**Research Article**

Photocatalytic Degradation of Azure B Dye using ZnO with Visible Irradiation

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Abstract

The photocatalytic degradation of an azure B in aqueous solution with ZnO as photocatalyst has been investigated under visible irradiation. The study on the effect of various photocatalysts reveals that ZnO is the best catalyst in comparison to other commercial photocatalysts. 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.
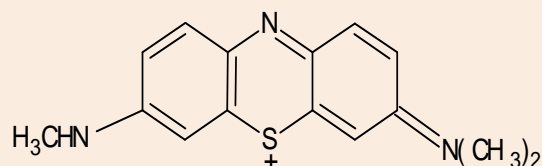
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Introduction

Water is an important natural resource for sustainable ecosystems, human life and economical development. The control of water pollution has become of increasing importance in recent years. Dyes make the world more beautiful through colored products, but cause a lot of problems in the environment. For decoloration and degradation of textile waste water many applicable methods have been developed. A variety of physical, chemical, and biological methods, such as coagulation, adsorption, membrane process, and oxidation-ozonation are presently available for treatment of dye wastewater [1-3]. 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 the formation of low-molecular-weight carboxylic acids or to complete degradation of pollutants to CO_2 and H_2O [4–6]. Nowadays, heterogeneous photocatalysis processes are one of the most efficient methods for destroying organic pollutants and dyes in aqueous media [7-8]. Photocatalytic oxidation is cost effective and capable of degrading any complex organic chemicals when compared to other purification techniques. ZnO is an important photocatalyst due to its strong oxidizing power, non-toxicity and long term photostability [9]. UV radiation sources commonly used are expensive and pollutant. Important criteria for a new energy source are low cost, ample supply, safety, and being pollution free. Therefore AOPs which can be driven by solar radiation are of special interest, making the development of suitable technologies for practical applications very attractive. As the majority of the solar radiation intensity reaching the earth surface is in the visible range (400–800 nm), visible light active system has become a priority for developing the future generation of photo catalytic materials.

In order to use sunlight energy effectively, the design and development of photocatalytic systems capable of operating under visible or solar light irradiation have been desired for the applications of photocatalytic system especially to the environmental concerns [10].
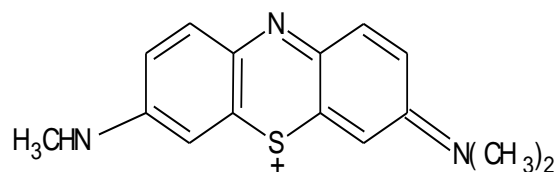
Figure 1 Azure B

Experimental

Azure B 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. 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±0.3°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: % 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 [11].

Result and Discussion

Effect of dye concentration variation

Effect of variation of dye concentration was studied by taking different concentrations of azure B from 1.0×10^{-5} mol dm^{-3} to 7.0×10^{-5} mol dm^{-3}. The results are reported in Figure 2. The photocatalytic degradation rate was found to be increased from 5.14×10^{-4} s^{-1} to 6.98×10^{-4} s^{-1} with increasing concentration of dye up to 3.0×10^{-5} mol dm^{-3}. Further increase in the concentration beyond this limit decreased the degradation rate from 4.10×10^{-4} s^{-1} to 1.91×10^{-4} s^{-1}. It was observed that the rate of photocatalytic degradation increased with an increase in the concentration of the dyes. It might be due to the fact that as the concentration of dye increased more dye molecules would be available for excitation and energy transfer and hence, an increase in the rate of photocatalytic degradation of the dyes was observed. The rate of photocatalytic degradation was found to be decreased with further increase in the concentration of the dye i.e. above 4.0×10^{-5} mol dm^{-3} for azure B [12]. This might be due to as the concentration of dye increased number of photons reaching to catalyst surface decreased resulted into lesser number of catalyst molecules underwent excitation and thus affect rate of formation of holes, hydroxyl radicals and supra oxide ions (o^-) got decreased, as a result the rate of degradation also decreased. Further due to fixed catalyst surface area the increase in concentration of dye rate of degradation decreased because limited number of dye molecules attach at the active site of the catalyst and remaining dye molecules persist in solution until earlier attached molecules are degraded and number of active site of catalyst also decreases due less availability of photons for excitation of catalyst molecules. Competitions between dye molecules to get attached on to the active site also affect rate of degradation. At higher concentration numbers of dye molecules are high so more will be the competition for attachment to active site of catalyst between the dye molecules and resulted into the reduction in the rate of degradation [13].
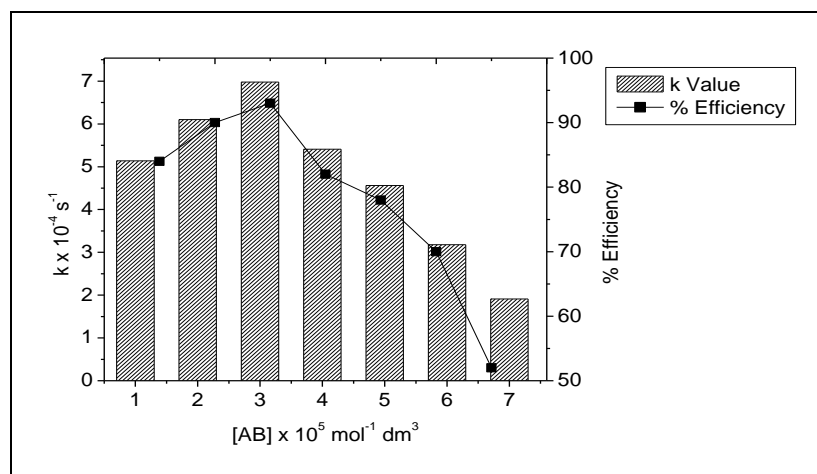
Figure 2 Effect of dye concentration variation: ZnO = 150 mg/100 mL, pH = 8.0
Light intensity $= 25 \times 10^3$ lux, Temperature $= 30 \pm 0.3 \, ^0C$

Effect of catalyst amount variation

To study the effect of catalyst loading on the photocatalytic system, the experiments were carried out by varying the catalyst loading from 50 mg/100 mL to 350 mg /100 mL. In the photocatalytic process, the reaction takes place on the surface of the catalyst, therefore amount of catalyst loaded to the system affect the efficiency of the reaction [14]. The results are shown in Figure 3. The rate of degradation of the azure B dye increased from 5.25×10^{-4} s^{-1} to 6.98×10^{-4} s^{-1} with the increase in amount of ZnO from 50 mg/100 mL to 150 mg/100 mL. Further increase in amount of ZnO from 200 mg/100 mL to 350 mg/100 mL resulted into decreased in rate constant from 5.29×10^{-4} s^{-1} to 4.10×10^{-4} s^{-1} of photocatalytic reaction. The azure B degradation rate found to be increased on increasing ZnO loading up to a certain value and then slightly decreased with increasing ZnO loading. The increased degradation rate that followed the increase in the catalyst loading could be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the compound solution molecules are adsorbed on ZnO no improvement was achieved by adding more catalyst. The decreased in efficiency, might be due to an increased opacity of the suspension and to an enhancement of the light reflectance, because of the excess of ZnO particles. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of ZnO which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction. The degradation rate was found to be maximum 6.98×10^{-4} s^{-1} at 150 mg/100 mL of catalyst loading [15].
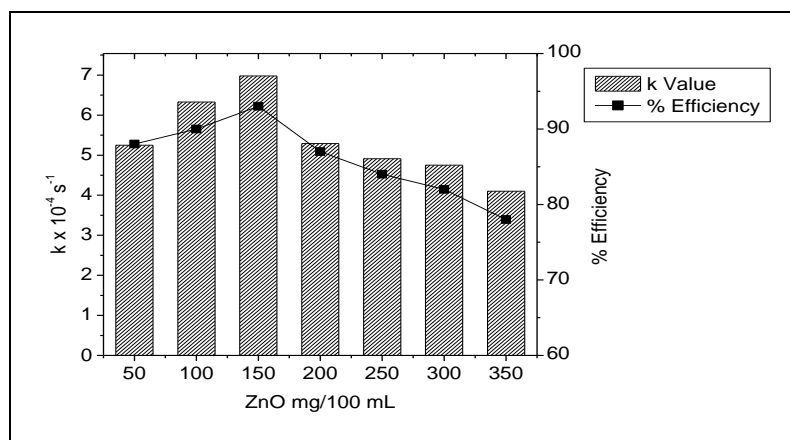

Figure 3 Effect of catalyst amount variation**:** [AB] $= 3.0 \times 10^{-5}$ mol dm^{-3}, pH = 8.0, Light intensity $= 18 \times 10^3$ lux, Temperature $= 30 \pm 0.3 \, ^0C$

Effect of pH variation

The pH of the medium plays a significant role on rate of degradation. Therefore, the effect of pH on the degradation rate of dye was studied in the pH range 5 to 10. The results are reported in **Figure 4**. The apparent first order rate constants values were obtained under different experimental conditions. The rate constants increased from 5.52×10^{-4} s^{-1} to 6.98×10^{-4} s^{-1} with the increase in pH 5.0 to 8.0. Thereafter, rate constant values decreased to $4.79 \times 10^{-4} s^{-1}$ on further increase in pH up to 10. Degradation studies could not be performed in lower pH because in highly acidic medium, semiconductor ZnO was soluble in water. It has been observed that rate of degradation increased with increase in pH but after a certain value of pH 8.0, the rate of reaction decreased under experimental conditions. However, it has been observed that the reaction rate got slightly increased with increasing the pH of the medium. The increased in rate of degradation in alkaline medium might be explained on the basis of the fact that larger number of hydroxyl ions ($^-$OH ions) were available at higher pH values $^-$OH ions would generate more ·OH radicals by combining with the hole and these hydroxyl radicals are considered responsible for the degradation of dye. But after a certain value of pH i.e. 8.0, a further increase in pH of the medium decreased the rate of degradation. It might be due to the fact that the dye could not remain in its cationic form due to the greater concentration of OH$^-$ ions and as such, the reaction rate decreased and it would not feel any force of attraction between negatively charged semiconductor surface (due to adsorption of OH$^-$ ions) and the neutral form of the dye. There is a greater probability for the formation of hydroxyl radicals ($^-$OH radicals) effect of photocatalysis. These ·OH radicals are actual oxidizing species responsible for the degradation of dye [16].
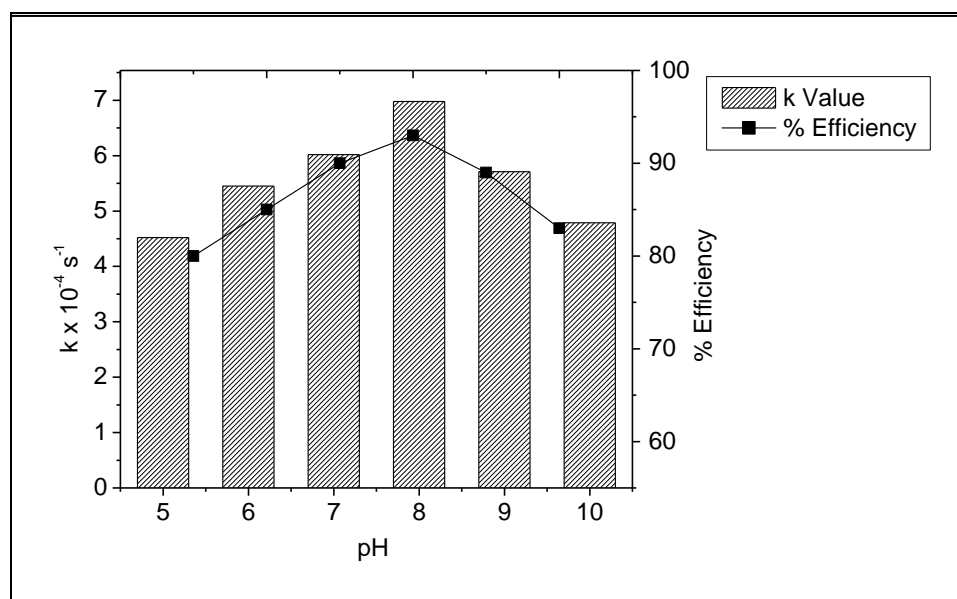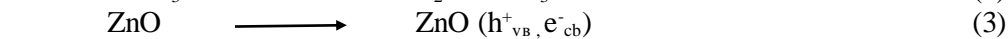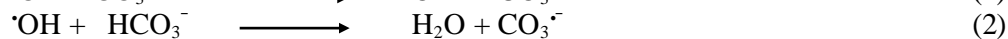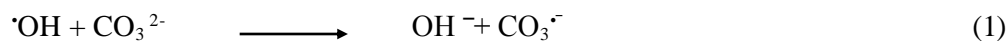

Figure 4 Effect of pH variation**:** [AB] = 3.0×10^{-5} mol dm^{-3} Light intensity = 25×10^3 lux, Temperature = 30 ± 0.3 ^{0}C

Effect of Na$_2$CO$_3$ and NaCl

Sodium carbonate is the common auxiliary chemical employed in textile processing operations. It is mainly used in the dyeing bath in order to adjust the pH of the bath as it plays an important role in fixing the dye on the fabrics and in the fastness of color. Therefore, the wastewater from the dyeing operations contain considerable amount of carbonate ions. Similarly sodium chloride also comes out in the effluents along with sectional wastes of textile mills. Hence it is important to study the influence of carbonate and chloride ions in the photodegradation efficiency of the dye under investigation. Experiments were performed in the presence of different quantities of sodium carbonate and sodium chloride. The effect of presence of Na$_2$CO$_3$ and NaCl ranging from 2.0×10^{-5} mol dm^{-3} to 14.0×10^{-5} mol dm^{-3} is shown in Figure 5. Reaction rate decreased from 3.60×10^{-4} s^{-1} to 1.76×10^{-4} s^{-1} and 3.49×10^{-4} s^{-1} to 1.68×10^{-4} s^{-1}

on increase in concentration of Na_2CO_3 and NaCl from 2.0 $\times$ 10^{-5} to 14.0 $\times$ 10^{-5} mol dm^{-3} respectively. The degradation rate constant values gradually decreased with the increasing carbonate and chloride ions concentration as shown in Fig. 5. The decrease in the degradation rate of dye in the presence of carbonate and chloride ions would be due to the hydroxyl scavenging property of carbonate and chloride ions which could be accounted from the following reactions (Eqs. (1) – (6).

$$^{\cdot}OH + CO_3^{\,2-} \longrightarrow OH^- + CO_3^{\cdot -} \tag{1}$$
$$^{\cdot}OH + HCO_3^- \longrightarrow H_2O + CO_3^{\cdot -} \tag{2}$$
$$ZnO \longrightarrow ZnO\,(h^+_{VB}, e^-_{cb}) \tag{3}$$
$$Cl^- + {}^{\cdot}OH \longrightarrow Cl^{\cdot} + OH^- \tag{4}$$
$$Cl^- + h^+_{VB} \longrightarrow Cl^{\cdot} \tag{5}$$
$$Cl^{\cdot} + Cl^- \longrightarrow Cl_2^{-\,\cdot} \tag{6}$$

Although chlorine radicals were formed slowly, they got instantaneously converted into chloride radical anion. Alternatively, surface sites normally would be available at the ZnO/dye solution interface for adsorption and electron transfer from the dye could be blocked by anions such as chloride which are not readily oxidisable but yet very effective inhibitors for the detoxification process. However, washing the catalyst with pure water can fully restore its photocatalytic activity when chloride ions are present in the wastewater [17,18].
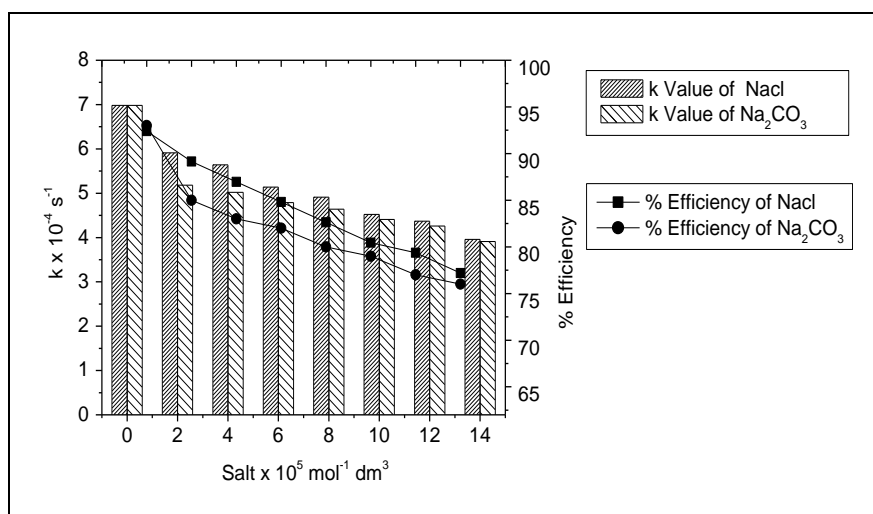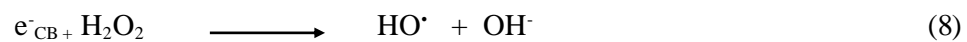

Figure 5 Effect of Na_2CO_3 and NaCl: [AB] = 3.0 $\times$ 10^{-5} mol dm^{-3} ZnO = 150 mg/100 mL, Light intensity = 25 $\times$ 10^3 lux, pH = 8.0, Temperature = 30 $\pm$ 0.3 ^{0}C

Effect of H_2O_2 and $K_2S_2O_8$

The degradation rate has been studied at different concentrations of hydrogen peroxide and potassium persulphate. The effect of addition of H_2O_2 in the range of 2.0 $\times$ 10^{-6} mol dm^{-3} to 14.0 $\times$ 10^{-6} mol dm^{-3} on the photocatalytic oxidation has been investigated. The results are shown in Figure 6. The addition of H_2O_2 in the range 2.0 $\times$ 10^{-6} mol dm^{-3} to 6.0 $\times$ 10^{-6} mol dm^{-3} increased the degradation rate from 7.71 $\times$ 10^{-4} s^{-1} to 8.98 $\times$ 10^{-4} s^{-1} in 30 min. Further increase in the H_2O_2 concentration limited the removal rate. Hence, 6.0 $\times$ 10^{-6} mol dm^{-3} H_2O_2 concentration found to be optimal for the degradation. Increase in H_2O_2 level enhanced the degradation rate up to the optimal load but beyond which inhibition occurred. Similar observations have been reported in dye degradation and organic contaminant degradation[19]. The enhancement of decolorization and degradation by addition of H_2O_2 could be due to increase in the hydroxyl radical concentration in following equations:
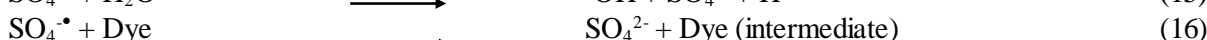
$$O_2 + e^- \longrightarrow O_2^{\cdot -} \tag{7}$$

$$e^-_{CB} + H_2O_2 \longrightarrow HO^\bullet + OH^- \tag{8}$$
$$H_2O_2 + h\upsilon \longrightarrow 2HO^\bullet \tag{9}$$
$$H_2O_2 + O_2^{\bullet-} \longrightarrow HO^\bullet + HO^- + O_2 \tag{10}$$

The inhibition of the degradation of the dye beyond the optimum load of H_2O_2 might be due to the hydroxyl radical scavenging effect of H_2O_2. The reaction between excess hydrogen peroxide and hydroxyl radical ($^\bullet OH$) generate hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of the dye (Eqs. (11) and (12)).

$$H_2O_2 + HO^\bullet \longrightarrow H_2O + {}^\bullet HO_2 \tag{11}$$
$${}^\bullet HO_2 + HO^\bullet \longrightarrow H_2O + O_2 \tag{12}$$
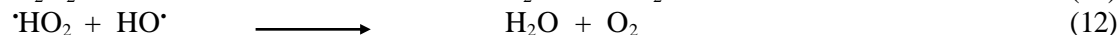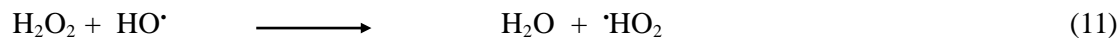
The effect of addition of $K_2S_2O_8$ on the photocatalytic oxidation of AB has also been studied by varying the concentration $K_2S_2O_8$ from 2.0×10^{-6} mol dm^{-3} to 14.0×10^{-6} mol dm^{-3}. The results are shown in Figure 6. Addition of 2.0×10^{-6} mol dm^{-3} to 6.0×10^{-6} mol dm^{-3} of $K_2S_2O_8$ increased the degradation rate from 7.06×10^{-4} s^{-1} to 8.48×10^{-4} s^{-1} in 30 min. Further increase in the addition (6.0×10^{-6} mol dm$^{-3)}$ decreased the degradation slightly. Similar enhancements by the addition of $S_2O_8^{2-}$ have been reported [20, 21]. Addition of persulphate to photocatalytic processes enhanced the degradation rate in following equations:

$$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^{-\bullet} + SO_4^{2-} \tag{13}$$
$$SO_4^{-\bullet} + e^-_{cb} \longrightarrow SO_4^{2-} \tag{14}$$
$$SO_4^{-\bullet} + H_2O \longrightarrow {}^\bullet OH + SO_4^{2-} + H^+ \tag{15}$$
$$SO_4^{-\bullet} + Dye \longrightarrow SO_4^{2-} + Dye\ (intermediate) \tag{16}$$
$$SO_4^{-\bullet} + Dye\ (intermediate) \longrightarrow Mineralization \tag{17}$$

At high dosage of $S_2O_8^{2-}$ the inhibition of reaction occurred due to the increase in concentration of SO_4^{2-} ion. The excess of SO_4^{2-} ion got adsorbed on the ZnO surface and reduced the catalytic activity. The adsorbed SO_4^{2-} ion would also react with photogenerated holes (Eq. (18)) and with hydroxyl radicals (Eq. (19)).

$$SO_4^{-\bullet} + h^+ \longrightarrow SO_4^{-\bullet} \tag{18}$$
$$SO_4^{2-} + {}^\bullet OH \longrightarrow {}^\bullet OH + HO^- \tag{19}$$
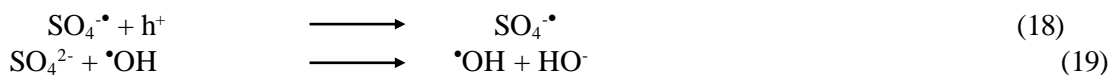
Since $SO_4^{\bullet-}$ is less reactive than $^\bullet OH$ radical and h$^+$, the excess SO_4^{2-} reduced the photodegradation of the dye.

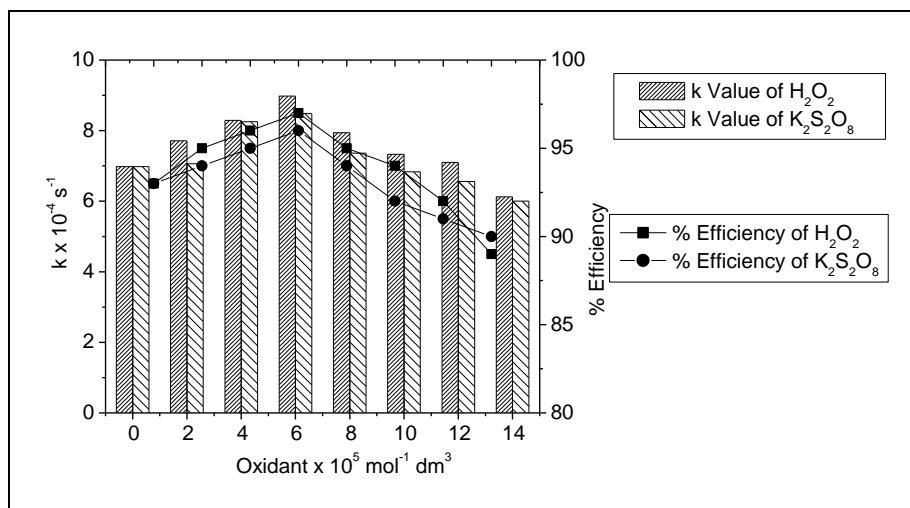

Figure 6 Effect of H_2O_2 and $K_2S_2O_8$: [AB] = 3.0×10^{-5} mol dm^{-3}, pH = 8.0 ZnO = 150 mg/100 mL, Light intensity = 25×10^3 lux, Temperature = $30 \pm 0.3\ ^0$C

Effect of light intensity

The effect of light intensity on rate of degradation has also been investigated. In order to determine the effect of light intensity, the experiments were performed by varying light intensity from 10×10^3 lux to 35×10^3 lux for dye solutions of 3.0×10^{-5} mol dm^{-3}/100 mL at pH 8.0. The results obtained are reported in Figure 7. The rate of degradation increased from 3.86×10^{-4} s^{-1} to 8.09×10^{-4} s^{-1} with increase in light intensity on the catalytic surface from 10×10^3 lux to 35×10^3 lux. We found that as light intensity was increased gradually the rate of degradation of dye molecules also increased. These changes in rate of degradation of dye molecules by variation in light intensity was due to the reason that as the light intensity was increased number of photons reaching the catalyst surface also got increased, so number of excited catalyst molecules increased and resulted into as increase in the number of holes, hydroxyl radicals and supra oxide ions (o$^-$). When the light intensity was increased more than 30×10^3 lux, temperature got increased therefore higher intensities were avoided [22-24].
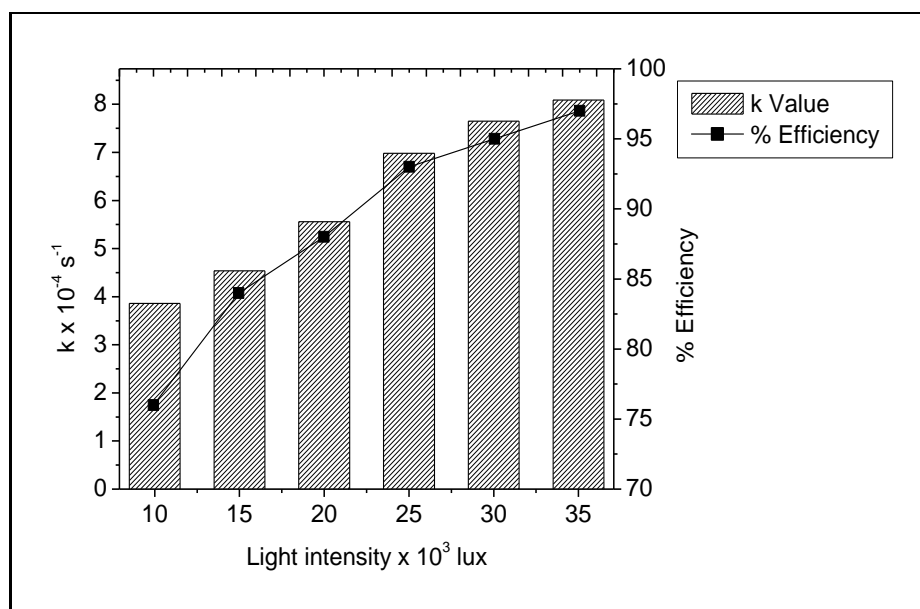

Figure 7 Effect of light intensity: [AB] = 3.0×10^{-5} mol dm^{-3}, ZnO= 150 mg/100 mL
pH = 8.0, Light intensity = 25×10^3 lux, Temperature = 30 ± 0.3^0C

Effect of other photocatalysts

The influence of different photocatalysts (ZnO, BiOCl, TiO$_2$, BaCrO$_4$ and CdS) on the photocatalytic degradation of azure B was investigated and results are shown in the **Table 1**. ZnO, TiO$_2$ and BiOCl are found to be more efficient than BaCrO$_4$ and CdS. The order of activities of the photocatalysts has been found to be ZnO > BiOCl > TiO$_2$ > BaCrO$_4$ > CdS. Thus ZnO has emerged as the most efficient catalyst [25]. 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 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 showed less activity since its conduction band is much lower than that of ZnO and TiO$_2$. The smaller band gap cause 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 [26].

Table 1 Effect of various photocatalysts: [AB] = 3.0×10^{-5} mol dm^{-3}, pH = 8.0
Light intensity $= 25 \times 10^3$ lux, Temperature $= 30 \pm 0.3$ ^{0}C

Photocatalysts 150 mg/100mL	Bandgap (eV)	k × 10^{-4} s^{-1}	t$_{1/2}$ × 10^3 s
CdS	2.3	3.37	2.05
BaCrO$_4$	2.6	3.64	1.90
TiO$_2$	3.2	3.76	1.84
ZnO	3.2	6.98	0.99
BiOCl	3.4	5.71	1.21

COD and CO$_2$ measurement during mineralization of AB

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 2** and **Figure 8**.

During 8 hours of irradiation, reduction in COD value from 224 mg/L to 0 mg/L and increase in CO_2 value from 22 mg/L to 189 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 [27, 28].
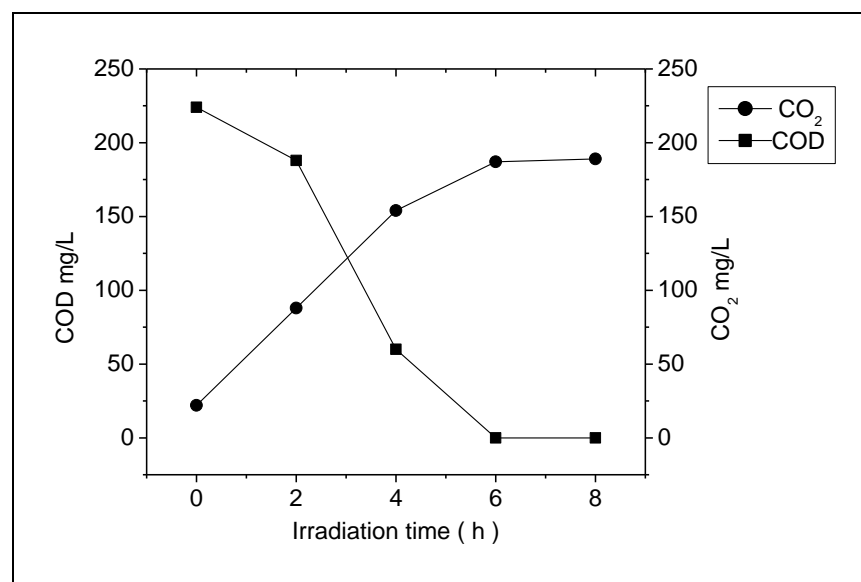

Figure 8 COD and CO$_2$ trend during mineralization of AB

Table 2 COD and CO_2 measurement during mineralization of AB; [AB] = 3.0×10^{-5} mol, ZnO= 150 mg/100 mL, pH = 8.0; Light intensity = 26×10^3 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	224	22	0	0	0	8.0
2	188	73	16	6.8	8.5	7.6
4	60	154	73	10.6	12.7	6.8
6	0	187	100	14.8	18.4	7.1
8	0	189	100	15.1	18.8	6.5

Spectral changes of azure B degradation

The UV–Vis analysis for the decolorization of azure B is shown in Figure 9. Azure B exhibit absorption peak at λ max 500 nm in visible region which gradually diminished and finally disappeared during the reaction, which indicated that the dye got decolorized. Similarly the peak in the UV region at λ max 215 and 310 nm got decreased with the passage .of time, thereby confirming the complete mineralization of dye. Complete mineralization of azure B was observed after 6 h of irradiation time [29].
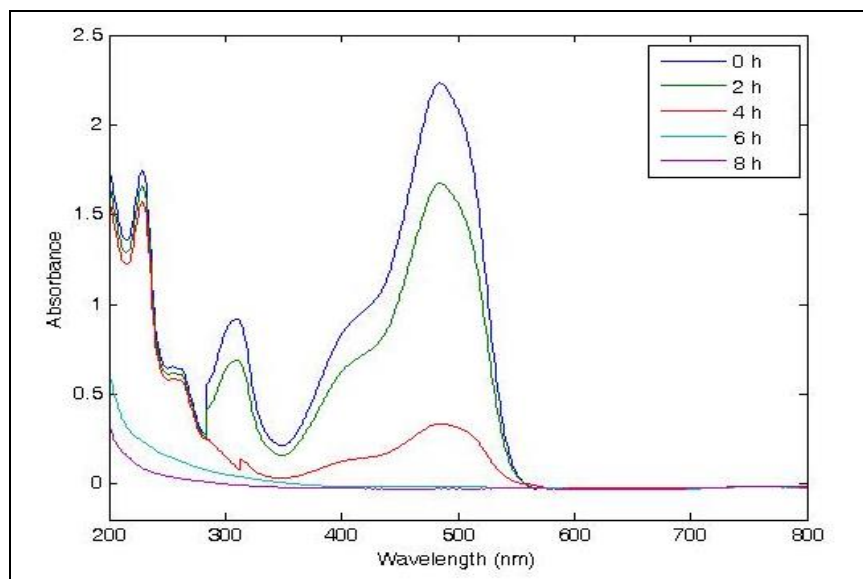

Figure 9 UV-Vis spectrum of AB at 0 to 8 h: [AB] = 3.0×10^{-5} mol dm^{-3}; ZnO = 150 mg/ 100 mL, Light intensity = 25×10^3 lux, pH = 8.0; Temperature = 30 ± 0.3 ^{0}C

Mechanism of azure B degradation

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.
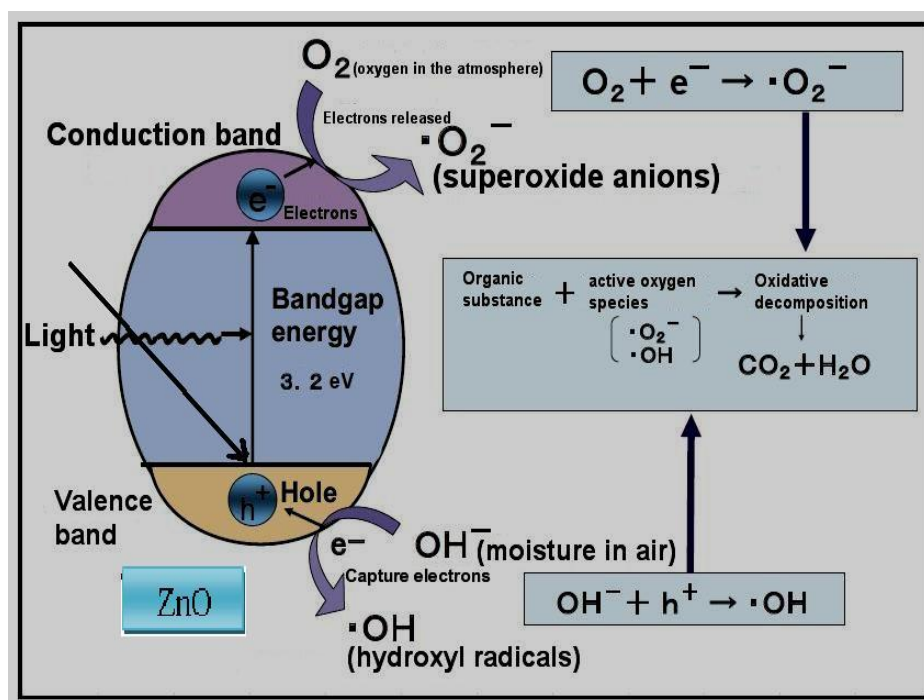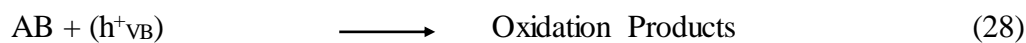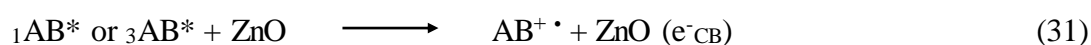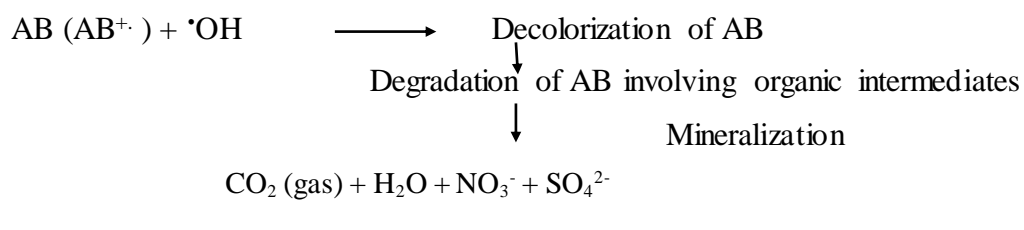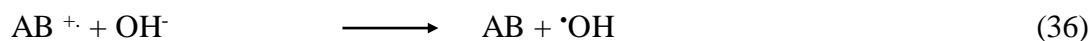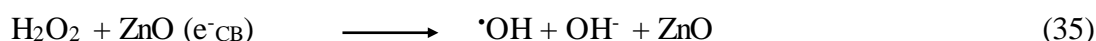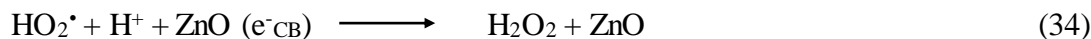
Figure 10 ZnO particle in water under visible light irradiation

The heterogeneous ZnO photocatalytic process is a complex sequence of reaction that can be expressed by the following (Figure 10) set of simplified equations shown below [30,31].

$$ZnO + h\upsilon_{visible} \longrightarrow ZnO\ (h^+_{VB} + e^-_{CB}) \tag{20}$$

$$ZnO\ (h^+_{VB}) + H_2O \longrightarrow ZnO + H^+ + {}^{\bullet}OH \tag{21}$$

$$ZnO\ (h^+_{VB}) + OH^- \longrightarrow ZnO + {}^{\bullet}OH \tag{22}$$

$$ZnO\ (e^-_{CB}) + O_2 \longrightarrow ZnO + O_2^{\bullet -} \tag{23}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \tag{24}$$

$$HO_2^{\bullet} + H^+ + ZnO\ (e^-_{CB}) \longrightarrow H_2O_2 + ZnO \tag{25}$$

$$H_2O_2 + ZnO\ (e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- + ZnO \tag{26}$$

$$AB + {}^{\bullet}OH \longrightarrow Degradation\ Products \tag{27}$$

$$AB + (h^+_{VB}) \longrightarrow Oxidation\ Products \tag{28}$$

$$AB + (e^-_{CB}) \longrightarrow Reduction\ Products \tag{29}$$

We anticipate a parallel mechanism in case of dyes. There may be direct absorption of visible light by the dye molecule can lead to charge injection from the excited state of the conduction band of the semiconductor as summarized in the following equation [32-34].

$$AB + h\upsilon_{visible} \longrightarrow {}_1AB^* \ or \ {}_3AB^* \tag{30}$$

$${}_1AB^* \ or \ {}_3AB^* + ZnO \longrightarrow AB^{+\bullet} + ZnO\ (e^-_{CB}) \tag{31}$$

$$ZnO\ (e^-_{CB}) + O_2 \longrightarrow ZnO + O_2^{\bullet -} \tag{32}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \tag{33}$$

$$HO_2^{\bullet} + H^+ + ZnO\ (e^-_{CB}) \longrightarrow H_2O_2 + ZnO \tag{34}$$

$$H_2O_2 + ZnO\ (e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- + ZnO \tag{35}$$

$$AB^{+\cdot} + OH^- \longrightarrow AB + {}^{\bullet}OH \tag{36}$$

$$AB^{+\bullet} + O_2^{\bullet -} \longrightarrow Degradation\ products \tag{37}$$

$$AB\ /\ AB^{+\bullet} + {}^{\bullet}OH \longrightarrow Degradation\ products \tag{38}$$

$$AB\ (AB^{+\cdot}) + {}^{\bullet}OH \longrightarrow Decolorization\ of\ AB$$

$$\downarrow$$

Degradation of AB involving organic intermediates

$$\downarrow \quad Mineralization$$

$$CO_2\ (gas) + H_2O + NO_3^- + SO_4^{2-} \tag{39}$$
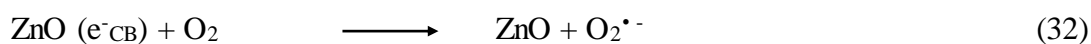
Conclusion

The role of various operating parameters on the photocatalytic degradation of azure B dye has been explored in the present study. ZnO has been found to be an efficient and viable photocatalyst for the degradation and mineralization of various toxic organic pollutants under investigation. It has also been concluded that various operating parameters such as dye concentration, catalyst amount, photocatalyst type, light intensity, initial pH of the reaction medium, 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 selected dyes. Estimated COD, determination of CO_2 further confirmed the mineralization of dyes 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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