Photo-Decolourization Kinetics of Acid Red 87 Dye in ZnO Suspension Under Different Types of UV-A Light

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Present study confirmed that the essential requirements for photo-decoulorizationof acid red 87 (Eosin yellow) dye solution are dependent on the presence of the UV light and a photocatalyst ZnO. A kinetics and thermodynamics studies of decolourization phenomenon involved in the photocatalytic decolorization of acid red 87 dye solutions was performed in suspension solution of the commercial ZnO, under the artificial light (high pressure mercury lamp) types 125 and 250 watt as UV A source.The photoreaction of this dye was obeyed to pseudo-first order kinetics and the calculated activation energies for this dye with using 125 and 250 watt were found to be 26.012 KJ and 29.397 kJ mol^{-1}, respectively, which indicated the fast photo-reaction and decreased energy barrier. On the other hand, the reaction is endothermic and non-spontaneously. The optimum conditions for the photocatalytic decolorization of Acid Red 87 were performed. The best dose of ZnO to remove 50 ppm from this dye is 300 mg/100 mL and maximum value for the initial pH of an aqueous solution of dye is 6.

Keywords: ZnO, Decolorization, Acid red 87 dye, Eosin yellow dye, Photocatalytic.

INTRODUCTION

Acid Red 87 dye also known as Eosin Yellow dye, is one of derivative of the xanthene dyes. Eosin yellow is classified according to application as an acid dye that means the dying process of either wool or nylon is performed in an acidic solution. This dye is freely soluble in water so its poor fastness on the textile, but slightly soluble in ethanol and described as anionic dye. Further, this dye is widely employed for dying of paper, drug, used as insecticides, silk, plastic, food colouring, cosmetics, ink, leather, *etc*. [1-6]. In most of the cases, xanthene dyes having special photophysics properties which caused the vast of applications in chemistry, biology and physics [7,8].

On the other hand, these dye employed in many different scientific and technological applications acted as an electron donor acted in photoelectron-chemical cell with present a surfactant solution [9]. It also employed as photosensitizer in biomimetic models (SDS, CTAB and Pluronic P-123 micelles) and studied the effects on their photophysical characteristics [10], using xanthene dyes with *Artemia salina* and LED irradiation to find a suitable quantitative for photodynamic

therapy (PDT) drug evaluation by photokilling of *Artemia salina* [11]. It also used as sensitizers for zinc oxide solar cells and the eosin yellow given a better results compared with the other used xanthene dyes [12]. The target of this study is to provide a compre-hensive analysis on the optimum conditions for photocatalytic decolourization process of acid red 87 under two different artificial light as UV-A source type (high pressure mercury lamp) in presence a commercial ZnO as catalysis.

EXPERIMENTAL

In all photocatalytic experiments, the chemicals used were employed without further purification. The physico-chemical properties of Acid red 87 dye (procured from CDH, India) are listed in Table-1, while 99.5 % purity of commercial zinc oxide was supplied by Fluka.

Photo-reactor and procedure: To perform all the experiments, different amount of ZnO were mixed with 100 mL of desired concentration of acid red 87 dye solutions (natural pH of this dye solution was found to be 8.65) by employing a Labtech magnetic stirrer to get a homogeneous suspension solution.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS
OF THE ACID RED 87 DYE

Parameters	Values
m.w. (g/mol)	691.86
m.f.	$C_{20}H_6Br_4Na_2O_5$
Synonym	Eosin yellow (eosin Y)
IUPAC name	2-(2,4,5,7-Tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate
λ_{max} (nm)	515-518

The mixture was adsorbed for 30 min (dark reaction) to make it ready to photocatalytic step. During each experiment, 3 mL of reaction mixture was pulled at regular time intervals; from the suspension solution using a plastic syringe and transfer to plastic test tube, then centrifuged at 4000 rpm for 10 min. The filtered solution was carefully removed by a new plastic syringe and centrifuged again at 4000 rpm for 5 min, to remove all the fine residue particles of ZnO [13]. Analyses were performed with UV-visible spectrophotometer (Labomad, USA) to measure the residual concentration of dye after adsorption or irradiation experiments that produced colourless solution at end of photoreaction and produced pH equal to 7. The residual concentration of dye analyzed was provided by the calibration curve of dye at 516 nm.

Moreover, the chemical actinometric solution [14] was used to calculate the light intensities that found to be 1.480×10^{-7} and 2.995×10^{-7} Ens. s^{-1} for the artificial UV-A radiation types Philips125 W and 250 W (high pressure mercury lamp-Germany), respectively.The inside whole reactor body must covered with polished aluminum thin layer as reflector to increase the efficiency of irradiation during all the experiments. On the other side, in order to prevent the escape of harmful radiation, the whole photocatalytic reactor must maintain to isolate by black wooden box.

RESULTS AND DISCUSSION

The results shown in Fig. 1 clearly explain the dark reaction (*i.e.*, reaction was preformed without light) under O_2 of atmosphere air was never happened becuse no electron-hole pairs generated. The reaction was very slow in absence the catalyst (photolysis process) to slow break of dye bond. while, the photocatalytic reaction by finding a dye, ZnO, O_2 of atmosphere air and light was clearly happend because all the top parametrs are regarded an essential parameters for the photooxidation process, that enhanced the generated electron-hole pairs that play an important role for formed hydroxyl
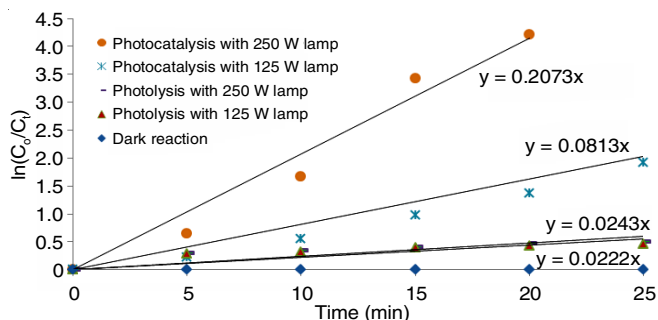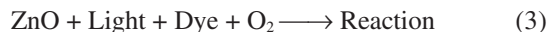

Fig. 1. Explained the preliminary experiment

radical that regarded as a power for pushing the reaction [15]. The summary of all this process will expained by the following suggested eqns. 1-3:

$$ZnO + Dye + O_2 \longrightarrow \text{No reaction} \tag{1}$$

$$\text{Light} + Dye + O_2 \longrightarrow \text{Slight reaction} \tag{2}$$

$$ZnO + \text{Light} + Dye + O_2 \longrightarrow \text{Reaction} \tag{3}$$

The efficiency for using high intensity lamp (250 W) is more than that using low intensity lamp (125 W), that interpenetration as increasing the number of photons that reached to solution and leads to generate electron-hole pairs [16].

Effect of irradiation time: The decolourization process for the any dissolved dyes in wastewater is regarded as a complex process that have many difficult reactions, thereby, the kinetic study for removal of colour for any dye solution can be assumed. Many researchers in photochemistry field [15,17-20] have reported that the kinetics of decolourization process depended upon the Langmuir-Hinshelwood (L-H) model. Based on the Langmuir-Hinshelwood kinetics model, there are four possible processes, according to the following equations [21-23]:

$$^\bullet OH_{ads.} + Dye_{ads.} \rightarrow \text{Decolourization or degradation} \tag{4}$$

$$^\bullet OH_{sol.} + Dye_{ads.} \rightarrow \text{Decolourization or degradation} \tag{5}$$

$$^\bullet OH_{ads.} + Dye_{sol.} \rightarrow \text{Decolourization or degradation} \tag{6}$$

$$^\bullet OH_{aqu.} + Dye_{sol.} \rightarrow \text{Decolourization or degradation} \tag{7}$$

In all cases, the reaction rate equation is similar. By assuming the initial dye concentration is low, hence, the rate of reaction follows pseudo first-order kinetics, therefore, the apparent rate constant (k_{app}) expression was calculated by the following equations [19,27]:

$$C_t = C_o \exp^{(-k_{app} \cdot t)} \tag{8}$$

whereas: C_o is an initial concentration of acid red 87 dye at time of irradiation equal to 0 min. C_t is a concentration of the same dye at time t of irradiation.

The eqn. 8 must be modified to give an apparent first order equation [20]:

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app} \cdot t \tag{9}$$

The % efficiency of dye decolourization was calculated from eqn. 10 [25]:

$$\text{Efficiency (\%)} = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \tag{10}$$

where: C_o is the concentration of acid red 87 dye at irradiation time equal to 0 min and C_t is the concentration of the same dye after time 't' min.

Effect of commercial ZnO dose: In order to study the effect of the non-needful excess of catalyst and to ensure a wholly absorption of light without any loss, hence, the dose of catalyst must be determined.

The effect of ZnO dosage under different light intensities (125 watt - Hg lamp and 250 watt - Hg lamp) is depicted in Figs. 2 and 3.

The results indicate that the apparent rate constant of this photo reaction were increased with increased the catalyst dosage
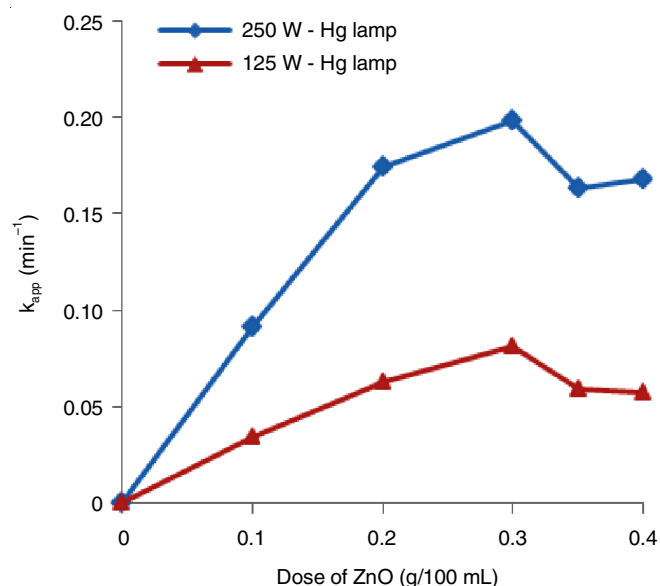
Fig. 2. Effect of catalyst dose on the apparent rate constant of reaction. At conditions: cat. dose = 100-400 mg/100 mL, acid red 87dye conc. = 50 ppm, initial pH of solution = 8.65 and T = 311.15 K
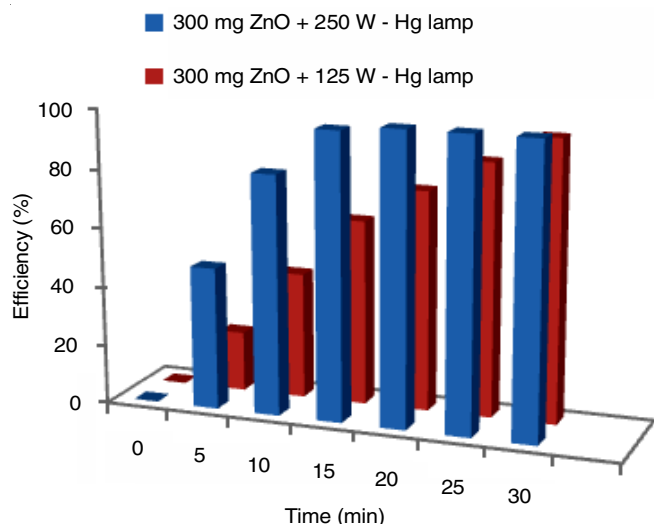

Fig. 3. % Efficiency of decolourization of dye by using different intensities light (125 watt - Hg lamp and 250 watt - Hg lamp) at best cat. dose = 300 mg/100 mL. At conditions: acid red 87 dye conc. = 50 ppm, initial pH of solution = 8.65 and T = 311.15 K

from 100 to 300 mg/100 mL, this behaviour reflects the increment in accessibility of the active sites of catalyst surface, which in turn increases the rate of radical formation [26,27]. The maximum decolourization rate levels are noted with 300 mg/100 mL. While, at high amount of catalyst (above the limiting value), the rate of reaction depresses the penetration of light with increase of the turbidity for a solution due to screening effect [28-30]. In Fig. 3, the percentages of efficiency by employing lamps type 250 watt - Hg lamp and 125 watt - Hg lamp were reached to 98.5 % after 20 min and 94.7 % after 30 min, respectively.

In the other word, the rate constant with employed a light source that have a capacity equal to 250 watt- Hg lamp is more active than that use light have a capacity equal to 125 watt - Hg lamp, because a high light intensity will increase the number of photons that reaching to surface of catalyst, thereby, number

of excited catalyst and number of hydroxyl radicals also increase [16].

Effect of initial pH of solution: The study of the initial pH of the aqueous solution is one of the important parameters that vital effects on the efficiency and the mechanism for the decolourization of dye, that interpenetration as affecting the surface charge of catalyst and the dye characteristics, hence that leads to alter the efficiency for adsorption of pollutants on the surface of any photocatalysts and then the ability for generation of hydroxyl radicals will change, so, the enhancements the photo decolourization of the dye or any pollutants decrease [26].

Fig. 4 demonstrated that the maximum bleaching of acid red 87 dye were obtained at initial pH equal 6 with 50 ppm. While, the minimum value of rate constant was recorded at initial acidic medium pH 3 and 5 and at initial basic medium from pH 8 to 12, which depended on two causes [31]:
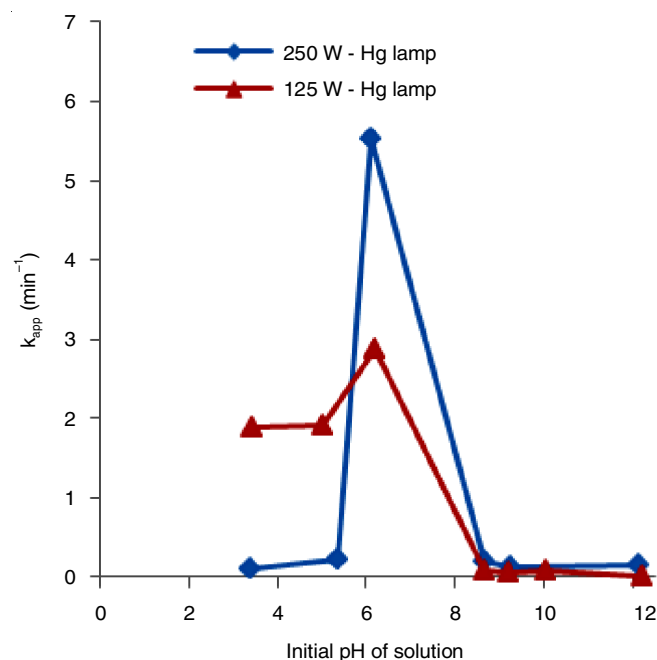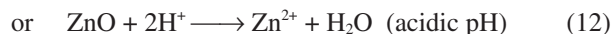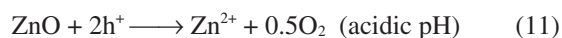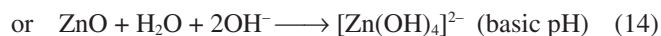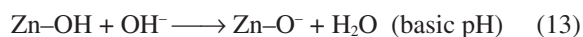

Fig. 4. Effect of initial pH of solution on the apparent rate constant of reaction. At conditions: cat. dose = 300 mg/100 mL, acid red 87 dye conc. = 50 ppm, initial pH of solution = (3-12) and T = 311.15 K

Surface state of catalyst, this cause can be related in acidic and basic medium, so, at acidic pH, ZnO undergoes photocorrosion through self-oxidation [25,27]:

$$ZnO + 2h^+ \longrightarrow Zn^{2+} + 0.5O_2 \text{ (acidic pH)} \quad (11)$$

$$\text{or} \quad ZnO + 2H^+ \longrightarrow Zn^{2+} + H_2O \text{ (acidic pH)} \quad (12)$$

While, at basic pH, the ZnO can undergo dissolution, hence, the photocatalytic activity of ZnO declines [27].

$$Zn–OH + OH^- \longrightarrow Zn–O^- + H_2O \text{ (basic pH)} \quad (13)$$

$$\text{or} \quad ZnO + H_2O + 2OH^- \longrightarrow [Zn(OH)_4]^{2-} \text{ (basic pH)} \quad (14)$$

Ionization state of ionizable organic molecules [31].

Fig. 5 explain that the percentages of efficiency with using lamps type 250 watt - Hg lamp is more than the efficiency with using lamps type and 125 watt - Hg lamp and reached to 99.2 % after 20 min and 97.7 % after 30 min, respectively.
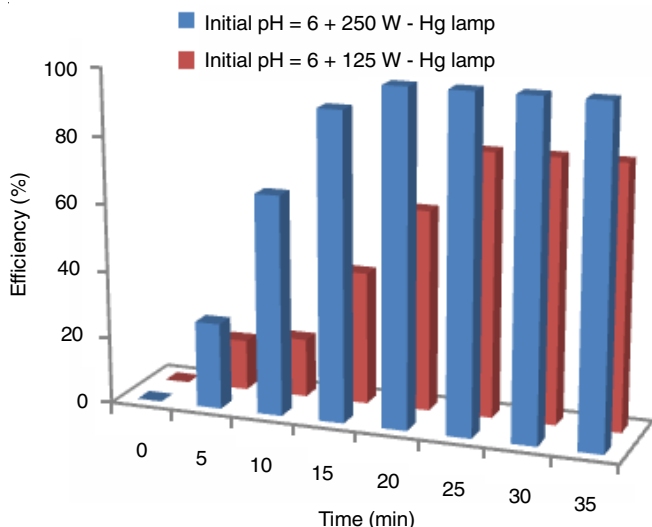
Fig. 5. % Efficiency of decolourization of dye by using different intensities light (125 watt - Hg lamp and 250 watt - Hg lamp) at best initial pH of solution = (6). At conditions: cat. dose = 300 mg/100 mL, acid red 87 dye conc. = 50 ppm and T = 311.15 K

Effect of temperature: This effect was monitored at various temperatures in the range (288.15-311.15) K. The results in Figs. 6 and 7 demonstrated that the decolourization process for acid red 87 dye is raised with increased the temperature this behaviour could be attributed by the thermodynamic parameters expression and enhancement of the photoreaction. On this basis, a linear relationship is produced. This relation is fitting with the graph of the Arrhenius equation (eqn. 15) and of Eyring-Polanyi equation (eqn. 16). Arrhenius equation was employed to calculate the apparent activation energy for photo-reaction [26,32,33].

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \qquad (15)$$

whereas: k_{app} is apparent rate constant (1st order min^{-1}), E_a is apparent activation energy, R is gas constant, T is temperature of reaction and A is a frequency constant.

Based on the Eyring-Polanyi equation (eqn. 16), $\Delta H^{\#}$ and $\Delta S^{\#}$ were calculated [18,33].
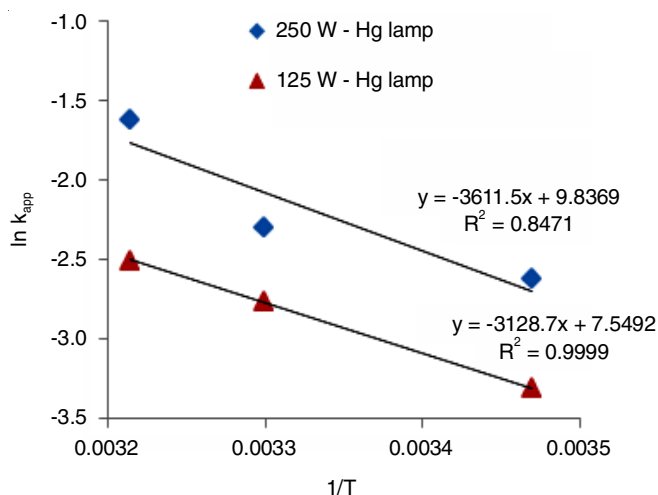

Fig. 6. Arrhenius equation plotted at varying temperature at (288.15-311.15) K. At conductions: dye conc. 50 ppm, semiconductor dosage 300 mg/100 mL and normal pH = 8.65
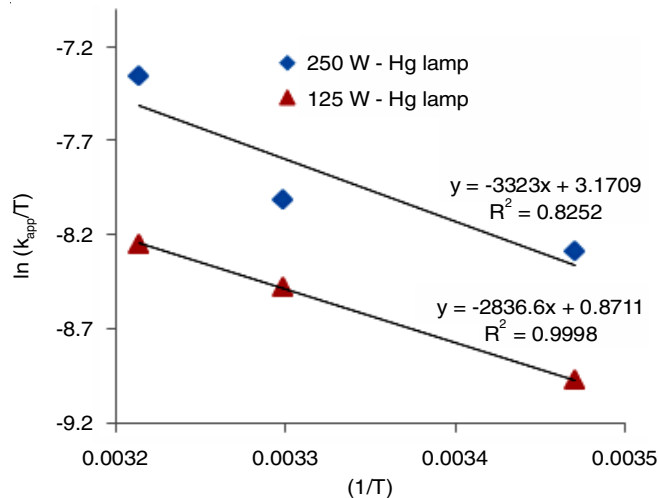

Fig. 7. Eyring plot of (ln (K_{app}/T)) vs. 1/T. At conductions: dye conc. 50 ppm, semiconductor dosage 300 mg/100 mL and normal pH = 8.65

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\#}}{R}\right) \qquad (16)$$

whereas: k_B is a Boltzmann's constant, h is a Plank's constant, R is a gas constant and T is the temperature of reaction.

Eqn. 17 (Gibbs equation) used to calculate $\Delta G^{\#}$ of photo-reaction [18,33].

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (17)$$

The fitted results of the thermodynamics functions and the apparent activation energy are listed in Table-2.

TABLE-2
ACTIVATION KINETIC AND THERMODYNAMIC PARAMETERS OF THE DECOLOURIZATION OF ACID RED 87 DYE UNDER LIGHT TYPE 125 watt AND 250 watt-Hg LAMP

Type of lamp (UV-A)	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1} K^{-1})	$\Delta G^{\#}_{311.15}$ (kJ mol^{-1})
At used 125 Watt	26.012	23.583	-0.190	82.735
At used 250 Watt	29.397	27.623	-0.171	80.804

Table-2 suggested that the calculated apparent activation energies are small and approximate values that due to the decolourization of this dye are happened in fast speed [32,34] and temperature independent (usually not very temperature sensitive) [34-36]. Based on the plot of Eyring-Polanyi equation in Fig. 6, the thermodynamic parameters were investigated. The positive $\Delta H^{\#}$ and positive $\Delta G^{\#}_{311.15}$ for decolourization of this dye indicate to the reaction is endothermic and non-spontaneous respectively. This was demonstrated that the transition state between the dye molecules and intermediates (hydroxyl radicals) is a well solvated structure. Moreover, those also supported the small negative values of $\Delta S^{\#}$ and indicate that the complex formed is less random than reactants. These results are similar behaviour with other photo reactions that observed by reorted studies [26,35,37].

Effect of solar light on decolourization efficiency: This study confirmed the opportunity of removing this dye was related to the intensity of used light. Hence, in order to investigate the comparative the % efficiency for decolourization of
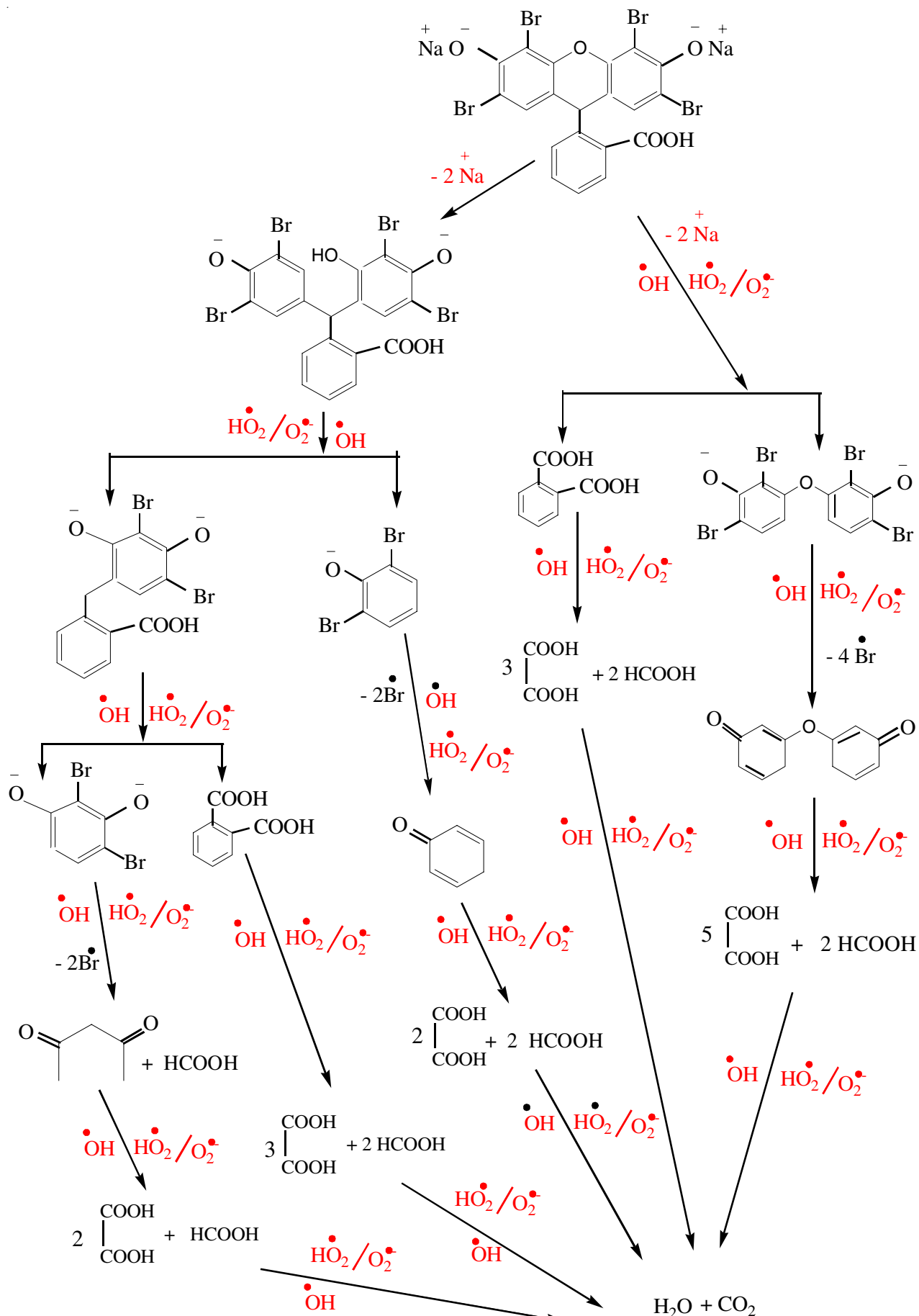
Scheme-I: Most probable degradation mechanism of acid red 87 dye in the presence of UV/ZnO

studied dye under different ranges of light. The sun light is an important source of illumination, hence, the influence of solar light on the decolourization of this dye was assessment at different intervals time and compared values with using artificial 125 watt-Hg lamp and 250 watt- Hg lamp as shown in Fig. 8.
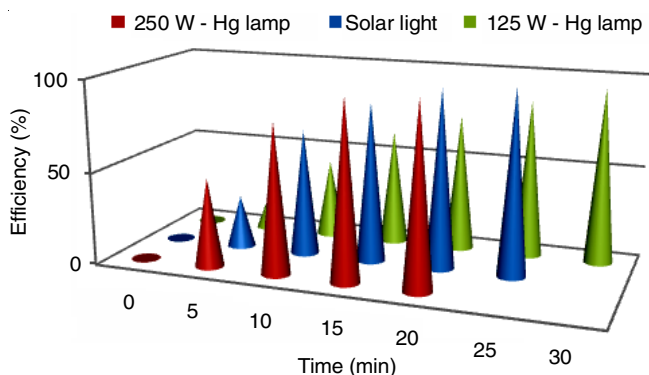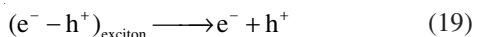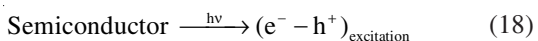

Fig. 8. % Efficiency of decolourization of dye by using different intensities light (Solar light, 125 watt - Hg lamp and 250 watt - Hg lamp) at standard initial pH of solution= (8.6). At conditions: cat. dose = 300 mg/100 mL and acid red 87 dye conc. = 50 ppm

The results explain that the maximum % efficiency value was found attributed to the sequence 250 watt - Hg lamp < Solar light < 125 watt - Hg lamp and reached to 98.5 %, 96.4 % and 74.4 % after 20 min, respectively. Inspirit on the solar light has a high light intensity and equal to 5.4×10^{-5} Ens s^{-1}, but, the % efficiency is less than that % efficiency under used 250 watt-Hg lamp, that can be ascribed to occur the thermal reaction further to the photoreaction under used solar light, because of solar light contains ultra-violate, visible and infrared part light, hence, that will lead to heat and increases the recombination process. This reason is in agreement with the results by Mills and Hunte [38]. They denoted the increased of temperature leads to enhance e^-/h^+ recombination.

Possible photocatalytic mechanism: On the basis of the above findings following proposed mechanism for the photocatalytic degradation of acid red 87 dye in ZnO suspension has been suggested. In outset, under UV irradiation, different mechanism involving band gap excitation of ZnO leaded to generate electron-hole pair. Electron-hole pair is inputted in series steps and produced radical intermediates such as: superoxide ion $O_2^{\bullet-}$, hydrogen peroxide radical $HO_2^\bullet$ then leads hydroxyl radical $HO^\bullet$ as powers force for starting a photo reaction as in equations from 18-25 [39-41].
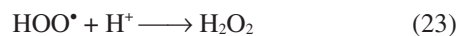
Photoexcitation:

$$\text{Semiconductor} \xrightarrow{h\nu} (e^- - h^+)_{excitation} \qquad (18)$$

$$(e^- - h^+)_{exciton} \longrightarrow e^- + h^+ \qquad (19)$$

Ionization of water:

$$H_2O \longrightarrow H^+ + HO^- \qquad (20)$$

Charge carrier trapping:

$$O_2 + e^- \longrightarrow O_2^{\bullet-} \qquad (21)$$

Protonation of superoxides:

$$O_2^{\bullet-} + H^+ \longrightarrow HOO^\bullet \qquad (22)$$

Protonation of hydrogen peroxide radical:

$$HOO^\bullet + H^+ \longrightarrow H_2O_2 \qquad (23)$$

Photodegradation of hydrogen peroxide:

$$H_2O_2 + h\nu \longrightarrow 2HO^\bullet \qquad (24)$$

Charge carrier trapping:

$$HO^- + h^+ \longrightarrow HO^\bullet \qquad (25)$$

Based on the formation of the radical intermediates, the mechanism of photocatalytic degradation of acid red 87 dye was deduced from other researches that studied the xanthene derivatives dyes [42,43]. The modified mechanism of degradation of acid red 87 dye is outlined in **Scheme-I**.

Conclusion

In the present work, the main conclusions are summarized as follows:

• The photo-decolourization of acid red 87 dye was kinetically studied and proved that the photoreaction obey the pseudo first order, beside, the UV-A light and a photo-catalyst (ZnO) were found to be an essential factors in the photodecoulorization ability of this dye.

• It's found that the method of decolourization by using two different light intensity high pressure mercury lamps (125 watt and 250 watt) is dependent on parameters such as dye concentration, catalyst dosages, initial pH of solution and temperature. The optimum concentration of dye was 50 ppm and the best dosage of ZnO found at 3.0 g/L, the maximum value of initial pH of dye solution was reached to 6.

• The rise of temperature was enhanced the rate of reaction. The activation energies for decolourization of this dye with employing high pressure mercury lamp (125 watt and 250 watt) were calculated and equal to 26.012 kJ mol^{-1} and 29.397 kJ mol^{-1}, respectively. The minimum values of activation energies for this dye onto ZnO, which indicated to lesser energy barrier.

• From the results, the thermodynamics functions were calculated by depending on Eyring equation. The photoreaction process was observed to be endothermic reaction, non- spontaneous and less randomness.

• The using of high capacity of Hg lamp, increased the rate of reaction, so, that depended on increase the number of photons that reaching to catalyst surface and ensure the generated a more number of photoelectron-photoholepairs, then increment the number of hydroxyl radicals.

• The maximum % efficiency value was found attributed to the sequence 250 watt - Hg lamp < Solar light < 125 watt - Hg lamp and reached to 98.5 %, 96.4 % and 74.4 %, respectively after 20 min. The use of solar light increases the speed and the collisions of species in solution and perhaps, leads to increase the heat and recombination process and then decline the efficiency.

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