Kinetic and thermodynamic study of Trifluralin photo-degradation by ultra violet light

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Abstract. The photo degradation of Trifluralin by ultra violet light region has been studied in liquid phase. In this research, different concentration with different temperature has been investigated. The results have shown that increasing temperature lead to increases rate constant, but when we change concentration the rate constant dose not changed regularly. That may be due to the fact that it is not pure secondary order photo-degradation reaction. All thermodynamic parameters have been measured using second order kinetic plot and Arrhenius plot.

Keywords: photo degradation, quenching, advanced oxidation process

1. Introduction

The widely spread of massive agricultural practices has become a universal problem. Due to world demand for agriculture to provide food that is necessary for population, many pesticides have been used as fertilizer to increase the production of food [1]. However, pesticides have had too much side effects that accumulate in body tissue causing chronicle disease [2] [3]. Pesticides are toxic chemical come in contact with local drinking water by hydrological cycle [4].they are introduced in to the environment for the purpose of killing living organisms. Moreover, removing pesticides is needful in order to avoid it is harmful effects. Removal of such chemicals occurs by process called degradation [5]. the term degradation is refer to breaking down the bonds in molecule structure in order to convert a toxic one to a nontoxic compound, or breaking down to it is original elements which is called mineralization [6]. The degradation usually occurs by chemical, biological, thermal or photochemical processes [7].Advanced oxidation process (AOPs) including Photo degradation is subject of this research. AOPs use metal oxides as semiconductors or organic dye as sensitizers with ultra violet or visible light to treat water sample [8].

1.1. Advanced oxidation process (AOPs)

In advanced AOP not only metal oxide is used with light sources, there are many different methods are in use, which we are going to mention them. The main purpose of AOP is production of hydroxyl radical from water molecule as follow fig.1 [9].
Schematic diagram illustrate the principal of semiconductor photo catalysis.

Photo-Fenton method uses ferrous or ferric ion mixed with hydrogen peroxide. This method is working even without light sources as below [10].

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{+2} & \quad \text{fenton process} \\
\text{H}_2\text{O}_2 + \text{Fe}^{+3} & \quad \text{fenton-like process} \\
\text{H}_2\text{O}_2 + \text{Fe}^{+2} / \text{Fe}^{+3} + \text{hv} & \quad \text{photo assisted fenton process}
\end{align*}
\]

Sensitizers have been used to degrade pesticides in drinking water. It is not easy applied as these sensitizers and semiconductors are not safe and cannot separate from water by filtration [9] [14].
Figure 2. Uses of sensitizer for photolysis process.

1.2. Kinetic and thermodynamic study

After the determination of rate constants, the activation energy has been measured by Arrhenius equation [11].

\[ k = Ae^{-E_a/RT} \] \hspace{1cm} (1)

When \( k \) is rate constant, \( A \) is a frequency factor, \( E_a \) is activation energy, \( T \) is absolute temperature and \( R \) is universal gas constant \((8.314 \times 10^{-3} \text{ KJ.mol}.^{-1}.\text{K}^{-1})\).

In addition, other thermodynamic parameters have been calculated, such as entropy \( \Delta S^* \), enthalpy \( \Delta H^* \) and Gibbs free energy \( \Delta G^* \) of activation by using the following equations [12] [13]:

\[ E_a = \Delta H^* + RT \] \hspace{1cm} (2)
\[ \Delta H^* = E_a - RT \] \hspace{1cm} (3)
\[ \ln \frac{k}{T} = \ln \frac{K_b}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \] \hspace{1cm} (4)
\[ \Delta G^* = \Delta H^* - T\Delta S^* \] \hspace{1cm} (5)

\( K_b \) is Boltzman constant \(1.3 \times 10^{-23} \text{J/K}\)

\( h \) is planck constant \(6.623 \times 10^{-34} \text{J/sec}\)

2. Experimental Parts:

Generally speaking, all chemicals have purchased from FLUKA and they are AnalaR grade, the experiments have been carried out in different temperatures, in order to calculate energy of activation. In addition, various concentrations are used, so that to investigate the effect of concentration on photo degradation process. Moreover, only ultra violet light has been used as a light source. The solvent was mainly consisting of water ninety percent and the remaining ten percent was acetonitrile. Acetonitrile is added in order to dissolve Trifluralin completely. The concentration change during photodegradation have been measured by spectrophoto meter at 280nm.
Figure 3. UV.-vis. Spectral change for the degradation of 50ppm Trifluralin by ultraviolet light at 25°C and at different time.

2.1. The photolytic system
The main part of part in photolytic system is shown in the following figure. This photolytic system contain double layer cell for circulation of water from thermostat.

Figure 4. Schematic block diagram for photo-degradation system (1) Light source ultra violet (UV.) Light (2) Stand and clamp they are used to hold a light source. (3) Photolytic cell is made from boro-silicate which is transparent for ultraviolet and visible light. The detail will explain in next section (4) Magnetic bar (5) Inlet and outlet tube of water from and to thermostat (6) Magnetic stirrer to make a solution adequately accept the light (7) Thermostat is used for a purpose temperature controlling.

2.2. Instrumentation
The pho-degradation have been done on special thermostatic cell as in the fig.4 UV-vis. Spectrophotometer type Perkin-Elmer lambda 25 is used, in order to determine the changes that occur during the degradation process with respect of time. Samples have been transferred to spectrophotometer and auto concentration and time is recorded.
3. Result and discussion
Trifluralin is sparingly soluble in water, but quite soluble in organic solvents at different ratios. Trifluralin gives two absorption spectra the high intensity peak absorb at (275nm) and the lower intensity at (390nm) this ratio varies from solvent to solvent this work has been done in water/acetonitrile 90/10 ratio. The calculations have been performed for 275nm absorption peak [9].

Table 1. Optical density and molar extinction coefficient of 15ppm Trifluralin in 10% acetonitrile + 90%H2O

| Wave length (nm) | O.D.    | $\varepsilon$ (mol/L.cm) |
|-----------------|---------|--------------------------|
| 280             | 0.476   | 10639                    |
| 400             | 0.2106  | 4707                     |

The rate of Trifluralin degradation has been estimated by examining degradation of peak (280nm) it appears that the degradation of peak 280nm is second order. The table 2 shows the photo-degradation of Trifluralin rate constant of different concentration with respect of temperature. The second table 3 illustrates calculated number of various thermodynamic parameters including enthalpy, entropy and Gibb’s free energy.

Overall, what stands out from Table 1 is that the rate constants are increased with increasing temperature throughout the experiments. In spite of increasing concentration, rate constant remain stable, in this experiment the rate constant is fluctuated. This may be due to the fact of quenching; during the degradation process new compounds are formed, which absorb the radiation causing less degradation [14].

And the following data have obtained:

Table 2. The rate constant $k$ (mol-.L.min- ) of Trifluralin degradation in different temperatures and concentrations.
Table 3. Activation energy, enthalpy, Gibbs free energy and entropy of activation for tow concentrations at 273k.

| Concentration in PPM | 30ppm | 60ppm |
|----------------------|-------|-------|
| Activation energy $E_a$ | 31.99 KJ/mol | 52.835 KJ/mol |
| Enthalpy of activation $\Delta H^*$ | 29.51 KJ /mol | 50.357 KJ /mol |
| Entropy of activation $\Delta S^*$ | -0.146 KJ /mol.K | -0.089 KJ /mol.K |
| Free energy $\Delta G^*$ at 298k | 73.018 KJ /mol | 76.879 KJ /mol |

The rate constant of degradation dose not remain constant by varying initial concentration. This may be due to secondary photo-chemical reactions that take place during photo-degradation process and also this change perhaps due to quenching process, in which some intermediates absorb a UV. Radiation and re-emit them as a form of heat do not undergo photolysis. Another striking point is that increase in temperature may change the order of degradation and therefore in some circumstances by increasing temperature the rate constant have been decreased [9].

The following figures show the calculation of rate constant for different temperature and concentrations.
Figure 6. Second order plot at 280nm for the degradation of 30ppm Trifluralin by ultraviolet light at 20, 25, 30 and 35°C
The Arrhenius plot is not good straight line that was due to the fact the degradation is not pure second order reaction and we used these plots to calculate the activation energies and thermodynamic functions.

4. Conclusion
All in all, the photo-degradation of this molecule of pesticide is composed of primary photo excitation, and then it decomposes by thermal reaction which they are approximately second order, that due to the fact this degradation plot of 1/A against time is not pure straight line although it is not first order. We calculate the rate constant as a second order reaction and we used these second order and rate constant to find activation energy through Arrhenius equation then all thermodynamics values have been calculated by classical thermodynamic equation.

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