



Influence The Addition of Fe²⁺ and H₂O₂ on Removal and Decolorization of Textile Dye (Dispersive Yellow 42 dye)



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THIS research compares the addition of some oxidant agents such as Fe²⁺, H₂O₂ and mixture from both to aqueous solution of disperse yellow 42 dye, which regarded as an organic contaminant. This work performed during the dark reaction and photo reaction under artificial UV-A light (HPML -125 watt). In reality, the addition of the oxidant agents led to raise the light resistance of this dye to decolorize, this result can be used to increase the life time for textile materials which painted by this dye. The removal percentage without addition oxidant agent at 20 °C was decreased from 32.710 % to 21.445, 11.439 and 8.785% for addition Fe²⁺, H₂O₂ and mixing of both respectively. Moreover, the decolorization percentage for mentioned materials was depressed from 94.444 to 60.869, 4.163 and 16.044 respectively. The effect of temperature determined with chose Fe²⁺ as oxidant agent and compared with reaction without any addition, because the change is less compared with the other studied cases. The kinetic study of the photo-decolorization process of this dye demonstrated that the generated response is pseudo-first order. The Fenton and photo-Fenton improve the resistance of dye to decolorize during illuminated by light. The dye removal rates depress with the temperature increases from 288 K to 303 K; that due to the dark reaction is exothermic, nonspontaneous and obeys the physical adsorption depending on the values of enthalpy and free energy. In contrast, the response of photodecolorization for this dye is found to be endothermic and non spontaneous and less random.

Keywords: Dispersive yellow dye, Dispersive dye Class C, Nitroarylamino disperse dye, nitrodiphenylamine dye, 4-anilino-3-nitro-N-phenylbenzenesulphonamide Fenton, Photo-Fenton, Activation energy.

Introduction

The large amounts of organic wastewaters are produced during the one year, which attitude to raise the human activities in different fields like: households, agriculture and industries. These human activities caused to vast interest for finding a new solutions to remove these pollutants, hence, the researchers reported many manuscripts in this field such as, adsorption process [1-4], bio-removal [5,6], coagulation [7,8], photocatalytic decolorization [9-15], extraction [16-18], Fenton, photo-Fenton, electro-Fenton, Fenton-like and photo-Fenton-like [19-23].

contamination for water such as azo, reactive and disperse dyes. Because of most textile dyes are non-ionic chemicals, good fastness, slight soluble in water, no strong solubilizing groups, bright color and relatively low molecular mass. Hence, they are mostly utilized for dyeing the polyester (like Terylene, Dacron), silk, cellulose acetate wool, nylon (polyamide), can also be applied on acrylic (Acrylan and Orlon) fibers [24-27]. The disperse dyes are widely employed in textile industries, and they classified by depended upon the molecular size and the sublimation fastness to four classes: class A, class B, class C and class D. The class D is having a large relative molecular size and high sublimation fastness. In contrast,

Textile dyes are regarded as the most source of

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class A has inversed characterizations compared with the characterizations of class D. Besides, class B and class C are owned the characterizations in ranged between class A and class D [28,29].

This work focuses on the removal process of dispersive yellow 42 dye (as Class C) in dark reaction, and studied the decolorization process of its under using UV-A. These processes will compared without and with using the oxidant agents such as Fe(II), H₂O₂ and mixing of both. The activation energy and thermodynamic functions will determine in dark and photo reaction to know the effect of resistance this dye to removal and decolorization with and without addition Fe²⁺.

Materials and Method

Materials

Dispersive yellow 42 dye (C₁₈H₁₅N₃O₄S) is called 4-anilino-3-nitro-N-phenyl benzenesulphonamide; with family's dye (nitro-diphenylamine dye); with M.wt 369.40 g/mol and λ_{max} 488 nm. It was provided by Hilla textile factory. The structure of this dye is displayed in figure 1. Commercial zinc oxide, 30% hydrogen peroxide and ferrous sulfate were supplied by Fluka Company. In this work, all chemicals were utilized without further treatment.

Method

The experiments of dark and photoreaction were executed employing the homemade photo reactor, which is depicted in Figure 2. Homemade photo reactor consists of (a) fan, (b) Pyrex container, (c) medium size Teflon bar, (d) magnetic stirrer type Heido-MrHei-Standard, (e) wooden box wrapped with Al foil in order to raise the focusing of UV-A light on dye solution and (f) UV-A lamp (Philips, HPML- 125 watt). The light intensity of this homemade photo reactor was measured employing the chemical actinometric solution [30] and found to be 9.14 x 10⁻⁸ Einstein s⁻¹.

First step in this procedure is dark reaction, it was performed using (100 mL, 25 ppm) of dispersive yellow 42 dye with and without the using the oxidant agents such as H₂O₂ and Fe²⁺, and then added 300 mg from ZnO. This suspension solution was mixed for 30 min to ensure the contacted all catalyst active sites with the studied dye solution [12-18]. Approximately, 2.5 mL from the suspension solution was collected and filtrated by using Centrifuge (Hettich). The filtered solution was analyzed with recording the absorbance at 488 nm employing (optima) UV-visible spectrophotometer. Using a previously constructed calibration graph, the residue concentrations of this dye in intervals time were found. The adsorption capacity q_e (mg/g) and the percentage of adsorption (removal) efficiency (E_{removal} %) were calculated using equation (1 and 2), which depended on substituted the mass (m in g) of dry adsorbent (ZnO), used volume (V in L) of dye aqueous solution and C_o and C_e that represented to the initial and equilibrium dye concentrations in solution[31-34].

$$q_e = \frac{(C_o - C_e) V}{m} \quad (1)$$

$$E_{removal} \% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

After 30 min of adsorption process; the second step is photo reaction. It was carried out by exposing the suspension solution to the UV-A light in intervals time. About 2.5 mL of suspension solution was isolated in a plastic test tube. Double centrifuged for collected samples were performed for 15 minutes to ensure all the fine ZnO particles were separated. The residual concentration of the studied dye was also determined at the same wavelength with using calibration curve of studied dye. The apparent rate constant (k_{app}) and the efficiency of decolourization (E_{decol} %) for this photo reaction were found [35-37] by the following equations.

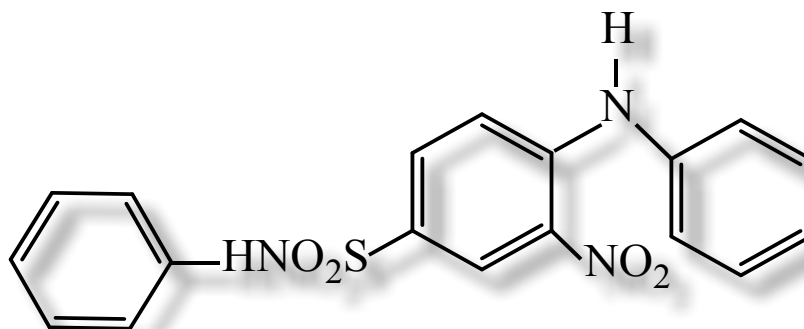


Fig. 1. The structure of dispersive yellow 42 dye.

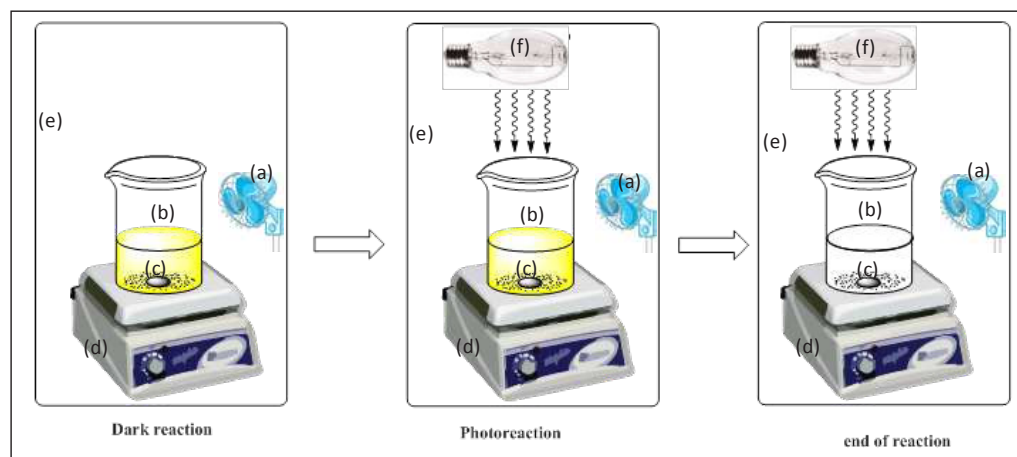


Fig. 2. Homemade photoreactor setup.

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app}.t \quad (3)$$

$$E_{decol.}\% = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (4)$$

Here C_0 is the initial concentration of studied dye without illumination (dark reaction for 30 min), and C_t is the residue dye concentration after time t of illumination.

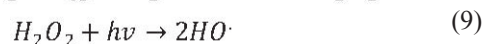
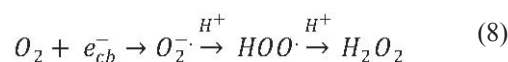
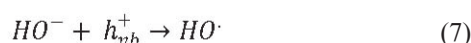
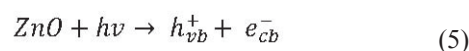
Results and Discussion

Effect of addition oxidant agents on dark reaction

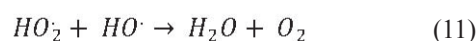
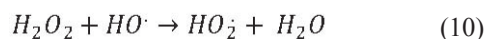
The series of dark reaction experiments were performed by adding H_2O_2 , Fe^{2+} and both to aqueous solution of 25 ppm dispersive yellow 42 dye in presence ZnO. Referring to Figure 3 and Table 1, the results clearly indicated to the adsorption capacity and $E_{removal}\%$ for using ZnO are had maximum values, but the values decrease with using 5×10^{-4} M of Fe^{2+} , 1% H_2O_2 and mixture of both via Fenton reaction. This behavior due to comparative between oxidant agents (Fe^{2+} and H_2O_2) and dye to adsorption on ZnO surface at pH 7.7 and 20 °C.

A. Effect of oxidant agents on photoreaction

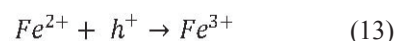
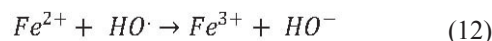
Figure 4 (a and b) illustrates that the maximum values for rate constant (k_{app}) and efficiency of decolorization ($E_{decolorization}\%$) occurred without using any oxidant agent at 30 min, that due to generate a maximum amounts of hydroxyl radical during illumination by using UV-A light [38,39], the hydroxyl radical will attach the chromophore groups in dye and decolorize it color from its solution.



Whereas, the rate constant and efficiency of decolourization reduce during addition of H_2O_2 under UV-A light, that denotes the high concentration of H_2O_2 , making H_2O_2 act as a trap of $HO\cdot$ by forming a high concentration of HO_2 [40- 42] in equations (10-11).



Besides, the results obtained the addition of Fe^{2+} to dye solution will also depress the rate constant and efficiency of decolorization, that investigated to decline the number of produced hydroxyl radicals, because, Fe^{2+} acts as scavenger of hydroxyl radical [43] or hole as shown in equation (12-13).



From other hand, the mixture of Fe^{2+} with H_2O_2 (photofenton reaction) will produce hydroxyl radicals in different media, but sometime that leads to decrease the activity of this reaction, if

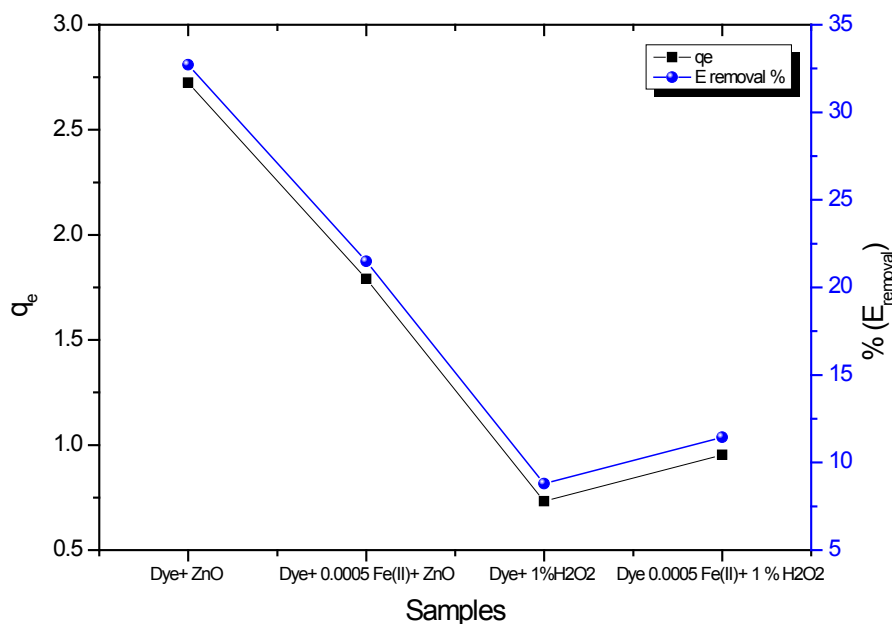
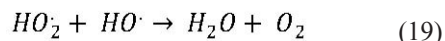
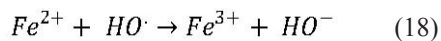
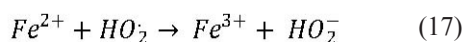
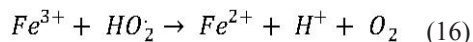
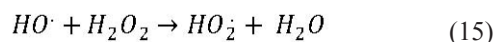
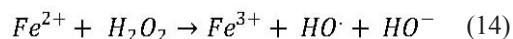


Fig. 3. $E_{\text{removal}}\%$ and q_e for dark reaction in (reactive yellow 42 dye/ oxidant agents/ ZnO).

TABLE 1. Relation between the adsorption capacity (q_e), $E_{\text{removal}}\%$ of Dispersive Yellow 42 Dye With and without addition of Fe^{2+} in finding ZnO.

Samples	q_e (mg/g)	$E_{\text{removal}}\%$
Dye+ ZnO	32.71	2.725
Dye+ 0.0005 Fe(II)+ ZnO	21.495	1.791
Dye+ 1% H_2O_2	8.785	0.732
Dye 0.0005 Fe(II)+ 1 % H_2O_2	11.439	0.953

found the excess from concentration of Fe^{2+} or H_2O_2 , hence, they may be reacted with the active formed species and inhibited them[40,43,44].



Effect of temperature on dark reaction

In order to demonstrate the effect of temperature on the adsorption process of reactive yellow 42 dye on ZnO surface, the activation energy and thermodynamics parameters such as

change in enthalpy (ΔH°), change in entropy (ΔS°) and change in Gibbs energy (ΔG°) were found with and without addition 5×10^{-4} M from Fe^{2+} as less effected oxidant agent in this study. The ΔG° value was calculated by depended on the value sorption distribution coefficient (k_d), which substituted in classical Van't Hoff equation (equation 21) [32,45].

$$k_d = \frac{C_{\text{ads.}}}{C_e} \quad (20)$$

$$\Delta G^\circ = -RT \ln k_d \quad (21)$$

Here, $C_{\text{ads.}}$ is the amount of adsorbate (dye) on the solid surface at equilibrium (mg/L), C_e is a totally dissolved adsorbate remaining (residual dye) in the solution at equilibrium (mg/L), R is universal gas constant (J/mol K) and T is absolute temperature in (K).

The ΔH° and ΔS° can be calculated by

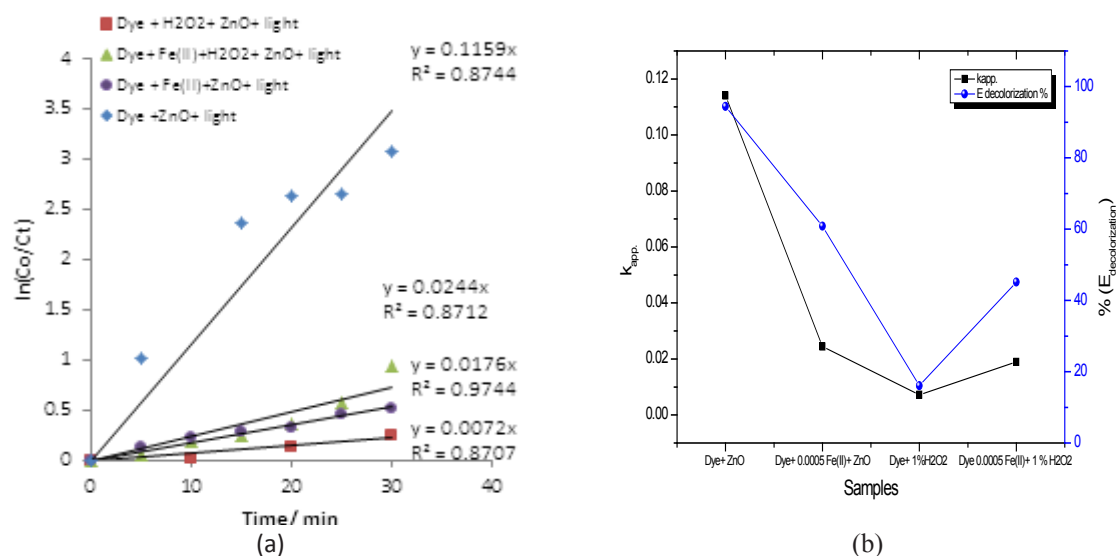


Fig. 4. Relation between $\ln(C_0/C_t)$ and time(a). $E_{\text{decolorization}}$, % and k_{app} for photo reaction in (reactive yellow 42 dye/ oxidant agents/ ZnO) systems(b).

plotting Van't Hoff equation [45,46]:

$$\ln k_d = \frac{-\Delta H^\circ}{RT} + \left(\frac{\Delta S^\circ}{R} \right) \quad (22)$$

The activation energy (E_a) equation was determined in dependence upon the ΔH° and gas constant at various temperatures [32,46].

$$E_a = RT + \Delta H^\circ \quad (23)$$

Figure 6: Relation of Gibb's free energy change (ΔG°) versus temperature for an exothermic process with and without addition Fe^{2+} for the aqueous solution of reactive yellow 42 dye in presence ZnO .

Referring to Figures 5 and 6 and Table 2, considering the adsorption reaction for dispersive yellow 45 dye on the ZnO surface with and without addition of Fe^{2+} , it can be deduced that the dark reactions of both are exothermic and ΔH° alters from $-174.320 \text{ kJ mol}^{-1}$ to $-10.089 \text{ kJ mol}^{-1}$ respectively. Moreover, the ΔG° values with and without addition Fe^{2+} are less negative than -20 kJ mol^{-1} that refers to occur electrostatic interaction between the charged molecules and the adsorbent surface as physical adsorption[46]. The negative values of ΔS° that calculated without and with addition Fe^{2+} is equal to $-0.6049 \text{ kJ mol}^{-1}$ and $-0.3061 \text{ kJ mol}^{-1}$ at 288 K respectively. That ensured the adsorption process has obtained without any change in the internal structure with associative adsorption mechanism[45]. The activation energy for this adsorption reaction

without and with addition Fe^{2+} is found to be $-171.926 \text{ kJ mol}^{-1}$ and $-7.695 \text{ kJ mol}^{-1}$ at 288 K respectively. This case can be interpenetrated to deal with the sorption process because of the calculated activation energies are less 4.2 kJ mol^{-1} [45].

Effect of temperature on photoreaction

This effect done in the temperature range (288-303) K, the activation energy (E_a) and thermodynamic function for active case in photo reaction (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) were measured using the Arrhenius equation (eq. 24), the Eyring-Polanyi equation (eq. 25), and the Gibbs equation (eq. 26), respectively [47- 49]:

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \quad (24)$$

$$\ln \left(\frac{k_{app}}{T} \right) = \frac{-\Delta H^\ddagger}{RT} + \left(\ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \right) \quad (25)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (26)$$

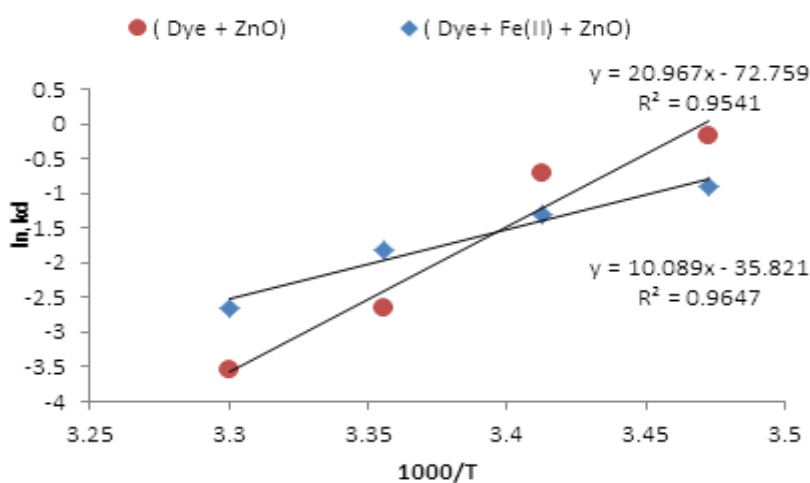
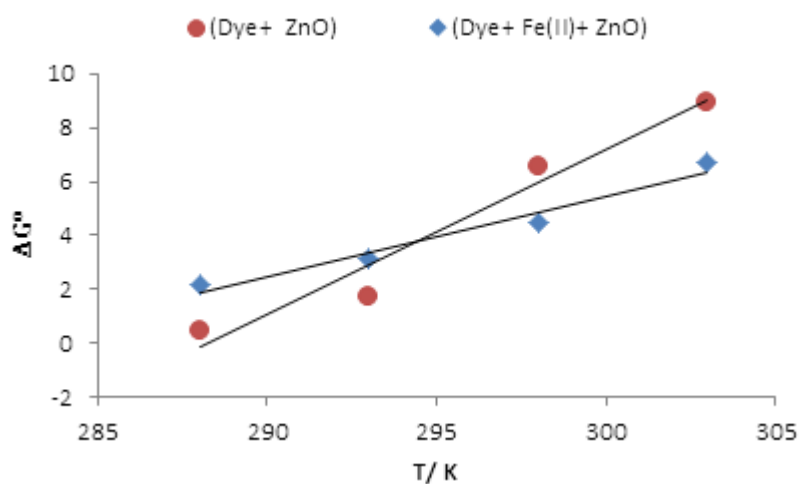
where k_{app} is the apparent rate constant (min^{-1}) and A is the frequency constant, R is the gas constant and T is the temperature of the reaction, k_B is the Boltzmann constant and h is the Plank constant.

Figure 7 Arrhenius equation plot for photodecolorization of dispersive yellow 42 dye from suspension solution of 300 mg/100 mL ZnO with and without $5 \times 10^{-4} \text{ M Fe}^{2+}$, at temperature range (288.15-303.15) K .

Figure 8 Eyring equation plot for photodecolorization of dispersive yellow 42 dye

TABLE 2. The Kinetic and Thermodynamic Parameters for Adsorption of Dispersive Yellow 42 Dye with and without Addition of Fe²⁺ on ZnO Surface.

Samples	(1000/T)	Ln k _d	ΔH°	ΔS°	ΔG°	T/K	E _a
			kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹		kJ mol ⁻¹
Without addition Fe(II)	3.472	-0.898	-10.089	-0.306	2.152456	288	-7.69537
	3.412	-1.298			3.162621	293	-7.6538
	3.355	-1.814			4.494328	298	-7.61223
	3.300	-2.659			6.699054	303	-7.57066
With addition Fe(II)	3.472	-0.18392	-174.320	-0.604	0.440391	288	-171.926
	3.412	-0.72155			1.757689	293	-171.884
	3.355	-2.65926			6.588508	298	-171.842
	3.300	-3.54738			8.936354	303	-171.801

**Fig. 5.** Relation between $\ln k_d$ versus $1000/T$ for adsorption reaction of reactive yellow 42 dye in colloid ZnO solution with and without addition Fe²⁺.**Fig. 6.** Relation of Gibb's free energy change (ΔG°) versus temperature for an exothermic process with and without addition Fe²⁺ for the aqueous solution of reactive yellow 42 dye in presence ZnO.

from suspension solution of 300 mg/100 mL ZnO with and without 5×10^{-4} M Fe^{2+} , at temperature range (288.15-303.15) K .

Figures 7 and 8, and Tables 3 and 4 explain the increases of the decolorization reaction of the dispersive yellow 42 dye with and without addition of Fe^{2+} when raising the temperature. The activation energy for reaction during addition of Fe^{2+} is found to be large than the value without addition Fe^{2+} that attitude to Fe^{2+} acts as scavenger for hydroxyl radical and increased the resistance for decolorization of dispersive yellow 42 dye. The both cases are endothermic, less random and non-spontaneous. These results are in good agreement with previous reported results [48,49].

Conclusions

1-In this work, the addition of the oxidant reagent (Fe^{2+} , H_2O_2 or mixing from both) in certain concentrations leads to depress the removal and photoreaction. This behavior leads to raise the resistance this dye under UV light so, that is useful from the industrial to increase the colored life in colored textile in this dye. The large value of activation energy in photoreaction enhances the importance of addition of Fe^{2+} to dye solution.

2-In dark reaction, the removal reaction for dispersive yellow 42 dye with and without addition Fe^{2+} as oxidant agent is exothermic and physical adsorption.

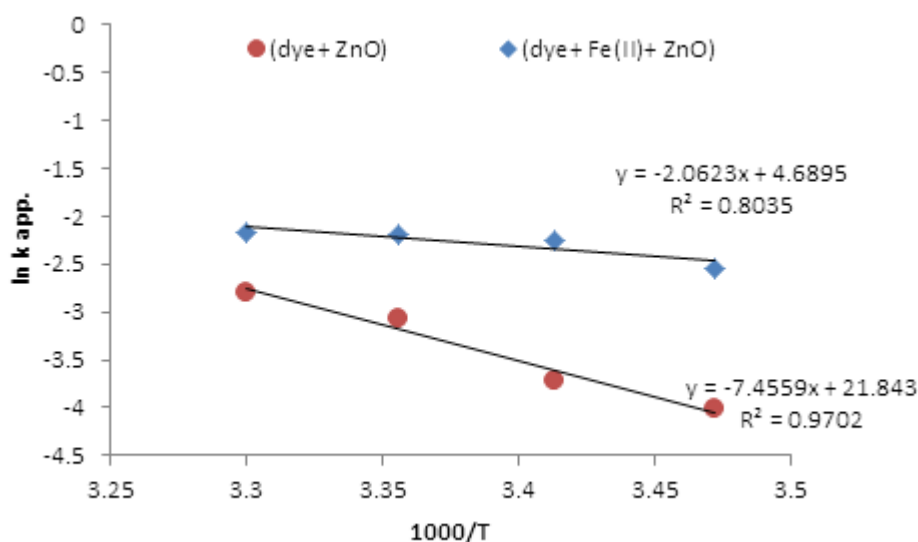


Fig. 7. Arrhenius equation plot for photodecolorization of dispersive yellow 42 dye from suspension solution of 300 mg/100 mL ZnO with and without 5×10^{-4} M Fe^{2+} , at temperature range (288.15-303.15) K .

TABLE 3. The Calculated Activation Energy from Arrhenius Equation for Photo Decolorization of Dispersive Yellow 42 Dye With and without addition of Fe^{2+} in finding ZnO.

(1000/T)	E_a kJ mol ⁻¹		E_a kJ mol ⁻¹	
	ln k _{app.} For Reaction without addition Fe^{2+}	ln k _{app.} For Reaction without addition Fe^{2+}	ln k _{app.} For Reaction with addition Fe^{2+}	ln k _{app.} For Reaction with addition Fe^{2+}
3.472	-2.540		-4.011	
3.412	-2.262		-3.713	
3.355	-2.191	17.145	-3.061	61.988
3.300	-2.173		-2.805	

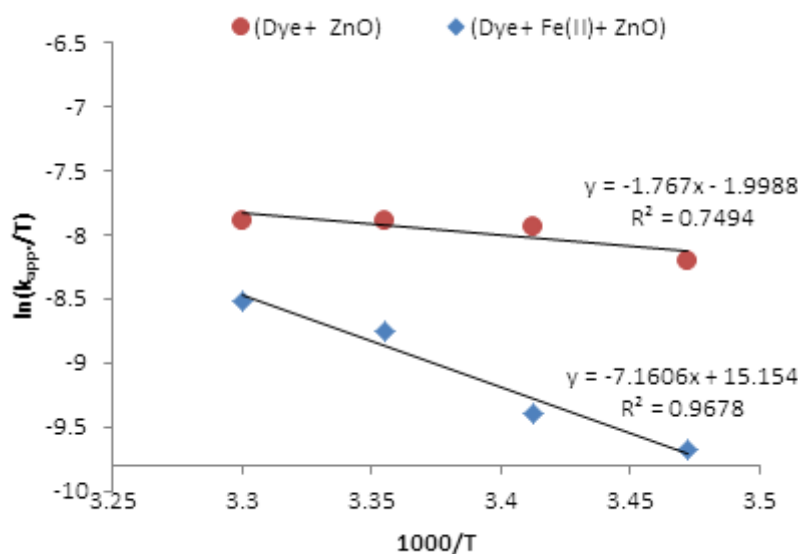


Fig. 8. Eyring equation plot for photodecolorization of dispersive yellow 42 dye from suspension solution of 300 mg/100 mL ZnO with and without 5×10^{-4} M Fe^{2+} , at temperature range (288.15-303.15) K .

TABLE 4. The Calculated Thermodynamic Parameters from the Eyring-Polanyi Equation and the Gibbs Equation for Photo Decolorization of Dispersive Yellow 42 Dye With and without addition of Fe^{2+} in finding ZnO.

(1000/T)	$\ln(k_{app}/T)$	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹				
					$\ln(k_{app}/T)$	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹
For Reaction without addition Fe^{2+}					For Reaction with addition Fe^{2+}			
3.472	-8.203				-9.674			
3.412	-7.942	14.690	-3.090	15.630	-9.393	59.533	-1.035	59.219
3.355	-7.889				-8.758			
3.300	-7.887				-8.518			

3-The photoreaction for decolorizing this dye with and without addition Fe^{2+} is endothermic, non-spontaneous and less random. The positive value of enthalpy and Gibbs free energy measured, that attitude to increase the solvation between hydroxyl radical and dye molecule.

4-The photoreaction for all samples is followed the pseudo first order kinetic reaction by depended on the dye concentration.

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