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PHOTOCATALYTIC DECOLOURIZATION OF DIRECT ORANGE DYE BY ZINC OXIDE UNDER UV IRRADIATION

SHAYMAA I. S. ZUAFUANI and LUMA M. AHMED*

Chemistry Department, College of Science, Kerbala University, KERBALA 5001 (IRAQ)

ABSTRACT

In this paper, photocatalytic decolourization of direct orange dye solution was made in the presence of commercial ZnO as catalyst under the artificial light (high pressure mercury lamp) as UV A source. Moreover the light intensity was measured. The decolourization of direct orange dye process was obeyed to pseudo-first order kinetics. Activation energies for dye was found to be 8.964 KJ mol^{-1} and the reaction is very fast, endothermic and spontaneously. The best conditions of decolourization for this dye was such as: initial dye concentration is 40 mg/L, best dose of ZnO is 350 mg/100 mL and the initial pH of an aqueous solution of dye is 9 were studied.

Key words: Direct orange dye, Photocatalytic, Decolourization, Zinc oxide, Apparent activation energy.

INTRODUCTION

Azo dyes are recognized as a common classification of dyes, that involves an approximately 60-70% of the available dyes. The most common colours of azo dye are reds, oranges, and yellows that caused of the colours is the azo bonds (–N=N–) in the molecule of dye to produce the monoazo, diazo, triazo, etc. The azo dye can be classified according to the structure and the method of applications to direct, disperse, developed, acidic, azoic[1].

Direct dye is one of the most popular dyes in the textile industry. It is water- soluble, contained one or more anionic sulphonic group, have linear structure, adhere with the hydroxyl group spacing in cellulose fibers without help from other chemicals by Van der Waals, hydrogen bond, dipolar force and non-specific hydrophobic interaction that depending on the polarity of dye and the chemical structure. This dye has advantages such as low cost, wide colour range, short dyeing time and using in dying of the animals or vegetables fibers, paper, leather, etc. But it's bleed thereby it's poor wash fastness that

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*Author for correspondence; E-mail: lumamajeed2013@gmail.com, luma.ahmed@uokerbala.edu.iq, alzafaaranysh@gmail.com

beyond to have a hydrophilic sulphonic group in molecule structure. In order to improve the fastness, there are some treatment like addition of cationic compounds, metallic salts, etc.[2-5]

The textile dyes can be produced an industrial effluents as a wastewater that caused polluting of the environment. So that must be treated of the wastewater by different researches. Mohan and coworkers[6] reported that the direct red dye was removed using *Aspergillus niger* and *Aspergillus flavus* under static and shaking conditions. This study referred to the most removal ability for this dye performed by *Aspergillus niger,* the adsorption isotherm for decolourization of direct red dye was followed by Freundlich model. In the other study, Tomczak and Tosik[7] found that the sorption capacity for direct orange 26 onto a cheap plant sorbent was more than its for reactive blue 81.

Many of researchers degraded some type of direct dyes by ozonation from the aqueous solution of them. These studies found that the results fitted well to pseudo first order kinetic[8,9]. Sudha and coworkers[10] found that the microbes could be used for decolourization of direct blue 15 with another type of dyes by both aerobic and anaerobic metabolism with different physicochemical parameters and application for treatment the wastewaters. Paniwnyk and coworker[11] employed the ultrasound to treatment the wastewater from dyes like direct orange 31, direct red 81 and the another type of textile dyes. This experimental work was performed by varies frequencies of ultrasound and found the active frequency as 850 KHz.

The aim of this work was to study the relationships between the rate of constant for decolourization of the direct orange dye and the different parameters like concentrations of dye, the dose of ZnO, initial pH of the solution and the temperatures. In order to find the optimum conditions for the photo-decolourization of dye.

EXPERIMENTAL

Direct orange dye is commonly employed in textile industries and it was supplied by the Hilla textile factory. Zinc oxide with 99.5% purity was supplied by Fluka and used as supplied. All the chemicals employed in photocatalytic experiment were of the highest purity available and of analytical grade. All photocatalytic experiments were performed by employing suitable amount of ZnO that mixed with 100 mL of direct orange dye employing a Labtech magnetic stirrer to produce a suspension solution. At a regular intervals; 2.5 mL of reaction mixture was withdraw from the suspension solution by a syringe to a plastic test tube, then centrifuged at (4,000 rpm, 10 minutes) in a Hettich centrifuge. The filtrated solution was carefully removed by a syringe to new plastic test tube and centrifuged again at the same top conditions, to remove the fine particles of ZnO. The concentration of residual direct orange dye was determined spectrophotometry at 416 nm, using UV-visible spectrophotometer type Labomad, USA.

The light intensity for Philips 250 W (high pressure mercury lamp-Germany) as a source for UV-A radiation was determined by employing the chemical actinometric solution[12-14] and found to be 2.995 x 10^{-8} Ens. s^{-1}. The whole photocatalytic reactor was isolated inside a wooden box to prevent the escape of harmful radiation.

RESULTS AND DISCUSSION

Effect of irradiation time

The decolourization experiments of direct orange dye by UV irradiation found that the aqueous solutions of this dye with presence of commercial ZnO obeys pseudo first order kinetics according to the Langmuir-Hinshelwood (L-H) model, thereby at the chemical concentration C_o is a small, hence the equation can be simplified to calculate the apparent rate constant (k_{app}) by the following equations[15,16]:

$$C_t = C_o \exp(-k_{app}.t) \qquad \ldots(1)$$

where: C_o is an initial concentration of dye at time of irradiation = 0 min (dark reaction). C_t is a concentration of dye at time t of irradiation.

$$\frac{C_t}{C_o} = \exp(k_{app}.t) \qquad \ldots(2)$$

$$\ln\frac{C_t}{C_o} = -k_{app}.t \text{ or } \ln\frac{C_o}{C_t} = k_{app}.t \qquad \ldots(3)$$

Effect of dye concentration

The effect of initial direct orange dye concentration in the range of 30-100 ppm is depicted in Fig. 1. The initial concentration of direct orange has a fundamental effect of the apparent rate constant for decolourization in the presence of the ZnO suspension solution. According to Fig. 1, the apparent rate constants were directly proportional with increasing the initial dye concentrations at ranged (25-50) ppm, that beyond to increase the quantity of intermediates that increased the photoreaction well. After 50 ppm of dye, the values of rate constant for decolourization of this dye decline. This behavior is due to the optical density of light that reached in the solution was depressed[17].

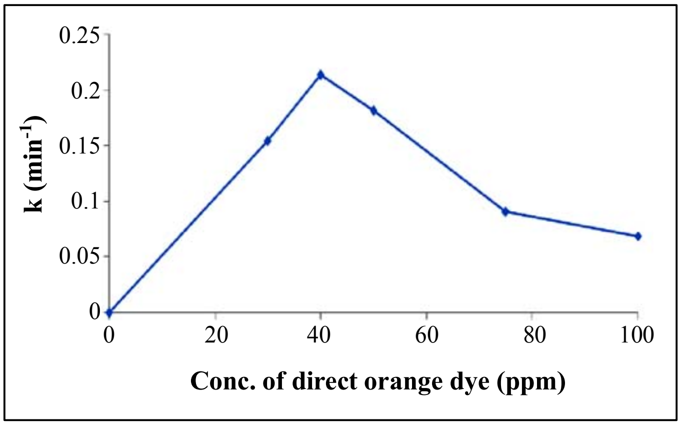


Fig. 1: Pseudo-first order rate constant at varying dye concentration. Conductions: semiconductor dosage = 350 mg/100 mL, pH = 6.68, temperature = 278.15 K, UV light intensity = 2.995 x 10^{-8} ensien.s^{-1}

Effect of ZnO dose

Fig. 2 shows the effect of ZnO dose on the photorcatalytic for decolourization of direct orange dye solution, The rates of reaction were found to be directly proportional to the catalyst dosage from 100 to 350 mg/100 mL that beyond to increase of active sites on the ZnO surface[18]. The decolourization rate levels reach maximum at 350 mg/100 mL as optimum catalyst ZnO dosage. While with increases of ZnO dosage more than 350 mg/100 mL the rate of decolourization is decreased with increased the turbidity of solution this called screening effect[19].

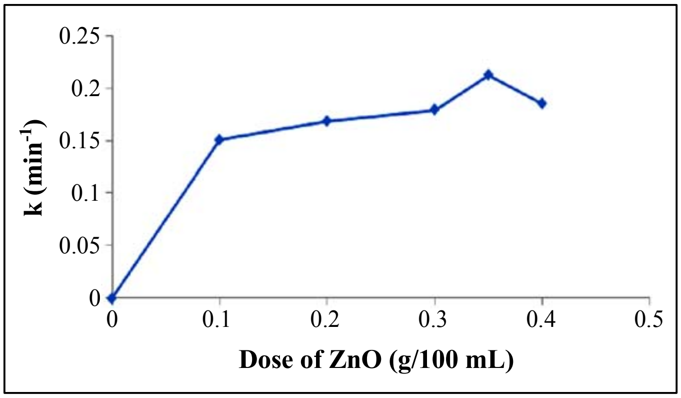


Fig. 2: Pseudo-first order rate constant at varying semiconductor dosages. Conductions: dye conc. = 40 ppm, pH = 6.68, temperature = 278.15 K, UV light intensity = 2.995 x 10^{-8} ensien.s^{-1}

Effect of initial pH

The most important parameter that influences the photocatalytic decolourization of dye is the initial pH of solution, so, it plays an important role in the characteristics of textile dye, the surface properties of catalyst and generation of hydroxyl radicals. Hence, this effect depends on three possible reaction mechanisms can decolorize of the dye with hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band [20]. In order to study the effect of pH on the decolourization of direct orange dye, experiments were carried out at different initial pH levels ranging from 4 to 11. The relationship between the rate constant and pH is shown in Fig. 3.

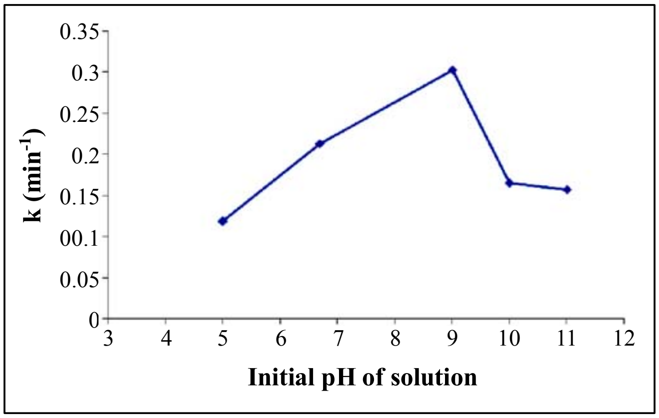


Fig. 3: Pseudo-first order rate constant at varying initial pH. Conductions: dye conc. = 40 ppm, semiconductor dosage = 350 mg/100 mL, temperature = 278.15 K, UV light intensity = 2.995 x 10^{-8} ensien.s^{-1}

It is clearly seen that the rate constant increases with increasing of the pH in the range 4-9. The interpretation of this behavior is due to the increasing of adsorption of dye and hydroxyl radicals on the ZnO surface. The maximum value of the rate of decolourization was found at pH 9. This is a zero point charge of ZnO surface, at this pH the net of charge on ZnO surface is equal zero[18]. However, at pH more than 9, the efficiency of decolourization of direct orange was depressed, that beyond to increase the amount of OH^- that will have a high ability to adsorb on the active sites of ZnO then react with him. According to equations 4 and 5, the ZnO can undergo dissolution, so the photocatalytic activity of ZnO reduce[18,20].

$$Zn-OH + OH^- \longrightarrow Zn-O^- + H_2O \quad \text{(Basic pH)} \qquad ...(4)$$

$$\text{or } ZnO + H_2O + 2\,OH^- \longrightarrow [Zn(OH)_4]^{2-} \quad \text{(Basic pH)} \qquad ...(5)$$

On the other hand, at pH less than pH of ZPC, the efficiency of decolourization for direct orange dye was low, that attitude to form a positive charged on ZnO surface and decrease the produced hydroxyl radical. Hence, ZnO undergoes photocorrosion through self-oxidation according to the following equations[18,21]:

$$\mathrm{Zn-OH} + 2\,\mathrm{H}^{+} \longrightarrow \mathrm{Zn}^{2+} + \frac{1}{2}\mathrm{O}_2 \quad \text{(Acidic pH)} \qquad ...(6)$$

$$\text{or } \mathrm{ZnO} + 2\,\mathrm{H}^{+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{H_2O} \quad \text{(Acidic pH)} \qquad ...(7)$$

Effect of temperature

The reaction was followed at different temperatures in the range 293.15-308.15 K. The results in Fig. 4 indicate that the decolourization efficiency of direct orange dye is having a linear relationship fitting the graph of the Arrhenius equation (Eq. 8)[22].

$$\ln k = \frac{-E_a}{RT} + \ln A \qquad \ldots(8)$$

Photocatalytic decolourization of direct orange dye was increased with increasing temperature. The calculated value of apparent activation energy on ZnO surface was found equal to 8.964 KJ mol^{-1}, hence the photocatalytic reaction is ended in 15 min.

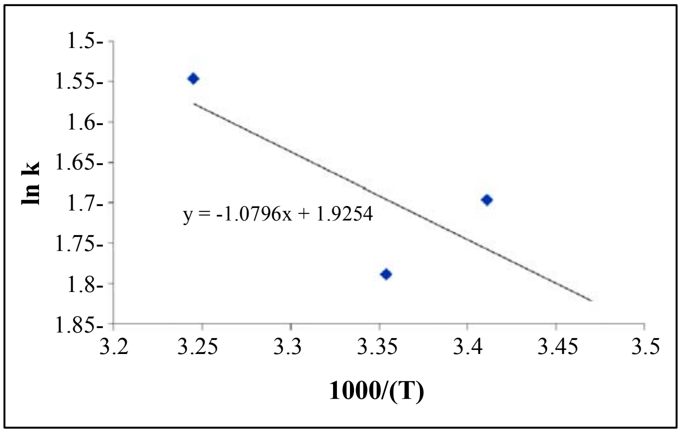


Fig. 4: Pseudo-first order rate constant at varying temperature. Conductions: dye conc. = 40 ppm, semiconductor dosage = 350 mg/100 mL, pH = 6.68, temperature = 293.15-208.15 K, UV light intensity = 2.295 x 10^{-8} ensien.s^{-1}

The $\Delta H^{\#}$ and $\Delta S^{\#}$ values can be determined from the plot of the Eyring Equation[22]:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\#}}{RT} + \left(\ln \frac{k_B}{h} + \frac{\Delta S^{\#}}{R} \right) \quad \ldots(9)$$

where: 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. The free energy $\Delta G^{\#}$ is calculated from equation (10):

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad \ldots(10)$$

The fitted results of the activation energy and the thermodynamics functions are shown in Table 1.

Table 1: The activation kinetic and thermodynamics parameters of the decolourization of direct orange dye

E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1} K^{-1})	$\Delta G^{\#}_{288.15}$ (kJ mol^{-1})
8.964	6.941	0.234	-61.890

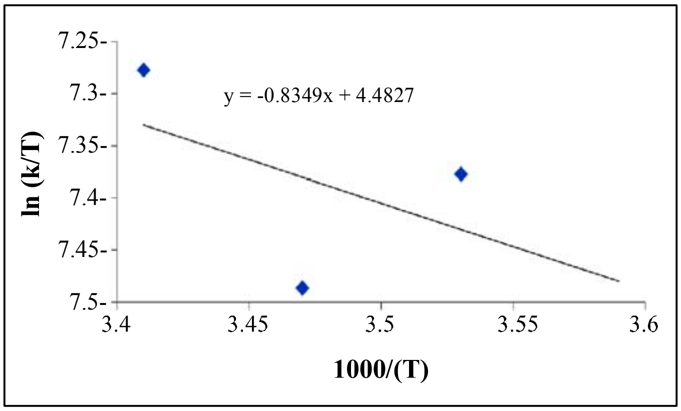
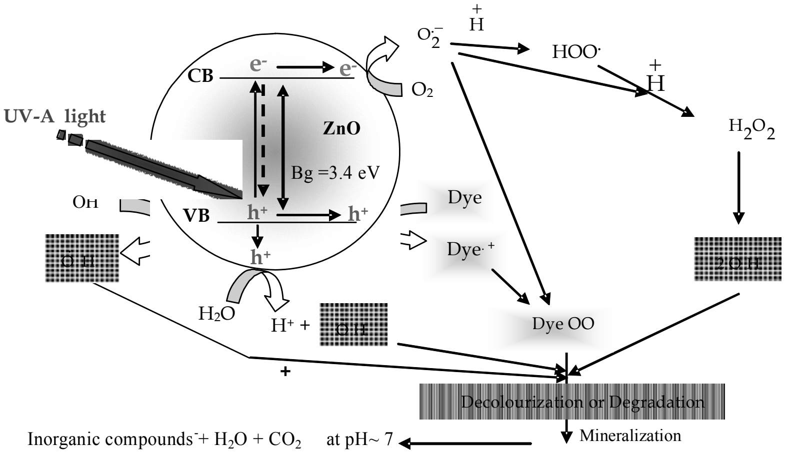


Fig. 5: Eyring plot of ($\ln(K_{app}/T)$) vs.1/T. Conductions: dye conc. = 40 ppm, semiconductor dosage = 350 mg/100 mL, pH = 6.68, temperature = 293.15-208.15 K, UV light intensity = 2.295×10^{-8} ensien.s^{-1}

From the calculated results in Table 1 and Figures (4,5) obtained shows that the rise in the temperature from 293.15 to 208.15 K was increases the rate of reaction, therefore the decolourization process of direct orange dye was endothermic reaction. In addition, the entropy was fewer that indicated to decrease in randomness, and the free energy of photocatalytic reaction was spontaneous. At temperature more than 298.15 K, the rate of reaction was diffused about the linearity, hence the solution was started to decrease the adsorption of the dye on the active sites of ZnO surface. On the other hand, the solubility of oxygen in water was less with increased the temperature of dye solution, that will depress the number of producing hydroxyl radical that regarded as a power of the photoreaction[23,24].

Suggested mechanism

When the UV-A light photon focuses on the colloid solution of direct orange dye with ZnO, that will produce a series of chain oxidative-reductive reactions. Hence, the photoelectrons and photoholes $(e^- -h^+)_{exciton}$ were created. Both will input in series of reactions as shown in **Scheme 1**.



Scheme 1: Schematic diagram for more accepted mechanism (Dye/semiconductor/UV light system) (modified from reference[25])

CONCLUSION

The essentially of photocatalytic experiments indicated that the presence of UV light, oxygen and zinc oxide were regarded the fundamental for the effective destruction of direct orange dye. The photocatalytic decolourization of direct orange dye employed a zinc oxide as a photocatalyst was proved that the photoreaction obeys the pseudo first order. The optimum conditions such as the dosage of catalyst, concentration of dye, initial pH, and temperature of solution were investigated.

The superior dosage of ZnO was obtained at 3.5 g/L, and the optimum concentration of dye was 40 ppm. The decolourization rate increases with increasing the initial pH of the dye solution, and the paramount value was reached to pH equal 9. Beyond that the increased the adsorbed ability for the hydroxyl group on the ZnO surface to generate a hydroxyl radical that regarded as a power for starting and continuously the photoreaction. The apparent activation energy is calculated by plotting Arrhenius equation. The value is small that prove the photocatalytic is useful to decolourization of direct orange dye from aqueous solution. The thermodynamics functions are also calculated, and indicated to that the decolourization of this dye is very fast, endothermic and spontaneously.

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