

Effects of the heterogeneous photo-Fenton oxidation and sulfate radical-based oxidation on atrazine degradation

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Received 16 September 2021; Accepted 8 February 2022

ABSTRACT

Atrazine is an organic compound composed of s-triazine rings and has a long half-life which can be found in the sediment. It is prohibited to be included in the list of 45 priority pollutants specified in the European Union Water Framework Directive. In this study, it is possible to evaluate the treatment of atrazine using the heterogeneous photo-Fenton oxidation and sulfate radical-based oxidation. The Box–Behnken statistical method was used to investigate the effects of different concentrations of oxidant, catalyst, and chelating agent on atrazine removals. The maximum atrazine removal efficiency was obtained as 90% at persulfate 5 ppm, magnetite 1 ppm, ethylenediamine tetraacetic acid (EDTA) 1 ppm concentration by sulfate radical-based oxidation. While the maximum atrazine removal efficiency was obtained as 92% at hydrogen peroxide 5 ppm, magnetite 5 ppm, EDTA 4 ppm concentration by heterogeneous photo-Fenton process. Although atrazine removal efficiencies were nearly the same value at these processes, the requirement of magnetite and EDTA concentrations in sulfate radical-based oxidation is lower than the heterogeneous photo-Fenton process. In addition, the sulfate radical-based oxidation process is more suitable than the heterogeneous photo-Fenton process due to not formation of deethylatrazine metabolites, which is more toxic than atrazine compound.

Keywords: Atrazine; Box–Behnken; Ethylenediamine tetraacetic acid; Heterogeneous photo-Fenton oxidation; Sulfate radical-based oxidation

1. Introduction

Recalcitrant organic compounds contain complex molecules that are bio-refractory or non-degradable in nature. These refractory and toxic organic compounds enter water bodies such as surface water, groundwater, using industrial effluents, domestic wastewaters, and agricultural activities. The existence of these refractory organic compounds in water bodies causes serious problems for human health, animal, and aquatic life due to toxic effects of these compounds.

Atrazine, an herbicide of the triazine class, is one of these organic compounds. Atrazine is used to control pre and postemergence broadleaf weeds in crops such as corn,

sorghum, rangeland, and sugarcane. Atrazine easily dissolves in water and is not volatile, or reactive.

Environmental Protection Agency (EPA) banned the atrazine usage due to its persistence in water and various adverse effects on humans. Only certified users may purchase or use atrazine in United States. EPA has set a maximum amount of atrazine in drinking water of 0.003 ppm [1]. Atrazine is also prohibited from being placed on the list of 45 priority pollutants specified in the European Union Water Framework Directive [2]. Atrazine has also been banned by Turkish Regulations. However, some people can be used atrazine, some fields without permission.

Atrazine has adverse effects such as endocrine-disrupting effects and possible carcinogenic effects. Intermediate products of atrazine can also negatively affect water bodies.

Metabolites or intermediate products of atrazine are still relatively unknown. Generally, deisopropylatrazine, deethylatrazine and hydroxyatrazine are the main metabolite of atrazine. Hydroxyatrazine (HA) has lower toxicity than its parent compound. However, deisopropylatrazine (DIA) and deethylatrazine (DEA) have toxic effects nearly the same toxic effects of atrazine.

Except for intermediate products of atrazine, atrazine usage is critical due to the existence and formation of N-nitrosoatrazine. N-nitrosoatrazine can be formed at acidic pHs after addition of atrazine and nitrate fertilizer. N-nitrosoatrazine has not been classified as carcinogenic but they are considered as carcinogenic [3].

For that reason, the treatment of atrazine is a significant subject. Atrazine treatment cannot be completely degraded by conventional biological treatment methods due to the inhibition of toxicity on biological treatment methods. The conventional biological methods to cope with wastewater containing micropollutants such as pesticides need prolonged reaction time to decrease limitations of toxic organics on microorganisms, in addition metabolites or by-products of micropollutants requiring further or advanced treatment before discharge. Thus, it is critical to investigate new technologies to mineralize these compounds such as atrazine, decrease toxicity effects of main and intermediate products before discharging water bodies. Last decades, the advanced oxidation process can be used or preferred to inhibit toxicity and endocrine-disrupting effects of these organic compounds and to decrease these negative effects before the biological treatment process.

Advanced oxidation processes (AOPs) have the capabilities of using the high reactivity of hydroxyl radicals in driving oxidation processes. Sulfate radical-based AOPs have been used as an effective solution for wastewater treatment recently [4,5]. Persulfate is inorganic, solid substance with strong oxidizing properties. It is more usable than other oxidants due to its solubility in water at room temperature and effectiveness of oxidation at high pH value and lack of by-product formation. Besides, it has relatively low cost and safe handling. The main disadvantage of persulfate requires activation, for example, a catalyst. So, persulfate compounds that produce sulfate radicals (SO_4^\bullet) were used with transition metals and UV radiation in the oxidation process [6]. In the presence of ultraviolet irradiation, persulfate can transform into two sulfate radical anions [7].

Except for persulfate, hydrogen peroxide is a highly reactive oxidant that can oxidize organic compounds. Persulfate anion and hydrogen peroxide are strong oxidants, with the oxidation potential of 2.12 V and 1.8 V, respectively [8]. Persulfate and hydrogen peroxide can form the hydroxyl radical, with the oxidation potential of 2.8 V in the presence of various activators (UV, metals, chelating agent) [9]. The hydroxyl radical, which is the second strongest oxidant preceded by the fluorine are nonselective reactive species, which attack most organic molecules [10].

Metal can initiate a free radical generation through the formation of the sulfate radical [11]. Efficient degradation of organic matters can be observed with homogeneous catalytic oxidation with metals by persulfate. However, due to the high solubility of transition metals, it is not technological feasible to recover the homogeneous catalyst, thus

leading to a secondary pollution caused by the residual metal ions. Therefore, researcher has focused on the heterogeneous catalysis of PS by insoluble metal oxides [12–15].

Magnetite (Fe_3O_4) is proffered from all kinds of irons due to mixed-valence properties. Due to its magnetic properties, magnetite can be separated easily from wastewater. Activating persulfate with irradiated magnetite leads to need low persulfate demand in oxidation processes and therefore to lower cost of the oxidant [16]. Even though the heterogeneous catalyst process provides sufficient degradation efficiency at acidic solutions, inorganic or organic ligands such as ethylenediamine tetraacetic acid (EDTA), EDDS and NTA can be added to system to enhance the oxidation rate of organic matter and the removal efficiencies [17–21]. Chelating agents promote H_2O_2 activation to generate hydroxyl radicals and promote the ferric ion reduction to ferrous ions to regenerate hydroxyl radicals and enhance the reduction of ferric ion to ferrous ion at neutral pH conditions to increase the hydroxyl radical formation. In the heterogeneous oxidation process chelating agent addition like as EDTA, sulfate radical, hydroxyl radicals can be generated, and these radicals have potential to treat refractory and toxic organic matters rapidly and significantly at neutral pH.

De Luca et al. [22] is mentioned that atrazine removal percentages were around 20% for Fenton, 60% for UV-A photo-Fenton and 70% for UV-C photo-Fenton treatments, respectively. Also, in this study, it is suggested that photo-Fenton can be considered an optional method for the removal of pesticides from wastewaters to perform the treatment at neutral pH. In this study, photo-Fenton experiments were designed to perform neutral conditions using chelating agents. So, the results of this study will meet the deficiencies and recommendations.

To show the advantages of chelating agent, magnetite and persulfate and hydrogen peroxide oxidants and to compare different oxidant effect on the treatment of atrazine, Box–Behnken statistical design was applied to synthetic atrazine wastewater. The effect of operating parameters (persulfate concentration, hydrogen peroxide concentration, magnetite concentration, and EDTA concentration) was investigated by means of different oxidation process in this study. In addition, it is possible to evaluate the treatment of atrazine using the heterogeneous photo-Fenton oxidation and sulfate radical-based oxidation with or without the addition of EDTA. Advantages of EDTA, magnetite and persulfate parameters on atrazine removal efficiency and reaction conditions can be evaluated and interpreted.

2. Material and methods

Atrazine ($\text{C}_8\text{H}_{14}\text{N}_5\text{Cl}$) was purchased from. Atrazine analyses were done by Agilent 1260 Infinity Binary LC. Agilent ZORBAX Eclipse Plus C18, (2.1 mm × 100 mm, 1.8 μm) column was used. 6550 iFunnel Q-TOF LC/MS is used for Q-TOF analysis. Reaction conditions of LC/MS/MS; injection volume: 10 μl , MS acquire time: 15 min, temperature of the column is 22°C, the velocity of flux is 0.35 mL/min, on source ESI (+). Mobile phase of atrazine analyses using LC/MS/MS; mobile phase A: water and % 0.1 formic acid. Mobile phase B: acetonitrile. Atrazine concentrations

between 1 and 100 ppb were used to determine the calibration curve with a linearity of $R^2 = 0.99$. In the heterogeneous photo-Fenton oxidation, magnetite as a source of iron was used and purchased from Merck (99%). Hydrogen peroxide as an oxidant (35% w/w) was used and obtained from Merck. In the sulfate radical-based oxidation process, potassium persulfate as an oxidant source was used to form $S_2O_8^{2-}$. EDTA as a chelating agent was used in both the oxidation process.

2.1. Experimental procedure

All oxidation parts were executed at room temperature ($23^\circ\text{C} \pm 2^\circ\text{C}$) with different magnetite, oxidants ($S_2O_8^{2-}/H_2O_2$) concentration and chelating agent (EDTA) which were determined by statistical program. Box–Behnken statistical program was designed for each process. Oxidant type and concentration were adjusted in the design program to occur and evaluate the effect of different oxidation processes. For all experiments, the concentration of atrazine was adjusted to 0.1 ppm due to the existing concentration in surface wastewater. The pH of wastewater was not adjusted; natural pH value was used in experiments. Because chelating agent addition in the oxidation process enhances to get Fe^{2+} as complex compounds at neutral pH conditions. So, pH value does not need to adjust pH 3. Raw wastewater pH was measured by Thermo Scientific Orion pH meter 720a.

For each oxidation process, first, synthetic solution was added to the UV reactor. Then, magnetite (catalyst) was added and mixed well. Then, oxidant (hydrogen peroxide or persulfate) was added to the reactor, immediately. The UV lamp was opened as soon as possible. At this time was accepted as the beginning of the experiment or time zero. Samples were taken from the reactor at the end of 1 h reaction time to evaluate atrazine removal efficiencies and pH variations. Raw and treated atrazine samples were immediately analyzed LC/MS/MS to avoid some reactions.

2.2. Experimental set-up

Heterogeneous photo-Fenton oxidation (UV/ H_2O_2 /magnetite) process and sulfate radical-based oxidation (UV/ $S_2O_8^{2-}$ /magnetite) process were conducted in a photochemical reactor, which is given in Fig. 1. The photochemical reactor is made of glass and its volume is 2.2 L. To protect eyes and overcome leakage from UV lamp to outside, the reactor was surrounded with an aluminum foil. A photochemical reactor includes some ports to feed oxidant and catalyst, to measure temperature and to withdraw samples. The reactor was placed on a magnetic stirrer to provide a proper mixing with a stirring bar.

The UV lamp was axially centered and placed in a quartz tube. UV lamp properties are a 16 W low-pressure mercury-vapor lamp and maximum emission at 254 nm. The UV radiation intensity was determined as a 4.98×10^{-6} einstein/s via ferrioxalate actinometry method. The UV lamp was placed in a water-cooling jacket to adjust temperature and execute runs at room temperatures, because of the production heat from the light source.

2.3. Regression model

The application of RSM offers an empirical relationship the objective function (Y) and the independent variables (X) can be approximated by a quadratic (second-order) polynomial equation as follows (1):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

This static design was preferred due to fewer combinations of the independent variables to estimate the second-order polynomial regression model. Nine coefficients were calculated such as one block term, three linear

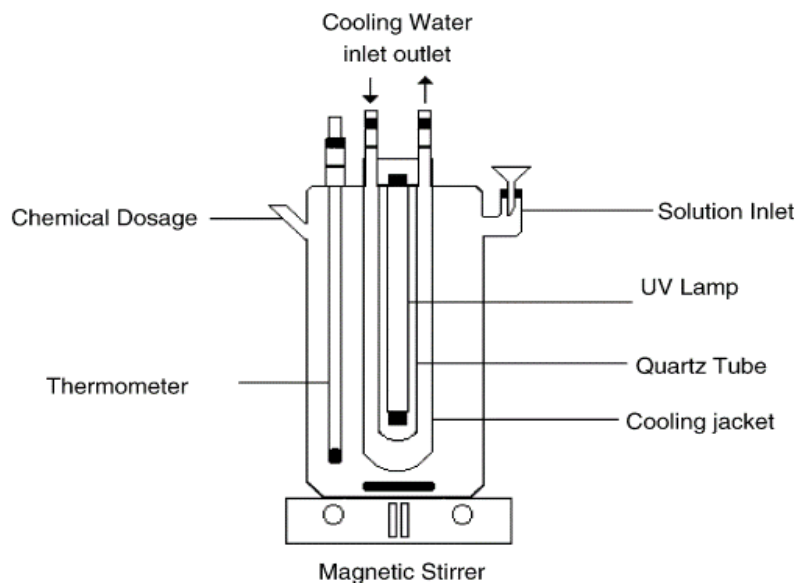


Fig. 1. Schematic of the UV reactor.

terms, three quadratic terms, and three interaction terms. Coefficients in the regression model were determined using 15 runs. Box–Behnken static design is carried out with minimum experimental runs also allow accurate experimental results. For that reason, Box–Behnken statistical design is chosen to investigate the effects of different concentrations of some parameters on atrazine removal. For each process, fifteen experiments were executed. Then these experiments were evaluated by Design-Expert 10 Program and some coefficients and regression squares were calculated. When a coefficient of determination (R^2) is larger than 0.95 for each process, predictions for atrazine removal efficiencies are in good agreement with the observed experimental data. P -values that are less than 0.05 were evaluated for all independent variables to determine the effectiveness of variables. Evaluation of experiments with Design-Expert 10 programme, all removal efficiencies can be calculated by regression model when dependent variables selected in the range concentrations.

For heterogeneous photo-Fenton oxidation (UV/ H_2O_2 /magnetite/EDTA) process, EDTA (X_1), H_2O_2 (X_2) and magnetite (X_3) as the independent variables were chosen in design. For sulfate radical-based oxidation (UV/ $S_2O_8^{2-}$ /magnetite/EDTA) process, EDTA (X_1), $S_2O_8^{2-}$ (X_2) and magnetite (X_3) as the independent variables were chosen in design. Percent atrazine removal efficiency (Y_1) as a dependent variable (or objective function) was chosen in Box–Behnken design. The low (–1), center (0) and high (+1) levels of each variable was determined by statically approach.

While the initial EDTA concentration (X_1) varied between 0 and 5 ppm, hydrogen peroxide concentration (X_2) altered between 0 and 6 ppm as an oxidant in photo-Fenton process. The magnetite concentration (X_3) was ranged from 0 to 5 ppm. Persulfate concentration (X_2) also altered between 0 and 5 ppm as an oxidant in sulfate radical-based oxidation experiments. Independent variable concentrations were chosen after doing some stoichiometric calculations

according to initial atrazine concentration, and molar ratio of hydrogen peroxide to ferrous ion.

3. Results and discussion

Heterogeneous photo-Fenton oxidation and sulfate radical-based oxidation experiments were designed by Box–Behnken design to determine the effect of oxidation processes on atrazine removal efficiencies. Independent variable effects (atrazine, hydrogen peroxide, persulfate and magnetite) on the objective function (percent atrazine removal efficiency) were evaluated by means of Box–Behnken design. Atrazine removal efficiencies as observed and estimated results via statical design are also given in Tables 1 and 2, respectively, for each process.

After oxidation experiments, equations were determined by statistical design program and their repeatable values were very high. The objective function for atrazine removal efficiencies with the determined coefficient is presented by Eq. (2) ($R^2 = 0.96$) and (3) ($R^2 = 0.99$) for heterogeneous photo-Fenton process and sulfate radical-based oxidation process, respectively.

$$Y_1 = 90.8 + 0.24X_1 + 2.21X_2 - 0.075X_3 - 0.325X_1X_2 + 0.8X_2X_3 - 0.946X_1^2 - 0.596X_2^2 - 0.821X_3^2 \quad (2)$$

$$Y_2 = 81.3 - 0.51X_1 + 1.1X_2 - 0.93X_3 + 0.23X_1X_2 + 0.65X_1X_3 + 0.33X_2X_3 - 1.73X_1^2 + 2.11X_2^2 + 3.68X_3^2 \quad (3)$$

According to the coefficients in Eq. (2), it can be that H_2O_2 (X_2), EDTA (X_1) are significant model terms. The H_2O_2 variable has a more significant effect on atrazine removal

Table 1
Atrazine removal efficiencies as observed and predicted results for heterogeneous photo-Fenton process

Run No.	EDTA	H_2O_2 (ppm)	Magnetite	Predicted ATZ rem. (%)	Observed ATZ rem. (%)
1	2.5	3	2.5	91.00	90.77
2	5	0	2.5	87.00	87.57
3	0	3	0	88.50	88.84
4	2.5	6	0	90.60	90.84
5	5	3	0	89.70	89.31
6	0	0	2.5	86.60	86.45
7	0	6	2.5	92.10	91.52
8	5	3	5	89.50	89.16
9	2.5	3	2.5	91.20	90.77
10	5	6	2.5	91.20	91.35
11	2.5	6	5	92.10	92.29
12	2.5	0	0	88.20	88.01
13	2.5	3	2.5	90.10	90.77
14	2.5	0	5	86.50	86.26
15	0	3	5	88.30	88.69

Table 2
Atrazine removal efficiencies as observed and predicted results for the sulfate radical-based oxidation process

Run No.	EDTA	S ₂ O ₈ ²⁻ (ppm)	Magnetite	Predicted ATZ rem. (%)	Observed ATZ rem. (%)
1	2.5	2.5	2.5	81.40	81.33
2	5	0	2.5	83.60	83.34
3	0	2.5	0	88.90	88.83
4	2.5	5	0	89.00	88.81
5	5	2.5	0	86.10	86.50
6	0	0	2.5	84.60	84.81
7	0	5	2.5	86.30	86.56
8	5	2.5	5	85.90	85.98
9	2.5	2.5	2.5	81.20	81.33
10	5	5	2.5	86.20	85.99
11	2.5	5	5	87.50	87.64
12	2.5	0	0	87.40	87.26
13	2.5	2.5	2.5	81.40	81.33
14	2.5	0	5	84.60	84.79
15	0	2.5	5	86.10	85.70

efficiency compared to magnetite or EDTA. Percent atrazine removal efficiency affected slowly after the addition of magnetite or EDTA as independent variables. Only hydrogen peroxide addition significantly increased the atrazine removal efficiencies.

According to the coefficients in Eq. (3), it can be said that EDTA (X_1), H₂O₂ (X_2), magnetite (X_3), X_1X_3 , X_1^2 , X_2^2 , X_3^2 are significant model terms. Although coefficients of independent variables affect atrazine removal efficiencies, only the persulfate as a variable has a more significant and positively affect atrazine removal efficiency compared to other independent variables. Predictions for atrazine removal efficiencies agree well with the observed experimental data. The coefficient of determination (R^2) is larger than 0.95 for each process. According to, the analysis of variance results, P -values less than 0.05 were evaluated for all independent variables to determine the effectiveness of variables.

3.1. Removal of atrazine

3.1.1. Removal of atrazine in heterogeneous photo-Fenton process

Variations of atrazine removal efficiencies in heterogeneous photo-Fenton process with the independent variables (EDTA, magnetite, and hydrogen peroxide concentrations) under different reaction conditions were estimated by coefficients determined from static design. Initial magnetite concentration effects on atrazine removal efficiencies at different H₂O₂ and EDTA concentrations during 60 min of reaction time are shown in Fig. 2. At these reaction conditions, initial atrazine concentration was selected as 0.1 ppm due to previous studies and existence concentration in surface water.

As can be shown in Fig. 2, atrazine removal efficiencies were 90%, 92%, and 93% when initial magnetite concentrations of 0, 2.5, and 5 ppm, respectively, at an EDTA

concentration of 2.5 ppm and a H₂O₂ concentration of 5 ppm. The addition of magnetite to the oxidation process increased the atrazine removal efficiencies due to the acceleration of hydroxyl radical formation by using magnetite, which consists of ferrous ion and ferric ions. When EDTA concentration increased to 5 ppm, percent atrazine removals were 85%, 89% and 90% when initial magnetite concentrations of 0, 2.5, and 5 ppm, respectively, at H₂O₂ concentration of 5 ppm EDTA addition helps the control of pH conditions, the oxidation process can occur all pH conditions after the addition of EDTA agent. The formation of Fe⁺² complexes at neutral and basic pH conditions. Fe⁺² complex in oxidation process at nonacidic conditions can be achieved by chelating agent.

Variations of atrazine removal efficiencies at different magnetite and EDTA concentrations during 60 min of reaction time in the heterogeneous photo-Fenton process are shown in Fig. 3. Atrazine removal efficiencies increased with high H₂O₂ concentration and atrazine degradation was not also completely achieved with low magnetite concentration, as shown in Fig. 3c.

As Fig. 3 shows, the hydrogen peroxide requirement to remove atrazine was approximately 5 ppm at high magnetite concentration. The most serious issue for the oxidation process is to evaluate the molar ratio of oxidant and catalyst. So, optimum reaction conditions should be determined using the static design approach according to initial atrazine concentration. When an inadequate amount of H₂O₂ or magnetite is used, complete atrazine degradation did not observe during reaction time. In other words, high H₂O₂/magnetite molar ratio produced low removal efficiencies due to inhibition of excess formation of hydroxyl radicals. At a molar ratio of 2, approximately 93% atrazine removal efficiency was obtained at 0.1 ppm initial atrazine concentration. Sufficient removal efficiencies were achieved with a low molar ratio.

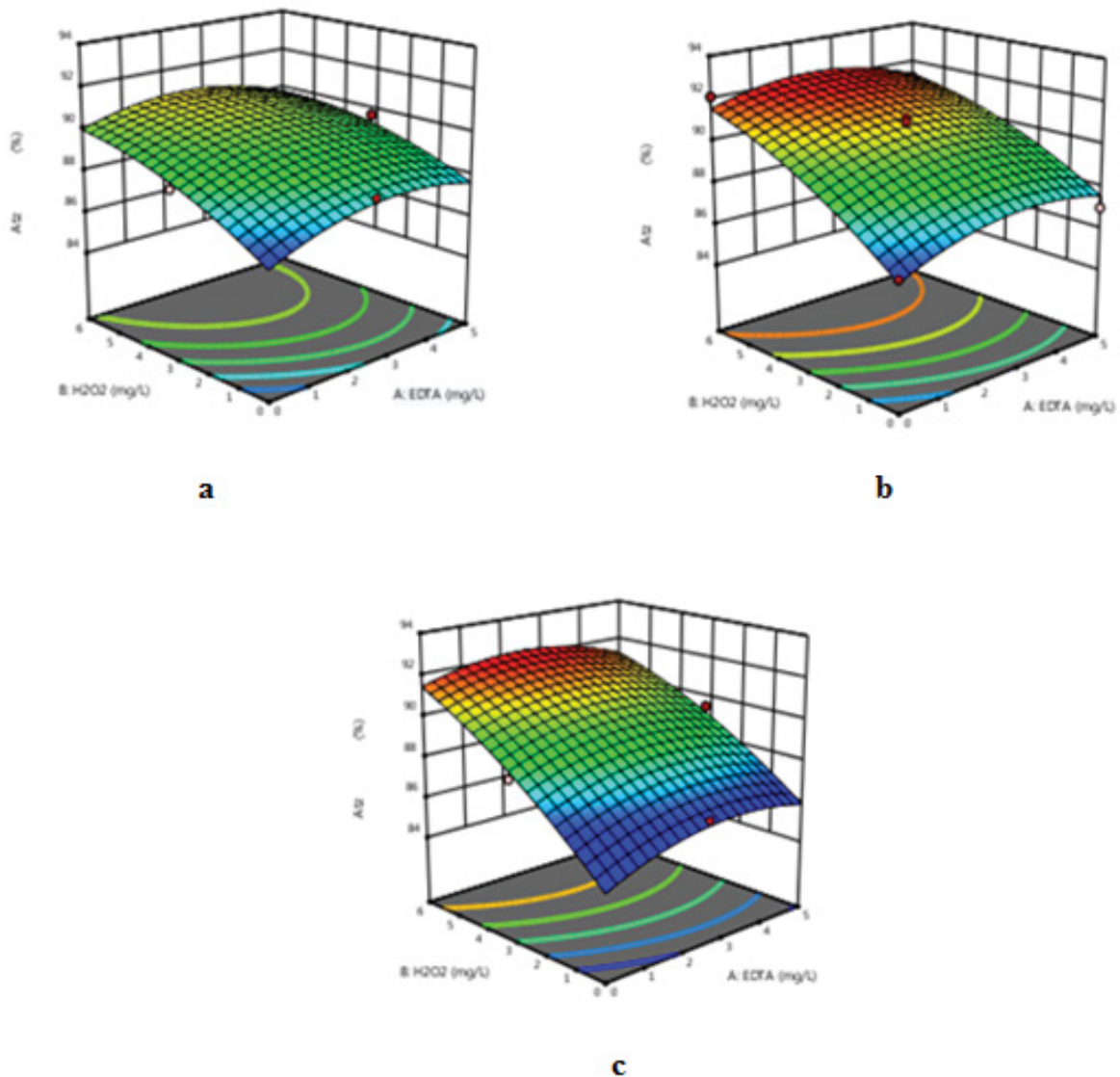


Fig. 2. Atrazine removal efficiencies achieved with different EDTA and H_2O_2 concentrations in heterogeneous photo-Fenton process [Reaction time: 60 min, (a) magnetite: 0 ppm, (b) magnetite: 2.5 ppm, and (c) magnetite: 5 ppm].

3.1.2. Removal of atrazine in the sulfate radical-based oxidation process

Variations of atrazine removal efficiencies in the sulfate radical-based oxidation process with the independent variables (EDTA, magnetite and persulfate concentrations) under different reaction conditions were estimated by coefficients determined from static design. Initial magnetite concentration effects on atrazine removal efficiencies at different $\text{S}_2\text{O}_8^{2-}$ and EDTA concentrations during 60 min of reaction time are shown in Fig. 4. At these reaction conditions, the initial atrazine concentration was selected as 0.1 ppm.

When magnetite did not add the oxidation process to degrade atrazine, percent atrazine removals achieved as 88% and 91% with initial sulfate concentrations of 2.5 and 5 ppm, respectively. As can be also shown in Fig. 4, atrazine degradation was not completely achieved with the addition

of magnetite. The addition of magnetite did not change the performance of the process and resulted in the same atrazine removal efficiencies. In addition to this, coefficients showed that magnetite as an independent parameter has not a positive effect on atrazine removal efficiencies. The maximum atrazine removal efficiency was obtained with a low concentration of magnetite as 91%.

Variations of atrazine removal efficiencies at different magnetite and EDTA concentrations during 60 min of reaction time in the sulfate radical-based oxidation process are shown in Fig. 5. Atrazine removal efficiencies increased with high $\text{S}_2\text{O}_8^{2-}$ concentration as shown in Fig. 5c.

As can be shown in Fig. 5, the addition of persulfate as an oxidant to the oxidation process significantly affects the atrazine removal efficiencies. When initial persulfate concentrations of 0, 2.5, and 5 ppm respectively were used with a magnetite concentration of 1 ppm and an EDTA concentration of 1 ppm, percent atrazine removals were 88%,

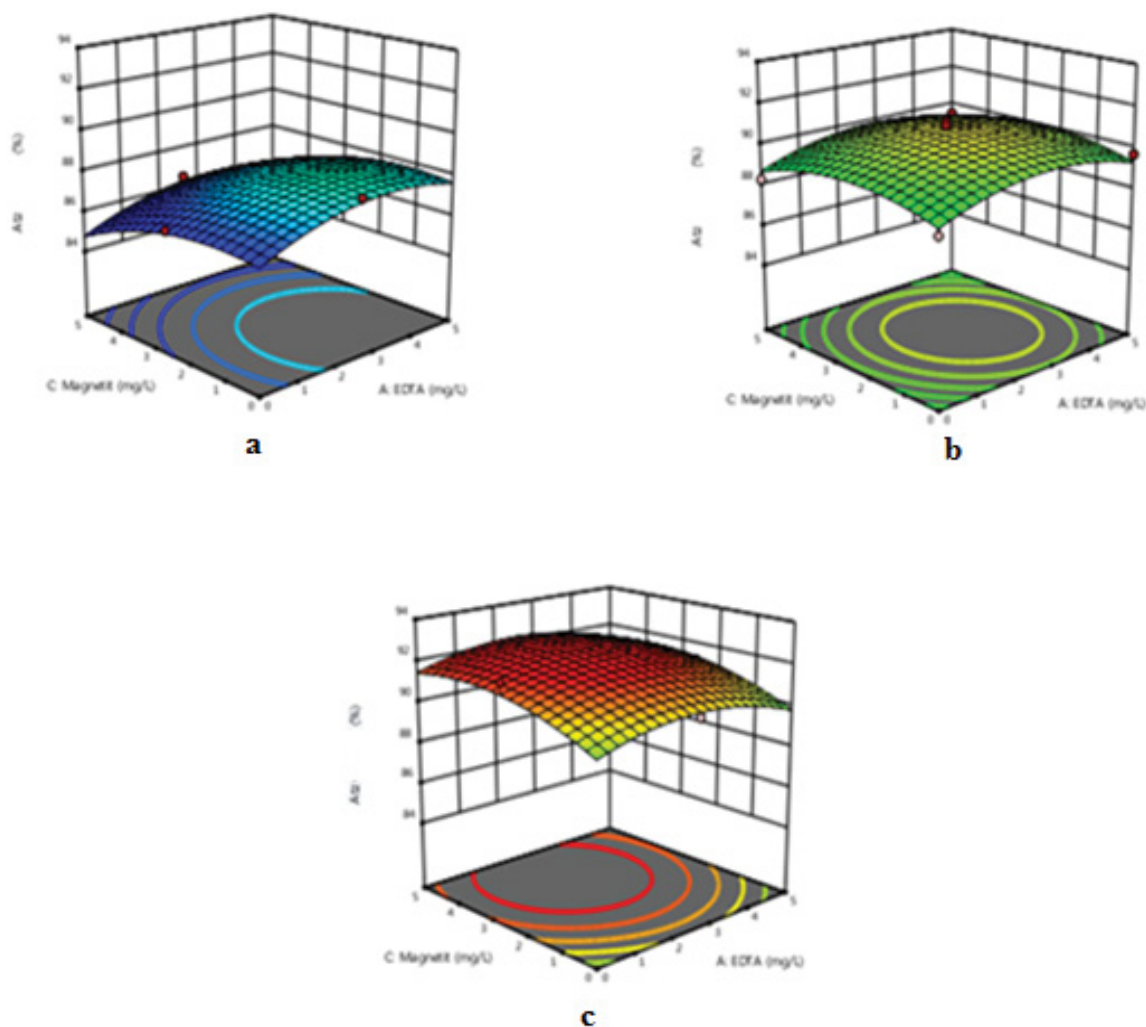


Fig. 3. Atrazine removal efficiencies achieved with different EDTA and magnetite concentrations in the heterogeneous photo-Fenton process [Reaction time: 60 min, (a) H_2O_2 : 0 ppm, (b) H_2O_2 : 3 ppm, and (c) H_2O_2 : 6 ppm].

86% and 90%, respectively. As can be shown in Fig. 5, at a molar ratio of 5, approximately 90% atrazine removal efficiency was obtained at 0.1 ppm initial atrazine concentration. In the sulfate radical-based oxidation process, the molar ratio of oxidant and catalyst to treat atrazine should be arranged as below the molar ratio, atrazine removal efficiencies decreased due to an inadequate amount of persulfate or magnetite. In other study, it is mentioned that low Fe^0 :PS molar ratio will lead to poor degradation effect on refractory organics due to lack of sufficient active sites for PS activation and $\text{SO}_4^{\cdot-}$ generation [23]. According to another study, UV/ S_2O_8 system was more effective than UV/ HSO_5^- and UV/ H_2O_2 systems for atrazine (ATZ) degradation under the same conditions. This study provided a comprehensive understanding of the effects of S_2O_8 on advanced oxidation processes [24].

3.1.3. By-products of atrazine and degradation mechanism

The degradation of atrazine was evaluated by a heterogeneous photo-Fenton process and sulfate radical-based

oxidation process. The irradiated atrazine samples were taken from the end of the oxidation process were analyzed by LC/MS/MS. All atrazine metabolites were identified and properties of by-products such as compound name, formula, structures, abbreviations, and retention times in LC/MS/MS are given in Table 3.

Samples taken from oxidation studies (heterogeneous photo-Fenton and sulfate radical-based oxidation processes) designed by Box–Behnken design were analyzed by LC/MS/MS. Intermediates of atrazine in samples were identified by LC/MS/MS. When oxidation processes were executed, deisopropylatrazine (DIA), deethylatrazine (DEA) and hydroxyatrazine (HA) are monitored as primary metabolites. Besides, hydroxysimazine (HS), betaine, dicyclohexylurea, phthalic acid mono-2-ethylhexyl ester, and dioctylphthalate were also identified as by-products.

After evaluation of analyze results from library of LC/MS/MS, DIA, DEA and HA, metabolites occurred by the applied oxidation process. Another study is also showed the dealkylation of ATZ occurred in the Fe_3O_4 -sep/PS system and the production of DIA and DEA, which underwent further

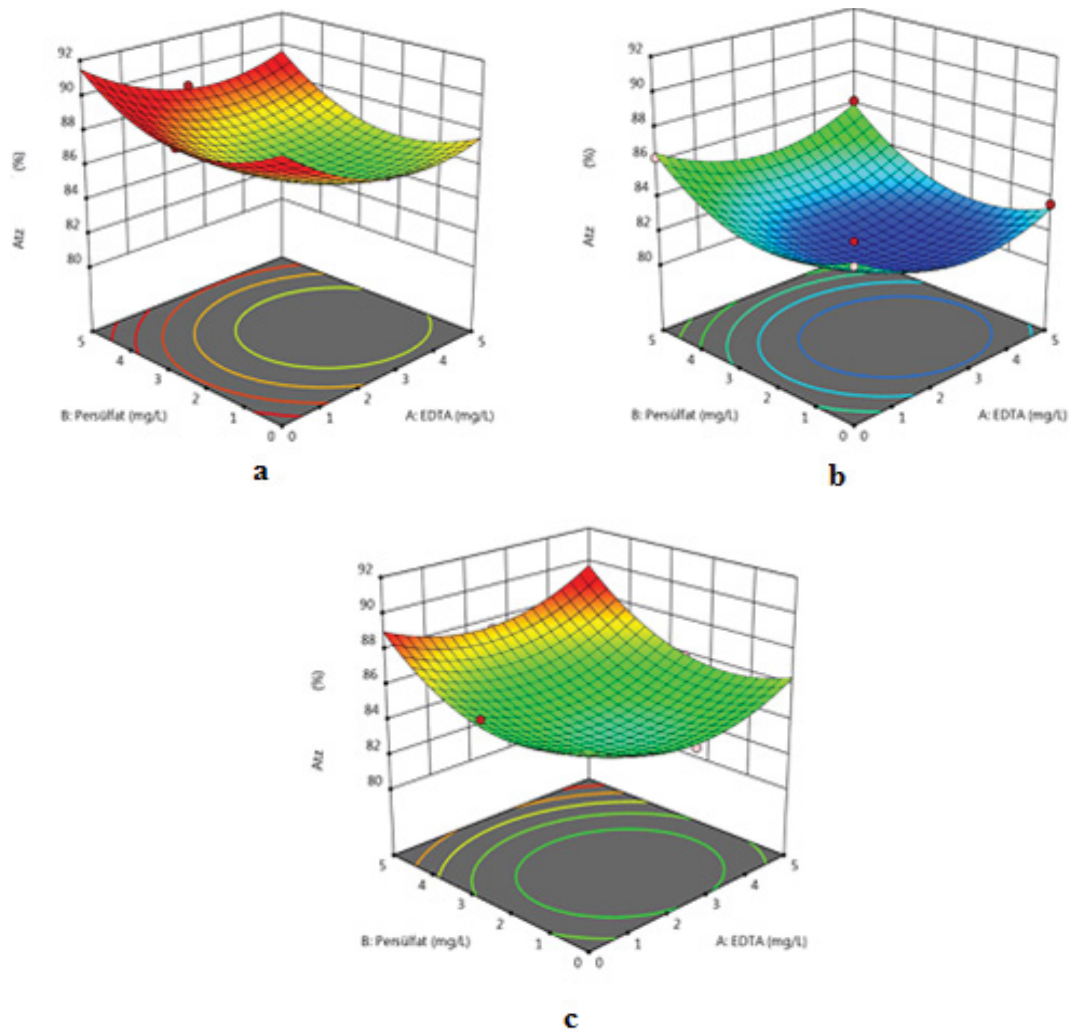


Fig. 4. Atrazine removal efficiencies achieved with different EDTA and $S_2O_8^{2-}$ concentrations in the sulfate radical-based oxidation process [Reaction time: 60 min, (a) magnetite: 0 ppm, (b) magnetite: 2.5 ppm, and (c) magnetite: 5 ppm].

dealkylation and generated DEIA [21,25]. It should be noted that some transformation products of ATZ by HO^\bullet or SO_4^\bullet (e.g., di-isopropyl-atrazine, diethylatrazine) are as toxic as ATZ [26]. After the evaluation of by-products, hydroxyatrazine metabolite was observed for all experimental runs. The amount of this metabolite is higher than other metabolites. Different from other studies, betaine and hydroxysimazine metabolites were also shown in the chromatogram. This means is that oxidation processes were positively affected by the treatment of atrazine. Both high removal efficiency of atrazine was obtained using these oxidation process and metabolites observed in treated samples were identified as nontoxic. For that reason, a heterogeneous photo-Fenton process and sulfate radical-based oxidation process were suitable for treating atrazine compounds and their metabolites.

In the heterogeneous photo-Fenton process, DIA, DEA and HA, HS and betaine were observed as by-products. Among these metabolites, betaine, hydroxyatrazine, and hydroxyl simazine were significantly monitored. This means that the chlorine ion attached to atrazine is broken down.

A small amount of DIA and DEA was observed with the heterogeneous photo-Fenton process.

In the sulfate radical-based oxidation process, DIA, HA, HS, atrazine-desethyl-2-OH and betaine were observed as by-products. Among metabolites, hydroxyatrazine and hydroxysimazine were significantly monitored. This means that chlorine ion bound in atrazine was also broken off. A small amount of DIA was observed with the sulfate radical-based oxidation process. DEA metabolites did not be identified by the sulfate radical-based oxidation process. For that reason, the sulfate radical-based oxidation process is more suitable than the heterogeneous photo-Fenton process due to not formation of DEA metabolites, which is more toxic than atrazine compound. Besides, the formation of hydroxyatrazine occurred in the sulfate radical-based oxidation process. This metabolite is less toxic than other by-products and the main compound.

Although atrazine removal efficiencies were nearly the same value at these processes, the requirement of magnetite and EDTA concentrations in the sulfate radical-based

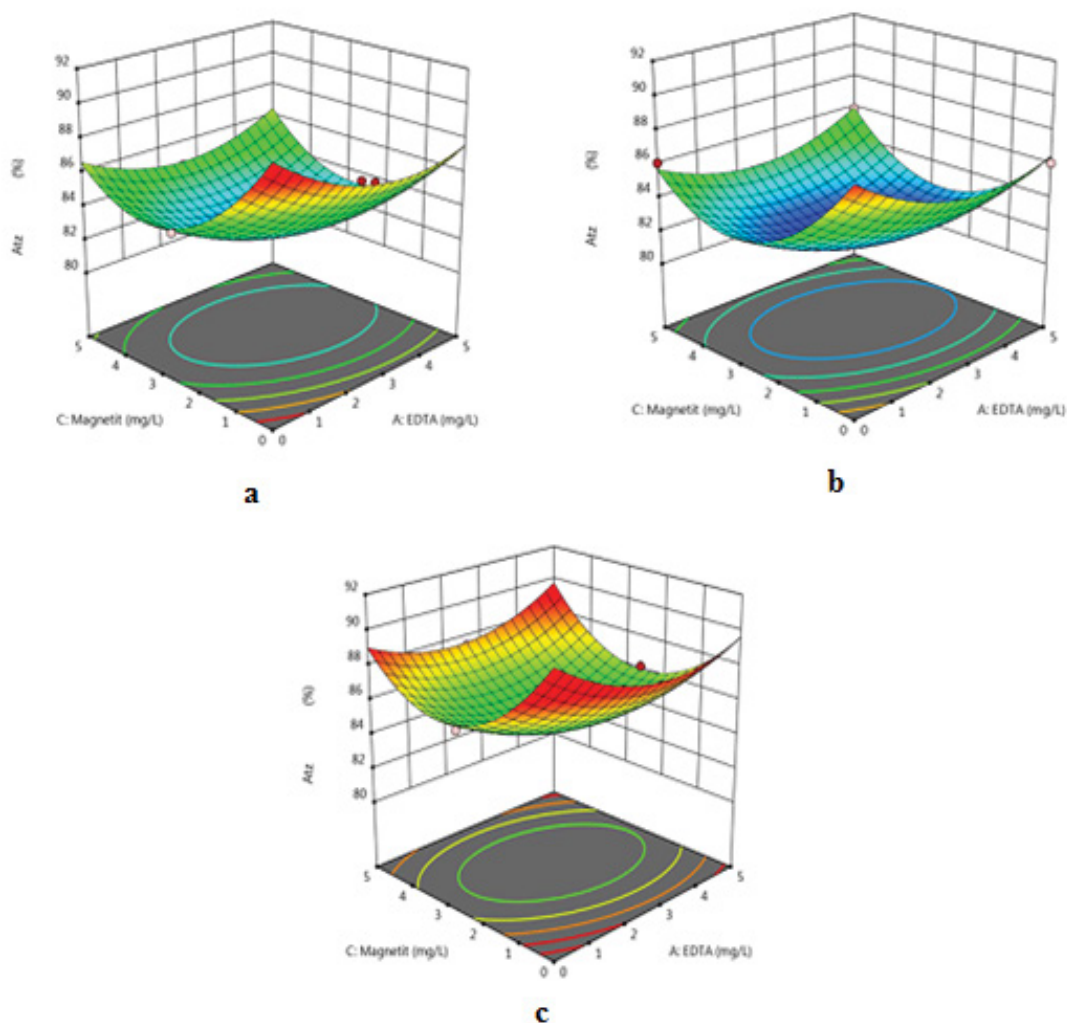


Fig. 5 Atrazine removal efficiencies achieved with different EDTA and Magnetite concentrations in the sulfate radical-based oxidation process [Reaction time: 60 min, (a) $S_2O_8^{2-}$: 0 ppm, (b) $S_2O_8^{2-}$: 2.5 ppm, and (c) $S_2O_8^{2-}$: 5 ppm].

Table 3
Retention times, compound name and formula of atrazine and its by-products

M+H ⁺ (m/z)	Retention time (min)	Compounds name	Formula
216	4.547	Atrazine (ATZ)	$C_8H_{14}ClN_5$
187	3.117	Deisopropylatrazine (DIA)	$C_5H_8ClN_5$
173	4.630	Deethylatrazine (DEA)	$C_6H_{10}ClN_5$
197	2.328	Hydroxyatrazine (HA)	$C_8H_5N_5O$
184	1.202	Hydroxysimazine (HS)	$C_7H_{13}N_5O$
198	2.329	Atrazine-desethyl-2-OH	$C_3H_{12}N_5O$
118	0.414	Betaine	$C_5H_{12}NO_2$

oxidation process is lower than the heterogeneous photo-Fenton method. This is the advantage of the sulfate radical-based oxidation process for treating atrazine compounds. Also, the sulfate radical-based oxidation process is more suitable than the heterogeneous photo-Fenton process due

to not formation of DEA metabolites, which is more toxic than atrazine compound.

The highest atrazine removal efficiency (90%) was obtained using an EDTA/ $S_2O_8^{2-}$ /magnetite ratio of 1/5/1 ppm to sulfate radical-based oxidation processes. Molar ratio of PS and magnetite was found at 5:1. These results implied that the optimum molar ratio of Fe^{2+} and PS for ATZ degradation was found at 1:1, which has been confirmed in other study [27].

4. Conclusions

Heterogeneous photo-Fenton and sulfate radical-based oxidation processes as an advanced oxidation process were applied to atrazine synthetic wastewater to degrade. Box–Behnken statistical design that is the most useful response surface methodology was used to optimize reaction conditions in the advanced oxidation process. H_2O_2 , $S_2O_8^{2-}$, EDTA, and magnetite concentrations were chosen as independent variables while atrazine removal efficiency was selected as the dependent variable (objective function).

The H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ variable has a more significant effect on atrazine removal efficiency compared to magnetite and EDTA independent variables. Atrazine removal efficiencies (nearly 90%) were achieved by heterogeneous photo-Fenton oxidation and sulfate radical-based oxidation processes. The highest atrazine removal efficiency (92%) was obtained with an EDTA/ H_2O_2 /magnetite ratio of 4/5/5 ppm to the heterogeneous photo-Fenton oxidation process. The highest atrazine removal efficiency (90%) was obtained using an EDTA/ $\text{S}_2\text{O}_8^{2-}$ /magnetite ratio of 1/5/1 ppm to sulfate radical-based oxidation processes.

Sulfate radical-based oxidation is more effective than a heterogeneous photo-Fenton oxidation. Although atrazine removal efficiencies were the nearly same value at these processes, the requirement of magnetite and EDTA concentrations in the sulfate radical-based oxidation is lower than the heterogeneous photo-Fenton method.

When heterogeneous photo-Fenton and sulfate radical-based oxidation processes were executed, DIA, DEA and HA are monitored as primary metabolites. The sulfate radical-based oxidation process is more suitable than heterogeneous photo-Fenton process due to not formation of DEA metabolites, which is more toxic than atrazine compound. Besides, the formation of hydroxyatrazine, which is less toxic than atrazine and its by-products occurred in the sulfate radical-based oxidation process.

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