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PHOTOCATALYTIC DEGRADATION OF ACRIDINE YELLOW IN AQUEOUS SUSPENSION OF ZNO USING VISIBLE IRRADIATION

Science

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ABSTRACT

A study of photocatalytic degradation of the acridine yellow dye has been carried out in aqueous heterogeneous medium using ZnO as photocatalyst in a batch reactor. The disappearance of the dye was monitored by spectrophotometric method and found that it follows pseudo-first order kinetics generally according to the Langmuir-Hinshelwood model. The total degradation of dye was studied using chemical oxygen demand (COD) method. The addition of an optimal amount of hydrogen peroxide and potassium persulphate increase the degradation rate while NaCl and Na_2CO_3 decrease the rate of degradation. The effect of addition of cationic and anionic surfactants has also been investigated. Bubbling of nitrogen in the reaction solution decreases the reaction rate. ZnO has been found experimentally to be a highly efficient photo catalyst for the degradation of acridine yellow dye.

KEYWORDS

Acridine yellow, Photocatalytic degradation, ZnO, Mineralization

1. INTRODUCTION

Dye pollutants are major source of environmental concern. The release of wastewater containing dye in the ecosystem is a dramatic source of aesthetic pollution and perturbations in aquatic life. [1, 2] Most of the organic dyes are not easily degradable by standard methods reported such as adsorption on activated carbon, ultra-filtration, reverse osmosis, coagulation, ion exchange and oxidation with peroxide etc. [3-5] Recently, the efficiency of advanced oxidation processes (AOP) for the degradation of recalcitrant compounds has been extensively used. The key advantage of this degradation method is that it can be carried out under ambient conditions and lead to complete mineralization of organic compounds. In pursuit of a better method for the detoxification of colored wastewater, heterogeneous photocatalysis stands uppermost. Many researchers have been attempting the photocatalytic degradation of dyes [6-8] using various photocatalysts, mainly with TiO_2/UV system but absorption of only small range of solar energy, it is essential to shift the absorption threshold towards the visible region. Keeping this in mind we have undertaken the ZnO assisted photocatalytic degradation of acridine yellow in the visible light. Acridine yellow is a water-soluble dye. It is used widely in coloration of leather and paper etc. Structure of acridine yellow is shown in **Figure 1**.

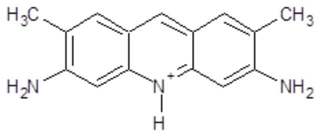

Figure 1: Acridine Yellow - G

2. EXPERIMENTAL PROCEDURE

All the chemicals used were of AR grade. Solutions were prepared by dissolving the desired amount of compound in distilled water. The photocatalytic reaction was carried out in a batch reactor with dimension of 7.5 × 6.0cm provided with a water circulation arrangement in order to maintain the temperature in the range of 25-30°C. The irradiation was carried out using a 500W halogen lamp. In all cases during the photolysis experiments, the slurry composed of the dye solution and catalyst was placed in the reactor and stirred magnetically with simultaneous exposure to visible light. The samples were withdrawn at periodic intervals from the reactor to assess the extent of decolourisation and degradation. Digital lux meter (Lutron LX-101) was used to measure the intensity of light. The pH was constantly monitored using pH meter. Absorbance of reaction mixture at different time intervals was measured at 490nm using UV-Vis spectrophotometer (Systronic 106). The chemical oxygen demand (COD) was measured by the closed reflux method using potassium dichromate as the oxidant under acidic condition. The amount of unreacted oxidant was determined by titration with ferrous ammonium sulphate using feroin indicator. [9]

The photodegradation efficiency for each sample was calculated from the following expression:

$$\eta = \frac{COD_0 - COD_t}{COD_0} \times 100 \qquad (1)$$

Where, η is photodegradation efficiency; COD_o and COD_t are COD of dye solution before irradiation and after irradiation for time t respectively.

3. RESULT AND DISCUSSION

A. Effect of dye concentration

The photocatalytic degradation of 2.0 x 10^{-5} mol dm^{-3} dye solution containing 400mg ZnO is tabulated in **Table-1**. The change in concentration of the dye in the solution is plotted as a function of irradiation time. It is seen that 95% of the initial concentration of the dye was degraded after 140min irradiation and complete decolourisation was observed in 150min.

Table-1 Effect of irradiation period

S.No.	Degradation (%)	Irradiation Period (min)	COD (mg dm^{-3}) %
1	100	0	0
2	84	30	16
3	56	60	46
4	40	90	60
5	20	120	80
6	00	150	100

Initial concentration of dye = 2.0 x 10^{-5} mol dm^{-3}, Amount of ZnO = 400mg/50ml

In contrast negligible decrease in the concentration of dye was observed by irradiation in the absence of ZnO or in the presence of ZnO without light source. **(Fig. 3)** The effect of initial concentration of the solute in the photocatalytic degradation rate is described by pseudo first order kinetics. This is rationalized in terms of the Langmuir-Hinshelwood model modified to accommodate reactions [10, 11] occurring at a solid-liquid interface as

$$r_0 = \frac{-dc}{dt} = \frac{k_r K C_0}{(1 + KC_0)} \qquad (2)$$

Where r_0 is the rate of disappearance of the dye and C_0 is the initial concentration of the dye. K represents the equilibrium constant for adsorption of the dye on ZnO particles and k_r represents the limiting rate of the reaction at maximum coverage under the experimental conditions. The integrated form is

$$t = \frac{1}{Kk_r} \ln \frac{C_0}{C} + \frac{(C_0 - C)}{k_r} \qquad (3)$$

where t is the time in minutes required for the initial concentration of dye C_0 to become C. At low concentration of the dye the second term in equation (3) is negligible compared to the first term. On neglecting the second term the final form of the equation is

$$\ln \frac{C_0}{C} = tKk_r = k't \qquad (4)$$

where k' is the apparent rate constant of the photocatalytic degradation.

$$t_{1/2} = \frac{0.693}{k'} \qquad (5)$$

The decrease of k' values with increase in initial concentration of the dye can be ascribed to the decrease in the path length of photons entering the solution due to impermeability of the dye solution. (Table-2)

Table-2: Effect of dye concentration

S.No.	[AY] x 10^{-5} mol dm^{-3}	$t_{1/2}$ x 10^3 s^1	k' x 10^{-4} s
1	1.0	0.36	19.1
2	2.0	0.78	8.81
3	3.0	0.78	5.31
4	4.0	1.23	4.02
5	5.0	1.84	3.81

AY=Acridine Yellow, Light intensity=17.5x10^3 lux, ZnO = 400 mg

At low concentration the reverse effect observed, thereby increasing the number of photon absorption by the catalyst that as the dye concentration increases requirement of catalyst also increases. [12] This decreasing phenomenon can further be explained as the concentration of dye increased the requirement of catalyst surface also increased. But here the irradiation time and amount of catalyst has been kept constant. Hence the relative numbers of O_2 and OH radicals formed on the surface of ZnO are also constant. As a result the relative number of O_2 & OH attacking the dye molecule decreases with increasing initial concentration of the dye. Hence, the rate of degradation decreases considerably with increase in concentration of the dye. The plot of C_0 versus $t_{1/2}$ should yield a straight line of which the slope is 1/k' and the intercept is 0.693/k_rK. The k_r and K values were calculated from the slope of the straight line and the intercept respectively. The product of k_rK = 19.1 x 10^{-4} s represents the apparent rate constant k' for low initial concentration of the dye and is in agreement with the values obtained from equation 4. (**Figure 3**)

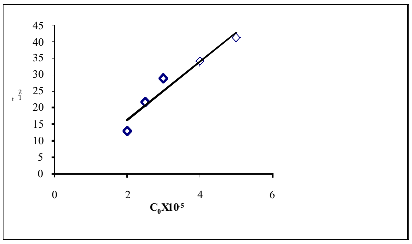

Figure-3

B. Effect of ZnO loading The effect of change in the amount of photocatalyst was performed in the range of 200-600mg/50ml of the dye solution. For the dye concentration of 2.0 x 10^{-5} mol dm^{-3} the change in the ZnO amount from 200-400mg/50ml has increased the apparent rate constant from 6.3 x 10^4 to 8.8 x 10^4s and decreased the $t_{1/2}$ value from 1.09 x 10^{-3} to 0.78 x 10^{-3} s. (Table-3).

Table-3: Effect of ZnO Loading

S. No.	Amount of ZnO(mg)	k' x 10^4 s	$t_{1/2}$ x 10^3 s^1
1	200	6.3	1.09
2	300	7.3	0.94
3	400	8.8	.078
4	500	8.5	0.81
5	600	8.0	0.84

Experimental studies have revealed that the catalyst loading of 400mg/50ml as the optimal dose for the degradation of 2.0 x 10^{-5} mol dm^{-3} dye in 60 minutes of irradiation time. Further increase in the amount of ZnO to 600mg, has decreased the k' value and increased $t_{1/2}$ values. These observations can be rationalised in terms of availability of active sites on ZnO surface and the penetration of photoactivating light into the suspension. Owing to an increase in the number of ZnO particle as the concentration of catalyst increased the availability of active sites increases but the light penetration and hence the photoactivated volume of the suspension shrinks. The transaction between these two effects is that at low solute concentration, when there are excess active sites, the balance between the opposing effects is evenly poise and change in the amount of ZnO makes little difference to the reaction rate. At high solute concentration availability of excess active sites outweighs the diminishing photoactivated volume and substantially high k' value is obtained at increase in ZnO concentration. [13] As well as the amount of ZnO increases the quantity of absorption of also increases. Further increase in catalyst concentration beyond 400mg/50ml may result in deactivation of activated molecules due to collision with ground state molecules as shown below: [14]

$$ZnO^* + ZnO \longrightarrow ZnO^\# + ZnO \qquad (6)$$

ZnO^* : ZnO with active species adsorbed on its surface

$ZnO^\#$: deactivated form of ZnO* shielding by ZnO may also take place.

C. Effect of H_2O_2

The decolarization of the dye solution found to be severely affected by the addition of hydrogen peroxide. On adding H_2O_2 in the concentration range from 4.0 x 10^{-4} to 1.0 x 10^{-3} mol dm^{-3}, rate constant values increases first but after reaching the highest value a fall in the k' values was found. The initial increase in the reaction rate on addition of H_2O_2 can be attributed to the formation of OH radicals responsible for the photocatalytic oxidation and it inhibits the electron-hole recombination as well. The oxidizing power of hydroxyl radical is 2.05 times more than chlorine, 1.58 times more than H_2O_2 & 1.35 times more than ozone[15,16]. H_2O_2 increases the rate of hydroxyl radical formation through three ways: Firstly, it could act as an alternative electron acceptor to oxygen (equation-7), which might restrain the bulk composite of the photo-excited electrons and holes. This should consequently increase the rate of photocatalytic process. Secondly, the reduction of H_2O_2 at the conductance band would also produce hydroxyl radicals. Even if H_2O_2 was not reduced at the conductance band it could accept an electron from superoxide again producing hydroxyl radicals (equation-8). Thirdly, the self- decomposition by illumination would also produce hydroxyl radicals (equation-9):

$$e_{CB}^- + H_2O_2 \longrightarrow OH^- + OH \qquad (7)$$
$$O_2 + H_2O_2 \longrightarrow OH^- + OH + O_2 \qquad (8)$$
$$H_2O_2 + hv \longrightarrow 2OH \qquad (9)$$

At high concentration, the hydrogen peroxide adsorbed on the photocatalytic surface could effectively scavenge not only the photocatalytic surface formed OH radicals (equation 10 and 11) but also the photo-generated holes (h_{CB}^+) (equation-12) and thus inhibit the major pathway for heterogeneous generation of OH radicals:

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (10)$$
$$Ho_2 + OH \longrightarrow H_2O + O_2 \qquad (11)$$
$$h_{CB}^+ + H_2O_2 \longrightarrow H^+ + HO_2 \qquad (12)$$

It is worth mentioning here that HO_2 radicals are less reactive than OH, therefore, have negligible contribution in the dye degradation.

TABLE IV: Effect of Effect of hydrogen per oxide

Concentration of k' x 10^4 s	$t_{1/2}$ x 10^3 s^1	[H_2O_2] x 10^{-4} mol dm^{-3}
0.0	8.8	0.78
4.0	8.3	0.71
6.0	11.3	0.60
8.0	7.1	0.96
10	6.8	1.0

Initial concentration of Dye = 2.0x10^{-5}mol dm^{-3} Amount of ZnO = 400 mg, Intensity of light = 17.5x10^3 lux

D. Effect of irradiation time

Figure 2 present the % degradation of the dye at different irradiation period at optimum catalyst loading and dye concentration. Under the experimental condition complete degradation of the dye occurred within 150 min of irradiation. The photocatalytic degradation of the dye takes place on the surface of ZnO where OH and O_2^- radicals are trapped in the holes of reactive species. Oxygen and water are essential for photocatalytic degradation. The OH radicals are strong enough to break the bonds in the dye molecules adsorbed on the surface of ZnO When the intensity of light and concentration of dye are constant, the number of OH and O_2^- radicals increase with increase in irradiation period and hence the dye molecules are completely degraded into smaller fragments[17].

E. Effect of pH

pH of 2.0 x 10^{-5} M aqueous dye solution was 6.12 .At this pH, k' value was found to be 8.83 x 10^{4} s and corresponding $t_{1/2}$ value was 0.7 x 10^{3} s for an irradiation period of 1 hr (Table 6) The photoadegradation of the dye was investigated in the pH range 6.12 pH can be one of the most important parameters for the photocatalytic process and it was of influence on the photooxidation of Acridine yellow. The presence of the solid-electrolyte interface i. e the electrical double layer, are modified as the pH of the medium changes and, consequently, the effectiveness of the adsorption-desorption process and spectrum of the photo generated electron-hole pairs also substantially affected[18-23].

In Table (5), The initial reaction rate values of the photooxidation of Acridine yellow are shown in the pH range from 5.2 – 10.2 for the alteration of pH in the acid and alkaline area 5M H_2SO_4 and 5M NaOH solutions respectively have been used. At pH values beyond that range a vigorous change of the adsorption spectrum of Acridine yellow was observed, thus preventing comparison of the results.

For ZnO system a sharper increase is observed as pH is increased from 5 to 8. At pH 8 the maximum initial rate is achieves and increasing further the pH values the photodegradation rate of Acridine yellow decreases. The low initial reaction rates at acidic or at alkali pH values due to dissolution and photodissolution of ZnO[24]. The semiconductor oxide presents here an amphoteric behaviour. At acidic pH, ZnO can react with acids to produce the corresponding salt and at alkalic pH, it can react with a base to form complexes like $[Zn(OH)_4]^{2-}$.

TABLE V: Effect of pH on photodegradation

pH (min^{-1})	k' x 10^{4} s	$t_{1/2}$ x 10^{3} s^{1}
5.23	6.60	1.0
6.12	8.83	0.7
7.33	9.50	0.7
8.21	9.83	0.7
9.26	8.00	0.8
10.2	7.60	0.9

Initial concentration of dye=2.0x10^{-5} mol dm^{-3}, Amount of ZnO=400 mg, Intensity of light = 17.5x10^{3} lux

F. Effect of persulphate ion

The effect of persulphate ion (electron scavenger) on the photocatalytic degradation was investigated by varying its concentration from 5.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} (Table 6). Rate constant values were found to increase with increasing amount of persulphate ion and attained an optimum value for 7.0 x 10^{-5} mol dm^{-3}. The increase in k' values may be due to the formation of SO_4^- as

$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^- + SO_4^{2-}$ (13)

The sulphate radical anion (SO^-) thus formed is a sufficiently strong oxidant (E = 2.6eV) and may act in following three possible ways with organic compounds (i) by abstracting a hydrogen atom from saturated carbon, (ii) by adding to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anions and from certain neutral molecules[25,26]. In addition, it can trap the photogenerated electron and/or generate hydroxyl radicals.

$SO_4^- + e^-_{cb} \longrightarrow SO_4^{2-}$ (14)
$SO_4^- + H_2O \longrightarrow OH + SO_4^{2-} + H^+$ (15)

The hydroxyl radical and sulphate radical anion being powerful oxidants degrade the dye molecule at a faster rate. The SO_4^- has the unique nature of attacking the dye molecule at various positions and hence the fragmentation of the dye molecules is rapid.

$SO_4^- + Dye \longrightarrow SO_4^{2-}$ + Dye (intermediate) (16)
So_4^- +Dye (intermediate) $\longrightarrow$ $SO_4^{2-} + CO_2 + NO_2$ + other inorganic compounds (17)

Further increase in persulphate concentration has decreased the degradation rate owing to the adsorption of sulphate ions formed during the reaction on the surface of ZnO deactivating a section of the catalyst.

TABLE VI: Effect of Potassium Persulphate

$[K_2S_2\ O_8]$ x 10^{-5} mol dm^{-3}	k' x 10^{4} s	$t_{1/2}$ x 10^{3} s^{1}
0	8.8	0.7
5.0	9.5	0.7
7.0	10.1	0.6
9.0	8.1	0.8
10	6.8	1.0

Initial dye conc.=2.0x10^{-5} mol dm^{-3}, Amount of ZnO=400 mg, Intensity of light = 17.5x103 lux

G. Effect of sodium carbonate

For the fixing of dye on the fabrics and fastness of the colour sodium carbonate is often used. Consequently, the wastewater from the dyeing operation contains substantial amount of carbonate ions. Hence, it is important to study the effect of carbonate ions in the photodegradation efficiency. Experiments were performed with sodium carbonate in the range 3.0x10^{-5} to 1.0x10^{-4} mol dm^{-3}. It is observed that k' value gradually decreases with increasing amount of carbonate ion (Table 8). The decrease in the rate of degradation in the presence of carbonate ion is due to the hydroxyl scavenging property of carbonate ions [27] as evident from the following reactions:

$OH + Co_3^{2-} \longrightarrow OH^- + CO_3^-$ (18)
$OH + HCO_3^- \longrightarrow H_2O + CO_3^-$ (19)

Hence, auxiliary chemicals like sodium carbonate may hinder the photocatalytic degradation of dyes.

TABLE VII: Effect of Sodium carbonate

$[Na_2CO_3]$ x 10^{-5} mol dm^{-3}	k' x 10^{4} s	$t_{1/2}$ x 10^{3} s^{1}
0	8.8	0.7
3.0	6.1	1.1
5.0	5.3	1.2
7.0	5.0	1.3
9.0	4.8	1.4
10	4.5	1.5

Initial dye conc. =2.0x10^{-5} mol dm^{3}, Amount of ZnO=400 mg, Intensity of light = 17.5x10^{3} lux

H. Effect of sodium chloride

The photocatalytic degradation efficiency was considerably decreased upon the addition of inert salts like sodium chloride, sodium sulphate and sodium phosphate. Hence, the effect of chloride ions on the photocatalytic degradation was studied. Photodegradation studies were carried out with sodium chloride in the range 3.0 x 10-5 to 1.0 x 10-4 M keeping dye solution concentration of 2.0 x 10-5 M. k' value of the degradation process decreases gradually with increase in the amount of chloride ions (Table 9). The decrease in the % degradation of the dye in the presence of chloride ions is due to the hole scavenging properties of these ions as shown in the following reaction sequence [28]. This is a typical example for competitive inhibition.

$ZnO + h \longrightarrow ZnO\ (h^+_{vb} + e^-_{cb})$ (20)
$Cl^- + h^+_{vb} \longrightarrow Cl + H^+$ (21)
$Cl + Cl^- \longrightarrow Cl_2^-$ (22)

TABLE VIII: Effect of Sodium chloride

[NaCl] x 10^{-5} mol dm^{-3}	k' x 10^{4} s	$t_{1/2}$ x 10^{3} s^{1}
0	8.8	0.7
3.0	6.1	1.1
5.0	5.5	1.2
7.0	5.0	3.8
9.0	4.8	1.4
10	4.5	1.5

Initial concentration of Dye 2.0x10^{-5} mol dm^{-3}, Amount of ZnO=400 mg, Intensity of light = 17.5x10^{3} lux

I. Effect of the light Intensity

The influence of light intensity on the rate of degradation has been examined at constant dye concentration (2.0 x 10^{-5} mol dm^{-3}) and catalyst loading (400mg/50ml). It is evident that the rate of decolourization and photodedradation increases with increasing light intensity (Table-9), because the visible radiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is independent on light intensity. The rate of degradation increases with increased radiation on the catalyst surface resulting in more hydroxyl radicals.

J. Effect of other photocatalysts

Experiments were performed with other photocatalysts as well. (Table-9) Generally, semiconductors having large band gaps are good photocatalysts. It has already been reported that semicondutors such as ZnO and TiO_2 have band gaps larger than 3 eV show strong photocatalytic activity. The conduction and valence band potentials of both ZnO and TiO_2 are larger than the corresponding redox potentials of H^+/H_2 and H_2O/O_2 and the photogenerated electron and hole can be separated efficiently. CdS with smaller band gaps show less activity since its conduction band is much lower than that of ZnO and TiO_2. Electron (CB) in these semiconductors rapidly falls into the hole thus showing reduced activity[14-29].

TABLE IX: Effect of other photocatalysts

Photocatalyst	k' x 10^4 s	Band gap (eV)
ZnO	8.6	3.2
TiO_2	8.1	3.1
CdS	6.1	2.3

Initial concentration of Dye = 2.0×10^{-5} mol dm^{-3}, Amount of catalyst = 400 mg, Light intensity = 17.5×10^3 lux

K. Effect of bubbling of nitrogen

The effect of bubbling of nitrogen through the aqueous suspension of the dye on the reaction rate constants has been studied. It is observed that photodegradation is severely retarded by bubbling of pure nitrogen because the dissolved oxygen in the solution plays an important role by trapping the conduction band electrons forming superoxide ions (O_2^-) and thus preventing the electron -hole recombination

$$(O_2 + e^- \longrightarrow O_2^-) \qquad (23)$$

and at same time H_2O_2 is formed from O_2^-[30].

K. Photodegradation products

When ZnO is irradiated in the presence of an aqueous solution the OH radicals formed on the illuminated semiconductor surface, are strong oxidizing agents with an oxidation potential of 2.8 eV. They can easily attack the adsorbed dye molecule or those in the vicinity of the surface of the catalyst, thus leading to their complete mineralization. The photocatalytic degradation of Acridine yellow certainly involves various chemical and photocatalytic stages and a few intermediates. The evolution of CO_2 during the degradation is the evidence of total destruction of dye in the aqueous medium. During the experiment the generation of CO_2 was identified by titrimetric method. And the decrease in pH indicates the formation of some mineral acid. The destruction of the dye has been confirmed by the COD method. The absence of any aromatic moiety has been further supported by the UV spectrum.

TABLE X: Concentration of photodegradation product

Time(min.)	CO_2(mg dm^{-3})
0	9.2
30	13.5
60	21.0
90	35.1
120	35.6
150	35.7

Initial dye conc. = 2.0×10^{-5} mol dm^{-3}, Amount of ZnO=400 mg, Intensity of light = 17.5×10^3 lux

L. Mechanism

It is a well established fact that by the irradiation on an aqueous ZnO suspension with light energy greater than the band gap energy of the semiconductor semiconductor (hυ >Eg = 3.2eV) conduction band electrons (e-) and valence band holes (h+) are generated. A fraction of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons act as powerful oxidants, respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the ZnO particle sites, reducing it to a superoxide radical anion O_2^-, while the photogenerated holes can oxidize either the dye molecule directly or the OH^- ions and the H_2O molecules adsorbed the ZnO surface to $^{\cdot}OH$ radicals. The $^{\cdot}OH$ radicals formed on the illuminated semiconductor surface are quite strong oxidizing agents with a standard electrode potential of 2.8 V. These can easily attack the adsorbed organic molecule or those located close to the surface of the catalyst, thus leading finally to their complete mineralization. In photocatalytic oxidation process, the generation of hydroxyl radicals takes places in two possible ways. Semiconductor ZnO, upon absorption of a photon of suitable energy can act as a photocatalytic substrate by producing electron-hole pair by the excitement of electrons from valence band to conduction band. The photogenerated holes that are able to migrate to the hydroxylated surface can create the highly reactive and short-lived hydroxyl radical $^{\cdot}OH$ [31-35].

$$ZnO + h \longrightarrow ZnO\,(e^- + h^+) \qquad (24)$$

$$h^+ + OH^- \longrightarrow OH \qquad (25)$$

In second way, the dye molecules act as a sensitizer by the absorption of visible light, and the transfer of photogenerated electrons from the dye molecule to semiconductor has been reported to be very effective. The various steps of overall mechanism envisioned are:

$$Dye + h \longrightarrow Dye^* \qquad (26)$$

$$Dye^* \longrightarrow Dye^+ + e^- \qquad (27)$$

$$ZnO + e^- \longrightarrow ZnO^{\cdot -} \quad . \qquad (28)$$

$$ZnO^{\cdot -} + O_2 \longrightarrow ZnO + O_2^{\cdot -} \qquad (29)$$

$$O_2^{\cdot -} + 2\,H_2O + e^- \longrightarrow 2\,H_2O_2 \qquad (30)$$

$$H_2O_2 + e \longrightarrow {}^{\cdot}OH + OH^- \qquad (31)$$

The equation (25) depicts the absorption of light by the dye molecule (Dye*). This excited dye (Dye*) injects an electron to the conduction band of ZnO in equation (27), where it is scavenged by O_2 to form active oxygen molecule as shown in equation (28). Further active oxygen molecule formed in equation (29) subsequently reacts with H_2O to generate OH radicals. These active radicals drive the photodegradation or minerlization of the dye molecule.

$$\begin{tikzcd}
Dye^{\cdot +} + OH \arrow[r] & \text{hydroxyl or peroxo} \arrow[d] \\
& \text{Intermediate degraded or mineralized products}
\end{tikzcd} \qquad (32)$$

$$h_{VB}^+ + dye \longrightarrow \text{oxidation of dye} \qquad (33)$$

$$e_{CB}^- + dye \longrightarrow \text{reduction of dye} \qquad (34)$$

4. CONCLUSION

The results obtained in this study demonstrate that photoassisted ZnO mediated degradation of acridine yellow in combination with H_2O_2 and persulphate ions is an effective treatment technology. While the presence of inorganic salts, surfactants such as C_{16}TAB and SDS and sodium carbonate hinder the photocatalytic degradation of acridine yellow. Complete mineralization of the dye may be possible in a short irradiation period if the concentration of the dye, catalyst loading, pH, amount of H_2O_2 and persulphate are optimized properly.

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