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To cite this article: Zainab A Hussein et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 454 012132

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UV-A activated ZrO₂ via photodecolorization of methyl green dye

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Abstract. This work was investigated from the decolorization of methyl green dye in presence of ZrO₂ under certain conditions. The raised of temperature leads to increase the rate of this photoreaction. The activation energy was found to be 26.005 kJmol⁻¹. Moreover, some oxidation agents was addition to dye solution with ZrO₂ and given the following sequence for increasing the rate of reaction Fe²⁺< K₂S₂O₈< without addition< H₂O₂. This result was indicated to the reaction is more fast under using different ratio from H₂O₂: from 0.5%, 0.75%, 1% and 1.5%. The Maximum efficiency was reached to 98.78% at 30 min under addition 1.5% from H₂O₂ to dye solution with ZrO₂.

1.Introduction

Zirconium Oxide or zirconia (ZrO₂) is deemed as one of the transition metal oxide that have a high chemical inert, a good optical properties (an n-type semiconductor with band-gap energy of about 5.0 eV) [1], a less toxicity, high melting point (thermally stable), high biocompatible, has an amphoteric surface (has a ZPC) with high surface area [2-4] and corrosion resistance with a high hardness hence, it is feavor to use in dentistry industry [5-7]. In fact, zirconia is a white crystalline insoluble in water, but it can be dissolved in HF and in H₂SO₄, witch be as very important ceramic material. Generally ZrO₂ has three polymorphs: monoclinic, tetragonal and cubic phases, these crystal phases can be transferred to another phases depended on varies temperatures with the following sequences [5,8-10].

\[
\text{monoclinic } \rightarrow \text{tetragonal } \rightarrow \text{cubic}
\]

The cubic phase of ZrO₂ is fully stable in room temperature while tetragonal is partially stable in the same temperature[11]. The bulk and nano particle of ZrO₂ are used in different applications[12] such as : using as photocatalyst [13-15] adsorption reaction [16, 17], using as sensor [18-20], using as a Dental Biomaterial or bioceramic[21, 22], in polishing of teeth[23,24] in crown of teeth[25].

The target of present work was to investigate the using ZrO₂ as photocatalyst to decolourize the methyl green dye under UV-A light . This was done with controlled ZrO₂ dosage, different oxidation agents like H₂O₂, Fe²⁺ and K₂S₂O₈ and H₂O₂ concentrations. The effect of temperature was applied to determine the activation energy and thermodynamic functions for decolorizing process.
2. Materials
The used chemicals in this work were employed without any purification. Commercial Zirconium oxide was supplied by Fluka-Germany. Methyl green dye was supplied by George T. Gurrl Td- England, which has a physico-chemical characteristics that is illustrated in Figure 1 and Table 1.

![Figure 1. The structural formula of methyl green dye [26].](image)

Table 1. Physico-chemical characteristics of the methyl green dye[26-29].

| Values                  | Parameters                  |
|-------------------------|-----------------------------|
| 608.778 g mol⁻¹         | Molecular Weight            |
| C₂₇H₃₅Cl₂N₃.ZnCl₂        | Molecular formula           |
| Ethyl green zinc chloride double salt | Synonym                   |
| Triphenyl methane       | Class                       |
| Basic (dicatonic dye)    | Natural                     |
| 629 - 635 nm            | λmax                        |

in medicine, biology, sensitize and photochromophor Most applications

3. Procedure
The photocatalytic experiments were performed by using the 100 mL of suspension solution from methyl green dye with ZrO₂, this solution virgous mixed by Labtech magnetic stirrer, and then illumination under artificial light type Philips 250Watt in light intensity value equal to 1.48 x 10⁻⁷ Ens. s⁻¹ which calculated by chemical actinometrical solution[30]. With regular intervals, certain amount of samples were collected and double separated by centerfuge to remove all ZrO₂ from dye solutions. The filtered dye solutions were analysed to determine the residue concentration of dye by recording the absorbance at 630 nm using UV-visible spectrophotometer.

By depended on Langmuir-Henshelwood mechanism, the rate constant was determined [31], and the photodecolorization efficiency (PDE %) was calculated by the following equation [32]:

\[
\ln \left( \frac{C_o}{C_t} \right) = k_{app} \cdot t
\]  

(1)

And

\[
PDE \% = \left( 1 - \frac{C_t}{C_o} \right) \times 100
\]  

(2)

Here: C₀ is an initial concentration of methyl green dye at no irradiation time (min). Cₜ is a concentration of the same dye at t time of irradiation (min).

4. Results and Discussion
4.1. Effect of ZrO₂ dose on photodecolorization of methyl green dye
As seen in Figure 2 (a & b), the increase in the doses of ZrO$_2$ from range (0.1-1.5) g in aqueous solution of methyl green dye solution was raised the decolorization speed. This behavior indicates to find the many active sites of catalyst (ZrO$_2$) surface with increasing the dose. the transmittanced light in dye solution is easy transmitted, hence, that entirely leads to enhance the producing of hydroxyl radical. The last is regarded as a vital species to start the photodecolorization of dye[33]. The maximum rate constant and PDE % are found at 1.5 g/ 100 mL of ZrO$_2$ and 92.31 % at 30 min. Besides, at dose more than 1.5 g, the rate of reaction inhibits that due to depress the reached light to dye solution that called screening effect[34].

![Figure 2](image)

**Figure 2.** Effect of catalyst dose on the (a) apparent rate constant of reaction and (b) PDE %, at conditions: cat. dose = (0.1-2) g/100mL, methyl green dye conc.= 25 ppm, initial pH of solution= 5.4 and T= 303.15K.

### 4.2. Effect of Oxidant agents on photodecolorization of methyl green dye

They are clear from Figure 3(a & b) that the addition of oxidant agents such as 0.5% H$_2$O$_2$, 1x10$^{-4}$ M from K$_2$S$_2$O$_8$ and 1x10$^{-4}$ M from FeSO$_4$ to dye solution are preferred.

![Figure 3](image)

**Figure 3.** Effect of oxidant agents on the (a) apparent rate constant of reaction and (b) PDE %, at conditions: cat. dose =1.5 g/100mL, methyl green dye conc.= 25 ppm, initial pH of solution= 5.4 and T= 303.15K.
From the results, it was observed that the addition of 0.5% from H$_2$O$_2$ is increased the rate of constant from 0.0822 to 0.1027 and raised the PDE% from 92.31 to 95.96 at 30 min. The 0.5% of H$_2$O$_2$ enhances generated of hydroxyl radical under UV light illumination that essentially to accelerate the photodecolorization of methyl green dye, according to the following equations[35-38].

\[
\begin{align*}
H_2O_2 + h\nu &\rightarrow 2 H^+ O^\cdot \\
H_2O_2 + e_{CB}^{-} of ZrO_2 &\rightarrow HO^\cdot + HO \\
H_2O_2 + O_2 &\rightarrow H^+ O^\cdot + HO + O_2
\end{align*}
\] (3) (4) (5)

The photodecolorization of methyl green dye activity with using the ZrO$_2$ was tested in varies ratios of H$_2$O$_2$ at range (0.5-1.5) % and found in figure 4. The maximum efficiency for addition of H$_2$O$_2$ is occurred at 1.5 %, that changed the PDE% from 92.31 % to 98.78% at 30 min.

![Figure 4. Effect of H$_2$O$_2$ addition on the PDE %, at conditions: cat. dose = 1.5 g/100mL, methyl green dye conc. = 25 ppm, initial pH of solution = 5.4, rage of H$_2$O$_2$ (0.5-1.5)% and T= 303.15K.](image)

On the contrary, the results in figure 2 explain, that the surplus addition of K$_2$S$_2$O$_8$ and Fe(II) in 1x $10^{-4}$ M are not enhanced the photodecolorization of methyl green dye, hence, that will attitude to the high concentrations of K$_2$S$_2$O$_8$ and Fe(II) act as scavenger of hydroxyl radicals, according to the following equations[38-39].

\[
\begin{align*}
S_2O_5^{2-} + e_{CB}^{-} &\rightarrow SO_4^{-} + SO_4^{2-} \\
SO_4^{-} + e_{CB}^{-} &\rightarrow SO_4^{2-} \\
SO_4^{-} + HO &\rightarrow SO_4^{-} + HO^- \\
Fe^{2+} + HO &\rightarrow Fe^{3+} + HO^- 
\end{align*}
\] (6) (7) (8) (9)

4.3. Effect of Temperature on photodecolorization of methyl green dye
The photocatalytic activity of methyl green dye solution with zirconia was tested in a fixed temperature in range (283-303)K in Fig. 5. This effect was reflected the increment inaccessibility of hydroxyl ions from his different sources to the active sites of catalyst surface that in turn raises the rate of radicals produced. Besides, the change in temperature can be utilized to determined the activation energy $\Delta E_a$ employing Arrhenius equation[40] and thermodynamics function such as $\Delta H^\circ$ with $\Delta S^\circ$ using Eyring equation[41,42] and the change in molar free energy $\Delta G^\circ$as Gibbs equation[42]. The values that calculated from Arrhenius equation, Eyring equation and Gibbs equation are summarised in Table 2.

![Figure 5](image_url)

**Figure 5.** Effect of temperature on photodecolorization of methyl green dye from colloidal solution of ZrO$_2$ at range in temperature (283-303) K (a) Arrhenius equation plot and (b) Eyring equation plot.

| Ea   | $\Delta H^\circ$ | $\Delta S^\circ$ | $\Delta G^\circ_{303.15}$ |
|------|------------------|------------------|--------------------------|
| 26.005 kJ mol$^{-1}$ | 23.571 kJ mol$^{-1}$ | -0.00273 K$^{-1}$ | 24.398 kJ mol$^{-1}$ |

According to the results of this investigation in table 1, it notices to the photoreaction of methyl green dye with ZrO$_2$ was fast, endothermic, less random and non- spontaneous. Nevertheless, the positive values of $\Delta H^\circ$ and $\Delta G^\circ_{303.15}$ in this photodecolorization, which attitude to increment in solvated of the transition state between methyl green dye molecules and hydroxyl radicals. This result was noticed in agreement with the mentioned in references[42].

### 4.4 Suggested mechanism

The suggested mechanism for the decolorization of methyl green dye with ZrO$_2$ is depicted in scheme1. On the basis of the photodecolorization processes described in reference [43], various redox process can conducted on surface of photosemiconductor under illumination of UV- A light. Firstly, electron-hole pair (exciton) on ZrO$_2$ surface was generated. The electron-hole pair is separated by reacting with the other species (H$_2$O, O$_2$) in series steps then formed groups of radical intermediates like: superoxide ion $O_2^{-}$, hydrogen peroxide radical (hydroperoxyl radical) $HO_2$ then leads hydroxyl radical $HO^-$ Which has a more activity then $HO_2$ [44-46].
\text{Semiconductor}(\text{ZrO}_2) \rightarrow (e^- - h^+)\text{ exciton} \quad (10)

\begin{align*}
H_2O & \rightarrow H^+ + HO^- \quad (11) \\
HO^- + h^+ & \rightarrow HO^\cdot \quad (12) \\
O_2 + e^- & \rightarrow O_2^- \quad (13) \\
O_2^- + H^+ & \rightarrow HOO^\cdot \quad (14) \\
HOO^- + H^+ & \rightarrow H_2O_2 \quad (15)
\end{align*}
Scheme 1. Schematic diagram for more accepted mechanism (methyl green Dye/semiconductor (ZrO$_2$)/UV-A light system) [43].
5. Conclusions
The essential conclusions are summarized with:

1- The photodecolourization of methyl green dye was conducted in controlled the ZrO2 dose, addition of oxidant agent like H2O2, Fe(II) and K2S2O8 and temperature. For all these influences the photoreaction is obey the pseudo first order.

2- It's found that the best dose of ZrO2 are 1.5 g in 100 mL of dye solution with PDE% 92.13.

The addition of oxidant agents, sometimes decreases the activity of decolorization of methyl green dye like Fe(II) and K2S2O8 and the PDE% decreases to 39.93 and 74.62 respectively. The addition of 1.5 % of H2O2 enhances this photodecolorization

1- of methyl green dye by raised the PDE % from 92.31 % to 98.78%.
2- The reaction is fast and the activation energy equal to 26.005 kJ/ mol, and the reaction is endothermic, less random and non- spontaneous.

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