Photocatalytic Degradation of Reactive Green-19 Dye Using Nano ZnO Catalyst

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Abstract. The present work investigates the ZnO nanoparticles synthesis by using sol-gel method. The characteristics of the produced nano ZnO were examined using X–ray diffraction (XRD) technique. The study aims to achieve photocatalytic degradation of (RG-19) reactive green dye in aqueous solution containing nano ZnO as the photocatalyst using batch reactor system. An endeavor has been made to investigate the effect of pH, ZnO dose, irradiation time, RG-19 concentration, H_2O_2 addition, and light intensity on the treatment process. The tests were accomplished by subjecting the RG-19 aqueous solutions containing nano ZnO to the UV irradiating. The concentrations of RG-19 before and after treatment was measured spectrophotometrically. The extent of decolorization reached to 100% under optimal conditions after 160 minutes of irradiation. The ideal pH for the photocatalytic decolorization of RG-19 dye within the existence of nano ZnO is pH 8. Optimum nano ZnO dose was 800 mgL^{-1}. Photocatalytic decolorization was directly proportional to initial RG-19 concentration and inversely with increasing temperature. The oxidizing agents (H_2O_2) improve the rate of decolorization. However, more addition of H_2O_2 decreases the decolorization rate. pseudo-first-order kinetics was followed for the decolorization process of RG-19 dye. An Arrhenius plot displays that the activation energy is equal to 7.855 $kJmol^{-1}$ and the reaction is endothermic in nature.

1. Introduction

Dyes represent a group of complex organics which enter into the environment from various industries like tanning, paper, paint, inks and textile industries. Some of these dyes are highly toxic [1]. Dyes in waste water can be treated by different methods. The traditional methods such as adsorption on waste materials, flocculation, adsorption on activated carbons, precipitation, ultrafiltration , reverse osmosis, and air stripping has used for the removal of dyes [2]. These methods are phase transferring methods and require further treatment for disposal [3]. The biological treatment of waste water is better to some extent over the above methods. But all of these methods are time consuming and produce a large quantity of sludge which cannot be recycled [4]. Also, many colorful waste waters are highly resistant to biodegradation. Thus, all the above methods are ineffective for removing the synthetic dyes that enter into water from various industries. A cost effective, simple and promising method to achieve complete dyes mineralization into H_2O and CO_2 is the advanced oxidation process (AOP) [5]. AOPs depend on the production of tremendously receptive species like hydroxyl radicals which has the ability to oxidize an expansive scope of organic pollutants non-selectively and quickly. The most important among them is the photocatalytic degradation by semiconductor-assisted. Semiconductors

have a unique electronic structure described by a vacant conduction band and an occupied valence band [6]. Under the irradiation, electrons of valence band are raised up to the conduction band abandoning an opening. These electron-gap sets may either interface independently or recombine with different particles. The gaps can react with donors electron of the solution, or with OH^- in order to create influential oxidizing species like super oxide radicals or hydroxyl [7]. In spite of the fact that, TiO_2 particularly anatase phase has utilized for some natural applications, ZnO is an appropriate option to be used., so far as hole band vitality is concerned. Zinc oxide is a fantastic wide band hole, natural n-type semiconductor material with a binding energy of 60 MeV, abundant in nature, non-toxic in nature, and is an environmentally friendly photocatalyst.

Sunlight is is a copiously accessible vitality source, however, UV irradiation as a high energy source is used for degradation of organic pollutants existing in the effluent wastewater. Electron-hole recombination is considered a great problem to circumvent in the process of photocatalytic.However, a UV irradiation source is preferred among the other energy sources to prevent this problem. So, in this study, we will use UV irradiation for degradation. In studies of photocatalytic degradation, ZnO nanosized is favored as compared to ZnO large sized particles. High surface area to volume ratio and the quantum confinement of nanoscale are considered the greatest important properties of a nanomaterial for application of catalysis as compared to macroscopic or microscopic particles. The main property brings about impetuses with high porosity and high surface zone, which guarantees upgraded response rates because of the abnormal state of communication between dynamic destinations and the reactants .The second property manages the transport of holes and electrons from the bulk to the surface of the material which its length scale of a few nanometers. Additionally, for photo applications, the catalyst should adsorb and not scatter or block by excitation of band gap. This could be possible only with   appropriate gap energy by using semiconductor materials of nanosized. Therefore, it is important to enhance molecular transport of the surface. it is clear that material of nanosized are useful as photocatalysts [8].

The purpose for this research is to explore the capability of ZnO nanosized in the oxidation of RG-19 dye in aqueous solutions as a photocatalyst material under radiation of UV. parameters effects like nano ZnO loading , pH, the addition of H_2O_2 , irradiation time, and initial RG-19 dye concentration on the rate of degradation were studied. These factors are the main parameters which effect on the efficiency of the process.

2. Materials and methods

2.1. Reactive dyes

Reactive Green-19 (RG-19) had been supplied from AL-Kut textile factory in south of Iraq, particularly from department of printing and dying. Simulated stock solutions of 1000 mg/L had been prepared by dissolving 1 g of dye in one liter of distilled water then diluted to the desired solution concentrations. Table. 1 shows specifications of this dye.

Table 1. Main characteristics of reactive dyes.

index name of Color	C.I. Reactive Green 19 (RG-19)
Chemical structure	
Chemical class	Anionic, Diazo
Color index number	68110-31-6
Molecular formula	$C_{40}H_{23}C_{12}N_{15}O_{19}S_6.6Na$

Mw (g/mol)	1418.92
λmax (nm)	630

2.2. ZnO as a photocatalyst

Zinc acetate dihydrate, zinc oxide (ZnO) hydrogen peroxide (H_2O_2), oxalic acid dihydrate, NaOH, HCl ,and all the organic reagents were bought from Merck (Germany). Double distilled water was utilized in all the expirements.

Nanocatalyst was synthesized by modifying the sol-gel method. A rotary evaporator under slightly reduced pressure at 60 °C was used to treat 5.49 g of Zinc acetate dihydrate with ethanol (150 mL). and it takes 10-15 minutes for the salt to be totally dissolved. Simultaneously, oxalic acid dihydrate (6.3 g) was dissolved in ethanol (100 mL) and under stirring at 50 °C for 10 minutes. Then, drop wiseof solution was added to the warm solution of ethan having Zn^{2+} ions. The white and thick gel gained was dried for 20 h at 80 °C to get xerogel which was calcined at 500 °C [9].

2.3. Photocatalytic experimental procedure

a batch photoreactor uas used to carry out All the experiments. a UV lamp was used as The radiation source (manufactured by Philips, Holland, λmax = 254 nm, $30W/m^2$, UV-C) which was located above 1 L reactor made of a Pyrex. Lux-UV-IR meter (Leybold Co.) was used to measure the light intensity in the photoreacto center. For the photocatalytic degradation of RG-19, a solution having identified concentrations of the nano ZnO and dye was prepared which was equilibrated in the darkness for 30 min, then prepared suspension (500 mL) was moved into the reactor. Then, the lamp was turned on to start the reaction. During irradiation, a magnetic stirrer was used to mount the glass reactor to save the suspension homogenous at assured reaction intervals. 10 mL of suspension was removed , and centrifuged. a UV–vis spectrophotometer at 630 nm (Ultrospec 2000, England) was used to analyze the dye concentration. Beer–Lambert's law was used to calibrate the plot which was established by linking the absorbance to the concentration. The decolorization efficiency (%) was calculated as:

$$\text{Efficiency of Decolorization } \% = \frac{c_i - c}{c_i} \times 100 \tag{1}$$

Where C_i is the dye initial concentration and C is the dye concentration after photoirradiation. Other experiments were done by changing the pH solution (pH 2-10), catalyst dose (100-900 mg/L), irradiation time (10-180 min), dye concentration (25-200 mg/L) and H_2O_2 concentration (10-50 mg/L).

3. Results and discussion

3.1. X-ray diffraction (XRD) study of ZnO nanoparticle

The XRD pattern of nano ZnO is shown in Fig. 1. All the peaks are in good agreement with wurtzite ZnO. The peaks match to the (101), (100), (002) (110), (102), (103), (112), and (200) of the ZnO nanoparticle planes., high crystallinity and purity of the as-obtained wurtzite ZnO nanoparticles with no impurities was noticed. Debye– Scherrer formula was used to calculate the ZnO nanoparticles average crystallite size at calcination temperature of 500 ℃ which is valued to be 26.3 nm:

$$P = \frac{0.9\,\alpha}{\beta \cos \theta} \tag{2}$$

Where: P: crystallite size, α : wave length (1.54 ^{O}A), β: full maxima half width, θ = diffraction angle.
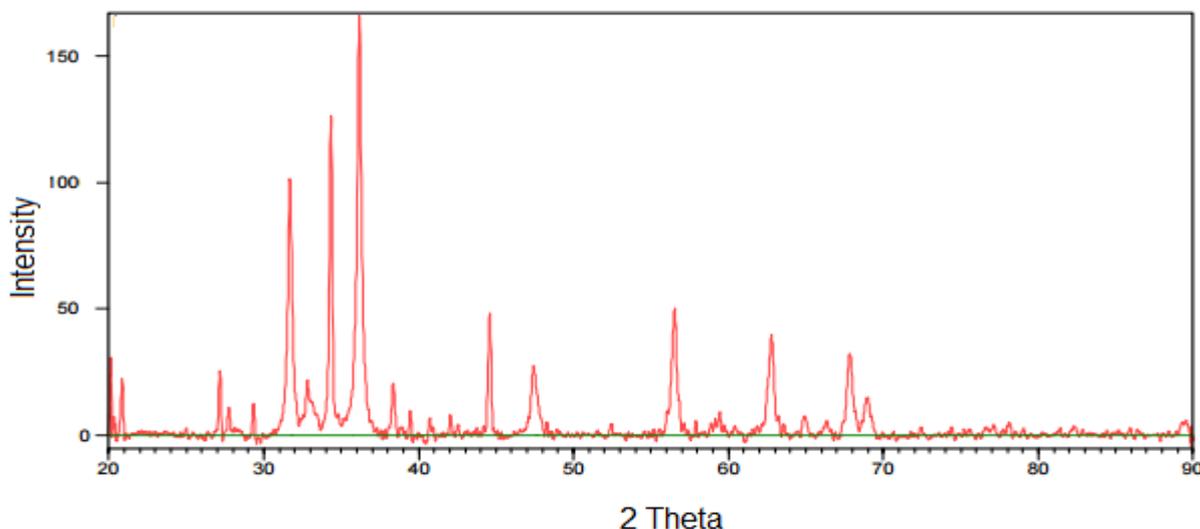
Figure 1. XRD of nano ZnO

The removal efficiency using normal and synthesized nano ZnO catalyst is presented in Fig. 2. As shown in this figure, nano ZnO had a greater decolorization efficiency than the normal one. For a ZnO and nano ZnO dose of 200 mg/L, reaction time of 60 min, and dye concentration of 50 mg/L, the efficiency of decolorization using ZnO was steady at 7%. However, for nano ZnO, the removal continued to increase and reached 35% in 60 mins. Thus, nano ZnO will be used for further experiments.
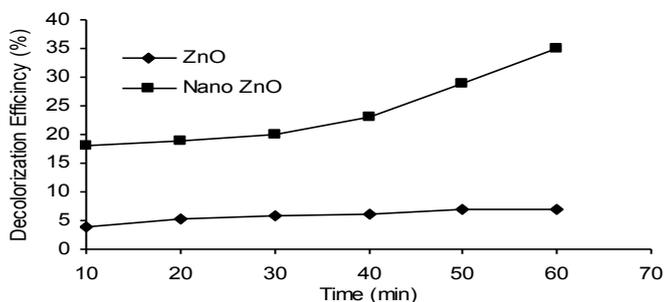
Figure 2. Removal of RG-19 using normal and Nano ZnO

3.2. pH Effect on photocatalytic degradation
The best important parameter that effects photocatalytic decolorization of dye is the initial value of pH of the solution. It has a crucial role in the surface properties of catalysts, the generation of hydroxyl radicals,and features of textile dye. Three possible mechanisms reactions will control this effect which are : direct oxidation by the positive hole, direct reduction of conducting band electrons, and dye decolorization with hydroxyl radical attack [10].

In this experiment, Nano ZnO, UV, H_2O_2 alone and in combination were used with different pH values. The nano ZnO photocatalyst samples (100 mg/L), and H_2O_2 (10 mg/L) were separately added to eight samples of dye solution (500 mL, 50 mg/L). By drop wise additions of HCl (0.1 M) and/or NaOH (0.05 M) solutions, the pH values of each sample of catalyst dye mixture were separately adjusted to 2, 3, 4, 5, 6, 7, 8 and 9. Each set was exposed to UV light for 60 minutes (arbitrary time) with continuous stirring. Fig. 3 displays efficiency of removal of RG-19 as a function of pH. It has noticed that the decolorization efficiency increases with increasing pH, displaying optimum degradation at pH 8, as presented in Fig. 3. Similar performance also has been described for the efficiency of photocatalytic of ZnO for azo dyes decolorization [11]. The interpretation effect of

pH on the photocatalytic degradation efficiency is a very hard mission because of its numerous roles.

First, it is associated with the property of acid base of metal oxide surface and may be described on the base of zero point charge. The water molecules adsorption at sites of surficial metal is followed by the OH^- charge groups dissociation leading to sheltering with metal hydroxyl groups which are chemically equivalent (M-OH) [12]. Because of the most metal hydroxides amphoteric behavior, the following two equilibrium reactions are tajen in account:

$$M\text{-}OH+H^+ \rightarrow M\text{-}OH_2^+ \tag{3}$$
$$M\text{-}OH \rightarrow M\text{-}O^- +H^+ \tag{4}$$
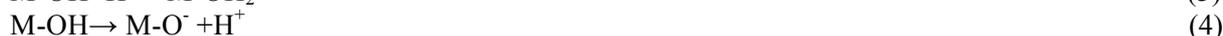
The zero point charge (zpc) for nano ZnO was determined, by the solid addition method, to be 8.0 [13]. The ZnO nano-sized surface is charged positively below pH= 8 and above this value, the surface is charged negatively by adsorbed OH^- ions. Huge amounts of OH^- ions existence on the surface of particle and in the reaction medium are suitable to the formation of $OH^{\bullet}$ radical, which is commonly recognized as the main oxidizing species in chargeof the process of decolorization at high or neutral levels of pH which are preferred in the enhancement of the process efficiency [14]. The efficiency of removal was 60, 10, 5, 65.2, 70.2, 15.1 and 77% for nano ZnO, H_2O_2, UV, nano ZnO+ UV, nano ZnO+ H_2O_2, UV+ H_2O_2 and nano ZnO+ H_2O_2+UV, respectively. Thus, ZnO+ H_2O_2+UV will be used in the next experiment at optimum pH.
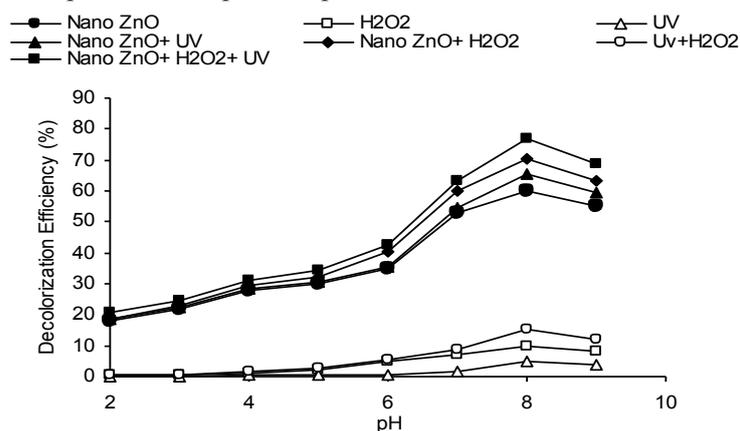
Figure 3. Effect of initial pH on photocatalytic degradation of RG-19

3.3. Effect of nano ZnO dose

To determine the catalyst loading effect, the experiments were achieved by changing the concentration of catalyst from 100 to 900 mg/L at optimum pH (8) for dye solutions of 50 mg/L. The efficiency of decolorization is shown in Fig. 4. Fig. 4 shows that initial slopes of the curves increase significantly as catalyst loading increasing from 100 to 800 mg/L, afterward, the decolorization efficiency rate stays nearly constant at 90%. It can be described as initial solute concentration control the optimum catalyst loading because with the increasing of dosage of catalyst, total active surface area increases and hence the obtainability of more active sites on the surface of catalyst. Simultaneously, because of an increasing in the suspension turbidity with high photocatalys doses, there will be a decrease in UV light penetration and hence decreasing the volume of photoactivated of suspension [15]. Therefore, it determined that a higher dose of catalyst may not be beneficial in vision of aggregation as well as irradiation field reduced because of scattering of light. Thus, the 800 mg/L dose of catalyst was permanent for additional studies.
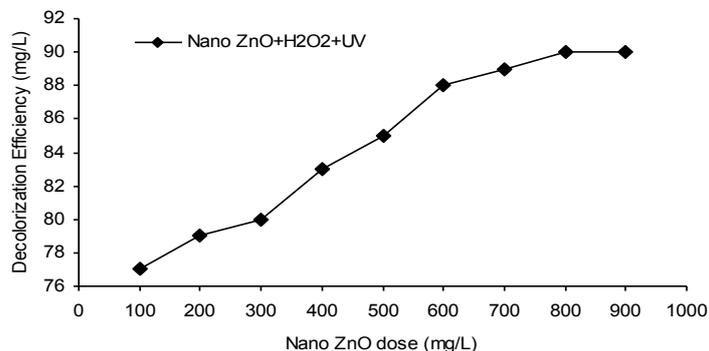
Figure 4. Effect of ZnO loading on photocatalytic degradation of RG-19

3.4. Irradiation Time Effect

irradiation time Effect on the decolorization efficiency of RG-19 is revealed in Fig. 5. The figure displays that as the time of irradiation increases, the efficiency removal of RG-19 increases until equilibrium is reached. Removal efficiency increases from 10 to 95% as the time of reaction increases from 10 to 160 min. The results obviously reveal that decolorization rate is higher at the beginning due to the occurrence of a huge number of active sites. When active sites are bushed, the rate is reduced [16]. Maximum removal was achieved at the first 160 min time of reaction. It seemed that there is no more advantage after 160 min. Thus, the time of equilibrium was fixed to be 160 min.
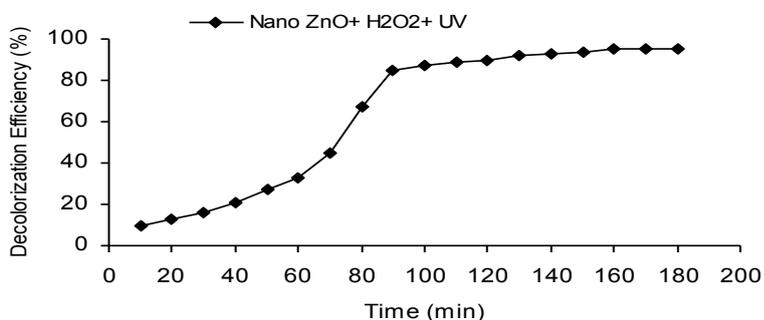
Figure 5. Effect of irradiation time on photocatalytic degradation of RG-19

3.5. Dye Concentration Effect

Initial concentration effect of solution of the dye on the degradation of photocatalytic is a significant feature of this research. Initial concentrations of RG-19 were changed in the range of 25-200 mg/L, while fixing pH, nano ZnO dose, and reaction time at 8, 200 mg/L and 160 min, respectively. The percentage of photodegradation decreased with initial concentration increasing of the dye solution as presented in Fig. 6. Maximum decolorization efficiency occurred at 25 mg/L where the value was 97%. this behavior is described as increasing of initial concentration, more dye molecules are adsorbed on the nano ZnO surface, thus, the production of hydroxyl radicals will be minimized because of only few active sites for the generation of hydroxyl radicals and adsorption of hydroxyl ions. More, as the dye solution concentration increases, the photons get interrupted before they reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and thus the percentage of degradation is reduced [17].
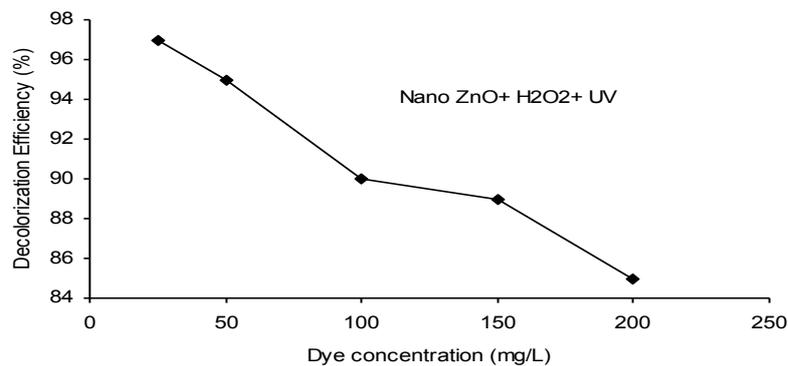
Figure 6. Effect RG-19 concentration on decolorization efficiency

3.6. H_2O_2 concentration Effect

The photocatalytic degradation rate of organic compounds is meaningfully enhanced by adding hydrogen peroxide or in the existence of oxygen. When concentration of hydrogen peroxide was increased, the photocatalytic degradation rate of RG-19 is increased and achieved a maximum value, but over optimal value, increasing concentration of H_2O_2 delays the reaction (Fig. 7). This double influence of H_2O_2 can be described by mechanisms radical reaction. The additional H_2O_2 could speed up the reaction by creating hydroxyl radicals from UV-light absorption and scavenging the electrons by the following reactions:

$$H_2O_2 + (ZnO)e^- \rightarrow {}^{\bullet}OH + {}^-OH \tag{5}$$
$$H_2O_2 + O^{2\bullet-} \rightarrow {}^{\bullet}OH + {}^-OH + O_2 \tag{6}$$
$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \tag{7}$$
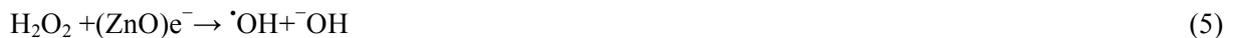
Adding of extra H_2O_2 is a reason to make it acts as hole scavenger or a hydroxyl radical to form perhydroxyl radicals ($HO_2{}^{\bullet}$) which are greatly weaker oxidants than hydroxyl radicals [18]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet} \tag{8}$$
$$H_2O_2 + h^+ \rightarrow H^+ + HO_2{}^{\bullet} \tag{9}$$
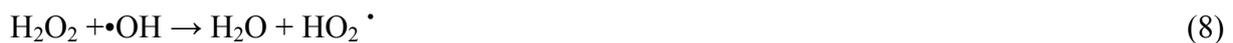
Thus, when hydrogen peroxide concentration is high, it inhibits the dye degradation reaction rate by competing with RG-19 for existing hydroxyl radicals.
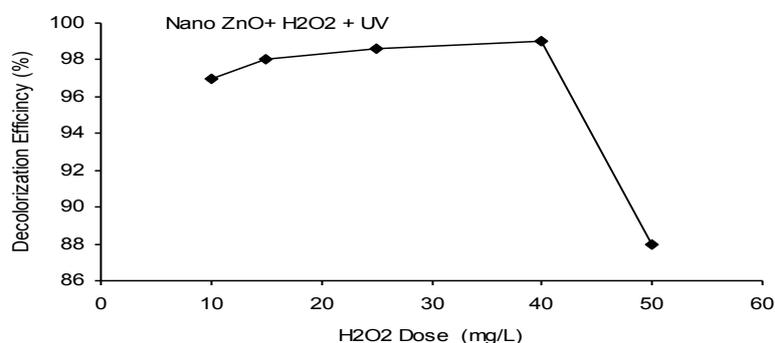

Figure 7. H_2O_2 dose Effect on photocatalytic degradation of RG-19

3.7. Light intensity effect

Light intensity effect on the efficiency of degradation was studied at optimum conditions obtained from previous experiments. It is obvious that increasing of light intensity leads to the increasing

percentage of photodegradation and decolorization as shown in Fig. 8. the photons necessary for the transfer of electron from the valence to conduction bands of the semiconductor photocatalyst materials are generated by the UV irradiation. The photon energy is associated with its wavelength, and the overall energy input to a photocatalytic process is influenced by intensity of light. The degradation rate increases as additional radiation reaches the surface of catalyst and hence more production of hydroxyl radicals` [19]. The decolorization efficiency reached 100% when using a UV lamp with light intensity of 40 W/m^2.
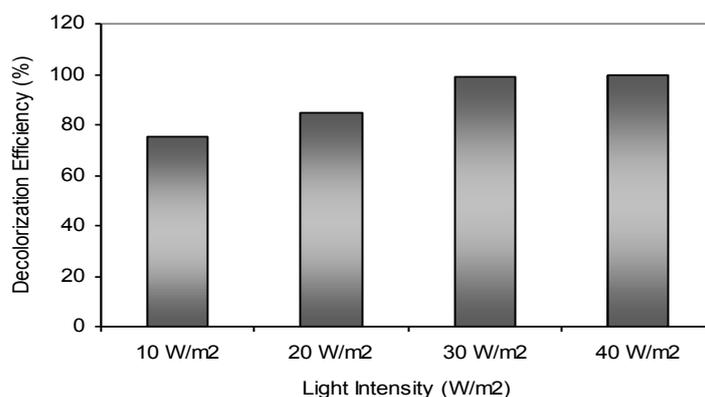
Figure 8. Effect of the light intensity on photocatalytic degradation of RG-19 under optimized conditions

3.8. Kinetic studies

The kinetics of disappearance of RG-19 are shown in Fig. 9 for 25 mg/L an initial concentration under optimized conditions. The results display thatthe decolorization of photocatalytic of RB-19 dye may be explained by the first order kinetic model, $\ln(C_o/C) = kt$, where t is the semi-logarithmic plots of the concentration data gave a straight line, C is the concentration at any time, and C_o is the initial concentration. The fitted line correlation constant was calculated to be $R^2 = 0.9417$. The constant of rate was calculated to be 1.34×10^{-4} s^{-1}.
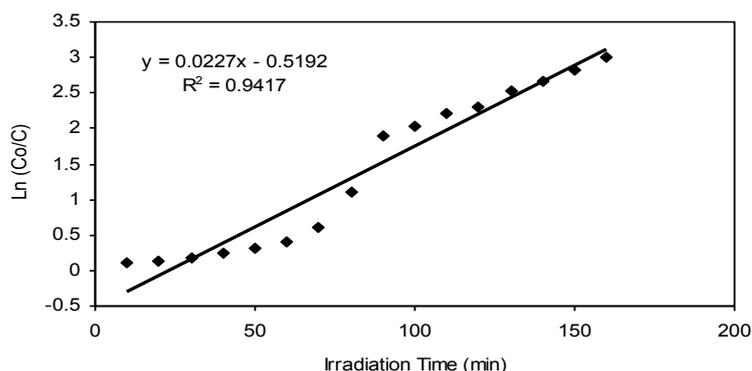
Figure 9. Kinetic analysis of RG-19 under optimized conditions

3.9. Temperature effect

The reaction was followed at different temperatures (293, 303, 313 and 323 K). The results in Fig. 10 show that, the efficiency of decolorization of RG-19 dye has a linear relationship with temperature, fitting the graph of the Arrhenius equation' (Eq. 10) [20].

$$LnK = \frac{-E_a}{RT} + \ln A \qquad (10)$$

Where, E_a: activation energy (KJ mol^{-1}), K: rate constant , R: gas constant (0.831 KJ K^{-1} mol^{-1}), A: frequency factor, and T: temperature of reaction (K)

As the temperature increasing, photocatalytic decolorization of RG-19 dye increased. The activation energy on the surface of nano ZnO was found to be equal to 7.855 KJ mol^{-1}. Eyring Equation plot was used to determine the values of ΔH^O and ΔS^O [21,22].

$$Ln\frac{K}{T} = \frac{-\Delta H^O}{RT} + (\ln \frac{KB}{h} + \frac{\Delta S^O}{R}) \qquad (11)$$

where: K_B: Boltzmann's constant and h: Plank's constant. The free energy ΔG^O is calculated from Equation (12):

$$\Delta G^O = \Delta H^O - T\Delta S^O \qquad (12)$$

The fitted results of the thermodynamics functions and the activation energy are as follows:

E_a= 7.855 (kJ mol^{-1}), ΔH^o= 5.852(kJ mol^{-1}), ΔS^o= 0.343 (kJ mol^{-1} K^{-1}), ΔG^o= -59.456 (kJ mol^{-1}).

The calculated results and Figures 10 and 11 show that the reaction rate increased as the temperature raised from 293 to 323 K, therefore the decolorization process of RG-19 dye was an endothermic reaction. Furthemore, the entropy was reduced representative a decrease in randomness, and the free energy of the photocatalytic reaction was spontaneous. the reaction rate was diffused about the linearity at temperatures higher than 323 K, hence the solution began to reduce the dye adsorption on the active sites of the surface of ZnO. Conversely, the oxygen solubility in water is less with increased temperature of the solution of dye, which depresses the number of hydroxyl radicals produced, regarded as a power of the photoreaction [23,24].
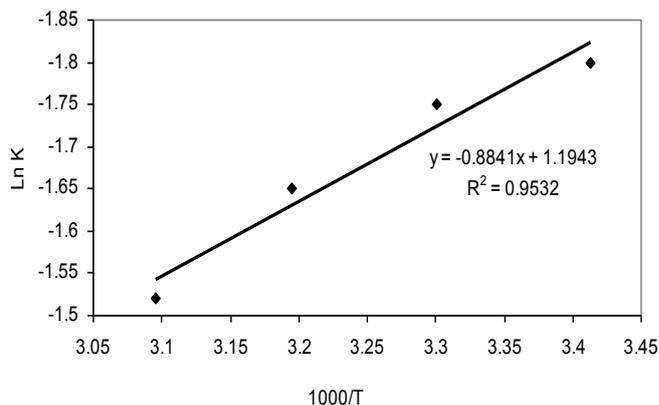
Figure   10. Pseudo-first-order   rate constant at varying temperature under optimized conditions
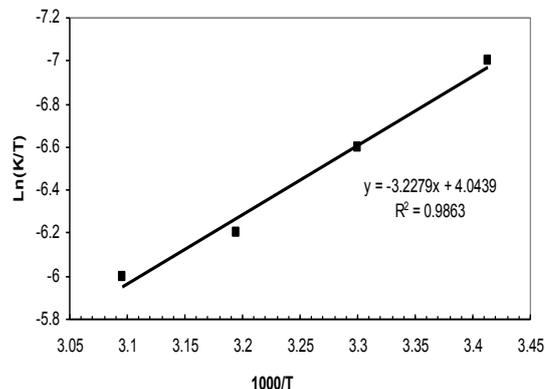
Figure 11. Eyring plot of (ln(K/T) vs.1/T at varying temperature under optimized conditions

4. Conclusions

The effected conditions such as pH, nano ZnO concentration, dye initial concentration, temperature, addition of H_2O_2 and light intensity onto photocatalytic decolorization of of RG-19 were studied.

800 mg/L dosage of nanosized ZnO was found to be the optimum value due to the ZnO surface have propionate active sites to this reaction. The rate of decolorization increased as an increasing in pH value and reach an optimum value at pH 8. Beyond the optimum value, the OH$^-$

adsorption on nano ZnO surface frees $^{\bullet}OH$ which is important for the process of photocatalysis. When dyes initial concentration was increased, the decolorization rate decreased. The decolorization rate of photocatalytic increased with an increase in the H_2O_2 concentration reaching an optimum at 40 mg/L. the rate photocatalytic decolorization was decreased as the H_2O_2 increase of above this value.because of the fact that more concentration of H_2O_2 acts as a scavenger for $^{\bullet}OH$. The photocatalytic decolorization of RG-19 dye showed that the reaction follows the pseudo first order. Plotting the Arrhenius equation was used to calculate the apparent activation energy. The value was small suggesting the photocatalytic process is valuable for the dye decolorization from aqueous solution.

Acknowledgment

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