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ZINC OXIDE ASSISTED PHOTOCATALYTIC DECOLORIZATION OF REACTIVE RED 2 DYE

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ABSTRACT

The photocatalytic decolorizations of aqueous solutions of Reactive Red 2 dye in the presence of ZnO suspension has been investigated with the use of artificial UV-A light sources. The effects of various parameters, such as time of irradiation, photocatalyst amount, pH, addition of H_2O_2 and temperature on photocatalytic degradation were investigated.

The rate of decolorization was found to increase significantly with time of irradiation. Under optimal conditions, the extent of decolorization was 100% after 30 minutes of irradiation. Optimum catalyst concentration $[\text{Catalyst}]_{\text{Opt}}$ was measured and found equal to 2.5 g L^{-1}. The oxidizing agents such as oxygen and hydrogen peroxide enhance the decolorization rate. However the addition of more amount of hydrogen peroxide decreases the rate of decolorization. The optimum pH for the photocatalytic decolorization of Reactive Red 2 dye in the presence of ZnO suspension is pH 10.0. Photocatalytic decolorization was found to increase with increasing temperature. Arrhenius plot shows that the activation energy is equal to 10.130 ± 1 kJ mol^{-1}.

The decolorization is not feasible in the absence of catalyst, oxygen and/or irradiation. The decolorization process of the dye follows pseudo-first order kinetics

Key words: Zinc oxide, Photocatalytic decolorization, Reactive red 2 dye, Activation energy.

INTRODUCTION

Azo dyes are regarded as the largest class of synthetic dyes and approximately 50-70% of the available dyes for commercial applications are azo dyes followed by the

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anthraquinone group[1]. Azo dyes are classified according to the present of azo bonds (–N=N–) in the molecule i.e., monoazo, diazo, triazo etc. and also sub-classified according to structure and method of applications such as acid, basic, direct, disperse, azoic and pigments[2].

Some azo dyes and their dye precursors are well-known class of dyes of high toxicity and suspected to be human carcinogens as they form toxic aromatic amines[3-5].

Decolorization of wastewaters is regarded more important process than the removal of other organic colorless chemicals[6].

Zhao and Zhang[7] reported that zinc oxide is an excellent photocatalytic oxidant for different types of pollutants in wastewater such as pharmacy wastewater, printing and dyeing wastes and papermaking wastewater. Kavitha and Palanisamy[8] found that ZnO is more efficient than TiO_2- P25 and TiO_2-UV-100 in photocatalytic degradation of Reactive Red 120; however, ZnO has the disadvantage of undergoing photocorrosion under illumination in acidic conditions. Photocorrosion of ZnO can take place as in the following equations[9]:

$$\mathrm{ZnO} \xrightarrow{h\upsilon} e^-_{CB} + h^+_{VB} \qquad \ldots(1)$$

$$\mathrm{ZnO} + 2\,h^+_{VB} \longrightarrow \mathrm{ZnO}^{2+} + \tfrac{1}{2}\,O_2 \qquad \ldots(2)$$

Hussein and co-workers[10-14] reported that titanium dioxide and zinc oxide have good photocatalytic properties and both catalysts are nominated to be promising substrates for photodegradation of different organic pollutants under artificial and solar irradiation.

Reactive azo dyes are not degradable aerobically[15,16], however recent study indicated that *Aspergillus parasiticus* fungal biosorbent is an effective candidate for textile dye Reactive Red 198 removals from aqueous solutions[17]. It was confirmed that Reactive Red 2 can be completely biodegraded in a two stage anaerobic - aerobic reactor and the reactor is also capable of achieving complete nitrification[18].

Photocatalytic decolorization of selected triazine and vinylsulfone type of reactive dyes clearly demonstrated the capability of visible light-TiO_2 photocatalytic system to remove the aesthetic appearance to a large extent either separately or in mixture [18]. Photocatalytic decolorization efficiency was found depends on the susceptibility and the intermediates formed[19].

The target of present work is to investigate the photocatalytic decolorization of Reactive Red 2 dye in ZnO suspension solution by light source type UV-A at different conditions.

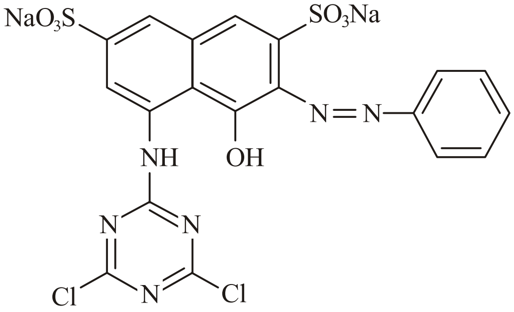


Fig. 1: The structure formula of Reactive Red 2 dye

EXPERIMENTAL

Zinc oxide with 99.5% purity was supplied by Carlo ERBA and used as supplied. In all experiments, the required amount of ZnO was suspended in 100 cm^3 of Reactive Red 2 dye using a magnetic stirrer. At predetermined times; 1.5 cm^3 of reaction mixture was collected and centrifuged (4,000 rpm, 15 minutes) in an 800B centrifuge. The supernatant was carefully removed by a syringe with a long pliable needle and centrifuged again at same speed and for the same period of time. This second centrifugation was found very important to remove fine particles of ZnO. The absorbance at 541 nm wavelengths of the supernatants was determined using ultraviolet-visible spectrophotometer (Apel-303 England). Photocatalytic reaction was carried out in a homemade photoreactor equipped with a Philips 125 W/542, high pressure mercury lamp (Holland) as a source for near-UV radiation. The reactor was consisted of graduated 400 cm^3 Pyrex glass beaker and a magnetic stirring setup. The lamp was positioned perpendicularly above the beaker. The distance between the lamp and the graduated Pyrex glass was 12 cm. The whole photocatalytic reactor was insulated in a wooden box to prevent the escape of harmful radiation and minimized temperature fluctuations caused by draughts.

RESULTS AND DISCUSSION

UV-Visible spectra of dye

Fig. 2 shows a time dependent UV-Visible absorption spectra of 50 ppm of aqueous solution of Reactive Red 2 dye during irradiation by UV-A light in the presence of ZnO. The complete disappearance of the band at 541 nm indicates the complete destruction of chromophore group. No additional bands were detected in the analyzed wavelength range after 30 minutes of irradiation.

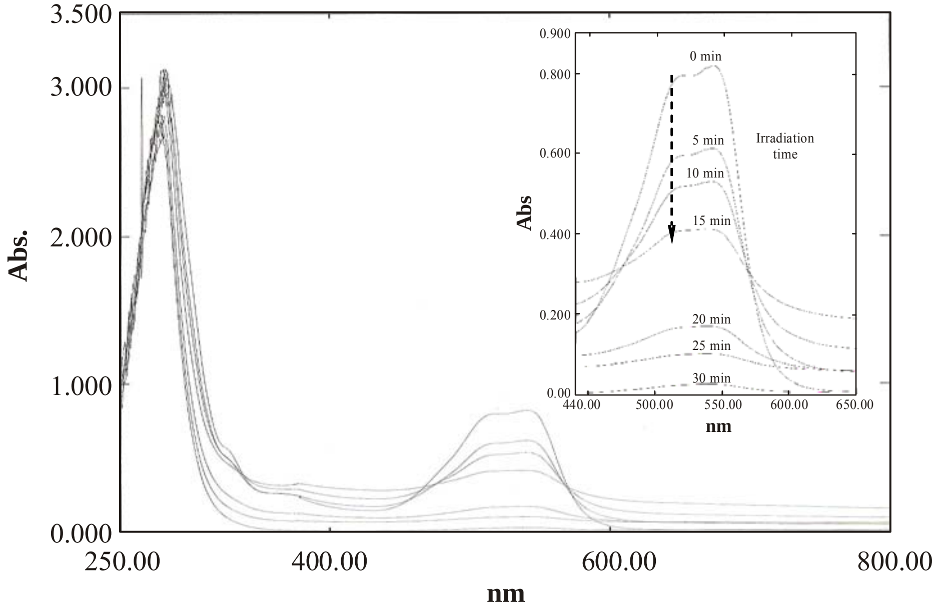


Fig. 2: UV-Visible absorption spectra change at different time intervals

Effect of irradiation time

The decolorization of Reactive Red 2 dye obeys pseudo first order kinetics according to the Langmuir-Hinshelwood (L-H) model[20-23], thereby the apparent rate constant (k_{app}) was calculated by the following equations:

$$C_t = C_o \exp(-k_{app}.t) \qquad \ldots(3)$$

where: C_o is an initial concentration of dye at time of irradiation = 0

C_t is a concentration of dye at time t of irradiation

$$\frac{C_t}{C_o} = \exp(-k_{app}.t) \qquad \ldots(4)$$

$$\ln \frac{C_t}{C_o} = -k_{app}.t \qquad \ldots(5)$$

or $$\ln \frac{C_o}{C_t} = k_{app}.t \qquad \ldots(6)$$

Effect of ZnO concentration

The initial reaction rates were found to be directly proportional to catalyst concentration. Above 2.25 g L^{-1}, the reaction rate level reaches maximum value and becomes independent of catalyst concentration and the curve takes a plateau form. The reaction rate levels reach maximum at 2.50 g L^{-1} of optimum catalyst concentration $[\text{Catalyst}]_{\text{Opt}}$. At higher catalyst concentrations the plateau region ends and reaction rate decreases, where screening effect is produced when the catalyst concentration is very high. Zhao and Zhang[7] found that the rate of degradation on ZnO increased with increasing of ZnO dosage and explained the reaching to maximum dosage was related to the entirely absorption of incident photons and the maximum dosage was changing with the changing of light intensity.

Effect of pH

The relationship between the apparent rate constant and pH is shown in Fig. 3. It is clearly seen that the apparent rate constant increases with increasing of pH in the range 6-10.

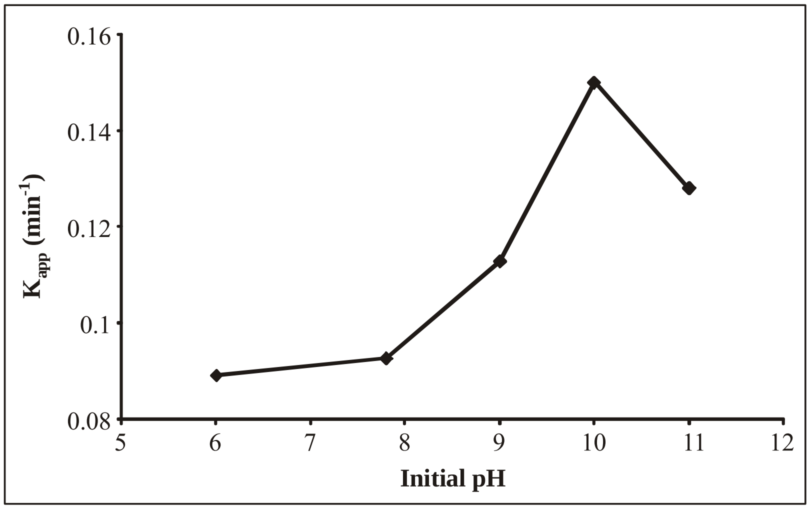


Fig. 3: Relation between k_{app} and initial pH of dye at different pH (5-11) and 50 mg/L of dye

This behavior is due to the increasing of surface dye concentration and hydroxyl radicals. Whereas the inhibitory effect seems to be started in the more alkaline range (pH > 10). Davis and Huang[24] explained the reduction of photoreaction rate with increasing pH due to the rapidly scavenging of hydroxyl radicals. At high pH, it may be also due to change in the behavior of dye molecule and also the surface of ZnO powder and as a result, the photocatalytic degradation of dye reduced[25].

Equations 7-10 indicate that at low pH, ZnO is dissolved in solution and at high pH ZnO is deprotonated or dissolute[23,26-29].

$Zn - OH + H^+ \longrightarrow Zn - OH_2^+$ (Acidic pH) …(7)

or $ZnO + 2\,H^+ \longrightarrow Zn^{2+} + H_2O$ (Acidic pH) …(8)

$Zn - OH + OH^- \longrightarrow Zn - O^- + H_2O$ (Basic pH) …(9)

or $ZnO + H_2O + 2\,OH^- \longrightarrow [Zn\,(OH)_4]^{2-}$ (Basic pH) …(10)

Effect of temperature

The results in Fig. 4 show the photocatalytic decolorization of Reactive Red 2 dye on ZnO with different temperature was represented a pseudo first order, and the apparent activation energy was calculated by Arrhenius plot.

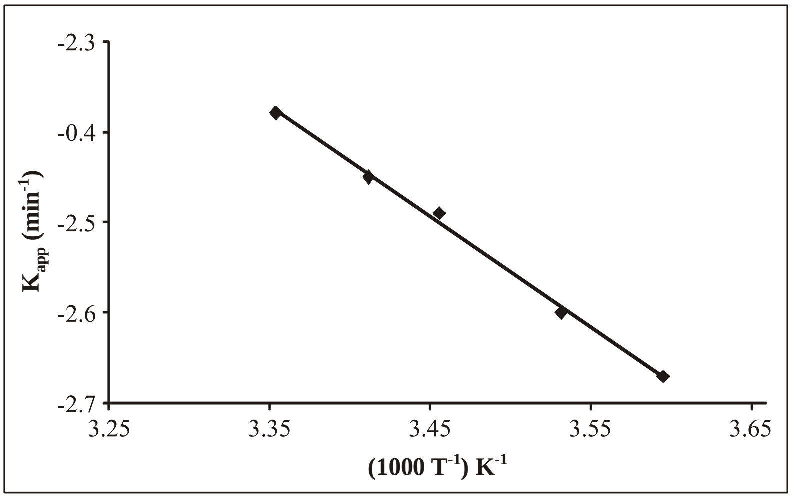


Fig. 4: Arrhenius plot for photocatalytic decolorization of Reactive Red 2 dye on ZnO at (278.15-298.15) K.

In photocatalytic reaction, the apparent activation energy deals with the elevation the photoelectrons from trapping centers to the conductive band of catalyst[20,30,31]. The value of apparent activation energy is very low (10.130 kJ.mol^{-1}) thereby the photocatalytic reaction is ending at 30 min.

Effect of addition of H_2O_2

From Fig. 5, the results show the apparent rate constant increased with increasing the concentration of H_2O_2 from 1.5 to 4.5 mmol/L, then $^{\bullet}OH$ decreased from 4.5 to 7.5 mmol/L, that refer to increase in the formation of $^{\bullet}OH$ radicals and besides inhibiting the recombination of hole-electron by following equations[29,32]:

$$H_2O_2 + e^-_{CB} \longrightarrow {}^{\bullet}OH + OH \quad \ldots(11)$$

$$H_2O_2 + {}^{\bullet}O_2 \longrightarrow {}^{\bullet}OH + OH + O_2 \quad \ldots(12)$$

While, at high concentration of H_2O_2, the photocatalytic processes decrease because H_2O_2 is a scavenger for $^{\bullet}OH$ radical, according to the following equations –

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO^{\bullet}_2 \quad \ldots(13)$$

$$HO^{\bullet}_2 + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad \ldots(14)$$

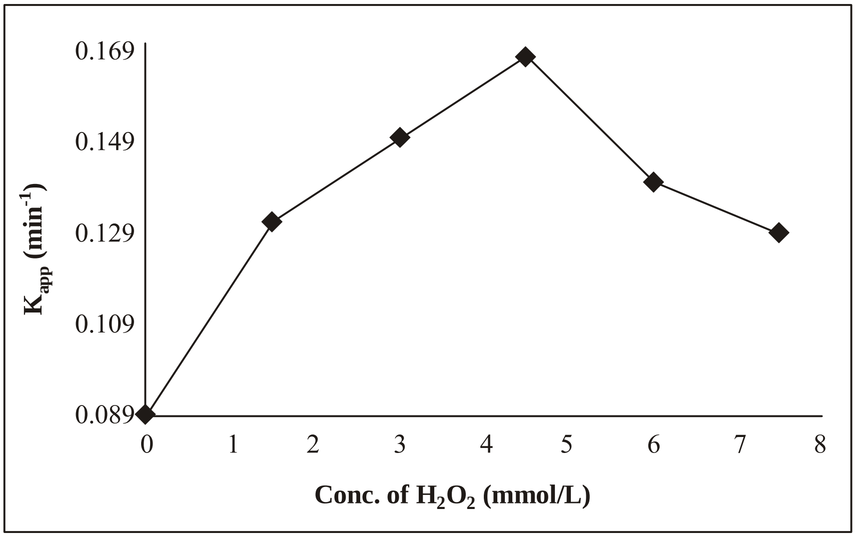
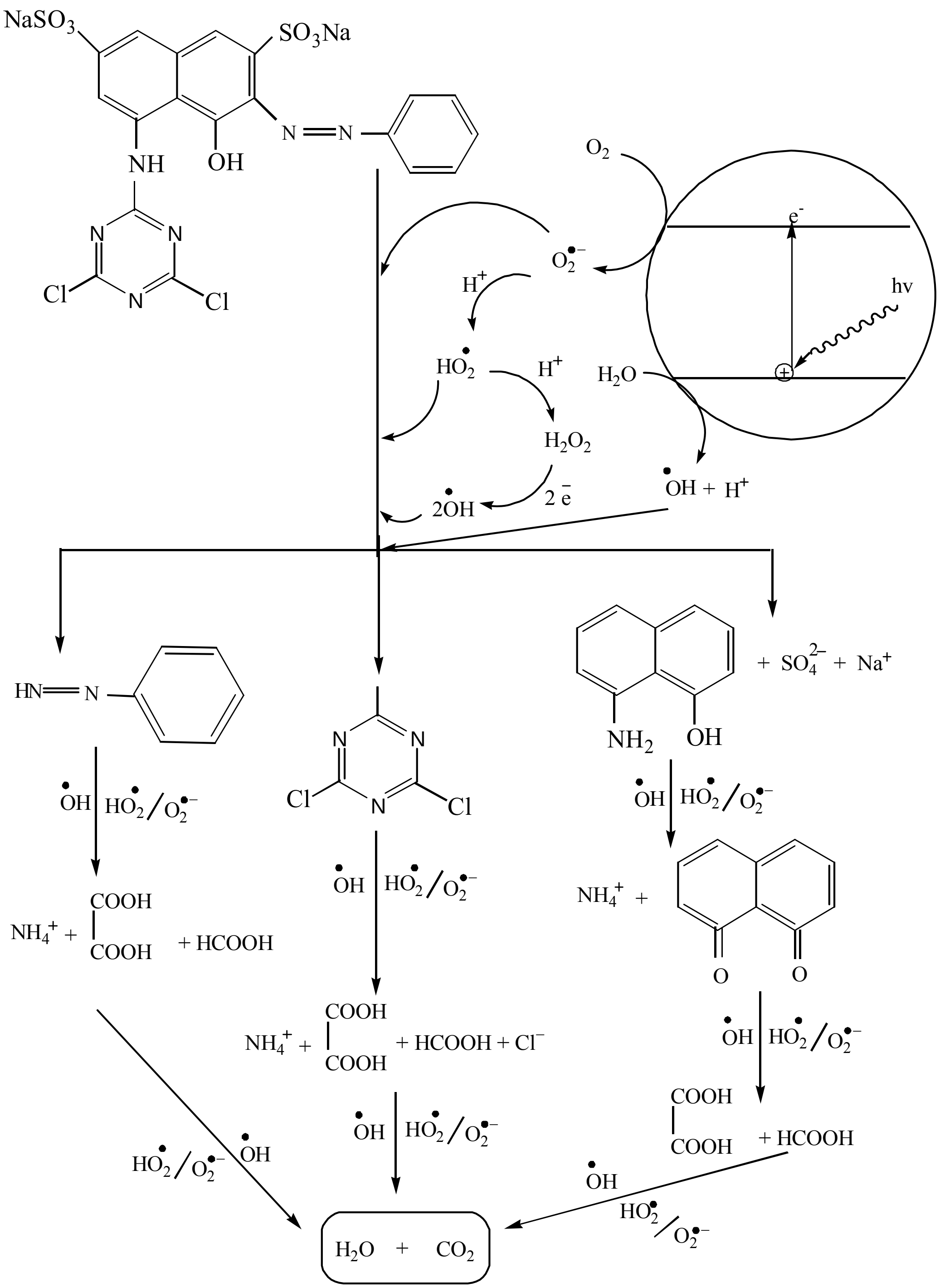


Fig. 5: Effect of addition of H_2O_2 on the apparent rate constant of photodecolorization of Reactive Red 2 dye



Scheme 1: Suggested mechanism

7-Suggested mechanism

Hydroxyl radicals photodegrades aqueous organic pollutants in the existence of semiconductor through one or more than one of the following mechanisms[33]:

1. Reaction of adsorbed $^{\bullet}OH$ with the adsorbed organic molecule.
2. Reaction of adsorbed $^{\bullet}OH$ with the free organic molecule in solution hitting the semiconductor surface,
3. Reaction between adsorbed organic molecule and free $^{\bullet}OH$ in solution.
4. Reaction between free organic molecules and free $^{\bullet}OH$ in solution.

Moreover, the organic pollutants can also degrade by another two mechanisms. These are direct oxidation by the positive hole in the valance band and direct reduction by the electron in the conducting band[34]. The suggested mechanism as shown in **Scheme 1** takes the rule of $^{\bullet}OH$ in consideration as well as the formation of $CaCO_3$ precipitate when $Ca(OH)_2$ was put in the exits of produce gases and the mechanism suggested before[19].

CONCLUSION

The photocatalytic decolorization of Reactive Red 2 dye proved that the reaction obeys the pseudo first order, and the optimum conditions such as ZnO concentration, pH, temperature and addition of H_2O_2 of photocatalytic decolorization of this dye were investigated.

The best dosage of ZnO found at 2.5 g/L, because the active sites of ZnO surface is propionate to this reaction.

The decolorization rate increases with increase in pH, and the maximum value at pH equal 10.0. Beyond this, an adsorption OH on ZnO surface liberate $^{\bullet}OH$, which is essential for photocatalysis process.

The apparent activation energy is calculated by plotting Arrhenius equation, the value is small that prove the photocatalytic is useful for decolorization of dye from aqueous solution.

The photocatalytic decolorization rate increases with increase in the concentration of added H_2O_2 and reached maximum when it reached 4.5 mmol/L. The increase in of H_2O_2

above this level led to decrease photocatalytic decolorization rate. This behavior may be due to that additional concentration of H_2O_2, which acts as a scavenger for $^{\bullet}$OH.

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