

# Removal of Titan Yellow GR from Water Using Advanced Oxidation Process (AOP) in the Presence of Suspended ZnO as a Catalyst

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## Abstract

Titan yellow GR indicator which is the type of azo dyes could be degraded by UV/ZnO process .In the photocatalytic degradation of dye by UV/ZnO process, effect of some parameters such as UV irradiation time, pH, concentration of dye, bromate anion and ethanol was examined and first order reaction rate constant through 150 min. was calculated equal to  $9 \times 10^{-3} \text{ min}^{-1}$ . at experimental conditions by plot of semi-log of dye concentration versus time which was linear . Increasing irradiation time increased dye removal while the increasing in the dye concentration decreased the efficiency .Ethanol had inhibitory effect on this process .The maximum efficiency of the photodegradation process was at neutral pH (pH=7).Increasing bromate anion concentration from 1 to 4 mmoles increased dye removal ,but at higher concentration of bromate anion (above 4 mmoles) , the efficiency of dye removal decreased .Also the adsorption of dye onto the surface of catalyst was studied .The adsorption isotherm was accepted Langmuir model suggesting occurring of chemical reaction.

إزالة Titan Yellow GR من الماء باستخدام عملية الأكسدة المتقدمة (AOP) بوجود عالق ZnO كعامل مساعد .

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الخلاصة

ان كاشف الـ Titan Yellow GR الذي هو من نوع إصباغ الازو يمكن ان يتفكك بعملية ZnO UV/ حيث تم دراسة بعض من العوامل في عملية التفكك الضوئي المحفز بوجود UV / ZnO مثل زمن التشعيع بالأشعة فوق البنفسجية والـpH وتركيز كل من الصبغة وايون البرومات السالب والايثانول وتم حساب ثابت السرعة لتفاعل المرتبة الأولى خلال فترة 150 دقيقة والذي كان مساويا إلى  $9 \times 10^{-3}$  دقيقة<sup>-1</sup> من خلال رسم لوغاريتم تراكيز الصبغة مقابل الزمن والذي كان خطا مستقيما . وان زيادة زمن التشعيع يزيد من عملية إزالة الصبغة في حين ان زيادة تركيز الصبغة يقلل من الكفاءة . للايثانول تأثير مثبط لهذه العملية والكفاءة القصوى لعملية التفكك الضوئي كانت عند الـpH المتعادل (pH=7) . ان زيادة تركيز ايون البرومات السالب من 1 الى 4 مليمول يزيد من عملية ازالة الصبغة , لكن عند التراكيز العاليه لايون البرومات (فوق 4 مليمول ) فان الكفاءه تنخفض . كذلك تم دراسة امتزاز ألصبغه على سطح العامل المساعد وكان منحي متساوي درجة الحرارة للامتزاز يتوافق مع نموذج لانكما ير الذي يقترح حدوث تفاعل كيميائي .

## 1-Introduction

Azo dyes are a class of colored organic compounds that have largely used in industry for many applications such as textiles, papers, leathers, additives and analytical chemistry<sup>(1)</sup>. During dye production and textile manufacturing process, a large quantity of waste water containing dye stuffs with intensive color and toxicity are introduced into the aquatic systems<sup>(2)</sup>. In such cases, it is important to remove color from wastes, because the presence of even small amounts of dye (below 1 ppm) is clearly visible and influences water environment considerably. The degradation of azo dyes has been reported in many papers.<sup>(3-7)</sup>

Lately, very extensive studies done by researchers on many photocatalytic systems (UV/ semiconductor), which they have been found to be very effective in degrading various organic dyes. They are able to photosensitize the complete mineralization of a wide range of compounds like dyes, phenols and pharmaceutical drugs, without producing harmful by-products at near room temperature and pressure<sup>(8-12)</sup>.

The wastewater treatment methods can be overcome by the application of advanced oxidation process (AOP)<sup>(13)</sup> defined by Glaze et al.<sup>(14)</sup>, which present a suitable alternative to remove color from water<sup>(13)</sup>. Common AOP involves Fenton, Fenton-like, photo-Fenton process, ozonation, photochemical and electrochemical oxidation, photolysis with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, high voltage electrical discharge (corona) process, semiconductor photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams and various methods<sup>(15-19)</sup>.

The principle of AOP is the generation of very reactive species such as hydroxyl radicals ( $\cdot\text{OH}$ )<sup>(20)</sup>, which have a very oxidation potential ( $E_0=+2.80\text{ v}$ ), second only to fluorine. Hydroxyl radicals rapidly oxidize a wide range of organic pollutants<sup>(21)</sup>.

Many researchers consider TiO<sub>2</sub> as the best photocatalyst that has the ability to treat water from a number of organic pollutants<sup>(22-24)</sup>. On the other hand, it has been proven similar efficiency of photocatalytic between ZnO and TiO<sub>2</sub>. ZnO has been reported to be a better substitution to TiO<sub>2</sub> in some applications, thus ZnO can be a suitable alternative for TiO<sub>2</sub><sup>(8-10)</sup>.

In this work, we studied various parameters influenced the removal efficiency of dye such as: irradiation time, pH, the concentration of dye, ethanol and bromate anion. Also we examined the kinetics of photoreaction and study the adsorption of dye on to the surface of ZnO particles.

## 2- Experimental

The photo cell was consisted of 100 ml three neck round bottom flasks as reactor which placed onto magnetic stirrer hotplate (obtained from GalenKamp) to make the homogeneous mixing and controlled temperature at 20C° for all experiments. Commercial mercury lamps (CAC 220 /240v 50/60 Hz 11 WCE with power of 160 w) were used as a source of light .To prevent another irradiations to reach the reactor, the last was surrounded by cubic box of aluminum with equal lengths about 50cm . The distance between the lamps and reactor was 10 cm. In each experiment , 50 ml of dye solution with 0.25 g of ZnO was irradiated at a period of time ,then centrifuged by centrifuge ( supplied from 80-1 Table Top Low Speed Centrifuge Truip International Corp. 120 cycle/ min ). Then the electronic spectra and measurements (purchased from Shimadzu Uv-vis. 1650 Spectrophotometer) were done for dye solution. The conversion fraction of dye was calculated using the equation 1:

$$X = (C_0 - C) / C_0 = 1 - (C / C_0) \dots\dots\dots (1)$$

Where x was conversion fraction, C was dye concentration (ppm) at time t (min) and C<sub>0</sub> was initial dye concentration (ppm) .NaOH and H<sub>2</sub>SO<sub>4</sub> for pH adjustment, ZnO and ethanol were from Merck, while titan yellow G.R and potassium bromate were from Aldrich.

## 3. Discussion

### 3.1. The determination of calibration curve

Various titan yellow GR solutions (which have the structural formula as illustrated in fig.1) at the range between (10-70) ppm were prepared.

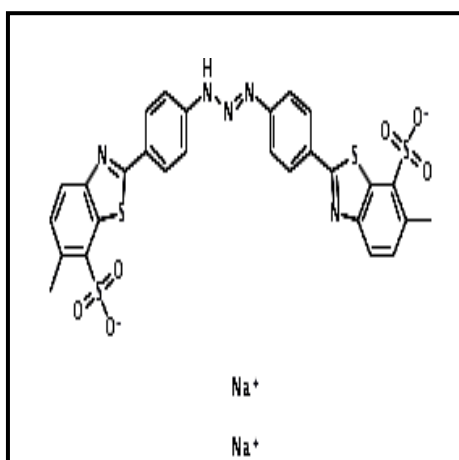
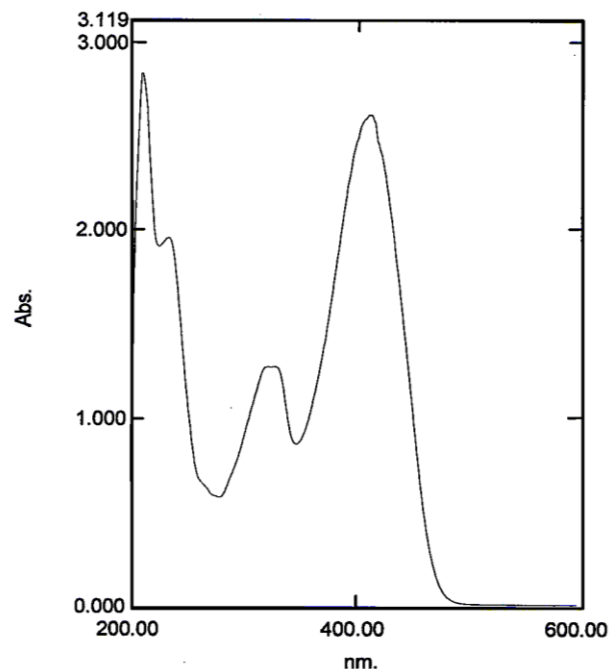


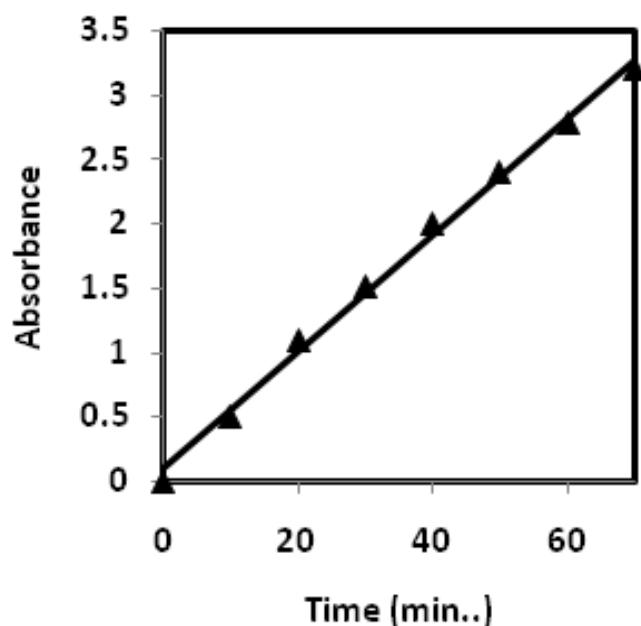
Fig. I: The structural formula of titan yellow GR.

The electronic spectrum of titan yellow GR that expressed by fig.2 showed three main peaks: 410 nm, 322nm and 232nm. The wave length at 410nm was selected to monitor the photodegradation of dye.



**Fig.2:** The electronic spectrum of titan yellow GR.

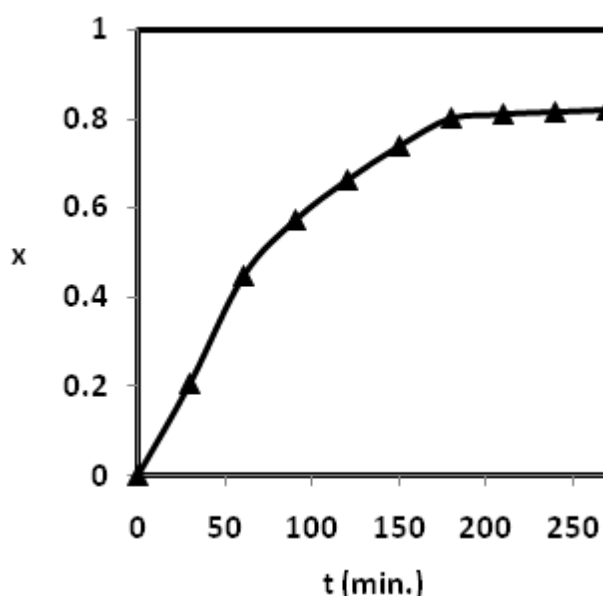
The calibration curve of dye was prepared by plot the values of absorbance at 410nm versus the values of concentration and linear relation was appeared which indicated agreement with the Lambert-Beer law (fig.3).



**Fig.3:** The calibration curve of titan yellow GR.

### 3.2 The effect of irradiation time

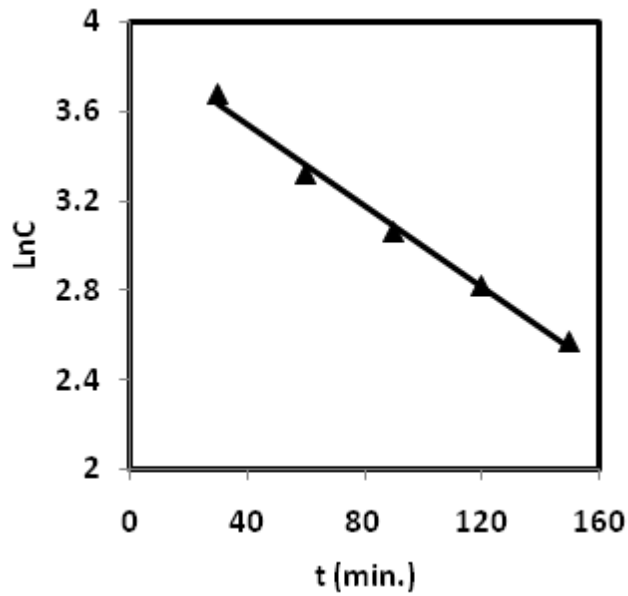
Fig.4 shows the effect of irradiation time on dye removal efficiency. It can be seen that the conversion fraction of the dye increases when the irradiation time increases and after 180 min. the conversion fraction remains constant. This is because of increasing the excited ZnO particles with time and therefore increasing the number of produced  $\cdot\text{OH}$  radicals and positive holes<sup>(25)</sup>.



**Fig.4:** The effect of irradiation time on the removal efficiency of dye. [dye]=50ppm, [ZnO]=0.25g/50ml, PH=7, temp. =20C°.

### 3.3 The determination of reaction order.

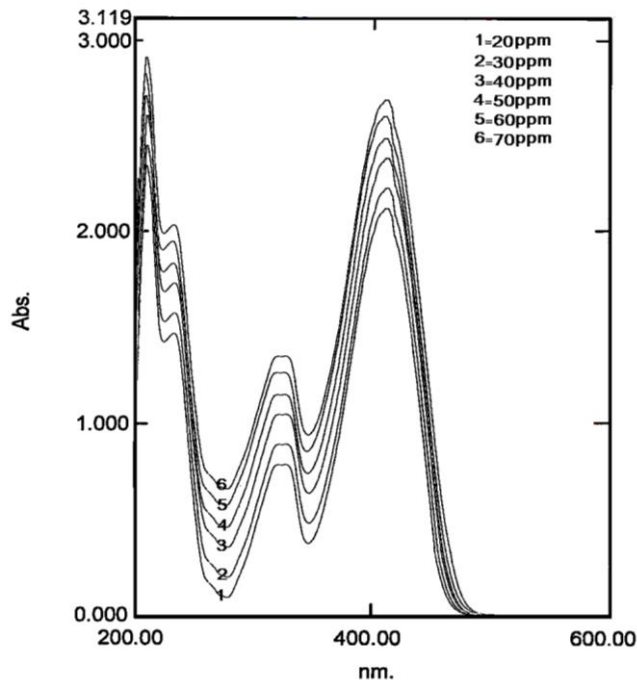
Using the data, which have been reported in section 3.2, it can be seen that the plot of  $\ln C$  vs. irradiation time (min.) was linear (30-150 min) and therefore the reaction belonged to first order rate system (fig. 5) and  $k$  value was calculated equal to  $9 \times 10^{-3} \text{ min.}^{-1}$ .



**Fig.5:** Plot of first order reaction of the dye.

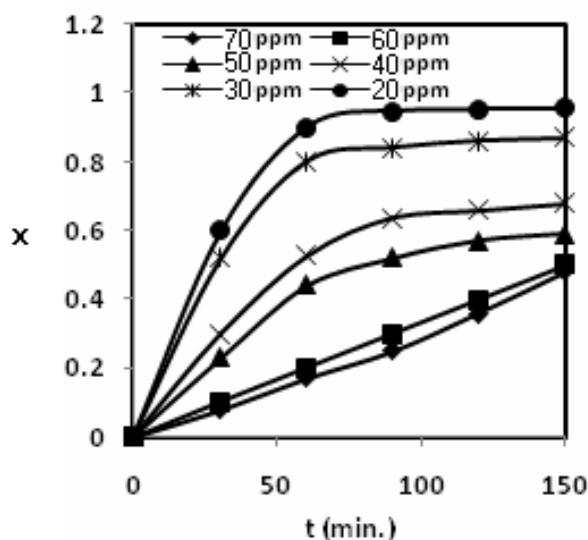
### 3.4 .The effect of dye concentration.

The pollutant concentration is a very important parameter in wastewater treatment .The effect of various initial dye concentrations on the photo degradation has been investigated from 20 to 70 ppm as illustrated by electronic spectra (fig. 6).



**Fig.6:** The electronic spectra of dye at different concentrations. [ZnO]=0.25g/50mL, pH=7, temp.=20C°, time=/50min.

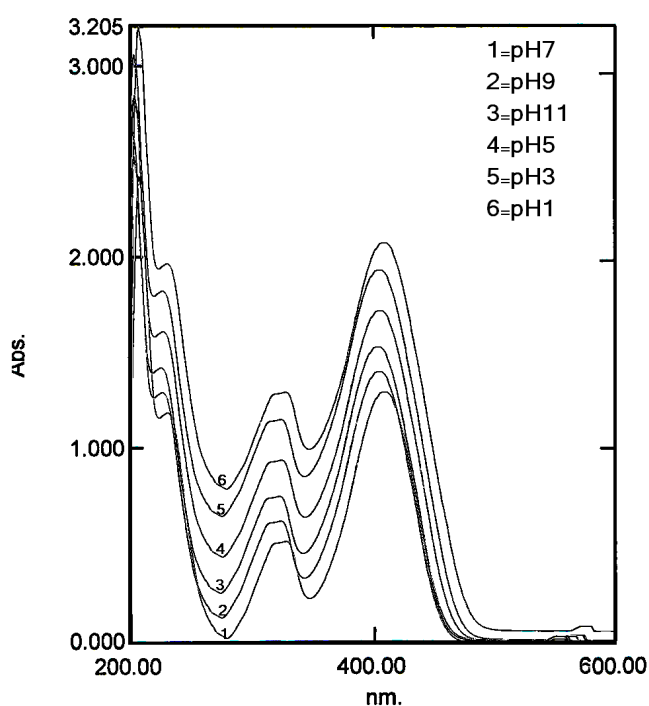
It is found from the results in fig .7 that the increase in the dye concentration from 20 to 70 ppm decreases the removal efficiency of dye .When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of ZnO. The increasing in dye concentration also decreases the path length of photo entering the dye solution. At high dye concentration a significant amount of solar light may be absorbed by dye molecules rather than the catalyst and this may also reduce the catalytic efficiency <sup>(26)</sup>.



**Fig.7:** The effect of dye concentration on its removal efficiency.  
 [ZnO]=0.25g/50mL,pH=7,temp.=20C°,time=150min.

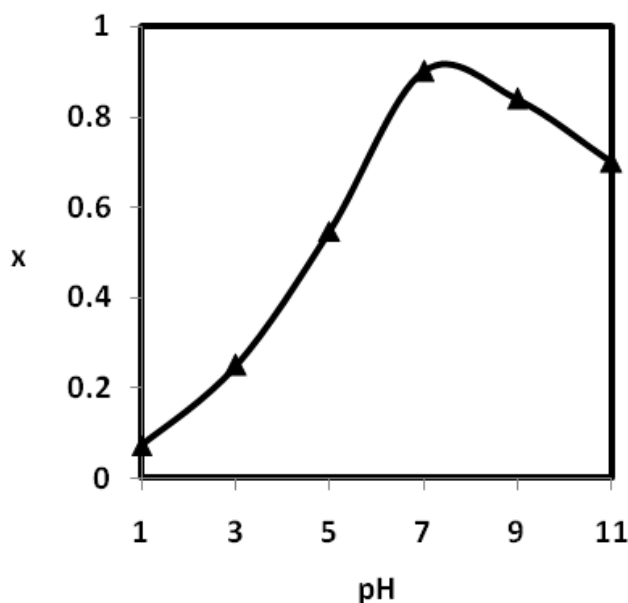
### 3.5. The effect of pH.

Fig .8 shows the electronic spectra of dye at different pH values.



**Fig.8:** The electronic spectra of dye at different pH.[dye]=20ppm,[ZnO]=0.25g/50mL,temp.=20C°,time=150min.

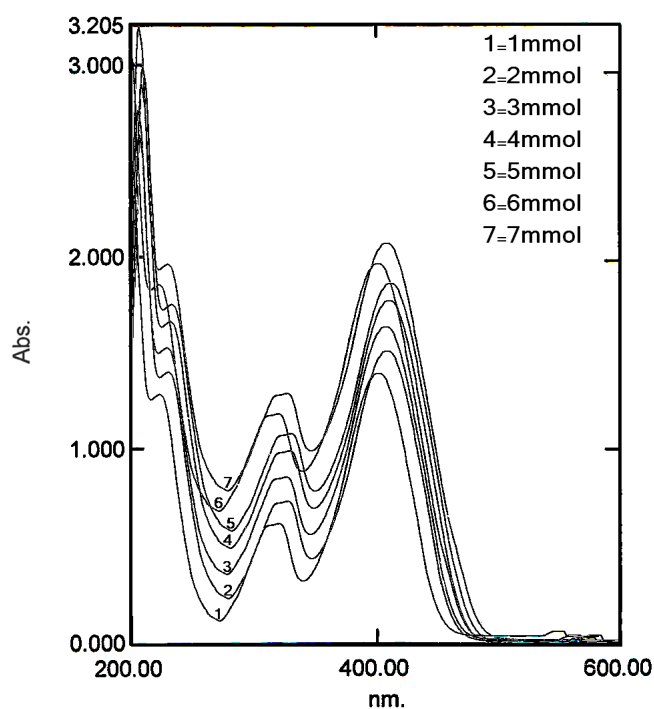
It can be seen from fig.9 that the removal efficiency was maximum at neutral pH. At acidic pH values, ZnO is dissolved as  $Zn^{+2}$  and has not any photocatalytic properties, at basic pH values, ZnO particles have negative surface charge and repulse dye anion molecules. Negative charges on dye molecules ordinate from  $SO_3$  group substituted on aromatic ring <sup>(25)</sup>.



**Fig.9:** The effect of pH on the dye removal efficiency. [dye]=20ppm, [ZnO]=0.25g/50mL, temp.=20C°, time=150min.

### 3.6. The effect of ethanol concentration.

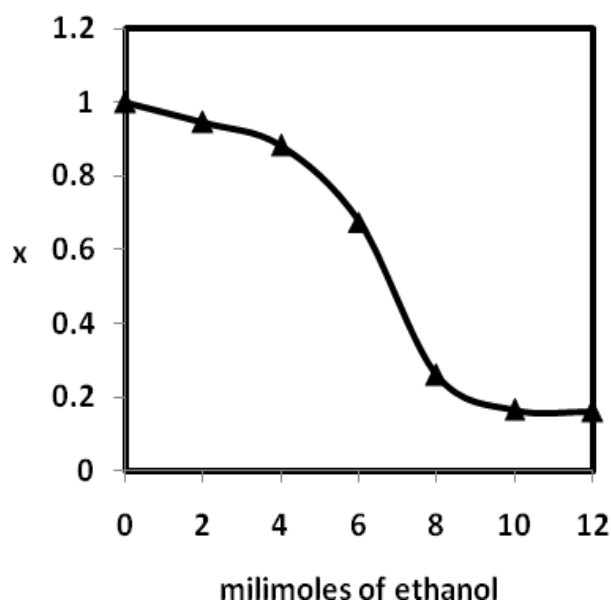
The electronic spectra of dye at different ethanol concentration are illustrated in fig.10.



**Fig.10:** The electronic spectra of dye at different ethanol concentrations. [dye]=20ppm, [ZnO]=0.25g/50mL, pH=7, temp.=20C°, time=150min.



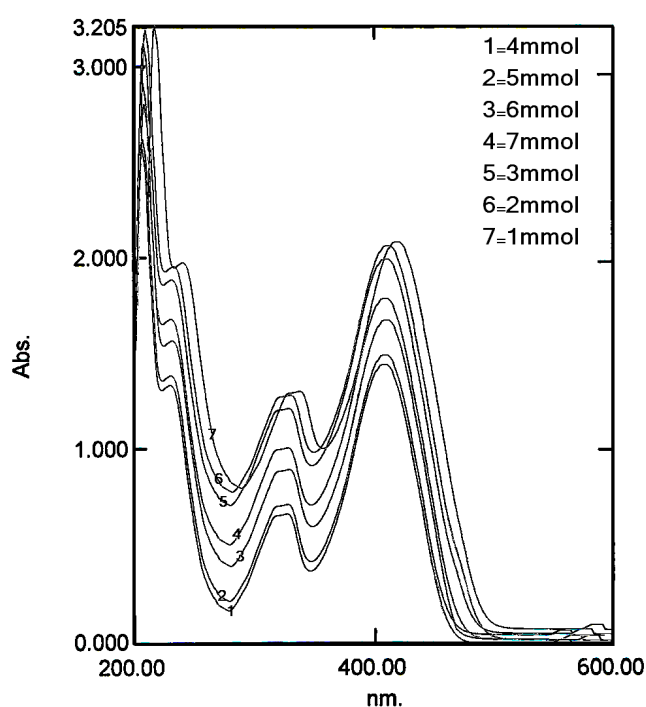
Fig.11 shows inhibitory effect of ethanol on dye removal efficiency .It can be seen that increasing ethanol concentration decreased the efficiency of dye removal, because ethanol quenches OH radicals <sup>(27)</sup>.



**Fig.11:** The effect of ethanol concentration on the dye removal efficiency. [dye]=20ppm, [ZnO] =0.25g/50mL, pH=7, temp. =20C°, time=150min.

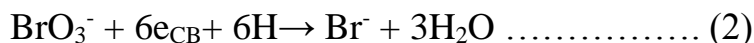
### 3.7. The effect of bromate anion concentration.

KBrO<sub>3</sub> is an efficient electronic acceptor and used as an additive to enhance photocatalytic degradation rate .Fig 12 shows the electronic spectra of dye at different bromate anion concentration.

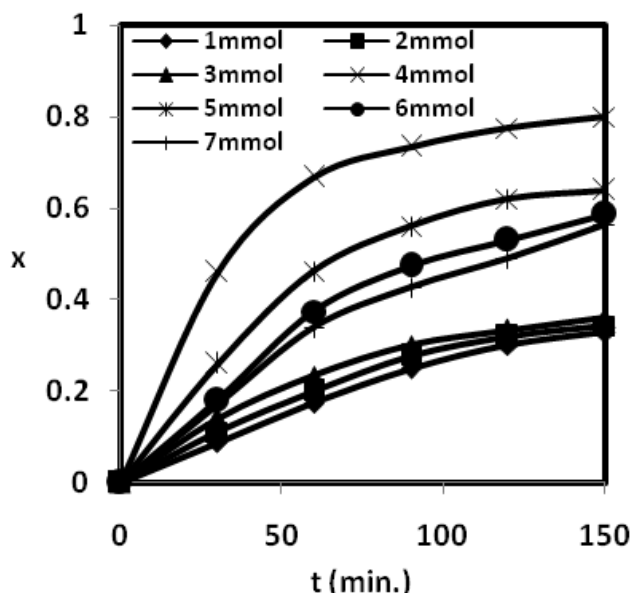


**Fig.12:** The electronic spectra of dye at different bromate anion concentrations .[dye]=20ppm,[ZnO]=0.25g/50mL,temp.=20C°,time=150min.

From fig .13 it can be seen that the addition of  $\text{KBrO}_3$  from 1 to 4 mmoles increase the removal efficiency of dye .The enhancement of the removal rate is due to the reaction between  $\text{BrO}_3^-$  anion and conduction band electron (eq.2) which reduces the recombination of electron-hole.



The further increase of  $\text{KBrO}_3$  from 4 to 7 mmoles, decrease the removal efficiency of dye. This is due to adsorption effect of  $\text{Br}^-$  ion on  $\text{ZnO}$  surface which affects the catalytic activity of  $\text{ZnO}$  <sup>(28)</sup>.



**Fig.13:** The effect of bromate anion concentration on the dye removal efficiency  
 .[dye]=20ppm,[ZnO]=0.25g/50mL,temp.=20C°,time=150min.

### 3.8. The adsorption studies.

In heterogeneous photocatalytic degradation process, the adsorption of dye onto the catalytic surface is the primary step of the reaction .The adsorptions experiments were carried by using Langmuir and Freundlich isotherms <sup>(29)</sup> as illustrated in fig. 14 and fig .15 respectively .Langmuir isotherm was done by using eq.3:

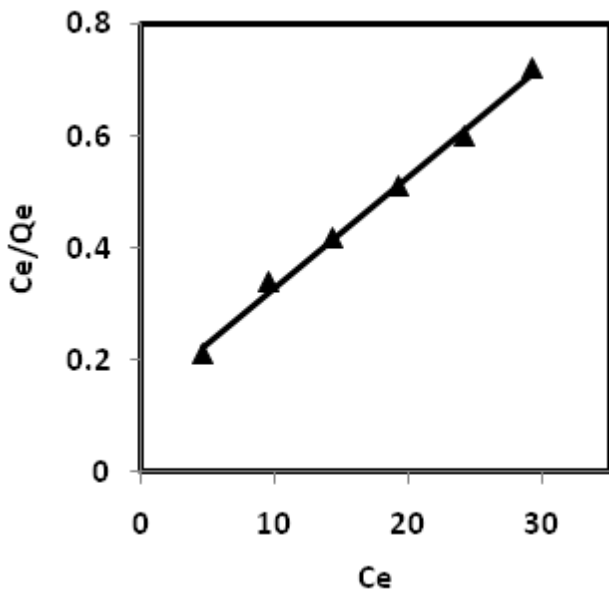
$$C_e/Q_e = 1/Q_m b + C_e/Q_m \dots\dots\dots (3)$$

Where  $Q_e$  is the amount of dye adsorbed (mg/L)  $Q_m$  is the amount adsorbed at equilibrium (mg /g), and  $b$  and  $Q_m$  are Langmuir constants

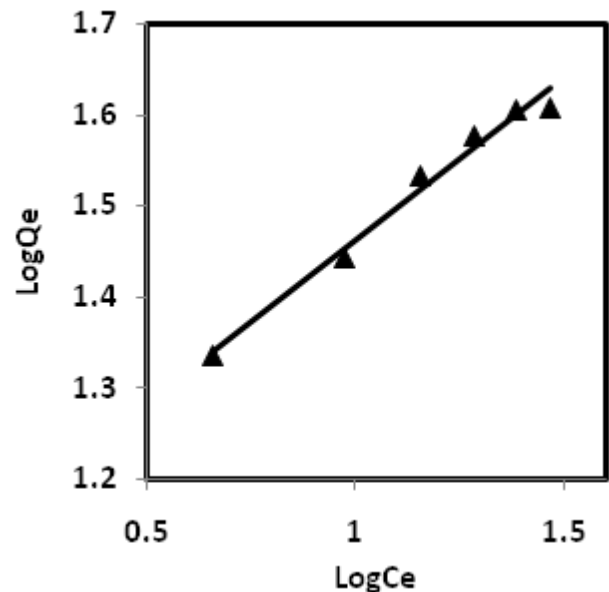
related to adsorption efficiency and energy of adsorption respectively .While freundlich isotherm was done by using eq.4:

$$\log Q_e = \log k_f + 1/n \log C_e \dots\dots\dots (4)$$

Where  $Q_e$  is the amount of dye adsorbed (mg /g),  $C_e$  is the equilibrium concentration of dye in solution (mg/L), and  $k_f$  and  $n$  are constants related to adsorption capacity and intensity of adsorption respectively.



**Fig.14:** Plot of Langmuir isotherm of the dye adsorption on ZnO surface.



**Fig.15:** Plot of Freundlich isotherm of the dye adsorption on ZnO surface.

The Langmuir and Freundlich constants are illustrated in table 1. From the results, it can be seen that the adsorption of dye onto ZnO surface was fitted with Langmuir isotherm. This means the adsorption was chemisorptions.

**Table 1:** The Langmuir and Freundlich constants.

Langmuir	$Q_m$	$b$	$R^2$
	52.632	0.143	0.995
Freundlich	$k_f$	$n$	$R^2$
	12.618	2.786	0.983

#### 4- Conclusions.

The photodegradation experiment showed that the dye removal efficiency increased with increasing irradiation time. The kinetics of photodegradation reaction expressed the pseudo first order reaction. The increasing of both dye and ethanol concentrations decreased dye removal efficiency. The maximum efficiency of dye removal was at neutral pH (pH =7). The concentration of bromate anion from 1 to 4 mmoles increased the photodegradation reaction, while the further increasing of bromate anion above 4 mmoles decreased the efficiency of reaction. Also the adsorption studies showed the appearance of adsorption isotherm with Langmuir model.

#### References

1. M. Dakiky and I. Nemcova, *J.Dyes Pigments*, 2000, **44**, 181.
2. M.A. Brown and S.C. De Vito, *J. Environ. Technol.*, 1993, **23** 249.
3. A.O. Ibadon, G.M. Greenway and Y. Yue, *J. Catal Commun.*, 2008, **9**, 153.
4. N. Sobana, M. Muruganadham and M. Swaminathan, *J. Mol. Catal. A: Chem.*, 2006, **258**, 124.
5. E. Bizani, K. Fytianos, I. Poulios and V. Tsiridis, *J. Hazard. Mater.*, 2006, **136**, 85.
6. C. Sahoo and A.K. Gupta, *J. Desalination*, 2005, **181**, 91.
7. S. Songa, L. Xua, Z. He, H. Ying, J. Chen, X. Xiao and B. Yan, *J. Hazard. Mater.*, 2008, **152**, 1301.
8. S. Chakrabarti and B.K. Dutta, *J. Hazard. Mater. B*, 2004, **112**, 269.
9. J. N. Daneshvar, D. Salari and A.R. Khataee, *J. Photochem. Photobio. A Chem.*, 2004, **162**, 317.
10. S.K. Kansal, A.H. Ali and S. Kapoor, *J. Desalination*, 2010, **259**, 147.
11. S.K. Pardeshi and A.B. Patil, *J. Sol. Energy*, 2008, **82**, 700.

12. M. El-Kemary, H. El-Shamy and I. El-Mehasseb, *J. Lumin.*, 2010, **130**, 2327.
13. M. Neamtu, A. Yediler, I. Siminiceanu, M. Macoveanu and A. Kettrup, *J.Dyes Pigments*, 2004, **60**, 61.
14. A. Rathi, H.K. Rajor and R.K. Sharma, *J. Hazard. Mater.*, 2003, **102**, 231.
15. PR. Gogate and AB. Pandit, *J.Advances in Environ. Res.*, 2004, **8**, 501.
16. PR. Gogate and AB. Pandit, *J. Advances in Environ. Res.*, 2004, **8** , 553.
17. H.S. El-Desoky, M.M. Ghoneim, R. El- Sheikh and N.M. Zidan, *J. Hazard. Mater.*, 2010, **175** ,858.
18. Y.H. Huang, H.T. SU and L.W. Lin, *J. Environ. Sci.*, 2009, **21**, 35.
19. A. Serra, X. Domenech, C. Arias, E. Brillas and J. Peral, *J. Appl. Catal. B: Environ.*, 2009, **89**. 12.
20. K.Wu. Y. Xie, J. Zhao and H.Hidaka, *J. Mol. Catal. A. : Chem.*,1999, **144** , 77.
21. N.Daneshvar, D. Salari and AR. Khataee, *J. Photochem. Photobiol. A: Chem.*, 2003, **157**, 111.
22. R.K. Wahi, W.W. Yu, Y. Liu, M.L. Mejia, J.C. Falkner, W. Nolte and V.L. Colvin, *J. Mol. Cata. A Chem.*, 2005, **242**, 48.
23. W.Z. Tang and H. An, *J. Chemosphere*, 1995,**31**, 4157.
24. C. Ahmed, M.G. Rasul, R. Brown and M.A. Hashib, *J. Environ. Managem.*, 2011,**92**, 311.
25. N.Daneshvar, D.Salari and A.R.Khataee, *J. Photochem. Photobiol. A: Chem.*,, 2004,**162**,317.
- 26.C.Minero, E.Pelizzeti, S.Malato and J. Blanco, *J. Chemosphere*, 1993, **26**,2103.

27.N. Daneshvars,S. Aber and, F. Hosseinzadeh, *J. Global Nest*, 2008, **10**, 16.

28.M.Murugandham and M. Swaminathan, *J. Solar Energy and Solar Cells*, 2004, **81**, 439.

29.D. G. Krishna and G. Bhattacharyya, *J. Appl Clay Sci*, 2002, **20**, 295.