ZnO Based Material as Photocatalyst for Treating the Textile Anthraquinone Derivative Dye (Dispersive Blue 26 Dye): Removal and Photocatalytic Treatment

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Abstract

The generation and accumulation of environmental pollutant of industrial contaminations gave it a big challenge to develop many removal strategies of pollution. Textile dyes as dispersive blue 26 dye affected by several decolorization parameters like as temperature, initial pH and initial concentrations of dye. These variables parameter were studied on ZnO-dye suspension solution in dark and photoreaction conditions. In dark reaction, with using thermodynamic and kinetic parameters such as $\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$ and $E_a$, the type of adsorption was determined and found as a physical adsorption, exothermic and fast reaction. Moreover, the results demonstrated that the photoreaction process under UV-light-A would elevated the rate of reaction, percentage of decolorization and accelerated the half-time of decolorization reaction in 50 ppm of dye. The photoreaction of decolorization of this dye acts as pseudo first order kinetics with endothermic, less random less, non spontaneous and fast reaction.

Keyword: Textile Anthraquinone Derivative Dye; Dispersive Blue 26 Dye; ZnO, Removal Treatment, Photocatalytic Treatment.

1. Introduction

The pollution of water resources by heavy metal solutions or dye-based effluent is already a worldwide problem, which has resulted in the scarcity of clean and healthy water. Most dyes are non-biodegradable, toxic in nature, and can affect water aesthetically at as little concentration as 1 ppm [1-2] which poses an environmental concern. Thus, the effective removal of dyes from aqueous systems became environmentally important [3]. Disperse
dyes are one of an important textile dye that has a low molecular weight, brightness color, fastness, non-ionic, relatively insoluble in water at room temperature, whereas they can be interaction with the acrylic, cellulose acetate and nylon fiber because of they contained non-ionic mono-azo, aniline and anthraquinone derivatives in their molecular structures, hence deep dyeing are produced [4-8]. Science 2008, the disperse dyes constitute the second largest sector in the dyeing industry, with produced capacity reached to more than 125 thousand tons in year with four classes: class A, class B, class C and class D, which depended on the sublimation fastness and molecular size [5,9,10]. In order to acquire adequate dye ability, the dyeing of polyester fabrics must be performed at high temperature and high pressure, or by utilizing a carrier as an organic compound, which quickens dyeing by separating or dissolving dye aggregates and carrying them to the fiber–water interface in little amounts. That is enough to be absorbed by the material, which suggests huge energy utilization and ecological [11], but last will lead to high amount of wastewater. Hence, many researches focused on the treatment methods of wastewater such as photocatalysis [12-15], Solar photocatalysis [16,17] adsorption [18-20], biosorption [21], biodegradation [22-24], fenton, photofenton and solar photofenton [25-29] and Electrochemical degradation [30]. Photocatalysis is one of the most common methods at the present time, the significant features of the photocatalytic system are the desired bandgap, suitable morphology, high surface area, stability, and reusability [30,31]. Metal oxides such as oxides of tungsten, chromium, titanium, zinc, zirconium, and manganese having these characteristics follow similar primary photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidize the organic substrates and hydroxyl ions under UV light or visible light [13, 31-33]. In this process, the photoexcited electrons are promoted from the valence band to the conduction band in metal oxide, forming an electron/hole pair (e⁻/h⁺) that leads to redox process. The photocatalytic activity of metal oxide comes from two sources: (i) generation of OH radicals by oxidation of OH⁻ anions on photohole, (ii) generation of O₂⁻ radicals by reduction of O₂. Both the radicals and anions can react with pollutants to degrade or otherwise transform them into lesser harmful products [34-36]. The current work aims to study the removal and photocatalytic decolorization of textile dye (dispersive blue 26 dye) with chemical structure as illustrated in Figure 1, using ZnO as a photocatalyst.

Figure 1. The structure of dispersive blue 26 dye.
2. Materials and Method

A. Materials

Zinc oxide was purchased from Fluka Company. All chemicals were employed without any purification. Dispersive blue 26 dye \((C_{16}H_{14}N_{2}O_{4})\) powder was supplied by Hilla textile factory, with molecular weight 298.29 g mol\(^{-1}\).

B. Dark and Photo reactions

In this work, many experiments were done to find the perfect conditions in dark and photo reactions of dispersive blue 26 dye aqueous solution. To perform the dark reaction, about 100 mL from dye was mixed with certain amount of ZnO for 30 min using magnetic stirrer. After adsorption step, photo reaction was made using the homemade photoreactor with wooden box, which contains magnetic stirrer, Pyrex glass beaker, Teflon bar, fan and UV-A lamp type Philips- 250 Watt as high pressure mercury lamp with 365 nm. The Light intensity of this lamp was measured using chemical actinometric solution \([38]\) that equal to \(2.995 \times 10^{-8}\) Ems. s\(^{-1}\). This homemade photoreactor is shown in figure 2.

![Homemade Photoreactor Diagram](image)

Figure 2. Schematic diagram of homemade photoreactor, with dark and photo decolorization of dispersive blue 26 dye.

After irradiation in regular time, 3.5 mL of suspended solution was collected in plastic test tube, and then double separated by Hettich centrifuge for 10 min. The residual concentrations of dye after adsorption and photoreaction were found using Shimdzu - UV-Vis spectrophotometer at 562 nm.
In dark reaction step, the adsorption capacities \( q_e \) (mg/g) and the percentage of removal \( (E_{\text{removal}}\%) \) were measured from this step depended on the following equations [20,37,39]:

\[
q_e = \frac{(C_0 - C_e)}{m} V
\]

(1)

\[
E_{\text{removal}}\% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

(2)

Here, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of dye in its solution, \( V \) is the volume of dye solution in L and \( m \) is the catalyst mass in g.

From the photoreaction, the apparent rate constant \( (k_{\text{app.}}) \), the photo decolorization efficiency \( (E_{\text{decol.}}\% ) \) and half time \( t_{1/2} \) were found using the following equations [40-42].

\[
\ln \left( \frac{C_0}{C_t} \right) = k_{\text{app.}} t
\]

(3)

\[
E_{\text{decol.}}\% = \left(\frac{C_0 - C_t}{C_0}\right) \times 100
\]

(4)

\[
t_{1/2} = \left(\frac{\ln 2}{k_{\text{app.}}}\right)
\]

(5)

whereas: \( C_0 \) and \( C_t \) are an initial concentration of dye in dark reaction and a concentration of the same dye at \( t \) time of irradiation.

3. Results and discussion

a. Influence of initial dispersive blue 26 dye concentration on dark reaction.

The estimation of this effect obtained with the equilibrium conditions 30 min, 38 °C and 0.3g ZnO in 100 mL of dispersive blue 26 dye concentration ranged (25-100) ppm. Based on results in figure 3, the adsorption capacity of ZnO \( (q_e \) per mg g\(^{-1}\)) raised by increasing concentration of the initial dispersive blue 26 dye However, the maximum removal percentage of dispersive blue 26 dye equals to 83.968% at 50 ppm, and then decreases from 83.968% to 60.973%. The decreased in removal efficiency is probably due to the non-ionic property of an organic disperse dye compounds [43], which reduces the adsorption of dispersive blue 26 dye into the solution.
b. Influence of dye concentration on photoreaction

The decolorization of dispersive blue 26 dye was performed in range (25-100) ppm of dyes concentration. According to figure 4 (a and b), the results observed to depress in the rate of reaction and the photodecolorization efficiency of dye after using 50 ppm from dye with kept the catalyst dose constant, that due to the screen effect which reduced the light penetration ability with increasing the concentration of colored solution[17,20].

Figure 4. Pseudo-first order rate constant at varying dye concentration. Conductions: ZnO dosage 0.30 g/100 mL, pH= 7.45, temperature 38 °C, UV light intensity 2.995 x10^{-8} ensien.s^{-1}. (a) $k_{app}$ vs studied dye concentrations and (b) $E_{decolorization}$ % vs concentrations of studied dye.
The fast decolorization of dispersive blue 26 dye illustrates with the lower half time that equal to 3.263 min. As indicated in figure 5.

![Figure 5. Relation between $t_{1/2}$ and concentrations of dispersive blue 26 dye.](image)

c. Influence of initial pH on dark reaction

The maximum adsorption capacities and percentages of removal for dispersive blue 26 dye at the initial pH were found equal to 7.45. At pH 7.45, the maximum adsorption capacity and removal percentage reached to 11.995 mg g$^{-1}$ and 83.968 % respectively, that attitude to the electrostatic force between the surface of ZnO and the unpaid electrons in oxygen and nitrogen of dye [44].

![Figure 6. The plot of adsorption the initial pH of dispersive blue 26 dye on ZnO surface.](image)

c. Influence of initial pH on photoreaction

The influence of initial pH in the photoreaction has been affected under UV-light and accelerated the efficiency of decolorization to 99.896 % at optimum initial pH 7.45. As clear in figure 7, the results found that the rate constant and the photo-decolorization efficiency of this dye decline with increasing the pH more than 7.45. This behavior ensures the increment in the electrostatic
repulsion of the negative charge of ZnO surface [45,46] and the pair's electron for nitrogen and oxygen atoms for dispersive blue 26 dye.

![Graph showing varying dye concentration](image)

**Figure 7.** Pseudo-first order rate constant at varying dye concentration. Conditions: ZnO dosage 0.30 g/100 mL, different range of pH, 50 ppm from dispersive blue 26 dye, temperature 38°C, UV light intensity 2.995 x10^-8 ensien.s^-1. (a) k_app vs studied initial pH and (b) E_decolorization % vs initial pH of studied dye.

d. Influence of temperature on dark reaction

The temperature has an obvious influence by increasing or decreasing adsorption process by depending on the type of adsorption. From figure 8, the Van’t Hoff equation applied to calculate the values of thermodynamics parameter such as change in enthalpy (ΔH°) and change in entropy of adsorption (ΔS°) [18,47].

\[
\ln k_d = \frac{-\Delta H^o}{RT} + \left(\frac{\Delta S^o}{R}\right)
\]

Where [48,20], k_d is sorption distribution coefficient which calculated from \( k_d = \frac{c_{ads}}{c_e} \) equation (where \( C_{ads} \) is the amount of dye (adsorbate) in the catalyst surface at equilibrium (mg/L) and \( C_e \) is total dissolved residual dye in the solution at equilibrium (mg/L).

The activation energy \( E_a \) obtained, depending on the magnitude of \( \Delta H^o \) as follow equation[18,20]:

\[
E_a = \Delta H^o + RT
\]
Figure 8. Relation between ln $k_d$ and $1/T$ for adsorption reaction of dispersive blue 26 dye on ZnO surface.

The Gibbs free energy $\Delta G^0$ [18, 49] can be calculated from equation 8, to detect the adsorption process type and deduction if the reaction spontaneous or not.

$$\Delta G^0 = -RT\ln k_d$$  \hspace{1cm} (8)

Table 1. The Kinetic and Thermodynamic Parameters for Adsorption dispersive blue 26 dye on ZnO Surface.

| $\Delta H^0$ | $\Delta S^0$ | $\Delta G^0$ | T/K | $E_a$ |
|---------------|---------------|---------------|-----|-------|
| kJ mol$^{-1}$ | kJ mol$^{-1}$ | kJ mol$^{-1}$ |     | kJ mol$^{-1}$ |
| -5.768        | -0.013        |               | 283 | -3.415 |
|               |               | -1.975        | 293 | -3.332 |
|               |               | -1.709        | 303 | -3.249 |

Figure 9. Relation of Gibb’s free energy change ($\Delta G^0$) for adsorption dispersive blue 26 dye versus temperature for an exothermic process.
From the result above that indicated in Figures 8 and 9 and Table 1, the adsorption process is exothermic with physical adsorption [18,20] due to negative values of thermodynamic parameter's, such as $\Delta H^\circ$ and $\Delta S^\circ$ that equals to -5.768 kJ mol$^{-1}$ and -0.013 kJ mol$^{-1}$. The temperature values, in above 303 K (i.e 311 K) ignorant in Figure 8, because it will shift the curve to endothermic reaction that may be to occur of sorption process. [18, 47,49]. The negative values of $\Delta G^\circ$ with the raising the temperature conformed the adsorption process are exothermic[20, 49], Moreover, the negative values of $E_a$ are being below 4.2 kJ mol$^{-1}$, these values illustrated that the adsorption process has really happened as associative mechanism and without change in the internal structures of the catalyst (ZnO) [47]

d. Influence of temperature on photoreaction

Under UV- light, the effect of temperature was illustrated to enhanced the photodecolorization of dispersive blue 26 dye in range (283.15-311.15) K, the activation energy by using Arrhenius equation[50,51] (in eq.9) assigned and with plotting Eyring-Polanyi equation [17,52](in eq.10), the thermodynamics parameters like $\Delta H^\ne$ and $\Delta S^\ne$ were determined. Moreover, used Free Energy equation($\Delta G^\ne$)[17,27] (in eq.11).

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A$$  \hspace{1cm} (9)

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^\ne}{RT} + \left(\ln\left(k_B\right) + \frac{\Delta S^\ne}{R}\right)$$  \hspace{1cm} (10)

$$\Delta G^\ne = \Delta H^\ne - T\Delta S^\ne$$  \hspace{1cm} (11)

Where $k_{app}$ is the apparent rate constant (min$^{-1}$), $h$ is the Plank constant, $R$ is the gas constant, $A$ is the frequency constant, $T$ is the temperature of the reaction and $k_B$ is the Boltzmann constant.

![Figure 10. Effect of temperature on photodecolorization dispersive blue 26 dye from colloidal solution of 0.3 g/100 mL ZnO at temperature range (283.15-311.15) K (a) Arrhenius equation plot of ($\ln k_{app}$) vs. 1/T, and (b) Eyring plot of ($\ln(k_{app}/T)$) vs.1/T.](image-url)
Table 2. Activation Energy and Thermodynamic Parameters values for Photo decolorization of dispersive blue 26 dye.

| \( E_a \) kJ mol\(^{-1} \) | \( \Delta H^\# \) kJ mol\(^{-1} \) | \( \Delta S^\# \) J mol\(^{-1} \) K\(^{-1} \) | \( \Delta G^{303.15} \) kJ mol\(^{-1} \) |
|----------------|----------------|----------------|------------------|
| 22.111         | 19.587         | -0.193         | 79.882           |

The elevation of temperatures with UV-light accelerated the decolorization of dispersive blue 26 dye, due to increase the velocity for generated of hydroxyl radical [14, 42] that explained in Figure 10 and Table 2. The positive value of \( \Delta H^\# \) and \( \Delta G^\# \) indicated to the photoreaction of decolorization of dispersive blue 26 dye are endothermic and non-spontaneous, respectively. Furthermore the negative value of \( \Delta S^\# \) indicated for the less random state of photoreaction. These results were considered as a good agreement with the previous published in references [52,53].

4. Suggested Mechanism of photodecolorization of dispersive blue26 dye

Indeed, hydroxyl radicals are produced in aqueous solution when the UV- A- light focused on suspension solution of ZnO-dye that leads to (e\(^-\) - h\(^+\)) pair in valance band (VB) or on Conductive band (CB). The adsorbed dispersive blue 26 dye on catalyst surface suffered to attract by hydroxyl radicals of ZnO[44,53], and the colorless solution appeared when the chromophor groups in dye will attract by hydroxyl radical with pH near 7 [27,41].

![Figure 11: The more accepted suggested mechanism in system (dispersive blue 26 dye /ZnO/ UV-A light) [54].](image-url)
4. Conclusions
Based on the results in photo and dark reaction, the adsorption of dispersive blue 26 dye is happened. With the raised of dye concentration from 25 ppm to 100 ppm at equilibrium time equal to 30 min, the adsorption capacity (qe) will raise, but the percentage will decrease. The maximum removal in the natural medium for ZnO-dye is the best. The removal reaction of dispersive blue 26 dye is physical adsorption, exothermic and less random. In photodecolorization of 50 ppm dispersive blue 26 dye has attained the optimum concentrations for decolorization and obtained the pH maximum decolorization efficiency for dispersive blue 26 dye equal to 7.45. The elevated influence of temperature enhanced the photoreaction with low values of activation energies and under these studied conditions illustrated the photodecolorization of dispersive blue 26 dye is pseudo first order kinetic reaction.

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