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PHOTOCATALYTIC MINERALIZATION OF ORANGE II DYE UTILIZING ZnO IN PRESENCE OF VISIBLE LIGHT

PRAKASH MORE, DAVID SWAMI, HEMANT PANDEY[a] and BRIJESH PARE[*]

Laboratory of Photocatalysis, Govt. Madhav Science Post Graduate College, Vikram University,
UJJAIN – 456010 (M.P.) INDIA
[a]Department of Chemistry, Hilslop College, NAGPUR (M.S.) INDIA

ABSTRACT

Advanced oxidation processes (AOPs) have been found to be very effective in treatment of wastewater containing the various hazardous organic pollutants. Photocatalytic degradation of orange II dye in the presence of an aqueous heterogeneous suspension of ZnO irradiated with visible light has been investigated. The degradation of the dyes under investigation depends on various parameters such as catalyst amount, dye concentration, pH, addition of hydrogen peroxide, Na_2CO_3, NaCl and effect of light intensity. The complete degradation of dye was tested using the chemical oxygen demand (COD) method and UV spectrophotometer.

Key words: Orange II, Photocatalysis, Zinc oxide, Orange II, Wastewater treatment, Visible light, Mineralization.

INTRODUCTION

Dyes are organic compounds, which are an increasing threat to the environment due to its use in manufacturing and textile manufacturing processes. After utilization these dyes are introduced in large quantities into water systems and cause serious ecological and environmental problems[1]. More particularly azo dyes are among the most widely used synthetic dyes and usually become major pollutants in textile wastewaters[2]. This is a known class of high toxic dyes that are carcinogenic to humans and animals and does not easily decompose[3]. Various physical, chemical and biological methods such as adsorption, coagulation, chlorination, ozonation, ion exchange and reverse osmosis have been in use to remove the colors have been used efficiently, although they are non-destructive[4]. Therefore, in recent years an alternative to conventional methods advanced oxidation processes (AOPs)

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[*] Author for correspondence; E-mail: brijeshpare2009@hotmail.com, prachem_more@rediffmail.com

based on the generation of very reactive species such as hydroxyl radical, which could oxidize a broad range of organic pollutants quickly and nonselectively have been developed[5,6]. AOP not only destroys the pollutants but also causes their complete mineralization to CO_2, H_2O and mineral acids[7-9]. In the past few years many catalysts like ZnO, TiO_2, WO_3, SnO_2, ZrO_2, CeO_2, CdS and ZnS have been attempted for photocatalytic oxidation of water contaminants[10]. ZnO has attracted considerable attention as a photocatalyst for the degradation of organic pollutants in wastewater because of its advantages as a non toxic nature, low cost, high reactivity and batter efficiency in visible light[11]. ZnO has been reported as more efficient photocatalyst than TiO_2 in visible light[12, 13]. Thus the aim of the present work is to investigate the efficiency of ZnO photocatalyst in removal of orange II dye (Fig. 1) from contaminated water using visible light.

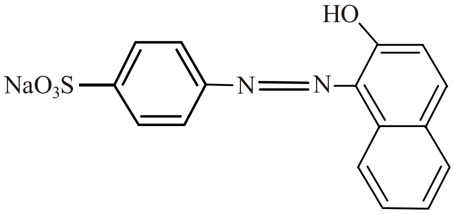


Fig. 1: Structure of orange II dye

EXPERIMENTAL

Reagents

Orange II dye was obtained from CDH chemical company. The photocatalyst ZnO was obtained from Merck Company India. H_2O_2 (30% aqueous), $FeCl_3$, $FeSO_4$, NaCl and Na_2CO_3 were of analytical grade and used without further purification. All the solutions were prepared by dissolving the calculated amounts of appropriate chemicals in doubly distilled water.

Apparatus and Procedure

The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor having pyrex vessel (ht. 7.5 cm x dia. 6 cm). The pyrex vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep temperature in the range of $30 \pm 0.3^{\circ}C$. The irradiation was carried out using 500 W halogen lamp surrounded with aluminium reflectors in order to avoid loss of irradiation. During the photocatalytic experiment, after stirring for ten minutes, the slurry was placed in dark for half an hour in the order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on the surface of photocatalyst. Now slurry containing aqueous dye solution and ZnO particles was stirred magnetically to ensure complete suspension of catalyst particle while exposing to visible light. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 minutes at the rate of 3500 rpm to remove ZnO particles form aliquot to assess the extent of decolorization photometrically. Changes in absorption spectra were recorded at 480 nm on UV-Vis spectrophotometer (Systronic Model No. 106). The intensity of visible radiation was measured by a digital lux-meter (Lutron Lx-101). The pH was constantly monitored using a pH meter. The COD and CO_2 estimation were performed also. The performance efficiency was calculated as:

$$\% \text{ efficiency} = \frac{C_0 - C}{C_0} \text{ x } 100 \quad \ldots(1)$$

Where C and C_0 are initial and final values for dye concentration or COD or CO_2 for reaction time t[14].

RESULTS AND DISCUSSION

Effect of dye concentration

From mechanistic and application point of view, it is essential to study the dependence of the photocatalytic reaction rate on dye concentration[15]. The concentration of dye was varied from 3.0 x 10^{-5} mol dm^{-3} to 9.0 x 10^{-5} mol dm^{-3} (Table 1 and Fig. 2). It has been observed that the rate constant values increased from 3.56 x 10^{-4} s^{-1} to 4.49 x 10^{-4} s^{-1} with the increase in dye concentration from 3.0 x 10^{-5} mol dm^{-3} to 6.0 x 10^{-5} mol dm^{-3}.

Table 1: Effect of dye concentration

ZnO = 200 mg/100 mL, Irradiation intensity = 25 x 10^3 lux, pH = 7

S. No.	Dye Concentration x 10^{-5} mol dm^{-3}	k x 10^{-4} s^{-1}
1	3.0	3.56
2	4.0	3.76
3	5.0	4.10
4	6.0	4.49
5	7.0	4.06
6	8.0	3.80
7	9.0	3.49

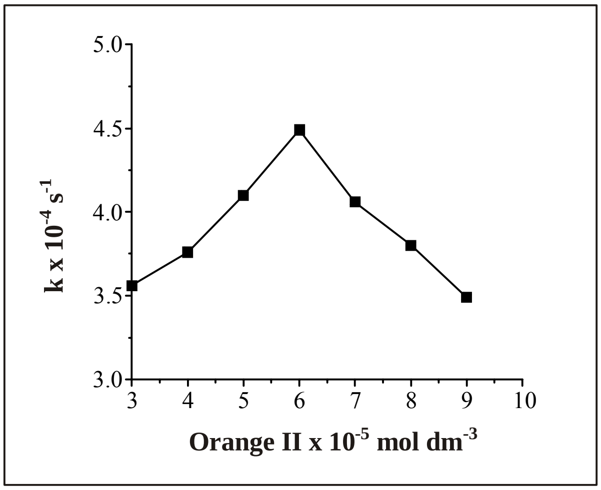


Fig. 2: Effect of dye concentration

Thereafter, on further increase in the dye concentration upto 9.0 x 10^{-5} mol dm^{-3} the rate constant got decreased. The initial increase in photocatalytic degradation rate might be due to the fact that as the concentration of dye was increased, more dye molecules got available for excitation and energy transfer. Consequently, rate constant values got enhanced. Later the rate of photocatalytic degradation was found to be decreased with further increase in the concentration of the dye. This might be attributed to the fact that the dye molecule could have acted as a filter for the incident light and thus hindering the desired intensity to reach the semiconductor particles[16].

Effect of catalyst amount

Table 2: Effect of catalyst amount

Orange II = 6.0 x 10^{-5} mol dm^{-3}, Irradiation intensity = 25 x 10^3 lux, pH = 7

S. No.	Photocatalyst (mg/100 mL)	$k \times 10^{-4}\ s^{-1}$
1	50	2.87
2	100	3.07
3	150	3.83
4	200	4.49
5	250	3.99
6	300	3.14
7	350	2.80

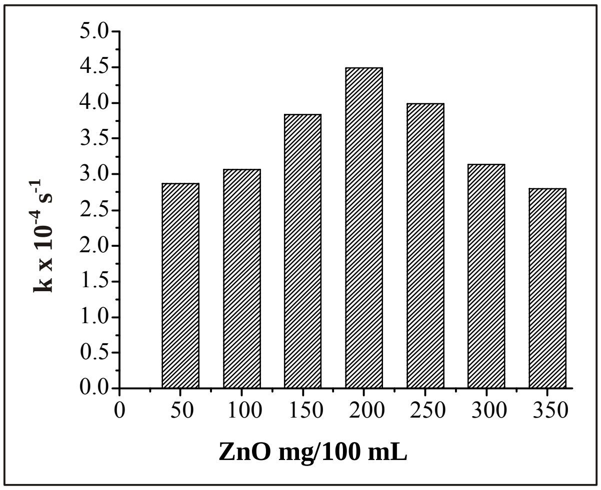


Fig. 3: Effect of catalyst amount

The amount of photocatalyst present in the system affect the rate of photocatalytic degradations therefore, the amount of catalyst has also been varied from 50 mg/100 mL to 350 mg/100 mL keeping all the other factors identical. The observed results are given in Table 2 and Fig. 3. Rate constant values increased from 2.87 x 10^{-4} s^{-1} to 4.49 x 10^{-4} s^{-1} with the increase in photocatalyst loading from 50 mg/100 mL to 200 mg/100 mL. Thereafter, rate constant values decreased to 2.80 x 10^{-4} s^{-1} with further increase in catalyst loading (350 mg/100 mL). The reaction rate was found to be maximal at 200 mg/100 mL of photocatalyst loading. This observation could be explained in terms of availability of active sites on the catalyst surface and the penetration of visible light into the suspension. The total active surface area increased with increasing catalyst dosage[17]. At the same time, due to an increase in the turbidity of the suspension, there was a decrease in visible light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreased. Since the most effective decomposition of orange II was observed with to 200 mg/100 mL of ZnO catalyst, all the other experiments were performed at this concentration of ZnO catalyst[18].

Effect of pH

The efficiency of the photocatalytic processes depends substantially on the pH of the reaction solution[19]. Therefore, the effect of pH on the rate of photocatalytic degradation of dye has been investigated in the pH range of 4.1 to 9.5. The rate constants increased from 3.68 x 10^{-4} s^{-1} to 4.49 x 10^{-4} s^{-1} with the increase in pH 4.1 to 7. Thereafter, rate constant values decreased to 3.72 x 10^{-4} s^{-1} on further increase in pH up to 9.5 (Table 3 and Fig. 4). This observation tend suggest to that the rate of degradation was higher in basic solution than acidic medium. The increase in rate of degradation might be due to more availability of hydroxyl ions in the pH range 7- 8 which will generate more hydroxyl radicals by combining with the holes. At lower pH the rate of degradation decreased due to the competition between hydroxyl groups to attach to the active site of catalyst thus rate of adsorption of hydroxyl group decreased. This resulted into the decrease in the formation of hydroxyl radicals and consequently rate of degradation also decreased[20]. On the other hand, orange II has a sulfuric group in its structure (Fig. 1), which is negatively charged in alkaline conditions; therefore, in the alkaline solution dye may not be adsorbed onto photocatalyst surface effectively[17]. All these factors are responsible for maximum value of photocatalytic degradation of orange II at pH 7.

Table 3: Effect of pH

Orange II = 6.0×10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL,
Irradiation intensity = 25×10^{3} lux

S. No.	pH	k x 10^{-4} s^{-1}
1	4.1	3.68
2	5.0	3.91
3	6.1	4.10
4	7.0	4.49
5	8.2	4.14
6	9.5	3.72

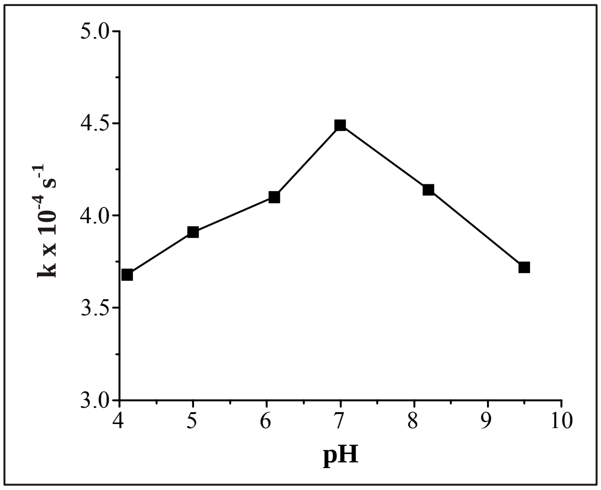


Fig. 4: Effect of pH

Effect of hydrogen peroxide

The study of photocatalytic degradation has been observed that molar concentration of H_2O_2 is an important factor that can significantly affect the degradation of dye[21]. The photocatalytic degradative removal of orange II has been studied at different H_2O_2 concentration. The removal rate of orange II increased with increasing H_2O_2 concentrations up to 8.0 x 10^{-6} mol dm^{-3} but above this concentration, degradation efficiency was found to decreased (Table 4 and Fig. 5).

Table 4: Effect of hydrogen peroxide

Orange II = 6.0 x 10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL,
Irradiation intensity = 25 x 10^3 lux, pH = 7

S. No.	H_2O_2 concentration x 10^{-6} mol dm^{-3}	k x 10^{-4} s^{-1}
1	2.0	4.98
2	4.0	5.29
3	6.0	6.06
4	8.0	7.56
5	10	6.67
6	12	5.75
7	14	5.10

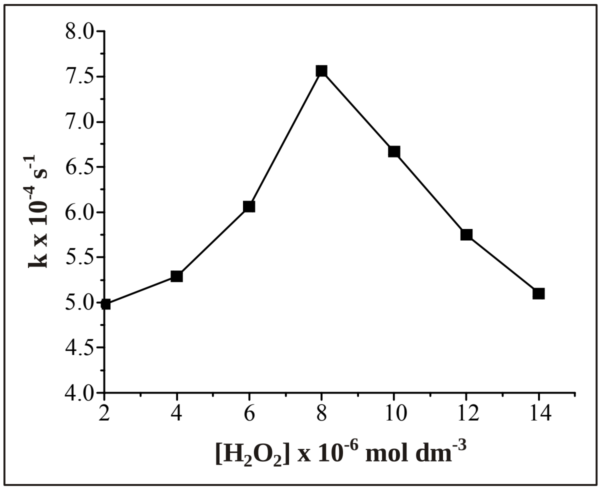


Fig. 5: Effect of H_2O_2

This might be due to the tendency of hydrogen peroxide to inhibit the electron hole recombination by accepting photogenerated electron from the conduction band of semiconductors and promote charge separation and also form $^{\bullet}OH$ radicals (Eq. 1-2). Hydrogen peroxide might also got splitted photocatalytically to produce $^{\bullet}OH$ radical directally (Eq. 3).

$$H_2O_2 + e^-_{CB} \longrightarrow {}^{\bullet}OH + {}^{-}OH \qquad ...(2)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow {}^{\bullet}OH + H^+ + O_2 \qquad ...(3)$$

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\bullet}OH \qquad ...(4)$$

At high concentration, the H_2O_2 adsorbed on the photocatalytic surface could effectively scavenge not only the photocatalytic surface formed $^{\bullet}OH$ radicals but also the photogenerated holes and thus inhibited the major pathway for heterogeneous generation of $^{\bullet}OH$ radicals. This is due to quenching of $^{\bullet}OH$ radical by H_2O_2. Perhydroxide radical has been reported significantly less reactive than OH radical[22-24].

$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2^{\bullet} + H_2O \qquad ...(5)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \qquad ...(6)$$

$$h_{VB}^{+} + H_2O_2 \longrightarrow H^+ + HO_2^{\bullet} \qquad ...(7)$$

Effect of inorganic anions

The waste water from dyeing operations normally contains considerable amount of carbonate and chloride ions. Therefore, it is important to study the influence of these ions on the treatment efficiency[25]. The two possible ways by which inorganic ions influence the photocatalytic reaction are: (1) By changing the ionic strength of reaction medium and (2) By inhibiting catalytic activity of the photocatalyst. The photocatalytic degradation rate constant decreased with the increase in CO_3^{2-} and Cl^- ions concentration from 2.0×10^{-5} mol dm^{-3} to 14×10^{-5} mol dm^{-3} (Table 5 and Fig. 6).

Table 5: Effect of inorganic anions

Orange II = 6.0×10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL,
Irradiation intensity = 25×10^3 lux, pH = 7

S. No.	[Salt] x 10^{-5} mol dm^{-3}	Na_2CO_3	NaCl
		k x 10^{-4} s^{-1}	k x 10^{-4} s^{-1}
1	2.0	3.49	3.60

Cont…

S. No.	**[Salt] x 10^{-5} mol dm^{-3}**	**Na_2CO_3**	**NaCl**
		k x 10^{-4} s^{-1}	**k x 10^{-4} s^{-1}**
2	4.0	3.03	3.18
3	6.0	2.87	2.95
4	8.0	2.41	2.61
5	10	2.14	2.26
6	12	1.80	2.07
7	14	1.68	1.76

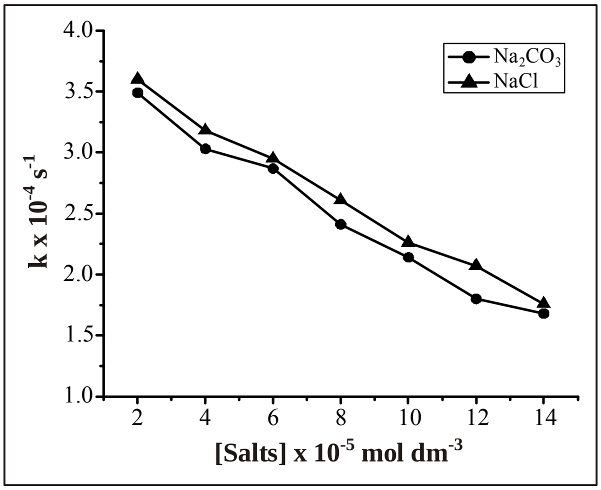


Fig. 6: Effect of inorganic anions

The obtained results clearly depicted that the addition of these inorganic anions resulted into the decrease of photocatalytic reaction rate. This decrease in the rate of degradation might be due to the hydroxyl scavenging property of CO_3^{2-} and Cl^- ions, as evident from the following reaction[26].

$$CO_3^{2-} + {}^{\bullet}OH \longrightarrow {}^{-}OH + CO_3^{\bullet -} \quad ...(8)$$

$$Cl^- + h_{VB}^+ \longrightarrow Cl^{\bullet} \quad ...(9)$$

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{\bullet -} \quad ...(10)$$

$$^{\bullet}OH + Cl^- \longleftrightarrow HOCl^{\bullet -} \quad ...(11)$$

$$HOCl^{\bullet -} + H^+ \longrightarrow Cl^{\bullet} + H_2O \quad ...(12)$$

Effect of light intensity

The effect of the variation of the light intensity on the rate has also been investigated and the observations are represented in Table 6 and Fig. 7. As the intensity of light was increased, more photons would be available for excitation at the semiconductor surface and in turn more electron hole pairs would be generated. This resulted into enhanced rate of photocatalytic degradation. In the degradation of orange II, the value of rate constant was found to be increased with the increase in light intensity, a typical characteristic of a photocatalytic reaction. However, higher intensities were avoided due to thermal effects[27].

Table 6: Effect of light intensity

Orange II = 6.0 x 10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL, pH = 7

S. No.	Light Intensity x 10^3 lux	k x 10^{-4} s^{-1}
1	10	1.94
2	15	2.72
3	20	3.83
4	25	4.49
5	30	6.71

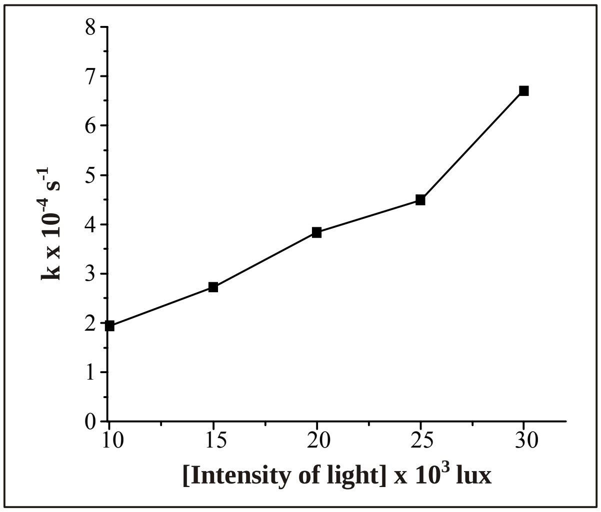


Fig. 7: Effect of light intensity

Effect of band gap of semiconductor

The excited photocatalytst has separated hole and electron pairs that induce the photocatalytic reactions, thus the band gap energy has vital role to play. Therefore, effect of band gap on the photocatalytic degradation has also been studied in the presence of different semiconductors having different band gap values. It was observed that the value of the rate constant of photocatalytic degradation increased as the band gap increased up to band gap of ZnO (3.2 eV), but after the band gap of 3.4 eV (BiOCl) the value of the rate constant of photocatalytic degradation decreased[28]. Results are given in Table 7.

Table 7: Effect of band gap of semiconductor

Orange II = 6.0×10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL,
Irradiation intensity = 25×10^{3} lux, pH = 7

S. No.	Photocatalyst 200 mg/100 mL	Bandgap (eV)	k x 10^{-4} s^{-1}
1	CdS	2.3	1.61
2	$BaCrO_4$	2.6	2.03
3	TiO_2	3.1	2.53
4	ZnO	3.2	4.49
5	BiOCl	3.4	3.10

COD and CO_2 measurements

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water. The COD of the dye solution before and after the treatment was estimated. The reduction in COD values of the treated dye solution indicated the mineralization of dye molecules along with the color removal and the results are given in Table 8. During 8 hours of irradiation, reduction in COD value from 220 mg/L to 4 mg/L and increase in CO_2 value from 33 mg/L to 242 mg/L indicated the photodegradation of treated dye solution. A decrease in pH of solution has also been observed with increase in the extent of mineralization[21,29].

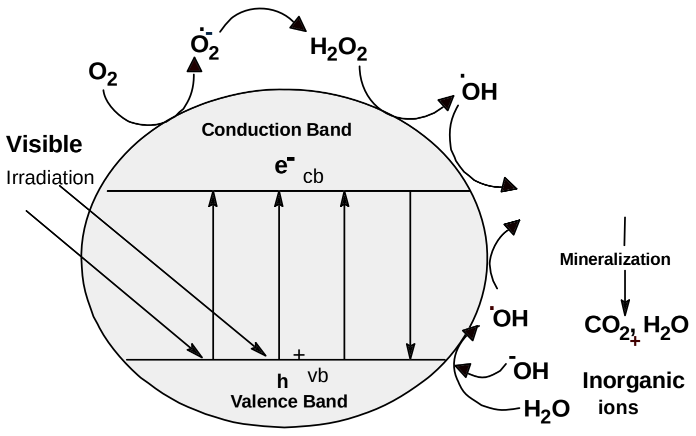
Table 8: COD and CO_2 measurements for degradation of Orange II dye

Orange II = 6.0×10^{-5} mol dm^{-3}, ZnO = 200 mg/100 mL, pH = 7,
Irradiation intensity = 25×10^3 lux

Irradiation time (h)	COD mg/L	CO_2 mg/L	% Efficiency	pH
0	220	33	0	7.0
2	148	77	32.7	6.3
4	84	121	61.8	5.1
6	40	176	81.8	4.6
8	4	242	98.1	4.2

Mechanism

Photocatalytic degradation of organic compounds is based on semiconductor photochemistry. The term photocatalysis consist of the combination of photochemistry and catalysis and thus implies that light and catalyst are necessary to bring about or to accelerate a chemical transformation. A semiconductor is characterized by an electronic band structures in which the highest occupied energy band, called valence band (VB) and the lowest empty band called the conduction band (CB), are separated by a band gap[30,31]. Certain semiconductors, notably zinc oxide (ZnO) and titanium dioxide (TiO_2) when illuminated by photons having an energy level that exceeds their band gap energy excites electrons (e^-) from the valence band to the conduction band and holes (h^+) are produced in the valence band (Fig. 8). The photogenerated valence band holes react with either water (H_2O) or hydroxyl ions (OH^-) adsorbed on the catalyst surface to generate hydroxyl radicals ($^{\bullet}OH$) which are strong oxidant. The photogenerated electrons in the conduction band may react with oxygen to form superoxide ions ($^{\bullet}O_2^-$). The superoxide ions can then react with water to produce hydrogen peroxide and hydroxyl ions. Cleavage of hydrogen peroxide by the conduction band electrons yields further hydroxyl radicals and hydroxyl ions. The hydroxyl ions can then react with the valence band holes to form additional hydroxyl radicals. Degradation of organic substances can be achieved by their reaction with hydroxyl radicals ($^{\bullet}OH$) or direct attack from the valence band holes. Recombination of the photogenerated electrons and holes may occur and indeed it has been suggested that preadsorption of substrate on to the photocatalyst is a prerequisite for highly efficient degradation. The heterogeneous ZnO photocatalytic process is a complex sequence of reaction that can be expressed by the following set of simplified equations shown below[17, 23, 32].



ZnO particle in water

Fig. 8: Mechanism of photocatalytic degradation of dye pollutants using ZnO illuminated by visible irradiation

$$\mathrm{ZnO} + h\nu_{\text{visible}} \longrightarrow \mathrm{ZnO}\,(h^+_{VB} + e^-_{CB}) \qquad ...(13)$$

$$\mathrm{ZnO}\,(h^+_{VB}) + H_2O \longrightarrow \mathrm{ZnO} + H^+ + OH^{\cdot} \qquad ...(14)$$

$$\mathrm{ZnO}\,(h^+_{VB}) + OH^- \longrightarrow \mathrm{ZnO} + OH^{\cdot} \qquad ...(15)$$

$$\mathrm{ZnO}\,(e^-_{CB}) + O_2 \longrightarrow \mathrm{ZnO} + O_2^{\cdot -} \qquad ...(16)$$

$$O_2^{\cdot -} + H^+ \longrightarrow HO^{\cdot}_2 \qquad ...(17)$$

$$HO^{\cdot}_2 + H^+ + \mathrm{ZnO}\,(e^-_{CB}) \longrightarrow H_2O_2 + \mathrm{ZnO} \qquad ...(18)$$

$$H_2O_2 + \mathrm{ZnO}\,(e^-_{CB}) \longrightarrow OH^{\cdot} + OH^- + \mathrm{ZnO} \qquad ...(19)$$

$$\text{Dye} + OH^{\cdot} \longrightarrow \text{Degradation Products} \qquad ...(20)$$

$$\text{Dye} + (h^+_{VB}) \longrightarrow \text{Oxidation Products} \qquad ...(21)$$

$$\text{Dye} + (e^-_{CB}) \longrightarrow \text{Reduction Products} \qquad ...(22)$$

We anticipate a parallel mechanism in case of dyes. There may be direct absorption of visible light by the dye molecule can leads to charge injection from the excited state of the conduction band of the semiconductor as summarized in the following equation[23].

$$\text{Dye} + h^+_{VB} \longrightarrow {}_1\text{Dye or } {}_3\text{Dye} \qquad ...(23)$$

$${}_1\text{Dye or } {}_3\text{Dye} + \mathrm{ZnO} \longrightarrow \text{Dye} + \mathrm{ZnO}\,(e^-_{CB}) \qquad ...(24)$$

$$\mathrm{ZnO}\,(e^-_{CB}) + O_2 \longrightarrow \mathrm{ZnO} + O_2^{\cdot -} \qquad \ldots(25)$$

$$O_2^{\cdot -} + H^+ \longrightarrow HO^{\cdot}_2 \qquad \ldots(26)$$

$$HO^{\cdot}_2 + H^+ + \mathrm{ZnO}\,(e^-_{CB}) \longrightarrow H_2O_2 + \mathrm{ZnO} \qquad \ldots(27)$$

$$H_2O_2 + \mathrm{ZnO}\,(e^-_{CB}) \longrightarrow OH^{\cdot} + OH^- + \mathrm{ZnO} \qquad \ldots(28)$$

$$\mathrm{Dye}^{+\cdot} + OH^- \longrightarrow \mathrm{Dye} + OH^{\cdot} \qquad \ldots(29)$$

$$\mathrm{Dye} + O_2^{\cdot -} \longrightarrow \text{Degradation products} \qquad \ldots(30)$$

$$\mathrm{Dye} + OH^{\cdot} \longrightarrow \text{Degradation products} \qquad \ldots(31)$$

The semiconductor photocatalysis mechanism is very complex in nature.

$$\begin{tikzcd}
\text{Dye (Dye}^{+\cdot}\text{)} + OH^{\cdot} \arrow[r] & \text{Decolorization of dye} \arrow[d] \\
& \text{Degradation of dye involving organic intermediates} \arrow[d, "\text{Mineralization}"] \\
& CO_2\text{ (gas)} + H_2O + \text{Inoganic ions}
\end{tikzcd} \qquad \ldots(32)$$

CONCLUSION

Photocatalytic processes are safe, low cost, ease of controlling parameters and their high efficiency in degrading recalcitrant organic and inorganic substances in aqueous systems. The reduction in COD of the effluent suggests that the dye molecules were completely mineralized. It can be concluded that the ZnO assisted photocatalytic degradation of textile dyes and textile effluent is a versatile, economic, environmentally benign and efficient method of treatment. The proper addition of hydrogen peroxide could improve the photocatalytic removal rate, but it was inhibited by the addition of salts. Hydroxyl radicals and positive holes are the main reactive species.

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