

Photocatalytic Degradation of Rhodamine b using Titanium Dioxide

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Accepted 10 Jan 2015, Available online 01 Feb 2015, Vol.3 (Jan/Feb 2015 issue)

Abstract

This research includes the study of Photocatalytic degradation of Rhodamine b using Titanium dioxide anatas , which is achieved by the irradiation of suspended solution consists of different concentration of Rhodamine b with 0.13gm/100ml of mixed metal oxide semiconductor titanium dioxide anatas by using mercury lamp 160 Watts from external source inside a pyrex photoreaction cell of 100 ml at room temperature 298 K. In order to study the effect of metal oxide Titanium dioxide anatas in Photocatalytic degradation of Rhodamine b, several experiments were carried out in various conditions to attain the best Photocatalytic degradation of Rhodamine b. These experiments include the effect of hydrogen per oxide , the effect of temperature. The products was studied by using UV-Vis spectrophotometer.

Keywords: Photocatalytic degradation , Rhodamine b .Zinc oxide , decolorization .

1. Introduction

In recent years, environmental contaminations has been major problem due to excess use of various dyes in the textile industry, this led to polluted the surface water and groundwater by releasing the toxic and colored effluents[1,2].

Many manner employed to wastewater treatment, one of them advanced oxide processes (AOP) method .It has attracted public concern for its ability to convert the pollutants into the harmless substances directly in the waste water[3].

Basically these method starting with generation of strong oxidizing agents such as hydroxyl radicals ($\cdot\text{OH}$) ($E = 2.8 \text{ V}$) ,this reactive radical capable of mineralizing organic pollutants [4].

Heterogeneous photo-catalytic oxidation, one of the Advanced Oxidation Processes, used to treated the organic pollutants to CO_2 and inorganic acids [5] . The most important metal oxide semiconductor used in this method was titanium dioxide as a catalyst best photo catalyst and has the ability to de-toxicate water from a number of organic and _complete destruction of dyes pollutants such as pesticides because titanium dioxide 1- Non toxic , 2- High photo- and Thermal-stability and , 3- Low cost [6] .

When titanium dioxide semiconductor irradiated using uv light with energy equal to or greater than the band gap(3.2 eV) [7] , electrons are promoted from the valence band to the conduction band of the titanium dioxide semiconducting oxide to give electron-hole pairs. The valence band hole (h^+) potential is positive enough to

generate hydroxyl radicals at the surface. Also, the conduction band electron (e^-) is negative enough to reduce the oxygen molecules, present in the solution, which in turn leads to the generation of another series of hydroxyl radicals [8,9] as shown in figure (1) :

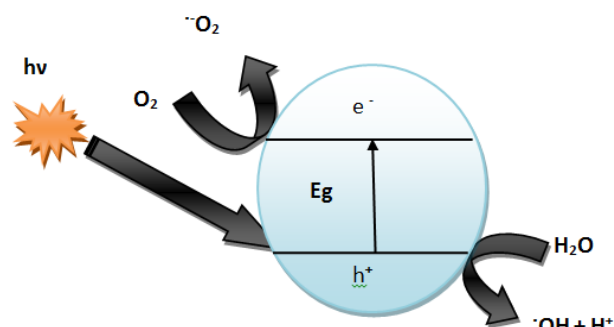


Fig.1: General mechanism of the photocatalysis on TiO_2 particle

2. Materials and Methods

2.1 Chemicals

- 1-Titanium dioxide anatas (TiO_2) : purity (99%) , particle size (100) mesh, supplied by Fluka AG.
- 2 – Rhodamine b supplied by sigma – Aldrich .

2.2 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 [10]. Schematic diagram of photochemical reaction as shown in figure (2):

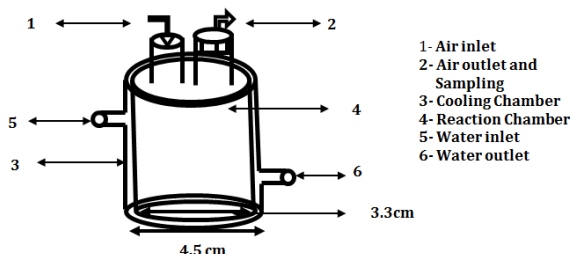


Fig.2: Main parts of the photocatalytic cell used in Photocatalytic degradation of Rohdamine b

2.3 Irradiation System

A block diagram of photolysis apparatus is shown in figure (3) a 160W mercury lamp source is a focusing fitted with a focusing lens to ensure parallel beam of light [11].

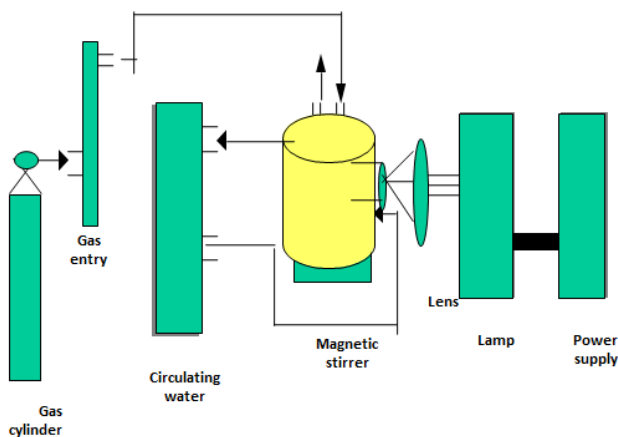


Fig. 3: Schematic diagram of the experimental apparatus

3. Result and Discussion

Effect of different parameters on Photocatalytic degradation of Rhodamine b

3.1. The Effect of titanium dioxide mass on photo catalytic degradation of Rohdamine b

The effect of mass of titanium dioxide on Photocatalytic degradation of Rohdamine b , was studied using 1 ppm of Rohdamine b, flow rate of air 10ml/min, room temperature 298 K.

Table (1) and Figure (4) represent photo catalytic degradation processes of Rohdamine b at different loaded mass of titanium dioxide. Photocatalytic

degradation of Rohdamine b. Gradually increases as the masses of titanium dioxide increases until reach to the mass titanium dioxide 0.13gm/100ml , then gradually decreases . When the mass of titanium dioxide equal 0.13 gm /100ml the semiconductor titanium dioxide can be provide the highest absorption of light. The decrease in the efficiency of phodegradation process at the masses of titanium dioxide higher than 0.13 gm /100ml due to the light absorption will be limited only to the first layers of Rohdamine b and the other layers of solution do not receive light photons. Moreover light scattering at high titanium dioxide loading , this lead to decrease the photon intensity, so 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]. At the loading mass of titanium dioxide below the optimum value 0.13 gm /100 ml the rate of photodegradation of Rohdamine b also decrease due to the quantity of mass of titanium dioxide decrease that mean the surface area decrease which lead to decrease of light absorption of light by titanium dioxide which cause lower photodegradation rate of Rohdamine b.

Table 1 The change of A_t / A_0 with irradiation time using different masses of titanium dioxide

Catalyst mass gm /100 ml	0.01	0.06	0.13	0.50	1.00
Irradiation Time/min	A_t / A_0				
0	1	1	1	1	1
10	0.64	0.76	0.45	0.84	0.89
20	0.44	0.53	0.19	0.68	0.76
30	0.28	0.36	0.11	0.52	0.62
40	0.19	0.24	0.10	0.38	0.48
50	0.14	0.20	0.09	0.30	0.44
60	0.11	0.16	0.08	0.27	0.43

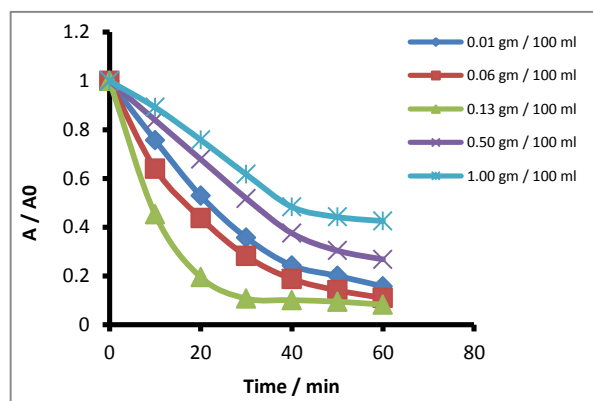


Fig. 4: The effect masses of titanium dioxide on Photocatalytic degradation of Rohdamine b

The results illustrated in Table 2 and plotted in figure 5 which shows the pseudo first order reaction curve for various catalyst concentration according to Langmuir Hinshelwood relationship.

The mass of TiO_2 0.13 gm/100 ml gives the optimum photodegradation efficiency which is equal to 91.82%. The results of the change in photodegradation efficiency (P.D.E) with catalyst concentration plotted in figure 6.

Table 2 The change of $\ln (A_0 / A)$ with irradiation time using different masses of titanium dioxide

Catalyst mass gm /100 ml	0.01	0.06	0.13	0.50	1.00
Irradiation Time/min	$\ln (A_0 / A)$				
0	0	0	0	0	0
10	0.34	0.42	0.78	0.26	0.19
20	0.56	0.74	1.37	0.43	0.33
30	0.81	1.08	2.13	0.63	0.49

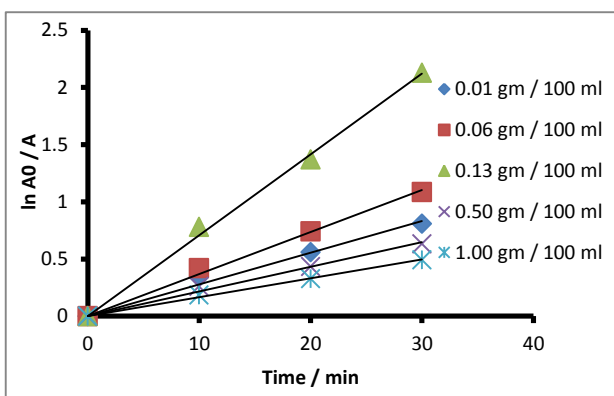


Fig.5 : The change of $\ln (A_0 / A)$ with irradiation time at different masses of TiO_2 on photocatalytic degradation of Rhodamine b

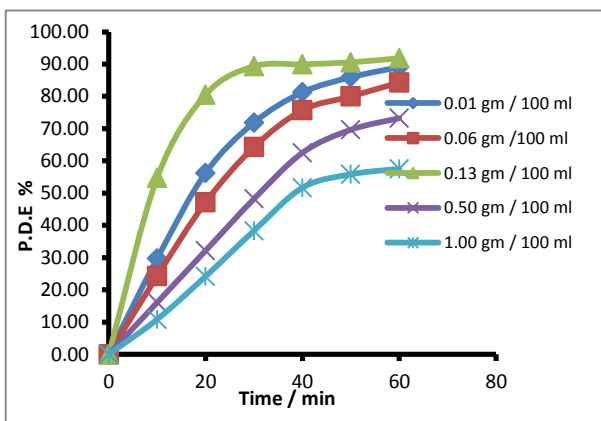


Fig.6 : The change of Photocatalytic Degradation Efficiency with irradiation time of different types of catalyst

3.2 The Effect of initial Rhodamine b concentration on photo catalytic degradation processes

A series of experiments have been done, the effect of change initial (1 – 10 ppm) on photocatalytic degradation process of Rhodamine b was studied using

0.13gm / 100 ml , the light intensity equal to 8.22 mW/cm^2 , and temperature equal to 298 K. The results are listed in Table 3 and plotted in figure 7. It has been observed that the rate of photocatalytic degradation gradually decreases with the increasing of initial Rhodamine b concentration. This behavior could be explained , the concentration 1ppm was the optimum concentration to cover the largest area of the titanium dioxide particles , therefore absorbed maximum exciting photons to generate higher concentration of the activated titanium dioxide semiconductor . Another reason for this behavior is the strong absorption of light by the Rhodamine b in the sample which contain high concentration that 1 ppm , Rhodamine b on 0.13 gm /100ml of titanium dioxide . The excess of Rhodamine b prevent the penetration of light through the successive layers of Rhodamine b on the titanium dioxide surface is weak to generate the required excited state of the Rhodamine b adsorbed on titanium dioxide [14,15] . The concentration of Rhodamine b 1ppm gives the optimum photodegradation efficiency which is equal to 91.82%. The results of the change in photocatalytic degradation efficiency (P.D.E) with concentration of Rhodamine b plotted in figure 9 .

Table3. The change of A_t / A_0 with irradiation time using different concentration of Rhodamine b

Concentration of Rhodamine b / ppm	1	2	3	5	10
Irradiation Time/min	A_t / A_0				
0	1.00	1.00	1.00	1.00	1.00
10	0.45	0.60	0.78	0.83	0.91
20	0.19	0.39	0.52	0.63	0.76
30	0.11	0.27	0.37	0.49	0.63
40	0.10	0.23	0.27	0.40	0.58
50	0.09	0.19	0.24	0.29	0.51
60	0.08	0.16	0.18	0.22	0.45

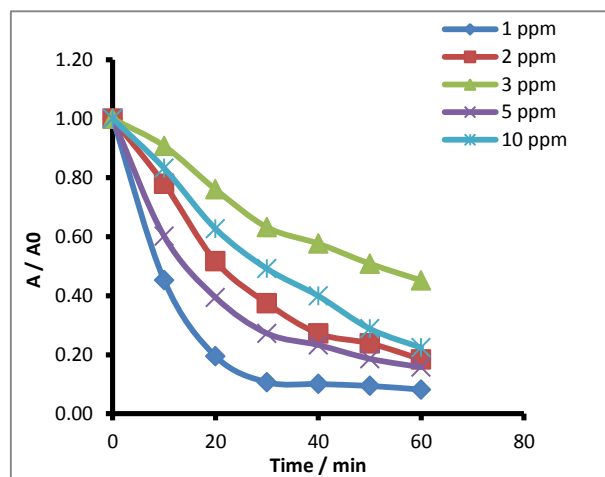


Fig.7: The change of (A / A_0) with irradiation time at concentration of Rhodamine b

Table 4 The change of $\ln (A_0 / A)$ with irradiation time using different Concentration of Rohdamine b

Concentration of Rohdamine b / ppm	1	2	3	5	10
Irradiation Time/min	$\ln (A_0 / A)$				
0	0.00	0.00	0.00	0.00	0.00
10	0.79	0.51	0.25	0.18	0.10
20	1.63	0.93	0.66	0.47	0.27
30	2.24	1.30	0.98	0.71	0.46

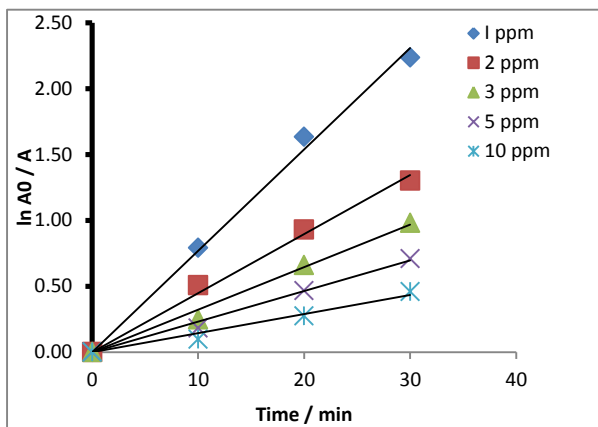


Fig.8: The change of $\ln (A_0 / A)$ with irradiation time at different concentration of Rohdamine b

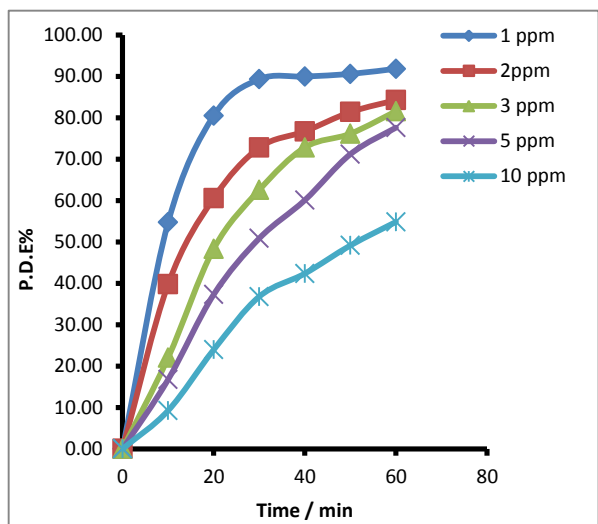


Fig.9: The change of Photocatalytic Degradation Efficiency with irradiation time of different types of concentration of Rohdamie b

3.3. Effect of light intensity on photocatalytic degradation process of Rohdamine b

A series of experiment were carry out to study the effect of light intensity rang (2.15 – 8.22) mW/cm^2 from high mercury lamp 160 watts, all experiments was studied using optimum condition ,the weight of loaded of titanium dioxide 0.13gm / 100 ml and the initial

concentration of Rohdamine b 1ppm, with flow rate of air bubbling is kept constant at 10ml/min, at room temperature 298K .

Table 5 and figure 10, illustrate the effect of light intensity on the photocatalytic degradation of Rohdamine b. The results indicate that the photocatalytic degradation of Rohdamine b increases with the increase of light intensity, the maximum value of light intensity 8.22 mW/cm^2 . In general the used lamp production photons ,this photons increase electrons transfer from valance band to conduction band in the titanium dioxide this process lead to increase photocatalytic process of Rohdamine b [16,17].

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	1.00
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

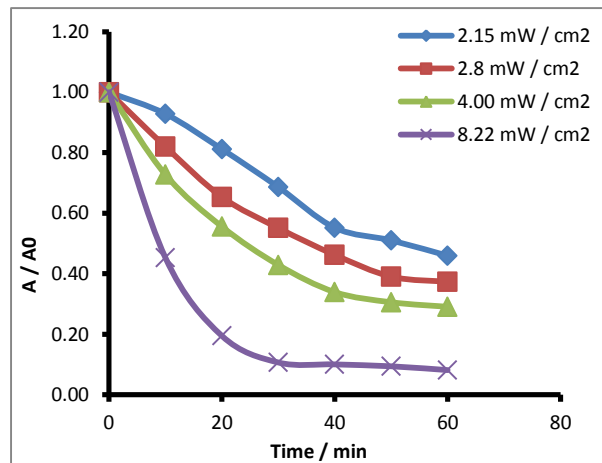


Fig.10: The change of (A / A_0) with irradiation time at different light intensity with 0.13 gm/100ml TiO_2 anatase on photocatalytic degradation of Rhodamine b

Table 6 The change of $\ln (A_0 / A)$ with irradiation time using different light intensity

Light intensity/ mW/cm^2	21.5	2.80	4.00	8.22
Irradiation Time/min	$\ln (A_0 / A)$			
0	0.00	0.00	0.00	0.00
10	0.07	0.20	0.32	0.79
20	0.21	0.43	0.59	1.63
30	0.38	0.60	0.85	2.24

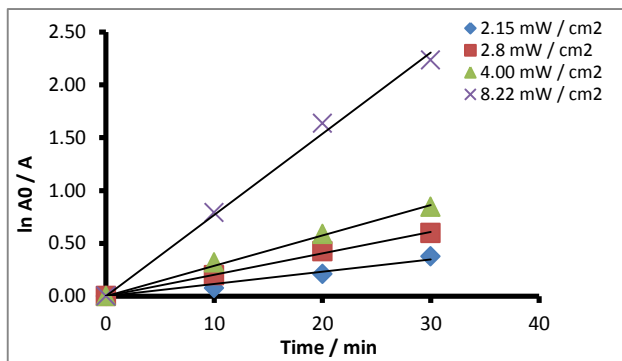


Fig.11: The change of $\ln (A_0 / A)$ with irradiation time at different light intensity

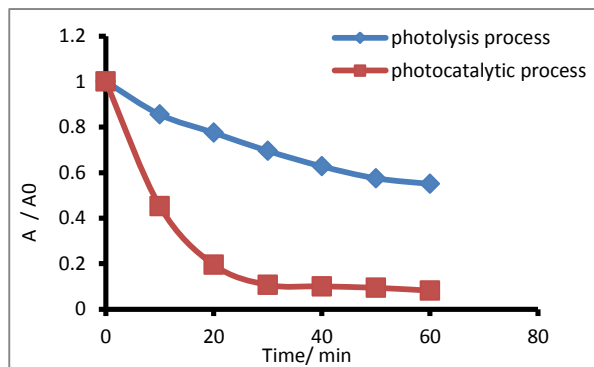


Fig.13 : The change of (A / A_0) with irradiation time for Photolysis process and Photocatalytic process

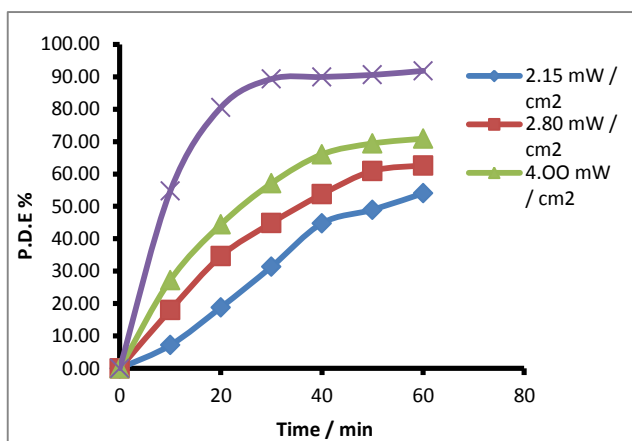


Fig.12: The change of Photocatalytic Degradation Efficiency with irradiation time of different light intensity

3.4. Comparison between photolysis process and photocatalytic process of photocatalytic degradation of Rhodamine b

Different experiments were carried out using photolysis process and photocatalytic degradation of rohdamine b with optimum condition ,were mass of TiO_2 0.13 gm / 100 ml ,1ppm of Rohdamine b ,and 298 k room temperature. Photolysis process experiments were carried out in the absence of the catalyst and the existence of the UV light. The results are shown in Table 7 and plotted in figure 13 show that the photolysis of Rohdamine b is under UV(A) light and photocatalytic degradation process.

Table 7 The change of A_t / A_0 with irradiation time for Photolysis process and Photocatalytic process

Irradiation Time/min	Photolysis process	Photocatalytic process
	A_t / A_0	
0	1	1
10	0.86	0.45
20	0.78	0.19
30	0.7	0.11
40	0.63	0.1
50	0.58	0.09
60	0.55	0.08

From theTable 7and figure 13 clear that the photocatalytic degradation of Rohdamine b using photocatalytic process more than photolysis process because the presence of TiO_2 catalyst lead to increases of photocatalytic degradation of Rohdamine b .

3.5 Effect of temperature on photocatalytic degradation of Rohdamine b

A series of experiments were carried out to study the effect of temperature on Photocatalytic degradation rate of Rohdamine b using titanium dioxide suspension at different temperature ranging from (278 – 303 k) [18,19]. Table 8 and figure 14 , shows the effect of temperature on the photo catalytic degradation rate of Rohdamine b at fixed initial concentration 1 ppm and 0.13 gm/100ml of titanium dioxide as catalyst . Figure 14 indicate that the photo catalytic degradation rate of Rohdamine b increases with increase of temperature increase temperature lead to increase photocatalytic degradation of Rohdamine b because increase temperature cause to increase generate free radicals and this lead to decrease recombination process. Figure 16 indicat that the percentage efficiency of degradation rohdamine b dye increases with increase of temperature equal (91.82%) . From the figure 17, the amount of activation energy 29.26 J / mole using Arrhenius equation.

Table 8 The change of A_t / A_0 with irradiation time using different Temperature

Temperature / K	278	283	293	303
Irradiation Time/min	A_t / A_0			
0	1.00	1.01	1.00	1.00
10	0.74	0.66	0.61	0.45
20	0.56	0.49	0.44	0.19
30	0.47	0.42	0.26	0.11
40	0.44	0.35	0.23	0.10
50	0.41	0.29	0.18	0.09
60	0.38	0.28	0.15	0.08

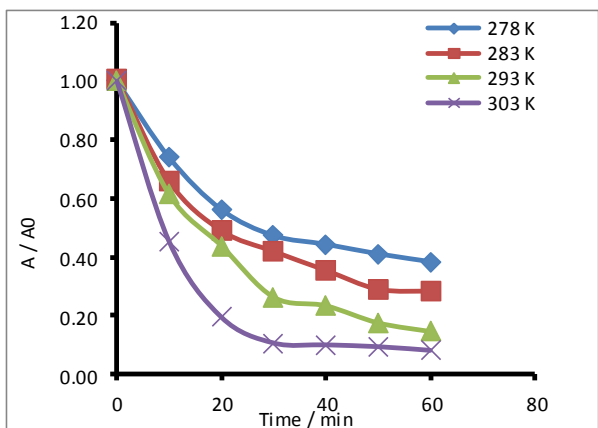


Fig.14: The change of (A / A₀)with irradiation time at different temperature for photo catalytic degradation rate of Rohdamine b by using titanium dioxide

Table 9 The change of ln (A₀ / A) with irradiation time using different temperature

Temperature / K	278	283	293	303
Irradiation Time/min	ln (A ₀ / A)			
0	0	0	0	0
10	0.3	0.42	0.49	0.79
20	0.58	0.71	0.82	1.63
30	0.75	0.87	1.34	2.24

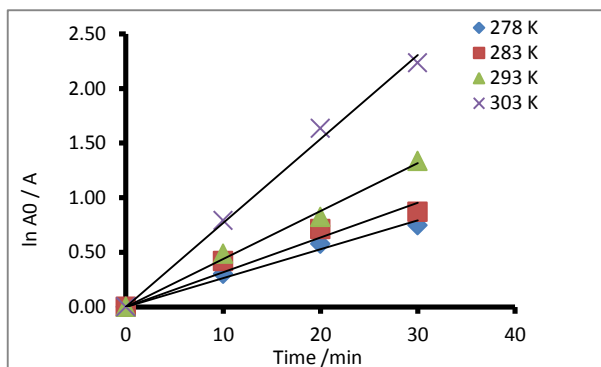


Fig.15 : The change of ln (A₀ / A)with irradiation time at different temperature

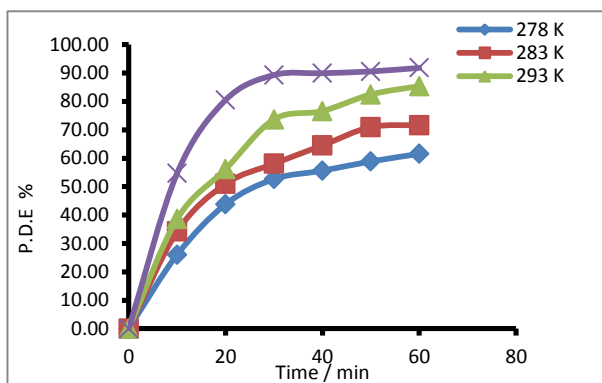


Fig.16: The change of P.D.E with irradiation time of different temperature

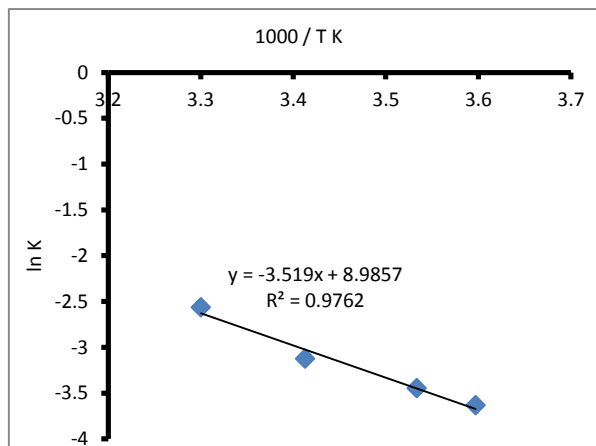


Fig.17: The change of ln K against 1000/T

Conclusion

1. The compound has been not degraded in case of absent 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 Rohdamine b equal 0.13 gm / 100ml mass of titanium dioxide and 1 ppm concentration of Rohdamine b and 8.22 mW/cm².
4. The activation energy = 29.26 J/mole.
- 5.The percentage efficiency of degradation rohdamine b equal 91.82% .

Acknowledgments

Insincerely thank for the university of Babylon, College of Science for Women, for providing the necessary infrastructural facilities during my research.

References

[1] Y. Su, Y. Yang, H. Zhang, Y. Xie, Z. Wu, Y. Jiang, N. Fukata, Y. Bando and Z. Wang, Nanotechnology, Vol. 24, pp6, 2013.
 [2] L. Sopyan, N. Hafizah, P. Jamal, Indian Journal of chemical Technology, Vol. 18, 2011, pp. 263-270.
 [3] C. Fernández, M. Callao, M. Larrechi, Talanta, Vol. 117, pp75-80, 2013.
 [4] Z. Lide, and M. Jimei, Nanophase Material and Nanostructure, Vol. 1, p140, 2001.
 [5] M. Mehra, and T. Sharma, Advances in Applied Science Research, Vol. 3, No. 2, pp849-853, 2012.
 [6] A. El Yadini, B. Marouane, A. Ahmido, P. Dunlop, J. Byrne, M. EL Azzouzi, S. EL Hajjaji, J. Mater. Environ. Sci., Vol. 4, No. 6, pp973-980, 2013.
 [7] P. Wilhelm, D. Stephan, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 185, pp 19-25, 2007.
 [8] D. Zhang, H. Liu, Sh. Han, W. Piao, Journal of Industrial and Engineering Chemistry, Vol. 19, pp 1838-1844, 2013.
 [9] S. Chen, M. Zhao, and Y. Tao, Taiyangneng xuebao, Vol. 16, pp234-239, 1995.

- [10] F. Gassim, A. Alkhateeb, and F. Hussein, *Desalination*, 2007, Vol.209,pp 342-349,2007.
- [11] N. Madhusudhana, K. Yogendra, and M. Mahadevan, *Res.J.Chem.Sci*, Vol. 2,pp 72-77,2012.
- [12] S. Kavitha, and P. Palanisamy, *International Journal of Civil and Environmental Engineering*,Vol. 3,No. 1, 2011.
- [13] Y.Chen, K.Zhang, and Y.Zuo, *Science of the total Environment*, Vol. 463,pp 802-809,2013.
- [14] J. Niu, L. Zhang, Y. Li, J. Zhao, S. Lv, and K. Xiao, *Journal of Environmental Sciences*,Vol.25,pp 1098–1106,2013.
- [15] B.Pare , S.B.Jonnalagadda , H.Tomar , P.Singh , and V. Bhagwat *Desalination*,Vol.232,pp 80-20,2008.
- [16] S. Alijani, M. Vaez, and A. Moghaddam, *International Journal of Environmental Science and Development*, Vol. 5, No. 1, 2014 .
- [17] O . Kmahadwad, P . Parikh, R . Jasra, and C. Patil, *Bull. Mater. Sci.*, Vol. 34, No. 3, p. 551–556, 2011.
- [18] Y. Tanga, and G. Smith, *Journal of Cultural Heritage*, Vol.14,pp 464- 470,2013.
- [19] V. Sanchez, J. Perez, R. Suarez, and I. Hndez, *Revista Mexicana de Ingeniería Química*, Vol. 11,pp 121-131,2012.