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Prepared coupled ZnO – Co_2O_3 then study the photocatalytic activities using crystal violet dye

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ABSTRACT

In this project coupled ZnO – Co_2O_3 powders was prepared using direct mixing of ZnO and Co_2O_3 and calcination at 500C, then studied the ability of prepared coupled semiconductor to degraded some pollutants such as crystal violet dye .The coupled ZnO – Co_2O_3 were prepared by mixing one gram of zinc oxide with one gram of cobalt oxide and calcing in furnace (500 ºC) for three hours. .The coupled characterized were investigated by using FTIR, XRD, and UV-visible techniques. The photo activity of coupled was testing using crystal violet dye.

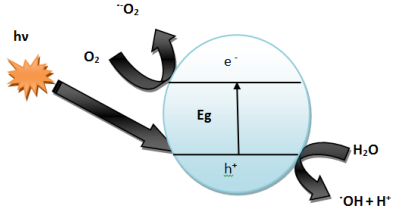
The synthesized coupled semiconductor powder photo activity were studied, which is achieved by the irradiation of suspended solution consists of different concentration of crystal violate dye with 0.14gm of mixed metal oxide (ZnO – Co_2O_3) by mercury lamp (125 W) from external source inside a pyrex photoreaction cell of 100 ml at 298 K, with flow rate of babul of air 10 ml/min. In this paper different experiments were studied such as: the effect of crystal violate dye concentration, the effect of loaded mass of coupled ZnO – Co_2O_3 semiconductors, and the effect of temperature.

KE WORDS: Photo degradation, semiconductor, crystal violate, oxidation.

1. INTRODUCTION

Many projects were carried out on photo catalytic (degradation, oxidation, and hydrolysis) using single metal oxide semiconductor oxide with excitation by UV-lamp. When pure semiconducting oxide exposure to photon with energy equal to or greater than the band gap of the semiconductor oxide, the electrons are transferring from the valence band to conduction band of semiconductor (Min, 2016; Manhal, 2015; Harufumi, 2015). The photoelectron produced on the conduction band inter photo reduction reaction and the holes produced by this process in valance band migrate to the surface of semiconductor and interact with adsorbed species **(**Zahra J.2015; Aline M.2016; Peidong H.2016) as in figure 1.

The perfect semiconductors should be stable, inexpensive, non-toxic, highly photoactive, and available. The coupled semiconductors is a famous method to increasing photocatalytic activity of pure semiconductor because increasing the charge separation and extending the energy range of photo excitation up to visible light region for the system (Hazim Y Al-gubury, 2016) as shown in Figure 2.



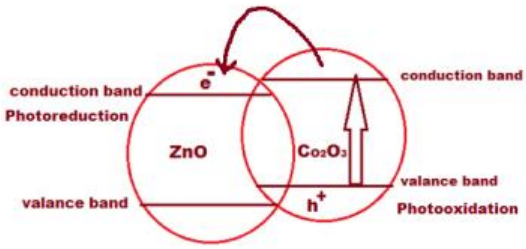


Figure.1.Direct excitation of Semiconductor oxide **Figure.2.Charge separation in mixed semiconductors**

2. EXPERIMENTAL PROCEDURE

Chemicals: 1-Zinc oxide (ZnO): The bang gap of zinc oxide (3.4 eV), purity (99%), particle size (100) mesh, supplied by Fluka AG.

2 – Cobalt oxide (Co_2O_3): The band gap of cobalt oxide (2.58 eV), purity (98%), supplied by Fluka AG.

3- Crystal violet, supplied by Fluka AG

Prepared mixed semiconductor (ZnO – Co_2O_3): The coupled semiconductors (ZnO – Co_2O_3) were prepared by using 99.9% pure ZnO and (98%) pure Co_2O_3 powders as the starting materials. The starting material were mixed by mortar for one hour, after that calcinate the mixture in furnace (500ºC) for three 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 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.

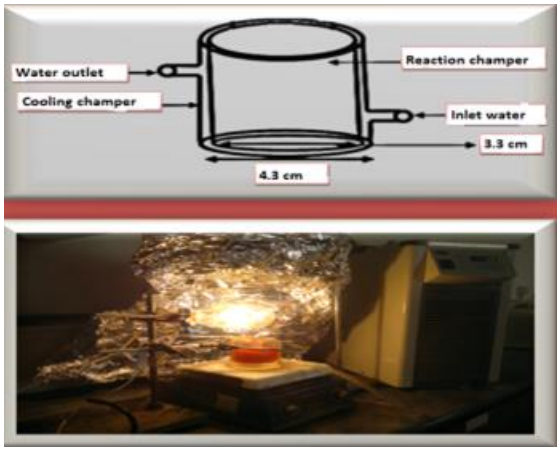


Figure.3. Main parts of the photocatalytic cell used in Photocatalytic degradation of crystal violet dye in presence of coupled ZnO-Co_2O_3

3. RESULTS AND DISCUSSION

Structural Characterization: The naked ZnO, Co_2O_3 and prepared coupled semiconductor (ZnO - Co_2O_3) were characterized by:

XRD Spectrum: In this technique (XRD) diffraction, we can study the effect of mixing of two semiconductors (ZnO – Co_2O_3) at temperature (500 ºC).

From the Fig.(4) below : The zinc oxide spectrum (5 - a), Cobalt oxide spectrum (5 – b) and coupled (ZnO – Co_2O_3) spectrum, with specific two theta 2Ɵ and intensity .

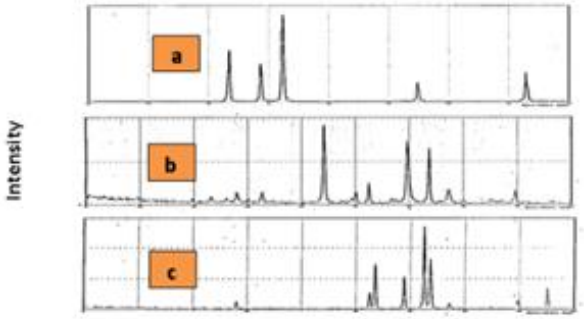


Figure.4. a) XRD diffraction spectrum of a- Zinc oxide b) Cobalt oxide c) coupled ZnO – Co_2O_3

From Figure 4a, different peaks (2Ɵ) appear in spectrum (33.5, 34.5, 36, 47.5, 56.5) represent naked zinc oxide. From Figure 4b, the peaks (2Ɵ) appear in spectrum (27.1116, 34.5810, 36.8634, 30.0746, 31.0420, 44.8190, 39.8839, 35.3376) represent naked cobalt oxide. From Figure 4c. Many peaks (2Ɵ) appear in spectrum (36.2900, 36.8753, 31.8047, 34.4567, 31.3045, 31, 6413, 31.8047, 36.5865, 36.8753, 38.5827, 44.8352, 47.5704) represent the mixed between zinc oxide and cobalt oxide. The mixed semiconductor ZnO – Co_2O_3 give new spectrum which indicates a shift in 2Ɵ and reduce its intensity .Also the mixed semiconductor ZnO – Co_2O_3 leads to appear of new peak 2Ɵ in spectrum not exist in the original spectrum, this may due to the distortion of the two crystal lattice of ZnO and Co_2O_3.

F.T.IR Spectrum: Figure 5a below show F.T. IR spectra of naked zinc oxide (488.01, 445.57) cm^{-1}, while Figure 5b show F.T.IR spectra of naked cobalt oxide. The peaks (667.39, 578.66, 547.80, 501.51, 462.93, 426.28) cm^{-1}. For mixed semiconductors (ZnO – Co_2O_3) Figure 5c show the peaks (675, 598, 475, 450) cm^{-1}. From the Figure 5c can see the shift in peaks and reduce its intensity, this mean the mixed between two semiconductors occurs.

Influence of Crystal violet concentration on Photcatalytic degradation process : The effect of initial Crystal violet concentration on the photocatalytic degradation of dye was investigated by change the concentration of crystal violet dye range (5- 60) ppm with keeping mass of coupled ZnO constant at 0.15 g /100 ml . From the Table 1 and Figure 6 degradation efficiency of crystal violet decreases with an increase in the initial dye concentration. The surface area on the catalyst is very suitable for the degradation process to take place and the concentration 5ppm represent the optimum concentration of dye, but when the dye concentration is increased and the catalyst amount is still constant, the case lead to minimise the active sites for the reaction on the surface of coupled. Therefor the photocatalytic degradation decrease. To explain this behaviour, when the dye molecules increases the solution became more intense coloured and the path length of photons penetration to the solution decreased and only fewer photons reached the active site on the surface of coupled and the photo catalytic degradation of dye was found to be decreased (Hazim Y Al-gubury, 2015)

Table.1.The change of A_t /A_0 with irradiation time using different masses of coupled ZnO-Co_2O_3

Catalyst Mass (gm /100 ml)	0.04	0.08	0.15	0.4	0.55
Irradiation Time/min	A / A_0				
0	1.00	1.00	1.00	1.00	1.00
10	0.33	0.46	0.66	0.75	0.84
20	0.17	0.28	0.47	0.58	0.71
30	0.11	0.20	0.34	0.44	0.58
40	0.09	0.15	0.28	0.38	0.52
50	0.07	0.13	0.23	0.33	0.47
60	0.04	0.11	0.19	0.29	0.45

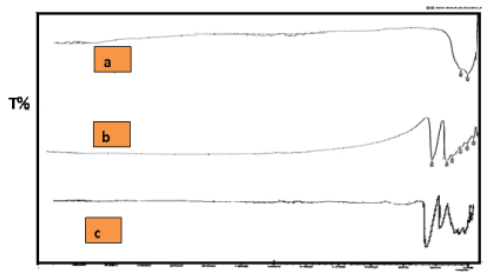


Figure.5.a) F.T.IR Spectrum for: a- Zinc oxide b) Cobalt oxide c) Coupled ZnO – Co_2O_3

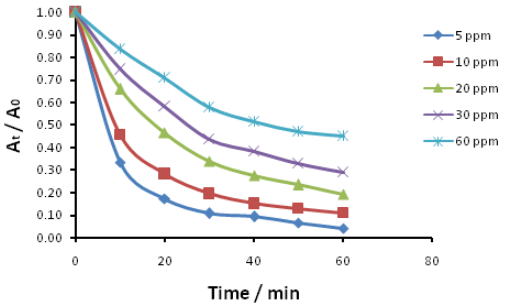


Figure.6.The change of (A_t / A_0) with irradiation time at concentration of crystal violet

The Effect of coupled ZnO – Co_2O_3 masses on Photcatalytic degradation of crystal violet dye: The effect of loaded mass of coupled ZnO – Co_2O_3 on Photcatalytic degradation of crystal violet dye was investigated using optimum conditions 5 ppm of crystal violet dye , flow rate of air 10ml/min, and room temperature = 298K . Table 2 and Figure 7 indicate that the rate reaction of photo catalytic degradation increases with increase of coupled masses. Gradually increases the masses of coupled ZnO – Co_2O_3 lead to increase the photocatalytic degradation rate of dye, until reach to (0.15) gm/100ml then gradually decreases the degradation rate of day, as in Figure 7. This behaviour could be explained that the mass of coupled of (0.15gm /100ml) was provided the highest absorption of light on the surface of coupled ZnO –Co_2O_3. The decreases in the reaction rate of photo catalytic degradation process at the masses of coupled ZnO – Co_2O_3 higher than (0.15 gm /100ml),because 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 (Ahmed H Shntaif, 2016; Chen Y, 2013; Ting H, 2013)

Table.2.The change of A_t /A_0 with irradiation time on different masses of coupled ZnO – Co_2O_3

Catalyst Conc. gm /100ml	0.04	0.08	0.15	0.4	0.55
Irradiation Time/min	A_t /A_0				
0	1.00	1.00	1.00	1.00	1.00
10	0.72	0.56	0.41	0.82	0.88
20	0.47	0.33	0.20	0.67	0.75
30	0.36	0.26	0.15	0.51	0.62
40	0.28	0.20	0.12	0.44	0.54
50	0.23	0.17	0.09	0.35	0.49
60	0.19	0.13	0.07	0.29	0.45

Effect of Temperature on photocatalytic degradation of crystal violet dye: A series of experiments were carried out to investigate the reaction rate of photocatalytic degradation of crystal violet using range of temperature (278 – 293 k) and to determine the activation energy. In all experiments the loaded mass of coupled equal (0.15 g / 100 ml), with 5 ppm concentration of crystal violet dye, and 10 ml/min the rate of babble of air. Table 3 and Figure 8 shows the effect of temperature on the photo catalytic degradation rate of crystal violet. It's clear that from the Figure 8. Photo catalytic degradation rate of crystal violet increases with increase of temperature due to the increases of electrons transfer from valance band to conduction band (Rong, 2015; Antonopoulou, 2016; Yi S, 2016).

Table.3.The change of A_t/A_0 with irradiation time at different temperatures using coupled ZnO – Co_2O_3

Temperature/ K	278	283	288	293
Irradiation time/min	A_t/A_0			
0	1.00	1.00	1.00	1.00
10	0.76	0.67	0.58	0.48
20	0.56	0.44	0.30	0.22
30	0.40	0.31	0.21	0.12
40	0.31	0.24	0.15	0.10
50	0.27	0.20	0.13	0.08
60	0.25	0.17	0.11	0.07

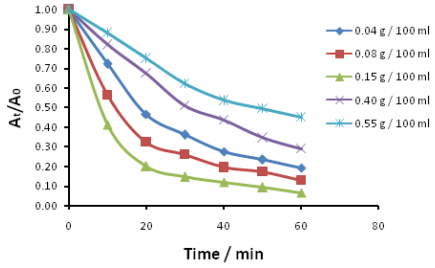


Figure.7.The effect masses of coupled ZnO – Co_2O_3 on Photcatalytic degradation of crystal violet dye

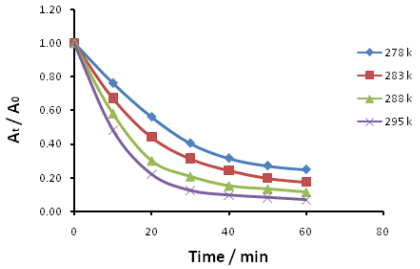


Figure.8. Effect of temperature on Photocatalytic degradation of crystal violet dye by using coupled ZnO-Co_2O_3

Table.4.The change of $\ln A_0/A$ with irradiation time at different temperatures

Temperature K	278	283	288	293
Irradiation time/min	$\ln A_0/A_t$			
0	0.00	0.00	0.00	0.00
10	0.27	0.40	0.54	0.72
20	0.58	0.82	1.21	1.51
30	0.91	1.16	1.58	2.08

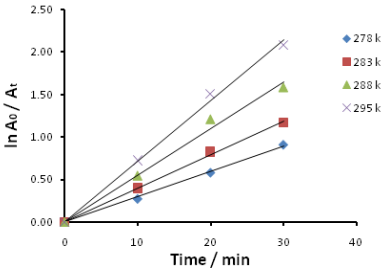


Figure.9. Effect of temperature on Photocatalytic degradation of crystal violet dye by using coupled ZnO-Co_2O_3

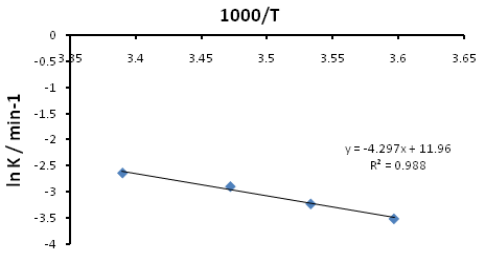


Figure.10. ln K against 1000/T

From the Fig. (10) above we can calculate the activation energy of the reaction (E_a), when plotted (1/ T k) against(ln K) (Arrhenius relationship).The activation energy for Photocatalytic degradation of crystal violet dye by using coupled ZnO-Co_2O_3 equal to (35.7 kJ.mol $^{-1}$) .

4. CONCLUSION

- The compound has been not degraded in case of absent of catalyst.
- The compound has been successfully degraded when used the catalyst with the light.
- The optimum condition for the Photocatalytic degradation of crystal violet dye by using coupled ZnO-Co_2O_3 (0.15 gm / 100ml mass of coupled ZnO – Co_2O_3 and 5ppm concentration of crystal violet dye.
- The activation energy =53.7 kJ/mole.

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