



Degradation of alachlor in aqueous solution by using hydrodynamic cavitation

Xikui Wang*, Yong Zhang

School of Light Chemistry and Environmental Engineering, Shandong Institute of Light Industry, Jinan 250353, China

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ABSTRACT

The degradation of alachlor aqueous solution by using hydrodynamic cavitation was systematically investigated. It was found that alachlor in aqueous solution can be decomposed with swirling jet-induced cavitation. The degradation can be described by a pseudo-first-order kinetics and the degradation rate was found to be $4.90 \times 10^{-2} \text{ min}^{-1}$. The effects of operating parameters such as fluid pressure, solution temperature, initial concentration of alachlor and medium pH on the degradation rates of alachlor were also discussed. The results showed that the degradation rates of alachlor increased with increasing pressure and decreased with increasing initial concentration. An optimum temperature of 40°C existed for the degradation rate of alachlor and the degradation rate was also found to be slightly depend on medium pH. Many degradation products formed during the process, and some of them were qualitatively identified by GC–MS.

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1. Introduction

Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide] is one of the most widely used chloroacetanilide herbicides that is used to control most annual grasses and many broadleaf weeds. It is a pre-emergence herbicide which is applied to the soil before cultivation. Alachlor has been detected in surface and ground water [1–3], despite its rapid microbial and photo-induced decomposition [4,5]. It is reported that alachlor has a potential to induce cancer in laboratory animals [6,7] and is classified as a group B2 carcinogen by the U.S. Environmental Protection Agency [8]. Even though pesticides are indispensable in modern civilization, society is aware of their potential toxicity for humans and animals, so the presence of their residues in water shows a potential hazard for both the environment and humans. Their elimination from wastewater effluents is now the subject of considerable concern of environmental remediation and has attracted many researchers in recent years. Since alachlor is toxic to many organisms, conventional biological remediation processes are not suitable to remove the herbicides from contaminated water and therefore alternative treatment methods are required. Among several available treatment methods the advanced oxidation processes (AOPs) are the most promising alternative to treat herbicide wastes because they involve the generation of hydroxyl radicals ($\cdot\text{OH}$) that are species nonselective and highly reactive oxidants. Ozonation [9,10], photolysis and photocatalysis [11,12], photo-Fenton degradation [13] of alachlor in water have been

reported. Sonochemical degradation of alachlor [14] and the effect of ultrasonic frequency on the sonolysis of alachlor [15] were also investigated.

The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid which produces unusual chemical and physical environments. The collapse of bubbles generates localized “hot spots” with transient temperature of about 5000 K, pressures of about 1000 at% [16,17]. Under such extreme conditions water molecules dissociate into $\cdot\text{OH}$ and $\cdot\text{H}$ radicals. These highly reactive species are capable of affecting secondary oxidation and reduction reactions. Ultrasonic radiation has been found to promote a wide range of physical and chemical reactions and to be capable of at least partially oxidizing dilute aqueous mixtures of organic compounds. However, the efficiency of such ultrasonic devices is limited by achieving cavitation in the form of a cloud of cavitation bubbles only in a relatively small region near the surface of the ultrasonic source.

Cavitation is a term used to describe a process, which includes nucleation, growth and implosion of vapor or gas filled cavities. These cavities are formed in a liquid when the pressure of the liquid is reduced below the vapor pressure of the liquid in current temperature. When cavities are carried to higher pressure region they implode violently and result in very high pressures and temperature. In fact, cavitation usually occurs in fluid power systems. But the occurrence of cavitation in fluid power is mostly detrimental. For example the efficiency of the system is reduced due to cavitation and vibration as well as noise level of a system is increased. On the other hand, the collapse of the cavitation bubbles also initiates shear forces, shock waves and reactive radicals. Similar to ultrasonic cavitation, the radicals produced from hydrodynamic cavitation such as $\cdot\text{H}$ and $\cdot\text{OH}$ can react with pollutants

* Corresponding author. Tel.: +86 531 86931 866; fax: +86 531 86931 111.
E-mail address: xk.wang@sdili.edu.cn (X. Wang).

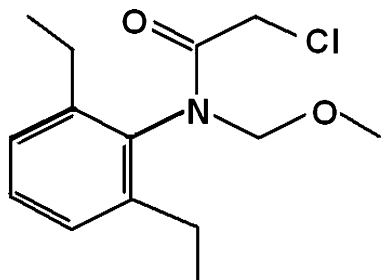


Fig. 1. The structure of alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide).

in water to promote degradation of pollutants. Ultrasonic cavitation has been extensively investigated in recent years, but there are not many studies on the applications of hydrodynamic cavitation to disintegrate water pollutants. Suslick et al. [18] have reported a conclusive experimental evidence for chemical reactions caused by hydrodynamic cavitation within a jet fluidizer in which I^- was oxidized to form I_3^- . Kalumuck and Chahine [19] have studied the degradation of *p*-nitrophenol in recirculating flow loops using a variety of cavitating jet configurations and operating conditions. The result showed that jet-induced cavitation can achieve oxidation with up to two orders of magnitude with greater energy efficiency compared to the ultrasonic means. Vichare et al. [20] have used KI decomposition as a model reaction and confirmed the occurrence as well as the intensity and thereby the efficiency of the multiple hole orifice plates in generating the cavitation. Sivakumar and Pandit [21] studied the degradation of a cationic dye rhodamine B by using multiple hole orifice plates and compared the efficiency of this technique with the cavitation generated by ultrasound. Gogate et al. [22] reported a cavitation efficiency assessment based on the oxidization reaction of potassium iodide.

In our previously work, the chemical effect of swirling jet-induced cavitation and the energy efficiency of the process were described [23]. In the present work, the effectiveness of swirling jet-induced cavitation for degradation of alachlor was investigated. It was found that alachlor in aqueous solution can be destroyed with swirling jet-induced cavitation and the effects of operating conditions such as pressure, temperature, initial concentration of alachlor and solution pH on the degradation of alachlor were also discussed. Some degradation products of alachlor were also analyzed.

2. Materials and methods

2.1. Reagents

Alachlor (99.7%, HPLC grade), which structure is shown in Fig. 1, was obtained from Riedel-de Haën. Hydrogen peroxide (30%, chemical reagent grade) was purchased from Tianjin chemical work and all other chemicals were of analytical reagent grade quality and were employed without further purification. Deionized and distilled water was used throughout.

2.2. Swirling jet cavitation reactor

A schematic illustration of the hydrodynamic cavitation reactor setup is presented in Fig. 2. It is a closed loop system designed to draw water from a holding tank of 40 L volume, then taking it into the swirling cavitation chamber and then discharging the treated solution back to the tank with a centrifugal pump (3000 rpm, 2500 W). The discharge from the pump branches into two lines: mainline and bypass line. The swirling cavitation chamber is fixed

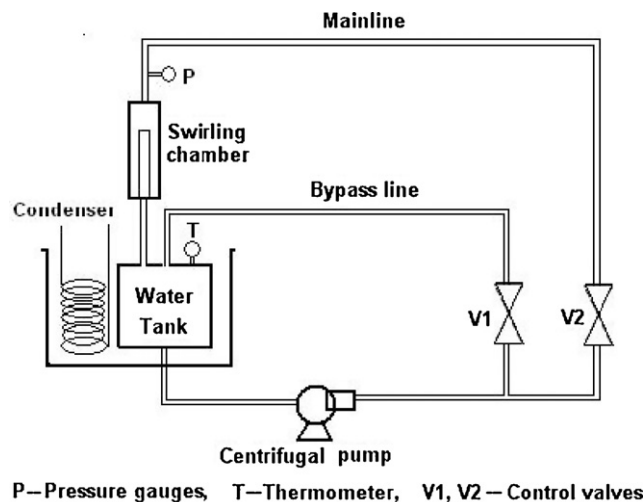


Fig. 2. Schematic representation of swirling cavitation reactor setup.

in the mainline. The bypass line is used to control liquid flow through the mainline.

The Cavitation was generated in the setup in a cylindrical swirling cavitation chamber that was positioned down within the combined chamber. Fig. 3 shows the cutaway side view (A) and cross-section (B) of the combined chamber. The swirling cavitation chamber was held to the cylindrical sidewall of the combined chamber and has four rectangular tangential injection ports in its cylindrical sidewall. Water was pumped into the combined chamber and then was injected into the swirling cavitation chamber through the tangential injection port. When water passes through the swirling cavitation chamber circularly, a swirling jet is formed that has a central pressure lower than the vapor pressure of water in which cavitation bubbles were generated. Then the swirling jet was ejected from the swirling cavitation chamber and dashed against the bottom surface of the combined chamber where the pressure raised rapidly and the cavitation bubbles collapsed.

2.3. Procedure

In a typical experiment, 25 L aqueous solutions of alachlor with 50 mg/L initial concentration were subjected to swirling cavitation chamber with a length of 100 mm and diameter of 10 mm (injection ports length 4.5 mm and width 0.2 mm) for degradation. The flow rate of water was fixed to 3.6 m³/h with 0.6 MPa inlet pressure in mainline. The pH of the test solution was maintained at 5.9 that

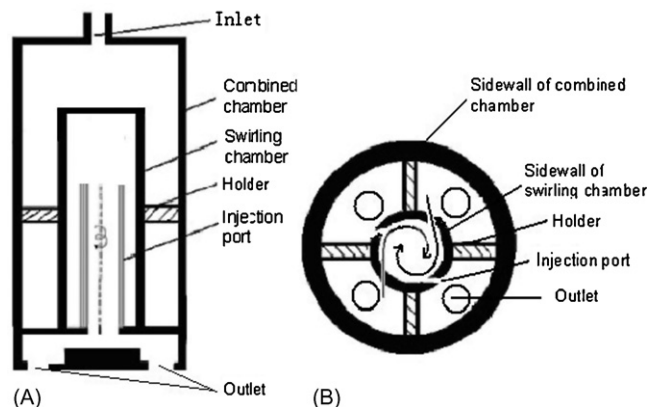


Fig. 3. Sketch of combined chamber and swirling cavitation chamber, (A) cutaway side view and (B) cross-section.

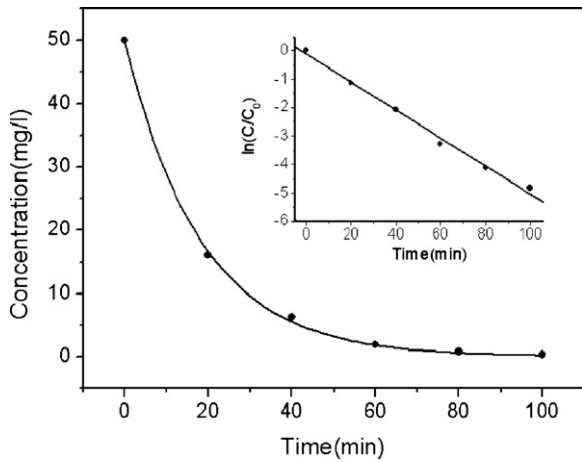


Fig. 4. Degradation vs. time dependency of alachlor. Inset is the degradation of first-order kinetics. Initial concentration 50 mg/L, temperature 40 °C, pH 5.9.

is the original pH of the solution. The pressure and the liquid flow in the swirling cavitation chamber can be controlled by adjusting valves. The temperature was controlled with the help of condenser in the water tank.

Samples were taken from the water tank at 20 min time intervals and analyzed for the residual concentrations of alachlor and formation of degradation products. 20 mL aqueous solution was withdrawn and extracted with 10 mL CH_2Cl_2 for two times, then the extract was concentrated to 1.0 mL. The residual concentrations of alachlor were determined by gas chromatography. 1.0 μL concentrated solution was injected to gas chromatography (Shimadzu GC 14-C, Japan) equipped with a flame ionization detector and DB-5 capillary column (length 30 m, i.d. 0.32 mm, with a 0.1 μm thin film coating). The operating conditions were as follows, carrier gas: nitrogen, flow rate: 1 mL/min, splitless injector temperature: 250 °C, detector temperature: 280 °C, column temperature program: initial temperature 50 °C for 1 min, ramped at 30 °C/min to 180 °C, then 10 °C/min to 280 °C and held for 10 min. The degradation products of alachlor were identified by using Finnigan-4570 GC-MS (Finnigan, USA). EI mass spectra were obtained at 70 eV electron energy with the ion source at 180 °C. The scan rate was 3 s and the mass range scanned was 29–500 amu.

3. Results and discussion

3.1. Degradation kinetics

The degradation of alachlor in aqueous solution by swirling jet-induced cavitation was investigated. It was found that the concentration of alachlor in water decreased exponentially with reaction time and the degradation rate can be expressed by the following equation:

$$C = C_0 \exp(-kt) \quad (1)$$

or

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (2)$$

where C is the concentration of alachlor at time t , C_0 the initial concentration, k the degradation rate constant, and t is the degradation time. This result indicated that the degradation of alachlor follows a pseudo-first-order kinetics (Fig. 4). The degradation rate constant k is found to be $4.90 \times 10^{-2} \text{ min}^{-1}$ with regression coefficient $R = 0.9968$ for 50 mg/L alachlor in aqueous solution at temperature 40 °C and pH 5.9.

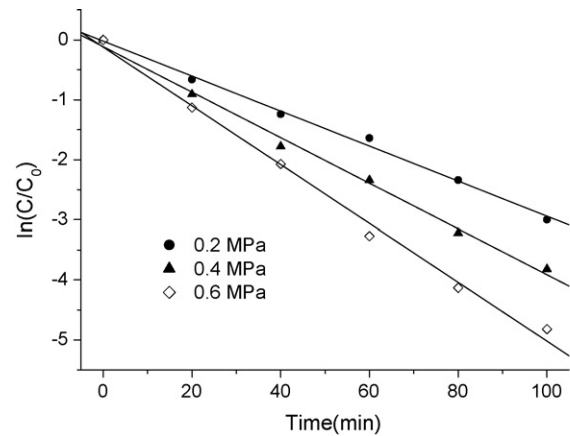


Fig. 5. The effect of pressure on the degradation rate of alachlor (initial concentration 50 mg/L) at temperature 40 °C.

3.2. Effect of pressure

The degradation of aqueous solution of alachlor (initial concentration 50 mg/L) was investigated under different inlet pressures at temperature of 40 °C. The results showed that the degradation rates were $2.92 \times 10^{-2} \text{ min}^{-1}$, $3.78 \times 10^{-2} \text{ min}^{-1}$ and $4.90 \times 10^{-2} \text{ min}^{-1}$ at pressure 0.2 MPa, 0.4 MPa and 0.6 MPa, respectively (Fig. 5). From the results it can be seen that the degradation rate is proportional to the fluid pressures. This result could be explained by the cavitation number σ , as defined in the following equation [18]:

$$\sigma = \frac{p_d - p_v}{p_u - p_d} \approx \frac{p_d}{p_u} \quad (3)$$

where p_d , p_u and p_v are the downstream, upstream, and vapor pressures of the fluid, respectively, and the approximation holds when $p_u \gg p_d \gg p_v$ as they do under our experimental conditions. Increasing upstream pressure should decrease the cavitation number σ and increase the number of cavitation events. This in turn should increase the degradation rate of alachlor.

3.3. Effect of the temperature

The influence of temperature to the degradation of alachlor was investigated with 50 mg/L alachlor aqueous solution at a pressure of 0.6 MPa and the results are depicted in Fig. 6. It was found that the degradation rates were $4.04 \times 10^{-2} \text{ min}^{-1}$, $4.90 \times 10^{-2} \text{ min}^{-1}$, $4.65 \times 10^{-2} \text{ min}^{-1}$ and $3.23 \times 10^{-2} \text{ min}^{-1}$ at temperature 30 °C,

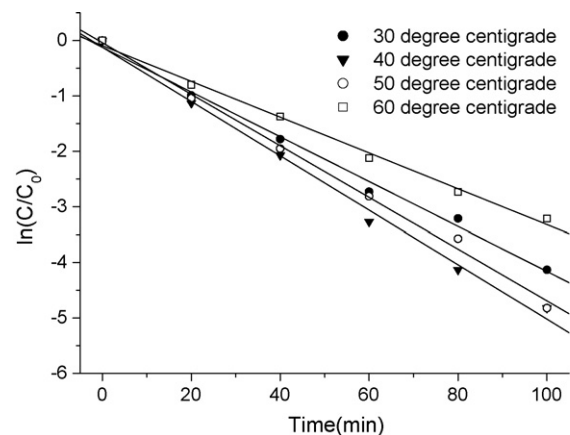


Fig. 6. The effect of temperature on the degradation rate of alachlor (initial concentration 50 mg/L) at a pressure of 0.6 MPa.

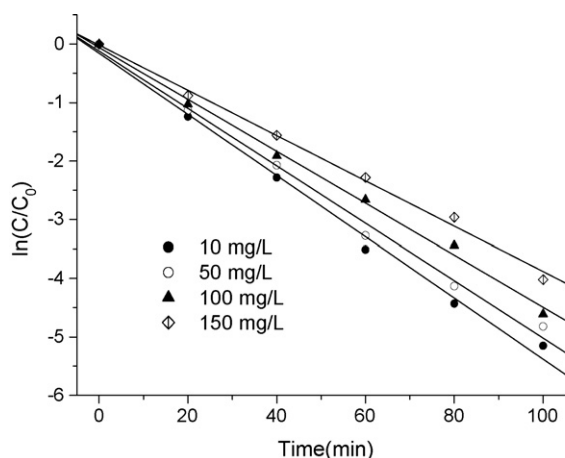


Fig. 7. Effect of initial concentration on the degradation rate of alachlor at a pressure of 0.6 MPa and temperature 40 °C.

40 °C, 50 °C and 60 °C, respectively. From the results it is evident that the effect of temperature is complicated. Comparing the degradation rates of alachlor at 30 °C and 40 °C, increasing temperature positively affects the degradation of alachlor. However, the degradation rates were decreased with increasing the water temperature in the temperature range of 40–60 °C. As we know, the formation of cavitation bubbles is not only a function of gas dissolution rate in water, but also affected by water vapor pressure. Higher temperatures can increase the quantity of cavitation bubbles and result in the increase of degradation. However, if the temperature was too high (e.g. at 60 °C), the water vapor would fill the cavitation bubbles and cushion the implosion phenomena. So the degradation efficiency of alachlor was decreased.

3.4. Effect of initial concentration

The effect of alachlor initial concentrations on the degradation rate was investigated at temperature of 40 °C, pressure 0.6 MPa and the result is shown in Fig. 7. It was found that the degradation rate decreased from $5.22 \times 10^{-2} \text{ min}^{-1}$ to $3.87 \times 10^{-2} \text{ min}^{-1}$ as initial concentration increased from 10 mg/L to 150 mg/L. However, the total mass of alachlor decomposed was increased with increasing its initial concentration.

It has been reported that there are two main mechanisms for the degradation of organic material by using cavitation [24,25]. One is that the organic material is pyrolysed directly in the gas phase within the cavitation bubble where elevated temperature and high pressure are produced, and the other is the oxidation of $\cdot\text{OH}$ radicals in the bubble–water interface where the temperature is lower than that inside the bubble but still high enough for a sonochemical reaction and in bulk solution at ambient temperature where reaction still takes place. When the cavitation condition is constant, the number of cavitation events and the amount of $\cdot\text{OH}$ radicals would be constant, but the total amount of alachlor in aqueous solution was increased with increasing its initial concentration. So the alachlor removal ratio must be reduced and the degradation rate was decreased. However, when alachlor concentration in bulk solution was increased, more alachlor molecules could enter the cavitation bubbles and water–bubble interface, and the total amount of contaminant removed was increased.

3.5. Effect of the medium pH

The solution pH is an important factor in determining the physical and chemical properties of the solution. The effect of different

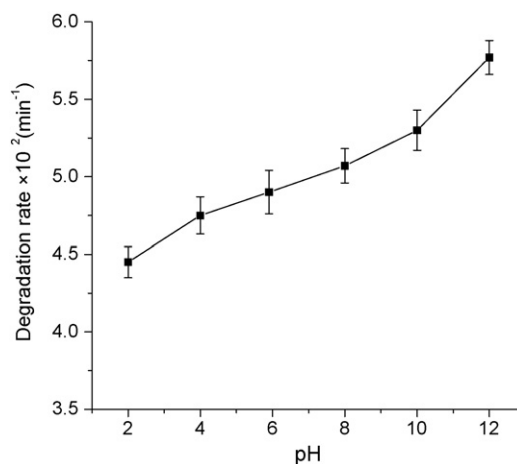


Fig. 8. Effect of pH on the degradation rate of alachlor (initial concentration 50 mg/L) at pressure 0.6 MPa and temperature 40 °C.

initial pH of the solution on the degradation rate of alachlor was also investigated. In general, the degradation rate was found to be slightly depend on pH, as shown in Fig. 8. About 30% increase (from $4.45 \times 10^{-2} \text{ min}^{-1}$ to $5.77 \times 10^{-2} \text{ min}^{-1}$) in rate constants were observed as pH increased from pH 2 to 12. At high initial pH, more hydroxide ions in the solution induced the generation of hydroxyl free radicals ($\cdot\text{OH}$). Since hydroxyl free radical is the dominant oxidizing species in the cavitation process, the degradation of alachlor is therefore accelerated in an alkaline medium [26,27]. On the other hand, the recombination reaction between protons and the hydroxyl radicals could occur as the pH decreases. Consequently the degradation decreases as hydroxyl radicals are scavenged by protons as pH decreases. Similar effects have been observed in photocatalytic degradation of alachlor [28] and sonochemical degradation of polycyclic aromatic sulfur hydrocarbons in aqueous solutions [12].

3.6. Degradation products and degradation pathway

When alachlor is decomposed with hydrodynamic cavitation for 30 min, a number of degradation products are formed. Fig. 9 shows the GC–MS total ion current chromatogram of alachlor and its degradation products. The mass spectral highlights of the principal degradation products are shown in Table 1 and their structures are given in Fig. 10. From the table and figure, it can be seen that some products (a, b, d, f) were due to bond scission or oxidation of the *N*-methoxymethyl group, which is consistent with sonochemical degradation [15], and some products (b and e) were characterized by substitution of chlorine by hydroxyl. The formation of product

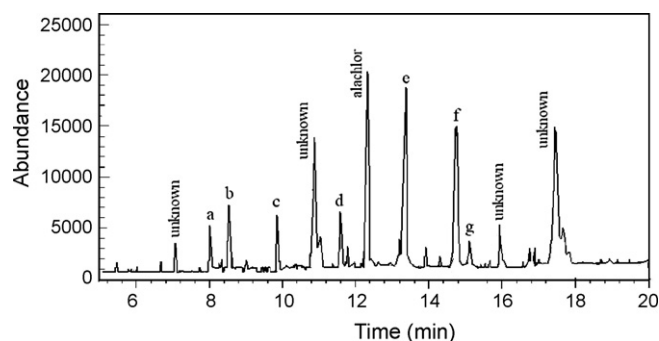


Fig. 9. GC–MS total ion current chromatogram of alachlor and its degradation products.

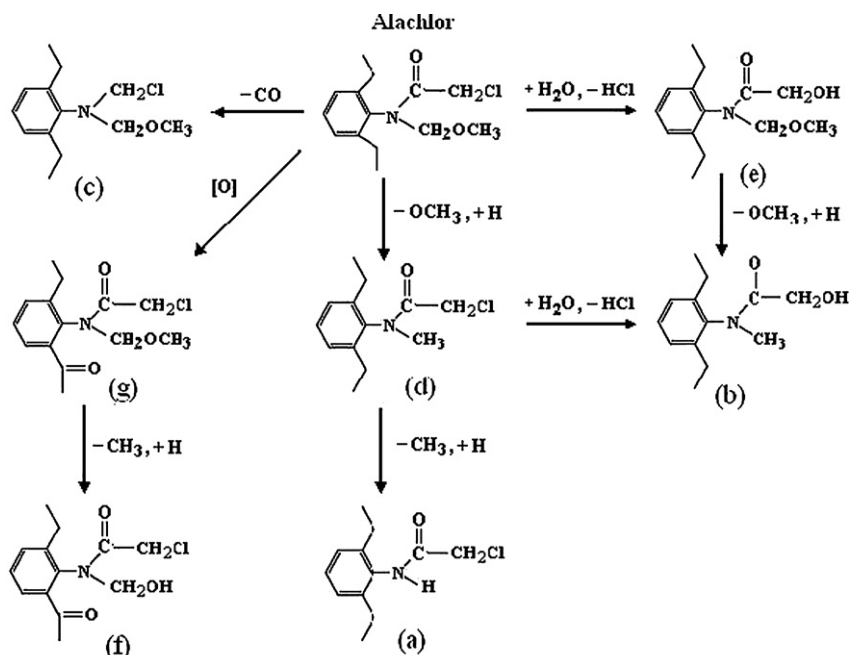


Fig. 10. Degradation pathway of alachlor.

Table 1
GC–MS characteristics of major degradation products of alachlor

Product	Molecular weight	Main ions–EI mode (relative abundance)
a	225	77 (85), 117 (22), 147 (53), 148 (16), 176 (100), 225 (8)
b	221	133 (17), 148 (45), 176 (76), 189 (91), 221 (100)
c	241	45 (100), 132 (44), 160 (28), 118 (12), 77 (10), 241 (6)
d	239	148 (50), 162 (36), 190 (100), 224 (8), 239 (5)
e	251	146 (24), 160 (100), 174 (72), 202 (57), 251 (35)
f	269	146 (16), 160 (100), 174 (19), 202 (12), 234 (27), 269 (2)
g	283	118 (30), 146 (36), 160 (71), 188 (100), 238 (15), 283 (5)

(f) and product (g) were typical of chemical oxidation processes involving alachlor [29], and suggested reaction with $\cdot\text{O}$ which is generated inside the cavitation site [30]. From the information obtained so far, a possible degradation pathway of alachlor may be proposed as Fig. 10.

4. Conclusions

The degradation of alachlor aqueous solution by using hydrodynamic cavitation was systematically investigated. The results showed that alachlor in aqueous solution can be decomposed with swirling jet-induced cavitation. It was found that the degradation can be described by a pseudo-first-order kinetics and the degradation rate constant k is found to be $4.90 \times 10^{-2} \text{ min}^{-1}$ with regression coefficient $R = 0.9968$ for 50 mg/L alachlor in aqueous solution at temperature 40 °C. The effects of operating parameters such as fluid pressure, solution temperature, initial concentration of alachlor and medium pH on the degradation rates of alachlor were also discussed. The results showed that the degradation rates of alachlor increased with increasing pressure and decreased with increasing initial concentration. An optimum temperature of 40 °C existed for the degradation rate of alachlor and the degradation rate was also found to slightly depend on medium pH. It also found that many degradation products formed during the process, and some of them were qualitatively identified by GC–MS. A possible degradation pathway of alachlor was also proposed.

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