مجلة القادسية للعلوم الصرفة المجلد (12) العدد (1) لسنة 2007

# *Kinetic Efffect of SDS and Rodamine 6G Dye on Photocatalytic Degradation of Hydroquinone Compound*

Nada Y . Fairooz
College of science
Babylon university

Fatima Al Zahra'a J . Jassim
College of Dentist
Babylon university

## Abstract :-

Photocatalytic degradation of Hydroquinone (HQ) dissolved in aqueous $TiO_2$dispersions under UV and near visible light has been investigated . The first experiments were used to determine the optimum value of $TiO_2$,it was found that using 10 mg of $TiO_2$ in 25 $cm^3$of aqueous solution produced the highest degradation of rate constant .

The effects of sodium dodecyl sulphate (SDS) and Rodamine 6G(Rod 6G) dye on the photocatalytic degradation of hydroquinone (HQ) have been studies .The results of degradation was observed that the rate of photodegradation was decrease with increasing of SDS concentration , while the results indicate that the rate of photodegradation was increased whenRod 6G dye was used. According the experimental results, the general reaction mechanism for this compound was suggested.

## الخلاصة :-

تضمن البحث الحالي دراسة الاكسدة الضوئية لتفكك مركب الهيدروكوينون المذاب في المحلول المائي بوجود $TiO_2$ كعامل مساعد وباستخدام الاشعة فوق البنفسجية والاشعة المرئية القريبة, حيث تم اجراء تجارب اولية لتحديد القيمة المثلى للعامل المساعد $TiO_2$ حيث وجد ان استخدام 10 mg من $TiO_2$ لكل 25 $cm^3$ من المحلول المائي تعطي اعلى سرعة تفكك ضوئي .

كما تمت دراست تاثير اسنخدام مادة SDS وتاثير استخدام صبغة الرودامين على سرعة التفكك الضوئي للمركب وقد اوضحت النتائج ان سرعة التفكك الضوئي تقل بزيادة تركيز مادة

SDS في حين تزداد هذة السرعة باستخدام صبغة الرودامين6G كمتحسس ضوئي . وعلى ضوء النتائج التجريبية تم اقتراح ميكانيكية الاكسدة الضوئية لمركب HQ باستخدام $TiO_2$.

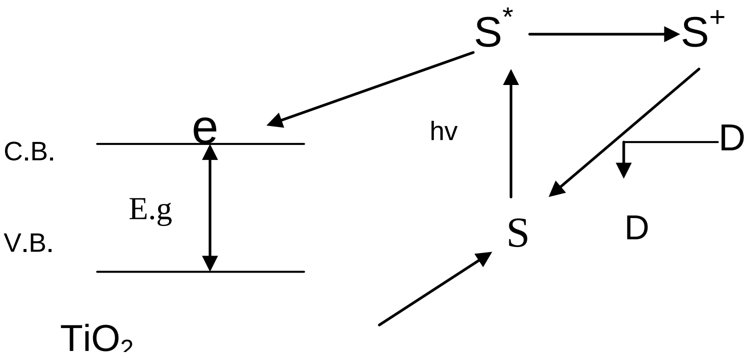
## 1- Introduction :-

Photocatalysis reaction is based on asequence of light induced redox process taking place at the semiconductor / solution interace upon irradiation of semiconductor particales with light of proper energy , higher than the band – gap. The production of electron – hole pairs is essential since these species have potentials capable to reduce or oxidise avarity of organic compound(1) .

Generally Titanium dioxide ($TiO_2$) is condider to be the best photocatalyst simicondoctor and has the ability to detoxification water from a number of organic pollutants(2). The band gap energy is approximately 3.2 ev for $TiO_2$ (anatase)(3)so that only light with 400 nm. Can be effective to drive photocatalytic process(4).Therefore, Kamat(5)investigated the successful sensitization of photocatalytic oxidation process by using sutable dyes such as Rodamin B(5) , Saframine(6), Riboflaven(7)and other dyes(8), these dyes are adsorbed on the $TiO_2$surface and extend the wave length of $TiO_2$ to the visible region. Sensitzer are quenched by $TiO_2$semiconductor particales via accepting the electrons in conduction band of semiconductor and converting charge to another a dsorbed substrate(9)a ccording to the following scheme :-

$$S \longrightarrow S^* \qquad \text{…….(1)}$$

$$S^* + TiO_2 \longrightarrow S^+ + TiO_{2\,(e^-)} \qquad \text{……..(2)}$$



The aim of the present work to study the effect of sodium dodecyl sulphate (SDS) and Rodmine 6G on photocatalytic degradation of hydroquinone (HQ) .

## 2- Experimental :-

### 2-1 Instraments :-

Photo cell (35 $cm^3$) with quartz window (2 $cm^2$) was used as a reaction vessel and Low Pressure Mercury Lamp (LPML) type OSRAM (125 watt) was used as a source of irradiation . Cintra-5 UV-visible spectrophotometer was used to determine the undegared (HQ) . The temperature was adjusted by reulator thermostat (Desaga Frigostat) , $TiO_2$ particaes were separated by using Ganetzki T scentrifuge.

### 2-2 Chemicals :-

Rodamine 6G supplied by BDH , Titanium dioxide (P-25) supplied by Dequssa , Sodium dodecyl sulfate (SDS) supplied by BDH .Double distill water was used in all experiments.

### 2-3 Photochemical Experiments :-

A queous solution of HQ was prepared by dissolving cerntain quantities of substrat. The concentration of stock solution was prepared at $1x10^{-4}$M and several cocentrations were prepared from this solution . All photochemical experiments were carried out by irradiation 25 $cm^3$aqueous $TiO_2$ suspension of HQ in presence of $TiO_2$ by light emitted from LPML in the photo cell fitted with quartz window. A magnetic stirrer was used to keep the solution in homogeneous suspension during the photolysis process. Oxygen gas was passed with rate of 10 $cm^3$/ min by using compressor. A small quantity (0.5 $cm^3$) of suspension solution was taken and centerfuged and filtrated to removed $TiO_2$.

Parker and Hautchard(9)method was used to measure the incedent light intensity, this method consist of irradiated actinometric solution potassium Ferrioxalate $K_3Fe(C_2O_4).3H_2O$ for 3nm.after passing $N_2$ gas about 15min.at 298 K. The average light intensity of LPML is $8.9 \times 10^{-8}$ Einstein $L^{-1}S^{-1}$.

## 3- Results and Discusion :-

A queous solution of HQ at 1x10$^{-4}$M was show two maximum absorption band at 223 nm. and at 287nm.as shown in figur(1) the second band at 238nm.was used monitor the photocatalytic degradation of HQ to study the optimum condition and effect of SDS and Rod 6G dye on the photodegradation of HQ.

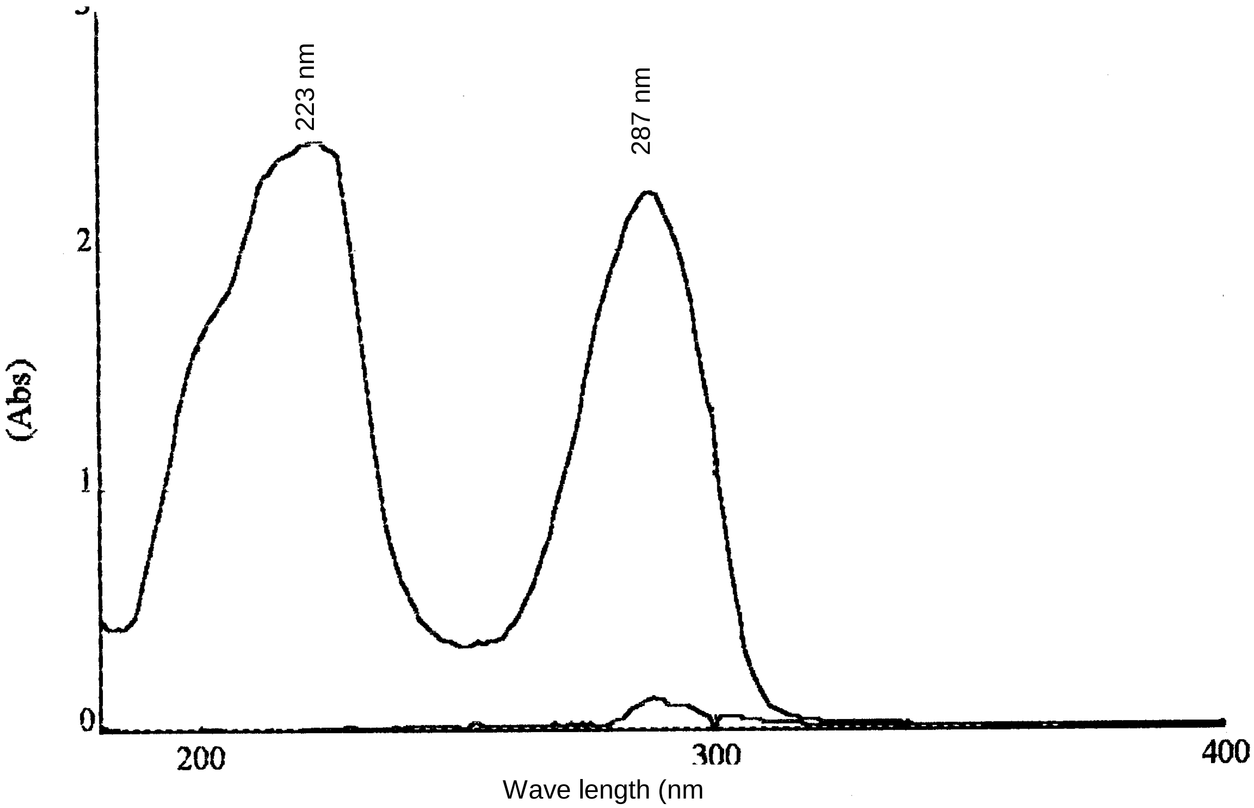


Figure (1) : Spectroscopic absorption spectrum of HQ dissolved in distilled water in concentration 1X10$^{-4}$ M at 298 K.

### 3.1- Effect of $TiO_2$ Masses :-

A number of experiments have been carried out by using different masses of $TiO_2$ in presence of light and $O_2$ at 298 K . The maximum rate of photocatalytic degradation was obtained at 10 mg of $TiO_2$ for 25 cm$^3$ of the solution. So that this quantity will be chosen to study the effect of SDS and Rod 6G on HQ photodegradation.

Figure(2) shows the rate of photocatalytic degradation was increased with increasing of $TiO_2$ mass due to complete adsorption of photons light potentially absorbable by $TiO_2$(10) .While using more than 10 mg /25cm$^3$ of $TiO_2$ leads to negative deviation in the HQ degradation and this observation can be explained to the large numbers of $TiO_2$ partical form inner filter(11) which absorb some of incedent photons and scatters others part of light.

Table (1): photocatalytic degradation of HQ with different weight of $TiO_2$ at 298 K

| Conc. of HQ x10$^3$ | | | | | |
|---|---|---|---|---|---|
| Irradiation Time (min) | Weight of $TiO_2$ mg | | | | |
| | 5 | 8 | 10 | 12 | 30 |
| 0.00 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| 5 | 1.08 | 1.07 | 1.05 | 1.08 | 1.09 |
| 10 | 1.05 | 1.01 | 0.95 | 0.98 | 1.05 |
| 15 | 0.97 | 0.93 | 0.9 | 0.93 | 0.99 |
| 20 | 0.9 | 0.87 | 0.82 | 0.85 | 0.95 |
| 25 | 0.85 | 0.82 | 0.75 | 0.79 | 0.9 |

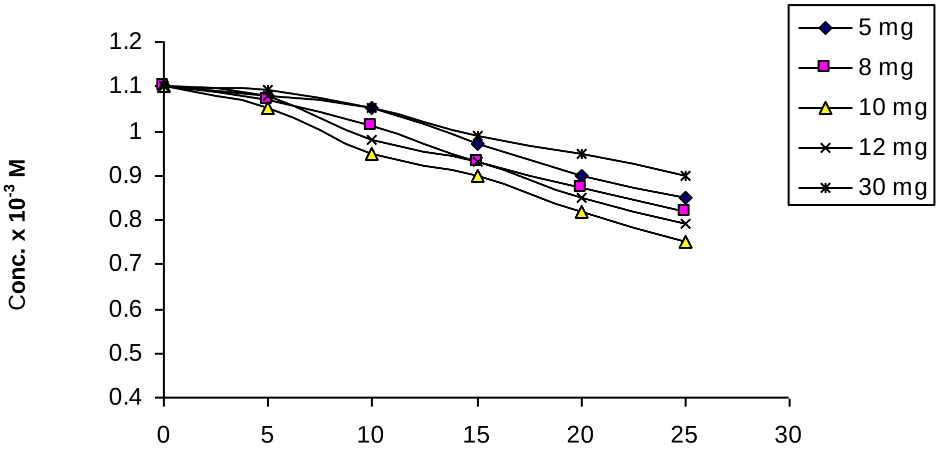


Figure (2): photocatalytic degradation of HQ with different weight of $TiO_2$ at 298 K

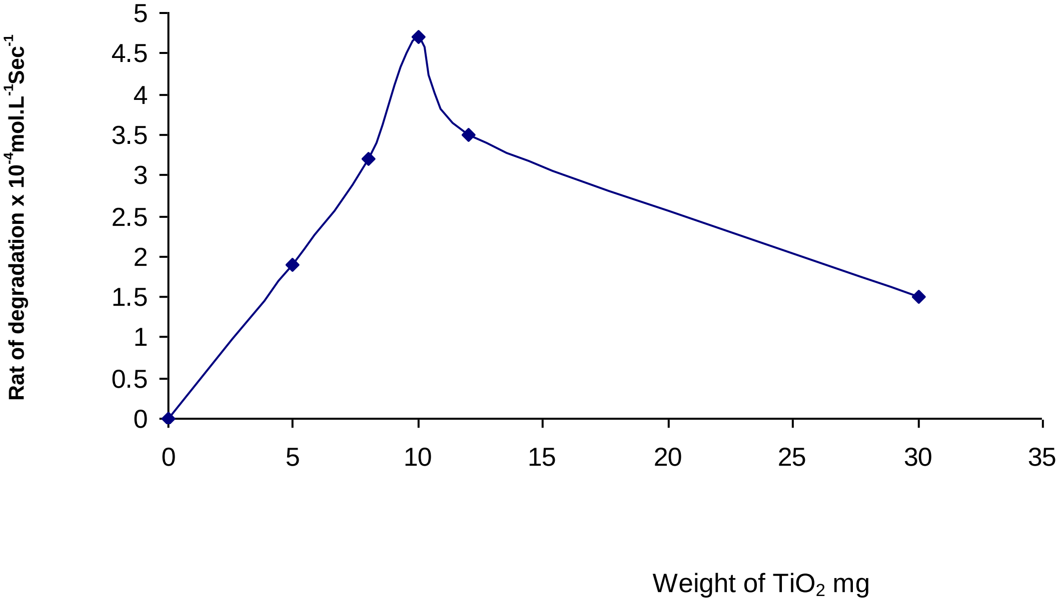


Figure (3) : the relationship between rate of degradation of HQ and weight of $TiO_2$

## 3.2-Effect of SDS Concentrations :-

Results of photocatalytic degradationof HQon 10 mg/25 cm$^3$ of $TiO_2$ at 298 K. in the presence of increasing SDS concentrations, ranging between (1 x 10$^{--1}$ M and 1 x 10$^{-3}$M ) are shown in figure(4).

Generally, HQ photodegradation was decreased with increasing of SDS concentration . This behaviour due to the competition between surfactant and HQ substrate molecules for the active sites of the $TiO_2$ catalyst(12) . The behaviour can be attributed to the adsorption of charged surfacetant molecules on the $TiO_2$ particaes , leading to the formation of bilayers effecting on the surface properties of the $TiO_2$ semiconductor and reduced the ability HQ degradation.

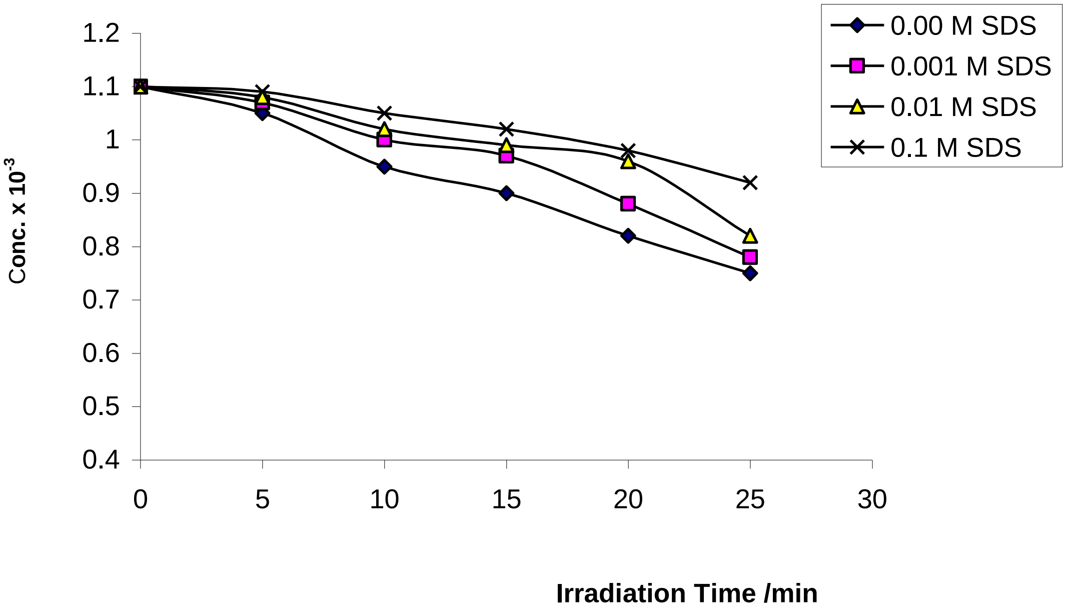


Figure (4): photocatalytic degradation of HQ with different concentrations of SDS at 298 K .

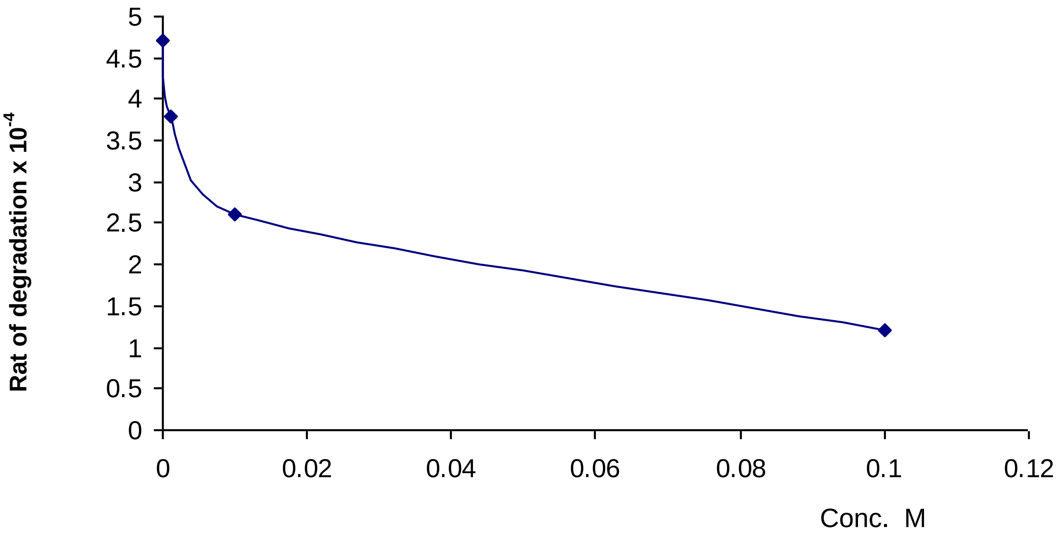


Figure (5) : the relationship between rate of degradation of HQ and weight of $TiO_2$ at 298 k .

## 3-3 Effect of Rod 6G :-

In this part. A seriers of experiments had been down with different concentrations of Rod 6G over rang inpresence of 10 mg of $TiO_2$ 25 $cm^3$ at 298 K.

Figure (7) shows that the ideal concentation of Rod 6G is ($0.25 \times 10^{-5}$M) to give maximum HQ photodegradation rate . Photocatalytic degradation of HQ was reduced when using concentration more then $0.25 \times 10^{-5}$M of Rod 6G this observation may be attributed due to form inner filter molecules of the dye which lead to absorbs high portions of incedent light and prevents it to pass the other parts of light photons, while using low concentration of Rod 6G (0.1 $X10^{-5}$ M ) lead to pass high portion of light to the other side of reactor with out sharing in reaction which reducethe rate of degradation(13).

Generlly, thre rat of photocatalytic degradation of HQ was increased by using Rod 6G dye and this result form stability, activity and wide adsorptionband in effective region spectrum of this dye(14).

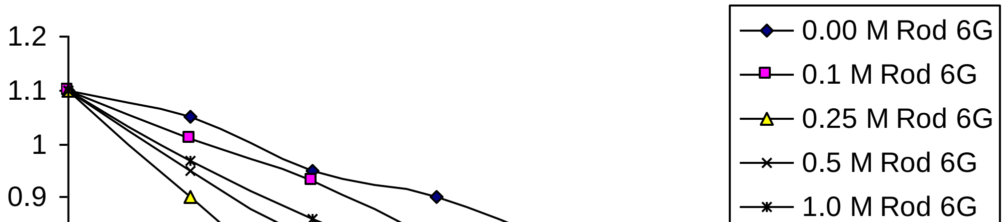


Figure (6): photocatalytic degradation of HQ with different concentrations of Rod 6G at 298 K .

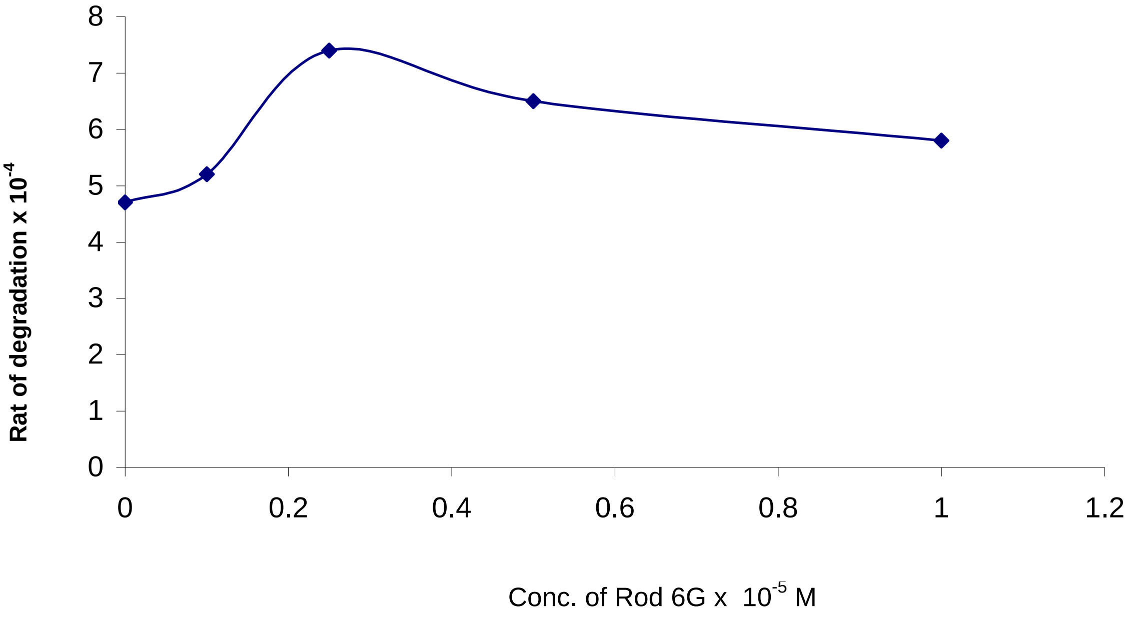


Figure (7) : the relationship between rate of degradation of HQ and concentrations of Rod 6G.

Table (2) **:-** photocatalytic degradation of HQ by using naked $TiO_2$ , SDS and Rod 6G **.**

| Reaction | Rate of degradation x $10^{-5}$ mol.$L^{-1}$.$Sec^{-1}$. |
|---|---|
| Naked $TiO_2$ | 4.7 |
| $TiO_2$ + SDS(0.1 M) | 1.2 |
| $TiO_2$ + Rod 6G (0.25 X$10^{-5}$M ) | 7.5 |

## Conclusions :-

The ideal weight of $TiO_2$ which gave an optimum efficiency for HQ degradation is 10 mg /25 $cm^3$. The rate of photocatalytic degradation has been increased with the amount of catalyst due to complete absorption of incedent light photons , potentially absorbale by $TiO_2$, while using more than 10 mg of $TiO_2$ decreased the HQ degradation because $TiO_2$ particales acte as inner filter which absorb high portions of incedent light and scatter the other part(12).

HQ photocatalytic degradation can be achieved in the presence of SDS. The decrease in the degradation rate is consistent with a competitive attributed between SDS particals and substrate for the acitve site of the catalyst and this process produced bilayers effectng on the surface properties of the catalyst(14 ).

Photocatalytic degradation of HQ was increased by using Rod 6G dye due to ability of dye to absorbs the incedent photones with the wave length greter than 400 nm. and injection the charge to the conduction band of $TiO_2$ partical and converting this charge to the adsorbing species (15).

## Mechnism of Photocatalytic $TiO_2$ in aqueous solution :-

Photocatalytic degradation of HQ inpresence of sensitsed $TiO_2$ and $O_2$ and light take place according to the following :-
The first step of degradation is excited of Rod 6G sensitizer molecules

$$\text{Rod} \xrightarrow{hv} [\text{Rod}]^* \qquad \text{. . . . . . . . . . . . . . . . .(3 )}$$

Excited state of sensitizer $S^*$ is quenched by injection of electrons inconduction band of $TiO_2$ semiconductor

$$S \longrightarrow S^* \qquad \text{.......(1)}$$

$$S^* + TiO_2 \longrightarrow S^+ + TiO_{2\,(e^-)} \qquad \text{........(2)}$$

Photo electrons are trapped by absorbed oxygen on the surface of excited sensitizer dye .

$Rod + TiO_2 \longrightarrow Rod^+ + TiO_2(e^-)$ . . . . . . . . . . . . . . . . .(4 )

$Rod^+ + H_2O \longrightarrow H^+ + H\dot{O} + Rod$ . . . . . . . . . . . . .. . . .(5)
$TiO_2(e^-) + O_2 \longrightarrow TiO_2 + \bar{O}_2 \longrightarrow H^+ \quad HO\dot{O}$ . . . . . . . . . . . . . . .(6)
$2HO\dot{O} \longrightarrow H_2O_2 + O_2$ . . . . . . . . . . . . .. . . . . (7)
$TiO_2 + H_2O_2 \longrightarrow TiO_2 + H\dot{O} + H\bar{O}$ . . . . . . . . . . . . . . . .(8)
$TiO_2(h^+) + H_2O \longrightarrow TiO_2 + H\dot{O} + H^+$ . . . . . . . . . . . . . .. . . . (9)
$\bar{O}_2$ + PCP molecule e (RH ) $\longrightarrow HO\dot{O} + R^{\cdot} \longrightarrow$ further products . . ..(10)
$R^{\cdot} + O_2 \longrightarrow RO\dot{O}$ . . . . . . . . . . . . . .(11)
$RO\dot{O}$+ HQ molecule (RH) $\longrightarrow$ ROH + $R^{\cdot}$ + further products . . . . . .(12)
$TiO_2(e^-)$ + HQ $\longrightarrow TiO_2$+ (HQ molecule) $\longrightarrow$ product . . . . . ..(13)

## 4- *References :*-

1- N.SerponeandE.Pelizzetti, Photocatalysis Fundamental and Applications , Wiley , Newyork,1989.
2- E.Pelizzetti , P.Piecinini , C.Minero,V.Maurino, N.Serpon, and H.Hidaka, J.Photochem. andPhotobiol.A:Chem.,1997,109,171.
3- A.L.Vogel, Test book of practical organic chemistry ,4th Edition,Longman,Newyork,USA,1978,356.
4- S.M.Aliwi and S.S.Abdul Kadir ,Nasional.J. of chemistry ,2001 , 2,272.
5- C.Kormann , D.W.Bahnaman and M.R. Hffman, Environ .Sci. Technol, 1991,25,494
6- Y.Liang, A.M.Ponte Goncalves and D.K. Negus, J.Phys.chem., 1983,87,1.
7- S.M.Bedir,M.Sc. thesis, Baghdad Univ. 1997,19.
8- C.S.Foote,Mechanisms of photosensitised oxidation ,Scince, 1968,162,963.
9- F.H.Hussein and H.A.Habeeb , Al-Qadisya , 2000, 1,3.
10- P.E.Toren and B.J.Henrich , Anal.chem.,1955 , 27, 1986.
11- P.Pichat , M.N.Mozzanega ,J.Disdier and J.M.Herrmann, Nour.J. Chem., 1982 ,6,559.
12- - A.J.Attia , and F.H.Hussein , National . J . Chem., 2001,2,230.
13- D.Fabbri , A.B.Prevot and Epramauro , Applied Catalysis , 2004, 49 , 233.

14- A.H.J.M.AL-Tai, M .Sc.Thesis, Baghdad univ.,June,2000,16
15- J.Lobebdank,E. Bellmann,J.Photo.Chem. and Photo. Biol.A: Chem. 1997,108