PHOTOCATALYTIC DEGRADATION OF 2,4-DICHLOROPHENOL AS A MODEL COMPOUND OF WATER POLLUTANTS.

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Abstract

Photocatalytic degradation of 2,4 - dichlorophenol (2,4-DCP) dissolved in aqueous solution. under UV and near visible light in the presence of TiO_2 as catalyst has been studied this reaction followed the first experiments were used to optimize the experimental parameters in the first set of experiments variable amounts of TiO_2 were used with affixed concentration of (2,4-DCP). It was found that 100 mg of TiO_2 gave the highest degradation rate constant. In the second set of experiments TiO_2 concentration was fixed at 100 mg/25 ml and study the effect temperature on the reaction and find the activation energy about 23.941 kJ/mole. The third set of experiments were the effect of PH solution and found that the highest rate constant at pH=4.

1-Introduction

TiO_2 has become the commonly catalyst employed in Photodegradation of organic environmental pollutants[1]. TiO_2absorbs light in UV region when irradiated with light of (λ<400nm.), promotes electron form valence band to the conduction band .This process produces conduction band electron (e^-_{cb}) in conduction band and positive hole (h^+_{vb}) in the valence band[2]according to the following equation:-

$$TiO_2 \xrightarrow{\lambda \leq 400\ nm} TiO_2(e^- — h^+) \qquad \text{- - - - - - - - - (1)}$$

Then the conduction band electron and valence band holes are separated from each other and transferred across the interface to reduce or oxidize surface. The absorbat environmental pollutants[3]as the following :-

$$h^+ + D \longrightarrow D^+ \qquad \text{- - - - - - - - - (2)}$$
$$e^- + A \longrightarrow A^- \qquad \text{- - - - - - - - - (3)}$$

Chlorophenols (CPs) are common organic contaminants found in the environment of most industrialized countries . CPs are toxic for a wide rang of organisms. A property that accounts for many of their use has been restricted. Some of these are still produced in large quantities. Lower CO2 serve as intermediates in the production of pesticides, such as those named commercially 2,4-Dichlorophenol and 2,4,5-Trichlorophenol[4,5].

CPs are present in drinking water as a result of chlorination of hypochlorination of phenols, as by products of the reaction of hypochorite with phenolic acid, as biocides, or as degradation products of phynoxy her biocides. Those most be to occur in drinking water as by products of chlorination are 2-CP, 2,4-DCPand 2,4,6-TCP[6].

Serpon and other workers[7-8]investigate the photodegradation of phenol , 4 – chlorophenol ,2,4 –dichlorophenol and 2,4,5 –trichlorophenol in presence of TiO_2 to produce CO_2 and HCl quantitatively as the following equation :

$$Cl_3C_6H_2OH + 5.5\ O_2 \xrightarrow[TiO_2]{h\nu} 6\ CO_2 + 3\ HCl \qquad \text{- - - - - - -(4)}$$

In this report the Photodegradation of 2,4-Dichorophenol have been studied as a model compound by near UV- visible light in the presence of TiO_2 as catalyst and study the influence of some parameters on this photoreaction such as pH of the solution , the loading of TiO_2 , and the effect the temperature in range between (283-303) K and determining the activation energy of this reaction.

2. Experimental

2.1 Chemicals:

All chemicals used without further purification. 2,4- Dichloro phenol supplied by Fluka purity better than 98% , Titanium dioxide (P-25) supplied by Degussa . The water was purified with a Millipore Millit tow system.

2-2 Instruments

Low pressure mercury lamp (LPML) type OSRAM (125 W) was used as a source of irradiation.

Photocell (35 cm^2) with quartz window (2 cm^2) was used as reaction vessel Cintra-5 UV Visible spectrophotometer was used to determination the undegarded 2,4-DCP in the λ max (284 nm). The temperature was adjusted by using regulator circulating thermostat (Desaga Frigostat) . The pH of suspension was controlled by using pH meter (Radiometer Copenhagen).

2-3 Photodegradation Experiments:

Aqueous solution of 2,4 DCP was prepared by dissolving certain quantities of subsrate.The concentration was prepared a 1×10^{-1} M in presence of 0.1 M $HCLO_4$ and prepare several solution . The photolysis experiments were carried out in the photolytic Pyrex cell. A magnetic stirrer was used to keep the solution in homogeneous suspension through the photolysis process. Oxygen gas was passed with rate of 10 cm^3 / min., during the photolysis experiments. all photodegradation experiments were carried out by irradiation the a aqueous suspension of 2,4-DCP by UV-visible light emitted from LPML in the reaction vessel fitted with quartz window. A small quantity (0.5 ml) of suspension was taken and centrifuged and filtrated to remove TiO_2 .

The inicedent light intensity was measured by using Parcker and Hautchard[9]method. This method consist of ferrioxalate actinometry $K_3Fe(C_2O_4)_2.3H_2O$ for 3 nm after passing 15 nm at 298 K. The average light intensity is 9.3×10^{-8} Einstein $L^{-1}S^{-1}$

3- Results and Discussion

Figure (1) shows spectrum absorption of (2,4-DCP) in distilled water . There are two absorption band. The first band observed at 225 nm and the second band at 284 nm. The second band was used to monitor the effect of photocatalysis on the degradation of 2,4-DCP to find the optimum condition and the effect of different parameters on the degradation of 2,4-D CP.

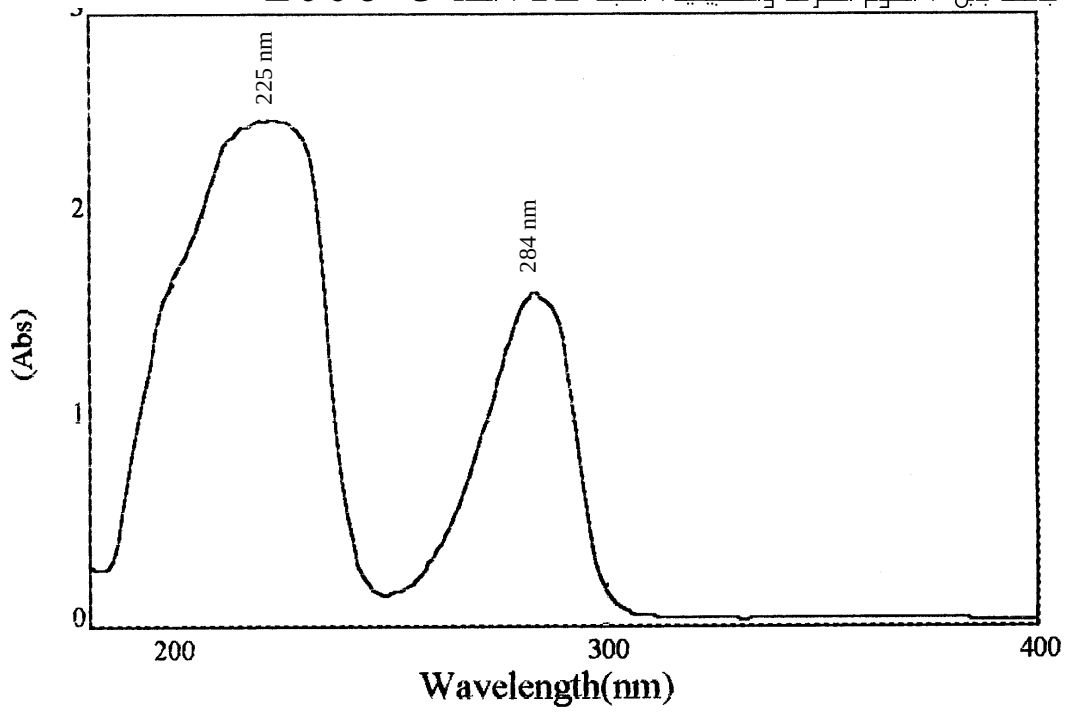


Figure (1) : UV – visible adsorption spectrum of 2,4-DCP (0.1M) dissolved in distilled water in concentration 0.1 M at 283 K.

3-1 Photocatalytic Degradation of 2,4-DCP Under Inert Atmosphere :-

Figure(2) shows photocatalytic degradation experiment at 283 K over TiO_2 in presence of air with out light and in presence of air and light with out using TiO_2 for 3 hours. It was noticed that 2,4-DCP is quite stable. This mean that the presence of light ,TiO_2 and O_2 are very essential for the Photocatalytic degradation of 2,4-DCP.

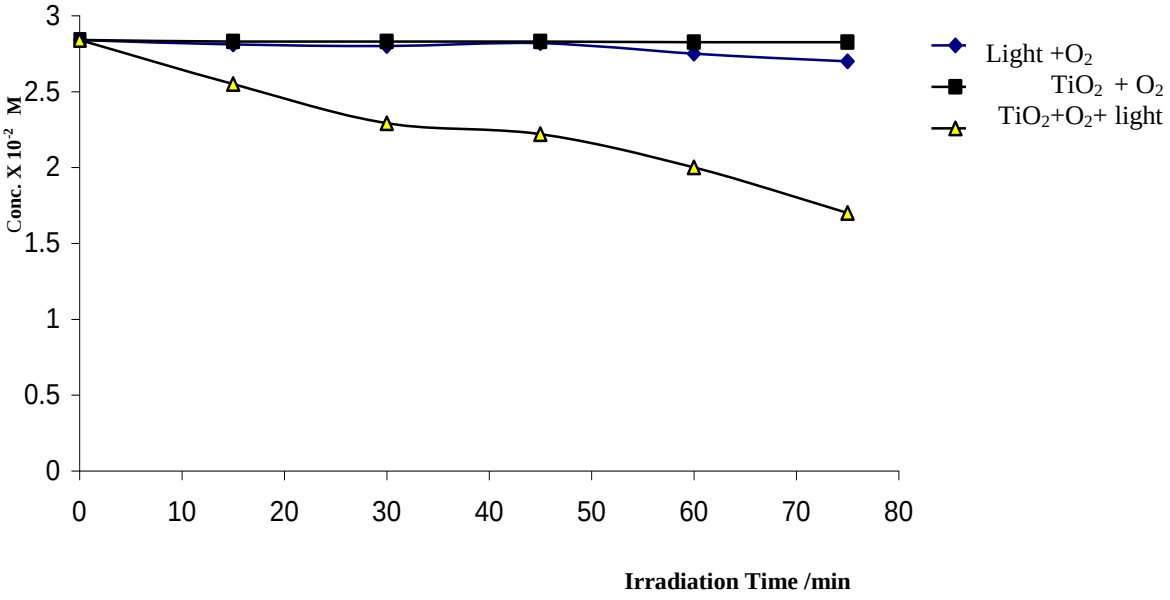


Figure (2) : photocatalytic degradation of 2,4-DCP under different conditions.

3-2 TiO_2 Concentration Optimization :-

A series of experiments have been done to determined the optimum conditions which led to high Photocatalytic activity in Photocatalytic reaction . Different masses of $TiO_2$was used in presence of air and light at 283 K. Figure (3) shows that weight 100 mg is sufficiently for the maximum rate of Photocatalytic reaction .This quantity will be used in all experiments has been down in this study.

Figure (3) shows that the lower weights of TiO_2(less than 100 mg) gave direct proportionality between weight of TiO_2 and the rate of degradation. This observation can be explained according to the second law of photo chemistry each atom or molecule absorbs one photo. While using a high weight of TiO_2 more than 100 mg leads to negative deviation in the 2,4-DCPdegradation because TiO_2 particles form inner filter which absorb some of incident photons and scatters others parts of light which lead to reduce the of degradation[9].

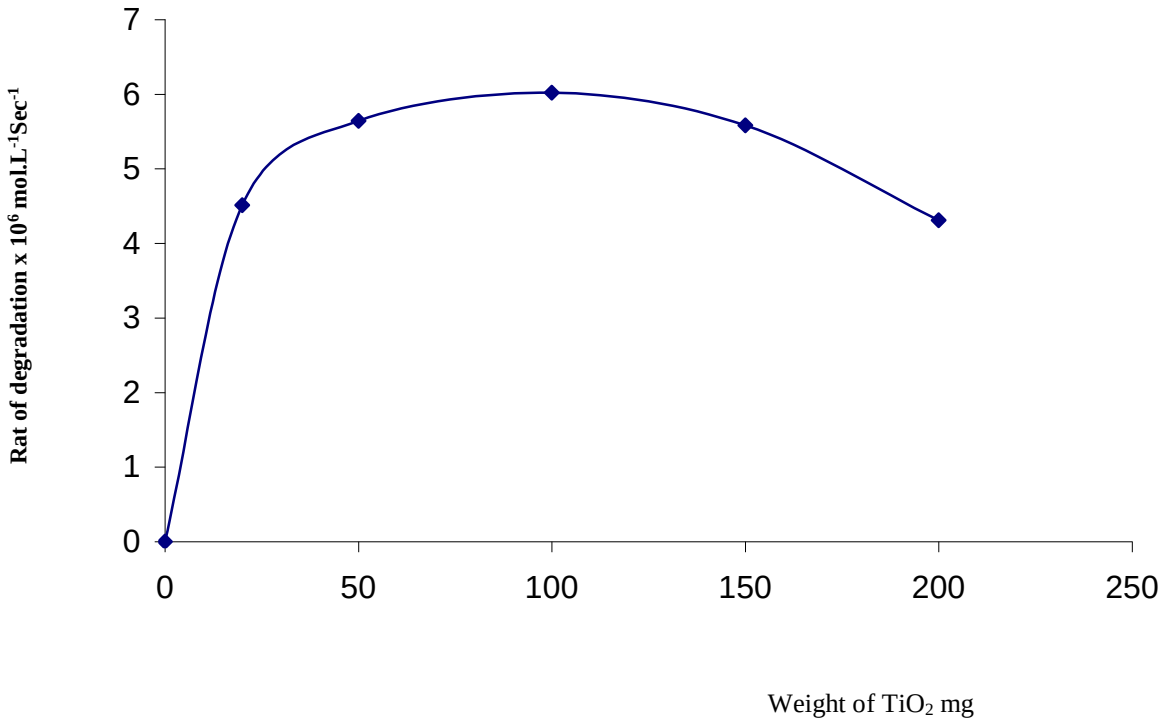


Figure (3) : the relation ship between rate of degradation of 2,4-DCP and weight of TiO_2

3-3 Effect of pH.

For a series of solution with 100 mg /25 ml of TiO_2 and starting PH in the rang (4-9). Figure (4) shows effect of PH solution on the Photocatalytic degradation of (2,4-DCP). The best degradation was obtained with PH=4.

Generally the initial rate of Photocatalytic reaction was decreased with increasing of the PH solution. The PH of the aqueous solution effects the practical size, the surface charge, and band edge position of the TiO_2 due to it is amphoteric character[11]. The PH at which the surface of an oxide is uncharged or also called the zero point charge (PH_{ZPC}), for TiO_2 is around 7. Above and below this value, the catalyst is negatively charge or positively charge according to equation (4) and (5).In

consequence the Photocatalytic degradation of organic compound is effected by the pH.

$$TiOH_2^+ \longrightarrow TiOH + H^+ \quad \text{----------} \quad (4)$$
$$TiOH \longrightarrow TiO^- + H^+ \quad \text{----------} \quad (5)$$

The adsorption and polar substances was enhanced when the surface of TiO_2 become positive charge, and this mean that initial photon catalytic rate was increased in acidic mediums[11].

3.3 Effect of Temperature:-

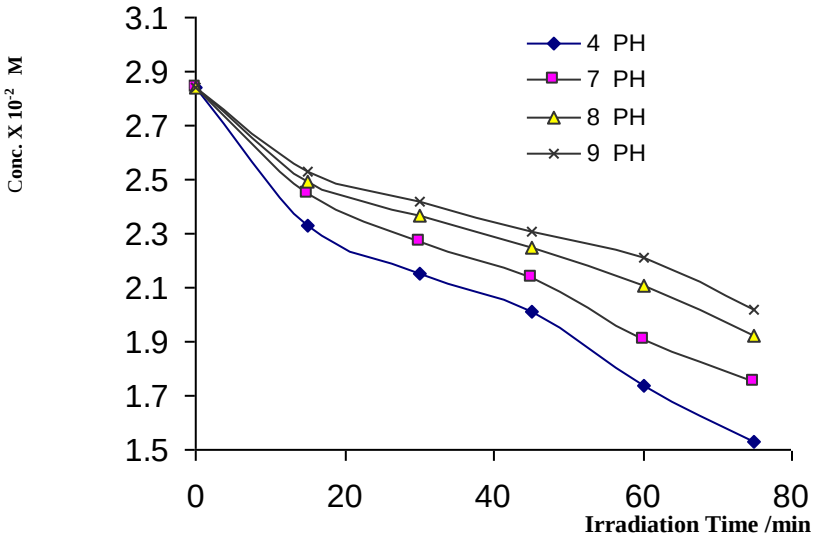
Results of Photocatalytic degradation of 2,4-DCP on TiO_2 in the rang of temperature (283-303)K are shown in table (2).

Generally, the rate of Photodegradation of 2,4-DCP.was increased with increasing of temperature and this behaviors may be attributed to the effect of temperature on the adsorption processes on the surface of TiO_2[12].

Figure (5) shows the Arrhenius-type plot in the temperature rang (283-303) K. The activation energy of 2,4-DCPwas deduced from the plot is equal 23.941 $K.Jmol^{-1}$, it indicates that the thermally activated step are negligible, i.e, this energy is required to promoted photo electrons from the valance band to the conduction band to be surface trapped by adsorbed oxygen molecules[13].

Table (1):Rates of Photocatalytic degradation of 2,4-DCP in the rang of pH (4-9) at 283 K .

pH	Rat of degradation x 10^6 $mol.L^{-1}Sec^{-1}$
4	6.42
7	5.98
8	5.69
9	4.85



Figure(4) : Photocatalytic degradation of 2,4-DCP under different pH at 283 K .

Table (2):Rates of Photocatalytic degradation of 2,4-DCP under different temperature

T/K	Rat of degradation x 10^6 mol.L^{-1}Sec^{-1}
283	6.00
288	6.21
293	6.46
298	6.71
303	6.90

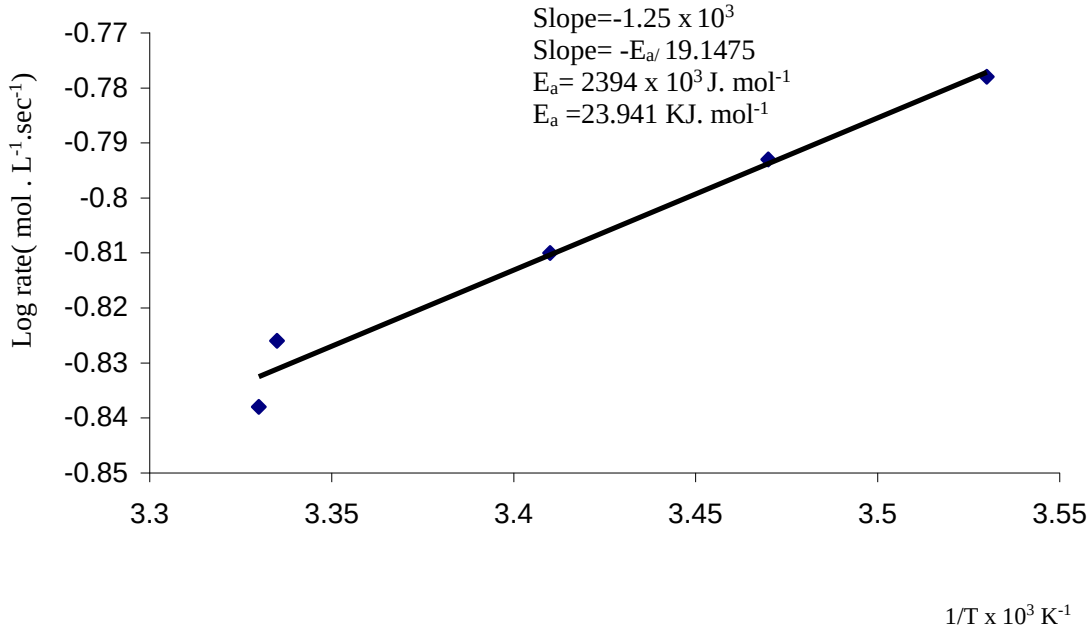


Figure (5) : Temperature dependence for the photocatalytic degradation of 2,4-DCP over TiO_2.

Conclusions

The oxidation of substrates by band gap irradiation of semiconductors in the presence of O_2 is well documented in the literatures[14]. The presence of oxygen is very essential for the trapping of photo electrons to reduce recombination process, which commonly occurs between (e^-_{cb}/h^+_{vb}) pairs in the naked TiO_2 according to the following reaction:-

$$e^- + O_{2(ads)} \rightarrow O^{\cdot-}_{2(ads)} \text{ - - - - - -- - - - - - - -(6)}$$

The rate for photocatalytic degradation of 2,4-DCP was reduced by using of TiO_2 band more than 100 mg and lower than 100 mg this mean that at this amount of catalyst there is complete absorption of the incident light by TiO_2 molecules.

The rate of Photocatalytic degradation of 2,4-DCP was change with the variation of the PH solution, it was found that this rate was increased with decreasing of PH solution due to the positive charge of the TiO_2 surface in the acidic medium which increased the adsorption of 2,4-DCP molecules on the surface of semiconductor molecules.

There is a direct proportion between rate of degradation and evaluation of temperature. Generally , photo reaction are not sensitive toward minor variations in temperature[15]. However the steps which are potentially dependent on the temperature such as adsorption and desorption and arrangement of the surface are not the rate determent steps in this type of reaction[15].

Mechanism of 2,4-DCP Photocatalytic Degradation:

The nature of the primary intermediatessuggests of the oxidation of 2,4-DCP by hydroxyl radicals these rasdicals can be propduced by the following reaction[1] .

$$TiO_2 \xrightarrow{h\nu} e^-_{cb} + h^+_{vb} \quad \ldots\ldots\ldots\ldots (7)$$

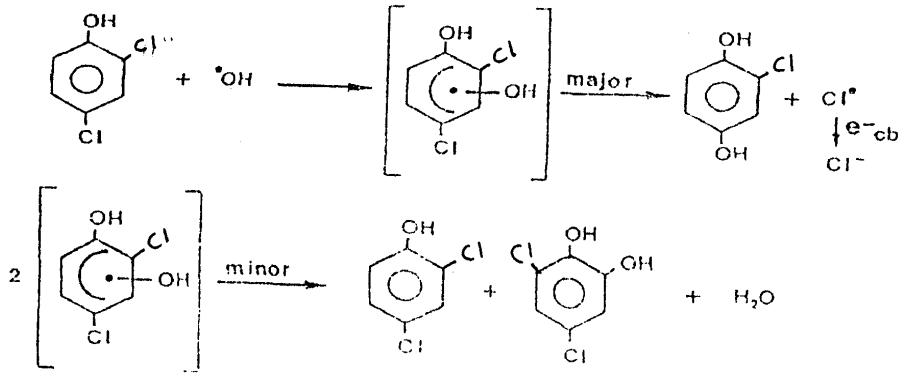
$$H_2O + h^+_{vb} \longrightarrow \dot{O}H + H^+ \quad \ldots\ldots\ldots\ldots (8)$$

$$H^+ + e^-_{cb} \longrightarrow \dot{H} \quad \ldots\ldots\ldots\ldots (9)$$

$$O_2 + e^-_{cb} \longrightarrow \dot{O}_2^- \xrightarrow{H^+} H\dot{O}_2 \quad \ldots\ldots\ldots\ldots (10)$$

$$2H\dot{O}_2 \longrightarrow O_2 + H_2O_2 \xrightarrow{O_2^-} \dot{O}H + \bar{O}H + O_2 \quad \ldots\ldots\ldots (11)$$

The $\dot{O}H$ (and $H\dot{O}_2$) can subsequently under go a series of reactions with 2,4-DCP to produce the following compounds[5] :-



Babeni and Morello[4] illustrate that the complete degradation of chloro phenols compounds in aqueous suspensions of TiO_2 in the presernce of air results rapid disappearance of chlorinated organic compounds to produce CO_2 and HCl.

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الخلاصة

تم خلال البحث الحالي دراسة الأكسدة الضوئية لتفكك 2و4- ثنائي كلورو فينول المذاب في المحلول المائي باستخدام الأشعة الفوق البنفسجية وقرب منطقة الطيف المرئي بوجود TiO_2 كعامل مساعد.

تم اجراء عدة تجارب اولية لتحديد الظروف المثلى لتفكك المركبات الفينوليه ففى المجموعة الأولى تم تحديد قيمة العامل المساعد TiO_2 المثلى التي تعطي اعلى سرعة تفكك وقد كانت هذه القيمه مساويه لـ 100 mg لكل $25\ cm^3$ من المحلول المائي وفي المجموعة الثانيه من التجارب تمت دراسة تاثير درجة الحرارة على سرعة التفاعل ضمن المدى (283-303) كلفن كما تم حساب طاقة التنشيط لهذا التفاعل وكانت مساوية لـ 23.941كيلوجول / مول.كما اجريت عدة تجارب لتحديد الظروف المثلىلـ pH حيث وجد ان االفضل تفكك تم بلوغه عند PH=4.