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Kinetic Study for Reduced the Toxicity of Textile Dyes (Reactive Yellow 14 Dye and Reactive Green Dye) Using UV-A Light/ZnO System

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SEVERAL parameters have been studied in this manuscript to investigate the effect of certain conditions on the removal and the decolorization of the textile dyes: reactive yellow 14 (RY 14) and reactive green (RG) dyes from aqueous solution. Parameters such as temperature, initial concentration of dye and initial pH were taken into consideration to reach the perfect removal and decolorization for both dyes. This work was achieved in both dark and photoreaction processes.

In dark reaction, the type of adsorption was determined based on Gibb's free energy values, activation energies and change in enthalpies, which were found that the physical adsorption for removal of both dyes is predominated, and the reaction is exothermic . The adsorption capacity and percentage of removal both dyes elevated with raised the dye concentration. The best initial pH for removal of RY 14 and RG dyes dyes was conducted and found equal to 5.14 and 9.75 respectively. The raised in temperature is not enhanced the adsorption process, that due to the dark reaction for both dye is exothermic. The small negative values of change in entropies are proved the associative mechanism of both dyes on ZnO surface.
On the other hand, the results under the percent UV-light showed, that the optimal conditions were found at 303.15 K, with 25 ppm and optimum pH=11.01 for reactive green(RG) dye, while the optimum conditions were appearing at 50 ppm and best pH= 6.075 for reactive yellow 14 at same temperature. The decolorization process for both studied dyes was found to be a pseudo-first-order kinetic, fast (low activation energies), endothermic reaction (positive change in enthalpies), non- spontaneous (positive change Gibbs free energies) and less random (negative change in entropies). The photoreaction is a completed to removal process to depress the toxicity for these studied textiles dyes.

Keywords: Decolorization, Textile dye, Cobaltous, Phthalocyaninate, Adsorption, Dark reaction and Photo reactions.

Introduction

Environmental pollution increased rapidly with development of industries and petroleum processing in our life. The biggest challenge for the researchers in an environment field is the pollution in our life [1, 2]. One of the most pollutants that discharged in water stream is dyes. Dyes are widely used in several industries which contribute to impact the damage in an environment. Industries such as pigment, textile, ink, painting, pharmaceutical industries, polymer production, paper processing and production

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cosmetics etc…[3]. The aspects of toxicity for dyes can classified as two classes according to the value of harmful to our bodies; acute aspect for the low conducting time like exposure for short time to the toxic materials. Second class is chronic toxicity for the high conducting time by exposure or intake multi dosages of toxic substances in our bodies [4]. Effect of dyes may be in other aspects of harmful (teratogenic, mutagenic and genotoxic) in addition to the health problems, which can be affected by exposure to this substances such as (damage in cerebral-system, des-function in digestive tracts system, damage in nervos and hepatics system [5]. A high percentage of dyes are used in coloring process, these dyes remain fixed which discharged into waste water or into water stream [6]. This dyes if it presence in the water would cause a several problems for the aquatic system and the life of organisms in this system [7]. A lot of papers were focused on the removal of inorganic dyes from textile fibers. The toxicity effect of these dyes is reported in several papers. Reactive dyes one of the most dyes those used in textile industry due to their properties like water solubility, cheap in cost, stability of colors during washing [8]. Several routs were followed to remove of these dyes by multi methods as example by extraction techniques, sorption by natural and synthesized surfaces, coagulation the dyes, filtration the polluted water and by advances oxidation processes (AOPs) [9-12]. In recent years methods of AOPs were applied to remove of pollutants from waste water [13,14]. Treatment of pollutants by AOPs most likely combined with using heterogeneous semiconductor in presence of photo. This process is called photo catalytic treatment. In which formation of hydroxyl radicals is release which act as oxidizing regent for this process. ZnO as semiconductor was applied in AOPs as photo catalyst for removal and decolorization of dyes from polluted water [15]. In this study, the removal and the decolorization of reactive yellow 14 and reactive green dyes in dark and in photoreaction were achieved under using the suspension solution of ZnO. Varies parameters were determined to find the best conditions in dark and photo reactions. Temperature influence was studied to investigate the impact of this parameter on efficiency of dyes removal and dyes decolorization. The structure of studied dyes illustrated in figure 1.

Materials and Method

Materials

The studied dyes were reactive green dye (RG) ($C_{32}H_{16}CoN_8$ and M .Wt 571.46 g.mol^{-1}) and reactive yellow 14 (RY14) ($C_{20}H_{19}ClN_4Na_2O_{11}S_3$ and and M .Wt 669.02 g.mol^{-1}), which supplied by Hilla textile factory. Zinc oxide was purchased from Fluka, with purity 99.5% which was used after calcinations process at 500 ºC for 2 hours. The rest chemicals were used without further purification in this work.

Dark and Photo reactions

Several experiments were achieved in this work to determine the perfect conditions for dark and photo catalyst removal of reactive yellow and reactive green dyes from aqueous solutions. The reactor was used for photo reaction made by locally materials equipped with a high pressure mercury lamp (365 nm), type Philips, Germany with power 250W. Light intensity was fixed for all experiments at Uv lamp height about 40 cm and measured using chemical actinometric solution [16] and found equal to 2.995 x 10^{-8} Ens s^{-1}. For every experiment done, the reactor was initially loaded with one hundred milliliter of 50 ppm of RY14 dye and like this volume with 25 ppm concentration of RG dye solutions was prepared using distilled water for dilution. For every mixture of dye a certain amount of zinc oxide was added according to the concentration of dye in mixture. The mixture was employed by magnetic stirrer type Labtich to distribute the catalyst among the solution of dye in completely dark place. Exactly 3.5 mL of suspended solution was transferred in test tube. The separation process for this solution was achieved by centrifuge (Hettich) with 4 thousand rpm for 10 min. And then the centrifuging process was repeated for the separated layer from the catalyst to get a clear solution at the same time and rate that top mention. The concentrations of residual dye during declorization process were measured using UV-Vis spectrophotometer type (AA-1800, Shimdzu) at 663 nm and 415 nm for RG dye and RY dye respectively. In dark reaction, the following conditions were applied for both dyes: (initial concentration for reactive yellow 14 is 50 ppm, while for reactive green was 25 ppm, weight of ZnO was 350 mg for both dyes, normal pH for reactive yellow 14 and reactive green were 6.75 and 7.21 respectively. The adsorption capacities q_e in (mg/g) and the percentage of removal ($E_{removal}$%) were determined as following the equations 4 and 5 [17,18]:

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

$$E_{Removal}\% = \frac{(C_o - C_e)}{C_o}.\ 100 \qquad (2)$$

Here, C_o and C_e are the initial and equilibrium dye concentrations in solution, m is the mass of the dry adsorbent in g and V is the volume of adsorbate (dye) in L.

The apparent rate constant ($k_{app.}$) of photo reaction for both dyes, the photo decolorization efficiency ($E_{decol.}$ %) and half time $t_{1/2}$ were calculated by depending on the following equations [19-22].

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

$$E_{decol.}\% = \left(\frac{C_o - C_t}{C_o}\right) x100 \quad (4)$$

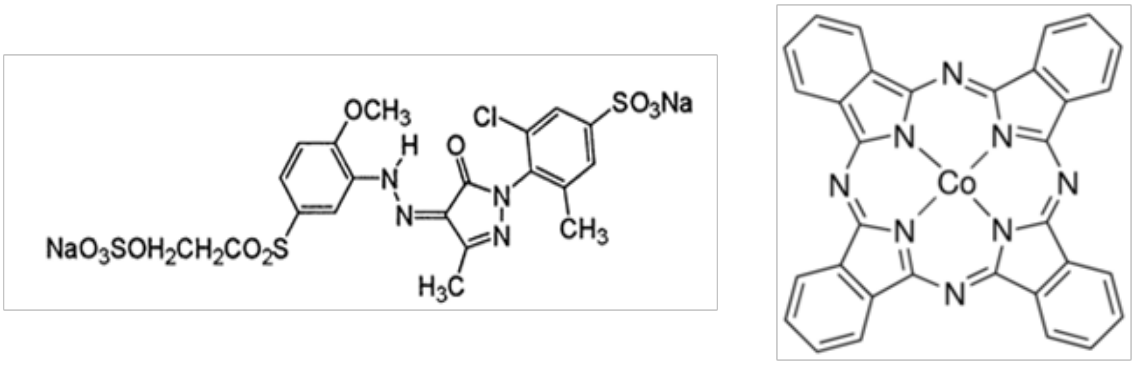
$$t_{1/2} = \left(\frac{\ln 2}{k_{app.}}\right) \quad (5)$$

whereas: C_o is an initial concent ration of reactive green and yellow 14 dyes in dark reaction at irradiation time equal to 0 min. Ct is a concentration of the same studied dye at t time of irradiation.

Results and Discussion

Influence of initial Reactive yellow (RY14) and reactive green (RG) dyes concentrations on dark reaction

This effect was estimated under the equilibrium conditions 30 min, 30 °C and 350 mg ZnO in 100 mL of RY 14 and RG dyes concentration ranged (25-100) ppm. By considering the amount of dye adsorbed per unit of ZnO (mg g^{-1}), adsorption capacity of ZnO raised as the initial RY14 and RG dyes concentration increased as presented in figures 2 and 3. Moreover, the percentages of RY14 and RG dyes removal are obviously supported from 63.276 % to 95.427% and 23.500% to 93.850% respectively. This behavior due to the raised the used dyes concentrations will increase the number of collisions between studied dye ions



(a) (b)

Fig. 1. Structures for reactive yellow (RY 14) (a) and reactive green (RG) (Cobaltous phthalocyaninate) (b).

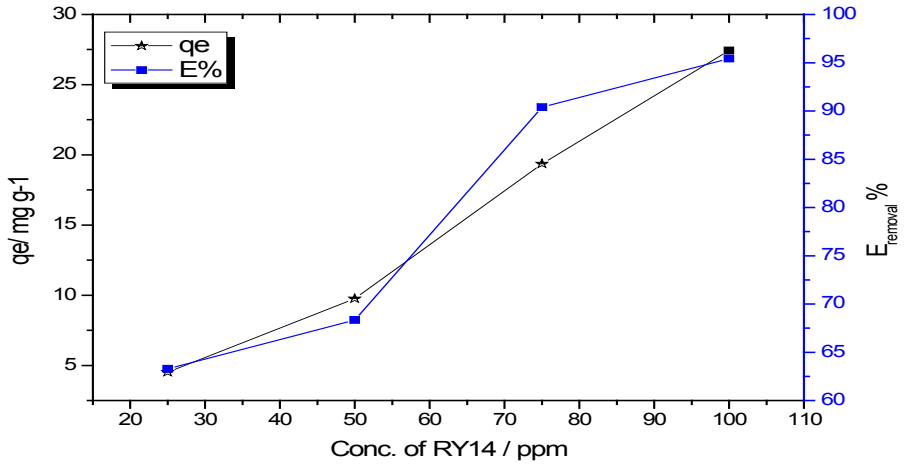


Fig. 2. The plot of adsorption the initial RY14 dye concentration on ZnO surface.

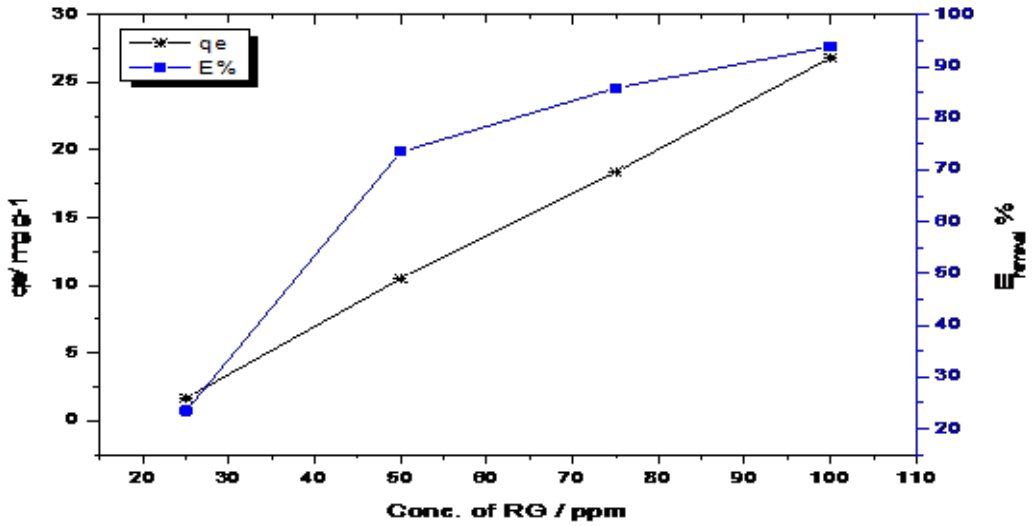


Fig. 3. The plot of adsorption the initial RG dye concentration on ZnO surface.

and the ZnO surface, and at last enhances the adsorption process[23,24].

Influence of dye concentration on photoreaction

After 30 min from dark reaction, the decolorization of RY 14 and RG dyes were carried out in batch operation. The concentrations of used dyes were varied within the range of (25-100) ppm. The results found that the optimum concentrations of RY 14 and RG dyes were obtained at 50 ppm and 25 ppm respectively. After these values, the rate of reaction and the efficiency depress with kept the catalyst dose constant, this is expected because the raised in dyes concentration will lead to decline the light passing through the solution that called screen effect[8,17,25]. As shown in figure 4 (a and b).

The rate of decolorization found to be more for decolorization of RY 14 than it's for decolorization of RG. That conformed by needing to low time and equal to 4.985 min at using 50 ppm but RG needed 9.705 min to decolorize it at 25 ppm respectively. As indicated in figure 5.

Influence of initial pH on dark reaction

In fact, the Initial pH acts as vital factor in adsorption of dyes on any surface. The maximum adsorption capacities and percentages of removal for RY 14 and RG are reveled in figures 6 and 7, which equal to 12.931 mg g^{-1}, 90.522 % and 4.785 mg g^{-1}, 67.000 % at pH 5.14 and 9.75 respectively. Based on the up mention results, that the optimum pH for adsorption RY 14 is 5.14, that deduce to the ZnO surface become positively charged, that will raised the electrostatic force between the active sites positive charge on ZnO surface and the unpaid electrons in oxygen, sulfur and nitrogen atoms that found in RY 14 dye structure. On the other hand, the optimum initial pH for RG dye adoption disclosed at basic pH 9.75, that attitude to the zero point charge of ZnO[25].

Influence of initial pH on photoreaction

Under UV-light, the influence of initial pH shifts compared with pH value under dark reaction, as occurred in figure 8 (a and b).As it is known, the hydroxyl radical that generates on ZnO surface and structure of dyes affect with increased the initial pH to 6.075 with efficiency of decolorization 96.900 % and 11.010 with efficiency 95.91% for RY 14 and RG at 25 min respectively. afterwards, the activity of decolorization depresses because of the ZnO can be undergone dissolution [17, 25] That conformed in acidic medium the surface of ZnO is positive and the chance for adsorption of hydroxyl group and RY 14 is high. When light focuses on suspension solution of ZnO, the photo hole will form and react with hydroxyl group to produce hydroxyl radical as key of starting the photoreaction [26,27]. From figures 8, they are clear that the best pH for decolorization of RG is 11.01, that due to raise the

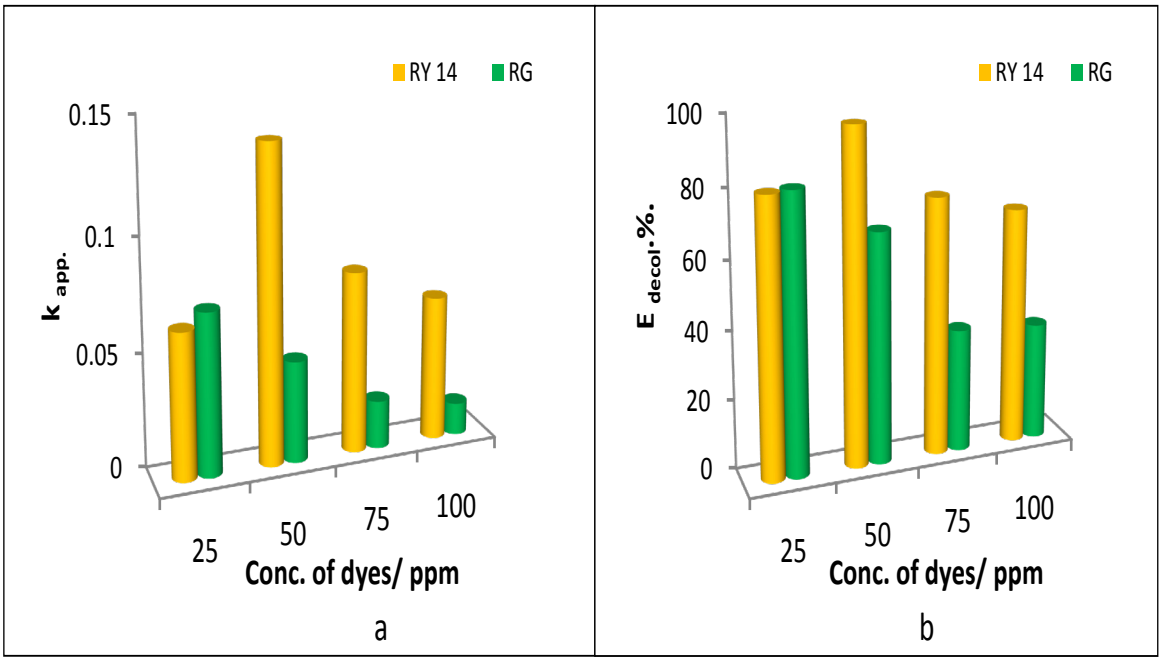


Fig. 4. Pseudo-first order rate constant at varying dye concentration. Conductions: ZnO dosage 350 mg/100 mL, pH= of RY 14 is 6.75 and RG is 7.21, temperature 15 °C, UV light intensity 2.995 x10^{-8} ensien.s^{-1}. (a) $k_{app.}$ vs studied dyes concentrations and (b) $E_{decolorization}$ % vs concentrations of studied dyes.

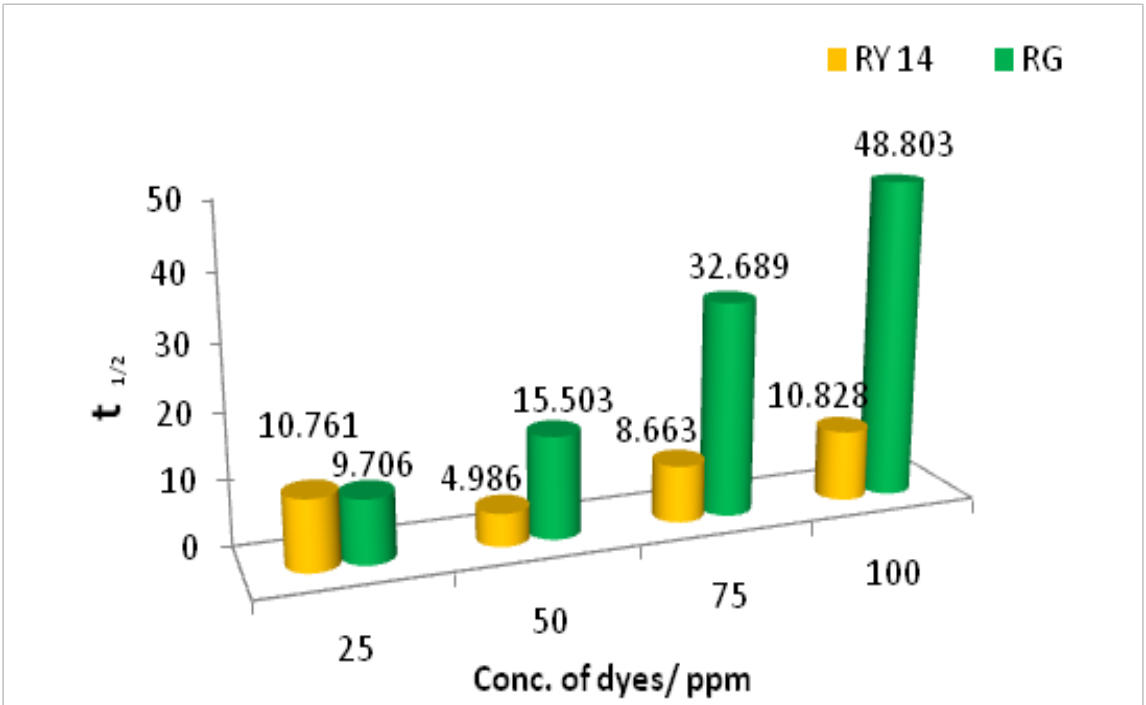


Fig. 5. Relation between $t_{1/2}$ and concentrations of studied dyes.

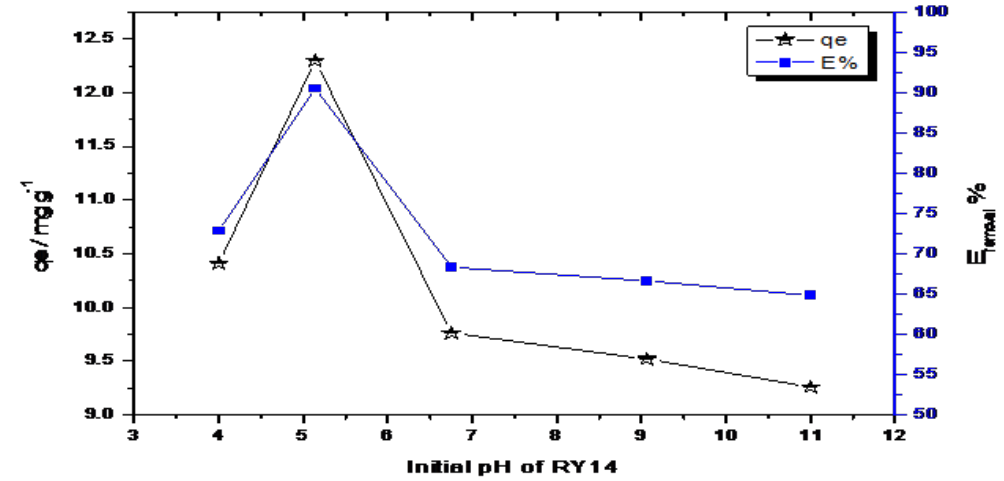


Fig. 6. The plot of adsorption the initial pH of RY14 dye on ZnO surface.

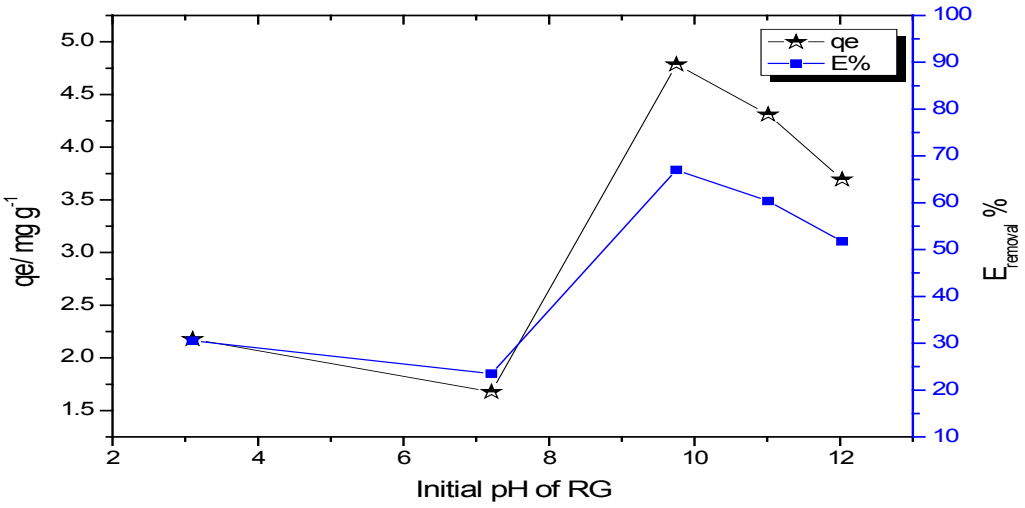


Fig. 7. The plot of adsorption the initial pH of RG dye on ZnO surface.

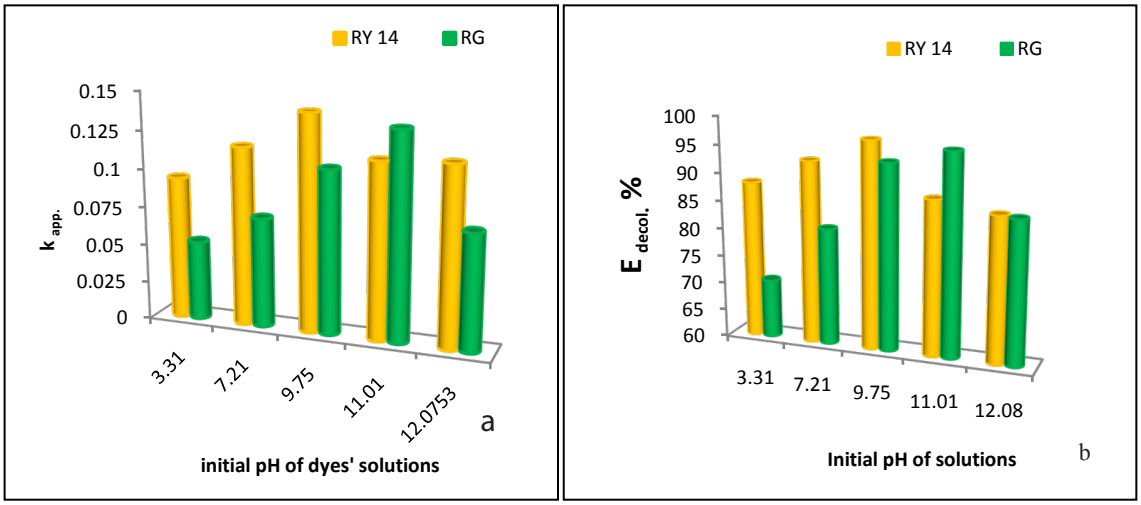


Fig. 8. Pseudo-first order rate constant at varying initial pH of dyes. Conductions: ZnO dosage 350 mg/100 mL, different range of pH, 50 ppm from RY 14 and 25 ppm from RG, temperature 15 °C, UV light intensity 2.995 x10^{-8} ensien.s^{-1}. (a) $k_{app.}$ vs studied initial pH and (b) $E_{decolorization}$ % vs initial pH of studied dyes.

number of generated hydroxyl radicals in basic medium [17].

Influence of temperature on dark reaction

The temperature has really pronounced influence on the adsorption process, because of temperature decreased or increased the adsorption by depended on the type o adsorption. The thermodynamics parameter can be calculated such as change in enthalpy (ΔH^o) and change in entropy of adsorption (ΔS^o) using Van't Hoff equation [26,28].These values are taken from figure 9.

$$\ln k_D = \frac{-\Delta H^o}{RT} + \left(\frac{\Delta S^o}{R}\right) \quad (6)$$

Here[29], k_d is sorption distribution coefficient which calculated from equation (where $C_{ads.}$ is the amount of dye (adsorbate) in the catalyst surface at equilibrium (mg/L) and Ce is total dissolved residual dye in the solution at equilibrium (mg/L).

Based on the magnitude of ΔH^o, the activation energy E_a as follow equation[26,29]:

$$E_a = RT + \Delta H^o \quad (7)$$

The ΔG^o can be calculated to detect if the reaction spontaneous or no and is adsorption process type physical or chemical, and it can be expressed as the following equation [26,29].

$$\Delta G^o = -RT \ln k_D \quad (8)$$

As indicated in Figures 9 and 10 and Table 1, the results obtained the adsorption reaction for RY 14 and RG dyes on the ZnO surface are exothermic and ΔH^o equal to -124.086 kJ mol^{-1} and -90.281 kJ mol^{-1} respectively. These values are less 100 kJ mol^{-1}, so this adsorption for RY 14 and RG dyes on ZnO regards physical adsorption [26,28,29]. The activation energies for the adsorption of both dyes on ZnO surface conformed the physical adsorption is really happened (activation energy below 4.2 kJ mol^{-1}) Furthermore, the small negative magnitudes of ΔS^o (-0.441 kJ mol^{-1} for RY14 and -0.303 kJ mol^{-1} for RG) insure the adsorption process has really happened as associative mechanism and without change in the internal structures of the catalyst (ZnO) [28]. The uptake positive ΔG^o values with the raising the temperature in figure 10, these ensures the process is exothermic with physical adsorption (less negative than -20 kJ mol^{-1})[26,29]. So, the adsorption process for RY 14 and above 298.15 K for RG that will require some energy from an external source to change reactants into products [29]. This case could be occurred because of the mobility of dyes ions or molecules in the solution, which increase with elevate in temperature and that depends on the high affinity for adsorbed the dye on catalyst surface. On the contrary, the uptake negative value of ΔG^o for adsorption of RG dye on ZnO surface ensures in low temperature will be the easy adsorption [26].

Influence of temperature on photoreaction

Figures 11 and 12 represents the increased the temperature under UV- light enhances the photo-decolorization of RY 14 and RG dyes at temperature ranged (288.15 -303.15) K. Based on plotted the Arrhenius equation[30-32] (in eq.9) in figure 11, the activation energy (E_a) assigned. Besides, the thermodynamics parameters like $\Delta H^{\#}$ and $\Delta S^{\#}$ were estimated by plotting Eyring-Polanyi equation [33,34](in eq.10)in figure 12, and used Gibbs equation($\Delta G^{\#}$)[35,36] (in eq.11).

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

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \left(\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R}\right) \quad (10)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (11)$$

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 11 (a & b) and Table 2 explain the elevated of temperature caused a fast decolorization of the studied dye, that attitude to increase the velocity for generated of hydroxyl radical [33,36] and indicated to the photoreaction of decolorization of both dyes are endothermic (positive $\Delta H^{\#}$). Furthermore, these photoreactions are less random (negative $\Delta S^{\#}$), non-spontaneous (positive $\Delta G^{\#}_{303.15}$) and fast (have low activation energies). The $\Delta G^{\#}$ and $\Delta H^{\#}$ have positive values, that can be interpenetrated as increment in solvated of the transition state between formed hydroxyl radicals and RY 14 dye or RG dye [34,36]. These up mentioned results are noticed in a good agreement with the previous published in references [8,19, 37-39].

Suggested Mechanism of photodecolorization of RG dye and RY14 dye

The essential principle for this mechanism

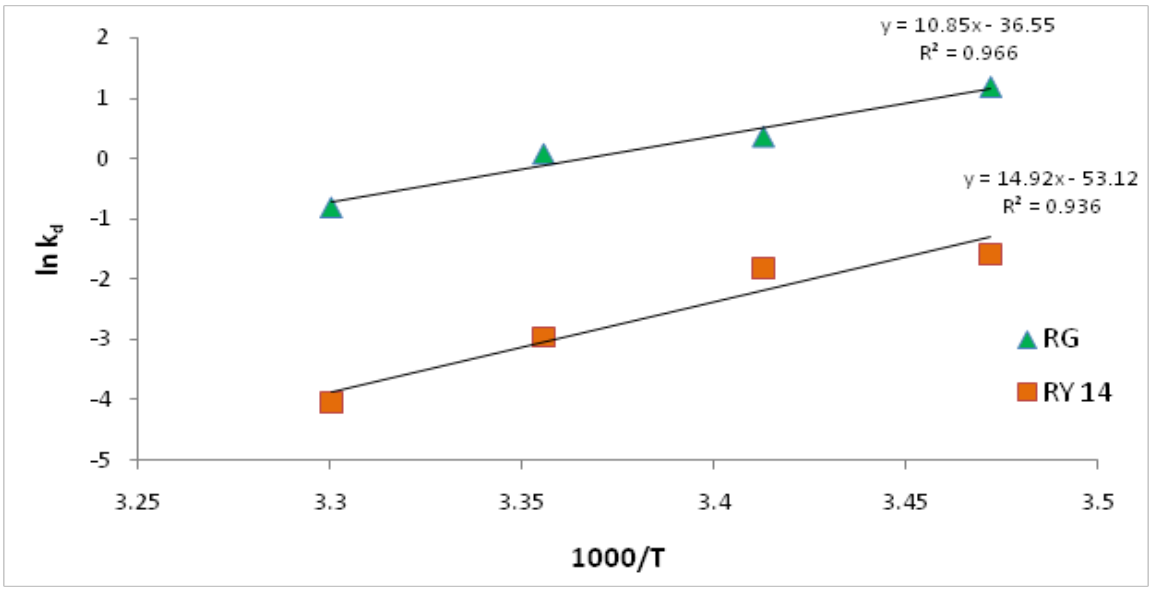


Fig. 9. Relation between ln k_d and 1/T for adsorption reaction of RY 14 and RG on ZnO surface.

TABLE 1. The Kinetic and Thermodynamic Parameters for Adsorption of Reactive Yellow 14 Dye and Reactive Green Dye on ZnO Surface.

Samples	ΔH° kJ mol^{-1}	ΔS° kJ mol^{-1}	ΔG° kJ mol^{-1}	T/K	E_a kJ mol^{-1}
RY 14	-124.086	-0.441	3.765	288	-81.884
			4.429	293	-81.843
			7.334	298	-81.801
			10.208	303	-81.759
RG	-90.281	-0.303	-2.826	288	-70.170
			-0.886	293	-70.128
			-0.198	298	-70.087
			2.015	303	-70.045

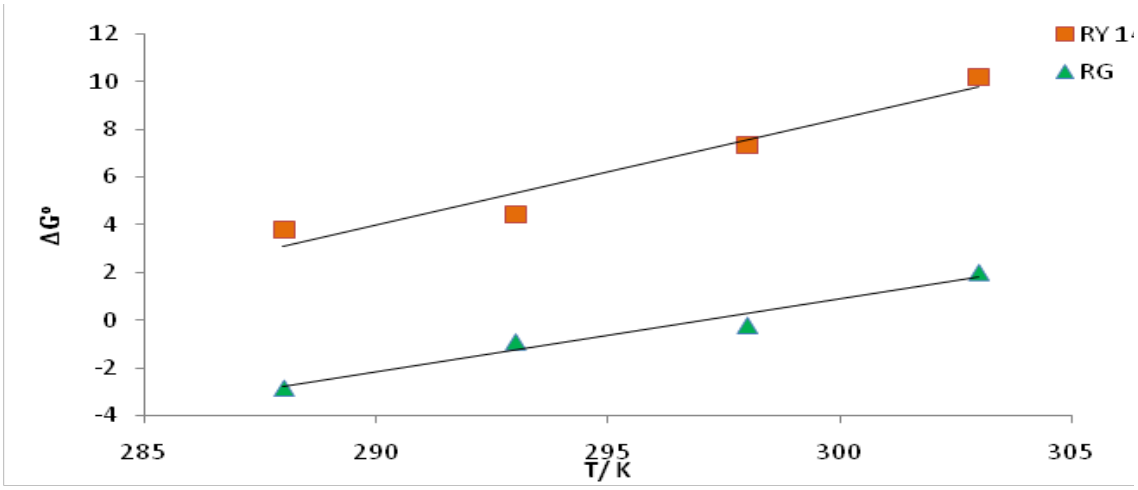


Fig. 10. Relation of Gibb's free energy change (ΔG^o) for adsorption RY 14 and RG dyes versus temperature for an exothermic process.

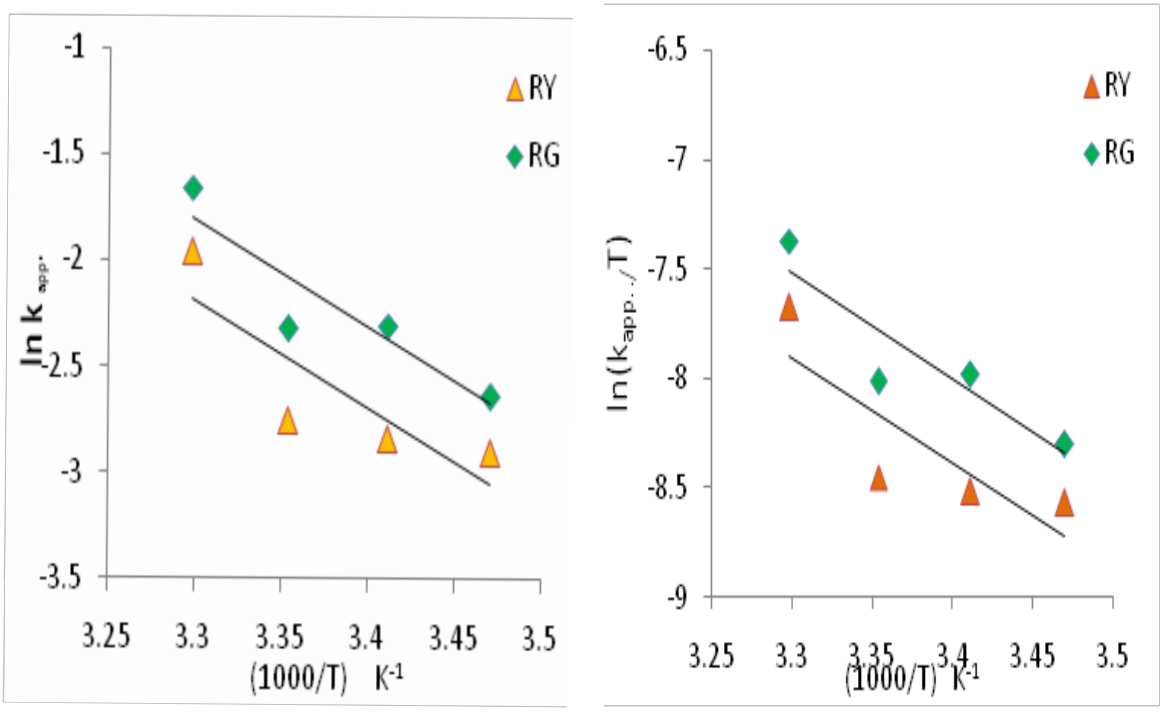


Fig. 11. Effect of temperature on photodecolorization of RY14 and RG dyes from colloidal solution of 350 mg/100 mL ZnO at temperature range (288.15-303.15) K (a) Arrhenius equation plot of (ln k_{app}) vs. 1/T, and (b) Eyring plot of (ln(k_{app}/T)) vs.1/T.

TABLE 2. Activation Energy and Thermodynamic Parameters values for Photo decolorization of RY 14 and RG dyes.

	E_a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J mol^{-1} K^{-1}	$\Delta G^{\#}_{303.15}$ kJ mol^{-1}
RY 14	42.0123	39.555	-0.132	79.792
RG	42.416	39.959	-0.128	78.814

is depended upon formed (e^- -h^+) pair, when the UV- A- light focused on suspension solution of ZnO[37,40]. The adsorbed dyes on ZnO surface are suffered to attract by hydroxyl radicals. Indeed, hydroxyl radicals are produced in aqueous solution under UV-A-light, either in presence the hole (h^+) on valance band (VB) or with presence the dissolved of environment oxygen with the (e^-) on Conductive band (CB) of ZnO[32,35]. The positive free radical of dyes molecules are formed during reacted them with holes of ZnO and then the chromophor groups in dyes will attract by hydroxyl radical. At last, the solution of these dyes will appear as a colorless with pH near 7[8,19]. The more accepted photocatalytic activity for RG dye and RY14dye was represented in figure 12.

Conclusions

On the basis of the results in dark and photoreactions, it can be concluded, that the adsorption of RY 14 and RG dyes on ZnO surface are happend. The adsorption capacity (qe) and percentage of removal for both dyes rise with elevated of the concentration from 25 ppm to 100 ppm at equilibrium time equal to 30 minutes. The

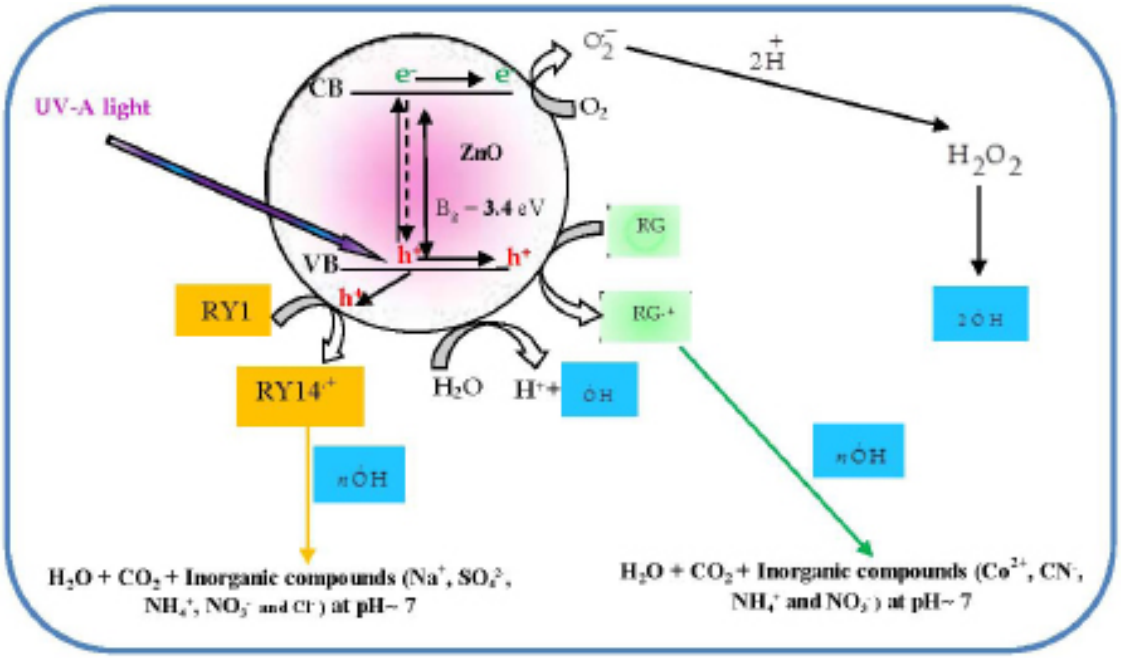


Fig. 12. The more accepted suggested mechanism in system (RG and RY14 Dyes/ZnO/ UV-A light) [8,19].

acidic medium is best to give a maximum removal for RG dye from the ZnO suspension solution, that attitude to attractive force between the electron pair on nitrogen atoms. On the contrary, the basic medium is favor media to remove RY 14 dye under the same conditions, this depended on the natural of the derivatives on aromatic dye. The removal reaction for both studied dye is physical adsorption, exothermic and less random. Indeed, to increase the activity for any photoreaction must pass the reaction in adsorption process to get best results. In photodecolorization for both mention dyes are found the optimum concentrations for decolorization are being to 50 ppm for RY 14dye and 25 ppm for RG dye. The maximum decolorization efficiencies for both dyes at initial pH were obtained at 9. 75 and 11.01 for RY 14 and RG dyes, that due to abundance of hydroxyl radical in basic medium under UV-light. The influence of temperature was illustrated that the elevated the temperature will enhance the photoreaction with low values of activation energies. The photoreactions for both dyes in presence ZnO are endothermic reaction. The photodecolorization of both dyes is pseudo first order kinetic reaction under studied conditions.

Acknowledgments

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