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# Effect of Oxidation Agents on Photo-Decolorization of Vitamin $B_{12}$ in the Presence of ZnO/UV-A System

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## ABSTRACT

*The aim of this work was to apply the many various oxidation agents namely $H_2O_2$, $K_2S_2O_8$ and $Fe^{2+}$ on the aqueous solution of vitamin $B_{12}$ with the presence of ZnO. The results indicated that the use of the mixture of $H_2O_2$ and $K_2S_2O_8$ in suspension of vitamin $B_{12}$ and ZnO gave a maximum efficiency percentage about 95.85% in 12 min; it was higher than that without the addition of oxidation reagent 79.33% in the same time. The obtained results demonstrated that the activation energy for this photoreaction without the addition of oxidation agent was more than that the apparent activation energy value with the used mixture of $H_2O_2$ and $K_2S_2O_8$. The thermodynamic study showed that both reactions were endothermic, less-random and non-spontaneous. The $\Delta H^{\#}$ with the oxidant agents (31.43 kJ mol$^{-1}$) is less than that without using oxidant agents (35.81 kJ mol$^{-1}$). Moreover, the addition of series of oxidant agent solution to vitamin $B_{12}$ solution led to change the photocatalytic activity for decolorization of vitamin $B_{12}$ in suspension solution of ZnO, and was found the activity sequence as follows: ($H_2O_2$ + $K_2S_2O_8$) > ($H_2O_2$ + Fe(II)) (Fenton reaction) > ($H_2O_2$) > ($K_2S_2O_8$) > (without the oxidation agents) > ($K_2S_2O_8$ + Fe(II)) > Fe(II).*

***Keywords***: *vitamin $B_{12}$; cyanocobalamin; cobalamin; decolorization; oxidant*

## ABSTRAK

*Tujuan dari pekerjaan ini adalah untuk menerapkan berbagai agen oksidasi, yaitu $H_2O_2$, $K_2S_2O_8$ dan $Fe^{2+}$ dalam larutan vitamin $B_{12}$ dengan keberadaan ZnO. Hasil penelitian menunjukkan bahwa penggunaan campuran $H_2O_2$ dan $K_2S_2O_8$ dalam suspensi vitamin $B_{12}$ dan ZnO memberikan persentase efisiensi sekitar 95,85% dalam waktu 12 menit; lebih tinggi daripada tanpa penambahan reagen oksidasi (79,33%) dalam waktu yang sama. Hasil yang diperoleh menunjukkan bahwa energi aktivasi untuk fotoreaksi tanpa penambahan oksidasi agen lebih besar daripada dengan campuran pengoksidasi $H_2O_2$ dan $K_2S_2O_8$. Kajian termodinamika menunjukkan bahwa kedua reaksi yang diteliti bersifat endotermik, kurang acak dan tidak spontan. Nilai $\Delta H^{\#}$ reaksi dengan agen oksidan (31,43 kJ mol$^{-1}$) lebih rendah daripada $\Delta H^{\#}$ tanpa agen oksidan (35,81 kJ mol$^{-1}$). Selain itu, penambahan serangkaian larutan agen oksidan pada larutan vitamin $B_{12}$ menyebabkan perubahan aktivitas fotokatalitik untuk dekolorisasi vitamin $B_{12}$ dalam larutan suspensi ZnO, dan didapatkan urutan akivitas sebagai berikut: ($H_2O_2$ + $K_2S_2O_8$) > ($H_2O_2$ + Fe(II)) (Reaksi Fenton) > ($H_2O_2$ > ($K_2S_2O_8$) > (tanpa agen oksidasi) > ($K_2S_2O_8$ + Fe(II)) > Fe(II).*

***Kata Kunci***: *vitamin $B_{12}$; sianokobalamin; kobalamin; dekolorisasi; oksidan*

## INTRODUCTION

In fact, the most drugs are sensitive toward the light, hence, they stores in non-clear containers [1]. Vitamin $B_{12}$ is deemed as one of the sensitive drugs to light [2]. It is known cobalamin, cyanocobalamin and hydroxocobalamin [3]. Cobalamin is an octahedral cobalt (III) complexes, this complex is arranged as an organometallic compound that is shaped by the arranged of the cobalt particle in a corrin ring of a porphyrin [2,4]. Four of the six coordination locales of triply ionized cobalt atom are tightly bound by creating a corrin ring, while the fifth linked is produced by a dimethylbenzimidazole gathering [5-6]. From the other side, the sixth coordination site is found in the focal point of reactivity, that can be a hydroxyl bunch (-OH), a cyano aggregate (-CN), a methyl gather (-$CH_3$) or a 5'-deoxyadenosyl gathering, which separate to produce a four coalmine frames, as shown in Fig. 1 [5-7].

Vitamin $B_{12}$ is red, red-orange, or yellow crystalline substances, water-soluble, liberated as free Co atom when reduced in present ascorbic acid and sensitive to light because of owing to the π–π transitions of the corrin nucleus [2,6]. Hence, many researchers interested in this object in different published in photo - decolorization of it from aqueous solution [8-10], used to surface-enhanced resonance Raman scattering [11-12], determined it by adsorption [13-14], Microbiological Assay of Vitamin $B_{12}$ [15], determined Vitamin $B_{12}$ in multivitamin by HPLC [16-17].

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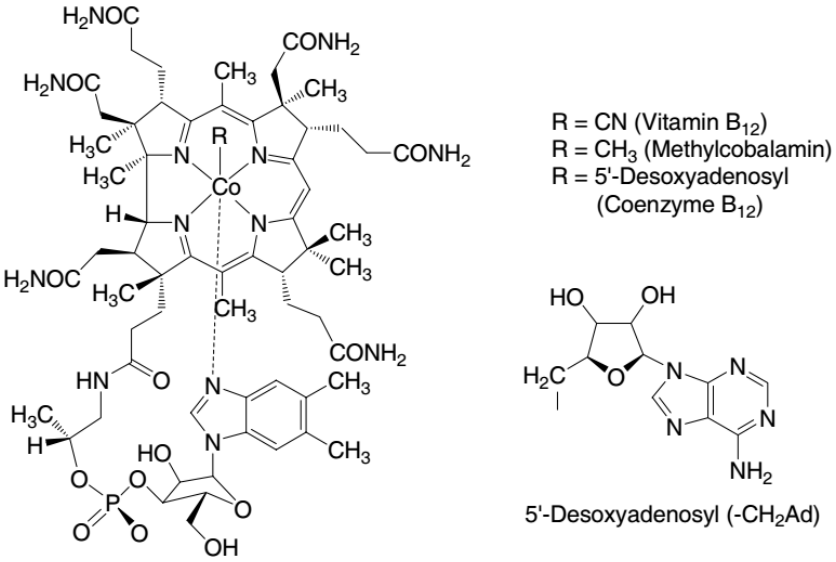


**Fig 1.** Structures formula of Vitamin $B_{12}$, methylcobalamin and coenzyme $B_{12}$ [7]

**Table 1.** Physico-chemical characteristics of the cobalamin dye

| Values | Parameters |
|---|---|
| $C_{63}H_{88}CoN_{14}O_{14}P$ | Molecular formula |
| Vitamin $B_{12}$ | Synonym |
| *α*-(5,6-dimethylbenzimidazolyl)cobamidcyanide | IUPAC name |
| 1355.37 g/mol | Molecular Weight |
| Phthalocyanine | Chemical class |
| 550 nm | $\lambda_{max}$ |

This work was focused on the kinetic and thermodynamics factors that influence on the photo-decolorization of Vitamin $B_{12}$ under various types of oxidant agents namely $H_2O_2$, $K_2S_2O_8$ and Fe (II).

## EXPERIMENTAL SECTION

### Materials

In this study, all used chemicals were utilized without further purification. Commercial ZnO was supplied by Fluka in 99.5% purity. Vitamin $B_{12}$ was supplied by GERDA–France as liquid tablets contain1000 µg/4 mL of it, this liquid sample was diluted with $H_2O$ to the appropriate concentration (25 ppm). The physicochemical properties of this vitamin (cobalamin dye) are listed in Table 1. The rest chemicals were supplied from Fluka and Merck.

### Instrumentation

The instruments used in this work included a sensitive balance (BL 210 S, Sartorius, Germany), hot plate stirrer (Heido-MrHei-Standard, Germany), centrifuge (Hettich-Universall II, Germany), water bath recirculation (Stuart-England). The absorbance of dye solution was measured using UV-Visible spectrophotometer (AA-1800, Shimadzu, Japan).

### Procedure

Photocatalytic decolorization reactions of cobalamin were carried out in using a batch homemade photoreactor with the radiation source type High-pressure mercury lamp- 250 Watts (Radium-Germany). The light intensity of this light source was calculated using a chemical actinometric solution [18], and found to be $9.545 \times 10^{-8}$ Ens. $s^{-1}$.

In this current work, 500 mg of commercial ZnO was suspended in 50 mL of 25 ppm of an aqueous solution of cobalamin. In the outset, the dark reaction was done for 30 min, after that the produced homogeneous suspension solution was illumination. At regular time intervals, about 2.5 mL of homogeneous suspension solution was removed and centrifuged at 4000 rpm for 10 min. The clear separated solution was centrifuged again at the same time and speed to ensure removed all fine particles of catalyst. The absorbance clear solution of dye was read with the using a UV-Vis spectrophotometer type optima at 550 nm, and then the concentration of this dye was analyzed with depending upon the calibration curve of

the same dye. The kinetic study of this photo-decolorization of cobalamin was obeyed to pseudo first-order kinetics, and the apparent rate constant $k_{app}$ was illustrated by equation 1, that depended on Langmuir-Hinshelwood kinetic expression at the low concentration of studied dye [19-22].

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

whereas, $C_o$ is an initial concentration of cobalamin dye in dark reaction at irradiation time equal to 0 min. $C_t$ is a concentration of the same studied dye at t time of irradiation.

The photo decolorization efficiency (PDE) of cobalamin was expressed by the following equation 2 [9,20]:

$$PDE = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \quad (2)$$

## RESULT AND DISCUSSION

Series of experiments were done to estimate how the light and the other parameters were affected on the photo-decolorization rate of cobalamin dye. This photoreaction was apparent to be followed by pseudo first - order kinetics, when plotted ln ($C_o/C_t$) verse time in min and given a straight line.

### Effect of Oxidant Agents on the Photo-Decolorization Rate

Fig. 2 and 3 explain the effect of addition for the different types of oxidant agents such as $H_2O_2$, $K_2S_2O_8$ and Fe(II) on the suspension solution of cobalamin with ZnO.

The results explain that the photoreaction rate constant was depressed under addition of $Fe^{2+}$ to an aqueous solution of cobalamin from 0.1438 $min^{-1}$ to 0.0531 $min^{-1}$ with PDE from 79.34 to 49.66% at 12 min, respectively. This behave was based on the oxidation forces and concentrations of this oxidation reagent, hence, the rate of reaction and efficiency of photo-decolorization of this dye decrease with the addition of $Fe^{2+}$ to dye solution, that due to scavenged Fe(II) by hydroxyl radical [23] that leads to depress the generated of hydroxyl radical from this side of photocatalyst.

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-} \quad (3)$$

The photoactivity of ZnO in light was performed according to the following equations [24-25].

$$ZnO + hv \rightarrow ZnO\left(e^{-}_{CB} + h^{+}_{VB}\right) \quad (4)$$

$$O_2 + e^{-}_{CB} \rightarrow O_2^{\cdot -} \quad (5)$$

$$O_2^{\cdot -} + H^{+} \rightarrow HO_2^{\cdot} \quad (6)$$

$$HO_2^{\cdot} + H^{+} \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 + hv \rightarrow 2HO^{\cdot} \quad (8)$$

$$H_2O + h^{+}_{VB} \rightarrow H^{+} + HO^{\cdot} \quad (9)$$

On the other hand, the fastest photoreaction was found at addition mixture from oxidant agent ($H_2O_2$, $K_2S_2O_8$) and the rate constant is equal to 0.1967 $min^{-1}$ at maximum PDE which equal to 95.858 at 12 min. As based on the next equations 10-12, the persulfate ion ($S_2O_8^{2-}$) can be reacted with light or with the electron of the conductive band of the photocatalyst, which leads to produce sulfate radical anion, which regarded as the strong one-electron oxidant to have a redox potential between 2.5 to 3.1 eV verses NHE. Sulfate

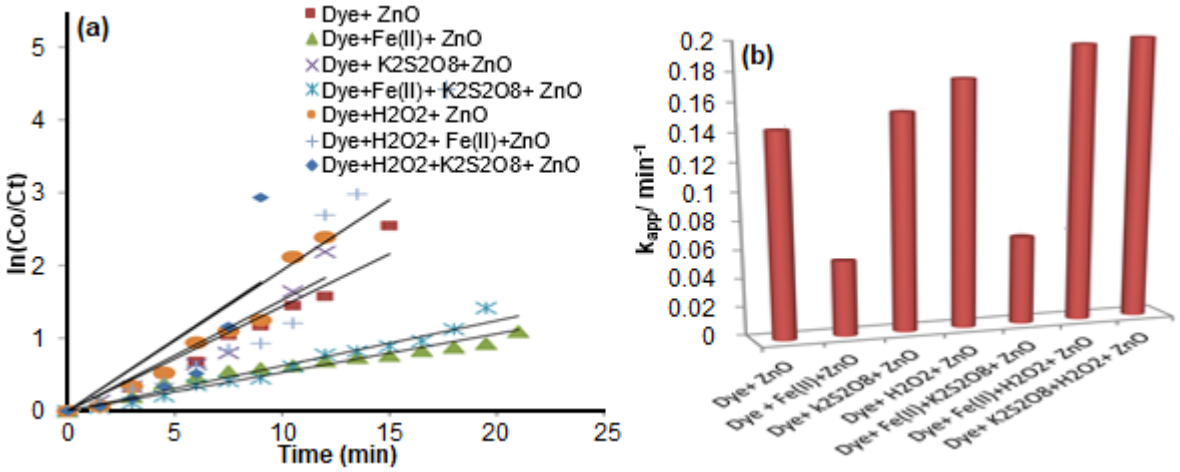


**Fig 2.** Effect of addition oxidant agents on the photo-decolorization of 25 ppm from cobalamin dye with 500 mg/50 mL of commercial ZnO, at 0.5% $H_2O_2$, 1x $10^{-4}$ M from $K_2S_2O_8$ and Fe (II). (a) The relation between ln($C_o/C_t$) verse Time and (b) relation between rate constant ($k_{app}$) verse used oxidation agent with the sample

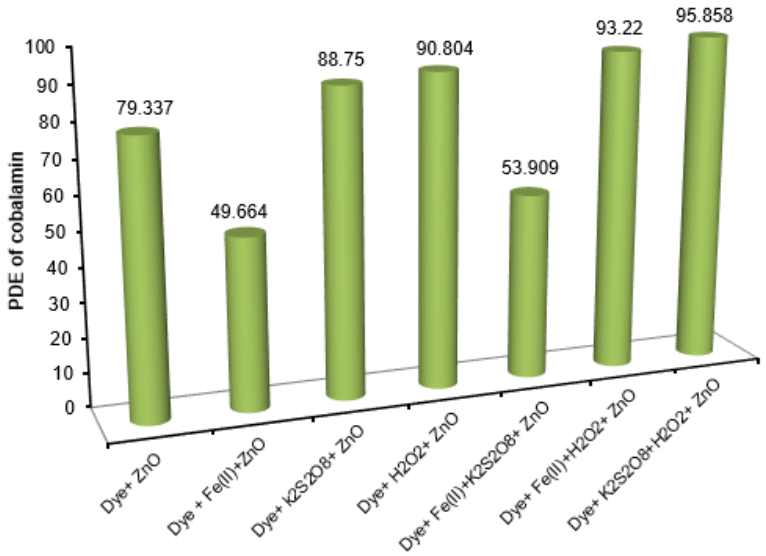


**Fig 3.** The relation between PDE and addition oxidant agents via photo-decolorization of 25 ppm from cobalamin dye with 500 mg/50 mL of commercial ZnO, at 0.5% $H_2O_2$, 1x $10^{-4}$ M from $K_2S_2O_8$ and Fe(II)

radical anion $SO_4^{\cdot-}$ reacts with water to enhance formed hydroxyl radical [26-30].

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\cdot-} \quad (10)$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (11)$$

$$SO_4^{\cdot-} + H_2O \rightarrow HO^{\cdot} + SO_4^{2-} + H^+ \quad (12)$$

From the other side, the used $H_2O_2$ as oxidant agent undertakes with increasing the rate of reaction by generated hydroxyl radicals [31-33], as shown in the following equations:

$$H_2O_2 + hv \rightarrow 2HO^{\cdot} \quad (13)$$

$$H_2O_2 + e_{CB}^- \rightarrow HO^{\cdot} + HO^- \quad (14)$$

$$H_2O_2 + O_2^{\cdot-} \rightarrow HO^{\cdot} + HO^- + O_2 \quad (15)$$

The Fenton's reaction was done by addition of mixture from $H_2O_2$ and $Fe^{2+}$ to an aqueous solution of cobalamin, hence the PDE increases from 79.33 to 93.22% this reaction was described in equations [34-38].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^- \quad (16)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad (17)$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \quad (18)$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \quad (19)$$

**Effect of Temperature on the Photo-Decolorization Rate**

This effect illustrates at the used temperature ranged (278–303)K, the raised of temperature enhances the photocatalytic decolorization of cobalamin when used oxidation agents (as the mixture for $K_2S_2O_8$ + $H_2O_2$) and without the using this mixture in presence ZnO. The activation energy (Ea), change in enthalpy ($\Delta H^{\#}$), change in entropy ($\Delta S^{\#}$) and change in free energy ($\Delta G^{\#}$) were determined using equations from 20 to 22 [39-41].

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \quad (20)$$

whereas, $E_a$ is an apparent activation energy, A is a frequency constant, R is gas constant and T is a temperature of reaction and $k_{app}$ is an apparent rate constant ($min^{-1}$).

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \left(\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R}\right) \quad (21)$$

where, $k_B$ is a Boltzmann's constant, T is a temperature of reaction, R is a gas constant, h is a Plank's constant, $\Delta S^{\#}$ is a change in entropy and $\Delta H^{\#}$ is a change in enthalpy.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (22)$$

whereas, $\Delta G^{\#}$ is a change in free energy.

The results of Fig. 4 and 5 gave the intuitional impression about the photoreaction, so, the rate of reactions increases with increasing the studied range of temperatures [42-43], this behave indicates the reaction is endothermic with and without the addition of a mixture of the oxidant agents from $K_2S_2O_8$ + $H_2O_2$. Based on the results in Table 2, the photo decolorization reaction of cobalamin dye with the using mixture of oxidant reagent ($K_2S_2O_8$ + $H_2O_2$) is faster than the photoreaction without using the mixture of oxidant reagent. The less value of activation energy confirms this fact. The positive values of $\Delta H^{\#}$ (endothermic reaction) and $\Delta G^{\#}$ (non-spontaneous

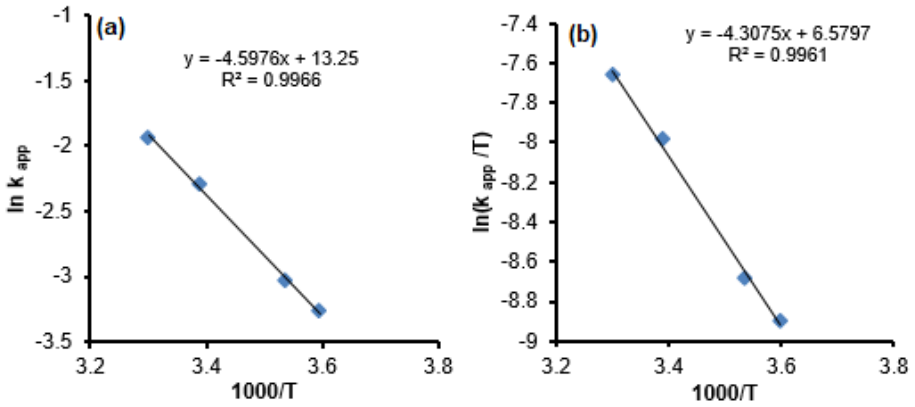


**Fig 4.** Effect of temperature on the photodecolorization of cobalamin dye from colloidal solution of 500 mg/50 mL ZnO at the range temperatures (288-303) K (a) Arrhenius equation plot of (ln $k_{app}$) vs. 1/T and (b) Eyring plot of (ln($k_{app}$/T)) vs.1

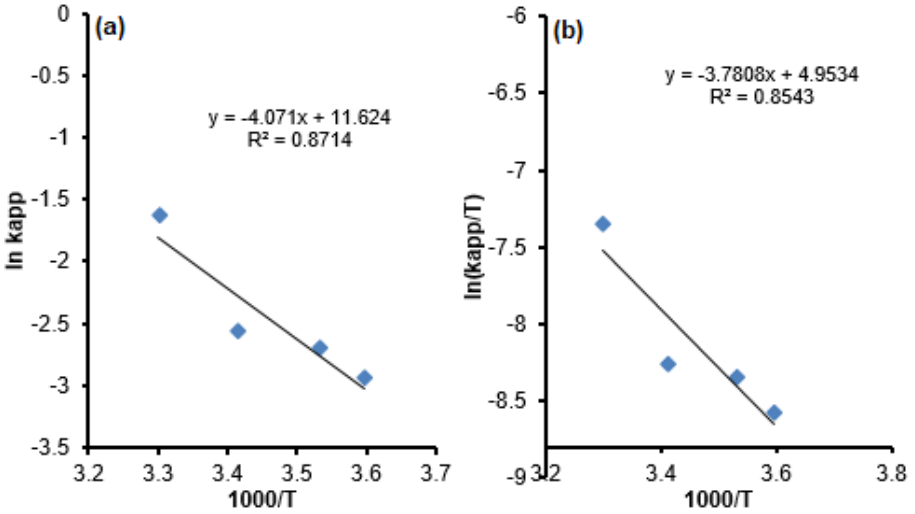


**Fig 5.** Effect of temperature on the photodecolorization of cobalamin dye from colloidal solution of 500 mg/50 mL ZnO with using 0.5% $H_2O_2$, 1x $10^{-4}$ M from $K_2S_2O_8$, at the range temperatures (288-303) K (a) Arrhenius equation plot of (ln $k_{app}$) vs. 1/T and (b) Eyring plot of (ln($k_{app}$/T)) vs.1/T

**Table 2.** The kinetic and thermodynamic parameters for photocatalytic decolorization of cobalamin with and without using oxidant agents.

| Condition | $E_a$ kJ mol$^{-1}$ | $\Delta H^{\#}$ kJ mol$^{-1}$ | $\Delta S^{\#}$ J mol$^{-1}$ K$^{-1}$ | $\Delta G^{\#}_{303}$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| Without oxidant agents | 38.224 | 35.812 | -2.066 | 36.620 |
| With oxidant agents | 33.846 | 31.433 | -2.262 | 35.809 |

reaction) observe without and with used mixture of oxidant reagent ($K_2S_2O_8$ + $H_2O_2$), that due to the high solvated of the transition state between hydroxyl radicals and the studied dye molecules, and this results in agreement with that found in references [21,41].

## CONCLUSION

In this work, series of photo-experiments of the photodecolorization of cobalamin dye were achieved by using the homemade photo-reactor with UV lamp of 250 watt. The produced results demonstrated that the photoreaction in this system obeyed to the pseudo first-order. The maximum decolorization of the dye was found in using the mixture of oxidant agents ($H_2O_2$+ $K_2S_2O_8$), whereas, the less decolorization was obtained when it was only used $Fe^{2+}$ solution. The thermodynamic study of photo-decolorization of cobalamin dye in ZnO/UV-A system was investigated by choosing this system without and with the using

oxidant agents, as the mixture from ($H_2O_2$+ $K_2S_2O_8$). Both reactions are found endothermic, less random and non-spontaneous. The $\Delta H^{\#}$ and $\Delta G^{\#}$ values for cobalamin dye in ZnO/UV-A system and cobalamin dye in ($H_2O_2$+ $K_2S_2O_8$) /ZnO/ UV-A system are positive. The activation energies for photo-decolorization of cobalamin dye in ZnO/UV-A system and cobalamin dye in ($H_2O_2$+ $K_2S_2O_8$)/ZnO/UV-A system were found to be 38.22 kJ $mol^{-1}$ and 33.84 kJ $mol^{-1}$, respectively. Hence, the photo-decolorization of cobalamin dye in ($H_2O_2$ + $K_2S_2O_8$)/ZnO/UV-A system is faster than that for using cobalamin dye in ZnO/UV-A system.

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