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Degradation of atrazine by microwave-assisted electrodeless discharge mercury lamp in aqueous solution

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Abstract

The present study investigates the degradation of atrazine (2-chloro-4-(ethyl amino)-6-isopropyl amino-*s*-triazine) in aqueous solution by a developed new method, namely by means of a microwave-assisted electrodeless discharge mercury lamp (MW-EDML). An experimental design was conducted to assess the influence of various parameters: pH value, initial concentration, amount of EDML, initial volume and coexisted solvent. Atrazine was degraded completely by EDML in a relatively short time (i.e. $t_{1/2} = 1.2$ min for 10 mg/l). Additionally, the identification of main degradation products during atrazine degradation process was conducted by gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS). This study proposes the degradation mechanism including four possible pathways for atrazine degradation according to the degradation products.

Keywords: Atrazine; Microwave; Electrodeless discharge mercury lamp; Photodegradation; Pesticide

1. Introduction

MW has been developed over than 30 years since in 1975 Abu-Samra first applied MW oven in laboratory. It has become a very attractive tool in synthetic organic chemistry because of its great ability to accelerate chemical reactions with improved yields and selectivity [1]. MW application is an active field of research, so it is also greatly applied in environmental science as a more effective, easier, cheaper extraction technique compared to traditional methods. The major advantages of MW extraction are decreased extraction time, reduced solvent consumption, increased sample throughput [2]. Application of MW in some other environmental research fields is still in progress [3,4]. An original photochemical reactor consisting of an electrodeless discharge lamp (EDL) was introduced in detail [5]. It was reported to be a prospective tool for photochemistry with good photochemical efficiency, simplicity and inexpensiveness by simultaneous application of UV and MW irradiation in experiment [6]. However, the MW-EDL was not widely employed in decomposition of organic pollutants especially in pesticides [7,8].

Atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-*s*-triazine) was introduced in the 1950s, and since then atrazine has become the most widely used herbicide in agricultural and forestry applications, with 70,000–90,000 tonnes applied annually in the world. Atrazine has high effectiveness in inhibiting the growth of target weeds including variety of plants and some species of algae by interfering with the normal function of photosynthesis [9]. In addition, atrazine has the properties of high leaching potential, persistence in soil, slow hydrolysis, low vapor pressure, solubility in water and high toxicity to aquatic organisms and lower for mammals [10]. Because of these properties, atrazine applied to cropland can be transported to groundwater by infiltration or to surface waters by water runoff [11]. Atrazine is more frequently detected in ground water and surface water of many countries than any other herbicides [9,12]. Atrazine persists under cool, dry conditions, in a stable pH environment. For these reasons, numerous studies have been carried out on degradation of atrazine applying different methods such as advanced oxidation method [13], catalytic oxidation process [14] and microorganism removal [15] for objective of resolving atrazine contamination and removing atrazine

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from water system. Both advanced oxidation method and catalytic oxidation process show higher efficiency in removal of atrazine in a mild condition and have received increasing attention. However, they are demanding preparation of catalyst and feasible regeneration of catalyst, thus, it is sometimes not desirable. Additionally, atrazine is toxic for microorganisms and the triazine-ring itself is quite resistant to the microbial attack [16]. As a result, conventional biological remediation processes are not efficient and unsuitable to remove higher concentration of atrazine from contaminated water rapidly. Therefore, all above methods are time costing and the application is restricted by limited conditions of the methods. Thus, until now, no completely efficient methods have been developed for remediation of atrazine-contaminated water. The degradation mechanisms and metabolic pathways of triazines have been also largely investigated [17,18], but the mechanisms of atrazine degradation still remain unclear and little information is available on the degradation mechanism of atrazine under MW-EDML irradiation, which serves as background data for environmental behavior of atrazine.

A MW-EDML reactor was developed in our laboratory and was applied to remove higher concentration of atrazine with impressive degradation capability. Several factors affecting the degradation of atrazine, such as the initial concentration of atrazine, pH value, the initial solution volume, the amount of EDML and trace coexisted solvent were studied in detail. In present study, applying LC–MS and GC–MS to identification of degradation products and according to the results of LC–MS and GC–MS, the possible degradation pathway and degradation products for atrazine are also predicted and proposed. It is also proved that MW-EDML is a very simple, economic, efficient, environmentally friendly and prospective tool for degradation of atrazine.

2. Materials and methods

2.1. Chemicals

Standard atrazine (99.0%) was purchased from Supelco (Bellefonte, PA, USA), and HPLC grade solvents (dichloromethane and methanol) used in the analysis were purchased from Tedia (Fairfield, OH, USA). Atrazine solution was prepared in methanol. Anhydrous sodium sulfate (analytical grade) was purchased from Nanjing Chemical Factory. Phosphate buffer solution with concentration of 0.02 mol/l was prepared in distilled water (pH 3.0, 5.0, 6.0, 7.0, 8.0, 9.0). All chemicals were used as received.

2.2. Methods

2.2.1. MW experiments

All MW degradation experiments was conducted in MW-EDML reactor, which consisted of a MW oven, Pyrex vessel, EDML, glass tube connector and water-cooling condenser (Fig. 1). A domestic MW oven (Midea, PJ23C-SCI, China) was one of the important parts of this reactor, which was modified as follows: a hole was drilled in the upper oven wall and an aluminum tube of the same diameter was attached to the hole in order to eliminate possible MW leaking. In the aluminum tube, a glass tube was attached connecting a water-cool condenser and a Pyrex vessel on its both sides. The EDML was placed into the vessel which was then put into the MW oven cavity. So, when the MW begins to work, the EDML is excited and causes UV–vis irradiation which is absorbed by the atrazine solution and induces the degradation of atrazine. The EDML was made of Pyrex with desired length, filled with argon and a few drops of mercury and as well as sealed under vacuum. The EDML lamp (10 mm × 50 mm) has prominent emission bands at 254, 313, 365, 405, 436, 546, 577 and 579 nm [19] and light intensity of 254–300 nm is 9–10 mW/cm^2 for four EDML with good stability more than 800 min. The MW power was adjusted to a maximal value (900 W), which guaranteed continuous MW radiation.

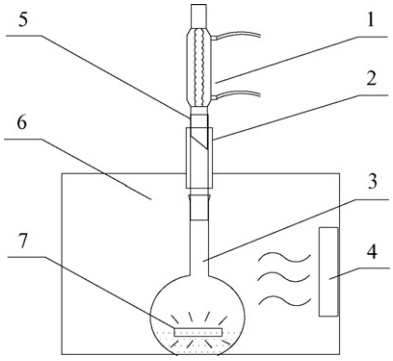


Fig. 1. The microwave-assisted photochemistry reactor: (1) water-cooled condenser; (2) aluminum tube (glass tube connector in it); (3) vessel; (4) magnetron; (5) glass tube; (6) microwave oven cavity; (7) electrodeless discharge mercury lamps (EDML).

When the experiment was started, the vessel with atrazine aqueous solution and EDML was placed into the MW oven cavity and connected to the glass tube connector and the water-cooling condenser systems. After installation, the reactor began to work and the solution for measurement of atrazine was obtained in time. The basic degradation experiments were carried out with above mentioned MW-EDML reactor. All the processes and the results described below were performed under this reactor.

2.2.2. HPLC analysis of atrazine

The degradation process followed a consecutive measurement of atrazine in time by a HPLC system (Agilent, USA, 1100 Series high-performance liquid chromatography) equipped with Zobax Extend-C18 HPLC column (150 mm × 4.6 mm i.d., 5 μm, Agilent, USA), a diode array detector (DAD) and an auto sampler controlling under a Chemstation data acquisition system. The measurement was performed in a methanol/water (60:40, v/v) phase at a flow rate of 1.0 ml/min. The wavelength was set at 220 nm which is the maximum absorption of atrazine and the column temperature was 30 °C. Retention time of atrazine was 4.67 min at the above conditions.

2.2.3. SPE enrichment of degradation products

According to previous literature [11], the C18 tube has a high efficiency on recovering atrazine and most of atrazine degradation products. In order to identify all degradation products of atrazine, the Supelclean ENVI^{TM}-18 solid phase extraction (SPE) tubes (Supelco, Bellefonte, PA, USA) were chosen for the enrichment of degradation products of atrazine. The SPE tubes were packed with 1 mg of silica gel bonded reversed phase parkings with average particle size at 56.0 μm. Before the enrichment, the SPE tubes were preconditioned with 10 ml of methanol and then 10 ml of distilled water and stored at distilled water until the enrichment procedure. The water solutions after degradation were trapped through the SPE tubes with a flow rate of 5 ml/min under vacuum pump. The SPE tubes enriched degradation products were eluted by 5 ml methanol twice and then the eluent was dried by adding anhydrous sodium sulfate and evaporated in an evaporator, then in a gentle stream of nitrogen until the volume was less than 1 ml.

2.2.4. Identification of degradation products by LC–MS and GC–MS

LC–MS and GC–MS are proved to be the appropriate and useful apparatus in the confirmation of many organic pollutants and their degradation products, which are widely applied in environmental science. However, an unambiguous identification of phototransformation products is often not readily possible because of the limitation of the apparatus. LC–MS–APCI is useful in detection of polar and thermally labile chemicals providing the molecular weight, but the information of molecular structure and inquiring laboratory system are unavailable or undesirable. GC–MS applies in nonpolar chemicals by providing the information of molecular structure following a relatively abundant inquiring laboratory system, but for some degree, GC is undesirable in polar organic pollutants. Therefore, the combination of LC–MS–APCI and GC–MS information might be more effective in getting more information about degradation products.

The identification of atrazine and its degradation products was first performed by LC–MS (ThermoQuestLCQ Duo, USA) with Beta Basic-C18 HPLC column (150 mm × 2.1 mm i.d., 5 μm, Finnigan, Thermo, USA). The final extract (10 μl) from SPE enrichment was injected automatically into the LC–MS system. The flow rate was 0.2 ml/min. The other LC conditions were described in Section 2.2.2. MS conditions were as follows: the MS was equipped with atmospheric pressure chemical ionization and electrospray ionization interface (APCI/ESI). The APCI interface was selected and the capillary temperature was set to 150 °C with a voltage of 10 V. The spectra were acquired in the positive scan mode, over the *m/z* range 40–500 at 1 scan/s. The discharge current was 5 μA and the sheath gas flow rate was 60 AU.

The identification of atrazine and its degradation products was also conducted by a Finnigan Thermo Trace gas chromatography interfaced with a Polaris Q ion trap mass spectrometer (GC–MS, Finnigan Thermo, USA). The instrument was controlled by the Xcalibur software from Finnigan. The final extracts (1.0 μl) were automatically injected into a 5% equivalent polysilphenylene-siloxane GC column (DB-5 fused-silica capillary column, 30 m × 0.25 mm i.d., 0.25 μm film thickness) with splitless mode. The oven temperature was programmed as follows: the initial temperature was 60 °C, then 60–200 °C at ramp rate of 10 °C/min hold 2 min, to 240 °C at 4 °C/min, to 280 °C at 10 °C/min holds 2 min. The MS conditions of the analysis were as follows: injector temperature and transfer line temperature was set at 250 and 200 °C, respectively. The carrier gas was helium with flow rate of 1.5 ml/min at constant flow with vacuum compensation. The mass spectra were scanned from 40 to 650 μm at 0.4 scan/s. The MS was operated with a 70-eV electron impact (EI) mode with positive ion mode.

3. Results and discussion

3.1. The factors affecting degradation of atrazine

3.1.1. Effect of initial concentration of atrazine

The effect of initial concentration of atrazine was examined with different concentrations at 5, 10, 20 and 50 mg/l (Fig. 2). As shown in Fig. 2, with the increasing of initial concentration of atrazine, the degradation rates were decreased. It indicates that initial concentration greatly affects the degradation rate of atrazine. When initial concentration was 5 mg/l, the degradation rate constant was 0.89 min^{-1}, and atrazine was degraded completely within 6 min. However, when the initial concentration was increased to 50 mg/l, degradation rate constant was decreased to 0.1459 min^{-1}, complete degradation of which needed 30 min. It might be the reason that degradation amount of atrazine is affected by light intensity of UV–vis irradiation. Therefore, under invariable light intensity, the degradation rate of atrazine decreases when the concentration of atrazine in the aqueous solution is increased. The degradation followed a first order rate equation, which is confirmed by the evidence of a straight line relationship of logarithmic atrazine concentration versus irradiation time ($r > 0.92$), this is coherent with the literature [20].

3.1.2. Effect of initial volume of atrazine

In order to estimate the effect of solution volume, degradation of atrazine with a series of different volumes was carried out.

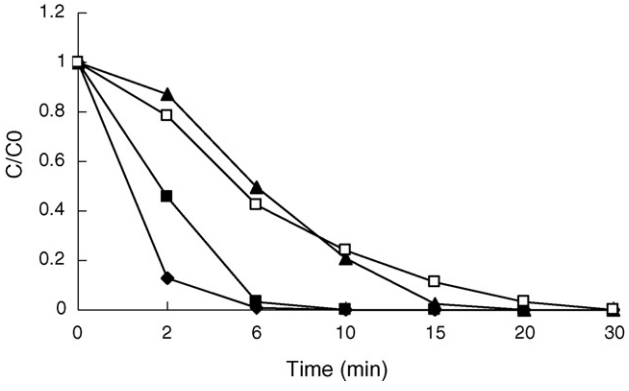


Fig. 2. Effect of initial concentration of atrazine: 5 mg/l (♦), 10 mg/l (■), 20 mg/l (▲) and 50 mg/l (□); solution volume of atrazine was 50 ml (pH 6.3, under one EDML irradiation).

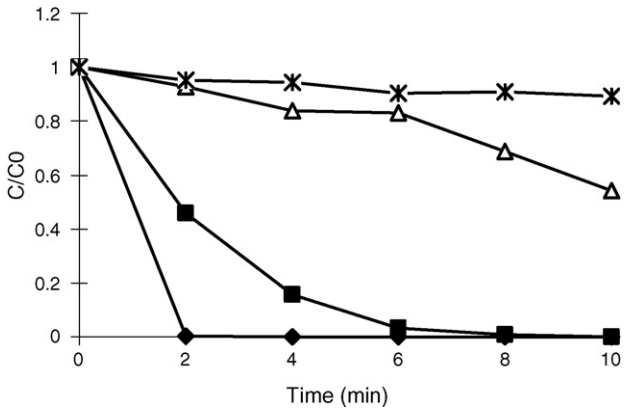


Fig. 3. Effect of initial volume of atrazine: the initial volume of atrazine was 25 ml (♦), 50 ml (■), 75 ml (△) and 100 ml (*); the concentration of atrazine was 10 mg/l (pH 6.3, without buffered, under one EDML irradiation).

Fig. 3 shows the experimental result when the same concentration of atrazine (10 mg/l) was conducted with different volumes at 25, 50, 75 and 100 ml. It was obvious that the solution volume has a great influence on atrazine degradation. The experiment with smaller volumes showed higher degradation rate than that of larger one. It might be the reason that degradation amount of atrazine is influenced by light intensity of UV–vis irradiation. With increasing the volume of arazine solution, the amount of atrazine increased but the light intensity of UV–vis irradiation not changed, as a result, degradation rate of atrazine decreased.

3.1.3. Effect of pH value

The effect of pH value on atrazine degradation was investigated by ranging the pH value of aqueous solution of atrazine from pH 3 to 9 (Fig. 4). As inferred from Fig. 4, atrazine degradation is also strongly dependent on pH. A significant enhancement of the degradation is experienced when increasing the pH value of aqueous solution of atrazine. Comparing the half-lives of atrazine at different pH values (not shown), it is concluded that degradation is slowed down in an acidic medium; on the contrary, the degradation of atrazine tends to be most efficient at the highest pH value, which might be a result of hydroxide ion concentration. The same behavior was reported by other literature [16].

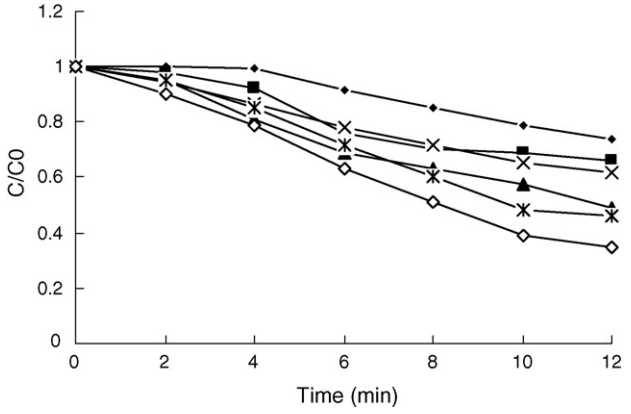


Fig. 4. Effect of pH value: pH 3 (♦), pH 5 (■), pH 6 (▲), pH 7 (×), pH 8 (*) and pH 9 (◊); atrazine concentration was 50 mg/l (phosphate buffer solution, under one EDML irradiation).

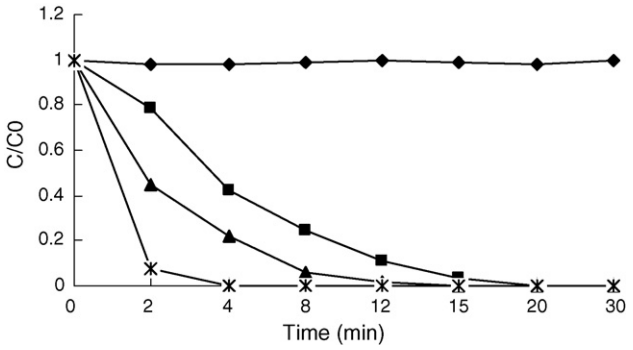


Fig. 5. Effect of EDML: 0 (♦), 1 (■), 2 (▲) and 3 (*); atrazine concentration was 50 mg/l (50 ml, pH 6.3, not buffered, under various amounts of EDML).

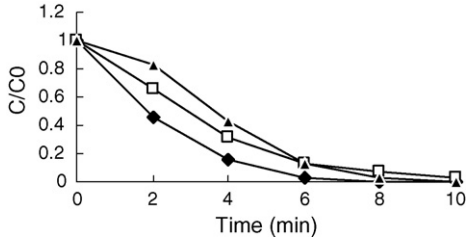


Fig. 6. Effect of solvent: no solvent (♦), methanol (□) and acetone (▲); atrazine concentration was 10 mg/l (50 ml, pH 6.3, not buffered, under one EDML irradiation).

3.1.4. Effect of EDML

The degradation experiments were conducted in various amount of EDML including the blank experiment. Following the degradation processes under different amounts of EDML which lead to a diagram, it is shown in Fig. 5 . The effect of EDML on degradation of atrazine is apparent in Fig. 5. It can be concluded

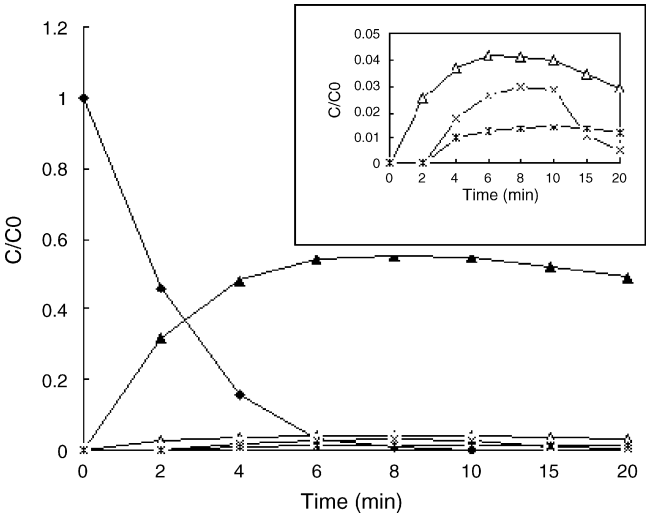


Fig. 7. Evolution of the concentration of atrazine and its first degradation products during microwave-assisted photolysis: AT (♦), HAET (▲), HIET (△), CDT (×), CAIT (*). The unclear parts of the figure have been enlarged and is shown in inset.

that there is a relationship between the amounts of EDML and the degradation efficiency of atrazine. When increasing the amount of EDML, the degradation rates apparently increase. It is worth pointing out that in blank experiment (without EDML), no degradation of atrazine was observed although the MW irradiation was still applied. This evidence implies that the existence of EDML can produce UV–vis irradiation which can degrade the atrazine, nevertheless the MW irradiation cannot degrade the atrazine. Additionally, the degradation efficiency strongly depends on the light intensity of EDML irradiated UV–vis which is correlated to the amount of EDML.

3.1.5. Effect of coexisted solvent

To assess a small volume of solvent (less than 1 vol.%) in the degradation process of atrazine, the experiment was conducted in an aqueous solution and with a small volume of methanol and acetone (Fig. 6). It was observed that a small volume of methanol and acetone slowed down the degradation rate of

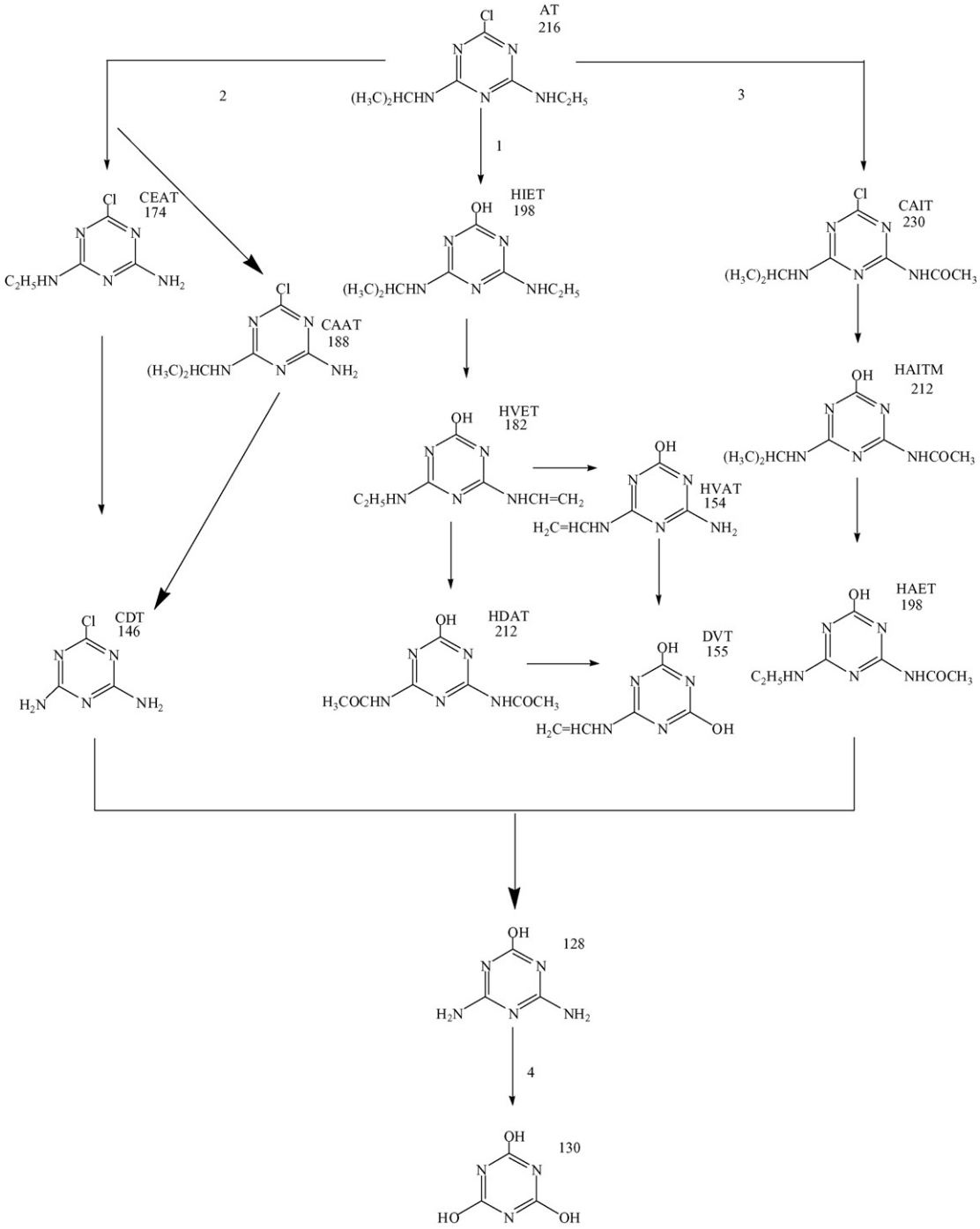


Fig. 8. Degradation pathways of atrazine under MW-EDML: (1) dechlorination–hydroxylation; (2) dealkylation; (3) alkylic-oxidation; (4) delamination–hydroxylation process.

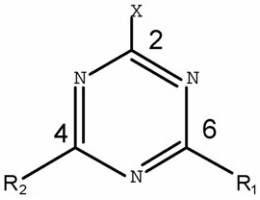
atrazine, respectively. The effect on the degradation of atrazine was notable at the beginning of degradation, but the solvents in the aqueous solution of atrazine were not apparent at the end of the experiment. It can be explained by the different characters of methanol and acetone. Known as a photosensitizer, acetone will compete with atrazine for absorption of UV–vis light. Moreover, as a quencher of radicals, methanol will trap the radicals and slow down the consequent degradation of atrazine. During the experiment, the solvent in the solution is volatilized gradually due to thermo-effect of MW.

3.2. Degradation products and degradation mechanism

In the present work, we focused mainly on the mechanism of atrazine degradation with particular care in the identification of degradation products. The degradation of 10 mg/l atrazine solution was investigated and the concentrations of first degradation products were evaluated as shown in Fig. 7. The experiment was conducted 20 min. As can be seen in Fig. 7, atrazine was degraded quickly and completely degraded in 8 min, and simultaneously some degradation products were formed and reached gradually the maximum, then they also began to degrade. Among the degradation products, one main degradation product was accumulated and its concentration was much higher than the other degradation products. According to the analysis of LC–MS and GC–MS, the main degradation product is HIET. From Fig. 7, it is observed that HIET is degraded slowly while the degradation time is increased. It indicates that formation of HIET (dechlorination–hydroxylation mechanism) is one of the main degradation mechanisms of atrazine in an aqueous solution by UV–vis irradiation of MW-EDML, which is in accordance with the previous studies [14,21]. The formation of HIET could result either from a homolytic cleavage of the C–Cl bond followed by an electron transfer from the carbon to the chlorine radicals processed by the carbocation reaction with water, or the heterolytic cleavage of the excited state atrazine molecule which is favored by polar solvents such as water [18].

In addition, some other degradation products were formed during 20 min degradation process. According to the result of GC–MS and LC–MS analysis, they were found to be the dealkylation products (CDT and CEAT) and alkylic-oxidation product (CAAT). However, from the evaluation of their concentration (Fig. 8), it is obvious that their formation is minor and they are also degraded under increased degradation time. It indicates that the dealkylation and alkylic-oxidation of atrazine are two other mechanisms for atrazine degradation.

Table 1
Structures, retention time and abbreviation of atrazine and degradation products



m/z or (*m* + 1)	Retention time	Detected	Abbreviation	Compounds	X	R_1	R_2
230	10.26	LC–MS	CAIT	2-Chloro-4-acetamindo-6-(isopropylamino)-*s*-triazine	Cl	$NHCOCH_3$	$NHCH(CH_3)_2$
226	9.60	LC–MS, GC–MS	M-HAITM	2-Hydroxy-4-acetamindo-6-(isopropylamino)-*s*-triazine	OCH_3	$NHCOCH_3$	$NHCH(CH_3)_2$
216	6.75	LC–MS, GC–MS	AT	2-Chloro-4-(isopropylamino)-6-(ethylamino)-*s*-triazine (atrazine)	Cl	NHC_2H_5	$NHCH(CH_3)_2$
212	6.25	LC–MS,	HAITM	2-Hydroxy-4-acetamindo-6-(isopropylamino)-*s*-triazine	OH	$NHCOCH_3$	$NHCH(CH_3)_2$
212	7.32	LC–MS,	HDAT	2-Hydroxy-4,6-diacetamindo-*s*-triazine	OH	$NHCOCH_3$	$NHCOCH_3$
212	8.63	LC–MS, GC–MS	M-HIET	2-Hydroxy-4-(isopropylamino)-6-(ethylamino)-*s*-triazine	OCH_3	NHC_2H_5	$NHCH(CH_3)_2$
198	2.55	LC–MS, GC–MS	HIET	2-Hydroxy-4-(isopropylamino)-6-(ethylamino)-*s*-triazine	OH	NHC_2H_5	$NHCH(CH_3)_2$
198	3.59	LC–MS, GC–MS	HAET	2-Hydroxy-4-acetamido-6-(ethylamino)-*s*-triazine	OH	$NHCOCH_3$	NHC_2H_5
198	5.30	LC–MS	CDVT	2-Chloro-4,6-(divinylamino)-*s*-triazine	Cl	NHC_2H_4	NHC_2H_4
198	5.71	LC–MS, GC–MS	M-HDT	2-Hydroxy-4,6-(diethylamino)-*s*-triazine	OCH_3	NHC_2H_5	NHC_2H_5
182	4.46	LC–MS, GC–MS	HVET	2-Hydroxy-4-(vinylamino)-6-(ethylamino)-*s*-triazine	OH	NHC_2H_4	NHC_2H_5
174	3.59	LC–MS, GC–MS	CEAT	2-Chloro-4-(ethylamino)-6-amino-*s*-triazine	Cl	NHC_2H_5	NH_2
154	2.61	LC–MS, GC–MS	HVAT	2-Hydroxy-4-(vinylamino)-6-amino-*s*-triazine	OH	NHC_2H_4	NH_2
154		GC–MS	DVT	2,6-Dihydroxy-4-(vinylamino)-*s*-triazine	OH	NHC_2H_4	OH
187		GC–MS	CAAT	2-Chloro-4-acetamido-6-amino-*s*-triazine	Cl	NH_2	NHC_2H_5
145		GC–MS	CDT	2-Chloro-4,6-diamino-*s*-triazine	Cl	NH_2	NH_2

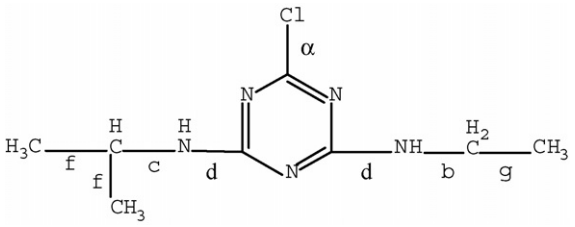


Fig. 9. Scissile bonds in atrazine molecular under MW-EDML.

In order to assess all the available degradation products during atrazine degradation, the same concentration of atrazine with longer degradation time (40 and 120 min) and higher concentration of atrazine with longer degradation time (50 mg/l, 40 and 120 min) in the degradation process were conducted. All the identified degradation products and their retention times, names, formulae and structures are presented in Table 1. Furthermore, according to Table 1, the possible degradation pathways are proposed in Fig. 8.

The degradation of atrazine in MW-EDML in an aqueous solution is a complicated process. Nevertheless, it still follows certain patterns of mechanism. According to previous literature [22], we suggest that the MW-EDML irradiation will lead to the promotion of atrazine to their excited singlet states, then may transit to the triplet states and then undergo the three possible processes, namely, homolysis, heterolysis and photoionization. According to the structure of atrazine, we suggest that there are several bonds (Fig. 9) which are easy to cleave when they get enough energy from UV–vis irradiation during MW-EDML degradation process. The bond α is the easiest to be scissile as compared to any other bonds. The cleavage of bond α lead to a dechlorination–hydroxylation process (the chlorine atom was substituted by a hydroxyl group): in this process, it is estimated that the chlorine atom which is connected to the carbon atom on the heterocyclic ring might cause a cleavage due to its higher polarity and is substituted by hydroxyl group at the same time. While the dechlorination occurs, the hydroxylation happens simultaneously. Consequentially, the degradation product HIET is being formed.

Additionally, the b, c, f and g bonds might also cleave easily and form dealkylation (alkylic lateral chain cleavage) degradation products including demethylation, deethylation and deisopropylation which are CDT, CAAT and CEAT identified by GC–MS and LC–MS, respectively. There is no evidence from GC–MS or LC–MS that the g bond is cleaved during the degradation process. Therefore, it is estimated that the order of those bonds cleavage from easy to difficult goes as follows: b > c > f > g. This is supported by the previous work showing that deethylation is easier than deisopropylation [23]. We suggest that the cleavage of those bonds might result in the formation of some neutral molecular such as alkenes or alkyl radicals.

In addition, an attack of the hydroxyl group on N-adjacent carbon atom of bonds b and c might result in an alkylic-oxidation (alkylamino lateral chain oxidation) process which is proved by the identification of CAIT, HAITM, HDAT and HAET. It is estimated that the abstraction of the hydrogen atom might occur in the case of hydroxyl radical's attacks on N-adjacent carbon atom. The observation of HVET might be explained by this mechanism.

If only amino group remained on the lateral chain of heterocyclic ring after complete dealkylation, bond d might cleave and cause the deamination–hydroxylation process (the amino group is substituted by a hydroxyl group). It should be pointed out that only after the dealkylation, the deamination–hydroxylation process is likely to occur. The cleavage of bond d and attack of the hydroxyl radicals on the carbon atom of heterocyclic ring happen simultaneously. This can be supported by the observation of DVT.

It may be pointed out that in the second step or ulterior steps, the above four degradation mechanisms may compete with one another, thus, the mixture of lateral chain losing, lateral chain oxidizing and hydrolyzing products are being formed.

In general, the common processes of degradation of atrazine are as follows: partial or complete loss of lateral chains; oxidation of lateral chains; substitution hydroxyl group for chlorine or amino group rather than opening the heteroatom ring. The degradation process may finally lead to the formation of ultimate production of cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine, CA) rather than causing the complete mineralization which is often observed for other chemicals. However, CA is not detected in our experiment, but it is eventually formed when a sufficient intensity of irradiation is provided with an extended time. It suggests that the heterocyclic ring has a much higher stability to decompose under the UV–vis light intensity irradiated by MW-EDML. As far as we know, the complete mineralization has not been reported in any other previous literature of photodegradation and biodegradation processes. Cyanuric acid was treated by Fenton Reagent and photocatalyst for 100 h, but no meaningful disappearance was observed [17]. Fortunately, it was reported that cyanuric acid had a low toxicity [17]. Therefore, the MW-EDML process shows a very efficient means for detoxification of atrazine.

4. Conclusion

Photodegradation of atrazine in an aqueous solution by MW-EDML was investigated in this study. The MW-EDML is proved to be a very simple, economic, efficient, prospective and environmentally friendly tool for detoxification of atrazine. The initial pH value, initial concentration of atrazine, volume of solution, amount of EDML and coexistent solvent are all the factors strongly affecting the atrazine degradation. In addition, the main degradation pathways proposed include the four ways: dealkylation, dechlorination–hydroxylation, alkylic-oxidation, and delamination–hydroxylation. In general, the most commonly degraded process of atrazine loses the lateral chains partially or completely, oxidizes and hydroxylates in the lateral chains rather than opens the heteroatom ring.

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