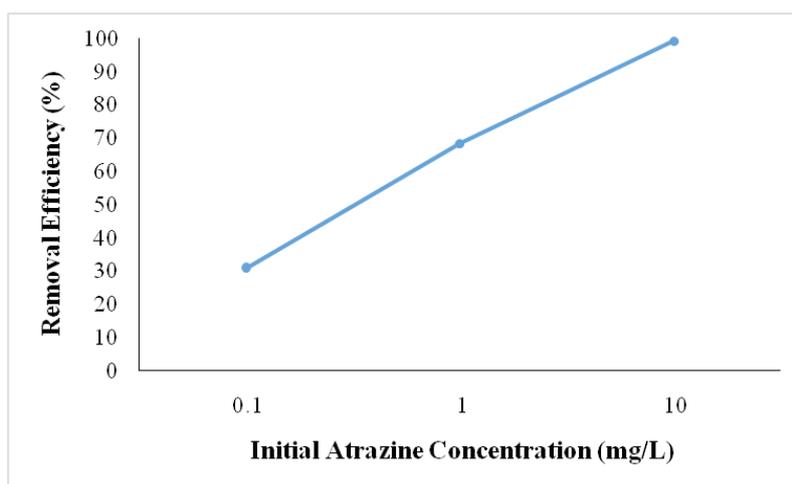

Figure 2: Atrazine chromatogram

Figure 3: Effect of pH on the removal efficiency of atrazine by UV-A process(In this condition, initial atrazine concentration was 10 mg/L and reaction time was 30 min).

Figure 4: Effect of initial atrazine concentration on the removal efficiency of atrazine by UV-A process(In this condition, pH was 11 and reaction time was 30 min).
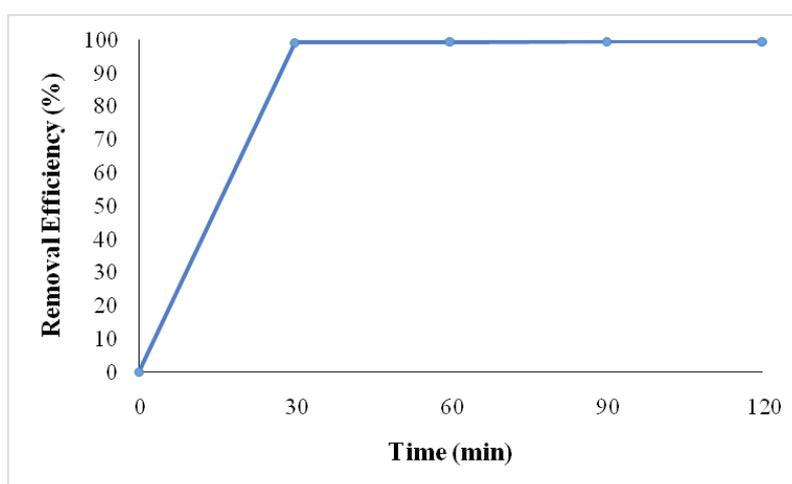

Figure 5: Effect of reaction time on the removal efficiency of atrazine by UV-A process (In this condition, pH was 11 and initial atrazine concentration was 10 mg/L).

of atrazine was very fast (30 min reaction time) and then it became slower until it reached the plateau (120 min). The results showed that the removal efficiency of atrazine increased with time and it reached 99.53% removal at 120 minutes. However, the results of regression analysis showed that there was a significant difference between the atrazine removal rates and reaction time ($P<0.05$).

Discussion

The optimization of influencing parameters including pH, initial atrazine concentration and the reaction time on the removal of atrazine herbicide from the aqueous phase using ultraviolet radiation (UV-A) process was studied in the current research.

Effect of pH on the Removal of Atrazine from the Aqueous Phase Using UV-A Process

pH is one of the most important factors that have an effect on the efficiency of many chemical and biological processes.[23] It has a significant role in the production of hydroxyl radical (OH°) as well. This *radical* has been shown to *oxidize many* different recalcitrant organic pollutants into *mineral end-products*.[25]

Our data showed that the maximum removal rate of atrazine occurred at alkaline condition (pH=11) due to the formation of high concentrations of hydroxyl radical.[26] It can be assumed that atrazine is degraded in this study through two possible ways including direct photolysis by UV-A radiation and oxidation by OH° radicals.[27]

A study conducted by Dehghani and colleagues showed that better removal of penicillin G occurred at acidic condition (pH=3)using UV-A radiation and the removal rate of antibiotic decreased by increasing pH.[23] But many other studies demonstrated that better removal of atrazine occurred at higher pH levels.[17,28] Bushnqe and colleagues showed that pH does not play an important role in direct photolysis of atrazine and the removal rate increased by increasing pH.[17] Prado and colleagues also showed that the maximum removal rate of atrazine is at pH=11.5

using ozonation process and the removal rate of atrazine increased as pH increased.[28] This result agrees with the research performed by Bushnqe [17] and Prado and colleagues.[28]

Effect of Initial Atrazine Concentration on the Removal of Atrazine from the Aqueous Phase Using UV-A Process

The maximum photodegradation of atrazine was related to the initial concentration of 10 mg/L. We also found that increasing the *atrazine concentration* led to *higher* photodegradation *rates* of the herbicide and followed first order *kinetic.[29]* The results of Baghapour and colleagues study[24] indicated that the removal efficiency increased with increasing the concentration of atrazine and the highest removal efficiency was obtained at atrazine concentration of 10 mg/L which was in the same line with the results of this survey. At the higher concentration of pollutant, the rate of atrazine removal was higher due to higher kinetic. However, Dehghani and colleagues[23] and Hemati and colleagues[26] reported that removal efficiency decreased by increasing the initial concentration of penicillin G and phenol.

Effect of Reaction Time on the Removal of Atrazine from the Aqueous Phase Using UV-A Process

This phenomenon may be related to the higher chance of atrazine photodegradation when the exposure time to the UV-A radiation is increased and more oxidation reaction proceeds in the presence of hydroxyl radicals as well. In fact, the reaction rate at equilibrium reached a plateau. Moreover, determining the required time to reach equilibrium is also very important to have a cost-effective and economical process.[30,31]

Vlaardingerboek showed that atrazine was completely degraded using UV/TiO$_2$after 150 min reaction time.[32] Bahena and colleagues demonstrated that complete oxidation of atrazine occurred at 75 min by TiO$_2$ in the presence of sunlight.[1]

Effect of UV-A Radiation on the Removal of Atrazine from the Aqueous Phase Using UV-A Process

The maximum rate of atrazine removal (99.53%) using UV-A radiation with 1020 μw/cm^2 occurred in pH=11 and atrazine concentration of 10 mg/L. Several studies have been done on the removal of pollutants using UV-A radiation with different intensities.

Bushnqe and colleagues showed that the atrazine removal rate at a concentration of 5 mg/L, in the presence of UV-A radiation with the intensity of 1.25 mwwas 11% after 5 hours.[17]

Dehghani and colleagues demonstrated that the maximum removal rate (38%) of penicillin G using UV-A radiation with the intensity of 8 W occurred in pH=3 and antibiotic concentration of 10 mg/L.[33]

Conclusion

Since atrazine is an endocrine disruptor herbicide with the evidence of carcinogenicity in laboratory animals (Group 2B carcinogen) and has been frequently detected in many waters resources, a method is needed to removes atrazine in a safe way so that UV-A process can remove more than 99% of atrazine from aqueous phase.It can be concluded that the UV-A process is an effective and commodious method for reducing atrazine in polluted water resources.

This study showed that the UV-A process can significantly reduce the concentration of atrazine in the aqueous solution. The results showed that different parameters (pH, initial concentration of atrazine and reaction time) affect the removal rate of atrazine. Moreover, the removal efficiency of herbicide increased by increasing the studied parameters. The maximum removal rate (99.53%) was achieved at pH=11 and 120 min reaction time.

Limitation

Because of the limitations of our budget for the current study and high cost of the analysis with HPLC, the effect of different parameters on the removal of atrazine from the aqueous phase was studied. Therefore, it is recommended that the future studies focus onthe effect of different intensities of UV lamp on the removal efficiency. Also, the effect of the lower initial atrazine concentration could not be determined because the detection limit of atrazine with the HPLC was 0.001 mg/L.

Acknowledgment

Conflict of Interest: None declared.

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