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The effect of coupled titanium dioxide and cobalt oxide on photo catalytic degradation of malachite green

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Abstract: Photcatalytic degradation of malachite green using coupled TiO_2-Co_2O_3, was studied, by the irradiation of suspended solution consists of 1ppm of malachite green with 0.12 g /100 ml of coupled TiO_2-Co_2O_3 metal oxide semiconductor. This process used external source 125Watts mercury lamp. Al photo reaction inside a Pyrex photoreaction cell of 100 ml, with flow rate of air 10ml/ min at room temperature 298 K. Several experiments were carried out in various conditions to create optimum Photcatalytic degradation of malachite green. These experiments include effect of mass of coupled TiO_2-Co_2O_3, concentration of malachite green, and the effect of light intensity. The products was studied by using UV-Vis spectrophotometer.
Keywords: Photcatalytic degradation, malachite green. coupled TiO_2-Co_2O_3, decolonization.

Introduction

Many semiconductors such as ZnO, TiO_2, CdS, …..,are used to degrade organic and inorganic pollutant(industrial dyes ,pesticides, heavy metals in waste water , …) using photo catalytic degradation processes[1,2]. Photo catalytic process include use direct semiconductors by UV lamp or indirect excitation using visible lamp. If semiconductor irradiated by UV lamp the electrons promote from valance band to conduction band produce electrons in conduction band undergo photo reduction leaving positive hole in valance band inter photo oxidation processes.

As shown in figure (1) :

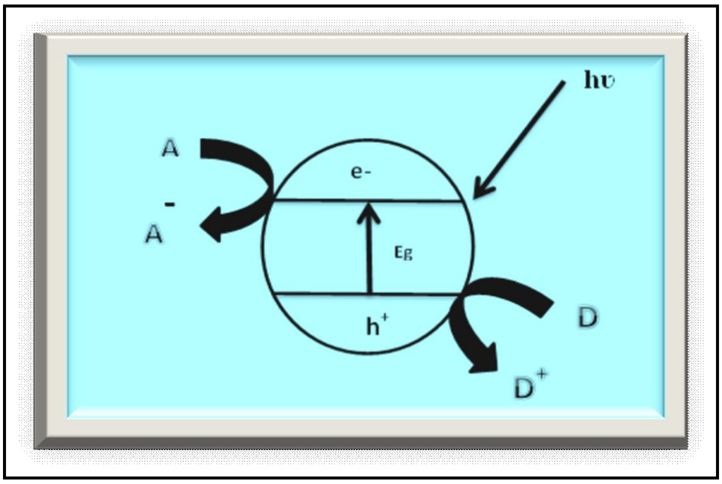

Figure1: General mechanism of the photocatalysis on semiconductor particle.

Recently researcher modified different types of semiconductors using couple between titanium dioxide and cobalt oxide to avoid the harmful of ultra violet radiation and to extend the response to visible light[3-5].

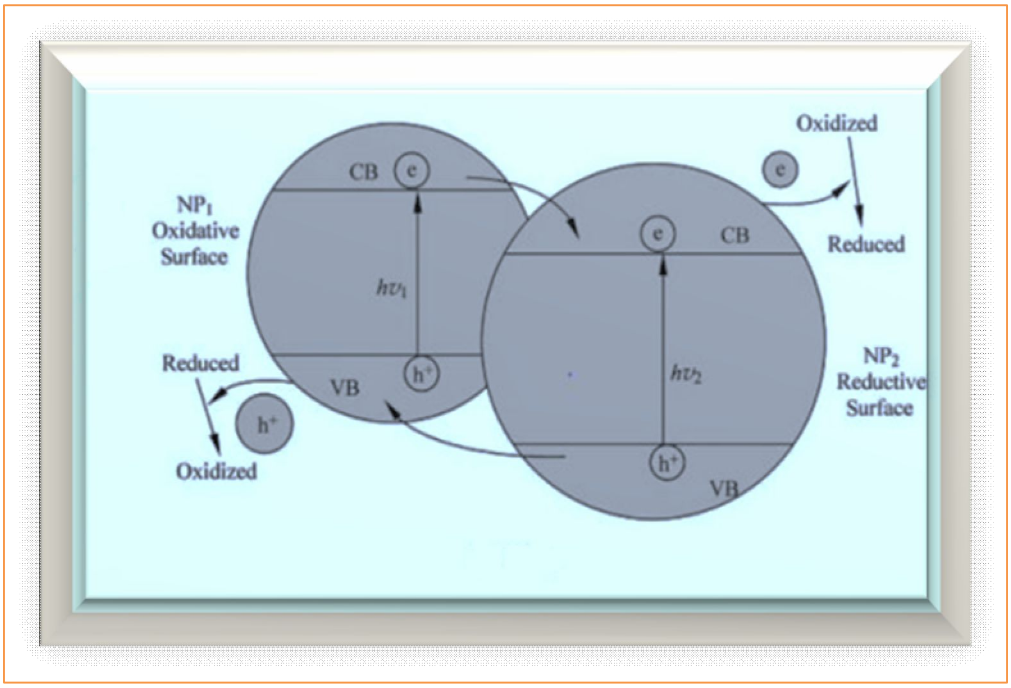

Figure (2) : Schematic diagram representing the injection between two semiconductors

Materials and Methods

A-Chemicals:

1. Titanium dioxide (TiO_2) : purity (98%) , supplied by Fluka AG.
2. Malachite Green supplied by sigma – Aldrich.
3. Cobalt oxide (Co_2O_3) supplied by sigma-Aldrich.

B-Prepared Coupled Semiconductor (TiO_2-Co_2O_3) :

The coupled semiconductors (TiO_2-Co_2O_3) was prepared by mixed 1g of titanium dioxide with different weights of Cobalt oxide. The mixture was crashed by mortar and pestle for 20 minutes. After that calcination the mixture in furnace (700C°) for three hours, after calculating the products was crashed again.

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 thecontinues 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.

Schematic diagram of photochemical reaction as shown in figure (3):

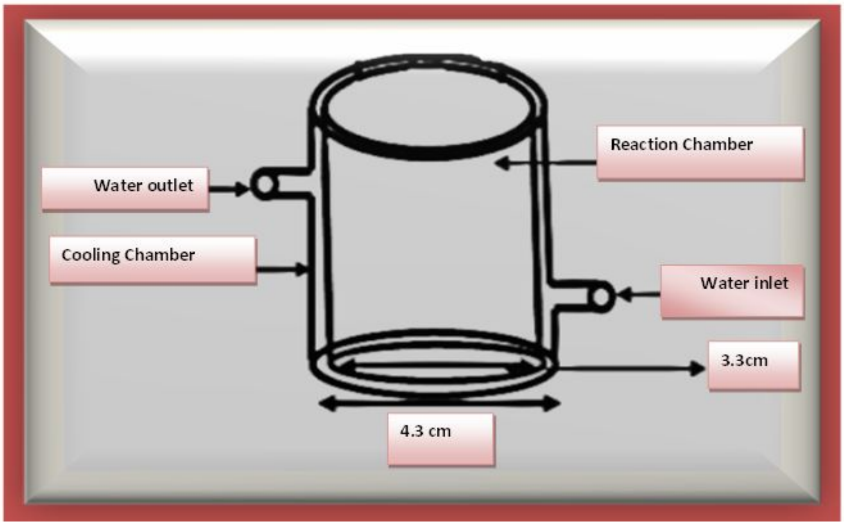

Figure 3 : Main parts of the photocatalytic cell used in Photcatalytic degradation of Malachite Green .

C- Irradiation System

A photo for photolysis apparatus is shown in figure (4) a 125Watts mercury lamp source is a focusing fitted with a focusing lens to ensure parallel beam of light.

Figure 4 : : photo for main parts of the photocatalytic degradation process cell

Result and Discussion

1 - Effect mass catalyst of coupled TiO_2-Co_2O_3 on photo catalytic degradation of malachite green :

These experiments include using different masses of coupled TiO_2-Co_2O_3 (0.03– 0.40 g/100 ml) to study Photcatalytic degradation of malachite green using 1 ppm of malachite green, flow rate of air 10 ml/min, and room temperature 298 K .

Table (1) and Figure (5) represent photo catalytic degradation processes of malachite green at different loaded mass of coupled TiO_2-Co_2O_3. Photocatalytic degradation of malachite green, gradually increases as the masses coupled TiO_2-Co_2O_3 increases until reach to the optimum photocatalytic activity 0.12 g /100ml, then gradually decreases. phtocatalytic degradation process at the masses of coupled TiO_2-Co_2O_3 higher than 0.12 g /100 ml were decreases due to the light absorption will be limited only to the first layers of malachite green and the other layers of solution do not receive light photons. The other reason light scattering at high mass of coupled TiO_2-Co_2O_3, this lead to decrease the photon intensity, so the absorption of light through the first layer of solution more than the other layers because the second layer prevent light from passing through the other layers in the reaction vessel .Many workers studied this effect[6,7]. At the loading mass of coupled TiO_2-Co_2O_3 below 0.12 g /100 ml the photo catalytic degradation of malachite green decrease due to the quantity of mass of coupled TiO_2-Co_2O_3 decrease so the surface area decrease which lead to decreases photodegradation rate of malachite green .

Table 1. The change of A_t /A_0 with irradiation time using different masses of zinc oxide.

Catalyst mass g /100 ml	0.03	0.06	0.12	0.22	0.40
Irradiation Time/min	A_t /A_0				
0	1.00	1.00	1.00	1.00	1.00
10	0.71	0.59	0.39	0.80	0.85
20	0.52	0.39	0.25	0.65	0.75
30	0.43	0.32	0.18	0.55	0.65
40	0.34	0.24	0.14	0.45	0.55
50	0.27	0.20	0.11	0.40	0.50
60	0.23	0.15	0.07	0.40	0.45

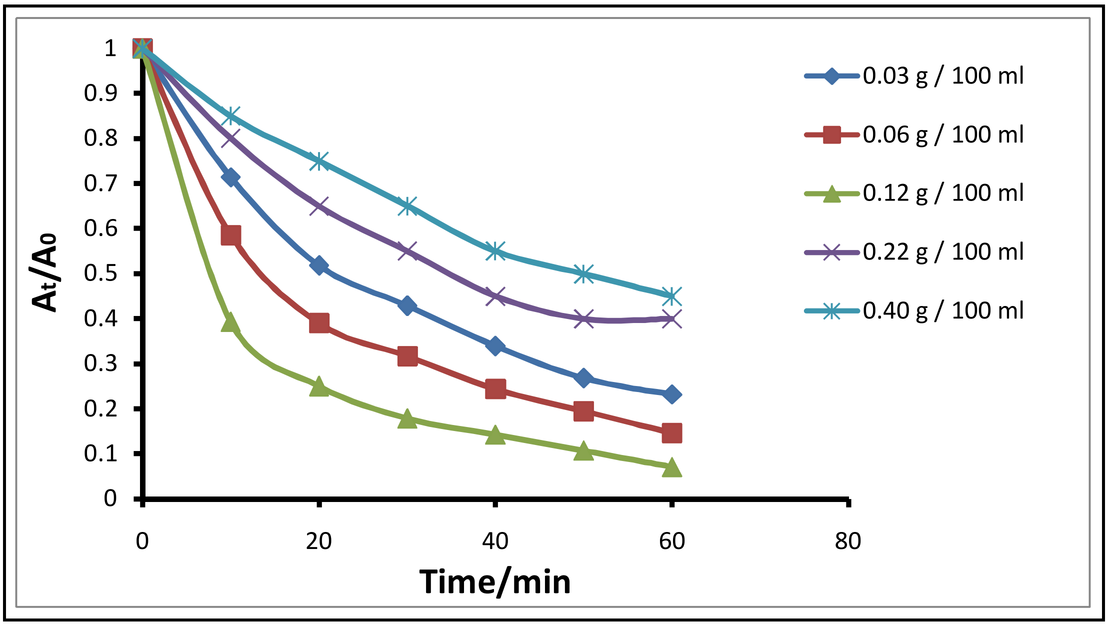

Figure 5 : The effect masses of coupled TiO_2-Co_2O_3 on Photcatalytic degradation of malachite green.

The results illustrated in table (2) and plotted in figure (6) which shows the pseudo first order reaction curve for various catalyst concentration according to Langmuir Hinshelwood relationship.

Table 2: The change of lnA0/At with irradiation time on different masses of coupled TiO_2-Co_2O_3.

Catalyst mass g/100ml	0.03	0.05	0.12	0.22	0.40
Irradiation time/min	LnA0/At				
0	0.00	0.00	0.00	0.00	0.00
10	0.34	0.54	0.93	0.22	0.16
20	0.66	0.94	1.39	0.43	0.29
30	0.85	1.15	1.72	0.60	0.43

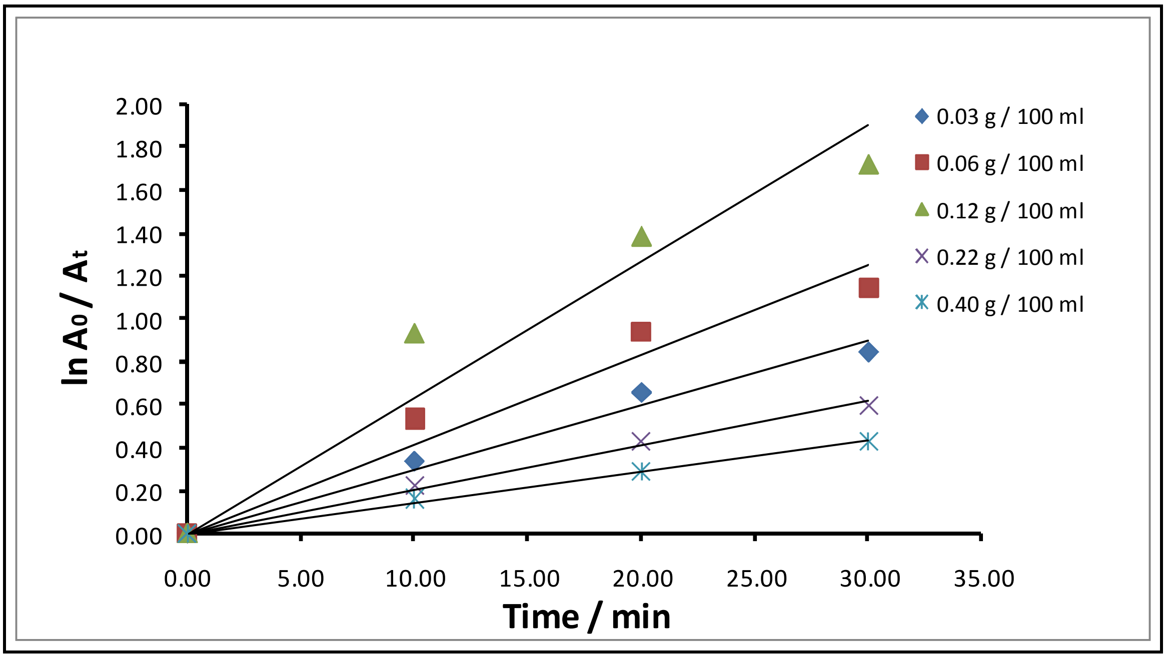

Figure 6 : The change of lnA0/At with irradiation time at different masses of coupled TiO_2-Co_2O_3.

The kinetic results are plotted in figure (7) which shows that the rate constant of reaction generally increases with increase of photocatalyst concentration.

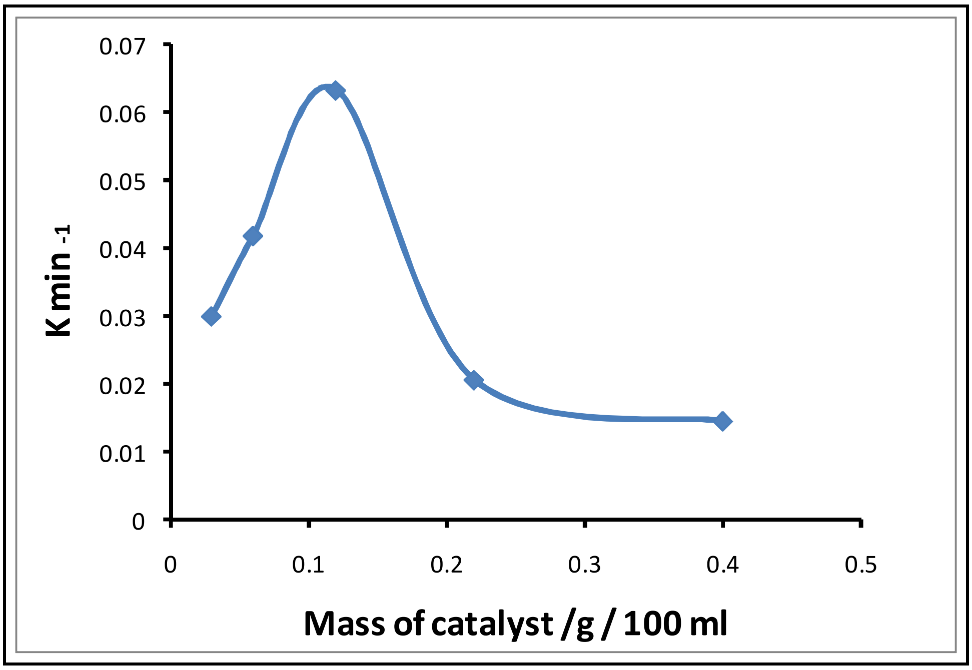

Figure 7: Effect of masses of coupled TiO_2-Co_2O_3 on rate constant.

2- The Effect of initial malachite green concentration on photo catalytic degradation processes :

A serious of experiments have been done , the change concentration of malachaite green (1 – 10 ppm) on photocatalytic degradation process was studied using the optimum mass of coupled TiO_2-Co_2O_3 0.12g / 100 ml , the light intensity equal to 8.22 mW/cm^2, and temperature equal to 298 K ,with flow rate of air 10 ml / min . The results are listed in Table (3) and plotted in figure[8]. It has been noted that the rate of photocatalytic degradation of malachite green gradually decreases with the increasing of initial concentration. This behavior due to , the low concentration 1ppm was the best value to cover the largest area of the coupled TiO_2-Co_2O_3

particles . The excess of malachite green prevent the penetration of light through the successive layers of malachite green on the coupled TiO_2-Co_2O_3 surface is weak to generate the required excited state of the malachite green adsorbed on coupled TiO_2-Co_2O_3 [8,10].

Table 3. The change of A_t /A_0 with irradiation time using different concentration of malachite green.

Concentration of malachite green / ppm	1	3	5	7	10
Irradiation Time/min	A_t /A_0				
0	1.00	1.00	1.00	1.00	1.00
10	0.65	0.73	0.84	0.88	0.93
20	0.49	0.61	0.73	0.78	0.85
30	0.38	0.51	0.67	0.71	0.79
40	0.32	0.44	0.61	0.66	0.75
50	0.24	0.39	0.55	0.60	0.69
60	0.23	0.35	0.54	0.59	0.67

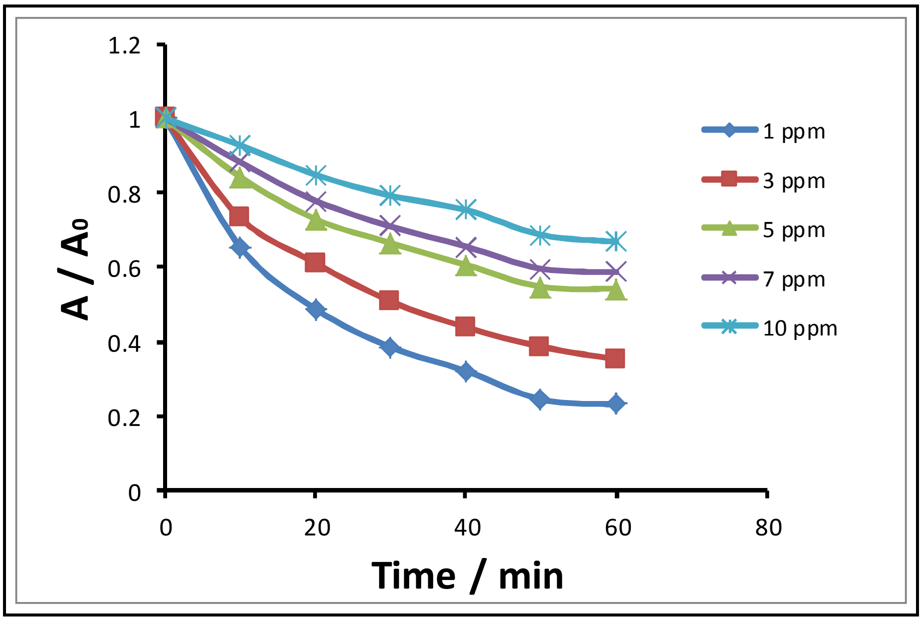

Figure 8: The change of (A / A_0)with irradiation time at concentration of malachite green.

The results illustrated in table (4) and plotted in figure (9) which shows the pseudo first order reaction curve for various catalyst concentrations according to Langmuir Hinshelwood relationship.

Table 4: The change of lnA0/At with irradiation time on different masses of coupled TiO_2-Co_2O_3.

Catalyst mass g/100ml	0.03	0.05	0.12	0.22	0.40
Irradiation time/min	LnA0/At				
0	0.00	0.00	0.00	0.00	0.00
10	0.34	0.54	0.93	0.22	0.16
20	0.66	0.94	1.39	0.43	0.29
30	0.85	1.15	1.72	0.60	0.43

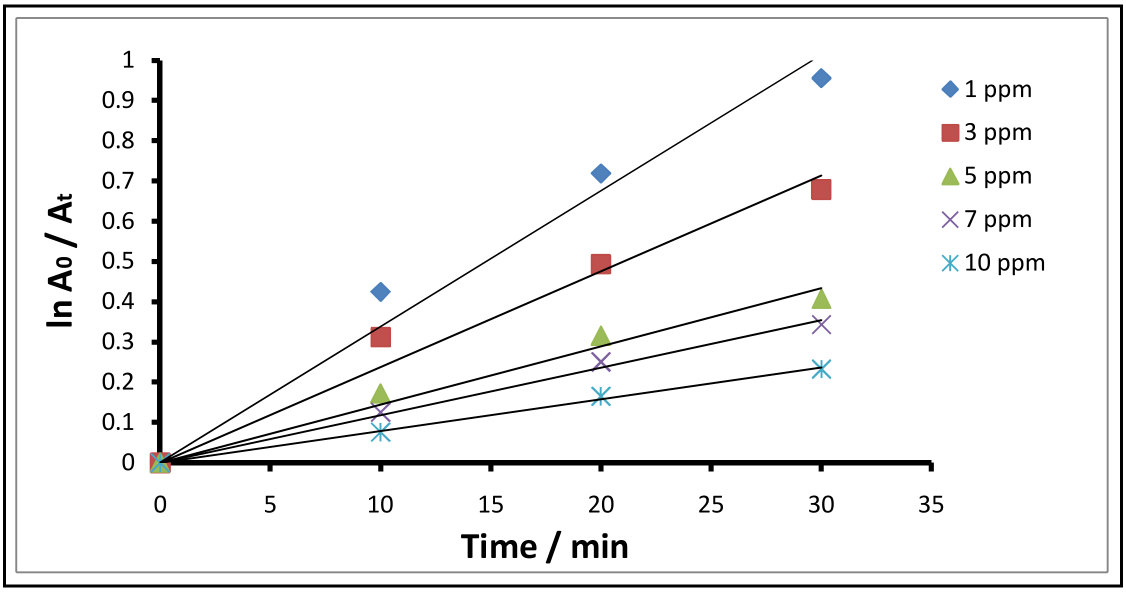

Figure 9 : The change of lnA0/At with irradiation time at different masses of coupled TiO_2-Co_2O_3.

3 – Effect of light intensity on photocatalytic degradation process of malachite green .

A serious of experiment were carry out to study the effect of light intensity rang (2.15 – 8.22) mW/cm^2 .All experiments performed using optimum condition of masses of coupled TiO_2 – Co_2O_3 (0.12 g / 100 ml) , with initial concentration of malachite green 1 ppm, using flow rate of air bubbling at 10 ml/min, at room temperature 298K .

Table (5) and figure(10), clear the effect of light intensity on the photocatalytic degradation of malachite green. photocatalytic degradation of malachite green increases with the increase of light intensity, the maximum value of light intensity 8.22 mW/cm^2. Basically lamp production photons ,this photons increase electrons transfer from valance band to conduction band in the coupled TiO_2-Co_2O_3 this process lead to increase photocatalytic process of malachite green[11,13].

Table 5. The change of A_t /A_0 with irradiation time using different light intensity.

light intensity/ mW/cm^2	2.15	2.80	4.00	8.22
Irradiation Time/min	A_t /A_0			
0	1	1	1	1
10	0.93	0.82	0.73	0.45
20	0.81	0.65	0.56	0.19
30	0.69	0.55	0.43	0.11
40	0.55	0.46	0.34	0.10
50	0.51	0.39	0.31	0.09
60	0.46	0.37	0.29	0.08

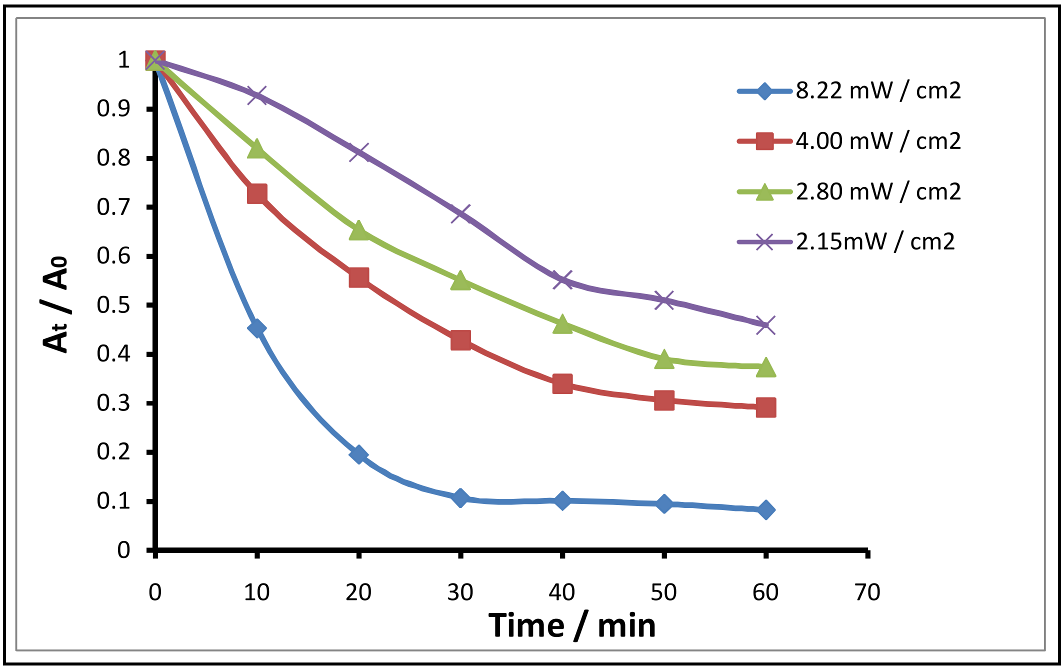

Figure 10 : The change of (A / A_0)with irradiation time at different light intensity with 0.12 g/100ml coupled TiO_2-Co_2O_3 on photocatalytic degradation of malachite green .

From the experiments photo catalytic degradation efficiency which is equal to 91.82 %. The results of the change in photocatalytic degradation efficiency (P.D.E) with light intensity plotted in figure 11 .

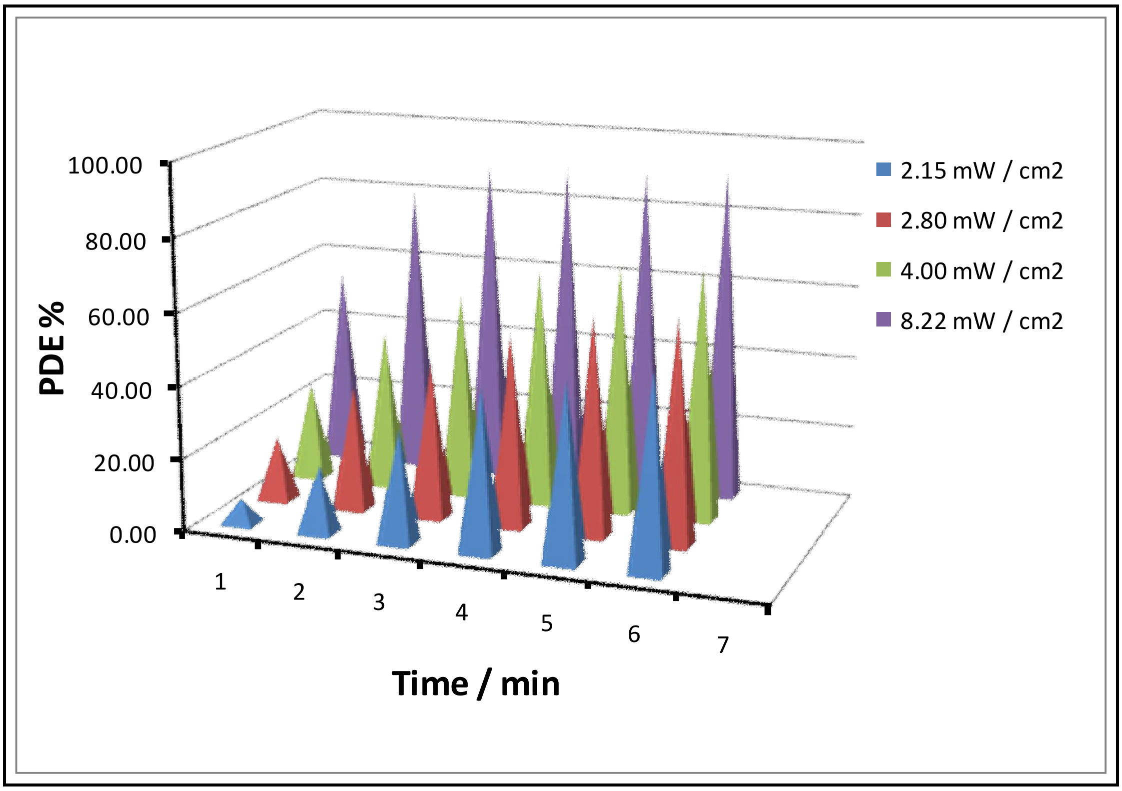

Figure 11 : The change of Photocatalytic Degradation Efficiency with irradiation time of different light intensity.

Conclusion

1. In the absence of coupled semiconductor titanium dioxide and cobalt oxide there is no degradation occur .
2. Malachite green has been successfully degraded in presence of the catalyst and the light.
3. The best condition for Photcatalytic degradation of malachite green equal 0.12 g /100ml mass of coupled semiconductor titanium dioxide and cobalt oxide and 1 ppm concentration of malachite green and 8.22 mW/cm^2 .

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