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Photocatalytic Cracking of P-nitro aniline using coupled ZnO – Sb_2O_3

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ABSTRACT

The research work consist of two main parts , the first part includes the preparation of coupled metal oxide(ZnO – Sb_2O_3) , which is done by mixing 1 g of ZnO with 1g of $Sb_20_3$and calcinig in oven at 900Cº for five hours. The mixing of semiconductor products was studied by using X-ray diffraction and Infra-red spectrophotometer techniques. The second part includes the study of photo degradation of P-nitro aniline using coupled metal oxides ZnO – Sb_2O_3 (first part) , which is achieved by the irradiation of suspended solution consists of different weights of P-nitro aniline dissolved in 100cm^3 of distilled water with 0.13 g of coupled metal oxide ZnO – Sb_2O_3 by mercury lamp(125 W) from external source inside a Pyrex photoreaction cell of 100 cm^3 at 298 K . In order to study the effect of coupled metal oxide ZnO – Sb_2O_3 in photo degradation of p-nitro aniline, several experiments were carried out in various conditions to attain the best degradation. These experiments include the effect of hydrogen per oxide, the effect of temperature. The product was studied by using UV-Visible spectrophotometer.

Keywords: P-nitro aniline, Photocatalytic Degradation, Aromatic compound, cracking.

INTRODUCTION

Large number of researches were carried out work on photo catalytic (degradation, oxidation, hydrolysis, cleavage of water, production of amino acid) using different semiconductor oxides with direct excitation by Ultra-Violet irradiation sources. When pure and metalized semiconducting oxide subjected to thermal or photon with energy equal to or greater than the band gap of the oxide, then the electrons are promoted from valence band to conduction band. The photoelectrons and photo holes produced by this process migrate to the surface and interact with adsorbed species [1,2] as in figure (1) .

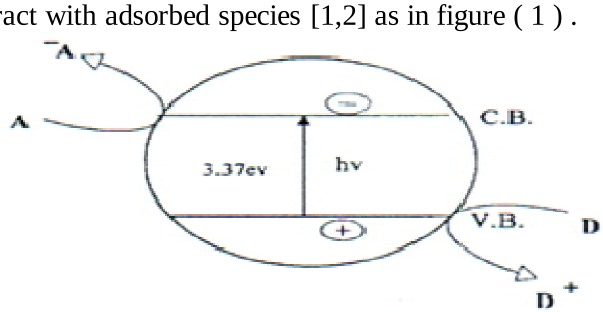


Fig. 1 Direct excitation of Semiconductor oxide

Modification of surface of semiconductor (sensitization) by using dyes such as (Crystal violet , Roadmen , Methyl red , …) , or by coupling with semiconductor have band gap less than the other semiconductor such as TiO_2 – CdS .Many researchers using the coupled semiconductors to photo catalytic degradation of particle systems such as TiO_2 – SnO_2 [3] , TiO_2 –MoO_3 [4] .An ideal photo catalyst should be stable, inexpensive, non-toxic and, highly photoactive . For increasing the efficiency of a photo catalytic process we used coupled ZnO-Sb_2O_3 due to increasing the charge separation and extending the energy range of photo excitation up to visible light region for the system. Recently many researchers [5, 6] were succeeded to improve the photo electrochemical processes using two or more semiconductors oxides owing large band gap . One of the semiconductor absorbed suitable light quail or greater than band gap of semiconductor and promoted to excited state which leads to inject an photoelectrons into the conduction band of the other semiconductor oxide [7,8].The activities of such type of semiconductors (mix semiconductors) shown in the degradation of azo aye by using coupled SnO_2 - TiO_2 [9] as in fig.2.

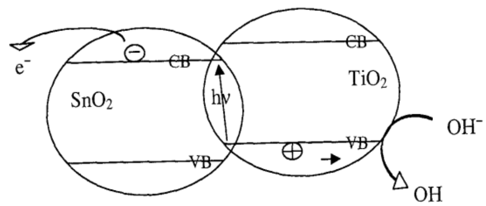


Fig.2: Charge separation in coupled semiconductors

MATERIALS AND METHODS

A-Chemicals:

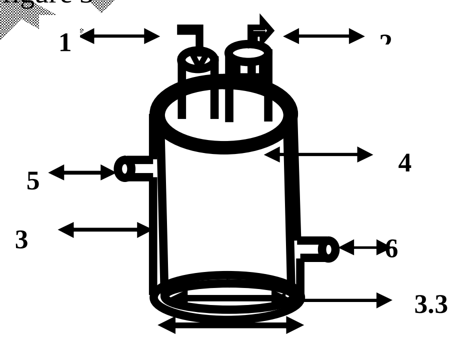
1. Zinc oxide (ZnO) : The bang gap is 3.4 ev [10] , purity - 99% , particle size- 100 mesh, supplied by Fluka AG. 2. Antimony tri oxide (Sb_2O_3) : The band gap is 3.74ev [11] ,purity- 98% , supplied by Fluka AG. 3 . P- nitro aniline, supplied by Fluka A.G.

B- Preparation of Coupled semiconductor (ZnO – Sb_20_3)

The coupled semiconductor ZnO- Sb_2O_3 was prepared by using 99.9% pure ZnO and 98% pure Sb_2O_3 powders as the starting materials . The starting material was mixed by mortar for one hour, after that calcinate the mixture in an oven at 900C° for five hours.

C - Photo reactor and Procedure

Experiments were carried out in glass photochemical reactor. The cylindrical annular – type reactor consisted of two parts. The first part was an outside thimble; Running water was passed through the thimble to cool the reaction solution. Owing to the continues cooling, the temperature of the reaction solution was maintained of room temperature. The second part was an inside thimble and the reaction solution (volume 100 ml) was put in the reaction chamber [12]. Schematic diagram of photochemical reaction is shown in figure 3



1- **Air inlet**
2- Air outlet and sampling
3-Cooling Chamber
4- Reaction Chamber
5- Water inlet
6- Water outlet

Fig 3 : Main parts of the photocatalytic cell used in photo degradation of p-nitro aniline.

D- Irradiation System:
A block diagram of photolysis apparatus is shown in figure (4) a 125 W mercury lamp source is a focusing fitted with a focusing lens to ensure parallel beam of light [13].

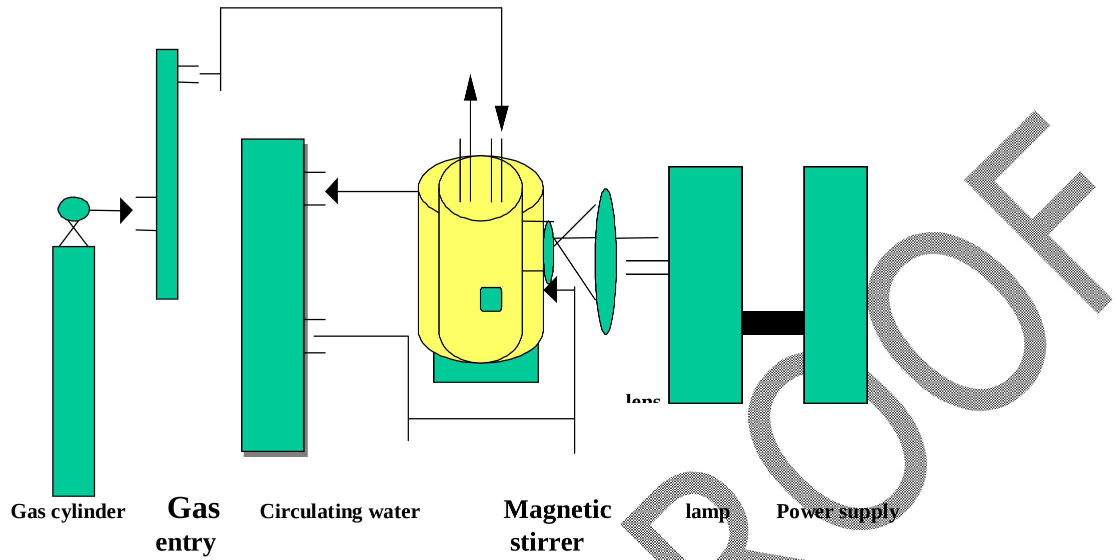


Fig 4: Schematic diagram of the experimental apparatus.

RESULTS AND DISCUSSION

Structural Characterization: The naked ZnO , Sb_2O_3 and prepared coupled semiconductor ZnO- Sb_2O_3 were characterized .

A- XRD Spectrum:
In this technique XRD diffraction, we had studied the effect of mixing of semiconductor ZnO- Sb_2O_3 at temperature 900Cº.

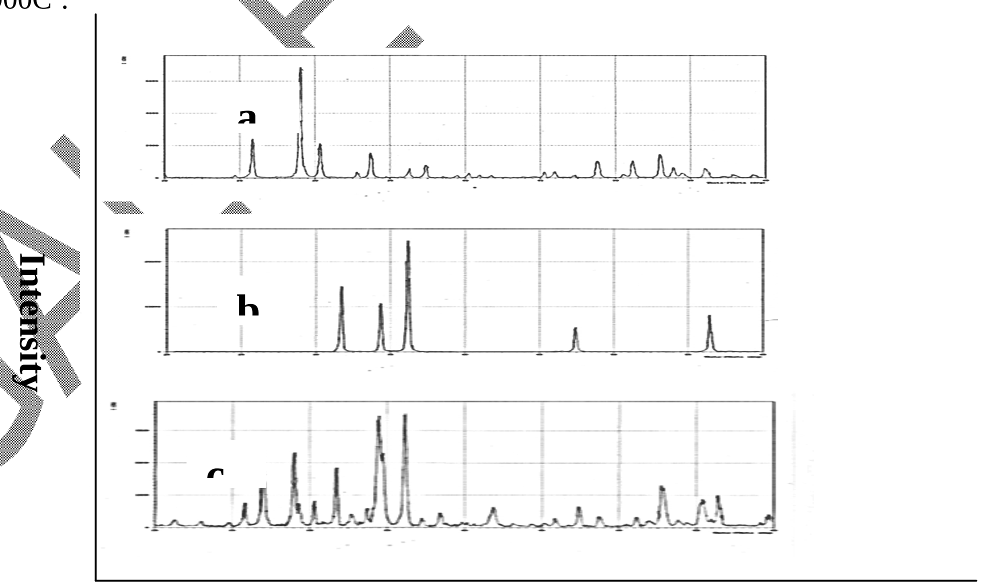


Fig.5: XRD diffraction spectrum of

a- Zinc oxide b- Antimony tri oxide c- Coupled ZnO - Sb_2O_3

From fig. 5- a , different peaks (2θ) appear in spectrum at 26 , 29 , 30.5, 33.5, 36.5, 37.5, 49, 51,54, 55, 56 and 59 represent naked antimony tri oxide . From fig. 5 - b, the peaks (2θ) appear in spectrum at 31.5, 34.5, 36 , 47.5 and 56.5 represent naked zinc oxide . From fig. 5 - c , many peaks (2θ) appear in spectrum at 21.5, 23, 24.5, 26 , 27, 29, 29.5, 30.5, 31.5, 32.5, 34, 34.5, 36, 37.5, 38.5, 42, 46, 47.5, 49, 51, 52, 53, 54, 55, 56.5 and 59.5 represent the coupled zinc oxide and antimony tri oxide. The coupled semiconductor ZnO- Sb_2O_3 give new spectrum which indicates a shift in 2θ and reduce its intensity .Also the coupled semiconductor gives new peaks (2θ) in the spectrum which cannot exist in the original spectrum .This may be due to the distortion of the two crystal lattices of ZnO and Sb_2O_3.

B- F.T.IR Spectrum:

Figure 6-a show F.T. IR spectra of naked antimony tri oxide .The peaks are at 754.19, 646.17, 601.81, 519.75, 472.58 and 437.86. Figure 6 - b show F.T. IR spectra of naked zinc oxide. The peaks are at 488.01 and 445.57. For coupled semiconductor, ZnO- Sb_2O_3, figure 6 - c show the peaks at 746.48, 669.32, 636.53, 590.24, 489.94 and 435.93 . From this we can see the shift in peaks and reduction in intensity. This means that the coupling occurs between two semiconductors.

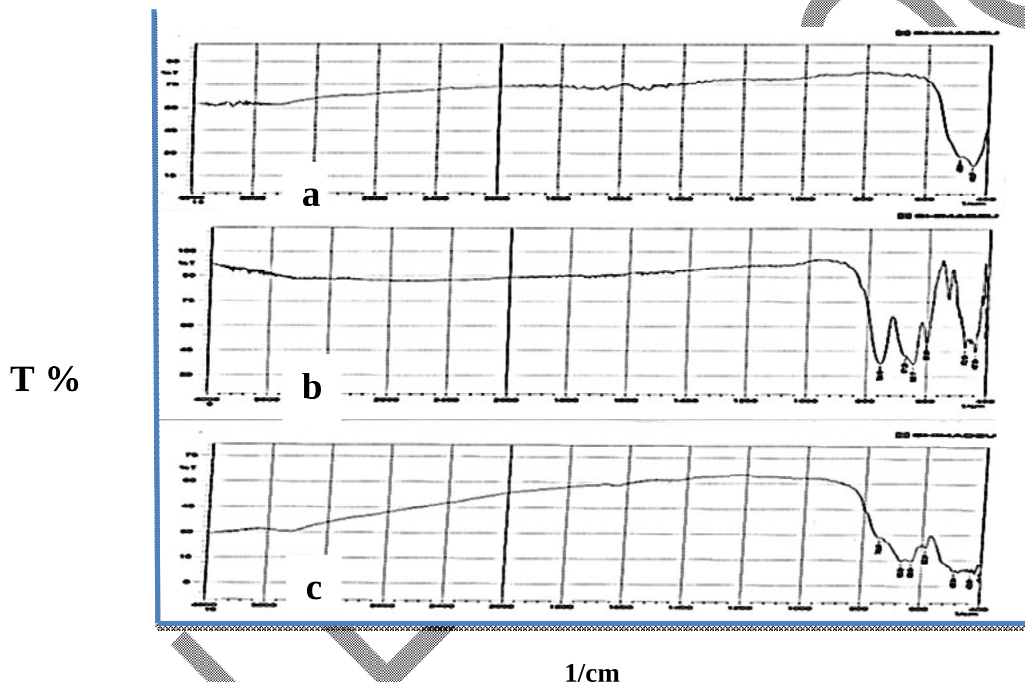


Fig. 6: F.T.IR Spectrum for:
a- Antimony tri oxide b- Zinc oxide c- Coupled ZnO - Sb_2O_3

C – UV-visible Spectrophotometer Analysis:

A series of experiments performed to study the effect of time on exposure in photocatalytic degradation of p- nitro aniline 5ppm, by using 0.13g $100mL^{-1}$ of coupled semiconductor, ZnO -Sb_2O_3 and mercury lamp (125W),at 25C°,with air flow=10mL min^{-1}. As indicate in the figure 7, the degradation of p- nitro aniline increase when the time of exposure increase.

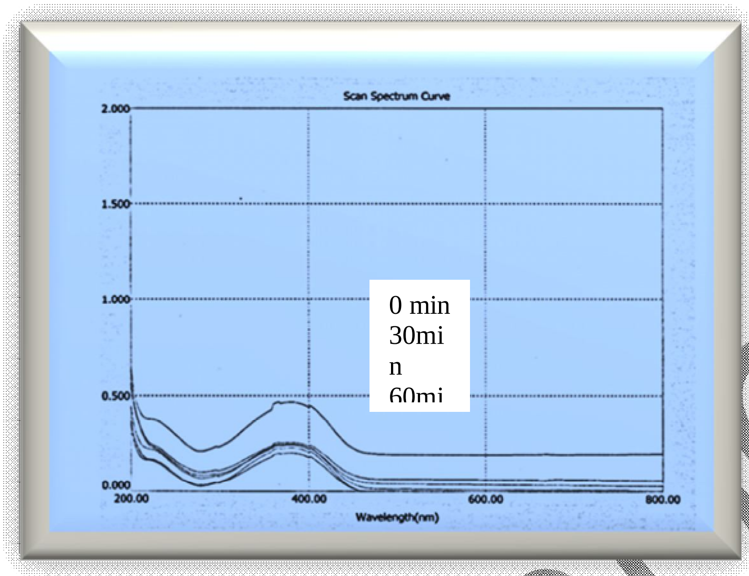


Fig. 7 : uv-visible Spectrum of photocatalytic degradation of p-nitro aniline

2 - The effect of H_2O_2 on photocatalytic degradation of p-nitro aniline:

Investigation of photocatalytic degradation of this compound performed by using optimum conditions of coupled $ZnO-Sb_2O_3$. Mass is 0.13g $100mL^{-1}$, P-nitro aniline is 5ppm. Irradiation of the suspension solution is with mercury lamp (125W). The air flow is 10mL min^{-1}, at25C□.

The amounts of hydrogen per oxide added to 100ml of suspension solution of p-nitro aniline are 0.003, 0.005, 0.01, 0.03, 0.0 5 mmoles. Hydrogen peroxide prevent the recombination processes between (h+) in the valance band and (e-) in the conduction band [14].

Table 1. The change of A/A0 with irradiation time on different mmoles of H_2O_2 using coupled $ZnO – Sb_2O_3$.

H_2O_2 add mmole	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**
Irradiation Time/min	**A /A0**				
0	1	1	1	1	1
10	0.711	0.658	0.459	0.772	0.883
20	0.613	0.511	0.254	0.691	0.799
30	0.447	0.338	0.119	0.563	0.784
40	0.337	0.188	0.081	0.447	0.732
50	0.289	0.146	0.079	0.431	0.711

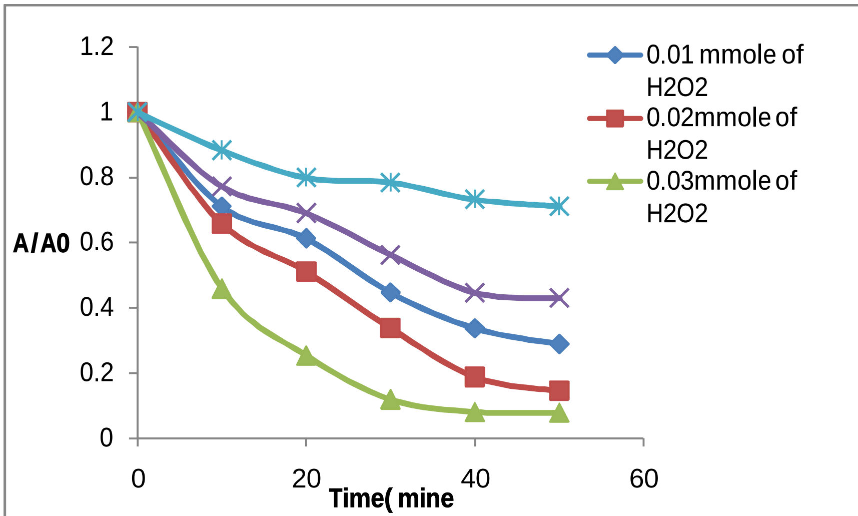


Fig. 8: The effect H_2O_2 on photoactalytic degradation of the p-nitro aniline using Coupled ZnO – Sb_2O_3.

From the table 1 and figure 8 it is clear that photocatalytic degradation processes of p – nitro aniline increase with increase in the amount of hydrogen per oxide added to the suspension solution of p-nitro aniline due to the formation of hydroxyl radicals until it reached optimum value of hydrogen per oxide i.e., 0.03 mmole. After this value of H_2O_2 the degradation process decrease because of the presence of access amount of H_2O_2, which leads to produce another species of hydroxyl radicals (•O_2H) .This radical is weaker than hydroxyl radical so that the degradation process decrease [15].

H_2O_2 + •OH → •O_2H + H_2O

3 - Effect of Temperature:

A series of experiments were carried out to study the effect of temperature on the photo catalytic degradation rate of p- nitro aniline in aqueous coupled ZnO –Sb_2O_3 suspension at different temperature ranging from 278.15 – 293.15 K[16,17]. Table 2 shows the effect of temperature on the photo catalytic degradation rate of p- nitro aniline at fixed initial concentration of p- nitro aniline and 0.13 g 100mL^{-1} of coupled ZnO –Sb_2O_3 as catalyst . From the fig. 9, it is clear that the photo catalytic degradation rate of p-nitro aniline increases with increase of temperature.

Table 2. The change of A/A0 with irradiation time at different temperatures using coupled ZnO –Sb_2O_3.

Temperature K	**278.15**	**283.15**	**288.15**	**293.15**
Irradiation time/min	**A/A0**			
0	**1**	**1**	**1**	**1**
10	**0.51**	**0.391**	**0.326**	**0.281**
20	**0.352**	**0.242**	**0.206**	**0.13**
30	**0.194**	**0.122**	**0.086**	**0.043**
40	**0.101**	**0.071**	**0.033**	**0.019**
50	**0.063**	**0.031**	**0.015**	**0.008**
60	**0.038**	**0.019**	**0.007**	**0.002**

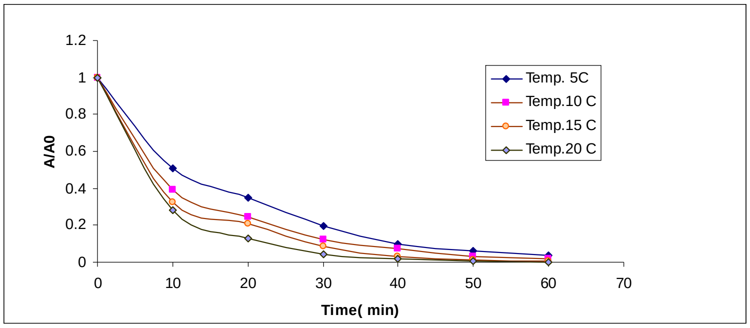


Fig. 9: Effect of temperature on photocatalytic degradation of p-nitro aniline by using coupled ZnO $-Sb_2O_3$.

Table 3. The change of $\ln A_0/A$ with irradiation time at different temperatures.

Temperature K	**278.15**	**283.15**	**288.15**	**293.15**
Irradiation time/min	**ln A0/ A**			
0	**0**	**0**	**0**	**0**
10	**0.673**	**0.94**	**1.12**	**1.27**
20	**1.045**	**1.42**	**1.58**	**2.04**
30	**1.64**	**2.1**	**2.45**	**3.14**
40	**2.29**	**2.64**	**3.4**	**3.98**
50	**2.77**	**3.46**	**4.2**	**4.8**
60	**3.28**	**3.97**	**4.91**	**5.82**

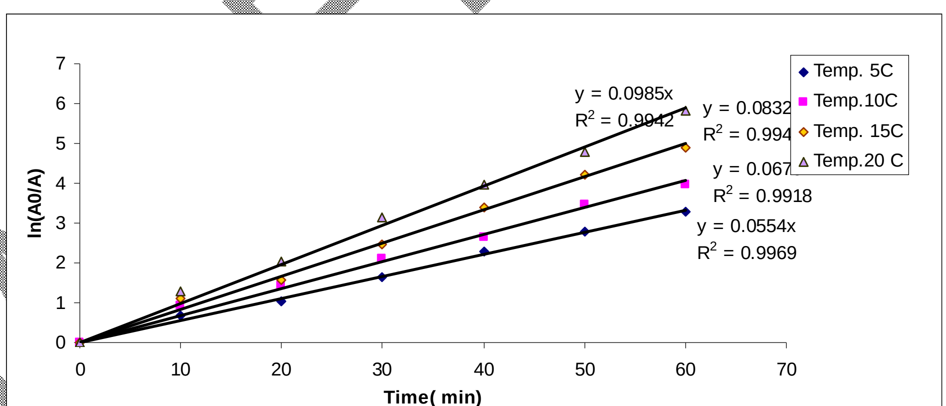


Fig. 10 : Effect of temperature on photocatalytic degradation of p-nitro aniline by using coupled ZnO $-Sb_2O_3$.

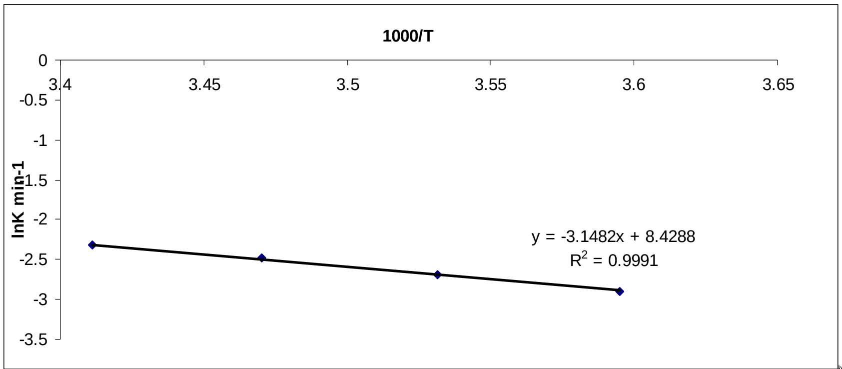


Fig. 11: lnK min^{-1} against 1000/T

From the fig. 11 we can calculate the activation energy of the reaction E_a, when plotted (1/ TK) against($lnKmin^{-1}$) (Arrhenius relationship).The activation energy for photo catalytic degradation rate of p- nitro aniline is equal to 26 $kJ.mol^{-1}$.

CONCLUSIONS

1. The Compound has not been degraded in the absence of catalyst.
2. The compound has been successfully degraded when used the catalyst with the light.
3. The optimum condition for the photocatalytic degradation of p-nitro aniline is 0.13 g 100mL-1 mass of ZnO - Sb_2O_3 and 5ppm concentration of p-nitro aniline
4. The activation energy =26KJ/mole.

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REFERENCES

[1] I.Izuml, F.F.Fan and A.J.Bard, *J.Phys.Chem.*, **1981**,85,218.
[2] E.Evgenidou, K.Futianos and I.Poulios, International Conference of environmental Science and Technology, LemnosIsland, Greece, 8 -10, 2003.
[3] X.Z., Li. F.B., Yang.C.L., Ge.W, K.,*J.Photochem . Photobiol. A: Chem.* **2001**, 209. 141
[4] K.Y.Song,K.M. Park,Y.T. Kwon ,H.W.Lee., ,W.J.Chung. , I.W.Lee., *Chem.Mater*, **2001**, 13, 2349.
[5] S.H.Leong, B.N.Park, S.B.Lee and J.H.Boo, *Surface and Coatings Technology*, **2005**,193, 340.
[6] C.Nasr,S.Hotchandani andP.V.Kamat,*J.Am.Chem.Soc.*,**1995**, 98, 9137.
[7] H.M.Sung-sub,J.R.Choi,H.J.Hah,S.M.Koo and Y.C.Bae,*J.of photo Chemistry and photobiology A: Chemistry* ,**2004**,163,37.
[8] C.Tang and V.Chen, *Water Research*, **2004**, 38, 2775.
[9] N.Y.Fairooz "Doctor of philosophy in Chemistry"Thesis, College of Science Babylon Universty, **2005**.
[10] M.S.Seyed-Dorrajl, N.Daneshva S.Aber, *Global Nest Journal*, **2009**, 11(4), 535-545.
[11] N.Tigau, *Rom.Journ*, **2006**, 51,641-647.
[12] S.F.Chen, M.Y.Zhao,Y.W.Tao, *Taiayangneng xuebao*, **1995**,16,234-239.
[13] F.G.Gassim, A.N.Alkhateeb, F.H.Hussein, *Desalination*, **2007**, 209,342-349.
[14] S.A.Abo-*Farah, researcher*, **2010**, 2(7).

[15] B.Pare, P.Singhand S.B. Jonnalgadda, *Journal of Scientific &IndustrialResearch*, **2009**, 68,724 – 729.
[16] F.H.Hussein, *International Journal of Photoenergy*, **2012**.
[17] K.Byrappa, A.K.subramani,S.ananda, K.M.lokanatha ARI, R.Dinesh,and M.Yoshimura.*Bull.*,*Matter .Sci.*, **2006**,29, 433-438.