American Journal of Analytical Chemistry, 2014, 5, 500-517
Published Online June 2014 in SciRes. http://www.scirp.org/journal/ajac
http://dx.doi.org/10.4236/ajac.2014.58059

Scientific Research

Investigations on the Degradation of Triazine Herbicides in Water by Photo-Fenton Process

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Received 16 April 2014; revised 31 May 2014; accepted 15 June 2014

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Abstract

In this work, the degradation of 2-chloro-4,6-diamino-1,3,5-triazine in aqueous solutions by photo-Fenton process has been investigated. The preliminary results have shown that the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process is more rapid and more effective than Fenton and UV/H_2O_2 processes. The effects of certain experimental parameters on kinetics and efficiency of the degradation of 2-chloro-4,6,-diamino-1,3,5-triazine by photo-Fenton process, have been evaluated. Under optimal conditions, photo-Fenton process achieved more than 90% of chloride release and about 30% of nitrate formation. The results of total organic carbon (TOC) and total Kjeldahl nitrogen (TKN) analyses have shown that no carbon dioxide and ammonia are formed during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. These results indicate that only substituent groups of triazine ring are released; however, nitrogen atoms of triazine ring remain unaffected. A simple mechanism of degradation of 2-chloro-4,6-diamino-1,3,5-triazine has been proposed. The degradation starts by a rapid release of chlorine atoms as chloride ions to form 2-hydroxy-4,6-diamino-1,3,5-triazine. The amino groups of 2-hydroxy-4,6-diamino-1,3,5-triazine undergo are oxidized into nitro groups by hydroxyl radicals to form 2-hydroxy-4,6-dinitro-1,3,5-triazine which undergoes a slow release of nitro groups and their substitution with hydroxyl groups to form cyanuric acid and nitrate ions. The degradation of cyanuric acid by photo-Fenton process has also been investigated. The results of TOC and TKN analyzes show that no carbon dioxide is formed during the treatment.

Keywords

Photo-Fenton Process, Hydroxyl Radicals, s-Triazine Herbicides, Degradation, Cyanuric Acid

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How to cite this paper: Dbira, S., Bedoui, A. and Bensalah, N. (2014) Investigations on the Degradation of Triazine Herbicides in Water by Photo-Fenton Process. *American Journal of Analytical Chemistry*, **5**, 500-517.
http://dx.doi.org/10.4236/ajac.2014.58059

1. Introduction

Pesticides are chemical substances widely used in agriculture to fight against different types of organisms that are harmful (bacteria, insects and weeds) for crops [1]-[3]. Pesticides are xenobiotic, toxic and non-biodegradable and can cause serious problems to human health and environment [4]-[6]. Herbicides constitute the principal class of pesticides especially used in agriculture to protect the crops plant against weeds. The class of s-triazine is the largest proportion of herbicides used in agriculture and horticulture. S-triazines are hetero-aromatic rings substituted with amino ($-NH_2$) and chloro (-Cl) groups. The hetero-aromatic rings contain alternately three nitrogen atoms and three carbon atoms. If nitrogen atoms are in positions 1,3,5 of hetero-aromatic ring, it is known as s-triazine ring. The chemical structures of s-triazines are given in **Figure 1**. Atrazine, simazine, cyanazine, prometon, propazine are the common triazines utilized in agriculture and horticulture. Atrazine is very commonly used to fight against weeds in crops and public gardens. Triazine herbicides are persistent, toxic and bio-resistant in the environment and have been detected in drinking water [3]-[9]. It is essential to find an effective and economic method of treatment capable to completely eliminate these pollutants from natural water. However, microbial degradation of triazines herbicides was limited to a partial degradation of these compounds [10]. Conventional physico-chemical methods used for the removal of herbicides from water such as flocculation, filtration and activated carbon adsorption are not suitable to reduce the concentration of s-triazines to concentrations less than maximum contaminant levels regulated by the environmental protection agencies.

Advanced oxidation processes (AOPs) have been considered as promising alternative to conventional methods of water treatment especially when the later fail to completely destroy or remove enough persistent and bio-resistant organic pollutants. Advanced oxidation processes are based on the production *in situ* of free oxidizing radical species mainly hydroxyl radicals ($HO^{\bullet}$). These radicals can be generated by chemical (Fenton (H_2O_2/Fe^{2+}) [11] [12], ozonation at alkaline medium [13], peroxonation (O_3/H_2O_2) [14], photochemical UV/TiO_2 [15] [16] UV/H_2O_2 [17] [18], UV/O_3 [19], photo-Fenton $UV/H_2O_2/Fe^{2+}$ [20] [21], and electrochemical (anodic oxidation, electro-Fenton) [22] [23]. Hydroxyl radicals are powerful oxidants (E° = 2.80 V/NHE), which react immediately and non-selectively with organic pollutants in water which leads in most cases to a complete mineralization these compounds or to transform them into readily biodegradable compounds. Advanced oxidation processes (AOPs) have been effective for the mineralization of several types of organic pollutants such as phenols, polyphenols, aromatic dyes, pharmaceuticals, etc. [24]-[29]. In particular, photo-Fenton UV/H_2O_2 is often successfully used in removing pollutants in various wastewater treatments. This method (Equations (1) and (2)) represents the decomposition of hydrogen peroxide into hydroxyl radical, which occurs through two routes: (1) catalytic decomposition by ferrous iron and (2) photodecomposition by UV irradiation.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{?} + HO^{-} \quad (1)$$

$$H_2O_2 + h\vartheta \rightarrow 2HO^{\bullet} \quad (2)$$

Several researchers have studied the degradation of atrazine by different advanced oxidation processes [30]-[32]. The results showed that atrazine was degraded rapidly with the formation of several intermediates such as 2-chloro-4,6-diamino-1,3,5-triazine and cyanuric acid (see **Figure 1**) [31]. However, this herbicide did not fully mineralize to CO_2, H_2O, Cl^- and NO_3^- (or NH_3). Rather, degradation of atrazine was stopped at 2-chloro-4,6-diamino-1,3,5-triazine and cyanuric acid. Watanabe *et al*. [33] showed that no degradation was obtained by treating cyanuric acid with Fenton's reagent and photolysis UV/TiO_2.

The aim of the present work was to 1) investigate the treatment process of synthetically prepared wastewaters contaminated with two intermediates of atrazine degradation: 2-chloro-4 ,6-diamino-1 ,3,5-triazine and cyanuric acid by photo-Fenton and 2) to evaluate the effects of certain experimental parameters such as H_2O_2 concentra-

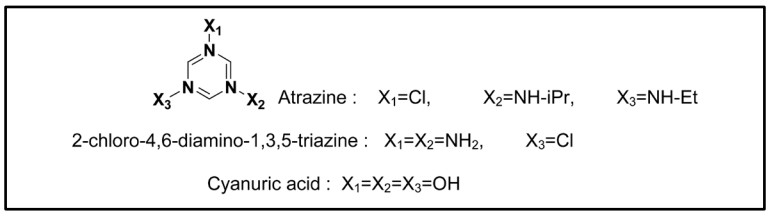


Figure 1. Structures of atrazine and its degradation intermediates.

tion, ferrous iron dose, initial pH, triazine concentration and UV light on the kinetics and efficiency of triazine degradation by photo-Fenton process to find out the optimal degradation and mineralization conditions.

2. Experimental

2.1. Chemicals

2-chloro-4,6-diamino-1,3,5-triazine and cyanuric acid were purchased from Fluka. Hydrogen peroxide was a 30% (w/w) solution (Fluka). Other chemicals such as hyptohydrated ferrous sulfate, sulfuric acid, sodium hydroxide and sodium sulfite were of analytical grade and were purchased from Sigma-Aldrich or Merck. All solutions were prepared with deionized water having 18 $m\Omega \cdot cm^{-1}$ resistivity from a Mill-Q^{TM} system.

2.2. Analytical Method

The formation of inorganic ions (nitrate, nitrite, chloride) was determined using a Dionex ICS 2000 ion chromatograph equipped with an AS autosampler, Ion Pac AG 19 (4 mm × 50 mm) guard column, Ion Pac AS 19 (4 mm × 250 mm) analytical column separation, ASRS 300 mm - 4 mm suppressor, DS6 conductimetric cell and EGC eluent generator. The mobile phase is an aqueous solution of potassium hydroxide KOH prepared by dilution of 1 M aqueous solution of KOH.

The total organic carbon (TOC) and total nitrogen (TN) were monitored with a Skalar Formacs^{HT} TOC/TN analyzer. Absorbance measurements were determined by a Perkin Elmer Lambda 5 UV-Visible spectrophotometer using a quartz cells (1 cm). To eliminate the influence of pH on the variation of UV-Visible spectra, all solutions were used at pH natural.

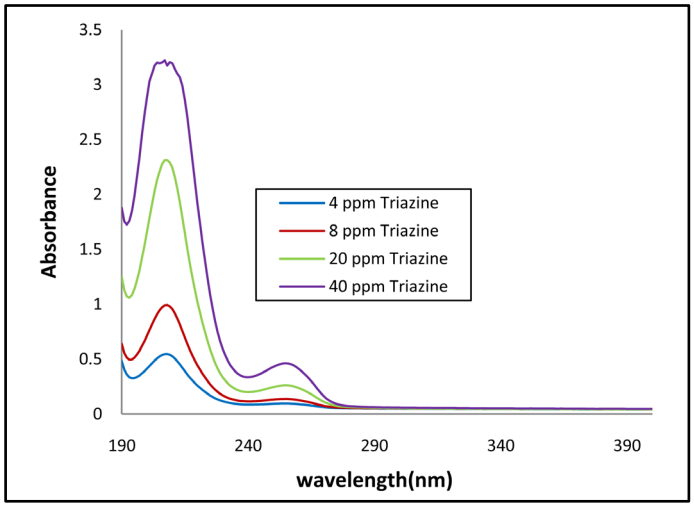
2.3. Photo-Fenton Process

The photochemical experiments were carried out in the reactor equipped with a UV lamp (TNN 15/32, 15 W) mercury vapor a magnetic stirrer and a thermometer. The photo-reactor (pyrex) of 0.5 L (500 mL) capacity was placed in the first part. The lamp was located in an axial position submerged in a vertical immersion tube contained in a vertical cooling tube and immersed in the solution. Water was circulated between the lamp and glass vessel. The experience was mounted on a magnetic stirrer. In this work, only mercury vapor lamps that emit irradiation primarily to about 254 μm coincide with the absorption of our reagent is H_2O_2. All experiments used 500 mL of the solution. The solution pH was adjusted to the desired values by addition of sodium hydroxide or sulfuric acid. After the light of the lamp, a precise amount of hydrogen peroxide 30% was mixed with 500 mL of the solution 10 mL samples were periodically collected. The reaction was quenched with Na_2SO_3, then analyzed immediately to determined pH. The samples were filtered through membranes and injected in the ion chromatograph, TOC and TKN.

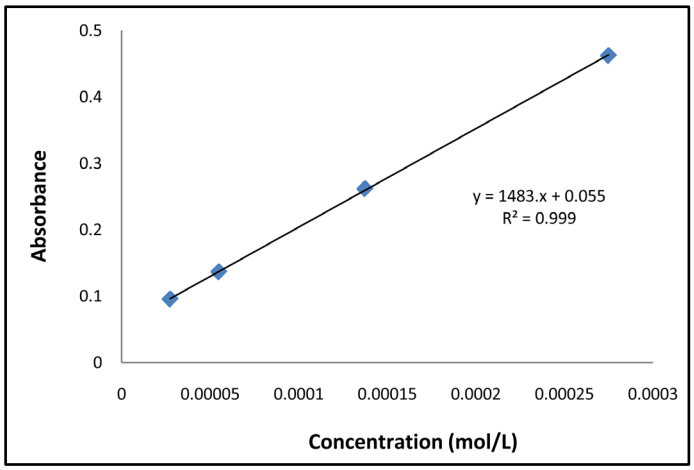
3. Results and Discussion

3.1. Degradation of 2-Chloro-4,6-diamino-1,3,5-triazine by Fenton, Photo-Fenton and UV/H_2O_2 Processes

The degradation of 2-chloro-4,6-diamino-1,3,5-triazine was followed with UV-visible spectrometry, ion chromatography analysis and TOC and TKN measurements. UV-Visible spectra of aqueous solutions containing various concentration of 2-chloro-4,6-diamino-1,3,5-triazine are shown in **Figure 2(a)**. The UV-Visible spectra of 2-chloro-4,6-diamino-1,3,5-triazine presents two absorption bands at 208 nm and 255 nm. The band at 208 nm can be attributed to $\pi \to \pi^*$ transition of the triazine ring. While, the band at 255 nm was most likely due to $n \to \pi^*$ transition in amino groups ($-NH_2$) substituent the triazine ring. The band at 208 nm cannot be used to measure the concentration of 2-chloro-4,6-diamino-1,3,5-triazine because the chemical species initially present in the reaction medium such as H_2O_2, Fe^{2+}, SO_4^{2-} or formed during the treatment by photo-Fenton process such as carboxylic acids, NO_3^- and NO_2^- absorb UV light in the same range from 200 to 220 nm. The band at 255 nm is characteristic of 2-chloloro-4,6-diamino-1,3,5-triazine in water. **Figure 2(b)** shows that the changes of absorbance at the wavelength λ = 255 nm with the concentration of 2-chloro-4,6-diamino-1,3,5-triazine in the field of concentration of 4 - 40 ppm. The change of the absorbance at 255 nm with the triazine concentration is linear curve passing by the origin which indicates that Beer's law is verified. This indicates that non-negligible



(a)



(b)

Figure 2. (a) UV-Visible spectra of triazine in water; (b) Calibration curve at λ = 255 nm.

portion of UV light emitted by the UV-L lamp at 254 nm can be absorbed by triazine molecules. This method was used to measure the concentration of 2-chloro-4,6,-diamino-1,3,5-triazine during the treatment of aqueous solutions containing 40 ppm of triazine herbicide at pH 3 by Fenton, photo-Fenton and UV/H_2O_2 processes as a function of time using 4000 mg/L H_2O_2 in absence and presence of 5 mg Fe^{2+}/L and by irradiation of UV light or not. The results given in **Figure 3**, showed that the concentration of 2-chloro-4,6-diamino-1,3,5-triazine decreases during the treatment which indicates the degradation of the triazine herbicide by Fenton, photo-Fenton photolysis UV/H_2O_2. It is also clear that the degradation of the triazine herbicide by photo-Fenton is more rapid and effective than by Fenton and UV/H_2O_2 processes. This can be explained by the supplementary hydroxyls radicals produced by catalytic as shown in Equation (1) and photo-decomposition of H_2O_2 as shown in Equation (2).

However, this analytical method cannot inform about the transformation of the triazine herbicide and the nature of by products and intermediates formed. Taking into account the fact that the treatment of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton processaimsto completely transforming this compound into CO_2, H_2O, Cl^- and NO_3^- (or NH_4^+), it is necessary to optimize the doses of chemicals and the nature of the UV light required to reach the goal. The experimental parameters studied were initial pH, H_2O_2 concentration, ferrous iron dose, triazine concentration and UV light. The optimization of these parameters will achieve high yields of mineralization and reduce the cost of treatment. The mineralization of organic pollutants was followed by measure-

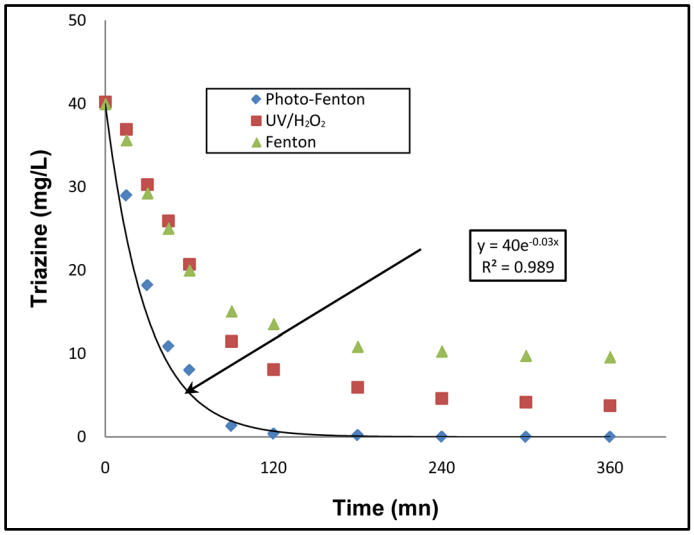


Figure 3. Changes of triazine concentration with time during the treatment of aqueous solutions containing 40 mg/L triazine using Fenton, photo-Fenton and UV/H_2O_2. Experimental conditions: 4000 mg/L H_2O_2, 5 mg/L Fe^{2+}, UV irradiation with UV-L lamp (λ = 254 nm), 300 rpm.

ing the chloride, nitrite and nitrate ions formed during the treatment by ion chromatography, the analysis of total organic carbon TOC and Kjeldahl nitrogen TKN.

3.2. Influence of the Experimental Conditions on the Efficiency of the Degradation of 2-Chloro-4,6-diamino-1,3,5-triazine by Photo-Fenton Process

3.2.1. Influence of Initial pH

Several authors have demonstrated that optimal pH for the production of hydroxyl radicals by the photo-Fenton process must be between 3 and 5 [34]-[36]. The pH is an important parameter that affects the efficiency of photo-Fenton process. The influence of the initial pH on the treatment of aqueous solutions containing 40 mg/L triazine by the photo-Fenton process was evaluated at different initial pH values ranging from 3.0 to 9.0 using 4000 mg/L H_2O_2, 5 mg/L Fe^{2+} and room temperature. **Figure 4** presents the changes of chloride ions concentration as function of time during the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process at different initial pH values. The results presented in **Figure 4** show that chloride ions released from the beginning of treatment for all values of initial pH studied here. In addition, the concentration of chloride ion undergoes a rapid and linear increase with time, and thenit reaches a plateau after 180 min of treatment. Theoretically, if all chlorine atoms are released as chloride ions during the treatment of 40 mg/L (0.275 mM) triazine, the maximum concentration of chloride ions should be equal to 9.75 mg/L. As shown in **Figure 4**, the amount of chloride ions measured at the end of treatment does not reach the theoretical value of 9.75 mg/L for all initial pH studied. This could be due to mass transfer limitation when the concentration of triazine becomes low and to higher affinity of the intermediates formed compared to the starting material relative to hydroxyl radicals, or the transformation of chloride ions into hypochlorous acid (ClOH) or hypochlorite acid (ClO^-) depending on the pH of the medium by oxidation of the hydroxyl radicals (Tatapudi *et al.*, 1994).However, the treatment of aqueous solutions containing 40 mg/L triazine by photo-Fenton process resulted in the release of 8.0 mg Cl^-/L at pH 3.0, 5.6 mg Cl^-/L at natural pH (pH = 5.3), 6.0 mg Cl^-/L at pH 7.0 and 9.0, respectively. This indicates that more than 80% of chlorine atoms were released at pH 3.0; while, the yield of chloride ions formation is between 57 and 62% for other initial pH studied.

Figure 5 presents the influence of initial pH on the formation of nitrates ions as a function of time during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine (2-chloro-4,6-diamino-1,3,5-triazine). These results show that the treatment of aqueous solutions of triazine by photo-Fenton process leads to the formation of nitrate ions at all initial pH values studied. Also, the concentration of nitrite ions during the treatment was measured; but only small amounts of nitrite ions (donot exceed 0.2 mg/L) were detected. These results in-

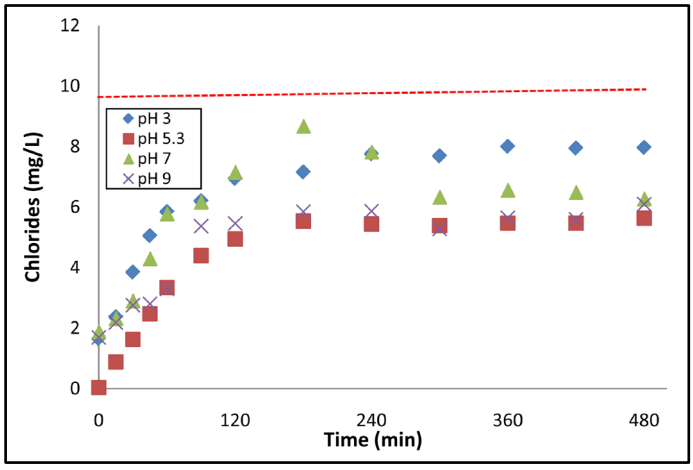


Figure 4. Influence of initial pH on the formation of chlorides during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental Conditions: 4000 mg/L H_2O_2, 5 mgFe^{2+}/L, UV-L (40 W) irradiation, pH 3 - 9, Room temperature (23 - 25˚C), 300 rpm.

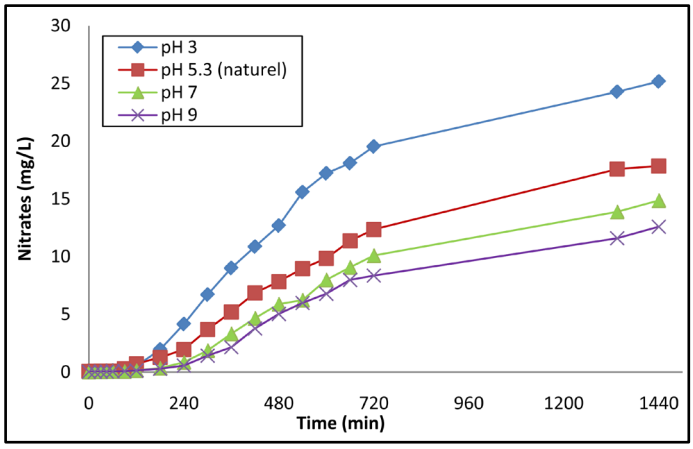


Figure 5. Influence of initial pH on the formation of nitrates during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental Conditions: 4000 mg/L H_2O_2, 5 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3 - 9, Room temperature (23˚C - 25˚C), 300 rpm.

dicate that part of the organic nitrogen of 2-chloro-4,6-diamino-1,3,5-triazine was released in the form of nitrates. It should be noted that if all organic nitrogen is released in the form of nitrate ions during the treatment of 40 mg/L (0.275 mM) triazine, the theoretical maximum concentration of nitrate ions is equal to about 85.25 mg/L; but all initial pH values tested did not result in the formation of the theoretical concentration of 85.25 mg/L. However, increasing the pH from 3.0 to 9.0 has decreased the amount of nitrate ions formed during the treatment. Amounts of nitrate ions from 17.8 mg/L, 14.9 mg/L and 12.6 mg/L, respectively, were measured at pH 5.3 (natural), 7.0 and 9.0 after 24 hours of treatment. The highest amount of nitrate ions (25.2 mg/L) was measured at pH 3.0 after 24 hours of treatment, which corresponds to about 30% of the theoretical nitrate concentration. These results indicate that the release of organic nitrogen of 2-chloro-4,6-diamino-1,3,5-triazine as nitrate ions involves several steps, consumes large amounts of hydroxyl radicals and absorbs important portion of UV Light. The results of **Figure 5** show that the photo-Fenton process failed to transform all organic nitrogen into nitrate or nitrite ions.

It can be concluded that:

- A pH 3.0 is optimal to achieve the highest yields of degradation of 2-chloro-4,6-diamino-1,3,5-triazine photo-Fenton process in terms of release of chlorine atoms as chloride ions and organic nitrogen as nitrate ions.

This could be due mainly to two factors: The first is related to the catalytic decomposition of hydrogen peroxide by ferrous ions to produce hydroxyl radicals which are accelerated in acidic, whereas the second phenomenon concerns the ionic or molecular characteristics of triazine which is probably in the cationic form at pH 3.0 which facilitates the attack by hydroxyl radicals.

- Increasing pH to values higher than 3.0, during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine with 4000 mg H_2O_2/L, 5 mg Fe^{2+}/L and UV-L irradiation, did not enhance the formation of chloride ions; in contrast, it decreases the formation of nitrates. This can be due to precipitation of ferric ions at neutral and alkaline pH which limits the regeneration of ferrous iron catalyst and then decreases the efficiency of the process
- The degradation of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process at pH 3.0 results in the release of about 80% of chlorine atoms as chlorides and 30% of organic nitrogen as nitrate ions.

3.2.2. Influence of the Initial Concentration of Fe^{2+}

The ferrous ions used as the catalyst for the decomposition of hydrogen peroxide according to the reaction Fenton to form of ferric ions (Equation (1)). These ions are excellent catalyst and a small catalytic amount may be sufficient to decompose H_2O_2 efficiently into hydroxyl radical $HO^{\bullet}$. High doses of ferrous ions can lead to the formation of insoluble hydroxo- and organo-ferriccomplexes. To study the influence of dose of Fe^{2+} ions on the efficiency of the treatment of aqueous solutions (pH 3.0) containing 40 mg/L of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process, the concentration of H_2O_2 was fixed to 4000 mg/L, and dose of Fe^{2+} was varied between 0 and 20 mg/L at room temperature. **Figure 6** and **Figure 7** present the changes of concentrations of chloride and nitrate ions as a function of time during the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process for different doses of Fe^{2+} ions in the range 0 - 20 mg/L. **Figure 7** shows a abrupt increase of chloride ions at the beginning of the treatment, and then it becomes eventually constant after four hours treatment. Contrarily, **Figure 8** shows that the formation of nitrate ions does not start from the beginning of the treatment, but after two hours of treatment nitrate ions start to form. The concentration of nitrate ions undergoes a continuous and slow increase for about 12 hours' treatment. It should be noted also that for relatively high amounts of ferrous ions, chloride and nitrate ions concentrations are lower than those measured without addition of catalyst. These results indicate that the release of chloride ions is faster that the formation of nitrate ions during the treatment of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process. However, these results clearly confirm that the amounts of chloride and nitrate ions generated during the treatment depends largely on the dose of ferrous ions: In absence of ferrous ions, photolysis UV/H_2O_2 resulted in the formation of 6.5 mg Cl^-/L and 17.3 mg NO_3^-/L corresponding to the release of 67% and 20.4% of chlorine and nitrogen atoms of 2-chloro-4,6-diamino-1,3,5-triazine. The addition of ferrous ions dose of 5 mg/L has improved yields of formation of chloride and nitrate ions to 8.0 mg Cl^-/L and 25.2 mg NO_3^-/L. However, the addition of a dose of Fe^{2+} greater than 5 mg/L decreases the efficiency of the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process in terms of chloride and nitrate ions formation. 20 mg/L Fe^{2+} ions result in the formation of 4.2 mg Cl^-/L and 17.3 mg NO_3/L. A dose of Fe^{2+} higher than 5 mg/L, does not have any significant influence on the formation of nitrate ions. The results obtained in this work are not in agreement with those mentioned in literature by many authors about the influence of Fe^{2+} ions on the efficiency of photo-Fenton process. Several research studies showed that increasing the dose of ferrous ions resulted into more efficient processes, since Fe^{2+} ions are found in sufficient amount when high doses are added which causes the acceleration of production radical hydroxyls by reaction Fenton as follows:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (3)$$

To explain these results, some basic concepts of coordination chemistry and the results reported in the literature should be taken into account. Szumera *et al*., [37] mentioned that Fe^{2+} and Fe^{3+} can form complexes with s-triazines with stability constants between 10^3 and 10^5. Gun *et al*., [38] have also described a photometric method of analysis of Fe^{3+} ions by complexation of Fe^{3+} by the bis-(hydroxyamino)-triazines. Based on these results, it seems that Fe^{2+} ions initially added and Fe^{3+} ions formed during the treatment may also form stable complexes with 2-chloro-4,6-diamino-1,3,5-triazine or one of its degradation intermediates. The formation of stabile Fe(II)-triazine complexes reduce the number of free triazine molecules available to react with hydroxyl radicals; while Fe(III)-triazine complexes consume large amount of UV light to dissociate into Fe^{3+} and free triazine molecules. Triazine molecule is a tridentate ligand, the formation of Fe(II)-triazine requires two moles of triazine

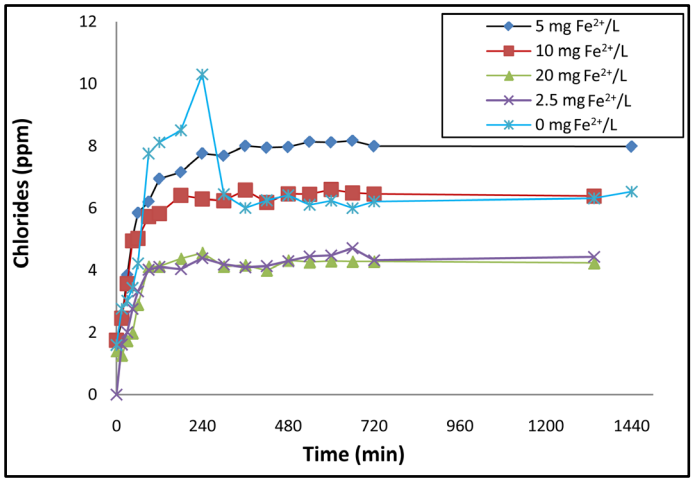


Figure 6. Influence of ferrous iron dose on the formation of chlorides during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental Conditions: 4000 mg/L H_2O_2, 0 - 20 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, Room temperature (23˚C - 25˚C), 300 rpm.

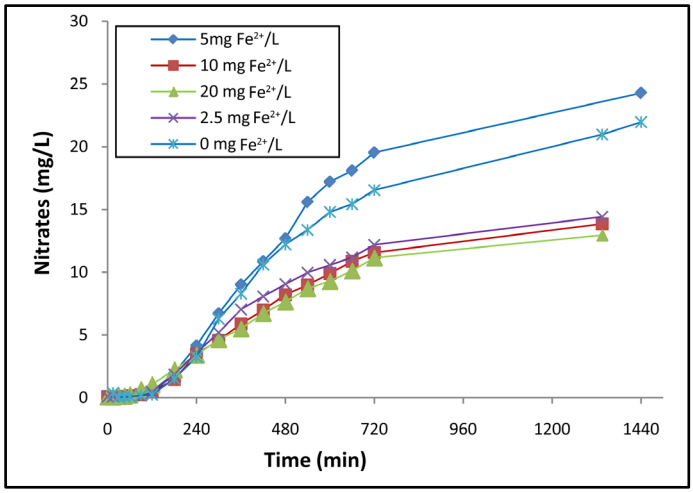


Figure 7. Influence of ferrous iron dose on the formation of nitrates during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental conditions: 4000 mg/L H_2O_2, 0 - 20 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, Room temperature (23˚C - 25˚C), 300 rpm.

per mole of Fe^{2+}. It is inferred that to complex all herbicide molecules initially contained in the solution of 40 mg/L (0.275 mM) minimum 0.1375 mM Fe^{2+} must be added which corresponds to 7.7 mg Fe^{2+}/L. It is then possible that for Fe^{2+} doses < 7.7 mg Fe^{2+}/L, Fe^{2+} ions as the triazine molecules are not completely complex. For doses > 7.7 mg Fe^{2+}/L, Fe^{2+} ions are in excess in the solution, which shifts the equilibrium of formation of Fe(II)-triazine to the right and therefore all triazine molecules are complex which makes their attack by hydroxyl radicals very difficult. In addition, if high doses of Fe^{2+} are added, the regeneration of the catalyst (Fe^{2+} ions) from Fe^{3+} ions becomes slow due to the precipitation of ferric hydroxide $Fe(OH)_3$. For these reasons, increasing the dose of Fe^{2+} ions has negatively influence the degradation of the herbicide studied in contrast to what is reported in the literature. A dose of 5 mg Fe^{2+}/L was optimal to form the highest chloride and nitrate amounts during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine at pH 3.0 using 4000 mg H_2O_2/L and UV-L irradiation. This can be explained by 1) lower ferrous doses than 5 mg Fe^{2+}/L are not sufficient to enhance the production of hydroxyls radicals, 2) the formation of stable triazine-ferric iron complexes that consume UV light to decompose which inhibits the regeneration of the catalyst and precipitation of ferric iron and

then lower the amount of ferrous iron catalyst in the media.

3.2.3. Influence of the H_2O_2 Concentration

The performance of photo-Fenton process is mainly related to the production of hydroxyl radicals by chemical and photochemical decomposition of hydrogen peroxide. Hydrogen peroxide is the main source of hydroxyl radicals although little amount of $HO^{\bullet}$ can be formed by water photolysis. Consequently, the initial concentration of H_2O_2 is considered as a fundamental factor that limits the production of hydroxyl radicals during the treatment by the photo-Fenton process [19] [21]. To study the effect of the concentration of hydrogen peroxide on the formation of chloride and nitrate ions during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine at pH 3.0, $[H_2O_2]/[Fe^{2+}]$ mass ratio was kept constant and equal 800 and UV irradiation was performed by low pressure mercury lamp (UV-L) emitting UV light at a wavelength of 254 nm. **Figure 8** and **Figure 9** present the changes of concentration of chloride and nitrate ions with time during the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process using 2000, 4000 and 6000 mg/L of H_2O_2. The results obtained show that the increase of the initial concentration of H_2O_2 from 2000 mg/L to 4000 mg/L increases both the rate and the yield of formation of chloride and nitrate ions. It should be noted that no nitrate formation was observed when 2000 mg/L H_2O_2 was used while 25.2 mg/L nitrate was measured using 4000 mg H_2O_2/L. These results can be interpreted by the fact that increasing the concentration of H_2O_2 and Fe^{2+} in the medium enhances the production of hydroxyl radicals $HO^{\bullet}$ and consequently accelerates the release of chlorine and nitrogen atoms of 2-chloro-4,6-diamino-1,3,5-triazine. However, when the initial concentration of H_2O_2 increases from 4000 mg/L to 6000 mg/L, different results were obtained. Indeed, the concentration of chloride ions increases rapidly at the beginning of the treatment, to reach a maximum of about 6.5 mg/L at 90 min, and then drops sharply and completely disappears after 300 min. Also, very low amounts of nitrate were measured during the treatment of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process using 6000 mg H_2O_2/L and 7.5 mg Fe^{2+}/L. These results indicate that chlorine atoms were released as chloride ions from the beginning of treatment, but the later undergo rapid oxidation into active chlorine (HClO and ClO^{-}) by hydroxyl radicals formed in large excess when high concentrations of H_2O_2 and $Fe^{2+}$are used according to the reaction below:

$$2Cl^{-} \rightarrow Cl_2 + 2e \quad (4)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^{+} + Cl^{-} \quad (5)$$

$$HOCl \leftrightarrow H^{+} + OCl^{-} \quad (6)$$

The fact that low amounts of nitrates were detected for the highest concentrations of H_2O_2 and Fe^{2+} does not indicate that there is no release of nitrogen as in the case of low concentrations of H_2O_2 and Fe^{2+}, but the nitrogen released from the triazine herbicide molecule can be rapidly transformed into ammonium ions by photochemical reduction of nitrite and nitrate by Fe^{2+} ions and UV irradiation (Fanning, 2000). Furthermore, the results of TOC and TKN analyses of samples taken during the treatment containing 40 mg/L triazine by photo-Fenton process using 6000 mg/L H_2O_2 and 7.5 mg Fe^{2+}/L (**Table 1**) showed that TOC does not change during photo-Fenton experiment. This indicates that photo-Fenton process was unable to open the triazine ring even with H_2O_2 concentration greater than 4000 mg/L. TKN results showed that photo-Fenton process can release up to 40% of the nitrogen of 2-chloro-4,6-diamino-1,3,5-triazine representing the nitrogen of the amino groups (-NH_2) oftriazine ring. For low concentrations of H_2O_2 (≤2000 mg/L), hydroxyl radicals generated by the chemical decomposition of hydrogen peroxideby the ferrous ions and its photochemical decomposition by UV irradiation are not sufficient to release all the chlorine atoms and even small part of organic nitrogen of 2-chloro-4,6-diamino-1,3,5-triazine. Also, higher concentrations of H_2O_2 than 4000 mg/L did not achieve higher nitrate formation than that obtained when 4000 mg H_2O_2/L was used. This result can be explained by 1) accelerating the decomposition of H_2O_2 into water and oxygen; 2) formation of triazine-ferric iron complexes which leads to lower quantum yield for hydrogen peroxide decomposition; 3) competition between triazine molecules and its intermediates such as chloride ions towards hydroxyl radicals with formation of chlorine species.

Also, UV irradiation using UV-L lamp was found to be more efficient than UV-M lamp which is related to the quantum yield of H_2O_2 photodecomposition that absorbs UV light between 200 and 260 nm and then UV irradiation at 254 nm achieves homolytic rupture of O-O bonds with a quantum yield close to unit.

$$H_2O_2 + h\nu \rightleftarrows 2HO^{\bullet} \quad (7)$$

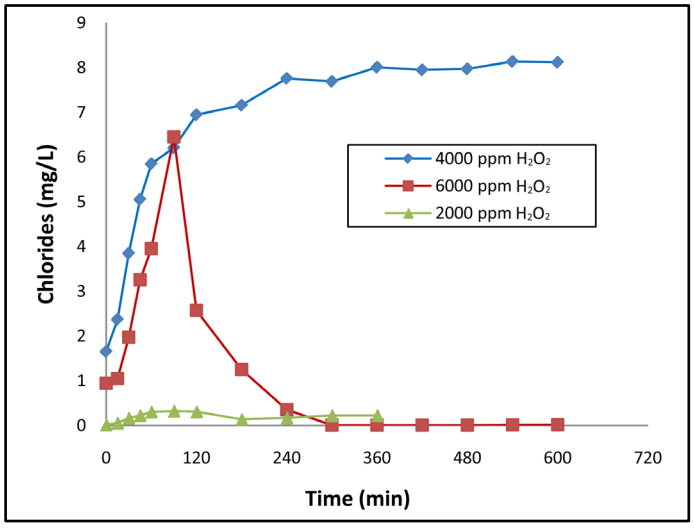


Figure 8. Influence of H_2O_2 concentration on the formation of chloride ions during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental Conditions: 2000 - 6000 mg/L H_2O_2, mass ratio $[H_2O_2]/[Fe^{2+}]$ = 800, UV-L (40 W) irradiation, pH 3, Room temperature (23˚C - 25˚C), 300 rpm.

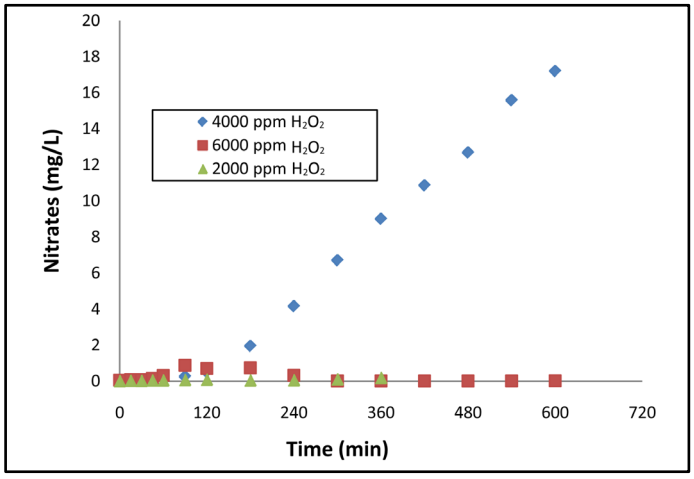


Figure 9. Influence of ferrous iron dose on the formation of nitrates during photo-Fenton treatment of aqueous solutions containing 40 mg/L triazine. Experimental conditions: 4000 mg/L H_2O_2, 0 - 20 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, Room temperature (23˚C - 25˚C), 300 rpm.

$$H_2O_2 + HO^{\bullet} \rightleftarrows HO_2^{\bullet} + H_2O \quad (8)$$

$$2H_2O_2 \rightleftarrows O_2 + 2H_2O \quad (9)$$

3.2.4. Influence of the Variation of Concentration of 2-Chloro-4,6-diamino-1,3,5-triazine

The initial organic matter has an important influence on the efficiency of advanced oxidation processes. For this reason we decided to also study the influence of the concentration of 2-chloro-4,6-diamino-1,3,5-triazine on the efficiency of treatment by photo-Fenton process. To study the influence of this parameter, the mass ratio $[H_2O_2]/[Fe^{2+}]$ and $[H_2O_2]$/[triazine] are maintained constant and equal to 100 and 800 respectively. **Figure 10** and **Figure 11** present the changes of concentrations of chloride and nitrateions with time during the treatment of aqueous solutions containing different concentrations of 2-chloro-4,6-diamino-1,3,5-triazine in the range of 20

Table 1. TOC and TKN analysis results of 2-Chloro-4,6-diamino-1,3,5-triazine degradation using photo-Fenton process (UV-L/H_2O_2/Fe^{2+}). Experimental conditions: 40 mg/L (0.275 mM) triazine, 7.5 mg/L Fe^{2+}, 6000 mg/L H_2O_2, UV-L (40 W) irradiation, pH 3, room temperature (23˚C - 25˚C), 300 rpm.

Time (min)	TOC (mg C/L)	TKN (mg N/L)
0	9.65	19.84
45	9.76	19.76
90	9.32	20.14
180	9.45	19.86
300	9.81	20.24
420	9.42	20.11
660	9.64	20.06

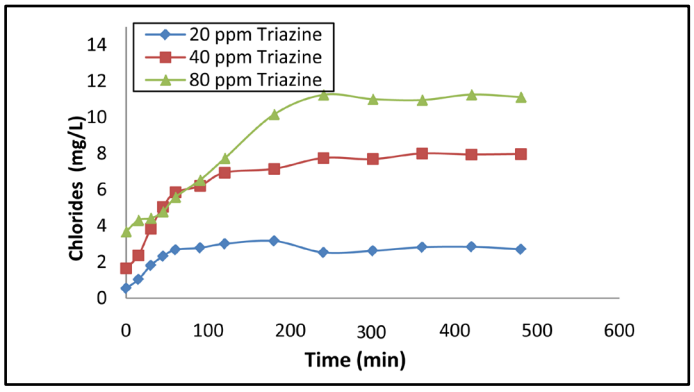


Figure 10. Influence of initial concentration of 2-chloro-4,6-diamino-1,3,5-triazine on the formation of chlorides during the treatment by photo-Fenton process (UV/H_2O_2/Fe^{2+}). Experimental Conditions: 20 - 80 mg/L of triazine, mass ratio [H_2O_2]/[triazine] = 100, 5 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, Room temperature, 300 rpm.

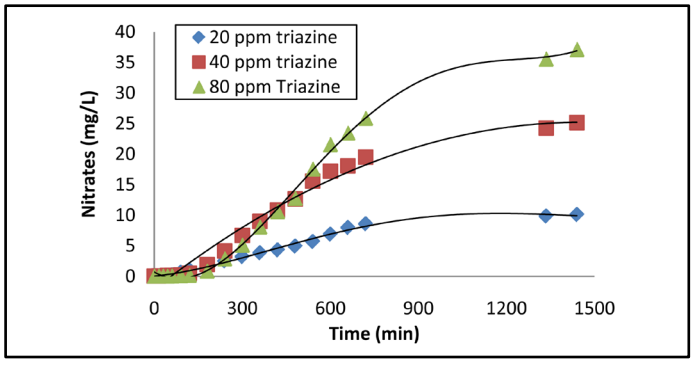


Figure 11. Influence of initial concentration of 2-chloro-4,6-diamino-1,3,5-triazine on the formation of nitrates during the treatment by photo-Fenton process (UV/H_2O_2/Fe^{2+}). Experimental Conditions: 20 - 80 mg/L of triazine, mass ratio [H_2O_2]/[triazine] = 100, 5 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, room temperature, 300 rpm.

to 80 mg/L by the photo-Fenton process at pH 3.0. Increasing the concentration of triazine leads to a significant increase in the amounts of chloride and nitrateions measured at the end of the treatment. The treatment of aqueous solutions containing 20 mg/L, 40 mg/L and 80 mg/L of triazine by the photo-Fenton process led to the

formation of 2.7 mg Cl^-/L and 10.1 mg NO_3^-/L, 8 mg Cl^-/L and 25.2 mg NO_3^-/L and 11.1 mg Cl^-/L and 37.1 mg NO_3^-/L, respectively. Although the treatment of 80 mg/L of triazine by photo-Fenton process led to the formation of higher amounts of chloride and nitrate ions, the yield of formation of chloride and nitrate ions are lower than those obtained with 20 mg/L and 40 mg/L as shown in **Figure 12**. The treatment of 40 mg/L of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process gives the highest yields of formation of chloride and nitrate ions. For low concentrations of triazine, H_2O_2 and Fe^{2+}, the collision of radicals $HO^\bullet$ with free triazine molecules is limited by mass transfer. When the concentration of triazine increases, the concentrations of H_2O_2 and Fe^{2+} are also increased which improves the production of radicals $HO^\bullet$ in the medium. These radicals react rapidly with free triazine molecules to release chlorineand nitrogen atoms as chloride as nitrate ions, respectively. The results obtained for higher concentrations of triazine than 40 mg/L can be explained by:

- A part of the UV radiation can be absorbed by organic molecules which reduces the quantum yield of production of radicals $HO^\bullet$ from H_2O_2;
- Ferrous ions form stable complexes with triazine molecules;
- Auto-decomposition H_2O_2 into O_2 and H_2O becomes more important;
- Recombination of hydrogen peroxide and hydroxyl radicals to generate super-hydroxyl radicals.

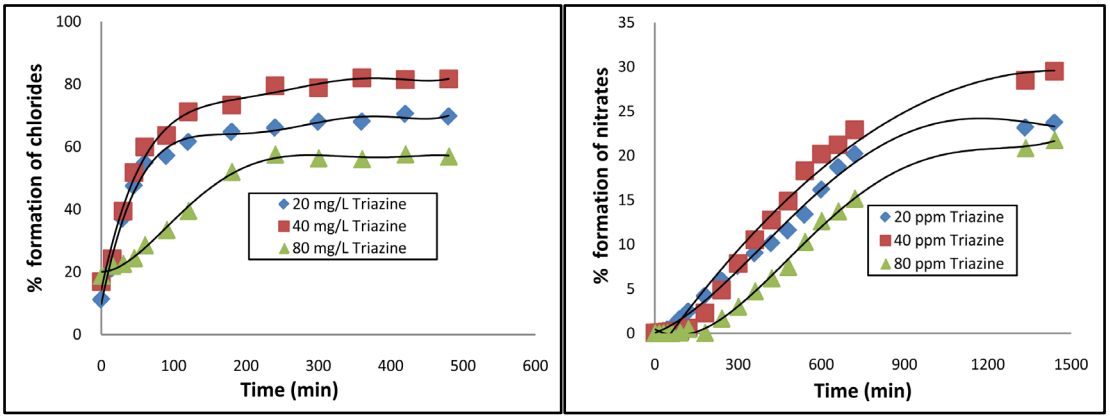
These phenomena participate in the reduction of the efficiency of degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process in terms of chlorine and nitrogen atoms release.

3.2.5. Influence of the Nature of the UV Light on the Efficiency of the Photo-Fenton Process

The source of UV irradiation has a high influence on the quantum yield of photo-decomposition of the hydrogen peroxide into hydroxyl radicals. It reported generally that the quantum yield of decomposition of H_2O_2 by UV irradiation at wavelengths between 200 - 300 nm is very close to unit. To study the influence of this parameter, we tested two types of UV light to treat aqueous solutions containing 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process. The first lamp is a low pressure mercury lamp (UV-L) emitting monochromatic UV radiation of wavelength λ = 254 nm. The second lamp is a medium pressure mercury lamp (UV-M) emitting polychromatic radiation between 200 - 600 nm. **Figure 13(a)** and **Figure 13(b)** show the evolution of the concentrations of chlorides and nitrates during the treatment of aqueous solutions at pH 3 containing 40 mg/L of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process using 4000 mg/L H_2O_2, 5 mg/L Fe^{2+}, at room temperature by UV-L and UV-M irradiation. It is clear that irradiation by UV-L is more effective than the UV-M. The irradiation by UV-M resulted in the formation of 5.3 mg Cl^-/L and 0.62 mg NO_3^-/L after 480 min of treatment, whereas the same period of treatment 8 mg Cl^-/L and 12.7 mg NO_3^-/L were formed. This result may be related to the efficiency of the photo-decomposition of hydrogen peroxide. We followed the variation of the concentration of H_2O_2 during the irradiation of aqueous solutions containing 4000 mg/L H_2O_2 by two types of lamp. **Figure 14** shows that the photo-decomposition of H_2O_2 follows a first order kinetics for both types of UV lamp used. It is clear that the photo-decomposition of H_2O_2 by UV-L irradiation is faster than that by UV-M irradiation. The best results obtained by UV-L irradiation can be explained by more efficient production of hydroxyl radicals and direct photolysis of triazine molecules which absorb at a wavelength close to that emitted by the UV-L.

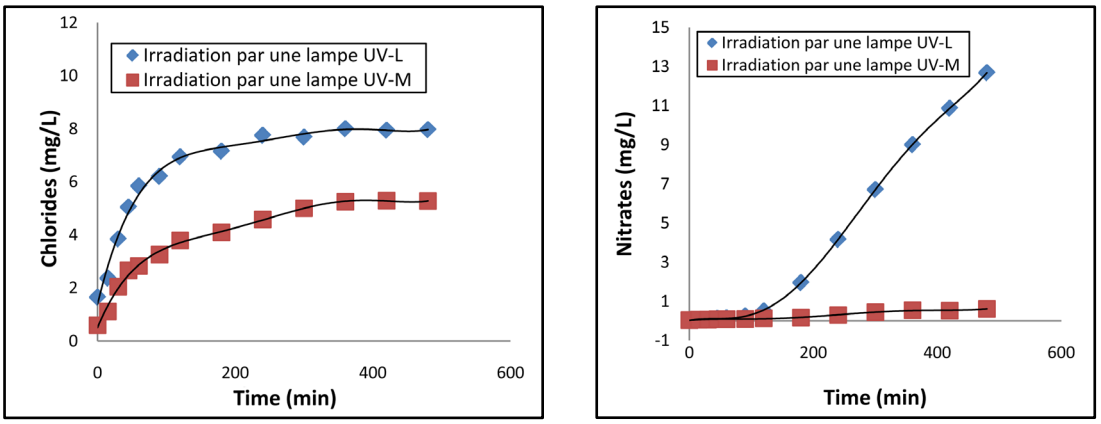
3.3. Mechanism of Degradation of 2-Chloro-4,6-diamino-1,3,5-triazine by the Photo-Fenton Process

The chromatographic analyses confirmed the almost total release of chlorine atoms as chloride ions and the partial release of nitrogen in the form of nitrate ions. Considering only these results, the steps involved in the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process cannot be precisely described. It is then mandatory to measure TOC and TKN during treatment of 40 mg/L triazine by the photo-Fenton process under optimal conditions. The results given in **Table 2** show that TOC value remains almost constant during the treatment which indicates that there is no formation of carbon dioxide during photo-Fenton treatment of 2-chloro-4,6-diamino-1,3,5-triazine. Furthermore, Kjeldahl nitrogen decreased by an amount equivalent to the amount of nitrate formed, while total nitrogen remains invariant throughout the experiment. Analysis of TOC and TKN indicate that the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process results in the release of chlorine and amino groups substituting the triazine ring, nevertheless the triazine ring were not open because no formation of carbon dioxide was formed considering that all carbon in the molecule is assembled in the triazine ring.



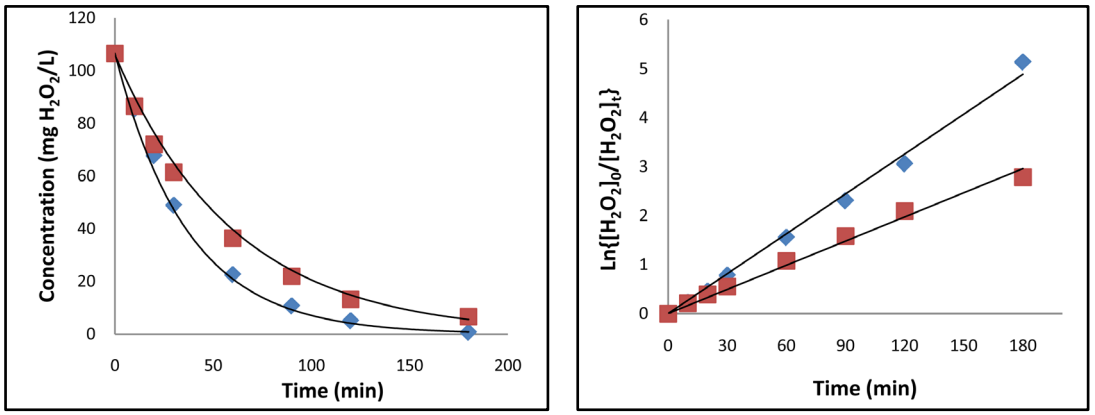
(a) (b)

Figure 12. Influence of initial concentration of 2-chloro-4,6-diamino-1,3,5-triazine on the formation of chlorides and nitrates during the treatment of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton ($UV/H_2O_2/Fe^{2+}$) process. Experimental Conditions: 20 - 80 mg/L of triazine, 4000 mg/L H_2O_2, 5 mg Fe^{2+}/L, UV-L (40 W) irradiation, pH 3, Room temperature, 300 rpm.



(a) (b)

Figure 13. Influence of the nature of the UV light on the formation of ions (a) chloride; (b) nitrate during the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process ($UV/H_2O_2/Fe^{2+}$). Experimental conditions: 40 mg/L of triazine, 4000 mg/L H_2O_2, 5 mg Fe^{2+}/L, pH = 3, Room temperature, 300 rpm.



(a) (b)

Figure 14. Kinetics of photo-decomposition of hydrogen peroxide by irradiation the light: (♦) UV-L and (■) UV-M. Experimental conditions: 4000 mg/L H_2O_2, naturel pH, Room temperature, 300 rpm.

Table 2. Results of TC (Total Carbon), IC (Inorganic Carbon), TOC, TN (Total Nitrogen), NN (Nitrate/Nitrite Nitrogen), and TKN analysis of 2-Chloro-4,6-diamino-1,3,5-triazine degradation using photo-Fenton process (UV-L/H_2O_2/Fe^{2+}). Experimental conditions: 40 mg/L (0.275 mM) triazine, 5 mg/L Fe^{2+}, 4000 mg/L H_2O_2, UV-L (40 W) irradiation, pH 3.0, room temperature (23˚C - 25˚C), 300 rpm.

Time (min)	pH	TC (mg C/L)	IC (mg C/L)	TOC (mg C/L)	TN (mg N/L)	NN (mg N/L)	TKN (mg N/L)
0	3.72	9.87	0	9.87	23.32	0	23.32
30	2.49	9.23	0	9.83	23.29	0	23.29
60	2.59	7.92	0	9.62	23.29	0.23	23.06
90	2.46	7.94	0	9.74	23.32	0.63	22.69
120	2.72	8.58	0	9.88	23.33	0.88	22.45
180	2.68	8.37	0	9.77	23.26	0.9	22.36
240	2.77	9.44	0	9.84	23.39	1.29	22.1
300	2.73	9.4	0	9.84	22.97	1.43	21.54
360	2.82	9.3	0	9.73	22.93	1.64	21.29

Based on chromatographic analyses and TOC and TKN results, a simple mechanistic scheme can be proposed for the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process. The main steps of this mechanism are given in **Figure 15**. According to the proposed mechanism, the degradation of 2-chloro-4,6-diamino-1,3,5-triazine begins by a rapid release of chlorine atoms as chloride ions and substitution of Cl group with hydroxyl group to form 2-hydroxy-4,6-diamino-1,3,5-triazine. This intermediate undergoes oxidation by hydroxyl radicals to convert amino groups in the nitro groups to form 2-hydroxy-4,6-dinitro-1,3,5-triazine. Nitro groups are released simultaneously or successively and are slowly substituted with hydroxyl groups. The release of the nitro groups leads to formation of nitrite which oxidizes instantly into nitrates. It appears that the final products of the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by the photo-Fenton process are chloride and nitrate ions, and cyanuric acid. The formation of cyanuric as final degradation product of triazine herbicides by advanced oxidation processes has been extensively reported in the literature acid. Several researchers have demonstrated that the degradation of other triazine herbicides stops at the stage of formation of cyanuric acid due the reversibility of the exchange between hydroxyl radicals and hydroxyl groups of triazine ring. This could explain the exceptional resistance of cyanuric acid degradation by advanced oxidation processes. To confirm these hypotheses the treatment of aqueous solutions containing cyanuric acid by photo-Fenton process was undertaken.

3.4. Degradation of Cyanuric Acid by Photo-Fenton Process

Cyanuric acid is widely used as a stabilizer in swimming pools to prevent the destruction of chlorine by solar irradiation [39]. Although many researchers [33] [40] [41] have shown that no degradation was obtained during the treatment of this compound by hydroxyl radicals generated by various chemical and photochemical advanced oxidation processes, it is decided to study its degradation by photo-Fenton process to explain the partial mineralization of 2-chloro-4,6-diamino-1,3,5-triazine and confirm that efficiency of photo-Fenton process is mainly linked to the formation of cyanuric acid as the final product.

Degradation of cyanuric acid by photo-Fenton process was carried out under the same optimal conditions determined in the case of 2-chloro-4,6-diamino-1,3,5-triazine. In fact, aqueous solutions containing 100 mg/L cyanuric acid were treated by 4000 mg/L H_2O_2 and 5 mg/L Fe^{2+} at room temperature. Concentrations of total organic carbon (TOC) and Kjeldahl nitrogen (TKN), nitrates were measured during the treatment. **Table 3** shows the TOC, TKN analysis results of cyanuric acid degradation using photo-Fenton process at different instant. These results show that the values of TOC are invariant during the treatment, while the TKN has been a slight decrease to the end of treatment. Very low amount of nitrates not exceeding 0.5 mg N/L were measured after ten hours of treatment. The amount of nitrate measured at the end of treatment has certainly resulted from irradiation by UV light because after 10 hours of treatment the hydrogen peroxide was completely decomposed. We also

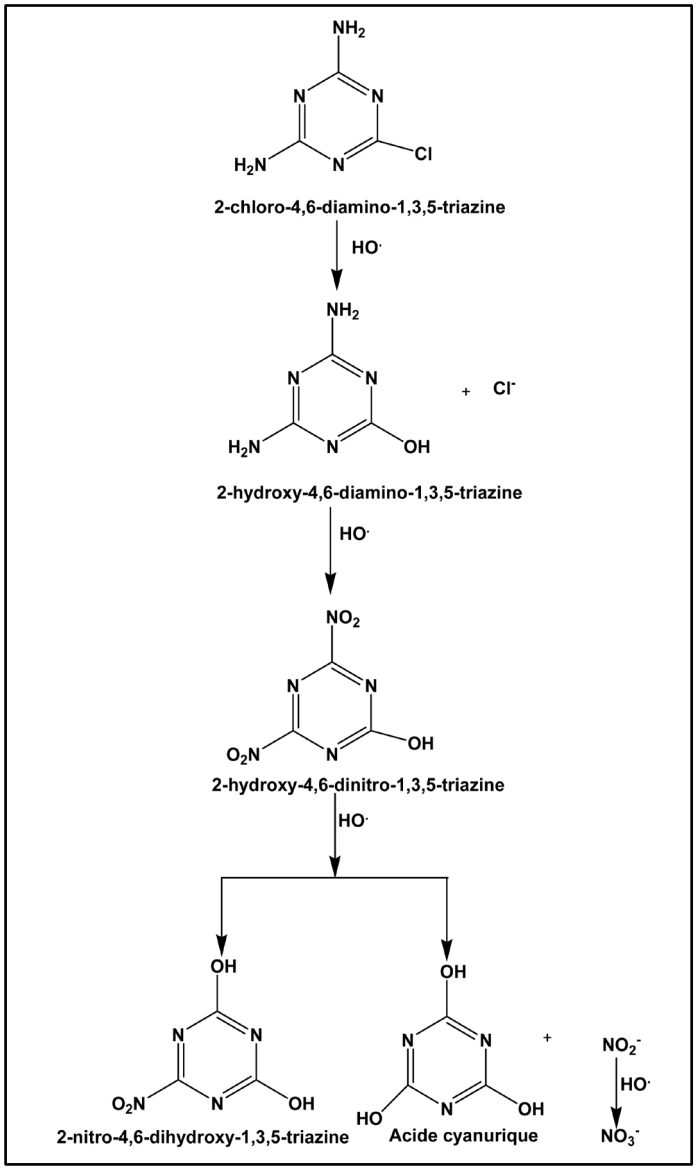


Figure 15. Simple mechanism proposed for the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process.

studied the influence of initial pH on the degradation of cyanuric acid. The results obtained at pH 3, 5.4, 7 and 9 coincide with those presented in **Table 2**. The overall results obtained have shown that no formation of carbon dioxide and nitrate were formed during photo-Fenton treatment of aqueous solutions containing 100 mg/L cyanuric acid. They are in good agreement with the results reported by Tetzlaff and Jenks, [41]. These researchers showed resistance of cyanuric acid by photocatalytic processes. The resistance of the cyanuric acid degradation by photo-Fenton process can be explained by: 1) No possibilityto oxidize the organic carbon of cyanuric acid because all carbon atoms are in the highest oxidation state (+IV); 2) the reversibility of exchange between hydroxyl radicals and OH groups of thetriazinic ring; 3) the formation of very stable complexes between ferrous or ferric iron and cyanuric acid molecules.

4. Conclusion

The results obtained have shown that the degradation of 2-chloro-4,6-diamino-1,3,5-triazine by photo-Fenton process is more rapid and effective than Fenton and UV/H_2O_2 processes. This can be explained by the additional

Table 3. Results of TC, IC,TOC, TN, NN, TKN, and nitrate analysis of cyanuric acid degradation using photo-Fenton process ($UV/H_2O_2/Fe^{2+}$). Experimental conditions: 100 mg/L cyanuric acid, 4000 mg/L H_2O_2, 5 mg Fe^{2+}/L, natural pH, room temperature, 300 rpm.

Time (min)	TC (mgC/L)	IC (mgC/L)	TOC (mgC/L)	TN (mgN/L)	NN (mgN/L)	TKN (mgN/L)	Nitrate (mg/L)
0	32.08	0	32.08	38.32	0	38.32	0.052
15	31.6	0	31.6	38.36	0	38.36	0.056
30	30.09	0	30.09	37.54	0	37.54	0.058
45	31.82	0	31.82	37.6	0	37.6	0.044
60	31.32	0	31.32	36.9	0	36.9	0.062
90	32	0	32	37.1	0	37.1	0.071
120	31.73	0	31.73	37.34	0	37.34	0.091
180	31.95	0	31.95	37.38	0	37.38	0.175
240	32.02	0	32.02	36.92	0	36.92	0.326
300	30.84	0	30.84	37.68	0	37.68	0.474
360	30.49	0	30.49	36.96	0	36.96	0.741
420	30.63	0	30.63	36.50	0	36.50	0.905
480	30.63	0	30.63	36.08	0	38.08	1.133
540	30.88	0	30.88	35.36	0	35.36	1.514
600	30.73	0	30.73	35.12	0	35.12	2.01

hydroxyls radicals produced by catalytic and photo-decomposition of H_2O_2. The study of the influence of certain experimental parameters on the efficiency of the photo-Fenton process was used to determine the optimal conditions for degradation 40 mg/L of 2-chloro-4,6-diamino-1,3,5-triazine at room temperature: an initial pH about 3, an initial concentration of hydrogen peroxide of the order of 4000 mg/L, a ferric iron dose not exceeding 5 mg/L and 300 rpm. In optimized operating conditions, photo-Fenton process achieved more than 90% of chloride release and about 28% of nitrate formation. By cons TOC and TKN analysis has shown that no carbon dioxide and ammonia were formed during photo-Fenton treatment of aqueous solutions. These results indicated that only the substituent groups (chloro and amino groups) are released; however, nitrogen atoms of triazine ring are stable. Also, the experiences of cyanuric acid degradation by photo-Fenton process indicated that no formation of carbon dioxide and nitrate was obtained. These results confirmed those reported in the literature [40] [41] that indicated that cyanuric acid is resistant to oxidation by hydroxyl radical which explains why no further nitrate ions and no carbon dioxide are formed for long period irradiation experiments.

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