Influencing the Artificial UV-A light on decolorization of Chlorazol black BH Dye via using bulk ZnO Suspensions

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Abstract. This manuscript is interested with the using Chlorazol black BH dye as a model compound. This photo reaction was obeyed first-order kinetics with low activation energy equal to 27.135 kJ/mol. Moreover, the thermodynamic parameters were calculated using the Arrhenius equation, the Eyring-Polanyi equation and the Gibbs equation, then proved this photo reaction is exothermic, with less random and spontaneous reaction. The best conditions were controlled with the using the artificial UV-A and found to be 100 mg/L (dye concentration), 200 mg (bulk ZnO), 7.63 as initial pH and 15 °C, from the other side, the photo-decolorization efficiency at these best conditions, was reached to 99.072% At final, the suitable mechanism for decolorization and degradation of Chlorazol black BH Dye was suggested.

Keywords: Chlorazol black BH dye; activation energy; bulk ZnO; decolorization.

Introduction

In the last decades, the dyes and pigments are deemed as important colorants to exercise a color or to alter the color of things. There are mostly soluble in the water, this behavior is regarded as a main point in the coloration methods. Azo dyes are the most major group of trading dyes, that have intensely red, orange, yellow, green or blue. In fact, these common colors are relying on the structure of the dye molecule. Hence, azo compounds are vastly used substances in the textile, cosmetics industries, paper, variegation tools for foods, employed to give a different of pleasant biological activities and pharmaceutical like antitumor, anti-inflammatory, anti-mycotic and antibacterial and antifungal agents. The purpose of the present work is to investigate the photodecolorization of chlorazol black BH dye in presence ZnO as a photocatalyst under UV-A radiation. Effects of varies parameters like dye concentration, catalyst dose and initial pH on the rate of photoreaction were carried out for 40 min. The effect of temperature was monitored to estimate the activation energy and essential thermodynamics parameters.

Materials and Method

Bulk Zinc oxide was purchased from Fluka. Chlorazol black BH dye has molecular formula C_{32}H_{21}N_{6}Na_{3}O_{11}S_{3}, molecular weight equal to 830.71 g mol^{-1}, chemical structure is illustrated in Fig. 1, Synonym is Direct Blue 2 and supplied by Merck. All chemicals were used without any treatment.
Batch experiments, for every photodecolorization of chlorazol black BH dye were performed in a homemade photoreactor. This reactor consists of a wooden box, high pressure mercury lamp type Philips-250 W, Pyrex glass beaker, teflon bar, magnetic stirrer, and fan. The used reactor was initially loaded with the mixture from 100 mL of chlorazol black BH dye with the suitable g from ZnO, and then continuous mixing by means of a magnetic stirrer. This mixture was maintained to irradiation using the artificial light, which has a light intensity equal to be $1.48 \times 10^{-7}$ Ens. s$^{-1}$ by employing chemical actinometrical solution.$^{12,13}$ Certain amounts of the mixture were collected at different times and separated by center fug. The residue concentration of chlorazol black BH dye was followed by determining the absorption of filtered solution at wavelength 550 nm using spectrophotometer. The kinetic study was conducted to find the apparent rate constant ($k_{app}$) for the photo reaction.$^{14,15}$

$$\ln \left( \frac{C_{dye,o}}{C_{dye,t}} \right) = k_{app} \cdot t$$

(1)

Here: $C_{dye,o}$ and $C_{dye,t}$ are an initial concentration at dark reaction and a concentration of the same studied dye at t time respectively. t is a time of reaction. The photodecolorization Efficiency % (PDE %) of photo decolourization for chlorazol black BH dye (removal it) was determined using the following relationship$^{14,16}$:

$$% \text{Efficiency} = \left( 1 - \frac{C_{dye,t}}{C_{dye,o}} \right) \times 100$$

(2)

The half- time for this reaction can be calculated$^{17}$ from the following equation.

$$t_{1/2} = \frac{\ln 2}{k_a}$$

(3)

Results and Discussion

Effect of Dye Concentration

As shown in Fig. 2a and b. It is obvious that the decolourization of chlorazol black BH dye in suspension solution of ZnO was obeyed to the first order, because of obtaining a linear relation when $\ln(C_{dye,o}/C_{dye,t})$ plot versus the time of reaction. On the other hand, the apparent rate constant for the decolorization process rises with increasing the dye concentration. That assesses to increase the numbers of intermediates that raised the rate and quantum yield of the photoreaction.$^{18,20}$
Figure 2. First order rate constant at varying dye concentration. Conductions: dye concentration (25-100)ppm, ZnO dosage 350 mg/100 mL, pH= 7.63, temperature 288.15 K, UV light intensity $1.48 \times 10^{-7}$ Ensiens. s$^{-1}$. (a) ln ($C_0/C_t$)$_{dye}$ vs time and (b) $k_{app.}$ vs concentration of the chlorazol black BH. Table 1 below illustrates, that the half time decreases with increasing the apparent rate constant and the less value at dye concentration equal to 100 ppm. This result clearly confirms with the results in Fig. 3, which refer to the maximum efficiency (PDE %) was seen equal to 90.804 % after 40 min of irradiation light.

Table 1. The chlorazol black BH dye conc. as functions for $k_{app.}$ and $t_{1/2}$.

| Chlorazol black BH dye conc. / ppm | Apparent rate constant $k_{app.}$ / min$^{-1}$ | Half time $t_{1/2}$ / min |
|-----------------------------------|-----------------------------------------------|---------------------------|
| 25                                | 0.0389                                        | 17.814                    |
| 50                                | 0.0438                                        | 15.821                    |
| 75                                | 0.0488                                        | 14.200                    |
| 100                               | 0.0612                                        | 11.323                    |

Figure 3. Effect of Concentration of chlorazol black BH on PDE % for decolourization of (25-100) ppm from studied dye, at 350 mg/100 mL of ZnO, pH 7.63, Temp. 288.15 K and UV light intensity $1.48 \times 10^{-7}$ Ensiens. s$^{-1}$.
Effect of ZnO dose

Various ZnO dose ranging from 100 mg/100 mL to 400 mg/100 mL was added to the 100 ppm of studied dye in order to examine the optimum amount of ZnO. The observed results in Fig. 4a and b, and Fig. 5 occurred, that the maximum removal efficiency was observed at 99.072% in used 200 mg/100 mL from ZnO dose after 40 min of irradiation time. On the contrary, the efficiency depresses of this reaction with excess the ZnO dose more than 200 mg/100 mL, this behavior is due to the decline the interpenetration of light in ZnO solution and increases the scatter of it, that beyond to screen effect.

Figure 4. First order rate constant at varying ZnO dose. Conductions: 100 ppm of dye concentration, ZnO dosage range (100-400) mg/100 mL, pH= 7.63, temperature 288.15 K, UV light intensity 1.48 x10^-7 ensien.s^-1. (a) ln (C_o/C_t)dye vs time and (b) k_app vs ZnO dose.

Figure 5. Effect of ZnO dose on PDE % for decolourization of 100 ppm from studied dye, at ZnO dose range (100-400) mg/100 mL, pH 7.63, Temp. 288.15 K and UV light intensity 1.48 x10^-7 Ensien. s^-1).
Effect of initial pH

In order to assess the effectiveness the initial pH, the used pH range from 2 to 10 was applied. The rate of this reaction increases from pH 2 to 7.63 (neutral pH) in E% equal to 99.072%, then decreases, as seen as in Fig. 6a and b, and Fig. 7. This behavior is attaining by depending on the ionization state of used dye and the ZnO surface charge (pH_ZC about 9.00). Based on ZnO amphoteric behavior, so, at pH below and above pH_ZC, the surface of the ZnO can be protonated (adsorbed H⁺) or deprotonated (adsorbed HO⁻) under acidic or alkaline medium respectively.20-24

![Figure 6](image1.png)

**Figure 6.** First order rate constant at varying pH. Conductions: 100 ppm of dye concentration, 200 mg/100 mL ZnO dosage, range of initial pH (2-10), temperature 288.15 K, UV light intensity 1.48 x 10⁻⁷ Ensien.s⁻¹. (a) ln \( (C_0/C_t)_{dye} \) vs time and (b) \( k_{app.} \) vs initial pH of solution.

![Figure 7](image2.png)

**Figure 7.** Effect of initial pH on PDE % for decolourization of 100 ppm from studied dye, at 200 mg/100 mL of ZnO dose, range of initial pH (2-10), Temp. 288.15 K and UV light intensity 1.48 x 10⁻⁷ Ensien. s⁻¹.

Effect of temperature

From Fig. 8 and Fig. 9, it is clear the optimum temperature for decolourization was 15 ºC. The increment in above this temperature leads to inhibit it; this might be due to the increased density of solution and turbidity, which depress the reached light to catalyst and decline of generated hydroxyl radical. Table 2 below explains the apparent activation energy (Arrhenius equation) and the values for some thermodynamics parameters like \( H^0, S^0 \) and \( G^0 \) (Eyring-Polanyi equation and Gibbs
equation)\textsuperscript{20,21,25} were calculated. The results illustrate the reaction is an exothermic and spontaneous reaction.

![Graphs showing Arrhenius equation](image)

**Figure 8.** Arrhenius equation plotted at the varying temperature at (278.15-298.15) K. At conductions: chlorazol black BH on dye conc. 100 ppm, semiconductor dosage 200 mg/100 mL and normal pH= 7.63

Table 2. The activation kinetic and thermodynamic parameters of the decolourization of chlorazol black BH on dye under light 250 watt -Hg lamp.

| Parameter | Value |
|-----------|-------|
| $E_a$ (kJ mol$^{-1}$) | 27.135 |
| $H^\circ$ (kJ mol$^{-1}$) | -30.527 |
| $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | -5.730 |
| $\Delta G^\circ$ (kJ mol$^{-1}$) | -28.881 |

**Suggested Mechanism**

The proposed mechanism of decolorization of chlorazol black BH was pictured in the following scheme.

![Scheme 1](image)

**Scheme 1.** The suggested mechanism of photo decolorization and degradation of Chlorazol black BH dye.
Conclusions

In this manuscript, the essential conclusions were done under UV-A light with a suspension solution of ZnO to investigate the photocatalytic decolourization of chlorazol black BH dye. The photo reaction of this dye solution was followed to first order. The neutral pH is the optimum condition with high efficiency equal to 99.072% in 40 min with 200 mg of ZnO, 100 ppm of dye and 15 °C. This reaction is fast, an exothermic at range (5-25) °C, less random and spontaneous reaction.

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