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Thermodynamic and aquatic photodegradation of herbicide butachlor

Sherif H. Abd-Alrahman[a,b,*], Z.H. Zidan[c], M.I. Abdel-Megeed[c], Monir M. Almaz[b], Aziza H Mohamady[d], A. Mostafa[e]

[a]*Biochemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia, Tel.+966 561776615; email: drsherif_hussein@yahoo.com (S.H. Abd-Alrahman)*
[b]*Agricultural Research Center, Pesticides Residue and Environmental Pollution Department, Central Agricultural Pesticide Laboratory, Giza 12618, Egypt, email: almazmonir@yahoo.com (M.M. Almaz)*
[c]*Faculty of Agriculture, Department of Plant Protection, Ain Shams University, Kalubia, Egypt, emails: zidan_hendy@yahoo.com (Z.H. Zidan), m_mgeed@yahoo.com (M.I. Abdel-Megeed)*
[d]*Agriculture Research Center, Bioassay Department, Pesticide Central Laboratory, Giza 12618, Egypt, email: Aziza_1972@yahoo.com*
[e]*Department of Botany and Microbiology, Collage of Science, King Saud University, P.O. Box 2455, Riyadh 11451 Kingdom of Saudi Arabia, email: ashraf812@yahoo.com*

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ABSTRACT

Thermodynamic and aquatic photodegradation kinetics of a chloroacetamide herbicide (butachlor), subjected to irradiation of ultraviolet light under different temperatures (20–50˚C), were investigated. Butachlor residues were determined using gas chromatography coupled with micro-electron capture detector (GC-ECD). The results showed that photochemical reaction of butachlor in water under UV light followed the first order kinetic equation, and the photodegradation efficiency was increased with temperature in the range of 20–50˚C. Photodegradation rate constants of butachlor exposed to temperatures of 20, 30, 40, and 50˚C were 0.004, 0.007, 0.041, and 0.12 h^{-1} and their half lives were 175, 100, 17.5, and 5.8 h, respectively. Activation thermodynamic parameters were determined for the degradation process. The reaction activation energy was calculated to be 11.7 kJ mol^{-1}. Results proved that the use of UV irradiation with increasing temperature is a good application to eliminate butachlor from contaminated water.

Keywords: Thermodynamic; Photodegradation; Herbicide; Butachlor

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1. Introduction

The chloroacetamide herbicide (butachlor), N-(butoxymethyl)-2-chloro-20,60-diethylacetanilide, is widely applied in agricultural fields, especially in paddy fields for control of annual grass and some broad leaf weeds. It is one of the herbicides heavily used in Egypt for control of weed-infested rice. The environmental degradation and dissipation studies showed that butachlor is a persistent pollutant in agricultural soil, threat to the agro-ecosystem and human health through food chains [1,2]. Fang et al. [3] concluded that butachlor sometimes adversely affected the growth and activities of beneficial microorganisms in soils.

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*Corresponding author.

Moreover, some researchers have demonstrated that butachlor is highly toxic to some aquatic organisms such as green algae [4] and fish [5], which brings a large water environment risk. Especially, after heavy application to paddy field, butachlor may be transferred into surrounding water easily through drainage, irrigation, farmland runoff and, consequently, causing contamination of river and ground water [6]. It has been proven that butachlor is genotoxic and cytotoxic [7,8]. Butachlor is a suspected carcinogen capable of stimulating cell proliferation and inducing malignant *in vitro* transformation [9,10]. It was also reported that butachlor could induce stomach tumors in rats [11,12].

In order to illuminate the degradation processes of butachlor in environment, some experiments have been done on its behavior in agricultural soils [12–15] and on its photodegradation under sunlight and UV irradiation as a thin film on glass [13]. Photolysis is one of the highly promising technics because it can operate at ambient temperature and pressure with low-energy photons, does not require expensive catalyst, and utilizes natural sunlight. An enormous literature is documented regarding photodegradation of organic pollutants. Very few studies have been published which consider the thermodynamic aspect of photodegradation. However, the quantitative data on thermodynamic parameters relating the degradation process is inadequate. To the best of our knowledge, there is lack of kinetic data, which relates thermodynamic parameters of activation with photodegradation of pesticides.

The present work investigates the kinetics and thermodynamic of butachlor photolysis by ultraviolet radiation under different temperature.

2. Materials and methods

2.1. Chemicals

Butachlor certified analytical standard of (purity > 95%) was purchased from Dr Ehrenstorfer GmbH, general structure of butachlor was illustrated in Fig. 1. All organic solvents were HPLC grade and supplied by Merck Ltd. Deionized water was prepared by a Milli-Q water purification system. Anhydrous magnesium sulfate and sodium chloride were of analytical grade and purchased from Merck Ltd. Anhydrous magnesium sulfate was activated by heating at 150˚C for 4 h in the oven before use and kept in desiccators.

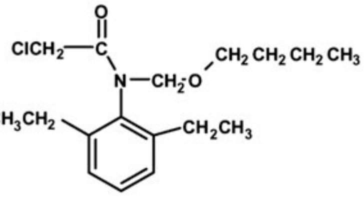

Fig. 1. Butachlor structural formula.

2.2. Standard calibration curves

The stock solution of butachlor was prepared by dissolving 50 mg of the analyte (accurate weight) in 50 mL acetone to obtain concentration of 1.0 mg mL^{-1}. Working standard solutions of 0.05, 0.1, 0.25, 0.5, and 1.0 μg mL^{-1} were prepared by appropriately diluting the stock solution with acetone. Stock solution was stored at −20 ± 2˚C, while working standard solutions were stored in ≤4˚C when not in use. Calibration curves were generated by plotting peak area vs. concentration.

2.3. Photodegradation procedure

Aliquots of butachlor stock solution (10 mg/ml acetone) were placed in 100 ml Pyrex flasks and made up to 100 ml with deionized water, then exposed to ultraviolet rays (UV-rays) at wave length 254 nm. Samples were taken at zero time and intervals 3, 6, 12, 24, and 48 h. Butachlor was extracted from water samples according to method validated by [16]. To determine the thermodynamic parameters of butachlor photo degradation, this experiment was done under different temperatures 20, 30, 40, and 50˚C.

Hydrolysis of butachlor in 10% acetone in water was performed. Butachlor of 1 mg/ml in hydrolysis solution was placed in 50 mL amber vials at 20, 30, 40, and 50˚C. The temperatures were controlled by keeping the vials in a room-temperature water bath, or a heated water bath. Samples were taken at zero time and intervals 3, 6, 12, 24, and 48 h. Sample was removed and analyzed in triplicate via GC-ECD against a set of butachlor standards.

2.4. Chromatographic analysis

Agilent 6890 (USA) gas chromatography coupled with micro-electron capture detector (GC-ECD) was used for determination of butachlor residues. The capillary column HP-5 (30 m × 0.25 mm × 0.25 μm) was used for separation. Nitrogen was used as the carrier gas at a flow rate 2 ml/min. The following temperature program was employed: initial temperature of 180˚C held for 1 min; increased at 25˚C min^{-1} to 220, held for 2 min; yet another increase at

3°C min^{-1} to reach 245°C. The injector temperature was 220°C. The injection volume was 1 µl for all standard and samples. Data analysis was performed using Chemistation software.

2.5. Statistical analysis

Data were statistically evaluated by one-way analysis of variance (ANOVA). Determination of the differences among means was carried out using the least significant differences (LSD) test. All statistical analyses were done using the Statistical Package for social sciences (SPSS 16.0) program.

3. Results and discussion

3.1. Butachlor photodegradation

Hydrolysis of butachlor is minimal at pH 7.2 over a period of 10 d, according to the literature [17], our data verified this result, as no noticeable hydrolysis occurred at 20, 30, 40, and 50°C. This is because butachlor is relatively stable in water [17].

To evaluate the fate of pesticides in the environment, the influence of both abiotic and biotic factors should be taken into account. Among the abiotic chemical factors affecting the behavior of pesticide, photochemical reactions are important. In the surface layers of aquatic system, photochemical reaction can play a dominant role in the conversion and degradation of pesticides. Table 1 and Fig. 2 showed the time profile of butachlor photodegradation under different temperature. The chosen temperature represents Egyptian local conditions which are almost tropical (or subtropical), where the temperature reaches 45 ± 5°C in summer. The results clearly showed that butachlor degradation varied according to time of exposure. The degradation increased as time increases. The degradation magnitude is proportional to the temperature. As the temperature increased, the curve shape changes. Much sharper curves were obtained at higher temperatures. The degradation was faster at 50°C where butachlor concentration reached lower than 5 ug/ml in about 25 h. The degradation at 40°C was slower compared with that taking place at 50°C. The curve at 20 and 30°C are very slow and did not reach to steady state in the studied time.

Table 1
Rate constants and half-lives of butachlor photodegradation under different temperatures

Parameters	20°C	30°C	40°C	50°C
K (h^{-1})	0.0035	0.007	0.041	0.12
R	0.997	0.9	0.98	0.99
$t_{0.5}$ (h)	175	100	17.5	5.8

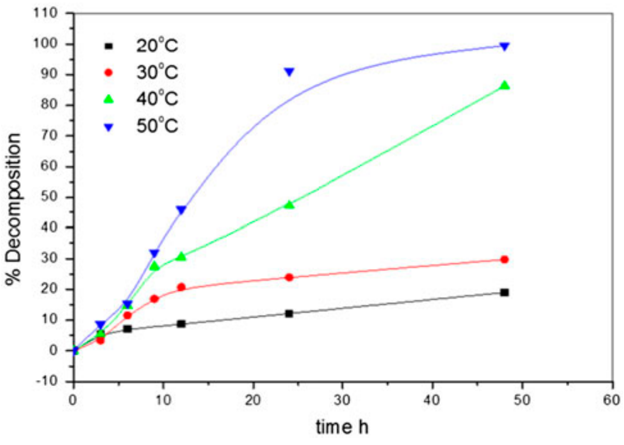

Fig. 2. Degradation kinetic of butachlor by UV at 254 nm at different temperature.

Data in Fig. 3 showed decomposition percent of butachlor at different temperature. Percentage was increased gradually with the exposure time and reached 2.4, 7.6, 13.2, 24.2, 34.7, and 54.5% after 1, 3, 6, 6, 12, 24, and 48 h exposure, respectively at 20°C. These results are in accordance to great extent with those obtained by Hegazy et al. [18], who studied the influence of acetophenone, benzoin, benzyl, p-nitrophenol and chlorophyll on the rate of photodegradation of the active ingredients of pirimiphos-methyl, The dissipation of pirimiphos-methyl, butachlor, malathion and prothiofos in methanol were 56.95, 16.4, 25, and 26.32% after 120 h, of exposure to UV-rays. The calculated residue half-life values were

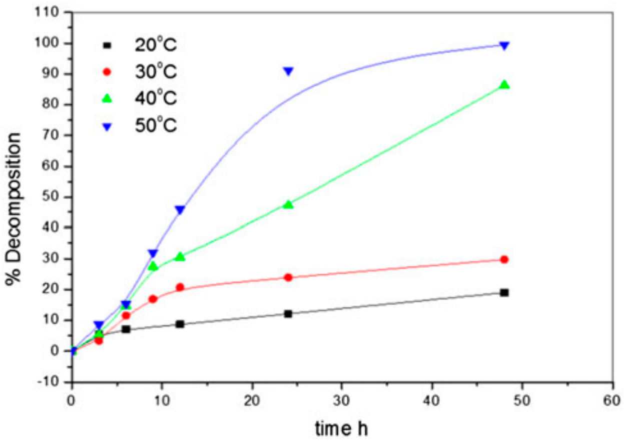

Fig. 3. Decomposition percentage of butachlor by UV at 254 nm at different temperature.

98.69, 464.4, 289.13, and 272.39 h, for pirimiphos-methyl, butachlor, malathion and prothiofos. Yoshichika et al. [19] assessed the photodegradation of two organophosphorus pesticides, fenthion, and disulfoton in the environment, degradation rates of their chemicals under UV irradiation. Result was reported that fenthion in the environment is more rapidly degraded by UVB irradiation in natural sunlight than disulfoton, and sulfoxide of both pesticides remains stable as photolysis products in the environment. The obtained results showed that butachlor was slightly stable under UV radiation with low temperatures, while it was rapidly degraded under UV light with high temperature, which suggested that the exposed temperature enhances the degradation of butachlor in contaminated water.

3.2. Kinetic analysis

To establish the photodegradation kinetics of butachlor, the effect of UV light exposure time (254 nm) on analytical response has been studied. For these studies, an aqueous solution containing 100 μg ml^{-1} of butachlor was exposed to UV irradiation for 0–48 h, subsequently, analyses were performed. From engineering point of view, it is useful to find out a simple user-friendly rate equation that fits the experimental rate data. According to many researchers, the photocatalytic degradation of organic pollutants is described by pseudo-first-order kinetics [20–22]. Pseudo-first-order kinetic behavior was demonstrated by plotting the Napierian logarithm of the percentage of undegraded compound against irradiation time (Fig. 3) according to the equation:

$$C_t = C_0 - e^{kt} \tag{1}$$

where C_t (μg ml^{-1}) is the mean concentration of butachlor as a function of time (t, h), C_0 (μg ml^{-1}) is the initial butachlor concentration, k (h^{-1}) is the rate constant. The resulting first-order rate constants have been used to calculate degradation rate for butachlor and thermodynamic parameters of activation. The required time for a response from the 50% of the initial concentration of reactants was calculated from the equation:

$$t_{0.5} = \ln 2/k \tag{2}$$

The kinetic parameters of butachlor are shown in Table 2 where the apparent rate constants and half lives are listed. In all cases, the kinetics of dissipation (Fig. 3) followed an apparent first-order degradation curve, with correlation coefficient R ranging from 0.9 to 0.999. The photolytic behavior of butachlor appeared strongly dependent on the temperature. The photolysis rate of butachlor was faster at high temperature compared to room temperature. The rate constant at 50°C was 34 times greater than the rate constant at room temperature. Increasing temperature reduces the half live of butachlor photodegradation. Half lives were 175, 100, 17.5, and 5.8 h at 20, 30, 40, and 50°C, respectively (Table 1). It highly decreased with increasing temperature. The degradation rate increased with increase in temperature (Fig. 3), which was probably a consequence of an increased frequency of molecular collisions in the aqueous solution. Recently, Mabury and Wilson have found that the photodegradation of butachlor in a solar simulator followed pseudo-first-order kinetics [23].

3.3. Photodegradation thermodynamic

This influence of the temperature must be considered in the kinetic analysis of photodegradation processes carried out in a wide range of temperatures. The apparent rate constant and temperature can be expressed by Arrhenius relation as follows:

$$k = A\, e^{-E_a/RT} \tag{3}$$

where k is the apparent rate constant, A is the frequency factor or pre-exponential factor, E_a is the activation energy of the reaction, R is general gas constant, and T is the absolute temperature. Translation of previous equation resulted in:

$$\ln k_\text{app} = \ln A - \frac{E_\text{a}}{RT} \tag{4}$$

A linear plot of ln k_app vs. $1/T$ yielded a straight line (Figs. 4 and 5) from which the activation energy can be obtained and are given in Table 2. The augmentation of the photodegradation activity is probably due to the increasing collision frequency of molecules in the solution. The other thermodynamic parameters, for instance, free energy of activation (ΔG), enthalpy of activation (ΔH), and entropy of activation (ΔS) were calculated (Table 2) using activation energy and apparent rate constant as follows:

$$\Delta G = -RT\, \ln k_\text{app} \tag{5}$$

Table 2
Thermodynamic parameters of butachlor photodegradation

T (°C)	E_a (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
20	11.7	13.75238	9.1	31.5
30		12.47854		30.2
40		8.29817		29
50		5.68421		27.8

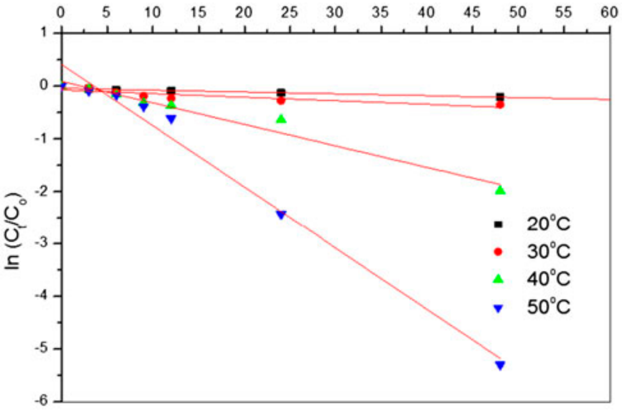

Fig. 4. Kinetics of butachlor pesticides.

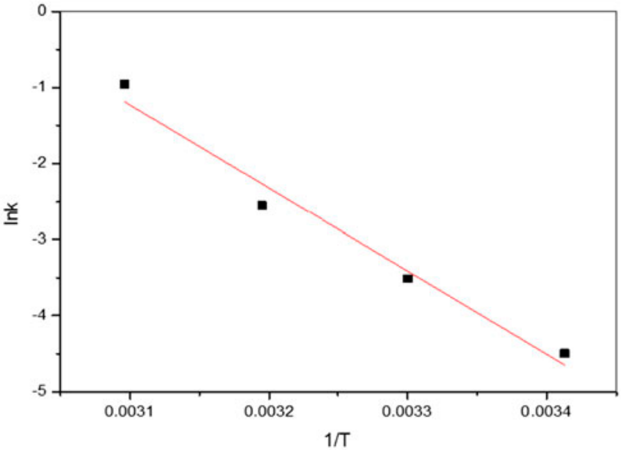

Fig. 5. Arrhenius plot of ln k against $1/T$ of butachlor photodegradation.

$$\Delta H = E_a - RT \tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

The overall apparent activation energy found to be 11.7 kJ mol^{-1}. This value is in good agreement with results reported in the literature [21–24], quoting the values of the overall apparent activation energy of photocatalytic oxidation of different substrates in the range from 5.5 to 28.4 kJ mol^{-1}. These results are in agreement with the finding of Hegazy et al. [24] who studied the influence of different temperatures, short ultraviolet, and direct sunlight on the rates of the decomposition of diazinon and pirimiphos-methyl insecticide. They stated that in general, increasing temperature degrees and prolongation of exposure were resulted in increasing the percentage loss of insecticides. The obtained results showed same trend of butachlor degradation rate when exposed to UV rays with different temperatures. The rate of butachlor degradation was varied according to the chemical structure, time of exposure, and the wave length of UV rays used. Butachlor was greatly deteriorated under UV radiation with high temperature at 50°C compared to low temperature at 20°C, half lives were 5.8 and 175 h, respectively. UV rays are found to be more effective with high temperature, in accelerating the photodecomposition of the pesticides. This may be due to thermal, evaporation, and light intensity considerations.

4. Conclusion

In our knowledge, this is the first study to examine thermodynamic photodegradation of the herbicide butachlor in water. The results provide evidence that the use of UV irradiation under increasing environmental temperature can significantly increase the pesticide degradation. The present study showed the kinetics and thermodynamics of the degradation of butachlor under irradiation by UV light. The degradation was examined to follow pseudo-first-order kinetic. An increase in the temperature has kind effect on kinetics and facilitates the degradation process to some extent. The effect of temperature from 20 to 50°C showed that the apparent rate constants follow the Arrhenius relation. The activation energies of the degradation of butachlor were found to be 11.7 kJ mol^{-1}.

Acknowledgments

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