Research Article

Photocatalytic Degradation of Direct Blue 1 Dye Using ZnO in Presence of Visible light

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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 direct blue 1 dye in the presence of an aqueous heterogeneous suspension of ZnO irradiated with visible light has been investigated. The degradation of the dye 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.

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Introduction

The presence of dyes in wastewater has become a major issue all over the world. These dyes constitute largest group of organic compounds. Environment pollution by organic dyes also sets several ecological problems, which are increased by the fact that most of them are difficult to degrade using standard biological and physical methods. For the removal of such recalcitrant pollutants, some traditional or physical techniques such as adsorption on activated charcoal, ultra-filtration, reverse osmosis, coagulation etc. are used efficiently. Nevertheless they are non-destructive [1]. The conventional processes are insufficient to purify the wastewaters. They transferred the compounds from aqueous to another phase, thus causing secondary pollution problem. Therefore, in recent years, special attention has been focused on the studies concerning the use of advanced oxidation processes (AOPs) that base on the production of highly reactive Oxygen species including hydroxyl radicals (HO·). AOPs can be an alternative for the treatment of wastewater or effluent containing hardly biodegradable organic compounds because they may lead to complete degradation of pollutants to CO_2 and H_2O [2-4]. The key advantage of this method is that can be carried out under ambient condition and lead to complete degradation of organic compounds. Among the advanced oxidation processes, heterogeneous photocatalysis appears as an emerging technology leading to the total mineralization of most of the organic pollutants. It is cost effective and capable of degrading any complex organic chemicals when compared to other purification techniques. Zinc Oxide is an important photocatalyst due to its strong oxidizing power, non-toxicity and long term photostability [5]. Thus the aim of the present work is to investigate the efficiency of ZnO photocatalyst in removal of direct blue 1 dye (Figure 1) from wastewater using visible light [6].
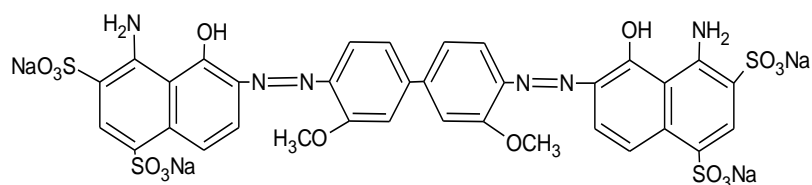
Figure 1 Direct Blue -1.

Experimental

Direct Blue 1 dye was obtained from Aldrich 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. 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 $30 \pm 0.3\ ^0C$. The irradiation was carried out using 500 W halogen lamp surrounded with aluminium reflectors in order to avoid loss of irradiation. During the photo catalytic 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: % efficiency = $C_0 - C / C_0 \times 100$. Where, C and C_0 are initial and final values for dye concentration or COD or CO_2 for reaction time t [7].

Result and Discussion
Effect of dye concentration variation

The effect of dye concentration on the rate of the reaction was studied by using different concentrations of direct blue 1 solution. It was observed that as the reaction was studied by using different concentrations of direct blue 1 solution. The initial concentration of dye has been varied from 0.5×10^{-5} mol dm^{-3} to 3.0×10^{-5} mol dm^{-3}. The results are represented in **Table 1** and **Figure 2**. Rate constant values increased from 4.98×10^{-4} s^{-1} to 5.29×10^{-4} s^{-1} with the increase in dye concentration from 0.5×10^{-5} mol dm^{-3} to 1.5×10^{-5} mol dm^{-3}. Thereafter, rate constant values decreased to 3.30×10^{-4} s^{-1} with the increased dye concentration (3.0×10^{-5} mol dm^{-3}). Rate constant has been found to be maximal at 1.5×10^{-5} mol dm^{-3} of dye concentration. It was observed that as the concentration of direct blue 1 was increased the rate of photocatalytic degradation also got increased, reaching a maximum at $1.5 \times$ mol dm^{-3}. Further increase in concentration of dye resulted into a decrease in the rate of photocatalytic degradation. This might be due to the fact that as the concentration of the dye increased, more dye molecules were available for excitation and consecutive energy transfer. As the dye surpassed the 1.5×10^{-5} mol dm^{-3} concentration it started screening / filtering the incident light and thus prohibited the incident light to reach to the dye molecules adsorbed on to the surface of photocatalyst. Thus, a decrease in the rate of photocatalytic degradation was observed [8].

Table 1 Effect of dye concentration variation: ZnO = 250 mg/100 mL, pH = 5.7, Light intensity = 22×103 lux, Temperature = $30 \pm 0.3\ 0C$.

[DB 1] $\times 10^5$ mol^{-1} dm^3	k $\times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
0.5	4.98	1.39
1.0	5.16	1.34
1.5	5.29	1.31
2.0	4.79	1.44
2.5	3.95	1.75
3.0	3.30	2.10

Effect of catalyst amount variation

The amount of catalyst is one of the main parameter for the degradation studies. In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst loading from 50 mg to 350 mg for dye solutions of 1.5×10^{-5} mol dm^{-3}/100 mL at pH 8.0. The results have been reported in **Table 2** and graphically represented in **Figure 3**. Rate constant values increased from 2.26×10^{-4} s^{-1} to 5.29×10^{-4} s^{-1} with the increase in photocatalyst

loading from 50 mg/100 mL to 250 mg/100 mL. Thereafter, rate constant values decreased to 4.45×10^{-4} s^{-1} with increased catalyst loading (350 mg/100 mL). Reaction rate has been found to be maximal at 250 mg/100 mL of photocatalyst loading [9]. The increase in the rate constant of direct blue 1 with an increase in the catalyst amount might be due to an increase in the active sites available on the catalyst surface for the reaction, which in turn made the rate of radical formation higher. The reduction in the rate constant when the catalyst amount was increased beyond 300 mg/100 mL was due to light scattering and reduction in light penetration through the solution. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates the reaction, thus reducing the rate of reaction [10].
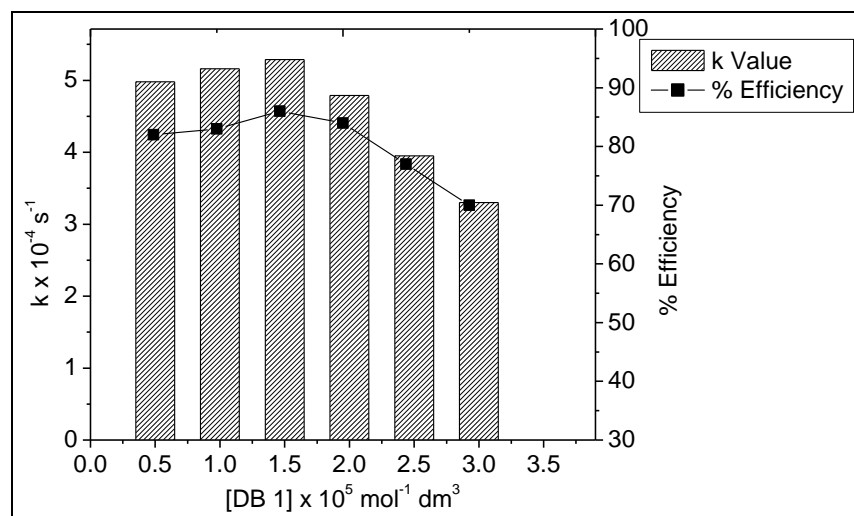

Figure 2 Effect of dye concentration variation.

Table 2 Effect of catalyst amount variation: [DB 1] = 1.5×10^{-5} mol dm^{-3}, pH = 5.7, Light intensity = 22×10^{3} lux, Temperature = 30 ± 0.3 ^{0}C.

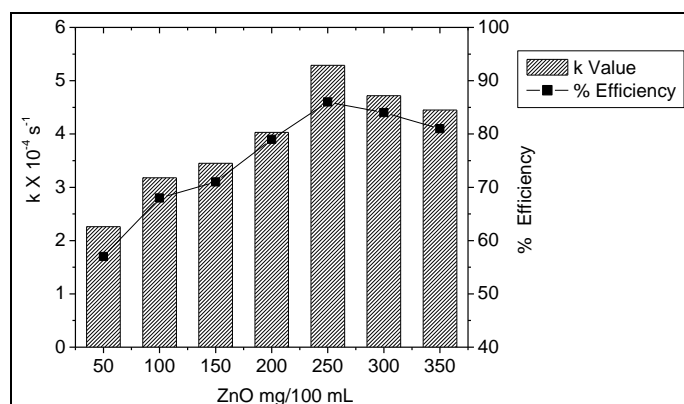| ZnO mg/100mL	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^{3}$ s
50	2.26	3.06
100	3.18	2.17
150	3.45	2.00
200	4.03	1.71
250	5.29	1.31
300	4.72	1.46
350	4.45	1.55

Figure 3 Effect of catalyst amount variation.

Effect of pH variation

The pH of the solution often affects the photocatalytic degradation of direct blue 1. The effect of pH on the rate of reaction was investigated in the pH range 3.5 to 9.6. The results are reported in **Table 3** and graphically presented in **Figure 4**. The rate constants increased from 4.41×10^{-4} s^{-1} to 5.29×10^{-4} s^{-1} with the increase in pH 3.5 to 5.7. Thereafter, rate constant values decreased to 4.37×10^{-4} s^{-1} on further increase in pH up to 9.6. Photocatalytic degradation of direct blue 1 was maximum at pH 5. 7. It was observed that the rate of photocatalytic degradation of direct blue 1 increased with increase in pH up to 5.7 and on further increasing the pH beyond 5.7, the rate of reaction decreased. This behavior might be explained on the basis that as pH was lowered the protonation of dye molecules will took place as well as the surface of the semiconductor became positively charged; thereby the dye molecules got experienced a force of repulsion from semiconductor. This resulted into of decreased the rate of reaction. On the other hand, the rate of photocatalytic degradation of direct blue 1 also got decreased with the increase in pH above 5.7. This might be due to the fact that at higher pH (alkaline), the $^{-}$OH ions are adsorbed on the surface of the semiconductor making it negatively charged and as a result, the anionic dye got experienced repulsion from semiconductor, causing a decrease in the rate of reaction. It means that the rate of photocatalytic degradation of direct blue 1 was optimum, when the dye remained almost in its neutral form (approx pH 5.7) [11].

Table 3 Effect of pH variation: [DB 1] = 1.5×10^{-5} mol dm^{-3}, pH = 5.7, Light intensity = 22×10^3 lux, Temperature = 30 ± 0.3 ^{0}C

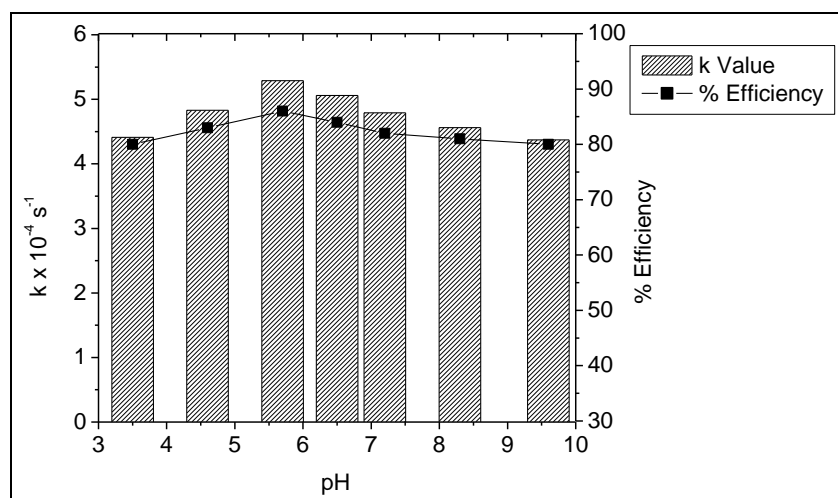| pH	k × 10^{-4} s^{-1}	t$_{1/2}$ × 10^3 s
3.5	4.41	1.57
4.6	4.83	1.43
5.7	5.29	1.31
6.5	5.06	1.36
7.2	4.79	1.44
8.3	4.56	1.51
9.6	4.37	1.58

Figure 4 Effect of pH variation

Effect of Na₂CO₃ and NaCl

Industrial effluents are composed of a large number of organic compounds, humic substances and inorganic substances like anions and metal ions. Hence, an evaluation of the degradability of the dyes under the influence of such externally added ions assumes importance. Therefore, the effects of added Na$_2$CO$_3$ and NaCl on the removal of direct blue 1 have been studies and are shown in **Table 4** and **Figure 5**. Degradation rate decreased from 4.83×10^{-4} s^{-1} to 3.14×10^{-4} s^{-1} and 4.91×10^{-4} s^{-1} to 3.37×10^{-4} s^{-1} on increase in concentration of Na$_2$CO$_3$ and NaCl from $2.0 \times$

10^{-5} to 14.0×10^{-5} mol dm^{-3} respectively. Na$_2$CO$_3$ strongly retarded the degradation rate due to the hydroxyl radical scavenging effect of carbonate ions [12, 13]. It has been very well reported that anions like carbonate, bicarbonate, and chloride ions retard the degradation of organic compounds by scavenging the hydroxyl radicals to form the respective anion radicals, according to the following reactions [14-17].
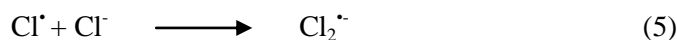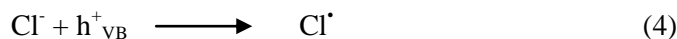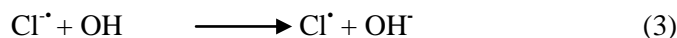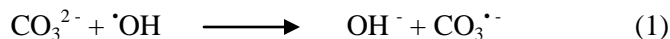
$$CO_3^{2-} + {}^\bullet OH \longrightarrow OH^- + CO_3^{\bullet -} \quad (1)$$

$$HCO_3^- + {}^\bullet OH \longrightarrow H_2O + CO_3^{\bullet -} \quad (2)$$

$$Cl^\bullet + OH \longrightarrow Cl^\bullet + OH^- \quad (3)$$

$$Cl^- + h^+{}_{VB} \longrightarrow Cl^\bullet \quad (4)$$

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^{\bullet -} \quad (5)$$

Table 4 Effect of Na$_2$CO$_3$ and NaCl: [DB 1] = 1.5×10^{-5} mol dm^{-3}, pH = 5.7. Light intensity = 22×10^3 lux, Temperature = 30 ± 0.3 ^{0}C.

[Salt] × 10^5 mol^{-1} dm^3	Na$_2$CO$_3$		NaCl	
	k × 10^{-4} s^{-1}	t$_{1/2}$ × 10^3 s	k × 10^{-4} s^{-1}	t$_{1/2}$ × 10^3 s
0.0	5.29	1.31	5.29	1.31
2.0	4.83	1.43	4.91	1.41
4.0	4.41	1.57	4.52	1.53
6.0	4.18	1.65	4.37	1.58
8.0	4.06	1.70	4.22	1.64
10.0	3.87	1.79	4.03	1.71
12.0	3.49	1.98	3.64	1.90
14.0	3.14	2.20	3.37	2.05
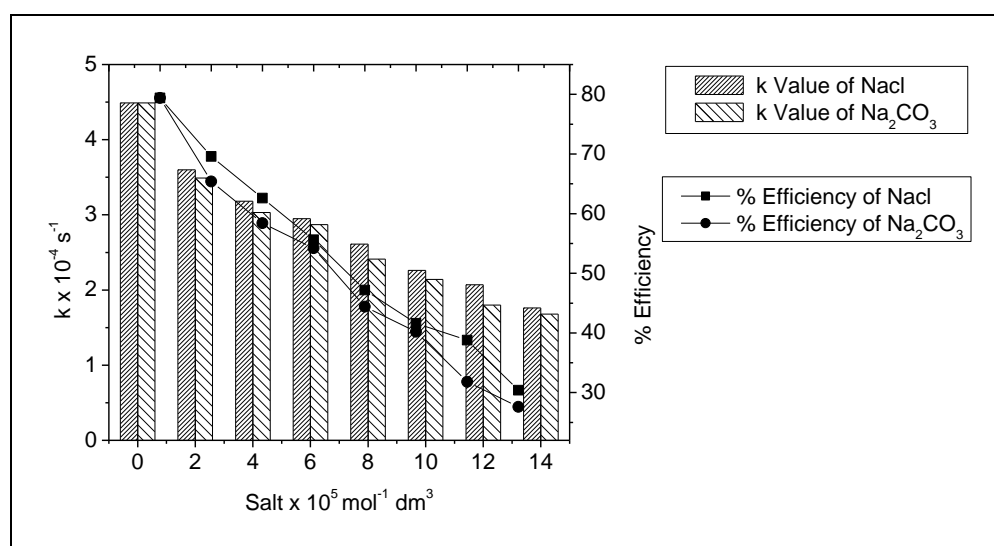
Figure 5 Effect of Na$_2$CO$_3$ and NaCl

Effect of H$_2$O$_2$ and K$_2$S$_2$O$_8$

H$_2$O$_2$ and K$_2$S$_2$O$_8$ play very important role of oxidizing agents in photocatalytic processes. The photocatalytic degradation of direct blue 1 was conducted at different concentration of H$_2$O$_2$ and K$_2$S$_2$O$_8$ as shown in **Table 5** and **Figure 6**. The results indicated that the rate of degradation of direct blue 1 increased with increasing concentration of H$_2$O$_2$ and K$_2$S$_2$O$_8$ up to 8.0×10^{-6} mol dm^{-3} but above this concentration, degradation efficiency was found to be decreased. This was because hydrogen peroxide has tangency to inhibit the electron-hole recombination by accepting photogenerated electron from the conduction band of semiconductor and promote charge separation and also form HO$^\bullet$ radicals according to Eqs. (6) and (7).

Table 5 Effect of H_2O_2 and $K_2S_2O_8$: [DB-1] = 1.5×10^{-5} mol dm^{-3}, pH = 5.7. ZnO = 250 mg/100 mL, Light intensity = 22×10^3 lux. Temperature = 30 ± 0.3 ^{0}C

[Oxidant] × 10^6 mol^{-1} dm^3	H_2O_2		$K_2S_2O_8$	
	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
0.0	5.29	1.31	5.29	1.31
2.0	5.64	1.22	5.56	1.24
4.0	5.98	1.15	5.75	1.20
6.0	6.83	1.01	6.14	1.12
8.0	6.56	1.05	5.87	1.18
10.0	6.06	1.14	5.64	1.22
12.0	5.18	1.33	5.41	1.28
14.0	4.95	1.40	5.25	1.32
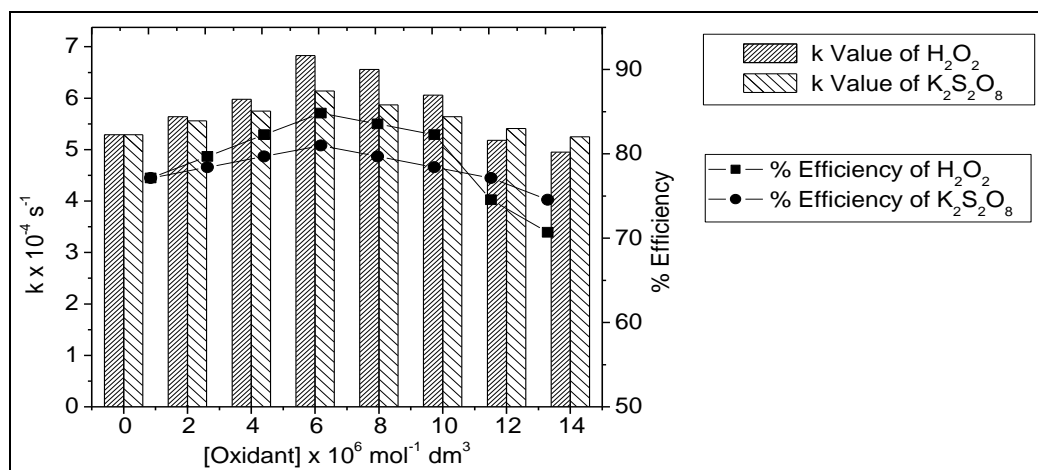
Figure 6 Effect of H_2O_2 and $K_2S_2O_8$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow HO^{\bullet} + HO^- + O_2 \qquad (6)$$
$$e^-_{CB} + H_2O_2 \longrightarrow HO^{\bullet} + OH^- \qquad (7)$$
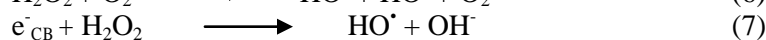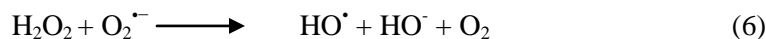
When H_2O_2 present in excess it might act as hole or $^{\bullet}$OH scavenger exerting detrimental effect on photocatalytic degradation. This phenomenon explains the need for an optimal concentration H_2O_2 for the maximal effect.

$$H_2O_2 + HO^{\bullet} \longrightarrow H_2O + HO_2^{\bullet} \qquad (8)$$
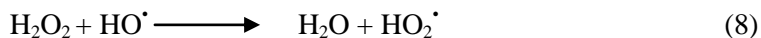
$K_2S_2O_8$ on the other hand, can also trap the photogenerated conduction band resulting in the formation of sulphate ion (SO_4^{-}) a strong oxidizing agent. In addition it can trap the photogenerated electrons and or generated hydroxyl radicals.

$$S_2O_8^{2-} + e^-_{CB} \longrightarrow SO_4^{2-\bullet} + SO_4^{2-} \qquad (9)$$

$$SO_4^{\bullet-} + e^-_{(CB)} \longrightarrow SO_4^{2-} \qquad (10)$$

$$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \qquad (11)$$

$$SO_4^{\bullet-} + DB\ 1 \longrightarrow SO_4^{2-} + Dye\ intermediates \qquad (12)$$

$$SO_4^{\bullet-} + Dye\ intermediates \longrightarrow Mineralization \qquad (13)$$
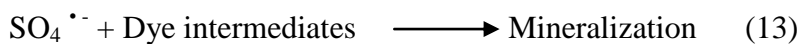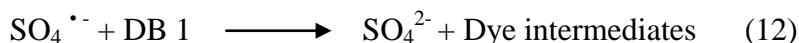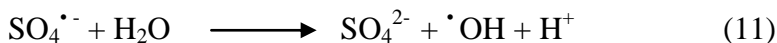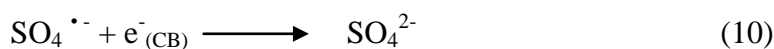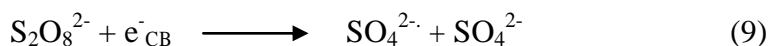
The decrease in rate of photodegradation above optimal concentration 10.0×10^{-6} mol dm^{-3} was due to the adsorption of sulphate ions formed during the reaction on surface of ZnO deactivating a section of photocatalyst [18].

Effect of light intensity and irradiation time

The variation of light intensity is one of the main parameter for the degradation studies. In order to determine the effect of light intensity, the experiments were performed by varying light intensity from 10×10^3 lux to 30×10^3 lux for dye solutions of 1.5×10^{-5} mol dm^{-3}, pH = 5.7. The results obtained are reported in **Table 6** and **Figure 7**. The above findings exhibit that an increase in light intensity increased the rate of photo catalytic degradation, since with the increase in light intencity the number of photons striking per unit area of the photocatalyst also increased. A linear behavior between light intensity and the rate of reaction has been observed. Since light intensity increase more than 30×10^3 lux increases the temperature of dye solution and a thermal reaction may occur, therefore higher intensities were avoided [19].

Table 6 Effect of light intensity: [DB 1] = 1.5×10^{-5} mol dm^{-3}, pH = 5.7. ZnO = 250 mg/100 mL, Temperature = $30 \pm 0.3\ ^0$C.

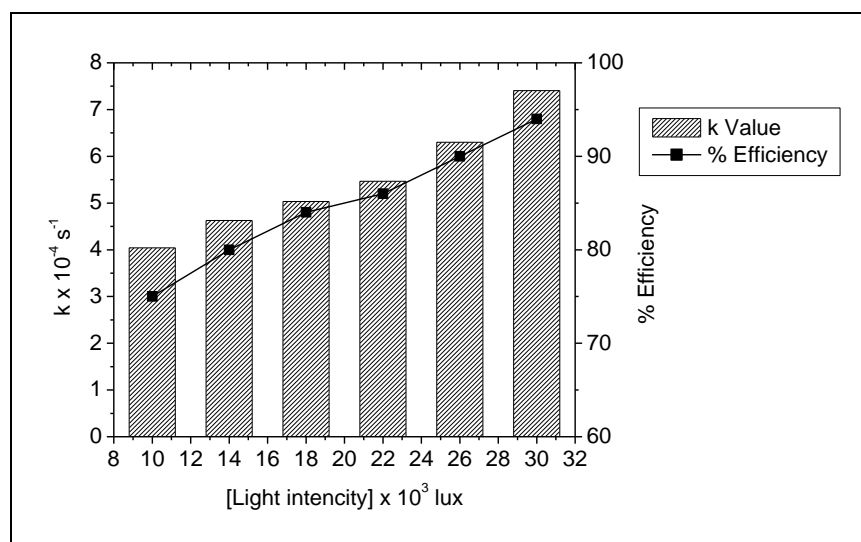| Light intensity $\times 10^3$ lux	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
10	3.91	1.77
14	4.48	1.54
18	4.87	1.42
22	5.29	1.31
26	6.10	1.13
30	7.17	0.96

Figure 7 Effect of light intensity

Effect of other photocatalysts

The influence of different photocatalysts (ZnO, BiOCl, TiO$_2$, BaCrO$_4$ and CdS) on the photocatalytic degradation of direct blue 1 was investigated and results are shown in the **Table 7**. ZnO, TiO$_2$ and BiOCl are found to be more efficient than BaCrO$_4$ and CdS. The order of activities of the photocatalysts are ZnO > BiOCl > TiO$_2$ > BaCrO$_4$ > CdS. Thus, ZnO has been found to be the most efficient catalyst [20]. Generally, semiconductors having large band gaps are good photocatalysts. It has already been reported that semiconductors such as ZnO, BiOCl and TiO$_2$ have band gaps larger than 3 eV should 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$_2$O/O$_2$ and the photogenerated electron and hole can be separated efficiently. BaCrO$_4$ and CdS with smaller band gap shows less activity since its conduction band is much lower than that of ZnO and TiO$_2$. It is quite evident that the smaller band gap permits rapid recombination of electron-hole and so electron in these semiconductors cannot move into the electron acceptors in the solution rapidly. Hence very low photocatalytic activity was observed in these catalysts [21].

Table 7 Effect of various photocatalysts: [DB 1] = 1.5 × 10-5 mol dm-3. pH = 5.7, Light intensity = 22 × 103 lux, Temperature = 30 ± 0.3 0C

Photocatalysts 250 mg/100 mL	Bandgap (eV)	$k \times 10^{-4} s^{-1}$	$t_{1/2} \times 10^3 s$
CdS	2.3	2.84	2.44
BaCrO$_4$	2.6	2.95	2.34
TiO$_2$	3.2	3.49	1.98
ZnO	3.2	5.29	1.71
BiOCl	3.4	4.03	1.31

COD and CO$_2$ measurement during mineralization of DB 1

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 colour removal and the results are given in **Table 8** and **Figure 8**. During 8 hours of irradiation, reduction in COD value from 248 mg/L to 0 mg/L and increase in CO$_2$ value from 33 mg/L to 154 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 [18, 22].

Table 8 COD and CO$_2$ measurement during mineralization of DB 1: [DB 1] = 1.5 × 10^{-5} mol, ZnO= 250 mg/100 mL, pH = 5.7, Light Intensity = 22 × 10^3 lux, Temperature = 30 ± 0.3 ^{0}C.

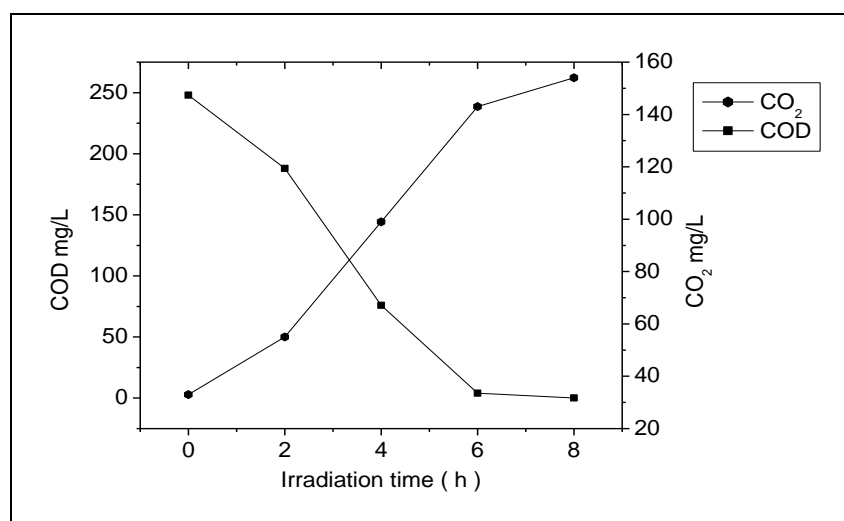| Time (h)	COD (mg/L)	CO$_2$ (mg/L)	Efficiency (%)	NO$_3^-$ (mg/L)	SO$_4^{2-}$ (mg/L)	pH
0	248	33	0	0	0	5.7
2	188	55	23	5	6.5	5.3
4	76	99	47	9.4	8.8	4.6
6	4	143	92	12.6	10.6	4.2
8	0	154	100	14.3	12.8	3.8

Figure 8 COD and CO$_2$ trend during mineralization of DB 1

Spectral changes of Direct Blue 1degradation

Figure 9 shows typical time-dependent UV–Vis spectrum of direct blue 1 dye during photo irradiation with ZnO. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region.

The prominent peak was observed at λmax i.e., 488 nm which decreased gradually and finally disappeared indicating that the dye had been decolorized. Similarly the peak in the UV region at λ max 220 and 310 nm got decreased with the passage of time, thereby confirming the complete mineralization of dye [23].
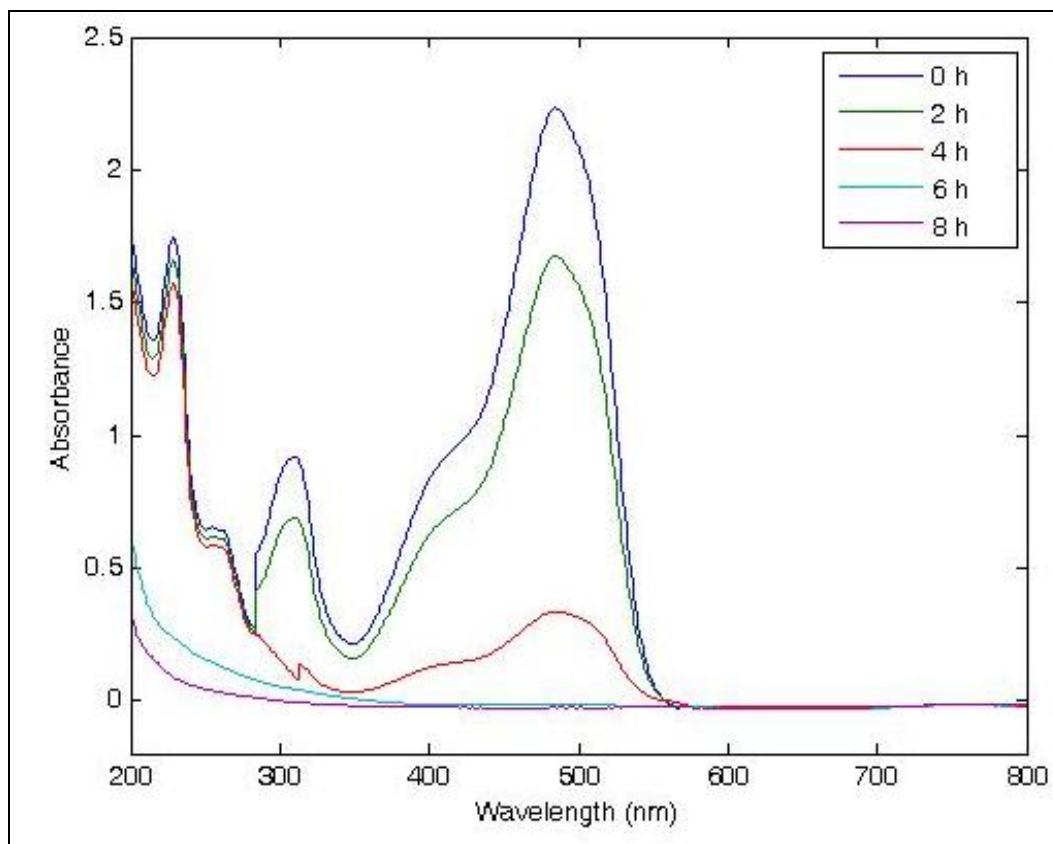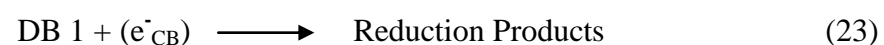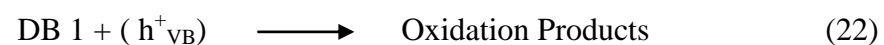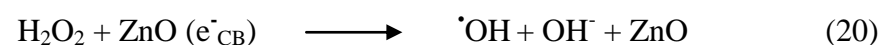

Figure 9 UV-Vis spectrum of Direct Blue 1 at 0 to 8 h: [DB 1] = 1.5×10^{-5} mol dm^{-3}, ZnO = 250 mg/ 100 mL, Light intensity = 22×10^{3} lux pH = 5.7, Temperature = $30 \pm 0.3\ ^{0}$C.

Mechanism of DB 1 degradation

Photocatalytic degradation of organic compounds depends largely 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 and 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 [24, 25]. On illumination of by zinc oxide (ZnO) photons ha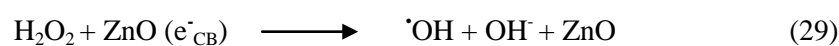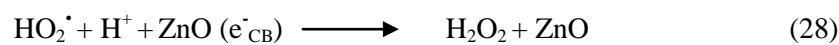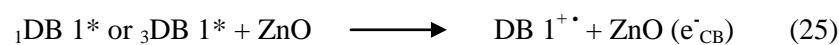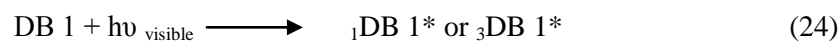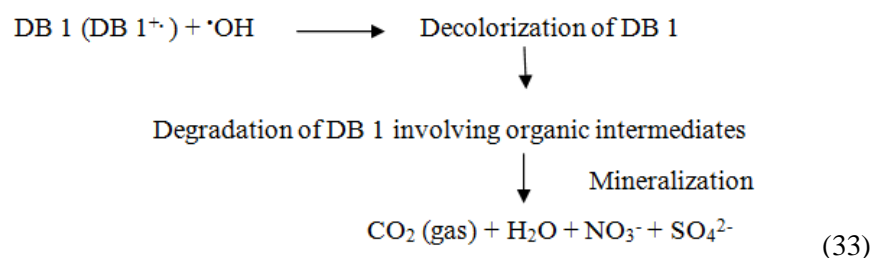ving energy level higher than, its band gap energy electrons (e^{-}) from the valence band goes to the conduction band and leaving a hole (h^{+}) valence band. The photogenerated valence band holes might react with either water (H$_2$O) or hydroxyl ions (OH^{-}) adsorbed on the catalyst surface to generate hydroxyl radicals (˙OH) that are strong oxidant. The photogenerated electrons in the conduction band might react with oxygen to form superoxide radical anions (˙O$_2{}^{-}$). The superoxide radical anions then subsequently 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 further react with the valence band holes to form additional hydroxyl radicals. Degradation of organic substances can be achieved by their reaction with hydroxyl radicals (˙OH) or direct attack from the valence band holes. Recombination of the photogenerated electrons and holes might occur and indeed it has been suggested that preadsorption of dye on to the photocatalyst could be prerequisite for highly efficient degradation. The heterogeneous ZnO photocatalytic process being a complex sequence of reaction that can be expressed by the following set of simplified equations shown below [26-28].

$$ZnO + h\upsilon_{visible} \longrightarrow ZnO\,(h^+_{VB} + e^-_{CB}) \tag{14}$$

$$ZnO\,(h^+_{VB}) + H_2O \longrightarrow ZnO + H^+ + {}^{\bullet}OH \tag{15}$$

$$ZnO\,(h^+_{VB}) + OH^- \longrightarrow ZnO + {}^{\bullet}OH \tag{16}$$

$$ZnO\,(e^-_{CB}) + O_2 \longrightarrow ZnO + O_2^{\bullet -} \tag{17}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \tag{18}$$

$$HO_2^{\bullet} + H^+ + ZnO\,(e^-_{CB}) \longrightarrow H_2O_2 + ZnO \tag{19}$$

$$H_2O_2 + ZnO\,(e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- + ZnO \tag{20}$$

$$DB\ 1 + {}^{\bullet}OH \longrightarrow \text{Degradation Products} \tag{21}$$

$$DB\ 1 + (h^+_{VB}) \longrightarrow \text{Oxidation Products} \tag{22}$$

$$DB\ 1 + (e^-_{CB}) \longrightarrow \text{Reduction Products} \tag{23}$$
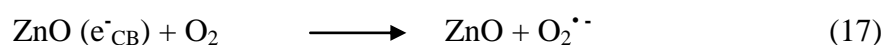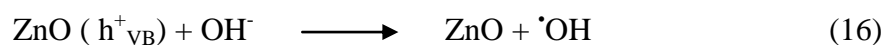
However in addition to the afore mentioned processes the ZnO photodegradation of dyes might also occur by photosensitization. The dye cation radical would react with molecular oxygen or with an oxygenated radical species to yield a mineralized product. We anticipate a parallel mechanism in case of dyes. There may be direct absorption of visible light by the dye molecule that could lead to charge injection from the excited state of the conduction band of the semiconductor as summarized in the following equation:

$$DB\ 1 + h\upsilon_{visible} \longrightarrow {}_1DB\ 1^* \text{ or } {}_3DB\ 1^* \tag{24}$$

$${}_1DB\ 1^* \text{ or } {}_3DB\ 1^* + ZnO \longrightarrow DB\ 1^{+\bullet} + ZnO\,(e^-_{CB}) \tag{25}$$

$$ZnO\,(e^-_{CB}) + O_2 \longrightarrow ZnO + O_2^{\bullet -} \tag{26}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \tag{27}$$

$$HO_2^{\bullet} + H^+ + ZnO\,(e^-_{CB}) \longrightarrow H_2O_2 + ZnO \tag{28}$$

$$H_2O_2 + ZnO\,(e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- + ZnO \tag{29}$$

$$DB\ 1^{+\bullet} + OH^- \longrightarrow DB\ 1 + {}^{\bullet}OH \tag{30}$$

$$DB\ 1^{+\bullet} + O_2^{\bullet -} \longrightarrow \text{Degradation products} \tag{31}$$

$$DB\ 1\,/\,DB\ 1^{+\bullet} + {}^{\bullet}OH \longrightarrow \text{Degradation products} \tag{32}$$
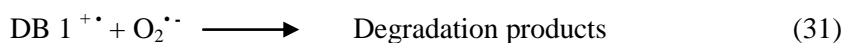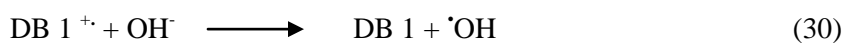
Dye molecules interact with $O_2^{\bullet -}$ $^{\bullet}OH_2$, or OH^- species to generate intermediates that ultimately led to the formation of degradation products. Hydroxyl radical ($^{\bullet}OH$) radical being very strong oxidizing agent mineralizes dye to end product. The role of reductive pathways in heterogeneous photocatalysis has been found to be in minor extent as compared to oxidation [24, 25].

$$DB\ 1\,(DB\ 1^{+\bullet}) + {}^{\bullet}OH \longrightarrow \text{Decolorization of DB 1}$$
$$\downarrow$$
$$\text{Degradation of DB 1 involving organic intermediates}$$
$$\downarrow \text{ Mineralization}$$
$$CO_2\ (gas) + H_2O + NO_3^- + SO_4^{2-} \tag{33}$$

Conclusion

The role of various operating parameters on the photocatalytic degradation of direct blue 1 dye has been explored in the present study. Photocatalytic processes are safe, low cost, ease of controlling parameters and their high efficiency in degrading recalcitrant organic and inorganic substances in aqueous systems. It has also been concluded that various operating parameters such as dye concentration, catalyst amount, photocatalyst type, light intensity, pH, and the presence of pottassium persulphate, hydrogen peroxide, sodium carbonate and sodium chloride in solution significantly influenced the photocatalytic degradation rate of dyes. UV-Vis spectra also ascertained the complete degradation of direct blue 1 dye. Estimated COD, determination of CO_2 further confirmed the mineralization of dye under investigation. Optimizing the degradation parameters has always been crucial and the investigated process is eco friendly way to reduce the pollution load of wastewater.

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