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# Photocatalytic decolorization of dispersive yellow 42 dye in ZnO/UV-A System

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**Abstract:**

This work is focused on the photocatalytic decolorization of dispersive yellow 42 dye as textile dye. The decolorization of this dye was done in present the suspension solution of the commercial ZnO and the artificial light (high pressure mercury lamp) type 125 Watt as UV-A source at light intensity equal to 1.48 x $10^{-7}$ Ensien. $s^{-1}$. The kinetic study for photocatalytic decolorization process of this dye was obeyed to pseudo-first order. The optimal variations for the decolorization of the studied dye at 25 mg/L were found. The best dose of ZnO is equal to 300 mg/100 mL and the maximum value of the initial pH of an aqueous solution is 7.7. Moreover, the effect of temperature was studied; and found that the photoreaction was endothermic and non-spontaneous. The apparent activation energy is small value, that make the photoreaction of this dye is fast.

**الخلاصة:**

ركز هذا العمل على الازالة اللونية المحفزة ضوئياً للصبغة المنتشرة الصفراء ٤٢ باعتبارها صبغة للنسيج. انجزت عملية الازالة اللونية لهذه الصبغة بوجود محلول عالق من ZnO التجاري بوجود ضوء اصطناعي (مصباح زئبقي عالي الضغط ) ذي قدرة ١٢٥ واط كمصدر للاشعة فوق البنفسجية نوع A وبشدة 1.48 x $10^{-7}$ انشتاين لكل ثانية. من خلال الدراسة الحركية لعملية الازالة اللونية المحفزة ضوئيا يتضح انها تطيع المرتبة الاولى الكاذبة. تم ايجاد الظروف الفضلى لعملية الازالة اللونية لهذه الصبغة عند تركيز 25 ملغم\ لتر. اذ ان افضل كمية للـ ZnO كانت مساوية الى ٣٠٠ ملغم\ ١٠٠ مللتر، واعلى قيمة عند دالة حامضية ابتدائية للمحلول المائي مساوية الى ٧.٧. علاوة على ذلك، تم دراسة تاثير درجة الحرارة، ووجد ان التفاعل الضوئي ماص للحرارة وغير تلقائي. كما وجد بان قيمة طاقة التنشيط الظاهرية للتفاعل الضوئي هي قيمة قليلة مما جعل التفاعل سريع.

Keywords: Dispersive yellow 42 dye, textile dye, ZnO, decolorization, wastewater.

## Introduction:

The textile industry is deemed as one of the oldest and wide used in world. This industry is essential depended upon dyes that used to dying the textile; hence, the thousand tons from the wastewater will produce as effluents emanating that often contain large amounts of colored organic pollutions. That will affect directly or indirectly on human healthy. In the manner, more than 3600 individual textile dyes manufactured to use in dyeing and printing, so, that will need to use more than 8000 chemicals in various processes during produced the textile and the major types of used dye in these processes are disperse dyes, vat dyes, sulphur dyes and reactive dyes [1,2].
In the last few decades, many research attentions focused on the treatment methods of wastewater such as photocatalysis [3-8], Solar photocatalysis [9-11] adsorption [12-14], biosorption [15], biodegradation [16-18], fenton and photofenton[19,20], solar photofenton [21] and Electrochemical degradation [22,23].
Disperse dyes are the wide used in textile industry, and they are mostly insoluble or slightly soluble in water, non-ionic chemicals, predominantly applied on polyester and although they have a poor wet-fastness properties but they applied on nylon, cellulose acetate and acrylic fibers[24-27]. In the 1970s, by depended on their sublimation fastness and dyeing properties, the ICI developed a new discerning method for the classification of these dyes to Class A to Class D [27]. The Class A is a small relative molecular size and low sublimation fastness like disperse orange 3 dye, while the Class D is revers of Class A like disperse blue 27. But, Class B (like disperse red 19 dye) and Class C (like disperse yellow 42 dye) are had properties between these two extremes [26].
This current work aims to investigate the photocatalytic decolorization reaction of 25 ppm of disperse yellow 42 dye as Class C by studying of the effect of loading of ZnO, initial pH of dye solution and temperature on the decolorization process.

## Material and Methods

All the used chemicals were employed without purification. Commercial zinc oxide was supplied by Fluka. Dispersive yellow 42 dye ($C_{18}H_{15}N_3O_4S$) has IUPAC name 4-anilino-3-nitro-N-phenylbenzenesulphonamide, molecular weight 369.40 g/mol; $\lambda_{max}$ 488 nm, this dye called as nitroarylamino disperse dyes (nitrodiphenylamine dye) and supplied by Hilla textile factory.

All the photocatalytic experiments were done inside a photo reactor (figure 1) that contains of source for irradiation as UV-A lamp type Philips (a), Pyrex glass beaker (b) as container of photoreaction, Teflon bar (c) and magnetic stirrer (d) used to mix a solution, fan (e) used to fix the temperature of reactor, and wooden box (f) to prevent the escape of harmful light[4,6].

(a)

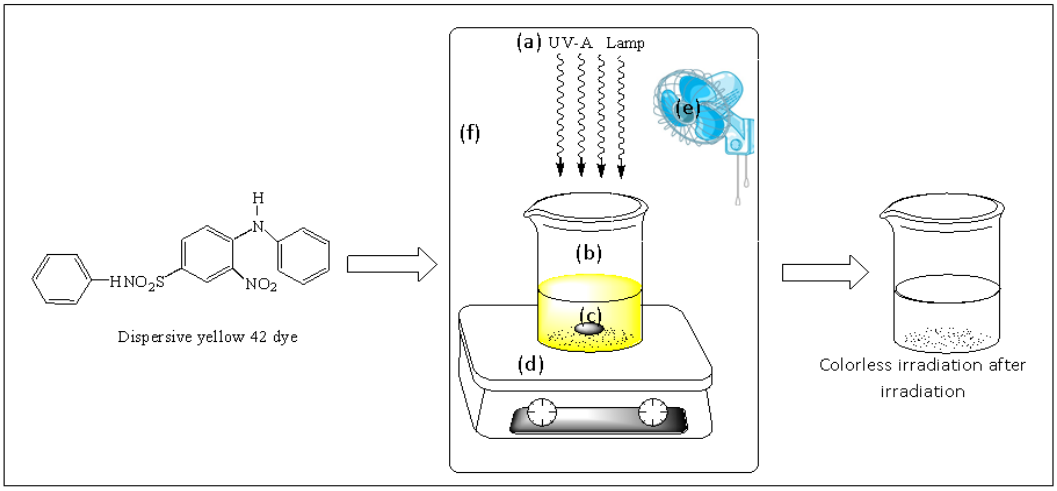



Figure1. Photo reactor setup.

100 mL from 25 ppm of dispersive yellow 42 dye was magnetically mingled with a required dose of ZnO to maintain even distribution of suspension solution in photo reactor. Before the illumination process, the dark reaction was done with stirring for 30 min to ensure contacting all the active sites of catalyst with the dye solution [6, 7, 28]. And then, the solution was exposed to125-Watt high pressure mercury lamp as the UV-A light source at light intensity equal to 1.48 x $10^{-7}$ Ens. $s^{-1}$ which calculated using the chemical actinometric solution [29].This process will lead to generate enough amount of hydroxyl radical that important to start the photoreaction [3,7].

In all runs of photocatalytic reaction, certain mL of mixture was eliminated from the bulk solution at specific time's gradient; and then centrifuged at 15 minutes to separate a filter solution. The produced filter solution was carefully transferred using a syringe to new plastic test tube and centrifuged again at 10 minutes to remove the fine particles of ZnO from this solution. After these steps, the residual concentration of reactive yellow 42 dye was measured at 488 nm by using (optima) UV-visible spectrophotometer.

The apparent rate constant ($k_{app.}$) for this reaction was conducted using the following equation [3, 5, 30]

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app} .t \qquad (1)$$

whereas: $C_o$ is an initial concentration of dispersive yellow 42 dye at (dark reaction). $C_t$ is a concentration of the same studied dye at t time of illumination.

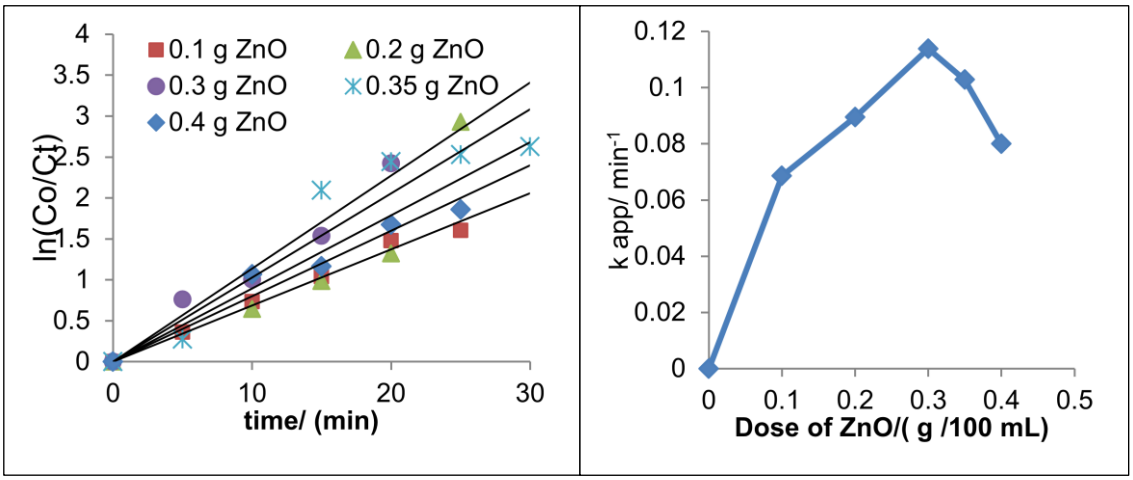
The % Efficiency of decolourization for dispersive yellow 42 dye (% E) was calculated using the following relationship [31]:

$$\%\ Effeciency = \left(\frac{C_o - C_t}{C_o}\right) x100 \qquad (2)$$

## Results and Discussion

### 1. Effect of ZnO dose

The effect of ZnO dose on photocatalytic decolorization of dispersive yellow 42 dye from aqueous solution was investigated in figures 2 and 3.




a b

Figure 2: Effect of ZnO dosage on decolourization of 25 ppm from dispersive yellow 42 dye, at ZnO dosage (100-400) mg/100 mL, pH 7.7, Temp. 311.15 K, UV light intensity 1.48 x $10^{-7}$ Ensien. $s^{-1}$). (a) ln (Co/C) vs time and (b) $k_{app}$vs ZnO dose.

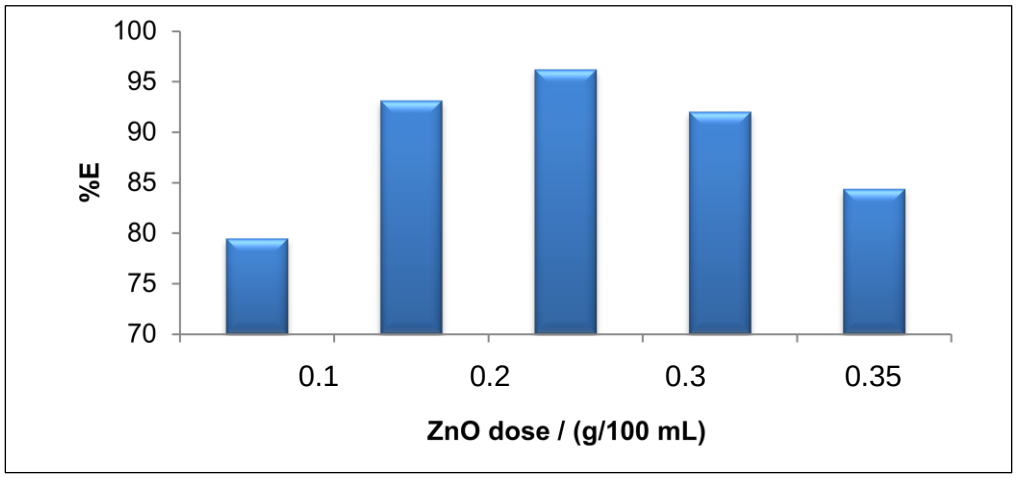



Figure 3: Effect of ZnO dosage on %E for decolourization of 25 ppm from dispersive yellow 42 dye. at ZnO dosage (100-400) mg/100 mL, pH 7.7, Temp. 311.15 K and UV light intensity 1.48 x $10^{-7}$ Ensien. $s^{-1}$).

The results clearly show that the decolorization of DY42 dye at 488 nm gradually increases with increasing irradiation time, and the maximum

apparent rate of reaction was reached at 300 mg/100 mL at % efficiency equal to 96.2%. However, on further rise in ZnO dose that sharply decreases the % efficiency to 84.3% at 400 mg/100 mL, that due to the aggregation of photocatalyst particle that will depress the contact area between the solution of dye and the photocatalyst. In other words, this rise will increase the turbidity of solution, and reduce the activity of photocatalyst that called screen effect [32-36].

## 2. Effect of initial pH

The results in figures 4 and 5 indicate that the pH of dye solution is very important parameter to accelerate the photocatalytic decolorization of dye. The rise the initial pH of dye solution from 3 to 7.7 that increase the % efficiency of decolorization from % 81.8 to 96.2% in 25 min, then decline to % 92.1 at pH equal to 10. This change can be explained on the natural and the ability of ionization of dye, moreover, the surface state of photocatalyst that related to the net charge of photocatalyst surface in basic and acidic medium [36]. This implies that the acidic medium and basic medium lead to positively charge and negatively charge of photocatalyst, hence the activity will decline. This result was in agreement with the results in the references [6, 37, 38].

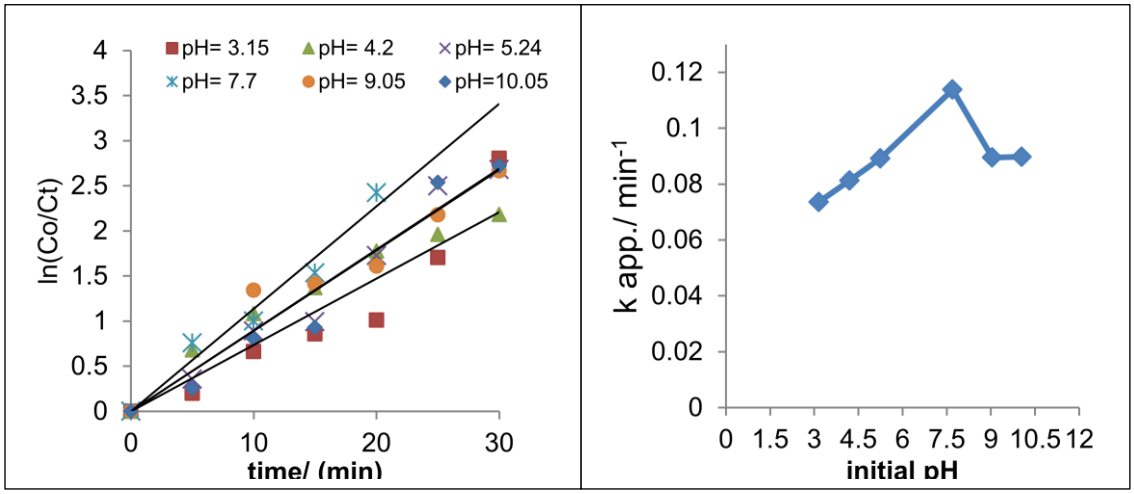



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Figure 4: Effect of initial pH on decolourization of 25 ppm from dispersive yellow 42 dye, at ZnO dosage (300) mg/100 mL, pH (3-10), Temp. 311.15 K, UV light intensity 1.48 x $10^{-7}$ Ensien. $s^{-1}$). (a) ln (Co/C) vs time and (b) $k_{app}$vs initial pH.

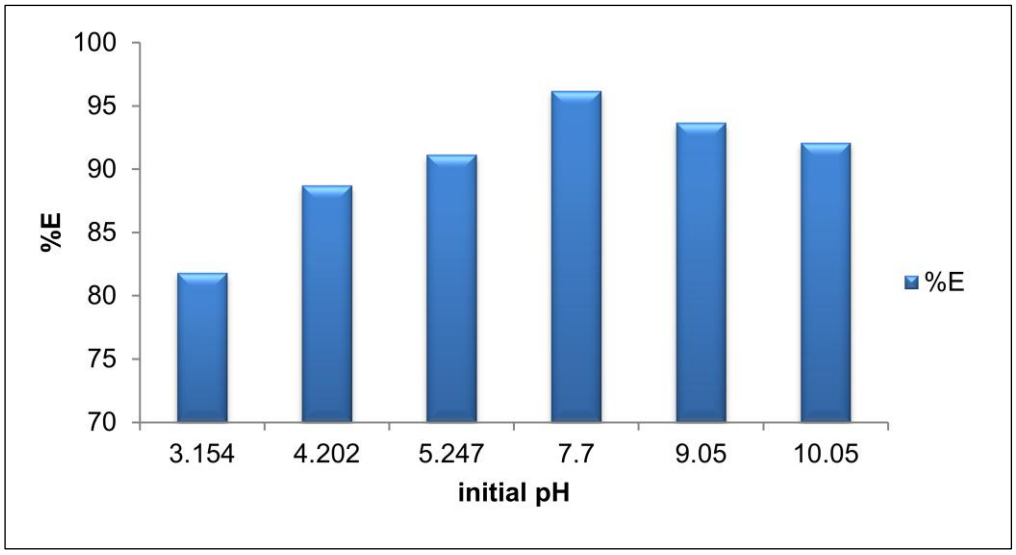



Figure 5: Effect of initial pH on %E for decolourization of 25 ppm from dispersive yellow 42 dye. at ZnO dosage 300 mg/100 mL, pH (3-10), Temp. 311.15 K and UV light intensity 1.48 x $10^{-7}$ Ensien. $s^{-1}$).

## 3. Effect of temperature

The photocatalytic reaction of dispersive yellow 42 dye was followed at four various temperatures in the range 283.15- 311.15 K employing 300 mg of ZnO under UV-A light. The essential goal of present article is describing a type, speed and is the reaction spontaneous or nonspontaneous of this photoreaction at calculated the apparent activation energy using Arrhenius equation and calculated the thermodynamic parameters using Eyring- Polanyi equation and Gibbs equation [6, 7, 39-41].

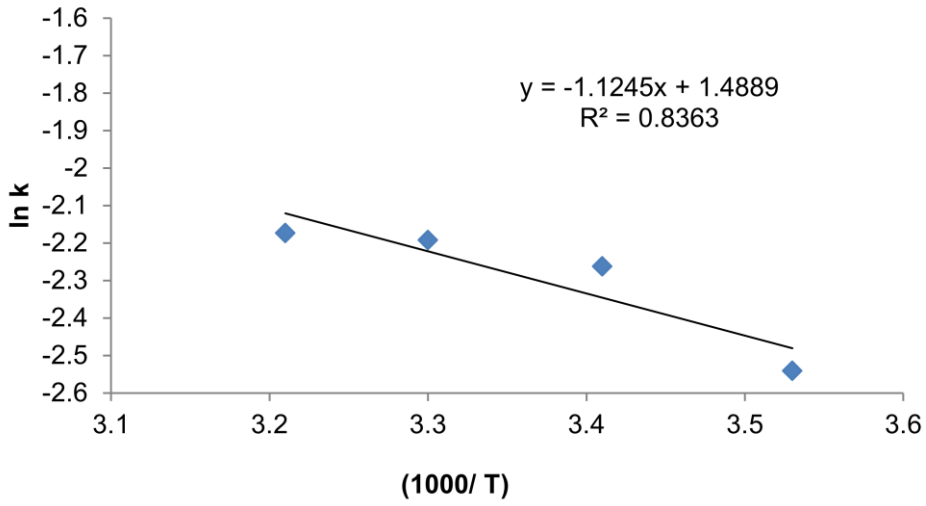



Figure 6: Arrhenius equation plot of (ln $K_{app}$) vs. 1/T. Conductions: Dispersive yellow 42 dye conc. = 25 ppm, ZnO dosage = 300 mg/100 mL, pH = 7.7, temperature = 283.15-311.15 K, UV light intensity = 1.48 x $10^{-7}$ Ens $.s^{-1}$.

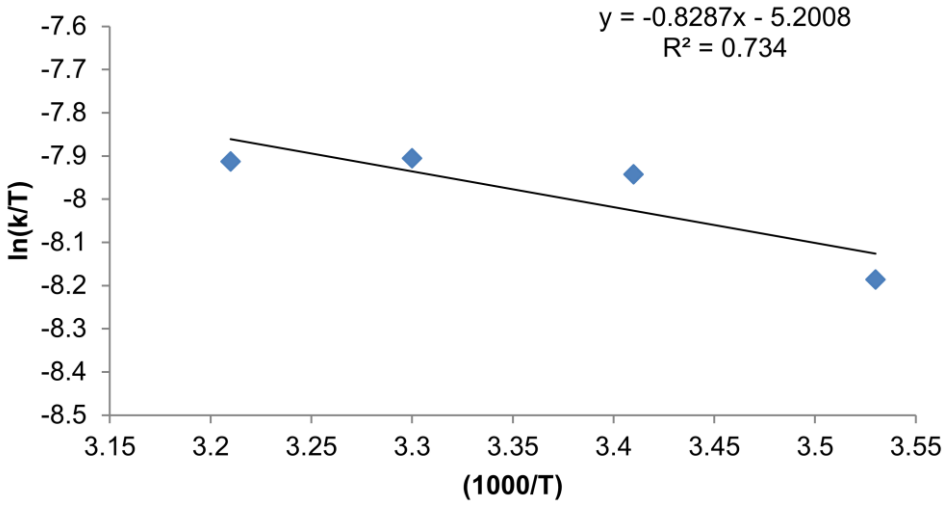



Figure 7: Eyring plot of (ln($K_{app}$/T)) vs.1/T. Conductions: Dispersive yellow 42 dye conc. = 25 ppm, ZnO dosage = 300 mg/100 mL, pH = 7.7, temperature = 283.15-311.15 K, UV light intensity = 1.48 x $10^{-7}$ Ens .$s^{-1}$

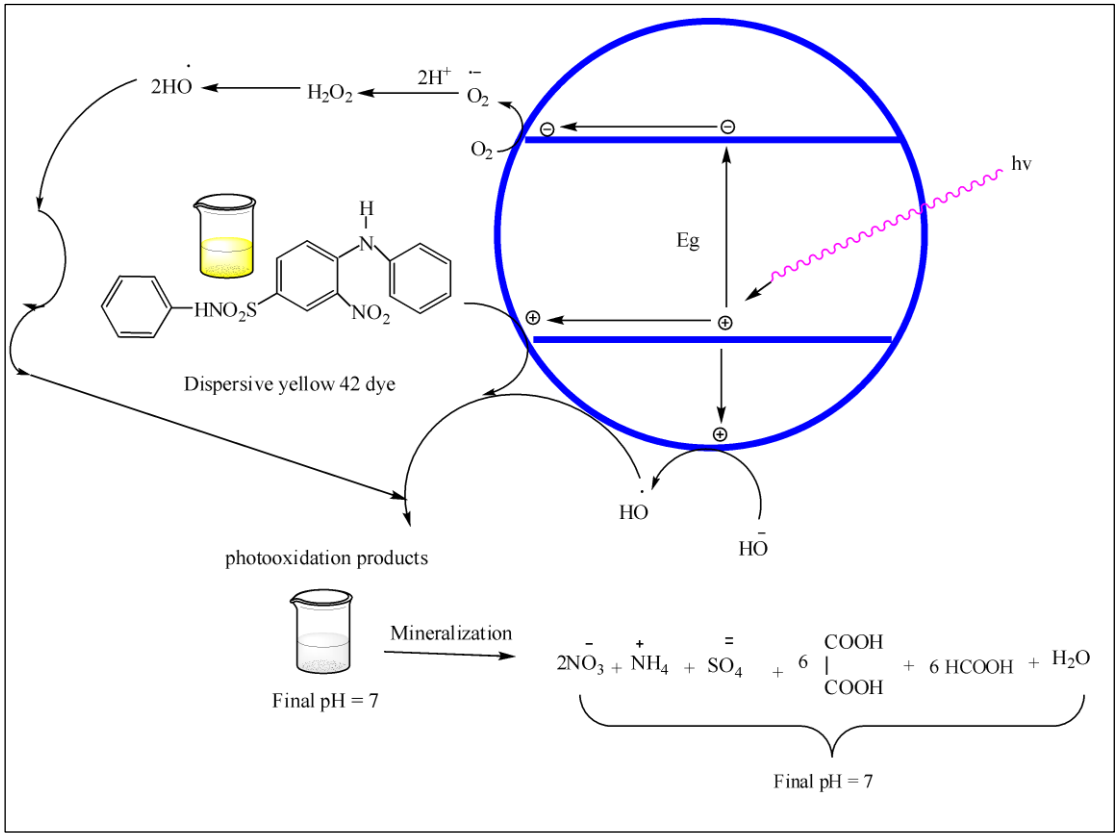
The rise in temperature would enhanced the photocatalytic, this reason can be ascribed to increase the creation of hydroxyl radical and depress the adsorption capacities associated with dye and dissolved oxygen [38, 42- 44]. Regression of the experimental data in figures 6 and 7 obtain that the photocatalytic decolorization of dispersive yellow 42 dye using ZnO is fast (low $E_a$), endothermic (positive $\Delta H^{\#}$), low randomness for the formed complex (negative $\Delta S^{\#}$) and nonspontaneous (positive $\Delta G^{\#}$). These results are summarized in table 1, and similar the results that reached by references [5-7, 41, 43]. The value of free energy changes $\Delta G^{\#}$ is positive, that confirming that the transition state between the dispersive yellow 42 dye molecules and hydroxyl radicals in intermediate state is being as a high solvated structure [6, 7, 45].

Table 1: The activation kinetic and thermodynamic parameters of the decoloration reaction of dispersive yellow 42 dye in present ZnO suspension under light type 125 watt -Hg lamp.

| $E_a$ kJ $mol^{-1}$ | $\Delta H^{\#}$ kJ $mol^{-1}$ | $\Delta S^{\#}$ kJ $mol^{-1}$ $K^{-1}$ | $\Delta G^{\#}_{311.15}$ kJ $mol^{-1}$ |
|---|---|---|---|
| 9.349 | 6.889 | -0.2407 | 81.783 |

## 4. Suggested Mechanism:

This mechanism depended upon the creating the electron- hole pairs, when UV-A light fill on the suspension solution ZnO with dye and in series steps that lead to produce hydroxyl radical as power for starting the photodecolorization of the color from dye in final pH equal to 7.While, with the continuous in the photocatalytic reaction that will produce $CO_2$ and $H_2O$ in mineralization process [5,6, 46,47].




Scheme 1. Schamitic diagram for suggested mechanism for decolorization of (Dispersive yellow 42 Dye/ZnO semiconductor/ UV-A light system).

## Conclusions:

In this project the photocatalytic decolorization process of dispersive yellow 42 dye using ZnO was estimated, by the following main conclusions:

1- The photoreaction is obey the pseud first order, when plot ln(Co/Ct) verse the time, that obtain linear line.
2- The percentage efficiency for decolorization of 25 ppm of dye was reached to 96% at 25 min at optimal conditions such as 300 mg/100ml, initial pH equal to 7.7.
3- The rise of reaction temperature that leads to enhance the photo reaction, and increase the speed of it. These results indicate the activation energy is small value and the reaction is endothermic.

## References:

[1] R. Kant, "Textile dyeing industry an environmental hazard ", *Natural Science*, vol.4, no.1, pp: 22-26, 2012. And reference there in.
[2] B.K. Handa, "Treatment and recycle of wastewater in industry". National Environmental Engineering Re-search Institute, Nagpur, p. 21, 65, 75, 76, 78, 82, 85, 94, 1991.

[3] M. Mashkour, A. Al-Kaim, L. Ahmed and F. Hussein, "Zinc Oxide Assisted Photocatalytic Decolourization of Reactive Red 2 Dye", *Int. J. Chem. Sci.*, vol. 9, no.3, 2011, pp. 969-979.

[4] S. Zuafuani and L. Ahmed, " Photocatalytic Decolourization of Direct Orange Dye by Zinc Oxide under Uv Irradiation ", *Int. J. Chem. Sci.,* vol. 13, no. 1, 2015, pp.187-196.

[5] E. S. Fathal and L. M. Ahmed, "Optimization of Photocatalytic Decolourization of Methyl Green Dye Using Commercial Zinc Oxide as catalyst ", *Journal of Kerbala University, Scientific* vol. 13, no.1, pp.53-63, 2015.

[6] L. M. Ahmed, F. T. Tawfeeq, M. H. Abed Al-Ameer, K. Abed Al-Hussein and A. R. Athaab, "Photo-degradation of Reactive Yellow 14 Dye (A Textile Dye) Employing ZnO as Photocatalyst", *Journal of Geoscience and Environment Protection,* vol. 4, pp: 34-44, 2016.

[7] M.T. Eesa, A. M. Juda and L. M. Ahmed,"Kinetic and Thermodynamic Study of the Photocatalytic Decolourization of Light Green SF Yellowish (Acid Green 5) Dye using Commercial Bulk Titania and Commercial Nanotitania", *International Journal of Science and Research IJSR*, vol. 5, no.11, pp.1495-1500, 2016.

[8] R. C. Meena Disha," A Study on Rate of Decolorization of Textile Azo Dye Direct red 5B by recently developed photocatalyst", International Journal of Scientific and Research Publications, vol. 3, no. 2, pp.1-4, 2013.

[9] A. Giwa, P.O. Nkeonye ,K.A. Bello, E.G. Kolawole and A.M.F. Oliveira Campos, "Solar Photocatalytic Degradation of Reactive Yellow 81 and Reactive Violet 1 in Aqueous Solution Containing Semiconductor Oxides", *International Journal of Applied Science and Technology,* vol. 2, no. 4, pp.90-105 2012.

[10] F. H. Hussein and T. A. Abass," Solar Photolysis and Photocatalytic Treatment of Textile Industrial Wastewater **",** *Int. J. Chem. Sci.,* vol. 8, no. 3, pp.1409-1420, 2010.

[11] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan,"Solar/UV-induced photocatalytic degradation of three commercial textile dyes", *Journal of Hazardous Materials*, B89, pp.303–317, 2002.

[12] S. Hashemian, B. Sadeghi, F. Mozafari, H. Salehifar and K. Salari, "Adsorption of Disperse of Yellow 42 onto Bentonite and Organo- Modified Bentonite by Tetra Butyl Ammonium Iodide (B-TBAI)", *Pol. J. Environ. Stud.*, vol. 22, no. 5, pp. 1363-1370, 2013.

[13] A. S. Gawade, A. K. Vanjara and M. R. Sawant, "Removal of Disperse Dyes from Water Using Surfactant Treated Alumina ", *Journal of the Chinese Chemical Society*, vol. 52, pp. 907-913, 2005.

[14] E. Porselvi and P. Krishnamoorthy, " Removal of Acid Yellow by Agricultural Waste ", *J. Mater. Environ. Sci.,* vol. 5, no. 2, pp. 408-415, 2014.

[15] S. Sharma, R. Saxena and G. Gaur, " Study of Removal Techniques for Azo Dyes by Biosorption: A Review ", *IOSR Journal of Applied Chemistry (IOSR-JAC),* vol. 7, no. 10, pp. 6-21, 2014.

[16] M. Siti Zuraida, C.R. Nurhaslina, and K. Halim Ku Hamid, "Removal of Synthetic Dyes from Wastewater by Using Bacteria, *Lactobacillus delbruckil*", *International Refereed Journal of Engineering and Science (IRJES)*, vol. 2, no. 5, PP. 1-*7*, 2013.

[17] H. Lade, A. Kadam, D. Paul and S. Govindwar, "Biodegradation and Detoxification of Textile Azo Dyes by Bacterial Consortium under Sequential Microaerophilic/Aerobic Processes", *EXCLI Journal,* vol. 14, pp. 158-174, 2015.

[18] V.V. Dawkar, U.U. Jadhav, S.U. Jadhav and S.P. Govindwar," Biodegradation of disperse textile dye Brown 3REL by newly isolated Bacillus sp. VUS", *Journal of Applied Microbiology,* vol. 105, pp.14–24, 2008.

[19] V. Simion, I.Cretescu1, D. Lutic, Co. Luca and I. Poulios,"Enhancing The Fenton Process By Uv Light Applied In Textile Wastewater Treatment", *Environmental Engineering and Management Journal*, vol.14, no. 3, pp. 595-600, 2015.

[20] M. S. Lucas and J. A. Peres, " Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation ", *Dyes and Pigments*, vol. 71, pp. 236-244, 2006.

[21] A. Tikhe and M. R. Gidde, "Decolourization of Nigrosine WS (AB2) Dye by Solar Photo-Fenton Process ", *The International Journal of Science & Technoledge*, vol. 2, no. 5, pp.68-73, 2014.

[22] A. Lopes, S. Martins, A. Morão, M. Magrinho and I. Gonçalves, "Degradation of a Textile Dye C. I. Direct Red 80 by Electrochemical Processes", *Portugaliae Electrochimica Acta,* vol. 22, pp. 279-294, 2004.

[23] M. Jović, D. Stanković, D. Manojlović, I. Anđelković, A. Milić, B. Dojčinović and G. Roglić, " Study of the Electrochemical Oxidation of Reactive Textile Dyes Using Platinum Electrode ", *Int. J. Electrochem. Sci.,*vol. 8, pp.168-183, 2013.

[24] N. M. Julkapli, S. Bagheri, and S. B. Abd Hamid, "Recent Advances in Heterogeneous Photocatalytic Decolorization of Synthetic Dyes", *The Scientific World Journal*, pp. 1-26, 2014. And reference there in.

[25] K. Ryberg, B. Gruvberger, E. Zimerson, M.Isaksson, L. Persson, O¨. S. Rensen, A. Goossens and M. Bruze, "Chemical investigations of disperse dyes in patch test preparations", *Contact Dermatitis*, vol. 58, pp. 199–209, 2008. And reference there in.

[26] M. Clark, " CH1-Fundamental principles of dyeing ", M. L. Gulrajani, "CH 10-Disperse dyes", Handbook of textile and industrial dyeing, Volume 1: Principles, processes and types of dyes, M. Clark (Ed.), First published, Woodhead Publishing Limited, Oxford, UK, p. 22, 23, 365, 2011.

[27] J. Koh, "Dyeing with Disperse Dyes", Textile Dyeing, P. Hauser (Ed.), ISBN: 978-953-307-565-5, InTech, 2011.

[28] N. Soltani, E. Saion, W. M. Mat Yunus, M. Navasery, G. Bahmanrokh, M. Erfani, M. R. Zare and E. Gharibshahi, " Photocatalytic degradation of methylene blue under visible light using PVP-capped ZnS and CdS nanoparticles", *Solar Energy*, vol. 97, pp. 147–154, 2013.

[29] S. Ahmed, "Photo electrochemical study of ferrioxalate actinometry at a glassy carbon electrode", Journal of Photochemistry and Photobiology A: Chemistry, vol. 161, PP. 151-154, 2004.

[30] S. Khezrianjoo and H. D. Revanasiddappa, "Langmuir-Hinshelwood Kinetic Expression for the Photocatalytic Degradation of Metanil Yellow Aqueous Solutions by ZnO Catalyst", *Chem. Sci. J.,* pp: 1-7, 2012. And reference there in.

[31] H. Nadi, M. Alizadeh, M. Ahmadabadi, A. R. Yari and S. Hashemi, "Removal of Reactive Dyes (Green, Orange, and Yellow) from Aqueous Solutions by Peanut Shell Powder as a Natural Adsorbent ", *Arch. Hyg. Sci*., vol.1, no. 2, pp. 41-47, 2012.

[32] L. Ahmed, F. Hussein and Ali Mahdi, "Photocatalytic Dehydrogen-ation of Aqueous Methanol Solution by Bare and Platinized $TiO_2$ Nanoparticles", *Asian Journal of Chemistry;* vol. 24, no. 12, 2012, pp. 5564-5568.

[33] F. Hussein, A. Halbus, H. Hassan and W. Hussein, "Photocatalytic Degradation of Bismarck Brown G Using Irradiated ZnO in Aqueous Solutions", *E-Journal of Chemistry* , vol. 7, pp. 540-544(2010).

[34] F. Hussein and T. Abass, "Solar Photocatalysis and Photocatalytic Treatment of Textile Industrial Wastewater", *Int.* J. *Chem. Sci.,* vol. 8, no. 3, 2010, pp. 1409-1420.

[35] Luma M. Ahmed, Falah H. Hussein," Quantum yield of formaldehyde formation from methanol in the presence of $TiO_2$ and platinized $TiO_2$ photocatalysts", Journal of Babylon University/Pure and Applied Sciences/ Babylon University Scientific Conference -College of Science, vol. 22, no. 1, pp. 464-469, 2012.

[36] N. P. Mohabansi, V. B. Patil and N. Yenkie, " A Comparative Study on Photo Degradation of Methylene Blue Dye Effluent by Advanced Oxidation Process by Using $TiO_2$/ZnO Photo Catalyst ", *Rasayan J. Chem*,Vol.4, No.4, pp.814-819, 2011.

[37] M. Chang, H. Shu, T.Tseng, and H.Hsu, " Supported Zinc Oxide Photocatalyst for Decolorization and Mineralization of Orange G DyeWastewater under UV365 Irradiation ", *International Journal of Photoenergy,* pp. 1-12, 2013.

[38] F. H. Hussein and A. F. Halbus, " Rapid Decolorization of Cobalamin ", *International Journal of Photoenergy,* pp. 1-9, 2012.

[39] K. M. Elsabawy and M. M. Bediwy," Application of Nano-Copper – Substituted Lead Zirconate as Surface Catalyst for Oxidative Degradation of Organic Dye", *WSN*, vol. 31, pp.134-147, 2016. And references there in.

[40] M. Salehi1, H. Hashemipour and M. Mirzaee, "Experimental Study of Influencing Factors and Kinetics in Catalytic Removal of Methylene Blue with $TiO_2$ Nanopowder ",

*American Journal of Environmental Engineering,* vol. 2, no. 1, pp. 1-7, 2012. And references there in.

[41] D. H. Mohsin , A. M. Juda and M. S. Mashkour, " Thermodynamic and Kinetic Study for Aromatic Rings Effect on The Photooxidation rate ", *International Journal of Engineering & Technology IJET-IJENS*, vol.13, no.04, pp. 34-41, 2013. And references there in.

[42] F. F. Karam, F. H. Hussein, S.J. Baqir, A. F. Halbus, R. Dillert and D. Bahnemann, " Photocatalytic Degradation of Anthracene in Closed System Reactor", *International Journal of Photoenergy*, pp. 1-7, 2014.

[43] K. Byrappa, A. K. Subramani, S. Ananda, K. M. Lokanatha Rai, R. Dinesh and M. Yoshimura, "Photocatalytic degradation of rhodamine B dye using hydrothermally synthesized ZnO ", *Bull. Mater. Sci.*, vol. 29, no. 5, pp. 433–438, 2006.

[44] H. A. Mills and S. L. Hunte, "An overview of semiconductor photocatalysis", *J. Photochem. & Photobiol. A: Chem.,* vol. 108, 1977, pp. 1-35.

[45] S.B. Gajbhiye , "Photocatalytic Degradation Study of Methylene Blue Solutions and Its Application to Dye Industry Effluent". International Journal of Modern Engineering Research, vol. 2, pp. 1204-1208, 2012.

[46] L.M. Ahmed, I. Ivanova, F.H. Hussein, and D. W. Bahnemann, "Role of Platinum Deposited on TiO2 in Photocatalytic Methanol Oxidation and Dehydrogenation Reactions", *International Journal of Photoenergy,* pp. 1-10, 2014.

[47] L. M. Ahmed and F. H. Hussein, Roles of Photocatalytic Reactions of Platinized $TiO_2$ Nanoparticales, 1st ed., LAP Lambert Academia Published, Germany, 2014