

# Photolysis of $\alpha$ -Naphtholbenzein Using $TiO_2$ as a Catalyst in the Presence of Sun Light

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## Abstract

The photolysis of  $\alpha$ -naphtholbenzein with  $TiO_2$  as photo catalyst has been investigated using solar light. The effect of various parameters such as: time of irradiation, light and dark reactions,  $TiO_2$  loading,  $H_2O_2$  and oxalate concentrations have been determined. The experiments explained that the photolysis was completed at 2.5 hr. In both light and dark reactions, the presence of  $TiO_2$  and  $O_2$  was an important factor to increase the rate of reaction. The optimum loading of the catalyst was 0.4g in which the rate constant was  $19 \times 10^{-2} \text{ hr}^{-1}$ . The rate of reaction increased with increasing the millimoles of  $H_2O_2$  until 12 millimoles. Also the experiments showed that the photolysis rate was increase with increasing the concentration of oxalate ion .The kinetics of reaction explained that the reaction was from pseudo first order.

التحلل الضوئي لـ  $\alpha$ - نفتول بنزين باستخدام  $TiO_2$  كعامل مساعد  
بوجود ضوء الشمس

احمد كاظم عباس

قسم الكيمياء ، كلية العلوم ، جامعة القادسية

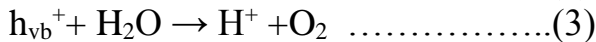
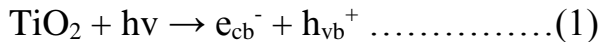
الخلاصة:-

تم دراسة تفاعل التحلل الضوئي لـ  $\alpha$ - نفتول بنزين مع  $TiO_2$  كعامل مساعد ضوئي باستخدام ضوء الشمس . وتم تعيين تأثير العوامل المختلفة مثل : زمن التشعيع وتفاعلات الضوء والظلام ووزن  $TiO_2$  وتراكيز  $H_2O_2$  والاوكزالات. وضحت التجارب بان التحلل الضوئي يكتمل عند الزمن 2 و30 ساعة وان وجود  $TiO_2$  و  $O_2$  كان عاملا مهما لزيادة سرعة التفاعل في الضوء والظلام . وكان الوزن الأمثل للعامل المساعد هو 0,4 غم حيث كان ثابت السرعة  $19 \times 10^{-2}$  ساعة<sup>-1</sup> . وان سرعة التفاعل تزداد بزيادة مليمولات الـ  $H_2O_2$  حتى 12 مليمول . كذلك بينت التجارب بان سرعة التحلل الضوئي تزداد بزيادة تركيز ايون الاوكزالات . وبينت حركية التفاعل بان التفاعل من المرتبة الأولى الكاذبة .

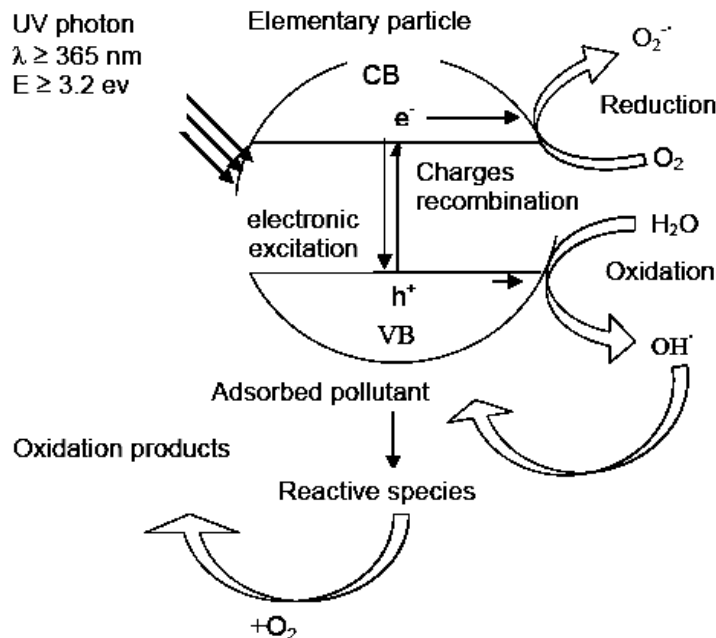
## Introduction

Solar radiation is regarded of interest being the existence of ultraviolet radiation the key of some homogeneous and heterogeneous photocatalytic Processes, such as  $\text{TiO}_2/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{Fe}^{+2}/\text{UV-vis}$  or  $\text{H}_2\text{O}_2/\text{Fe}^{+3}/\text{UV-vis}$ . system (Photo-Fenton)<sup>(1-3)</sup>. Heterogeneous photocatalytic process includes the use of UV radiation to Photoexcite semiconductor catalyst in the presence of oxygen. Under these conditions, oxidizing components-bound hydroxyl radical or free holes are Generated <sup>(4)</sup> . The photocatalyst titanium dioxide ( $\text{TiO}_2$ ) is a wide band gap Semiconductor (3.2eV) and it is used as a photocatalyst for the treatment of organic <sup>(5-8)</sup> and dye pollutants <sup>(9-15)</sup> .

$\text{TiO}_2$  is regarded as the best photo catalyst due to high stability, good performance and low cost <sup>(16)</sup> .In  $\text{TiO}_2/\text{UV}$  light system, a titanium Peroxide semiconductor absorbs UV light and generates hydroxyl radicals. During UV illumination of  $\text{TiO}_2$ , conduction band electrons and valence band holes are initially yielded (eq.1). Band electrons interact with surface adsorbed molecules oxygen to yield super oxide radical anions (eq.2) , while band holes interact with water to produce hydroxyl radical (eq.3) <sup>(17)</sup> .



The photo catalysis processes that take place on the  $\text{TiO}_2$  -semiconductor can be represented by fig.1 <sup>(18)</sup>.



**Fig.1:** Mechanism diagram of photocatalytic degradation.

Photodegradation of pollutant using  $\text{TiO}_2$  with solar light is an economically process because the solar energy is an abundant natural energy source .This solar energy can be used instead of artificial light source. The artificial light sources need high electrical power which is costly and hazardous. Solar energy has been successfully used for photo catalytic degradation of pollutants <sup>(19-29)</sup> .

In the present investigation we have under taken  $\alpha$ -naphtholbenzein and examined the various parameters to find out the optimum conditions for removal of color and aromatic part of the dye.

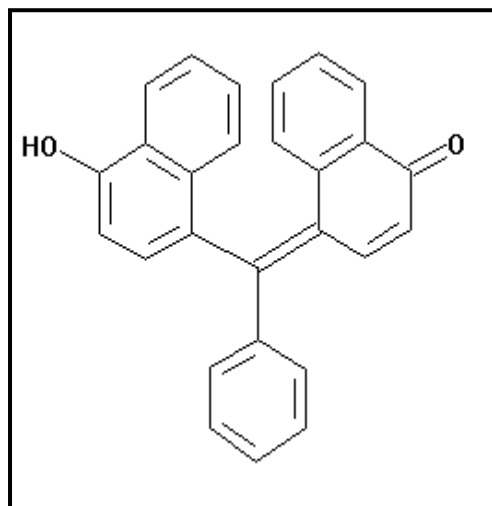
## **2-Experimental**

All experiments were carried out under similar conditions on sunny days of April-May between 11 Am and 2 Pm . 100ml three neck round bottom flask was used as reaction vessel which placed onto magnetic stirrer hotplate(obtained from GallenKamp)to reach the homogeneous mixing .The suspensions were magnetically stirred in the dark and light in the presence of dye only , dye- $\text{O}_2$  , dye- $\text{TiO}_2$  (supplied from Degaussa) and dye- $\text{TiO}_2$ - $\text{O}_2$  . Fifty milliliters of dye solution with  $\text{TiO}_2$  were continuously aerated by open part of the flask for complete mixing of reaction solution. At specific time intervals 3ml of the sample was withdrawn and centrifuged using centrifuge (supplied from 80-1 Table Top Low Speed Centrifuge Truip International Corp.120 cycle/min) .The electronic spectra and measurements(purchased from Shimadzu UV\_vis . 1650 Spectrophotometer) of dye samples then determined .ethanol(supplied from Fluka) was used as a solvent of the dye.

## **3. Disussion**

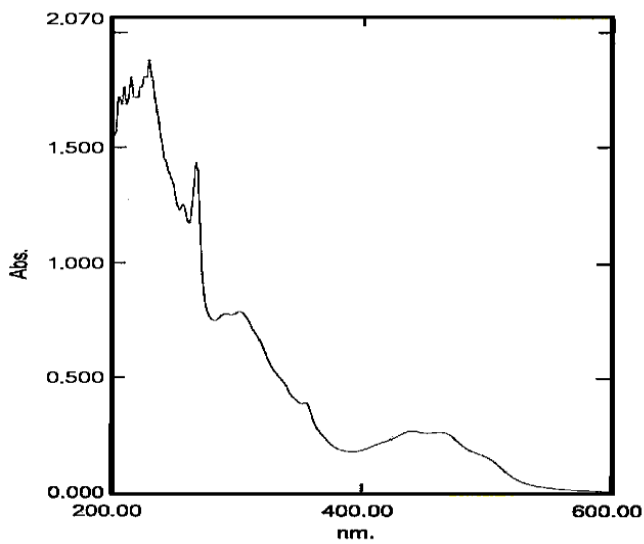
### ***3.1.The preparation of calibration curve***

The preparation of calibration curve solutions of  $\alpha$ -naphtholbenzein-which have the structure as illustrated in fig.2-at the range between (5-90)  $\text{mg.L}^{-1}$  were prepared using 96% ethanol as a solvent.

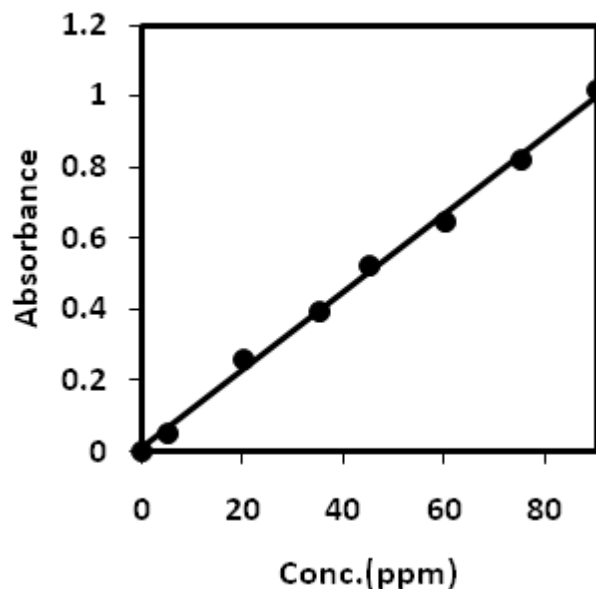


**Fig.2:** The structural formula of  $\alpha$ -naphtholbenzein.

The UV-visible spectrum of the concentration  $40 \text{ mg.L}^{-1}$  was taken to identify the maximum wave length which was 463 nm (fig.3) then the a absorbance at 463 nm was determined for each solution to represent the calibration curve by plot the values of a absorbance against the values of concentration which showed an straight line that obeyed the law of Lambert-Beer(fig.4)



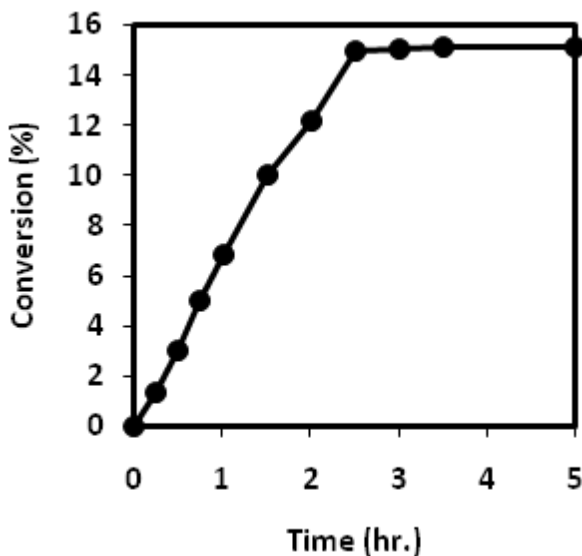
**Fig.3:** The electronic spectrum of  $\alpha$ -naphtholbenzein in 96 % ethanol.



**Fig.4:** Absorbance vs. concentration to prepare the calibration curve of photolysis.

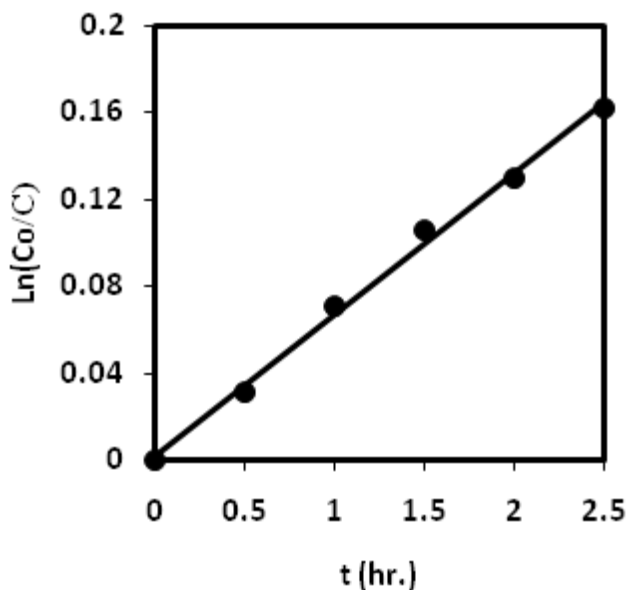
### ***3.2.The kinetics of photoreaction***

The irradiation of the substance at different irradiation time at the range between (0.25-5) hr. was examined. The experiments showed that the percentage of conversion was increase with increasing the irradiation time (fig.5) and the optimum conversion % was at time 2.5 hr.



**Fig.5:** Conversion % vs. irradiation time.

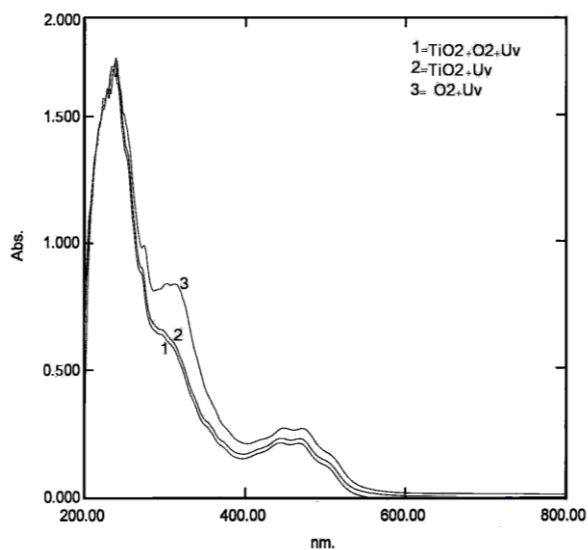
The reaction was from pseudo first order at range of time between (0.25-2.5) hr. because the plot of  $\ln(C_0/C)$  against  $t(\text{hr.})$ - where  $C_0$  is the initial concentration,  $(C)$  is the residual concentration and  $(t)$  is the time-yielded a straight line which represent the first order of reaction<sup>(30)</sup> and the rate constant  $(k)$  was determined by the slope (fig .6)



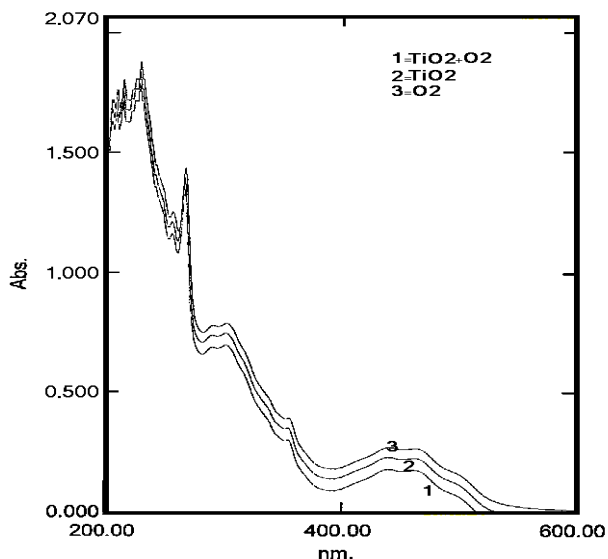
**Fig.6:**  $\ln(C_0/C)$  vs. irradiation time of first order reaction of photolysis process.

### ***3.3. The effect of various conditions on the photolysis process***

The reaction of  $\alpha$ -naphtholbenzien at different conditions in the presence of  $\text{TiO}_2$ ,  $\text{O}_2$  and  $\text{TiO}_2\text{-O}_2$  in the light and dark as illustrated by electronic spectra (fig.7 and fig.8) was achieved.



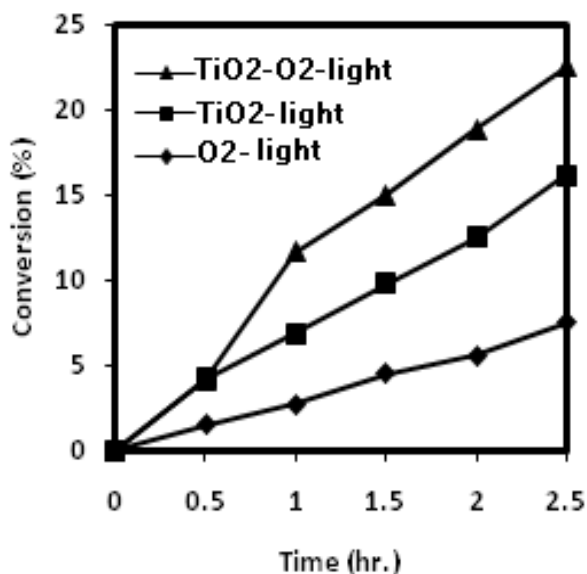
**Fig.7:** Electronic spectra of  $\alpha$ -naphtholbenzein irradiated by uv.-vis. light at different conditions. [ $\alpha$ -naphtholbenzein] = 40 mg/L, [ $\text{TiO}_2$ ] = 0.2 gm/50 mL, pH = natural, solvent = 96 % ethanol.



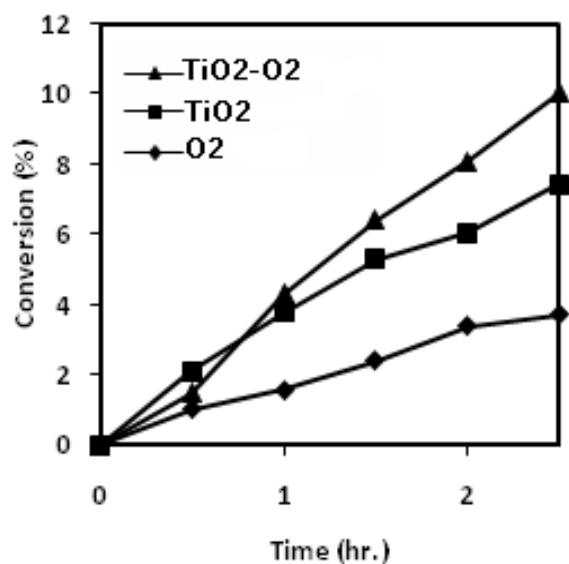
**Fig.8:** Electronic spectra of  $\alpha$ -naphtholbenzein in the absence of uv.- vis. light at different conditions. [ $\alpha$ -naphtholbenzein] = 40 mg/L, [ $\text{TiO}_2$ ] = 0.2 gm/50 mL, pH = natural, solvent = 96 % ethanol.

In the light reaction  $\text{TiO}_2$  semiconductor particles illuminated yielded excited holes in valance band and excited electrons in conduction band. Both OH groups-founded at the surface of  $\text{TiO}_2$ -and molecular oxygen are induce the photolysis process (31, 32).

While in the dark reaction only adsorption process was formed at the surface of  $\text{TiO}_2$  and molecular oxygen was unable to from the super oxidized oxygen ( $\cdot\text{O}_2$ ). Thus, the percentage of conversion in the case of light was higher than that in the dark (fig.9 and fig.10) and rate constant .Also the rate constant for light reaction was higher than in the dark reaction (table 1 and table 2).



**Fig.9:** Conversion % vs. irradiation time of  $\alpha$ -naphtholbenzene irradiated by uv.-vis. light at different conditions. [ $\alpha$ -naphtholbenzene] = 40 mg/L, [TiO<sub>2</sub>] = 0.2 gm/ 50 mL, pH = natural, solvent = 96 % ethanol.



**Fig.10:** Conversion % vs. irradiation time of  $\alpha$ -naphtholbenzene in the absence of uv.-vis. light at different conditions. [ $\alpha$ -naphtholbenzene] = 40 mg/L, [TiO<sub>2</sub>] = 0.2gm/ 50 mL, pH = natural, solvent = 96 % ethanol.

**Table 1:** The values of rate constants of photolysis of  $\alpha$ -naphtholbenzene in the presence of light at different conditions

Condition	Rate constant( $k$ ) $\times 10^{-3}$
O <sub>2</sub> -light	31.1
TiO <sub>2</sub> -light	65.7
TiO <sub>2</sub> -O <sub>2</sub> -light	102.2

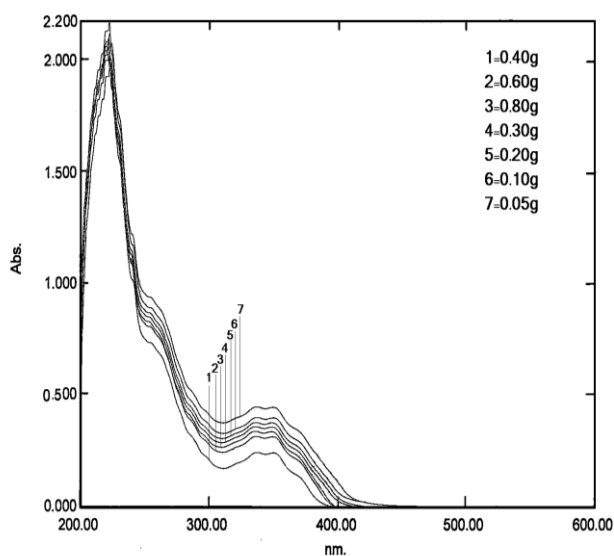
**Table 2:** The values of rate constants of photolysis of  $\alpha$ -naphtholbenzene in the absence of light at different conditions.

Condition	Rate constant( $k$ ) $\times 10^{-3}$
O <sub>2</sub>	14.7
TiO <sub>2</sub>	27.2
TiO <sub>2</sub> -O <sub>2</sub>	44.4



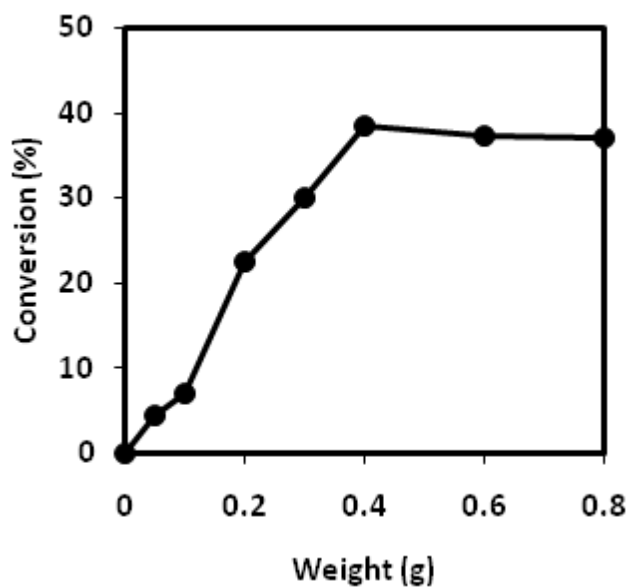
### 3.4. The effect of TiO<sub>2</sub> loading

The amount of catalyst is one of the main parameters for the photolysis studies. In order to avoid the use of excess catalyst, it is important to find out the optimum loading for efficient removal of substance. Several authors have investigated the reaction rate as function of catalyst loading in the photolysis process<sup>(33-35)</sup>. The effect of catalyst weight of TiO<sub>2</sub> on the percentage of conversion of  $\alpha$ -naphtholbenzien was investigated from 0.05 to 0.8 g as illustrated by electronic spectra (fig.11).



**Fig.11:** Electronic spectra of  $\alpha$ -naphtholbenzenin irradiated by uv.-vis. light at different TiO<sub>2</sub> loading. [ $\alpha$ -naphtholbenzenin] = 40 mg/L, pH=natural, solvent=96% ethanol.

The results showed that the increase of catalyst weight from 0.05 to 0.4 g increases the photolysis rate due to (i) the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed (ii) the increase in the density of particles in the area of illumination. But at weights from 0.6 to 0.8 g the photolysis rates are almost constant (fig.12 and table 3).



**Fig.12:** Conversion % vs. weight of TiO<sub>2</sub> in the presence of uv.- vis. light. [ $\alpha$ -naphtholbenzein] = 40 mg/L, pH = natural, solvent = 96 % ethanol.

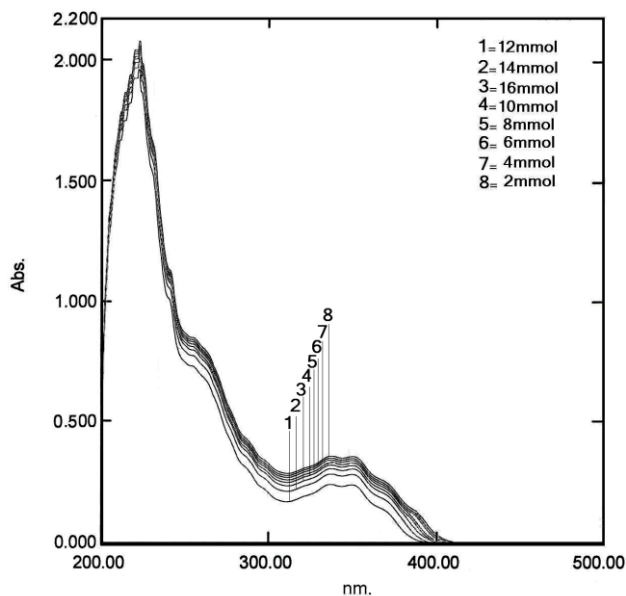
**Table 3:** The values of rate constants of photolysis of  $\alpha$ -naphtholbenzein at different TiO<sub>2</sub> weights.

Weight(g)	Rate constant ( k )x10 <sup>-2</sup>
0.05	1.94
0.1	3.08
0.2	10.22
0.3	14.62
0.4	19.0
0.6	18.62
0.8	18.53

This may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration<sup>(36)</sup> .

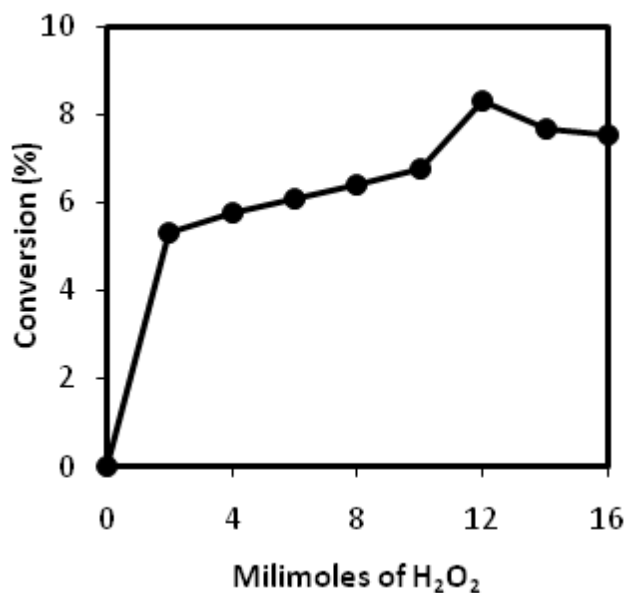
### 3.5. The effect of addition of H<sub>2</sub>O<sub>2</sub>

The effect of addition of H<sub>2</sub>O<sub>2</sub> (2-16 mmol) on the photolysis process has been investigated as illustrated by electronic spectra (fig .13).



**Fig.13:** Electronic spectra of  $\alpha$ -naphtholbenzein irradiated by uv.-vis. light at different H<sub>2</sub>O<sub>2</sub> concentrations, [ $\alpha$ -naphtholbenzein] = 40mg/L, [TiO<sub>2</sub>] = 0.4g/50mL, pH=natural, solvent=96% ethanol.

The results are shown in fig .14 and table 4 .The addition of H<sub>2</sub>O<sub>2</sub> (2-12 mmol) increases the photolysis rate, while further increase of H<sub>2</sub>O<sub>2</sub> concentration from 12 to 16 mmol decreases the rate of photolysis process.

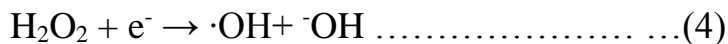


**Fig.14:** Conversion % vs. milimoles of H<sub>2</sub>O<sub>2</sub> irradiated by uv.-vis. light. [ $\alpha$ -naphtholbenzein] = 40 mg/L, [TiO<sub>2</sub>] = 0.4 gm/ 50 mL, pH =natural, solvent = 96 % ethanol.

**Table 4:** The values of rate constants of photolysis of  $\alpha$ -naphtholbenzein at different H<sub>2</sub>O<sub>2</sub> concentrations.

Milimoles	Rate constant ( $k$ )x10 <sup>-2</sup>
2	21.2
4	22.0
6	23.6
8	24.7
10	25.2
12	26.3
14	26.0
16	25.6

12 mmol of H<sub>2</sub>O concentration appears to be optimal for the photolysis. The enhancement of photolysis by addition of H<sub>2</sub>O<sub>2</sub> is due to increase in the hydroxyl radical concentration as in the following equations:



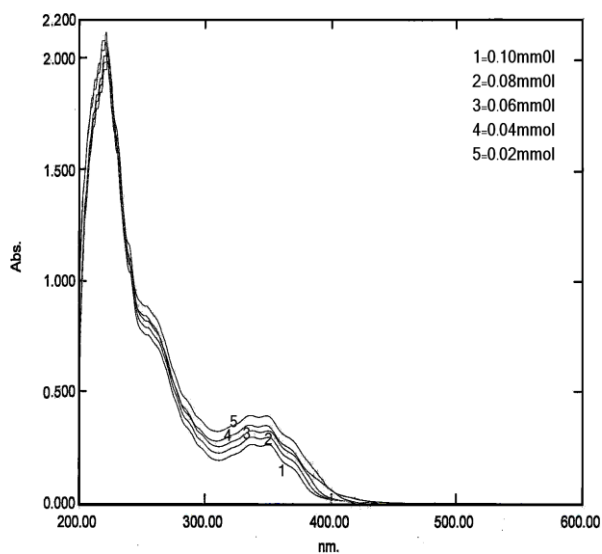
H<sub>2</sub>O<sub>2</sub> also reacts with superoxide anion to form ·OH radical:



While at high H<sub>2</sub>O<sub>2</sub> dosage (12-16 mmol ) the photolysis rate decreases due to its hydroxyl radical scavenging effect <sup>(37 and 38)</sup> .

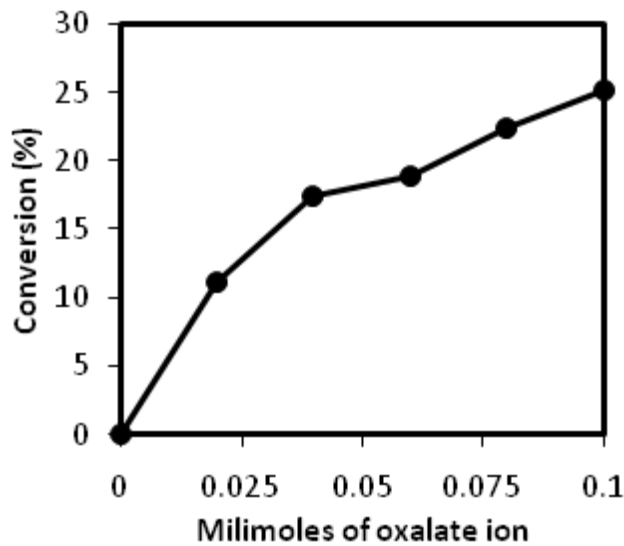
### 3.6. The effect of oxalate anion

Fig. 15 illustrates the electronic spectra of α-naphtholbenzein at different oxalate concentrations.



**Fig.15:** Electronic spectra of α-naphtholbenzein irradiated by uv.-vis. light at different oxalate concentrations, [α-naphtholbenzein] = 40mg/L, [TiO<sub>2</sub>] = 0.4g/50mL, pH=natural, solvent=96% ethanol.

It can be seen that increasing the oxalate concentration increased  $\alpha$ -naphtholbenzein removal efficiency (fig .16 and table 5) which is due to increasing the  $\cdot\text{OH}$  concentration <sup>(39)</sup>.



**Fig.16:** Conversion % vs. milimoles of oxalate irradiated by uv.-vis. light. [ $\alpha$ -naphtholbenzein] = 40 mg/L, [ $\text{TiO}_2$ ] = 0.4 gm/ 50 mL, [ $\text{H}_2\text{O}_2$ ]=12mmol, pH =natural,solvent=96%ethanol.

**Table 5:** The values of rate constants of photolysis of  $\alpha$ -naphtholbenzein at different oxalate concentrations.

Milimoles	Rate constant ( $k$ ) $\times 10^{-2}$
0.02	45.2
0.04	68..1
0.06	80.3
0.08	87.4
0.1	92.8

#### 4. Conclusions

The optimum time of irradiation that gave a higher percentage of conversion of  $\alpha$ -naphtholbenzein was at 2.5 hr. and the reaction was from pseudo first order at the range of time between (0.5-2.5 hr.). In the dark reaction the rate was approximately constant without any effect, while in the light the existence both UV-vis. light and  $\text{TiO}_2$  with molecular oxygen was the main role to increase the photolysis rate. The optimum weight of catalyst and  $\text{H}_2\text{O}_2$  concentrations were 0.4 g and 12 mmole respectively. Also the experiments illustrated that the rate of photolysis increase with increasing oxalate anion concentration.

#### References

1. A.Adeyeye and O.Osibanjo, "Aquatic and surface photochemistry", Lewis Publishers, 261, (1999).
2. S.Malato, "Solar photocatalytic decomposition of pentachlorophenol dissolved in water", Editorial CIEMAT., Madrid, Spain, 22, (1999).
3. J.Blanco, and S.Malato, "Solar detoxification", UNESCO. Natural Sciences, World Solar Programme, 45, (2001).
4. S.Malato, J.Blanco, A.Vidal, and C.Richter, *J.Appl. Catal. B:Environ.*, 2002, **37**, 1.
5. C.Komann, D.W. Bahnemann and M.R. Hoffmann, *J.Environ. Technol.*, 1991, **25**,. 494.
6. C. Y. Hsiao, C.L. Lee and D.F. Ollis, *J. Catal.* , 1983, **82** ,418. Abstract
7. O.Zahraa, H.Y. Chen and M. Bouchy, *J. Adv. Oxid. Technol.* , 1999, **4** ,167.
8. C. Shifu, *J.Environ. Sci.* , 1996, **17**, 33.

9. L.C. Chen and T.C. Chou, *J.Mol. Catal.* , 1993, **85** ,201.
10. S. Zheng, Q. Huang. J. Zhou and B. Wang, *J. Photochem. Photobiol A: Chem.* , 1997, **108**, 235.
11. I. Poulios and I. Aetopoulou, *J. Environ. Technol.*, 1999, **20**,479.
12. G.A. Epling and C. Lin,*J.Chemosphere* , 2002, **46**,561.
13. W.Z. Tang and H. An, *J.Chemosphere* , 1995,**31**, 4171. Abstract
14. W.Z. Tang, Z. Zhang, H. An, M.O. Quintana and D.F. Torres,*J. Environ. Technol.* , 1997, **18**,1.
15. S. Lakshmi, R. Renganathan and S. Fujita, *J. Photochem. Photobiol A: Chem.* , 1995, **88**,163.
16. R.Andreozzi, V.Caprio, A.Insola, and R.Marotta, *J.Catalysis Today*, 1999,**53** 51.
17. J.C.Crittenden, R.R.Trussell, D.W.Hand, K.J Howe. and G.Tchobanoglous,"Water treatment: Principles and Design", second ed., Wiley, New Jersey,67, (2005).
18. A.Mills, , S.Le Hunte, *J. Photochem. Photobiol*,1997, **108**,1.
19. H. Wu and X. Dong,*J. Acta Energia Solaris Sinica*, 1997, **18**,380.
20. Y. Wang and Y. Fu. Chin. *J. Biomed. Eng.*, 1998, **17**,,117.
21. L. R. Mathews,*J. Sol-Gel Sci. Tecnol.* , 1997, **8**,619.
22. J. C. Crittenden, Y. Zhang, D.W. Hand, D.L. Perran and E.G. Marchand, *J. Water Environ. Res.*, 1996, **68**,270.
23. Y. Waang, *J. Water Res.* , 2000, 24,990.
24. C. Minero, E. Pelizzeti, S. Malato and J. Blanco,*J. Chemosphere*, 1993, **26**, 2103. Abstract



25. J.M. Herrmann, J. Disdier, Pichat, S. Malato and J. Blanco, *J. Appl. Catal. B. Environ.* , 1998, **17**, 15.
26. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, *J.Chemosphere* , 2002, **46** ,1173.
27. S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, *J. Sol. Energy Mater. Sol. Cells* , 2003, 77,65.
28. W.S. Kuo and P.H. Ho, *J. Chemosphere* , 2001, **45**,77.
29. C. Minero, E. Pelizzetti, S. Malato and J. Blanco, *J.Sol. Energy* , 1996, **56**,421.
30. V. Mirkhani, S. Tangestaninejad, M. Moghadam, M.H. Habibi and A. Rostami Vartooni, *J. Iran. Chem. Soc.*, 2009, **6**, 800.
31. R. W.Matthews, *J. Water Res.*, 1986, **20**, 569.
32. C.Kormann, D. W.Bahnemann and M. R.Hoffmann, *J.Environmental Science and Technology*, 1991, **25**, 494..
33. N.San, A.. Hatipoglu, G. Kocturk and Z. Cinar, *J. Photochem. Photobiol A: Chem.* , 2001, **139**,225.
34. C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Duran, N. Nagata and P.P. Zamora, *J. Chemosphere* , 2000, **40**,96.
35. M. Saquib and M.Munner, *J. Dyes Pigments* , 2002, **53**,,237.
36. M.Murugandham and M. Swaminathan, *J. Solar Energy and Solar Cells*, 2004, **81**, 439.
- 37.A.P. Davis and C.P. Huang, *J.Water Sci. Technol.* , 1990, **21**,,455.
38. S. Malato, J. Blanco, C. Richter, B. Braun and M.I. Maldonado, *J.Appl. Catal. B: Environ.* , 1998, **17**,455.
39. A.A.Safarzadeh, J.R. Bolton and S.R.Cater , *J.Water. Res.*, 1997,**31**, 787.