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# Optimization of Photocatalytic Decolourization of Methyl Green Dye Using Commercial Zinc Oxide as catalyst

# التحفيز الضوئي المثالي لازالة صبغة المثل الاخضر باستخدام اوكسيد الخارصين التجاري كعامل مساعد

Eitemad[*] S. Fathal , Luma[**] M. Ahmed
Chemistry Department, College of Science, Karbala University, Karbala, Iraq
Author for correspondence; E-mail:
* Eitem3d@gmail.com, ** Lumamajeed2013@gmail.com.

## Abstract

This study describes the results for series of experiments on photocatalytic decolourization of methyl green dye from aqueous solution in the presence of commercial ZnO suspension. The photocatalytic decolourization has been studied as a function of initial dye concentration, best dose of ZnO, initial pH of aqueous solution, and temperature by regular intervals from experiments. The decolourization of methyl green dye process was found to follow pseudo-first order kinetics with the use of artificial UV (A) light sources.

The optimum dye and catalyst concentration was measured and found equal to be 50 ppm and 700 mg/ 200 mL$^{-1}$ respectively. The best value of pH for the photocatalytic decolourization of methyl green dye in the presence of ZnO suspension is pH 5.4. The Photocatalytic decolourization reaction of dye was endothermic and found the rate of reaction increased with increasing temperature. Arrhenius plot obtains that the activation energy for this reaction is equal to 24. 914 kJ mol$^{-1}$, this value is small that beyond to be associated with the transport of photoelectrons through the catalyst to the adsorbed oxygen on the surface.

**Key words**: Zinc oxide, Photocatalytic decolourization, methyl green dye, treatment of wastewater.

## الخلاصة:

تصف هذه الدراسة النتائج التي تم الحصول عليها خلال سلسة من تجارب الازالة اللونية المحفزة ضوئياً للمحلول المائي لصبغة المثل الاخضر بوجود عالق من اوكسيد الخارصين ZnO التجاري. تم دراسة عملية الازالة اللونية المحفزة ضوئياً كدالة لـ تركيز الصبغة الابتدائي، و افضل جرعة من الـ ZnO ، والدالة الحامضية pH الابتدائية للمحلول، و درجة الحرارة عند تجارب ذات ازمنة متسلسلة.

حسب كل من تركيز الصبغة والعامل المساعد، وكانت تساوي 50 جزء من المليون و 700 ملغم \ مللتر على التوالي. كما وجدت افضل قيمة للدالة الحامضية لعملية الازالة اللونية المحفزة لصبغة المثل الاخضر بوجود عالق من الـ ZnO وكانت تساوي 5.4. وجد ان تفاعل الازالة اللونية المحفز ضوئيا ماص للحرارة وان سرعة التفاعل تزداد بزيادة درجة الحرارة. حسبت قيمة طاقة التنشيط من خلال معادلة ارينوس وكانت تساوي 24.914 كيلو جول\مول ، هذه القيمة تعتبر قليلة ويعود ذلك الى تجمع وانتقال الالكترونات الضوئية خلال العامل المساعد ولامتزاز الاوكسجين على سطحه.

## 1.Introduction:

Zinc oxide (ZnO) is an n-type metal oxide semiconductor that regards as one of the most common photocatalysts, having a wide direct band gap semiconductor with an energy gap (Eg) 3.436 eV at 0 K, while at room temperature the value of energy gap is equal to (3.37± 0.01) eV with a large electron-hole couple (exciton) binding energy that about equals to 60 meV. It is operated in the visible and near ultraviolet spectral regions[1]. The areas in which it is employed include, photocatalytic decolourization and photocatalytic degradation of textile dyes[2,3],treatment of wastewater[4,5], gas sensor[6], Chemical sensor[7], destruction of microorganisms[8], protection of skin from solar irradiation [9,10], produced of self- cleaning glass[11,12] and using in manufacture of solar cell[13,14]. On the other hand, ZnO has the disadvantage of undergoing photocorrosion through self-oxidation under illumination, so it tendency to dissolve in acidic conditions. The photocorrosion of ZnO can occur as in the following equations[15]:

$$\mathrm{ZnO} \xrightarrow{h\upsilon} e^{-}_{CB} + h^{+}_{VB} \qquad \ldots(1)$$

$$\mathrm{ZnO} + 2h^{+}_{VB} \rightarrow \mathrm{ZnO}^{2+} + 1/2\,O_2 \qquad \ldots(2)$$

$$\mathrm{ZnO} + 2H^{+} \rightarrow \mathrm{Zn}^{2+} + H_2O \qquad \ldots(3)$$

The target of present work is to investigate the photocatalytic decolourization of Methyl Green dye in ZnO suspension solution by light source type UV (A) at different conditions.

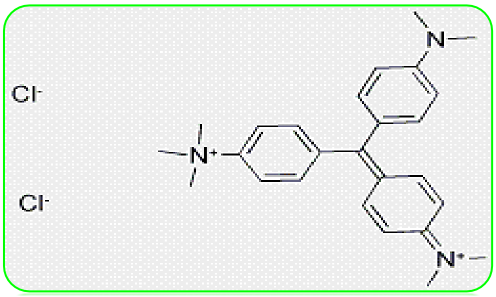
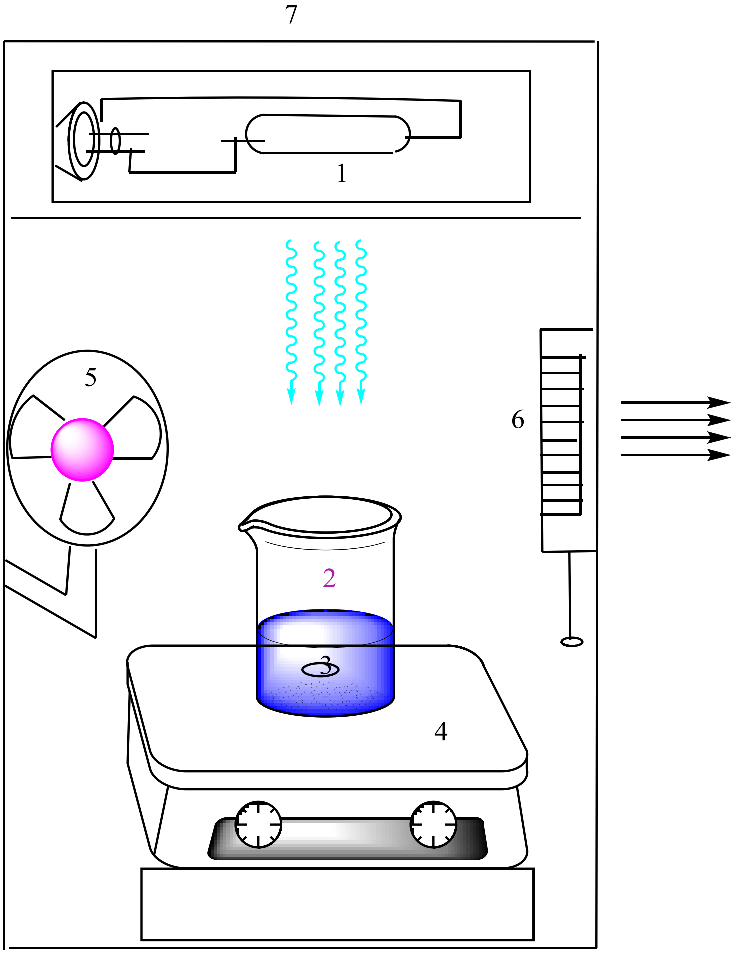


Figure 1: The structure formula of Methyl Green dye.

## 2.Experimental

All chemicals employed in photocatalytic experiment were of analytical grade. Zinc oxide with 99.5% purity was supplied by Fluka. Suitable amount of ZnO was suspended in 200 mL of methyl green dye ($C_{27}H_{35}\ C_{l2}N_{3}.ZnCl_{2}$) employing a Labtech magnetic stirrer. At a regular intervals; 3 mL of reaction mixture was withdraw from the mixture and centrifuged (4,000 rpm, 15 minutes) in a Hettich centrifuge. The collected solution was carefully removed by a syringe to a new plastic test tube and centrifuged again at same speed and for the 10 minutes. The second centrifugation was very important to separate the fine ZnO particles. The concentration of residual methyl green dye was determined spectrophotometrically at 630 nm, using UV-visible spectro-photometer type Labomad, USA. The Photocatalytic reaction was carried out in a photoreactor equipped with a Philips 400 W(high pressure mercury lamp- Germany) as a source for UV-A radiation. A general diagram of the experimental set-up is shown in Scheme 1.



Scheme 1: Schematic Diagram of Experimental Set-up. Where: High pressure mercury lamp(400 W)(1), 400 $cm^3$ Pyrex glass beaker (2), Teflon bar (3), magnetic stirrer (4), fan (5), pump fan (6) and wooden box (7).

The UV lamp was positioned perpendicularly above the Pyrex glass beaker. The wooden box was used to insulate the photocatalytic reactor contents in order to prevent the escape of harmful radiation [2].

## 3.Results And Discussion

### 1. UV-Visible spectra of dye:

A series of experimental was carried out in the containing ZnO particles with illumination of high pressure mercury lamp, dyes were found to be decolorized due to photocatalytic reaction as shown in figure 2. The time dependent on UV-Visible absorption spectra of 50 ppm of aqueous solution of methyl green dye during irradiation by UVA light in the presence of ZnO. The complete disappearance of the band at 630 nm was obtained after 20 minutes of irradiation, that indicates to complete the destruction of chromophore groups in dye.

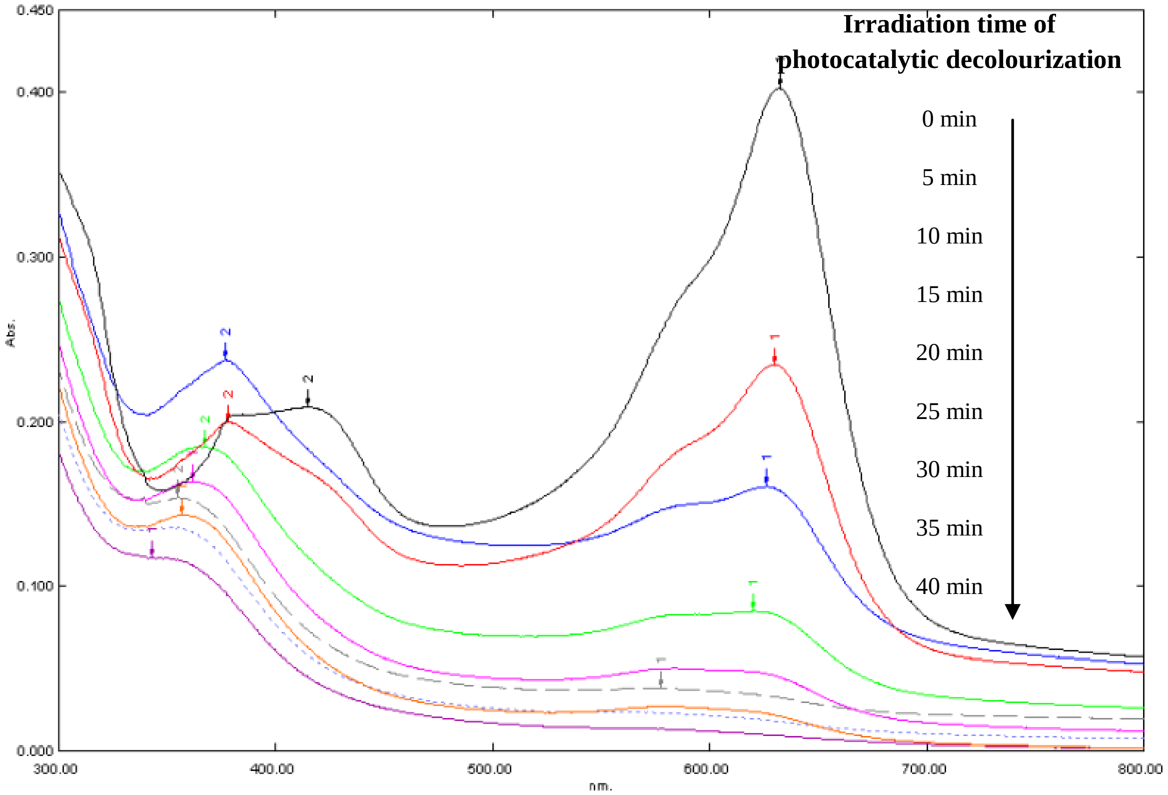


Figure 2: UV-Visible absorption spectra change at different time intervals.

## 2. Effect of irradiation time:

At low initial methyl green dye concentration, the decolourization experiments by UV irradiation of this dye aqueous solutions with presence of ZnO obey the pseudo-first order kinetics according to the Langmuir-Hinshelwood (L-H) model, so the apparent rate constant ($k_{app}$) expression was calculated by the following equations[16,17]:

$$C_t = C_o \exp^{(-k_{app}.\, t)} \qquad \text{…(4)}$$

where: $C_o$ is an initial concentration of methyl green dye at time of irradiation = 0 min Ct is a concentration of methyl green dye at time t of irradiation.

$$\frac{C_t}{C_o} = exp^{(-k_{app}.t)} \qquad \text{…(5)}$$

$$\ln \frac{C_t}{C_o} = -k_{app}\ .t \qquad \text{…(6)}$$

$$or \quad \ln \frac{C_o}{C_t} = k_{app}\ .t \qquad \text{…(7)}$$

## 3. Effect of Dye Concentration:

The effect of initial methyl green dye concentration in the range of 25- 100 ppm is depicted in figure 3.

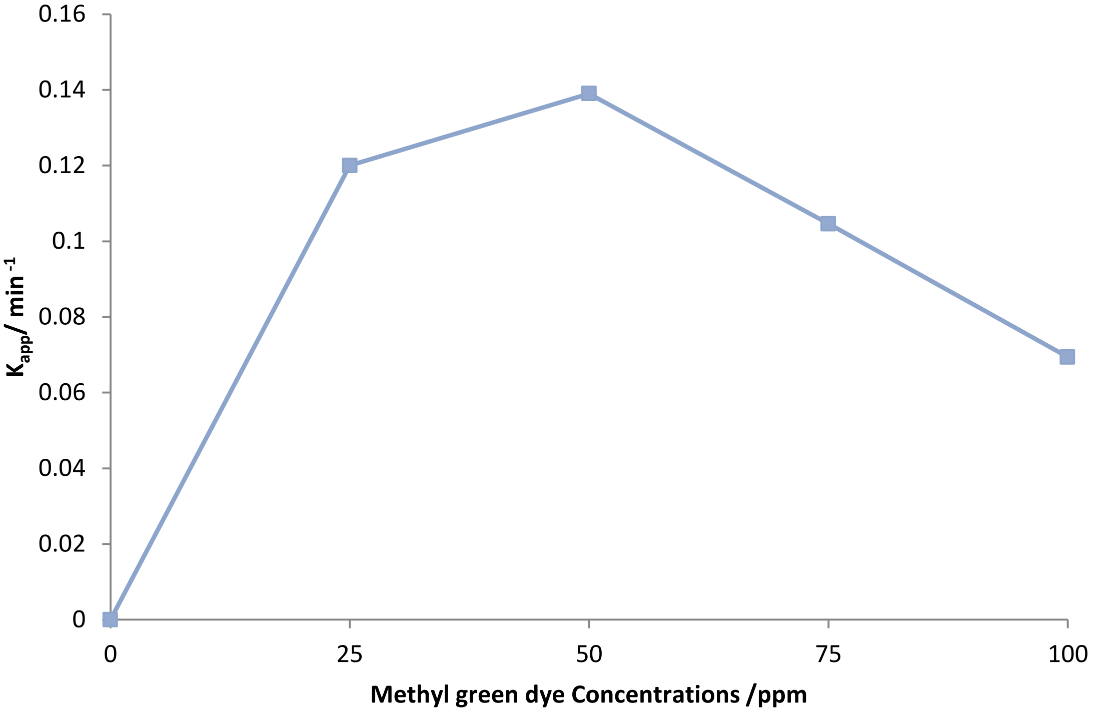


Figure 3: Pseudo-first order rate constant at varying dye concentration. Conductions: semiconductor dosage 700 mg/200 mL, pH= 5.4, temperature 278.15 $^{o}$K, UV light intensity 6 x10$^{-5}$ ensien.s$^{-1}$.

The values of apparent rate constant for decolourization of methyl green dye in presence of aqueous ZnO solutions were found to be directly proportional to initial dye concentration at ranged (25-50) ppm, according to the Lambert- Beer law, that beyond to increase the quantity of intermediates that increased the photoreaction well. Then the values of apparent rate constant for decolourization of methyl green dye decline. This behavior is due to the optical density in the solution was lower and fewer the amount of photons that must reach to catalyst's surface in photoreaction[18].

## 4. Effect of ZnO Dose:

For economic removal of methyl green dye from the wastewater must find the optimum amount of catalyst ( ZnO) for determining the efficient decolourization. From figure 4, the initial reaction rates were found to be directly proportional to ZnO dosage from 100 to 400 mg/200 mL that beyond to increase the active sites on the ZnO surface. Further increases of ZnO dosage beyond 400 mg/200 mL do not affect the decolourization significantly and the curve takes a plateau form. The decolourization rate levels reach maximum at 700 mg/200 mL as optimum catalyst ZnO dosage. At higher catalyst dosage, the decolourization rate starts declining, where screening effect is produced when the penetration of UV light (increased the turbidity)into the suspension is decreased, hence reducing the optical path and increased the turbidity of solution [2,19,20].

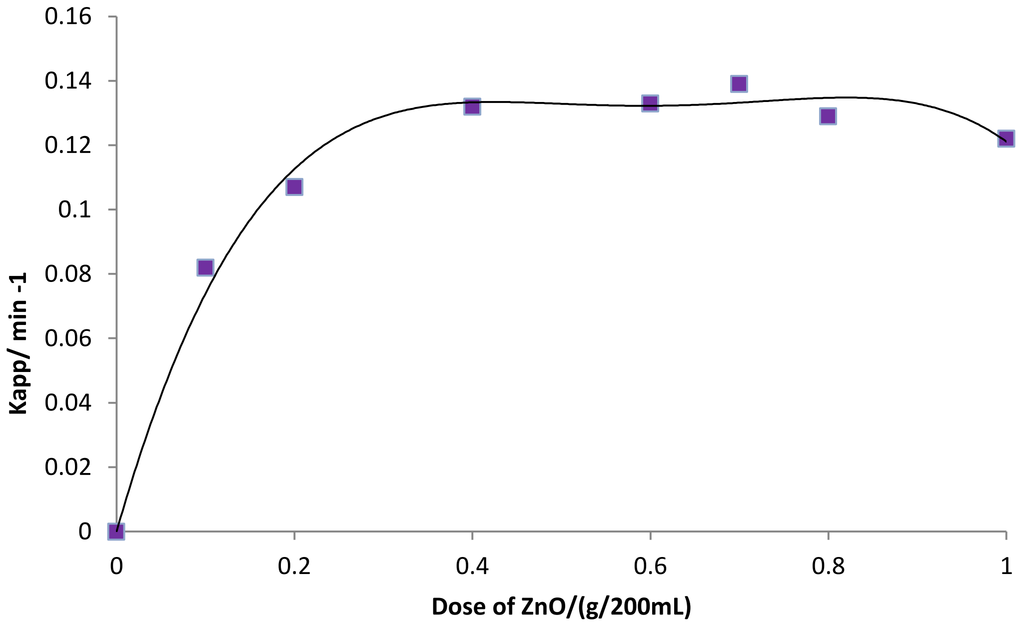


Figure 4: Pseudo-first order rate constant at varying semiconductor dosages. Conductions: dye conc. 50 ppm, pH= 5.4, temperature 278.15 $^{o}$K, UV light intensity 6 x10$^{-5}$ ensien.s$^{-1}$.

## 5. Effect of pH:

The initial pH of solution plays a vital role in the characteristics of textile dye and generation of hydroxyl radicals, moreover, the surface properties of catalyst. Hence, the interpretation of pH effects on the efficiency of the decolourization process is a very difficult task. This effect depends on three possible reaction mechanisms can contribute to dye decolourization with hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band[21].

The decolourization of methyl green dye was studied at different initial pH levels ranging from 2 to 10. The relationship between the apparent rate constant and pH is shown in Figure 5. The apparent rate constant increases with increasing of pH in the range 2-5.4. This behavior is due the increasing of adsorption of cationic (methyl green) dye on ZnO surface. Whereas at initial pH of solution less than 5.4, the surface of ZnO become positively charged that will increase the electrostatic repulsion between the positive charge of ZnO surface and the positive charge in solution, i.e; (hydronium cation ($H_3O^+$) and dye). Hence, at high concentration of hydronium cation will prevent the formation of hydroxyl radicals[22].

On the other hand, at pH more than 5.4, the efficiency of decolourization of methyl green was fewer, in spirit of increasing the speed of hydroxyl radicals formation, that due to increase the ability of an anion $Cl^-$ to react with hydroxyl radicals and lead to inorganic radical ions($ClO^{-\bullet}$). This inorganic radical anion has a lower reactivity than hydroxyl radicals, hence, it do not share in the dye decolourization or degradation[23].

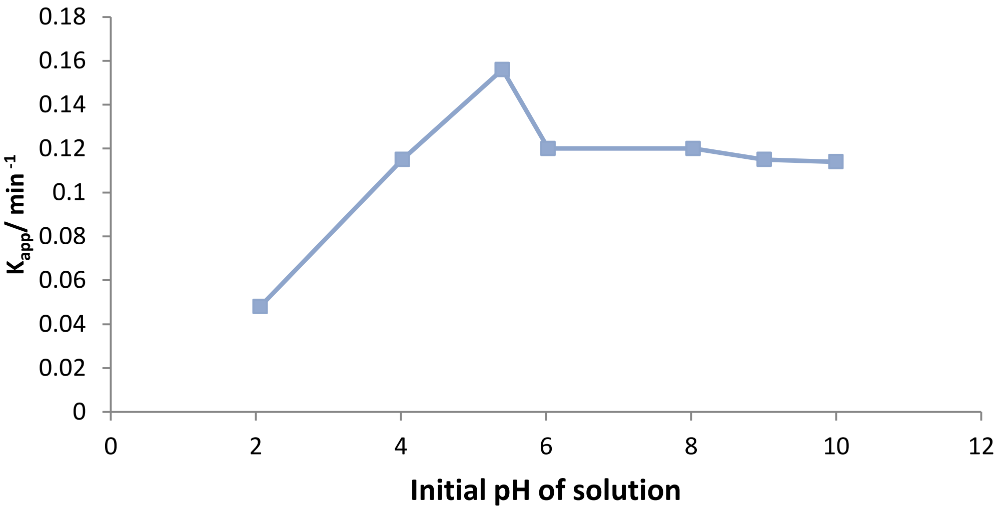


Figure5:Pseudo-first order rate constant at varying initial pH.Conductions:dye conc.50ppm, semiconductor dosage 700 mg/200 mL,temperature 278.15 °K, UV light intensity 6 x$10^{-5}$ ensien.$s^{-1}$.

## 6. Effect of temperature:

In a range of 278.15-293.15 °K, a linear relationship fitting the graph of Arrhenius equation (equation 8) was obtained for photodecolourization of methyl green dye in figure 6.

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \qquad ...(8)$$

Photocatalytic decolorization was found to increase with increasing temperature. Results indicated that the apparent activation energy was found equal to 24.914 kJ $mol^{-1}$, hence the photocatalytic reaction is finishing at 20 min.

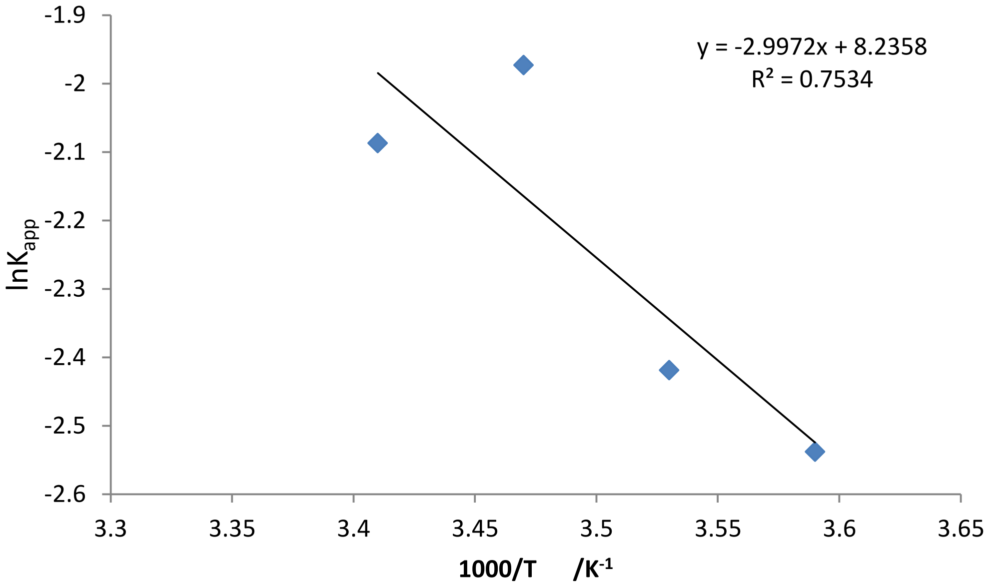


Figure 6: Pseudo-first order rate constant at varying temperature. Conductions: dye conc. 50 ppm, semiconductor dosage 700 mg/200 mL, pH= 5.4, temperature 278.15-293.15 °K, UV light intensity 6 x$10^{-5}$ ensien.$s^{-1}$.

The $\Delta H^{\#}$ and $\Delta S^{\#}$ values can be calculated from the plot of the Eyring equation[24]:

$$ln\frac{k_{app}}{T} = \frac{-\Delta H^{\#}}{RT} + \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\#}}{R}\right) \qquad \ldots(9)$$

Where: $k_B$ is Boltzmann's equation, h is Plank's constant, R is gas constant and T is temperature of reaction. The free energy $\Delta G^{\#}$ is equal to equation(10):

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad \ldots(10)$$

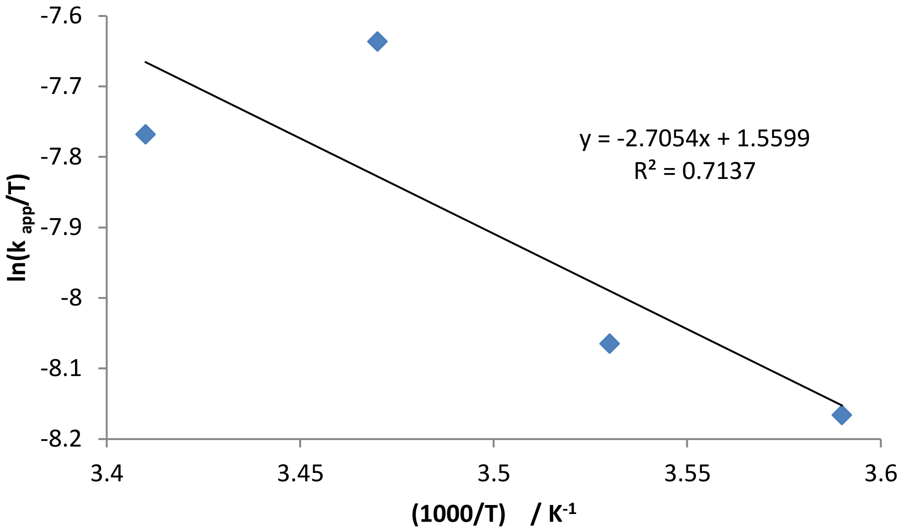


Figure 7: Eyring plot of $(\ln(K_{app}/T))$ vs.1/T. Conductions: dye conc. 50 ppm, semiconductor dosage 700 mg/200 mL, pH= 5.4, temperature 278.15-293.15 $^{o}$K, UV light intensity 6 x$10^{-5}$ ensien.$s^{-1}$ .

The activation energy and the other thermodynamics functions were listed in table1.

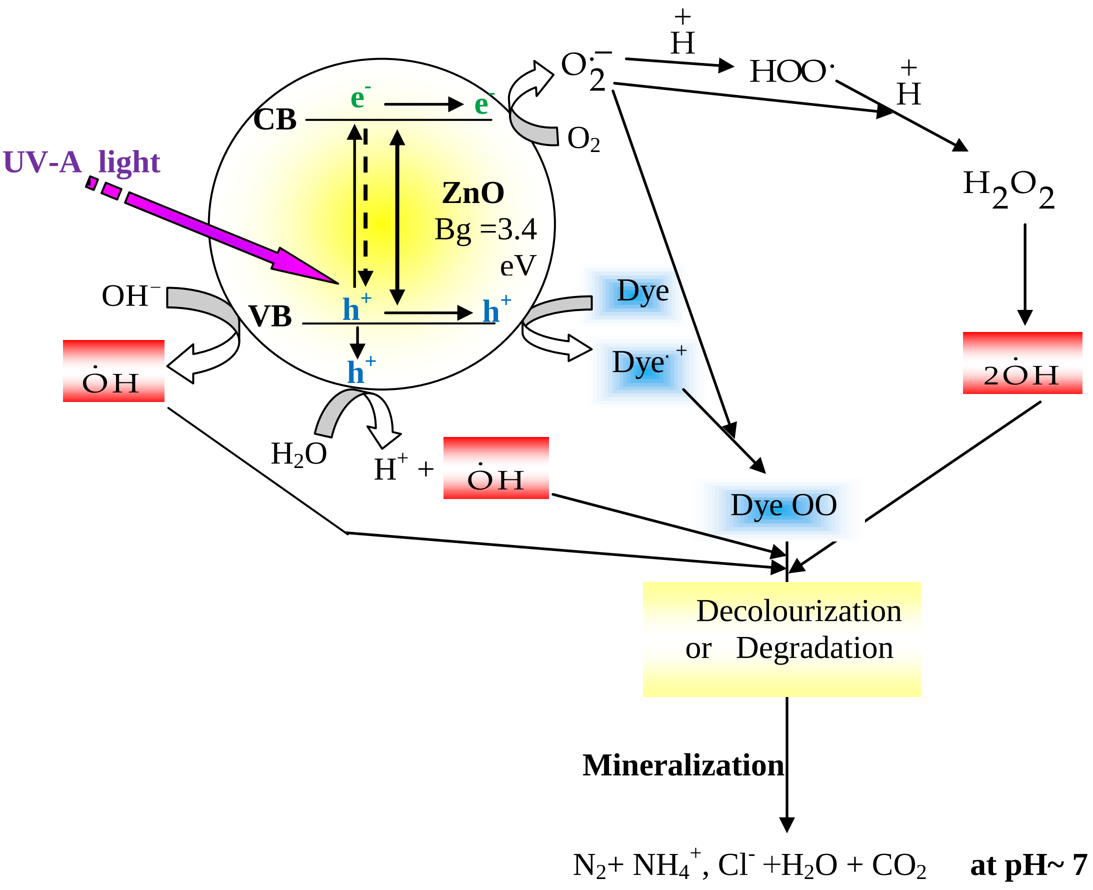
Table(1): The activation kinetic parameters of the decolourization of methyl green dye.

| $E_a$ kJ $mol^{-1}$ | $\Delta H^{\#}$ kJ $mol^{-1}$ | $\Delta S^{\#}$ kJ $mol^{-1}$ $K^{-1}$ | $\Delta G^{\#}_{288.15}$ kJ $mol^{-1}$ |
|---|---|---|---|
| 24.914 | 22.489 | -0.184 | 75.675 |

The results in table 1 and figures (6 ,7) were observed, that the rise in the temperature from 278.15 to 288.15 $^{o}$K was increased the rate of reaction, hence the photo-decolourization of methyl green dye was endothermic reaction. Moreover, the entropy was fewer that indicated to decrease in randomness, and the reaction was non spontaneous. Tabbara and Jamal [24] explained the results of thermodynamics functions for photoreaction were given a good in agreement with results of this work. However, at temperature more than 288.15 $^{o}$K the rate of reaction was decreased, thereby the solution was started to depress of dye adsorption on active sites of ZnO surface, moreover, the solubility of oxygen in water was less, that will decrease the number of produced hydroxyl radical [23].

## 7. Suggested mechanism:

The series of chain oxidative-reductive reactions occurs ,when the photon of UV-A light focuses on the colloid solution which contain methyl green dye with ZnO, the photoelectron and photohole $(e^- -h^+)_{exciton}$ were created, then the photohole and photoelectron input in serious of reactions as follow in scheme 2.



Scheme 2:Schamitic diagram for more accepted mechanism (Dye/semiconductor/ UV light system)(modified from reference [25]).

The rate limiting step consisting of hydroxyl radical formation or attack, therefore the Hydroxyl radicals in all photoreaction acts as power of decolourization or degradation of organic compounds like dyes, hence the mechanism of reaction can be passed through one or more than one of the following mechanisms [2,26,27]:

a. Reaction of adsorbed $^{\bullet}OH$ with the adsorbed organic molecule (dye).

$$^{\bullet}OH_{ads.} + Dye_{ads.} \longrightarrow \text{Decolourization or degradation} \quad \ldots(11)$$

b. Reaction of adsorbed $^{\bullet}OH$ with the free organic molecule(dye) in solution .

$$^{\bullet}OH_{ads.} + Dye_{aqu.} \longrightarrow \text{Decolourization or degradation} \quad \ldots(12)$$

c. Reaction between adsorbed organic molecule (dye) and free $^{\bullet}OH$ in solution.

$$^{\bullet}OH_{aqu.} + Dye_{ads.} \longrightarrow \text{Decolourization or degradation} \quad \ldots(13)$$

d. Reaction between free organic molecules(dye) and free $^{\bullet}OH$ in solution.

$$^{\bullet}OH_{aqu.} + Dye_{aqu.} \longrightarrow \text{Decolourization or degradation} \quad \ldots(14)$$

## 8. Conclusions

A series of experimental was carried out in the presence of ZnO particles, illumin- ation of high pressure mercury lamp and oxygen, that strongly regarded as an essential requirements for photocatalytic decolourization of methyl green dye. According to the results of this invistigation,the decolourization process of this dye follows pseudo-first order kinetics. The optimum conditions for this studied were 50 ppm of methyl green dye, the best ZnO dose is 700 mg/ 200 mL, and the initial pH equal to 5.4. At the temperature range 278.15–293.15 $^{o}$K, the activation energy for decolourization of dye were calculated and equal to 24.914 kJ mol$^{-1}$ by using Arrhenius equation. Also the thermodynamics functions were calculated by depending on Eyring equation. The photoreaction process was observed to be endothermic reaction and fewer randomness.

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