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ORIGINAL ARTICLE

Insight into the Oxidant Agents Effect of Removal and Photo-decolorization of Vitamin B_{12} Solution in Drug Tablets using ZrO_2

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KEYWORDS

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ABSTRACT: The purpose of this manuscript was to remove and decolorize vitamin B_{12} from an aqueous solution of drug tablets using ZrO_2 as an environmentally friendly method via advanced oxidation processes. Some oxidant agents such as Fe^{2+}, H_2O_2, $K_2S_2O_8$ and their mixture of were performed, and the best adsorption sequences have occurred with increased adsorption capacity: $q(K_2S_2O_8 + H_2O_2) > q(H_2O_2) > q(K_2S_2O_8) > q(Fe^{2+} + H_2O_2) > q(Fe^{2+}) > q$ (without) Endothermic and physical adsorption occurred of this vitamin on the ZrO_2 surface with and without the addition of $K_2S_2O_8 + H_2O_2$. On the other side, the photoreaction for this vitamin with and without the addition of $K_2S_2O_8 + H_2O_2$ was found to be quick, endothermic, less random, and spontaneous. At 15 min, 33.223 % and 98. 684% were calculated as the maximum percentage of removal in the dark reaction and the maximum decolorization in the photocatalytic reaction respectively.

INTRODUCTION

In the past few decades, photocatalysis has been one of the most vital processes, using photo-semiconductor molecules that largely interfere with various molecules in the liquid or gaseous state under light [1]. Indeed, the nature of any photoreaction depends on the photo-semiconductor absorbing of ultraviolet, visible, or solar light, leading to the generation of a free radical as hydroxyl radical in all aqueous solutions [2, 3]. photocatalysis is commonly used in the treatment of water contaminations from colored organic compounds using photocatalysts such as ZnO[4], TiO_2[5], ZrO_2[6]. etc. Zirconium oxide (ZrO_2) is recognized in this area as one of the significant and active photo-semiconductors in the spirit of having a large bandgap of about 5 eV [7]. It is has a high negative potential value of the conduction band [8], reached approx. 2400°C with high density, chemical deadlock, resistance to firmness [9]. ZrO_2 comprises many shapes, including cubic, monoclinic and tetragonal, depending on the temperature as shown in equation 1 and its preparation process [10-14].

$$(\text{monoclinic} \xrightarrow{1170\ ^oC} tetragonal \xrightarrow{2370\ ^oC} cubic\ ) \qquad 1$$

ZrO_2 or its composite is typically used to decolorize the colored compounds as dyes and complexes from its aqueous solution in photocatalysis [6, 15]. On the other side, many-colored materials like cobalt amine (vitamin B_{12} an industrial form) have been photo-cataysed[16-18]. Vitamin B_{12} contains cobalt with a coronoid molecule that

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has a dark red color, can quickly dissolve in aqueous solutions[19,20] and is known to be one of the essential vitamins present in many food sources or in medicinal substances in the human body[14,21]. Generally, when cobalt amine is exposed to ultraviolet light in the presence of hydroxide and hydrogen ions, it progresses to photolysis and creates hydroxocobalamin (B_{12b}). The photochemical conversion rate is enhanced by stimulation, even though the kinetic reaction has zero-order kinetics at various pH values. As illustrated in the following equations [22], this process has been

$$[Co^{3+}CN] \overset{hv}{\rightarrow} [Co^{3+}CN]^{*} \overset{ISC}{\longrightarrow} [Co^{3+}CN]^{***} \qquad 2$$

Singlet excited state Triplet excited state

$$[Co^{3+}CN]^{***} \overset{H_3O}{\longrightarrow} [Co^{3+}OH] + CN^{-} \qquad 3$$

The goal of the present work was to explore the role of the ZrO_2 photocatalyst in Vitamin B12 (cobalt amine dye) adsorption and photocatalysis and to study the several active factors that raised the rate of dye removal and decolonization efficiencies in a short time.

MATERIALS AND METHODS

Chemicals

The Vitamin B_{12} or cobalt amine dye in formula structure ($C_{63}H_{88}CoN_{14}O_{14}P$, with M. wt 1355.37 g mol^{-1}, λ_{max} 550 nm and Phthalocyanine class was supplied as liquid tablets (containing 1000 µg/4 mL of this vitamin) by GERDA – France. ZrO_2 with 99.5% purity was supplied from Fluka-Germany. All the rest chemicals in these performed experiments were carried out without any purification and supplied from Fluka and Merck companies.

Adsorption process

Using a magnetic stirrer, 25 ppm of cobalamin was vigorously shacked with 25 mg of commercial ZrO_2 for 30 minutes to ensure contacting of the solution with the active sites of the used catalyst's surface. The amount of cobalamin dye uptake onto ZrO_2 was determined employing the mass balance equation below [23-25].

$$q = (C_o - C_e)x\,\frac{V}{m} \qquad 4$$

Here: q is adsorption capacities at equilibrium state in (mg g^{-1}), m is the mass in g for dry adsorbent (ZrO_2) used, C_o and C_e are the initial and equilibrium cobalamin concentrations in solution at time 0 and equilibrium time respectively, V is the volume of adsorbate (cobalamin solution) in L.

The percentage of removal (adsorption) efficiency ($E_{removal}$%) of cobalamin can be obtained from the following relation[5,26]

$$E_{removal}\,\% = \frac{(C_o - C_e)}{C_o}\ \mathrm{x}\ 100 \qquad 5$$

Photocatalysis

High-pressure mercury lamp (250 watts, radium-Germany) was used as a source of ultraviolet light (type UV-A light) with a light intensity equal to 9.545×10^{8} Ens. s^{-1}, which was calculated by actinochemical solution [27].

In this current work, UV- A light illumined 50 mL of 25 ppm of suspended cobalamin solution with 25 mg of ZrO_2. Relevant volumes of the illuminated solution were withdrawn at regular intervals, these solutions were then separated for 15 minutes at 4000 rpm to expel the suspended substance from the solution. The absorbance of produced filtered solution was read at 550 nm using (optima) UV-visible spectrophotometer, and then the concentration of this dye was analyzed based upon the calibration curve of the same dye. To calculate the apparent rate constant ($k_{app.}$) [28-30]and the % Efficiency of decolorization ($E_{decol.}$%) [31-33]for this photoreaction, the following equations below were applied to calculate them.

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app}\ .t \qquad 6$$

$$E_{decol.}\,\% = \left(\frac{C_o - C_t}{C_o}\right) x100 \qquad 7$$

whereas: C_o is an initial concentration of cobalamin dye in a dark reaction. C_t is the concentration of the same dye at t various times of irradiation respectively.

RESULTS AND DISCUSSION

The Influencing of adding oxidizing agents on the removal of vitamin B_{12}

The adding of different oxidizing agents such as (Fe(II), H_2O_2, Fe(II) + H_2O_2, $K_2S_2O_8$, and $K_2S_2O_8$ +H_2O_2) via the removing process of vitamin B_{12} by ZrO_2 surface were done for 30 min of stirring. Referring to Figure 1, the results obtained that the addition of mixture from peroxide Hydrogen with potassium persulfate give a great effect in removing of vitamin B_{12} with using ZrO_2 surface, and the $E_{removal.}$% alters form 6.578 % to 33.223 % at 30 min. This behaves due to the nature of the ZrO_2 surface to adsorption these species.

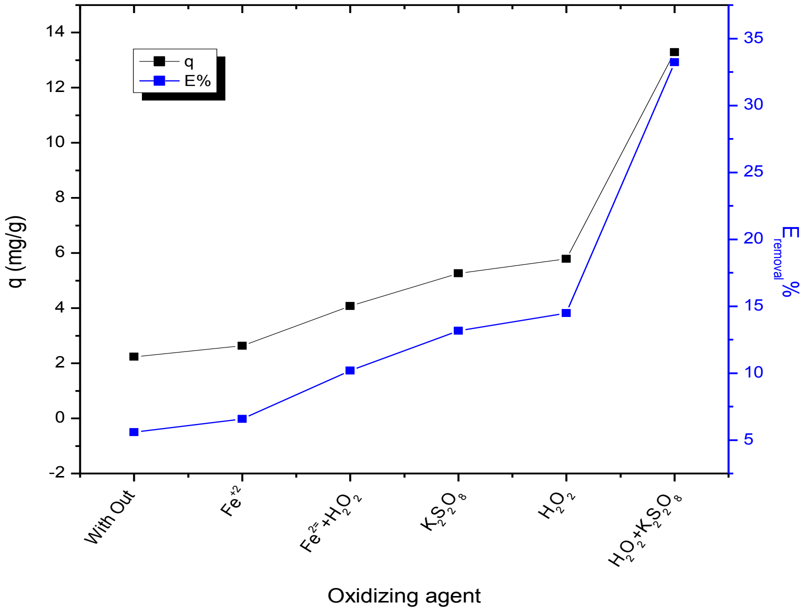

Figure 1. Influencing of adding oxidizing agents on $E_{removal.}$% and q during the process of removing vitamin B_{12} by ZrO_2

The Influencing of adding oxidizing agents on decolorization of vitamin B_{12}

Figures 2 and 3 explain the effect of the addition of the oxidizing agents under UV-A light enhances the decolonization of vitamin B_{12} with present ZrO_2. At the outset, the focus of UV-A light on suspension solution of ZrO_2 with vitamin B_{12} under environmental oxygen was adopted by the following equations below, which are essential to produce the hydroxyl radicals in the presence of any photocatalyst in an aqueous solution[6, 34-36].

$$ZrO_2 + h\nu \rightarrow ZrO_2(e_{CB}^- + h_{VB}^+) \qquad 8$$

$$O_2 + e_{CB}^- \rightarrow O_2^{\cdot -} \qquad 9$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \qquad 10$$

$$HO_2^{\cdot} + H^+ \rightarrow H_2O_2 \qquad 11$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \qquad 12$$

$$H_2O + h_{VB}^+ \rightarrow H^+ + HO^{\cdot} \qquad 13$$

The maximum reaction rate and the photodecolorization efficiency ($E_{decol.}$ %) occur when mixing hydrogen peroxide with persulfate as oxidant agents and the efficiency rises from 75.698 % to 98.684 % for 15 min and 15°C. This case attitude to react the persulfate ion with light or the photoelectron of photo-semiconductor (ZrO_2) [9, 37] and produce a sulfates radical anion ($SO_4^{\cdot -}$), which interacts with water molecules and generates the free hydroxyl radical [37]. Besides, hydrogen peroxide with or without the addition of the persulfate ion can give another amount of free hydroxyl radical in present light as shown in the following equations[37-39].

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\cdot-} \qquad 14$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \qquad 15$$

$$SO_4^{\cdot-} + H_2O \rightarrow HO^{\cdot} + SO_4^{2-} + H^+ \qquad 16$$

$$H_2O_2 + hv \rightarrow 2\,HO^{\cdot} \qquad 17$$

$$H_2O_2 + e_{CB}^- \rightarrow HO^{\cdot} + HO^- \qquad 18$$

$$H_2O_2 + O_2^{\cdot-} \rightarrow HO^{\cdot} + HO^- + O_2 \qquad 19$$

While the addition of Fe (II) alone (as an equation 20 and 21) or with the hydrogen peroxide (as an equation from 22 to 25) is caused to reduce the effectiveness compared with other used oxidant agents, that due to scavenging the generation of free hydroxyl radicals on ZrO_2 surface by Fe(II), and produced Fe(III). Fe(II) can be interacted with electron and reproduced Fe(II) in solution[26,40]. Moreover, sometimes, hydrogen peroxide acts as a scavenger of free hydroxyl radicals and formed water molecules [18, 39].

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \qquad 20$$

$$Fe^{3+} + e_{CB}^- \rightarrow Fe^{2+} \qquad 21$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^- \qquad 22$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \qquad 23$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad 24$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \qquad 25$$

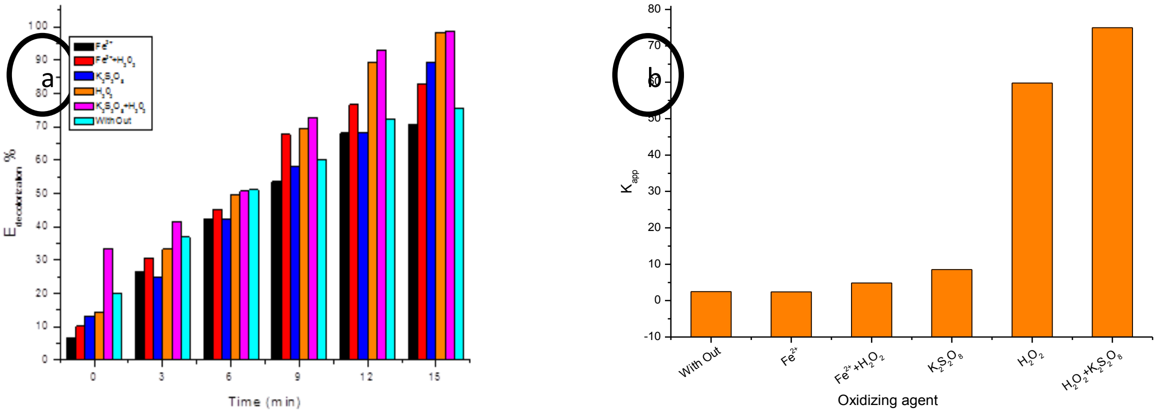

Figure 2. a) Influencing of adding oxidizing agents of $E_{decolorization.}$% and time to decolorization of vitamin B_{12} by ZrO_2 under UV light. B) Influencing of adding oxidizing agents with k_{app} on decolorization of vitamin B_{12} by ZrO_2 under UV light.

The Influencing of Temperature on the removal of vitamin B_{12}

Figure 3 represents the influencing the raised of temperature on the removal of vitamin B_{12} with and without using a mixture of oxidant agents ($K_2S_2O_8$ +H_2O_2) in ZrO_2 suspension solution. The adsorption constant (sorption distribution coefficient) k_d and the change in free molar energy (ΔG^o) were calculated using eq. 26 and classical Van't Hoff equation[26, 41] (eq. 27).

$$k_d = \frac{C_{ads.}}{C_e} \qquad 26$$

$$\Delta G^o = -RTlnk_d \qquad 27$$

Here, C_e is the concentration of the remaining vitamin B_{12} in solution in mg.L^{-1} at equilibrium state, $C_{ads.}$ is the concentration of vitamin B_{12} (mg L^{-1}) present on the zirconium oxide surfaces as an adsorbate material in equilibrium, R is the universal gas constant (J mol^{-1} K^{-1}) and T is the absolute temperature in (K).

On the other hand, the ΔH^o and ΔS^o were calculated, after plotting the Van't Hoff equation (eq. 28) [4,25, 42].

$$lnk_d = \frac{-\Delta H^o}{RT} + \left(\frac{\Delta S^o}{R}\right) \qquad 28$$

The activation energy (E_a) of the dark reaction was calculated depending upon the ΔH^o [5, 42].

$$E_a = \Delta H^o + RT \qquad 29$$

Referring to Figure 3 and Table 1 that the rise in the temperature would enhance the absorption of vitamin B_{12} on ZrO_2 surface and the change in enthalpies for the addition oxidant agent and without that are found to be positive. Indeed, the solvent molecules may be desorbed from the adsorbent surface and, at the same time, the solid surface adsorption can be the substance species present in the solution. When the increased the displacement of adsorption species (vitamin B_{12}) by solvent, the positive value of enthalpy will be produced [41]. The magnitude of ΔH^o is being less than 80-200 kJ mol^{-1} to ensure that physical adsorption happened. The positive magnitudes of ΔS^o reflect the affinity between the adsorption species (vitamin B12, water, and oxidant agents) and adsorbent surface, hence, the increased of random on the solid/ solution interface[41, 42]. The activation energy with the addition of mixing from ($K_2S_2O_8$ +H_2O_2) is less than value without addition, that due to the absorption of vitamin B_{12} is being more oriented in present $K_2S_2O_8$ and H_2O_2 with the temperature range 10 -25°C.

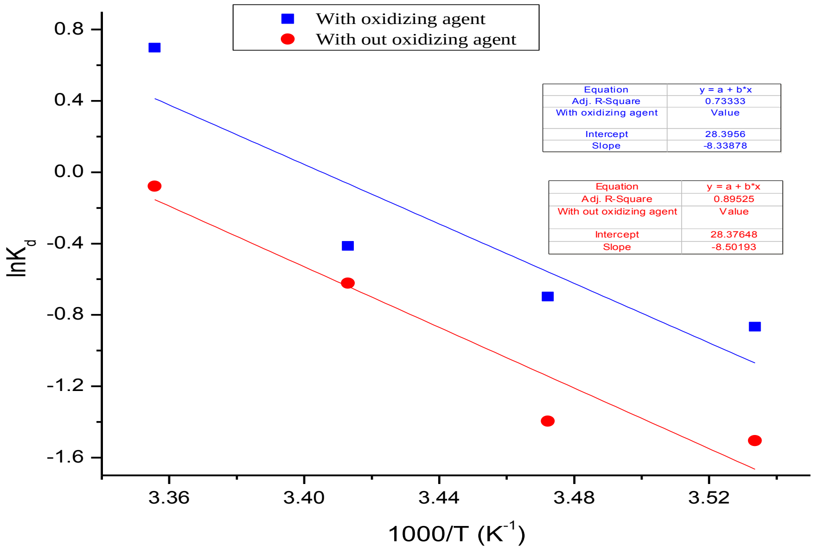

Figure 3. Relation between ln k_d verse 1000/T for the process of removing vitamin B_{12} by ZrO_2 with and without addition (H_2O_2 + $K_2S_2O_8$)

Figure 4 explains that the ΔG^o magnitudes for both reactions with and without the addition of mixing of (H_2O_2 + $K_2S_2O_8$) are exothermic. This pathway indicates that the studied adsorption processes are spontaneous and more favorable with increased temperatures[41,42].

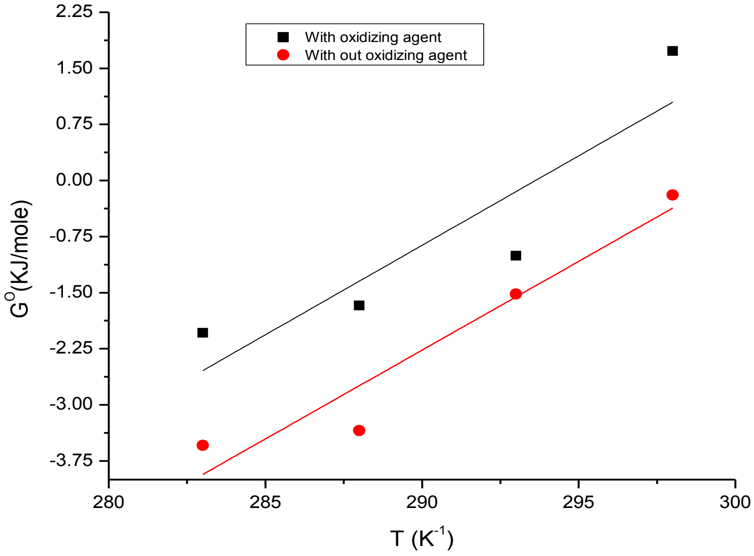

Figure 4. Relation of Gibb's free energy change (ΔG^{o}) versus temperature for an exothermic process with and without addition(H_2O_2 + $K_2S_2O_8$) during removing of vitamin B_{12} by ZrO_2

Table 1. The thermodynamics parameters and activation energies for removal process of vitamin B12 by ZrO_2 with and without the addition of (H_2O_2 + $K_2S_2O_8$) to the solution.

Studied Process	**ΔH^{o} (kJ mol^{-1})**	**ΔS^{o} (J mol^{-1} K^{-1})**	**$E_{a\ 298}$ (kJ mol^{-1})**
process of removing vitamin B_{12} by ZrO_2 with addition(H_2O_2 + $K_2S_2O_8$)	69.329	0.236	71.806
process of removing vitamin B_{12} by ZrO_2 without addition (H_2O_2 + $K_2S_2O_8$)	7.0685	0.236	73.162

The Influencing of Temperature on decolorization of vitamin B12

Based on the Arrhenius equation [43-45](eq. 30) and the Eyring-Polanyi equation[46-50] (eq. 31), the activation energy (E_a) and the thermodynamic functions ($\Delta S^{\#}$ and $\Delta H^{\#}$) were calculated during the photocatalytic reaction.

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \qquad 30$$

$$\ln(\frac{k_{app}}{T}) = \frac{-\Delta H^{\#}}{RT} + \left(\ln(\frac{k_B}{h}) + \frac{\Delta S^{\#}}{R}\right) \qquad 31$$

Where, (k_{app}) represents a rate constant for a first-order reaction, where (T) is the absolute temperature, the rate constant is (R), and the Eyring-Polanyi equation where (k_B and h) are the Boltzmann constant and Planck constant respectively.

The Gibbs energy (eq. 32) was calculated depending on the values of $\Delta S^{\#}$ and $\Delta H^{\#}$[49, 51].

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad 32$$

Figures 5 and 6 deduce the raised temperature from 10 to 25°C, enhance the photoreaction for decolorization of vitamin B12 using the photocatalyst (ZrO_2). Based on achieved results in Table 2, the activation energy magnitude with used mixing from (H_2O_2 + $K_2S_2O_8$) as an oxidant agent is more than the value for the activation energy without using the mixing of oxidant agents (H_2O_2 + $K_2S_2O_8$), that denotes to increase the mobility of H_2O_2 and $K_2S_2O_8$ to adsorption on the surface of catalyst and $S_2O_8^{2-}$ may be reacted with H_2O_2 and formed peroxide radical $HO_2^{-\cdot}$, which be less activity compared with hydroxyl radicals, so the reaction is slow with different ranges of temperature [52].

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\cdot-} \qquad 33$$

$$SO_4^{\cdot-} + H_2O_2 \rightarrow HO_2^{-\cdot} + HSO_4^{-} \qquad 34$$

The positive magnitudes for $\Delta H^{\#}$ reveal this photodecolorization of vitamin B_{12} with and without the addition of mixing from H_2O_2 and $K_2S_2O_8$ in present ZrO_2 are be endothermic. The $\Delta S^{\#}$ magnitudes (negative values) for both up mention cases are less random after decolorization. These results are in good agreement with reported in references [29, 31], the $\Delta G^{\#}$ for these studied reactions is negative that refers to spontaneous processes [46, 53]

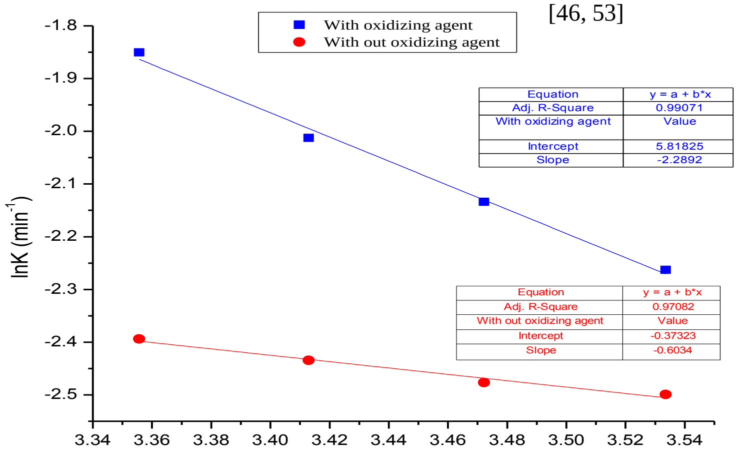

Figure 5. Arrhenius equation plot for photodecolorization of vitamin B_{12} by ZrO_2 with and without addition (H_2O_2 + $K_2S_2O_8$)

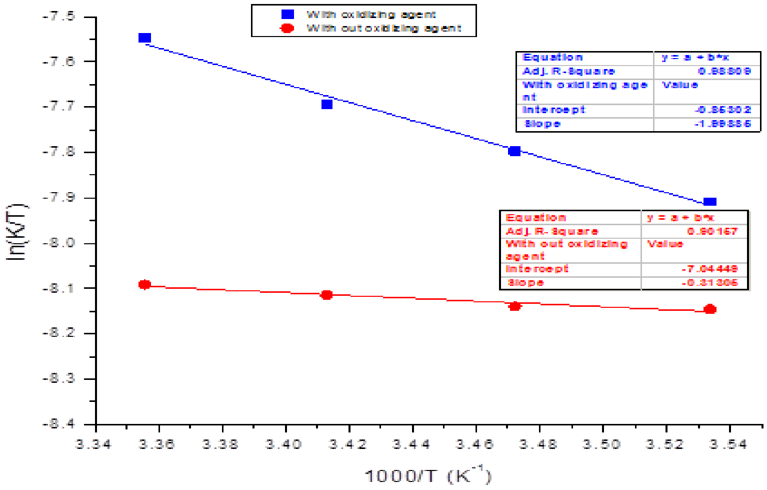

Figure 6. Eyring equation plot for photodecolorization of vitamin B_{12} by ZrO_2 with and without addition (H_2O_2 + $K_2S_2O_8$)

Table 2. The thermodynamics parameters and activation energies for decolorization process of vitamin B_{12} by ZrO_2 with and without the addition of (H_2O_2 + $K_2S_2O_8$) to solution in present UV-A- light.

Reactions type	**E_a (kJ mol^{-1})**	**$\Delta H^{\#}$ (kJ mol^{-1})**	**$\Delta S^{\#}$ J (mol^{-1} K^{-1})**	**$\Delta G^{\#}_{298}$ (kJ mol^{-1})**
with addition(H_2O_2 + $K_2S_2O_8$)	19.032	16.618	-204.629	-44.361
without addition (H_2O_2 + $K_2S_2O_8$)	5.016	2.602	-139.222	-38.886

CONCLUSIONS

The ZrO_2 is the activated surface for removal and photo-decolorization of vitamin B_{12} as drug amble. These processes were performed with and without the addition of the oxidant reagent such as (Fe^{2+}, H_2O_2, $K_2S_2O_8$, and mixing from them). The best removal happens when added mixing from (H_2O_2 and $K_2S_2O_8$).

The removal process for this reaction was found to be endothermic (ΔH^o is positive) and the type of adoption is physical. While the photoreaction with and without the addition of (H_2O_2 and $K_2S_2O_8$) is endothermic also and spontaneous.

Moreover, the activation energy for using oxidant agents is more than without using them, this indicates to increase in the scavenger in an aqueous solution. The photoreaction of vitamin B_{12} obeys pseudo-first-order kinetics under UV-light in the presence ZrO_2.

The decolorization percentage of vitamin B_{12} is found to be more magnitude than the removal percentage in using dark reaction with using and without using the oxidant agents.

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Conflict of interests

No conflict.

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