Kinetic study for the decolorization of dispersive blue 26 dye from suspension solution of commercial ZnO

الدراسة الحركية للازالة اللونية للصبغة الزرقاء المنتشرة 26 من محلولها العالق مع ZnO التجاري

Luma[*]*. M. Ahmed, Q. M. Mahdi, F. S. Mahmoud, M. J. Mahammed and N. S. Ahmed*
Chemistry Department, College of Science, Karbala University, Karbala, Iraq
* E-mail: lumamajeed2013@gmail.com

Abstract

In this work, the photocatalytic decolorization of dispersive blue 26 dye solution was performed in suspension solution of the commercial ZnO, under the artificial light (high pressure mercury lamp) type 250 Watt as UV A source. The photoreaction of this dye was obeyed to pseudo-first order kinetics. The optimum conditions for the photocatalytic decoloration of this dye were determined such as the optimum concentration of dye that equal to 50 ppm, the best dose of ZnO is 300 mg/100 mL, and the maximum value at the initial pH of an aqueous solution is 7.45. Moreover, the apparent activation energy is equal to 22.116 kJ/mol. From other the hand, the some thermodynamics parameters were calculated and $\Delta H^{\#}$ = 19.591 kJ/mol, $\Delta S^{\#}$ = 0.201 kJ/mol and $\Delta G^{\#}$ = -43.043 kJ/mol. There data clear due to the reaction is fast, endothermic and spontaneous reaction.

الخلاصة :

في هذا العمل، اجريت دراسة لعملية الازالة اللونية المحفزة ضوئياً للصبغة الزرقاء المنتشرة 26 في محلول العالق لـ ZnO التجاري، باستخدام مصدر للضوء التجاري (مصباح الزئبق عالي الضغط) كمصدر للاشعة فوق البنفسجية نوع A وبقدرة 250 واط. وجد بان التفاعل الضوئي لهذه الصبغة يخضع للمرتبة الاولى الكاذبة. كما عينت الظروف الفضلى للازالة اللونية المحفزة ضوئياً من خلال دراسة افضل تركيز لها وكان مساوياً الى 50 جزء بالمليون، ووجد بان افضل كمية للـ ZnO هي 300 ملغم لكل 100 مللتر من محلول الصبغة، وان اعلى قيمة للازالة كانت عند دالة حامضية ابتدائية للمحلول مساوية الى 7.45. علاوة على ذلك، وجد بان قيمة طاقة التنشيط الظاهرية مساوية الى 22.116 كيلو جول لكل مول. من ناحية اخرى تم احتساب قيم بعض الدوال الثرموديناميكية وكانت قيمة التغير بالانثالبي مساوية الى 19.591 كيلو جول لكل مول، ومقدا التغير بالانتروبي مساويا الى 0.201 كيلو جول لكل مولوالتغير بالطاقة الحرة المولية مساويا الى -43.043 كيلو جول لكل مول. من خلال هذه النتائج يظهر بوضوح ان التفاعل سريع، وماص للحرارة وتلقائي.

1. Introduction

Disperse dyes are one of an important textile dye that have a low molecular weight, brightness colour, fastness, relatively insoluble in water at room temperature, whereas they soluble in the fiber because of they contained of non-ionic mono-azo and anthraquinone derivatives in their molecular structures, hence deep dyeing are produced [1]. Anthraquinone disperse dyes, are usually 1-hydroxy or 1-amino derivatives, that have a bright colours ranging from red through to blue while, azo disperse dye structures are more wide than the anthraquinone disperse dyes because of the numerous substitution patterns possible in the diverse diazonium ion and coupling components, and the possible colours are greenish-yellow and blue. These dyes are dispersion by the surface-active agent compounds and employed as synthetic textile dyes for dying the polyester, nylon or acetates [1-3]. In textile industries, the effluent contain varies dyes in different concentrations which are

caused a serious of environmental problems. These problems are due to produce a carcinogen and mutagen chemicals; hence, the produced wastewaters must be removed. In this manner, many of studies were performed in different conventional methods that include adsorption [4,5], Coagulation-Flocculation Method [6], biodegradation [7,8] and photodegradation [9].
The present study focused on the optimal conditions for decolorization dispersive blue 26 dye. This study was described the effects of, concentration of dye, dose of catalyst, initial pH of solution, and temperature on photoreaction rate.

2. Materials and Method

All chemicals were employed in photocatalytic experiment that used without further purification. Commercial Zinc oxide (99.5% purity) was supplied by Fluka. Dispersive blue 26 dye ($C_{16}H_{14}N_2O_4$) has molecular weight equal to 298.29g mol^{-1}, and supplied by the Hilla textile factory, that has a chemical structure is illustrated in Figure 1.

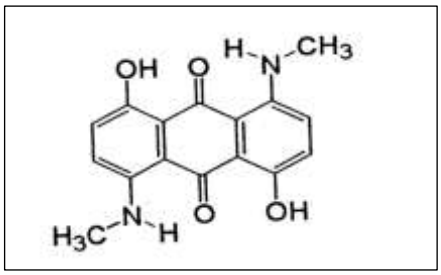
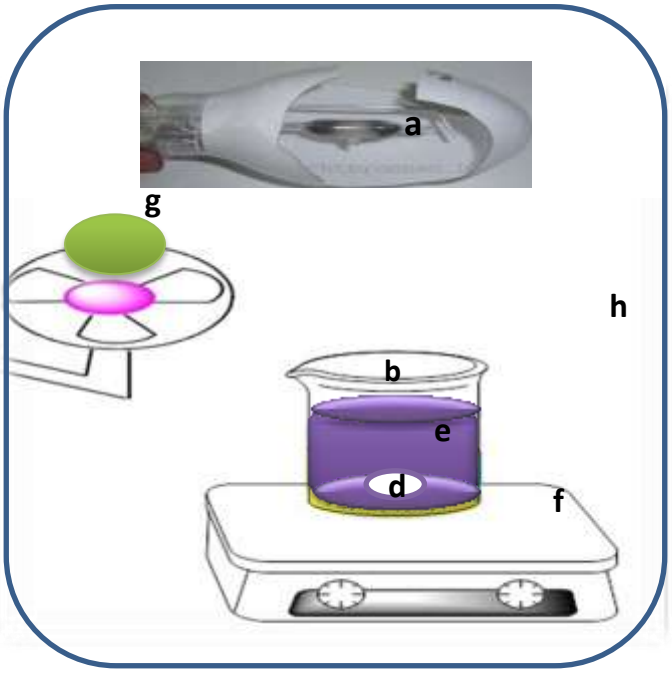


Figure 1: The structure formula of dispersive blue 26 dye.

To perform the photocatalytic experiments, 100 mL from dispersive blue 26 dye concentration and the know amount of the catalyst (ZnO), were taken in (400 mL) Pyrex beaker, and then mixed by (Labtech) magnetic stirrer to keep suspension homogeneous. The produced suspension solution was exposed to artificial light (Philips 250Watt, high pressure mercury lamp), the light intensity of this lamp was calculated by the chemical actinometrical solution [10] and the value found to be 2.995 x 10^{-8} Ens. s^{-1}.
About 3- 3.5 mL of the suspension solution was taken out at predetermined times; then put in plastic test tube, and centrifuged (Hettich, centrifuge) for 10 minutes at 4000 rpm. The produced filtration solution was transformed to a new plastic test tube then centrifuged again at the same speed and time to separate the fine ZnO particles. This procedure is sanctioned in references [11-14]. The residual concentrations of dispersive blue 26 dye before irradiation (dark reaction) and after irradiation (photoreaction) were measured by standard calibration curve obtained from recorded the absorbance at 562 nm using UV-visible spectrophotometer (model: Labomad). The experimental reactor was designed as Scheme 1



Scheme1. Schematic diagram of photo-reactor components. Whereas, a) (250 W) High pressure mercury lamp,(b) 400 cm^3 Pyrex glass beaker, (c) dispersive blue 26 dye with ZnO as suspension solution, (d)Teflon bar, (e)suspension solution (Dye with photo-catalyst), (f) magnetic stirrer, (g) fan and (h) wooden box.

3. Results and discussion

A series of experiments were carried out to investigate the effects of relevant parameters such as initial dye concentration, catalyst loading, initial pH of solution, and temperature on the rate constant of the discoloration of dispersive blue 26 dye.

In most cases, the final products of dispersive blue 26 dye were colorless, and followed to pseudo-first order kinetics.

At low concentration of studied dye, and by depended on Langmuir-Hinshelwood Kinetic Expression, the apparent first order rate constant resulting from fitting equation (1) can be transferred to equation (2) [15,16] by basing on calibration curve of dispersive blue 26 dye at 562 nm.

$$A_t = A_o \exp\left(-k_{app}.t\right) \qquad (1)$$

whereas : A_o is an initial absorbance of dye at (dark reaction) time of irradiation equal to 0 min. A_t is an absorbance of the same dye at t time of irradiation.

$$C_t = C_o \exp\left(-k_{app}.t\right) \qquad (2)$$

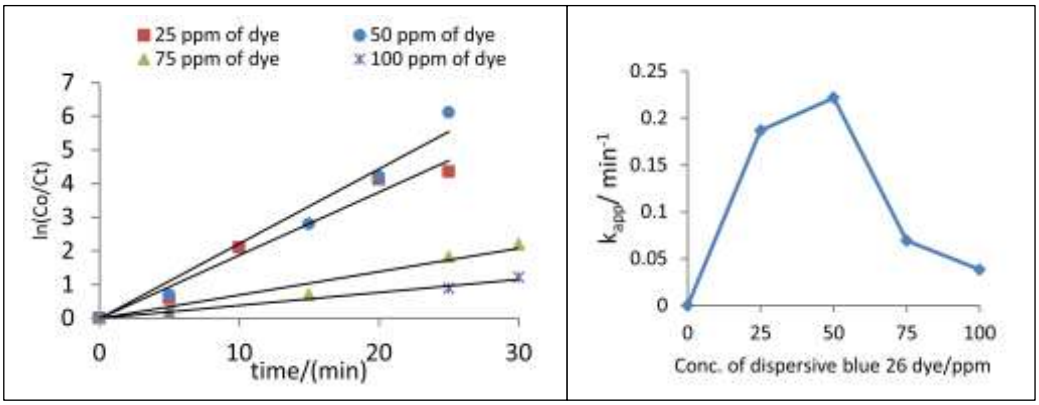
whereas : C_o is an initial concentration of studied dye at (dark reaction) time of irradiation equal to 0 min. C_t is a concentration of the same studied dye at t time of irradiation.

The apparent first order equation can be measured from modified of equation (2)[16]:

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app}.t \qquad (3)$$

3.1. Effect of Initial Dye Concentration.

Figures 2 illustrates, that the reaction is obeyed the pseudo first order. On other hand, this effect is interesting to explain that the discoloration rate for the dispersive blue 26 dye increases with the increase in substrate (dye) concentration and reaches to 50 ppm, then reduces that leads to decline in penetration of light through the solution. This results is in agreement with the reported by Ahmed and coworker [11, 12].

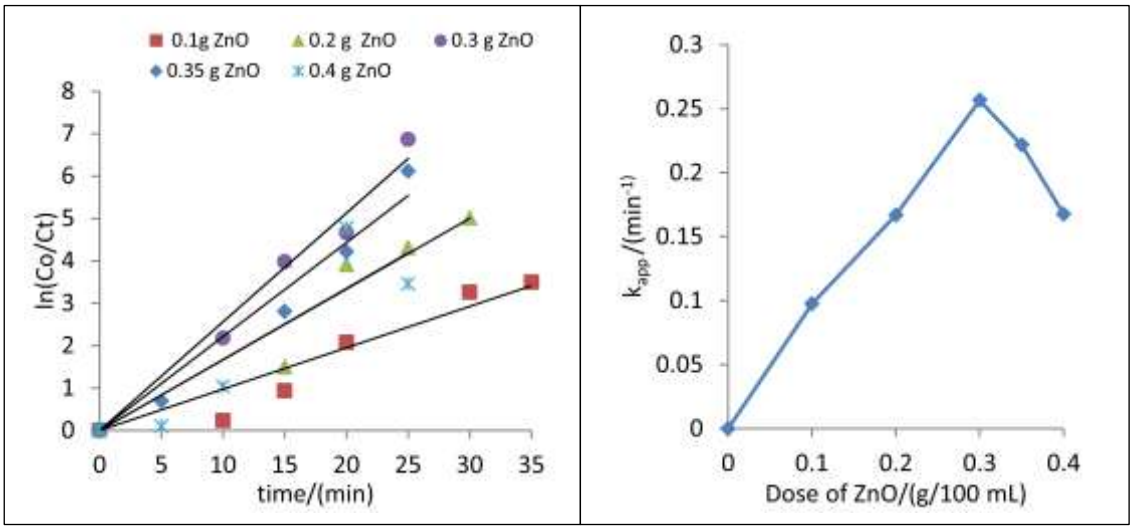


a b

Figure 2: Effect of initial dye concentration on the apparent rate constant of dye decolourization, at dye concentration (25-100) ppm, ZnO dosage 350 mg/100 mL, pH 7.45, Temp. 311.15 K, UV light intensity 2.995 x 10^{-8} Ens $.s^{-1}$). (a) ln (Co/C) vs time and (b) k_{app}vs concentration of dye.

3.2. Effect of Catalyst Loading.

The study of this effect is essential to dominate on the amount of consuming of photo catalyst. From the results in figures 3 (a) and 3(b), it seems that the apparent rate constant increases linearly with catalyst loading from 100 to 300 mg/100 mL, that attitude to increase the active sits on ZnO surface which leads to increment the chances of dispersive blue 26 dye adsorption on his surface, moreover, the absorbed light photons increase on ZnO surface [17, 18]. After 300 mg/100 mL, the apparent rate constant reduces with increasing number of free particles of ZnO. This result can be taken as evidence to formed screening effect [14, 17, 19].



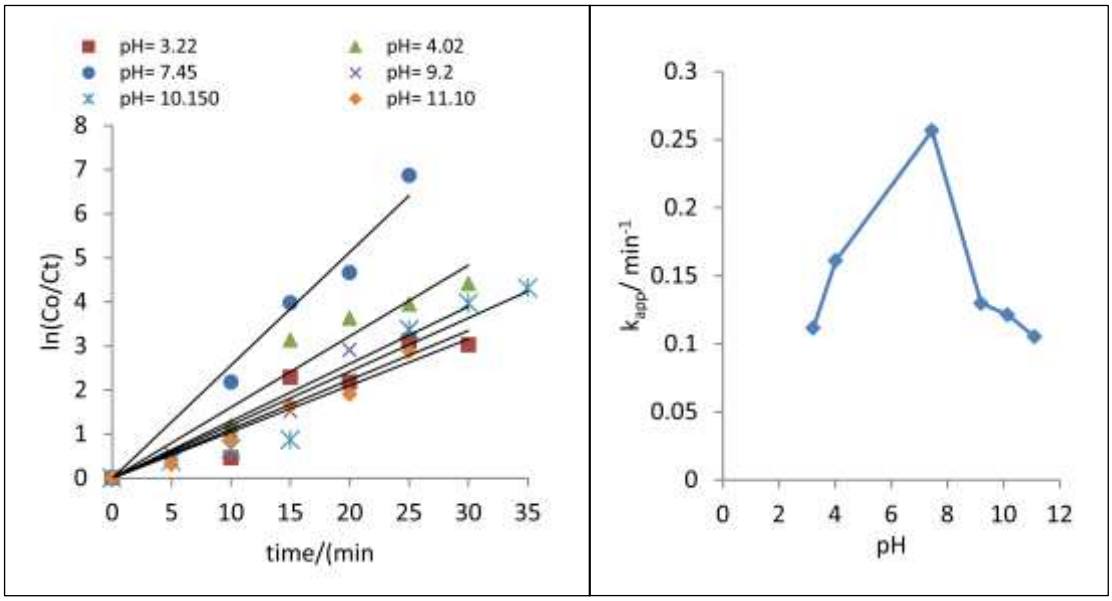
a b

Figure 3: Effect of ZnO dosage on the apparent rate constant of dye decolourization, dye concentration 50 ppm, ZnO dosage (100-400) mg/100 mL, pH 7.45, Temp. 311.15 K, UV light intensity 2.995 x 10^{-8} Ens .s^{-1}). (a) ln (Co/C) vs time and (b) k_{app}vs initial ZnO dose.

3.3 Effect of pH.

The initial pH of solution is an important parameter in the photocatalytic reactions, whereas, the properties of photo catalyst surface can be altered such as the charge and size of aggregates that depended on the electrostatic interactions between the photocatalyst surface and type of solvent respectively [20]. That leads to effect called zero point charge, some references refer to the value of the zero point charge for ZnO is 9.0, at above this value, the surface of ZnO is charged by negative charge (increased adsorption of hydroxyl ions), but at less value the surface of ZnO should be charged by positive charge (increased adsorption of hydrogen ions)[17, 21].

The effect of pH on the apparent rate constant for discoloration of dispersive blue 26 dye was examined in the range 3.22–11.10 in suspension solution of ZnO and depicted in figures 4 (a) and 4 (b). The results obtain, the discoloration of this dye is increment with increasing the pH value at 7.45 (natural pH of dye), and then depresses in basic medium. This decline is taking place before reach to zero point charge of ZnO. The more accepted interpenetration is beyond to increase the electrostatic repulsion between the positive charge of ZnO surface and the pair's electron for nitrogen and oxygen atoms that found in structure of studied dye. That caused shifts in value of zero point charge of ZnO.



a b

Figure 4: Effect of initial pH on the apparent rate constant of dye decolourization, dye concentration 50 ppm, ZnO dosage 300 mg/100 mL, pH range (3.22-11.10), Temp. 311.15 K, UV light intensity 2.995 x 10^{-8} Ens .s^{-1}). (a) ln (Co/C) vs time and (b) k_{app}vs initial pH of solution.

3.4 Effect of temperature.

The fixed fact in photoreaction is increasing the rate of reaction and rate constant with increasing the temperature, that deduced to the increase of temperature will depress the physical and chemical adsorption, and then enhance photoreaction, this reactional steps are favored [22]. This concept is identifying with the results in figures 5 and 6. The apparent activation energy and some essential thermodynamics parameters were calculated by the following equations [23, 24]:

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \qquad (4)$$

whereas: k_{app} is apparent rate constant (pseudo first order min^{-1}), E_a is apparent activation energy, R is gas constant, T is temperature of reaction and A is a frequency constant, the upper equation is called Arrhenius equation.

The Eyring- Polanyi equation was used to determine $\Delta H^{\#}$ and $\Delta S^{\#}$ [11, 14, 24].

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\#}}{R}\right) \qquad (5)$$

Whereas: k_B is a Boltzmann's constant, h is a Plank's constant, R is a gas constant and T is the temperature of reaction.

$\Delta G^{\#}$ of photo reaction was calculated by using Gibbs equation [12, 14, 24].

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (6)$$

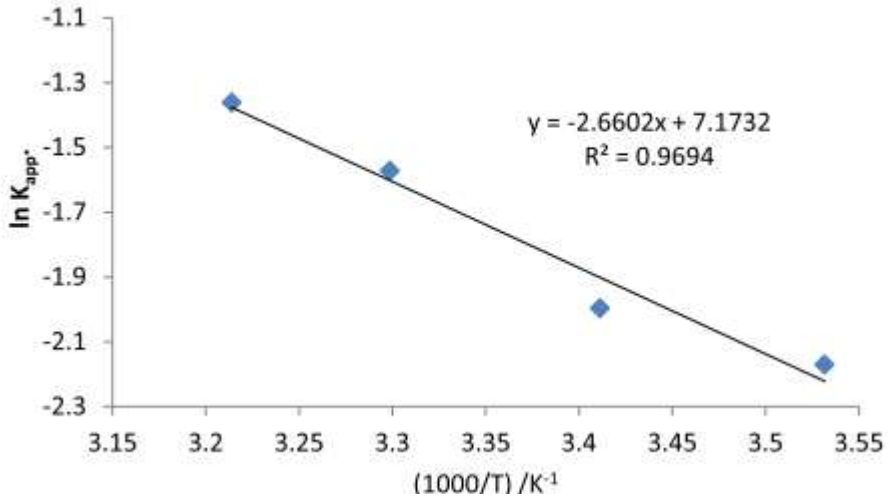


Figure 5: Arrhenius equation plot of (ln K_{app}) vs. 1/T. Conductions: Dispersive blue 26 dye conc. = 50 ppm, ZnO dosage = 300 mg/100 mL, pH = 7.45, temperature = 283.15-311.15 K, UV light intensity = 2.995 x 10^{-8} Ens $.s^{-1}$.

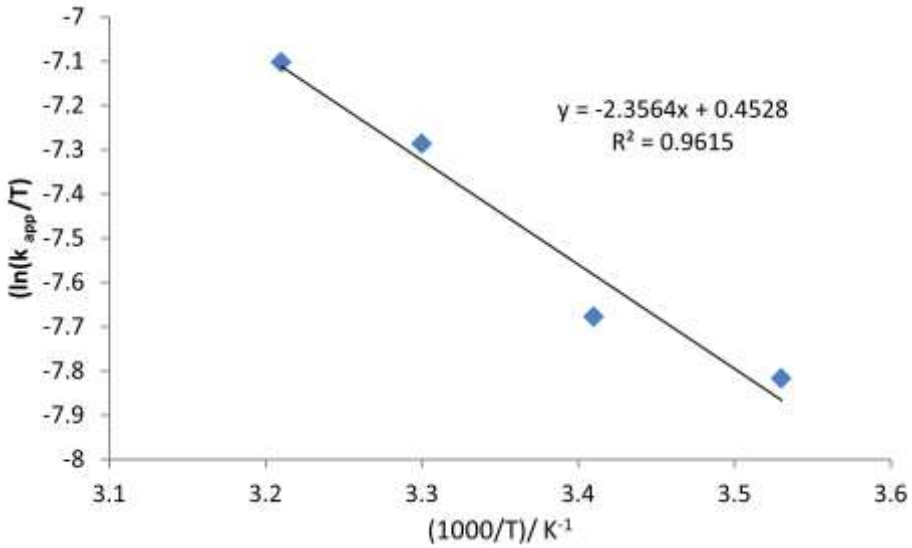


Figure 6: Eyring plot of (ln(K_{app}/T)) vs.1/T. Conductions: Dispersive blue 26 dye conc. = 50 ppm, ZnO dosage = 300 mg/100 mL, pH = 7.45, temperature = 283.15-311.15 K, UV light intensity = 2.995 x 10^{-8} Ens $.s^{-1}$.

On basis on produced dada from figures 5 and 6 and equations from 4 to 6, the apparent activation energy and some thermodynamics functions are calculated then listed in Table 1.

Table 1: The activation kinetic and thermodynamic parameters of the discoloration of dispersive blue 26 dye in present ZnO suspension under light type 250 watt -Hg lamp.

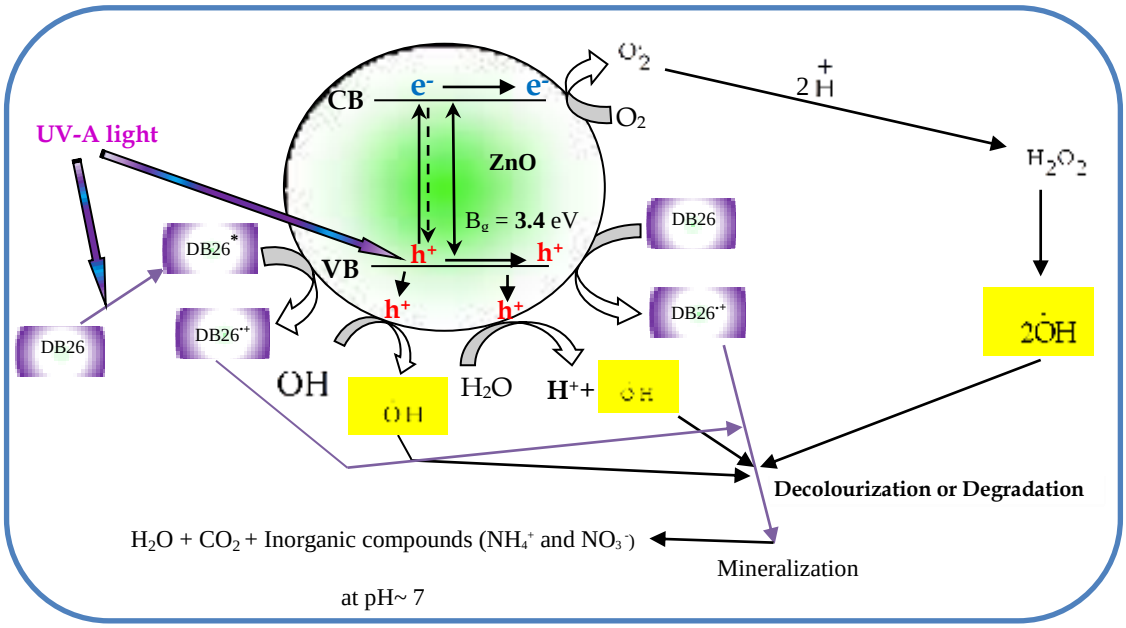
E_a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ kJ mol^{-1} K^{-1}	$\Delta G^{\#}_{311.15}$ kJ mol^{-1}
22.116	19.591	0.201	-43.043

The results demonstrate that the photoreaction for discoloration of dispersive blue 26 dye in found ZnO suspension is endothermic (positive $\Delta H^{\#}$), fast (low E_a) and spontaneous (negative $\Delta G^{\#}$). In the other side, the change in entropy was low that indicated to reduce in randomness. These results similar observations have been reported by Zuafuani and Ahmed [11].

3.5 Proposed mechanism.

The proposed mechanism for discoloration of dispersive blue 26 dye (DB26) from ZnO suspension solution is being as system (Dye/semiconductor/ UV light). The mechanism is outlined in Scheme 2.

Generally, the UV-A light photon fills on the ZnO suspension solution with dispersive blue 26 dye, that will lead to some series of chain oxidative-reductive reactions, which at last produced the final pH solution is equal to 7[11,12,13].



Scheme 2: Schematic diagram for more accepted proposed mechanism as system (Dye/semiconductor/ UV light) (modified from reference [12, 25]).

4.Conclusions

From the results of decolorization one can conclude that:

1. The results clearly show that dispersive blue 26 dyes can be decolorized after irradiation with present ZnO suspension solution.
2. By depended on Langmuir-Hinshelwood Kinetic Expression, the photo-discoloration of dispersive blue 2 dye is followed the pseudo first order kinetics at low concentration.
3. In photocatalytic treatment, the formation of hydroxyl radical may represent an important step for complete the discoloration and then degradation of textile dye the dispersive blue 26 dyes.

4. The decolorization process efficiency seems to be assessed of parameters such as dosage of ZnO (300 mg/ 100mL), concentration of dye (50 ppm), pH of solution (7.45) and temperature of solution (311.15 K).
5. According to the results of kinetics and thermodynamics for this photoreaction, it seems that the discoloration of dispersive 26 dye from ZnO suspension solution is fast, endothermic and spontaneous reaction.

References:

1- A. D. Broadbent, Basic Principles of Textile Coloration, Society of Dyers and Colourists, Canada, CH 15, 2011.
2- W. Ingamells, *Colour for Textiles: A User's Handbook*, SDC, ISBN 0-901956-56-2, Bradford, UK, (1993).
3- A.E. Ghaly, R Ananthashankar, M. Alhattab and V.V. Ramakrishnan, Production, "Characterization and Treatment of Textile Effluents: A Critical Review", *J Chem Eng Process Technol*, vol. 5, pp: 1-19, 2014.And reference there in.
4- A.A. Ahmad, B.H. Hameed and A.L. Ahmad, "Equilibrium And Kinetics of Disperse Dye Adsorption on Activated Carbon Prepared from Rattan Sawdust by Chemical Activation", *International Conference On Environment 2008,*, pp: 1-8, (Icenv 2008).
5- A. F. Halbus, Z. H. Athaba and F. H. Hussein, "Adsorption of Disperse Blue Dye on Iraqi Date Palm Seeds Activated Carbon", *Int. J. Chem. Sci*, vol.11, no. 3, pp:1219-1233, 2013.
6- S. P. Buthelezi, Ademola O. Olaniran and B. Pillay, "Textile Dye Removal from Wastewater Effluents Using Bioflocculants Produced by Indigenous Bacterial Isolates", *Molecules*, vol. 17, pp:14260-14274, 2012.
7- 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.
8- 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.
9- I. Arslan-Alaton and S. Dogruel,"Photodegradation of hydrophobic disperse dyes and dye-bath effluents by silicadodecatungstate (SiW12O404-/5-) nanoparticles", *Water and science technology*, vol. 49, no. 4, pp:171-176, 2004.
10- 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.
11- S. I. Zuafuani and L. M. Ahmed, "Photocatalytic Decolourization of Direct Orange Dye by Zinc Oxide Under Uv Irradiation ", *Int. J. Chem. Sci*., vol. 13, no. 1, pp: 187-196, 2015.
12- 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*, vol. 13 no.1 Scientific, pp: 53-63, 2015.
13- M. Mashkour, A. Al-Kaim, L. Ahmed and F. Hussein, "Zinc Oxide Assisted Photocatalytic Decolorization of Reactive Red 2 Dye", *Int. J. Chem. Sci.*, vol. 9, no.3, pp: 969-979, 2011.
14- 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.
15- F. P. van der Zee, G. Lettinga and J. A. Field, "Azo dye decolourization by anaerobic granular sludge", *Chemosphere*, vol. 44, pp: 1169-1176, 2001.

16- 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.

17- H. C. Yatmaz, A. Akyol and M. Bayramoglu,"Kinetics of the Photocatalytic Decolorization of an Azo Reactive Dye in Aqueous ZnO Suspensions", *Ind. Eng. Chem. Res.*, vol. 43, pp: 6035-6039, 2004. And reference there in.

18- N. Daneshvar,S. Aber, M.S. Seyed Dorraji, A.R. Khataee and M.H. Rasoulifard, "Preperation and Investigation of Photocatalytic Properties of ZnO Nanocrystals: Effect of Operational Parameters and Kinetic Study", *World Academic of Science, Engineering and Technology*, vol. 29, pp: 267-272, 2007.

19- A. Dixit, A. Mungray, and M. Chakraborty, "Photochemical Oxidation of Phenol and Chlorophenol by UV/H_2O_2/TiO_2 Process: A Kinetic Study", *International Journal of Chemical Engineering and Applications*, vol. 1, no. 3, pp: 247-250, 2010. And reference there in.

20- M. Abu Tariq, M. Faisal, M. Saquib and M. Muneer, "Heterogeneous photocatalytic degradation of an anthraquinone and a triphenylmethane dye derivative in aqueous suspensions of semiconductor", *Dyes and Pigments*, vol. 76, pp: 358-365, 2008.

21- A. A. Khodja, T. Sehili, J. Pilichowski and P. Bolue, "Photocatalytic Degradation of 2-penylphenol on TiO_2 and ZnO in Aqueous Suspensions", *J. Photochem. Photobiol. A: Chem.*, vol.141, pp: 231–239, 2001.

22- A. Boukhennoufa, M. Bouhelassa and A. Zoulalian, "Photocatalytic Degradation of Solophenyl Red 3 BL in an Aqueous Suspension of Titanium Dioxide", *Journal of Advanced Chemical Engineering*, vol. 1, pp:1-8, (2011).

23- M. QADRI, S. Nisar and N. Fatima, "Photokinetics of the oxidation of Coomassie Brilliant Blue by Potassium dichromate in acidic medium ", *International Journal of Advanced Research*, vol. 3, no. 2, pp. 888-898, 2015.

24- M. A. Tabbara, and M. M. Jamal, "A kinetic study of the discoloration of methylene blue by Na_2SO_3, comparison with NaOH", *J . of the Uni. of Chem. Tech. and Metall.*, vol. 47, no. 3, pp. 275-282, 2012.

25- F. Hussein,"Photochemical Treatments of Textile Industries Wastewater", *Advances in Treating Textile Effluent*, Peter J. Hauser (Ed.), ISBN: 978-953-307-704-8, InTech, 2011.