Photocatalytic degradation of n- Hexacosane Using coupled ZnO-Sb$_2$O$_3$ and tungsten lamp

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ABSTRACT

The photo degradation of n-hexacosane (n- C26H54) by coupled ZnO -Sb$_2$O$_3$ was investigated. The coupled ZnO- Sb$_2$O$_3$ was prepared by using pure solid materials of ZnO -Sb$_2$O$_3$(1: 1) then calcend in suitable furnace for five hours The photodegradation of n-hexacosane using coupled ZnO-Sb$_2$O$_3$, which is achieved by the irradiation of suspended solution consists of 1x10^{-4}Mn-hexacosane dissolved in 100 cm^3 of n-nonane with 0.1 g of coupled ZnO- Sb$_2$O$_3$ by using tungsten lamp from external source of a Pyrex photo reaction cell of 100 cm^3 at 298.15 K.. Several experiments were carried out at various conditions to reach the best degradation of n-hexacosane using coupled ZnO- Sb$_2$O$_3$. These experiments include the amount of n- hexacosane on fixed mass of ZnO-Sb$_2$O$_3$, the amount of coupled ZnO-Sb$_2$O$_3$, and the temperature effects .The main photolytic products of n-hexacosane photo degradation processes were heptane, octane, nonane, dodecane and tetradecane. Gas chromatographic using FID and IR, UV-Visible spectrophotometric techniques were used to identify the photocalalytic degradation products. Also the coupled ZnO - Sb$_2$O$_3$ studied by using X-Ray Diffraction spectrometric technique.

Keywords: Hexacosane, photocatalytic, Degradation, Hydrocarbons, Cracking**.**

INTRODUCTION

Hexacosane is a type of saturated hydrocarbon, consist of twenty six carbon atoms and fifty four hydrogen atoms. This compound consists of single bonds between adjacent carbon atoms. Hexacosane not very reactive white solid heavy alkane, with boiling point (412.2C°), melting point (56C°). Hexacosane compound undergo cracking and broking down into light hydrocarbons. In the past several years, the scientist study how could improve the activity of semiconductors. They used different ways for this paupers:

1. Modification of semiconductor by using metal such as (pt, Ag, Au, ….).
2. Coupled semiconductors such as (TiO2-SnO2).
3. 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 (TiO2-CdS).

Many researchers using the coupled semiconductors to photocatalytic degradation of particles systems such as TiO_2-SnO_2 [1], TiO_2 –MoO_3 [2].

An ideal photo catalyst should be stable, inexpensive, non-toxic and, highly photoactive. For increasing the efficiency of a photo catalytic process could use 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 [3, 4] were succeeded to improve the photo electrochemical processes using two or mosemiconductors 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 [5, 6] .

The activities of such type of semiconductors (mix semiconductors) shown in the degradation of azo aye by using coupled SnO_2 -TiO_2 [7] (figure1).
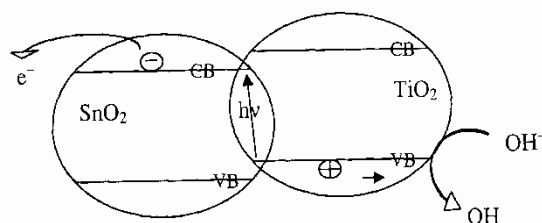
Fig.1: Charge separation in coupled semiconductors

The aim of present work: To extend the range of photo catalysis longer wavelength 400-700 nm by coupling zinc oxide with antimony tri oxide.

MATERIALS AND METHODS

Chemicals :Zinc oxide (ZnO) : The band gap of zinc oxide (3.4 ev) [8] , purity (99%) , particle size 100 mesh, supplied by Fluka AG.2.Antimony tri oxide (Sb_2O_3) : The band gap of antimony trioxide (3.74ev) [9] ,purity (98%) ,supplied by Fluka AG.3- Normal Hexacosane with melting point 56.4C° was supplied by Merck .

Preparation of Coupled semiconductor ZnO- Sb_2O_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 were mixed by mortar for one hour, after that calcinate the mixture in oven (900C°) for five hours.

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 cation 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 [10] . Schematic diagram of photochemical reaction is shown in figure 2.
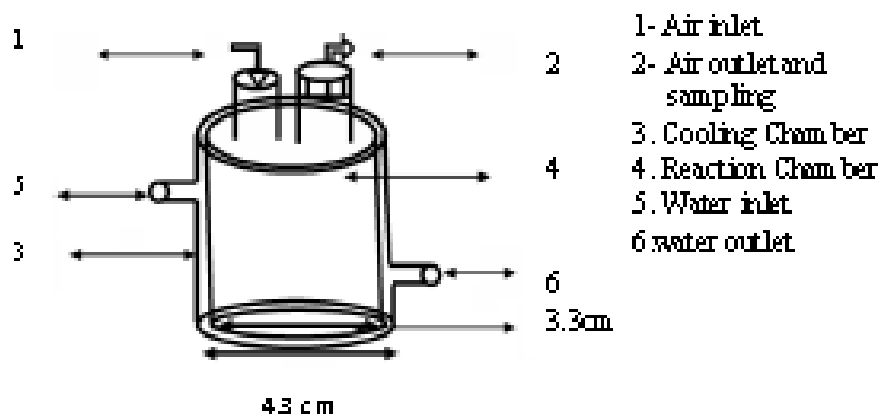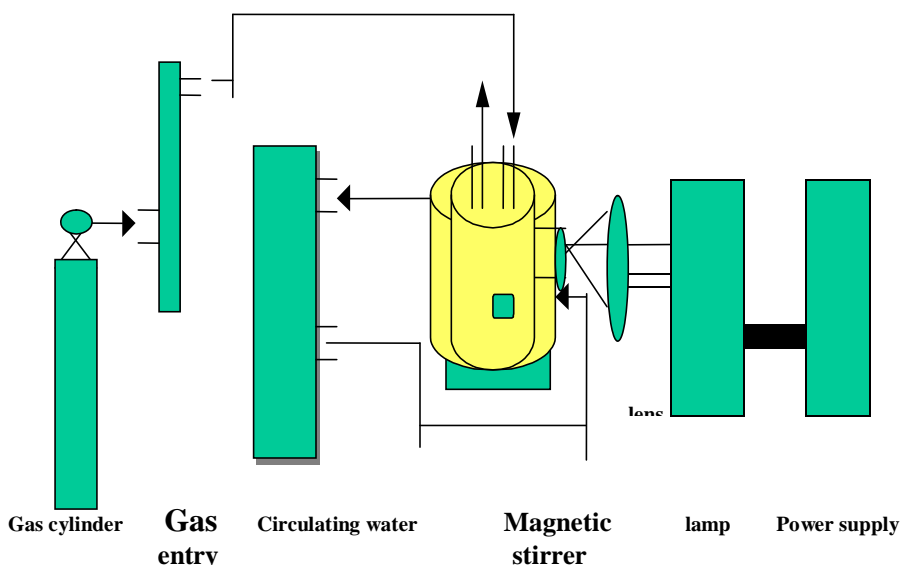
Fig. 2 : Main parts of the photocatalytic cell used in photo degradation of n –Hexacosane

Irradiation System: A block diagram of photolysis apparatus is shown in figure3 A300 W tungsten lamp source is focusing which is fitted with a focusing lens to ensure parallel beam of light [11].

| Gas cylinder | **Gas entry** | **Circulating water** | **Magnetic stirrer** | **lamp** | **Power supply** |

RESULTS AND DISCUSSION

Structural Characterization: The naked ZnO, Sb_2O_3 and prepared coupled semiconductor (ZnO-Sb_2O_3) were characterized by **XRD Spectrum**: In this technique (XRD) diffraction (XRD-6000, SHIMADZU), we can study the effect of mixing of two semiconductors (ZnO- Sb_2O_3) at temperature 900C°. The antimony trioxide spectrum (4- a), zinc oxide spectrum (4-b) and coupled (ZnO-Sb_2O_3) spectrum, with specific two theta 2θ and intensity are shown in fig,4

24
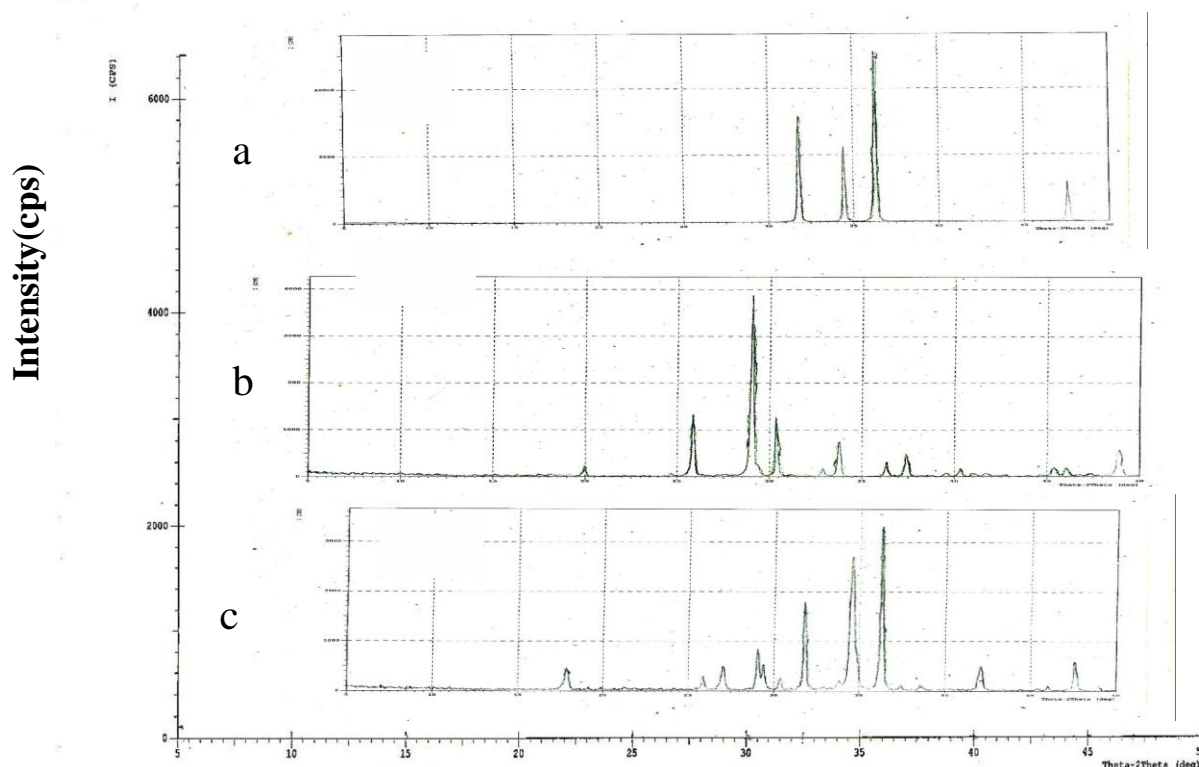
Fig.4: XRD diffraction spectrum of a- Zinc oxide b-Antimony tri oxide c- Coupled ZnO - Sb_2O_3

From figure 4-a, different strong peaks (2θ) appear in spectrum at 29.0753, 25.8860, 30.3901 represent naked antimony tri oxide. From figure 4-b, the strong peaks (2θ) appear in spectrum at 36.2911, 31.8105, 34.4626 represent naked zinc oxide. From figure 4-c, different peaks (2θ) appear in spectrum at 13.8132, 46.0407 and another peak disappear at 19.9855 and different peaks shift from position 27.7397, 36.2972, 46.0407 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 ZnO- Sb_2O_3 leads to appear of new peak 2θ in spectrum not exist in the original spectrum .This may due to the distortion of the two crystal lattice of ZnO and Sb_2O_3.

FTIR Spectrum : Figure 5-a show FTIR (FTIR-8400S, SHIMADZU) spectra of naked antimony tri oxide The peaks appear at 754.19, 646.17, 601.81,519.75, 472.58 ,437.86 . Figure 5-b show FTIR spectra of naked zinc oxide. The peaks are at 488.01, 445.57. For coupled semiconductors ZnO- Sb_2O_3 (figure 5-c) show the peaks at 746.48, 669.32, 636.53, 590.24, 489.94, 435.93. From the figure 5-c we can see the shift in peaks and reduce its intensity. This mean that two semiconductors are coupled IR

25

spectrometry (PERKINS-ELMER 1330 K Brdisc) was used to identify the functional groups created during the photo degradation of n-hexacosane. It is well known that the C = O give stretching vibration for aliphatic carbonyl compound in the range between
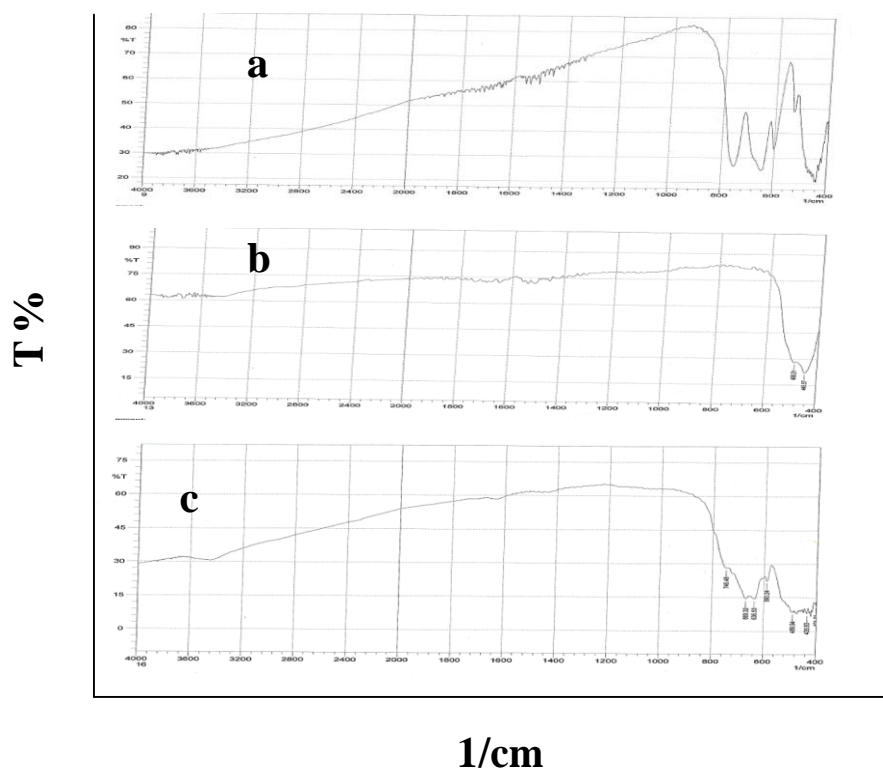
T %

1/cm

Fig. 5: FTIR Spectrum For: a- Antimony trioxide b- Zinc oxide c- Coupled ZnO - Sb_2O_3

I.R Spectrum:
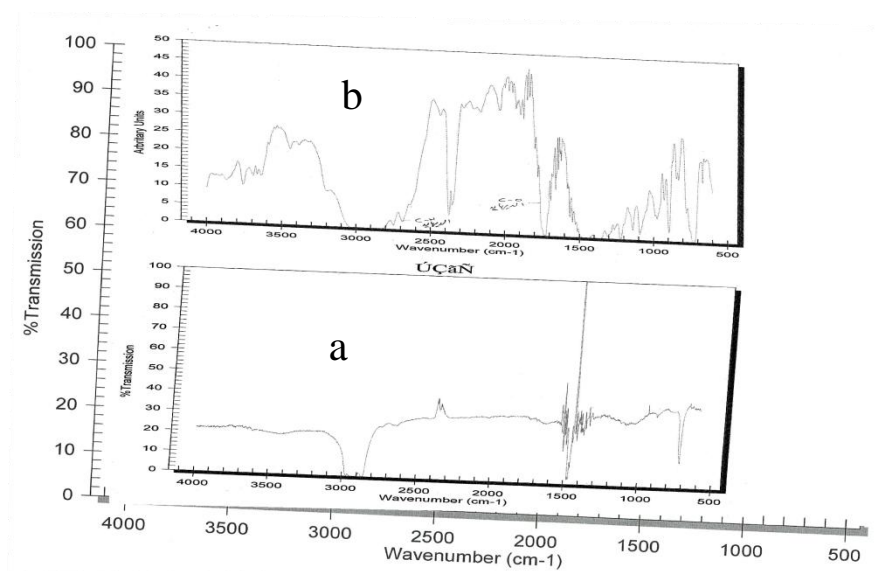
Fig. 6: I.R Spectrum of: a- n-hexacosane before irradiation b- n-hexacosane after irradiation.

26

1720 - 1740cm^{-1}(figure - 6a). The photolysis system using coupled ZnO-Sb$_2$O$_3$ showed a carbonyl band at 1690 cm^{-1}as shown in (figure 6-b), not present in the original substrate n-nonane + n-hexacosane spectrum (figure 6-a).

Gas Chromatography analysis:
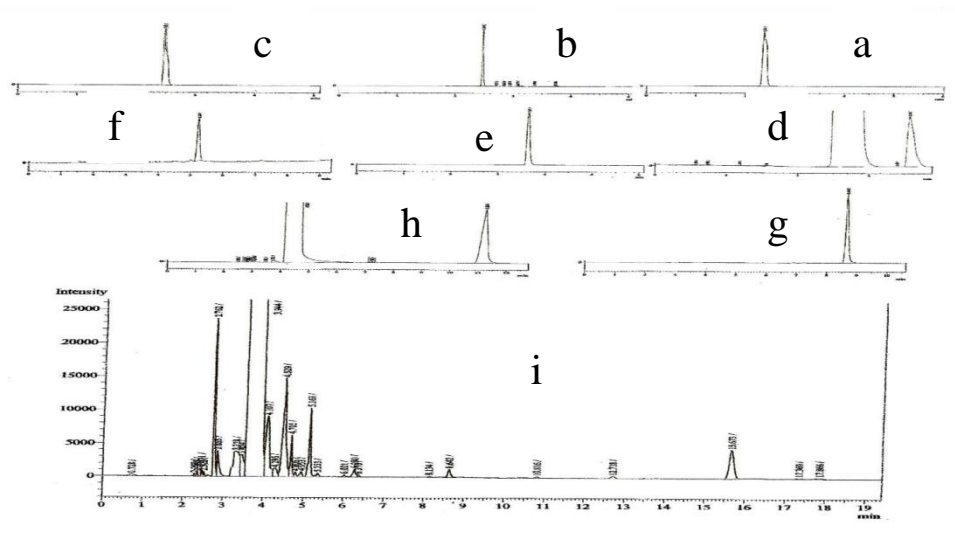
Fig. 7 : G.C. Spectrum : (a,b,c,d,e,f,g,h)standard hydrocarbons(pentane, hexane, heptane, n-Nonane, decane, unidecane, dodecane) (i) : products of photo degradation.

The Gas- Chromatography spectrum of n-hexacosane (PYE UNICAN-304 ,FID ,PHILIPS) after irradiation for 25 hours shows new peaks area percentage of light hydrocarbons are generated that means the photo degradation of n- hexacosane occur .

Table 1. Retention time of some standard hydrocarbons

| Light hydrocarbons	Retention time
n – Pentane	2.369
n-Hexane	2.469
n-Heptane	2.471
n-Nonane	3.637
n- Decane	5.234
n-Unidecane	8.660

The Effect of coupled semiconductor ZnO-Sb$_2$O$_3$ mass on photo catalytic degradation of n-hexacosane : The effect of mass of coupled semiconductor ZnO- Sb$_2$O$_3$ on photocatalytic degradation of n – hexacosane was studied under suitable conditions - 1x10^{-4} Mof n- hexacosane , light intensity equal to 16.36x10^{-5} Enis. Sec^{-1}, flow rate of air is 10ml min^{-1}, room temperature is 298.15 K.

The rate of photo catalytic degradation processes of n- hexacosane are listed in (Table 1) and plotted in figure 8. Gradually increases as the concentration of coupled semiconductor ZnO-Sb$_2$O$_3$ increases as a function of irradiation of each experiment until the concentration become 0.1 g 100ml^{-1} then gradually decreases as in figure 8. This behavior could be explained by the idea that the

27

concentration of 0.1 g 100ml^{-1} of coupled ZnO-Sb$_2$O$_3$ was provides the highest absorption of light by coupled ZnO-Sb$_2$O$_3$ and assures homogeneous absorption. The decrease in the efficiency of light through the lavers of reaction vessel photodegradation process at the concentration of coupled ZnO-Sb$_2$O$_3$ higher than 0.1 g 100ml^{-1} might be explained by the strong absorption of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel .Many workers studied this effect [12,13].

Table 2. The change of Absorbance with irradiation time on different masses of ZnO- Sb$_2$O$_3$.

Catalyst Conc. g/100ml	0.01	0.03	0.05	0.1	0.15	0.23
Irradiation Time/min	A					
0	0	0	0	0	0	0
20	0.11	0.41	0.5	0.21	0.14	0.33
40	0.12	0.63	0.74	0.34	0.23	0.54
60	0.17	0.82	0.96	0.46	0.34	0.63
80	0.24	1.12	1.27	0.54	0.44	0.82
100	0.32	1.24	1.47	0.73	0.53	0.93
120	0.39	1.42	1.68	0.91	0.71	1.15
140	0.58	1.56	1.79	1.06	0.86	1.28
160	0.56	1.52	1.71	0.97	0.79	1.21
200	0.58	1.42	1.65	0.92	0.73	1.13
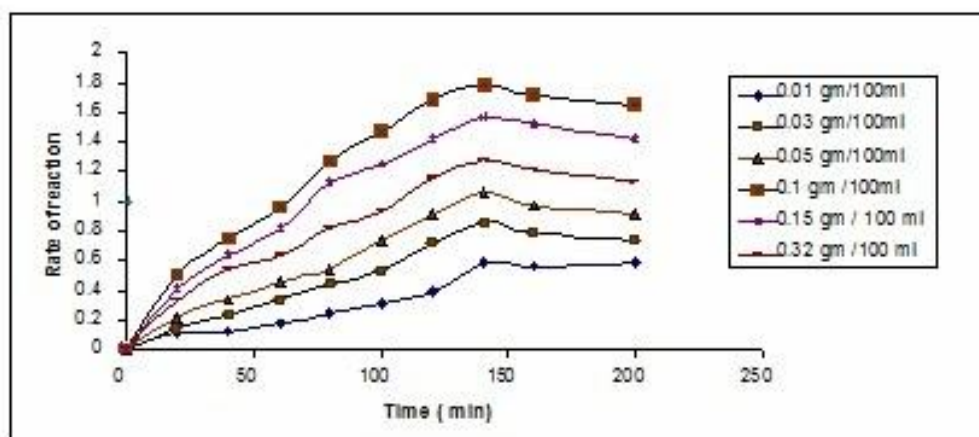
Fig. 8: The effect masses of ZnO – Sb$_2$O$_3$ on photocatalytic degradation of the
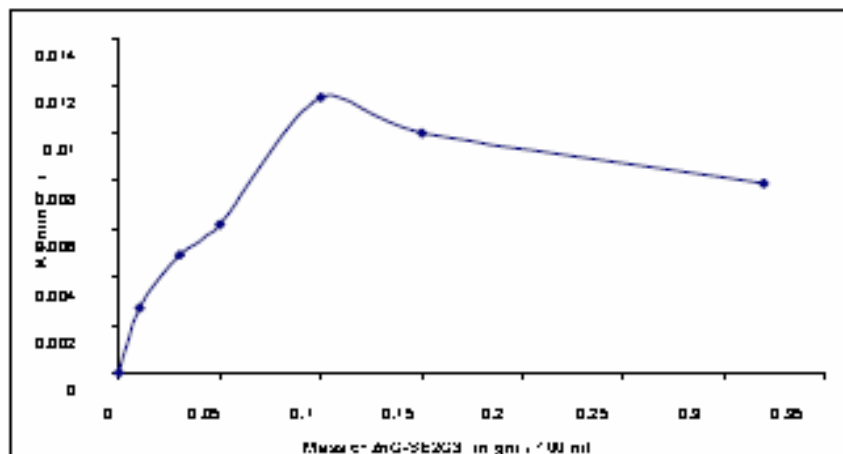
rate of n-hexacosane

Fig. 9: Effect of masses of (ZnO – Sb$_2$O$_3$) on rate constant.

The Effect of concentration of n-hexacosane: A series of experiments were carried out to study the effect of variation of initial concentration of n-hexacosane on the photo catalytic degradation of n-hexacosane was studied under optimum conditions (0.1 g of coupled ZnO -Sb$_2$O$_3$, light intensity equal to 16.36x10^{-5} Enis Sec^{-1} , flow rate of air 10ml min^{-1}, room temperature is 298.15 K**.** . The concentration of n-hexacosane is 5x10^{-5}– 2x10^{-3}M and the mass of coupled one is 0.1 g 100ml^{-1}. The Table 3 and the figure10 shows the rate of photo catalytic degradation of n -hexacosane increase with increase the concentration of   n-hexacosane until the concentration 7x10^{-4} M, then gradually decreases. This behavior could be explained by the idea that the concentration of 7x10^{-4}M on coupled ZnO–Sb$_2$O$_3$ (0.1 g 100ml^{-1}) was the optimum concentration to cover the largest area of the coupled ZnO –Sb$_2$O$_3$ particles, therefore absorbed maximum exciting photons to generate higher concentration of the activated coupled ZnO –Sb$_2$O$_3$ semiconductor. Another reason for this behavior is the strong absorption of light by the n-hexacosane, in the sample which contains high concentration that is 7x10^{-4}M, n-hexacosane on 0.1 g 100ml^{-1} of coupled ZnO –Sb$_2$O$_3$. The excess of n-hexacosane prevent the penetration of light through the successive layers of n-hexacosane on the coupled ZnO –Sb$_2$O$_3$ surface is weak to generate the required excited state of the n-hexacosane adsorbed on coupled ZnO –Sb$_2$O$_3$. This effect was studied by different scientists [14-16].

Table 3. The change of Absorbance with irradiation time on different n-hexacosane concentrations by (ZnO – Sb$_2$O$_3$).

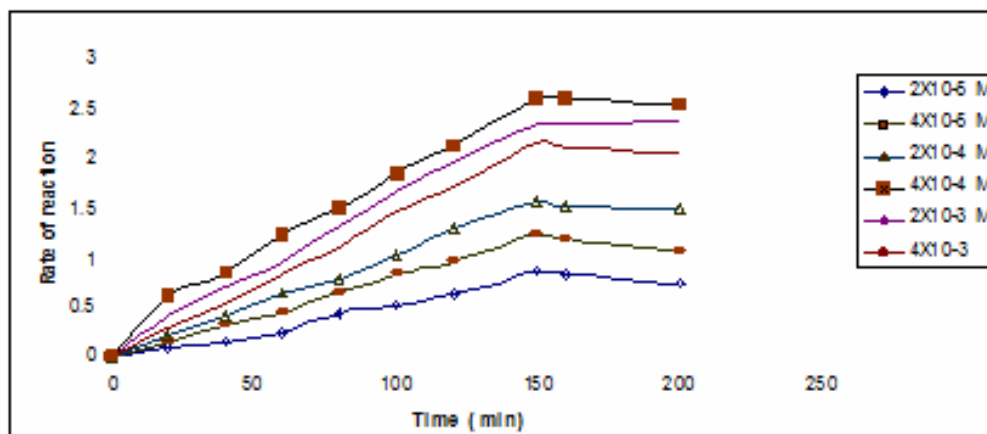| Concentration of n – hexacosane	2x10^{-5} M	4x10^{-5} M	2x10^{-4} M	4x10^{-4} M	2x10^{-3} M	4x10^{-3} M
Irradiation Time/min	A					
0	0	0	0	0	0	0
20	0.09	0.16	0.21	0.61	0.42	0.29
40	0.16	0.32	0.41	0.87	0.71	0.54
60	0.25	0.45	0.64	1.25	0.98	0.85
80	0.44	0.66	0.81	1.51	1.34	1.13
100	0.52	0.85	1.04	1.87	1.68	1.49
120	0.63	0.98	1.31	2.15	1.98	1.73
140	0.89	1.25	1.58	2.61	2.35	2.17
160	0.85	1.21	1.53	2.62	2.37	2.12
200	0.75	1.09	1.52	2.56	2.39	2.07

Fig. 10: Effect of of initial n-hexacosane concentration on rate constant by
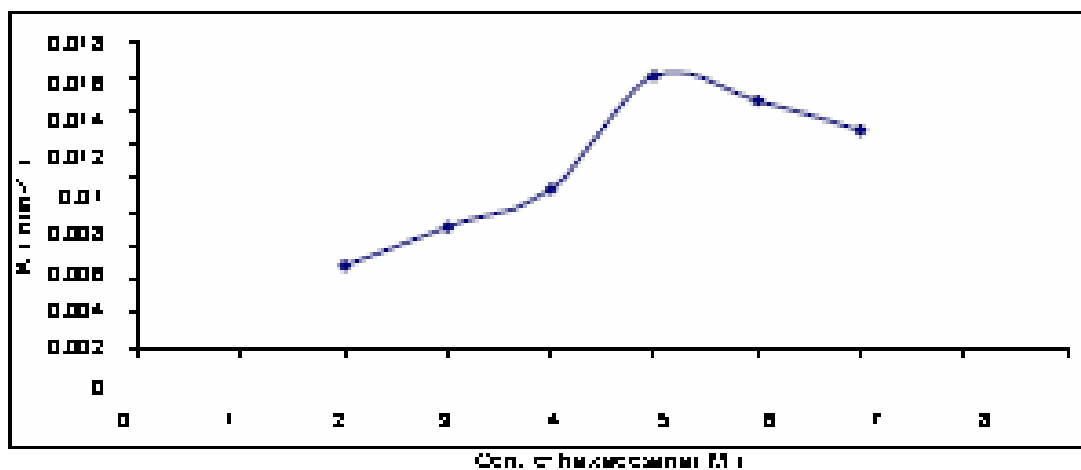$(ZnO – Sb_2O_3)$.

Fig. 11: Effect of initial n-hexacosane concentration on rate constant by
$(ZnO – Sb_2O_3)$.

Effect of Temperature : A series of experiments were carried out to study the effect of temperature on the photo catalytic degradation rate of n-hexacosane in aqueous coupled $ZnO– Sb_2O_3$ suspension at different temperature ranging from (278.15 – 293.15 k) [17,18]. Table 4 shows the effect of temperature on the photo catalytic degradation rate of n-hexacosane at fixed initial concentration of n-hexacosane and 0.15 g 100ml^{-1} of coupled $ZnO –Sb_2O_3$ as catalyst. The figure 12 indicate that the photo catalytic degradation rate of n-hexacosane increases with increase of temperature.

30

Table 4 . The change of Absorbance with irradiation time at different temperatures.

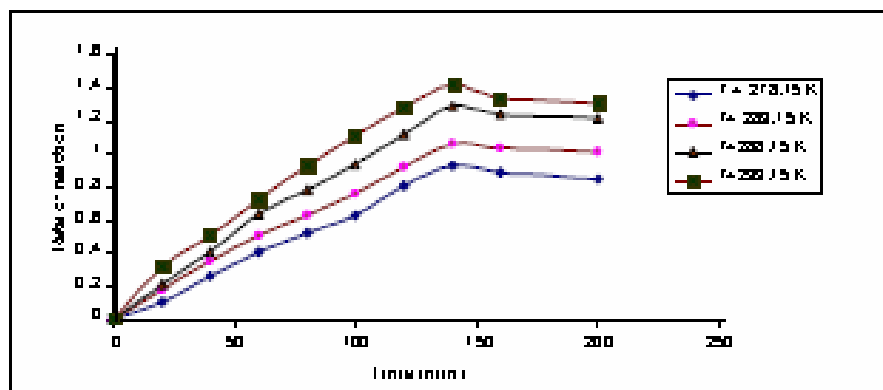| Temperature K	278.15	283.15	288.15	293.15
Irradiation time/min	A			
0	0	0	0	0
20	0.11	0.18	0.21	0.32
40	0.26	0.35	0.41	0.51
60	0.41	0.51	0.64	0.73
80	0.52	0.63	0.78	0.93
100	0.63	0.76	0.94	1.11
120	0.81	0.92	1.12	1.28
140	0.93	1.06	1.29	1.42
160	0.89	1.04	1.24	1.34
200	0.85	1.01	1.22	1.31

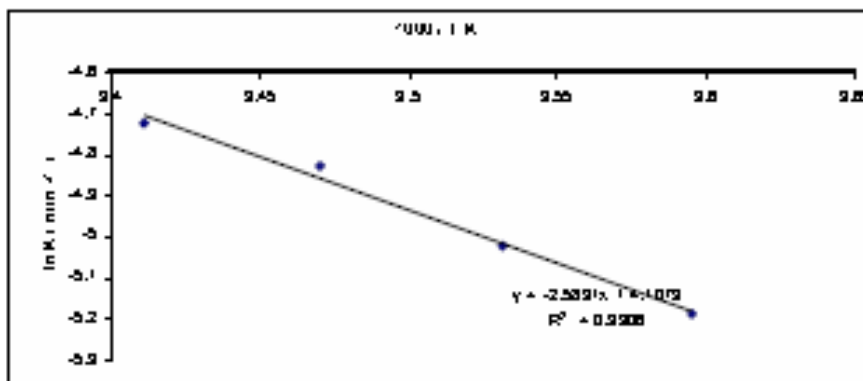**Fig. 13:** Effect of temperature on photo catalytic degradation rate of n-hexacosane by coupled ZnO –Sb$_2$O$_3$.

Fig. 14 : ln K min^{-1}against 1000 T^{-1}

From the figure14 we can calculate the activation energy of the reaction (Ea), when   plotted 1000 T^{-1} against ln K min^{-1} (Arrhenius relationship).The activation energy for photo catalytic degradation rate of n-hexacosane is equal to 26 $kJ.mol^{-1}$.

APPLICATION

This method is useful to study photo degradation in the absence and presence of catalyst.

CONCLUSIONS

1. The compound has not 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 n – hexacosane 0.1 g $100ml^{-1}$ mass of ZnO – Sb2O3 and $4x10^{-4}$ M concentration of n –hexacosane.
4. The activation energy 26KJ $mole^{-1}$

ACKOWLEDGMENTS

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