Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2010 Desalination Publications. All rights reserved
doi: 10.5004/dwt.2010.1466

24 (2010) 132–139
December

Influence of operational parameters on photodegradation of Acid Black 1 with ZnO

B. Krishnakumar, K. Selvam, R. Velmurugan, M. Swaminathan*

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India
Tel. +914144225072; Fax +914144225072; e-mail: chemres50@gmail.com

Received 29 June 2009; accepted 12 May 2010

ABSTRACT

The photodegradation of Acid Black 1 (AB 1) using ZnO as photocatalyst in aqueous solution has been investigated under different conditions. The degradation is higher with UV/ZnO process than with UV/TiO_2-P25 process at neutral pH 7. The influence of operational parameters such as the amount of photocatalyst, dye concentration and initial pH on degradation by ZnO has been analyzed. At pH 7, maximum degradation efficiency is observed and the leaching of Zn^{2+} due to photocorrosion is also significantly reduced when compared to pH 3 and 5. The addition of oxone increases the dye removal where as KIO_4, KIO_3 and H_2O_2 fails. The degradation of AB 1 follows pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. GC-MS analysis reveals the formation of azobenzene, 3-aminobenzene-1,2-diol, 2-aminobenzene-1,4-diol and 5-aminobenzene-1,3-diol as intermediates. The degradation of AB 1 has also been confirmed by COD measurements.

Keywords: Acid Black 1; Degradation; Photocatalysis; Oxidants; Metal ions

1. Introduction

The color of wastes is the most apparent indicator of waste pollution and it should be reduced before their drop. The presence of small amount of dyes (below 1 ppm) is clearly visible and considerably influences the water environment. Removal of color from wastes is often more important than other colorless organic substances. Azo dyes are the most important class of synthetic organic dyes used in the textile industry and so they are common industrial pollutants [1–6].

The disadvantage of commonly used traditional methods of wastewater purification is the fact that they are not destructive but only transfer the pollutants from one phase to the other. New technologies of wastewater purification leading to the complete mineralization of organic pollutants are now considered as the most suitable solution of the problem connected with more and more drastic requirements concerning the contamination levels in water and wastewater. Nowadays advanced oxidation processes (AOPs) have been proposed as the alternative methods for water purification [7–9]. AOPs generate a powerful oxidizing agent hydroxyl radical, which completely destroy the pollutants in wastewater quickly and non-selectively. Among AOPs, semiconductor photocatalysis has emerged as important destructive technology leading to the total mineralization of most of the organic pollutants [10]. Most of the AOPs (except Fenton process) use atmospheric air as an oxidant under ambient conditions. Moreover, these processes utilize cheaply available nontoxic semiconductors (TiO_2, ZnO) and leads to total mineralization of organic compounds to CO_2, water and mineral acids.

---

*Corresponding author

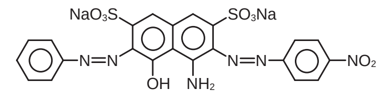
Name	Chemical structure of AB 1	Absorption maxima (nm)
Acid Black 1		320, 615

Fig. 1. The chemical structure and absorption maxima of AB 1.

Different forms of TiO_2 [11] dye-sensitized TiO_2 [12], ZrO_2 [13] and Bi_2O_3 [14–17] have been used as catalysts for photodegradation. Zyoud et al. reported CdS sensitized TiO_2 system for the degradation of phenazopyridine [18]. Non-metal doped TiO_2 catalysts have also been used for photodegradation of dyes [19–21].

Though TiO_2 is the most commonly used photocatalyst for a wide range of organic compounds, ZnO is found to be a suitable alternative to TiO_2 since its photodegradation mechanism has been proved to be similar to that of TiO_2 [22]. ZnO has been reported to be more efficient than TiO_2 under certain conditions. Its higher efficiency than TiO_2 has been reported in the photocatalytic oxidation of paper and pulp mill bleaching wastewater [23], 2-phenylphenol [24] and phenol [25].

Earlier, Grzechulska and Morawski [26] reported the photocatalytic decomposition of azo dye AB 1 using TiO_2 with UV light and also Shu et al. [27] reported the decolourization of AB 1 by the UV/H_2O_2 process. So far the degradation of AB 1 by ZnO had not been investigated. In our earlier work, we have reported photodegradation of a number of toxic chemicals with commercial ZnO using UV and solar light [28–32]. In the present work, we report the photocatalytic degradation of AB 1 with ZnO and the effect of operational parameters on this process.

2. Experimental

2.1. Materials

The commercial azo dye AB 1 (dye content 80.0%) obtained from Aldrich was used as such. The chemical structure is given in Fig. 1. The photocatalyst ZnO was purchased from E. Merck (99% purity). ZnO has a particle size 0.1–4 μm and surface area 5 $m^2\ g^{-1}$. AnalaR grade reagent H_2O_2 (30 w/w%), KIO_3, KIO_4, oxone, Na_2CO_3, Na_2SO_4, $NaHCO_3$, $NaNO_3$ and NaCl were used as received. Double distilled water was used to prepare experimental solutions. The pH of the solutions was adjusted using H_2SO_4 or NaOH.

2.2. Irradiation procedure

For the degradation by UV-A light (365 nm), a Heber Multilamp-photoreactor HML MP 88 was used (Fig. 2). This model consists of 8 W medium pressure mercury vapor lamps set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflector made of highly polished aluminum and built in cooling fan. Cooling fan reduces the heat produced by the lamps in the reaction chamber. It is provided with a magnetic stirrer and 50 mL capacity reaction glass tubes. The light exposure length is 330 mm. As the degradation was significant with four lamps the irradiation was carried out using four parallel 8 W medium pressure mercury lamps. The solution with ZnO and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

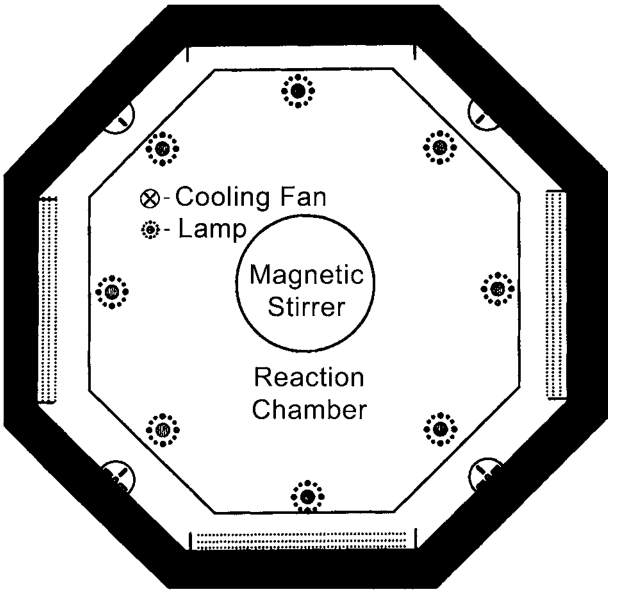


Fig. 2. Schematic diagram of photoreactor.

Fifty milliliters of AB 1 (2×10^{-4} M) with the appropriate amount of catalyst was stirred for 30 min in the dark prior to illumination in order to achieve maximum adsorption of AB 1 onto the semiconductor surface. During the illumination time no volatility of the solvent was observed. At specific time intervals 2 mL of sample was withdrawn and catalyst particle was removed by centrifugation. The changes in the concentration of AB 1 were monitored from their characteristic absorption at 320 and 615 nm using UV-visible spectrophotometer. The absorbance at 615 nm is used to monitor the decolourization of AB 1. The absorbance at 320 nm represents the aromatic part of AB 1 and its decrease indicates the degradation of aromatic part of dye. UV spectral measurements were made using Hitachi U-2001 spectrometer. The pH of the solution was measured by using ELICO LI-10 T model digital pH meter. The leaching of Zn^{2+} was determined by AAS

(Atomic Absorption Spectrometer), ELICO SL 176 Model Double Beam Atomic Absorption Spectrometer. For GC analysis, Perkin-Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used. GC/MS analysis was carried out using GC model: Varian GC-MS-Saturn 2200 Thermo, capillary column VF5MS (5% phenyl–95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness, temperature of column range from 50°C to 280°C (10°C min^{-1}) and injector temperature 250°C. For sample preparation, solution obtained after 15/30 min irradiation was extracted using dichloromethane (DCM) by three times. All the samples were collected and evaporated and dissolved with HPLC grade methanol. Then it was subjected to GC-MS analysis.

2.3. Chemical oxygen demand (COD) measurements

COD was determined using the following procedure. Sample was refluxed with $HgSO_4$, known volume of standard $K_2Cr_2O_7$, $AgSO_4$ and H_2SO_4 for two hours and titrated with standard Ferrous Ammonium Sulfate (FAS) using ferroin indicator. A blank titration was carried out with distilled water instead of dye sample. COD was determined using the following equation

$$\text{COD} = \frac{(\text{Blank titre value} - \text{dye sample titre value}) \times \text{normality of FAS} \times 8 \times 1000}{\text{Volume of sample}}. \tag{1}$$

3. Results and discussion

The UV–vis spectra of AB 1 (2×10^{-4} M) solution at different irradiation times are shown in Fig. 3. The absorption peaks in UV and visible region decrease gradually and finally disappear indicating the complete degradation of the dye. There is no significant change in UV spectra during irradiation and the intensity at 320 and 615 nm decreases during the degradation. This reveals that the intermediates do not absorb at the analytical wavelengths of 320 and 615 nm.

3.1. Photodegradability of AB 1

Fig. 4 shows the percentage of AB 1 (2×10^{-4} M) degradation on irradiation under different conditions. It is found that 88.4% degradation of AB 1 takes place at the time of 60 min in the presence of both ZnO and UV light. This is contrasted with 5.6% decrease in dye concentration for the same experiment performed in the absence of UV light and negligible degradation (0.2%) in the presence of UV without ZnO. The decrease in dye concentration with ZnO in the absence of UV light is due to adsorption of dye on the catalyst. These observations reveal that both UV light and photocatalyst are needed for effective destruction of AB 1. When the photocatalyst TiO_2-P25 was used under same conditions only 57.0% degradation occurred. This shows that UV/ZnO process is more efficient in AB 1 degradation than UV/TiO_2-P25 process for this experimental condition. Since the degradation was effective with ZnO, the influence of

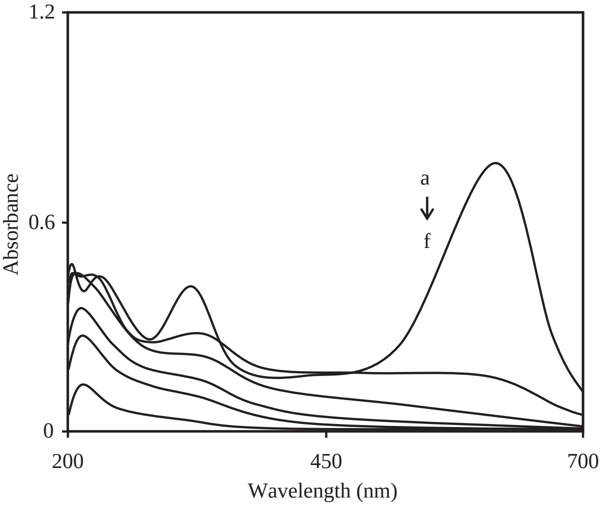


Fig. 3. The changes in UV–vis spectra of AB 1 on irradiation with UV light in the presence ZnO: [AB 1] = 2×10^{-4} M; pH = 7; catalyst suspended = 5 g L^{-1}; airflow rate = 8.1 mL s^{-1}; I = 1.381×10^{-3} einstein L^{-1} s^{-1}. (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min and (f) 60 min.

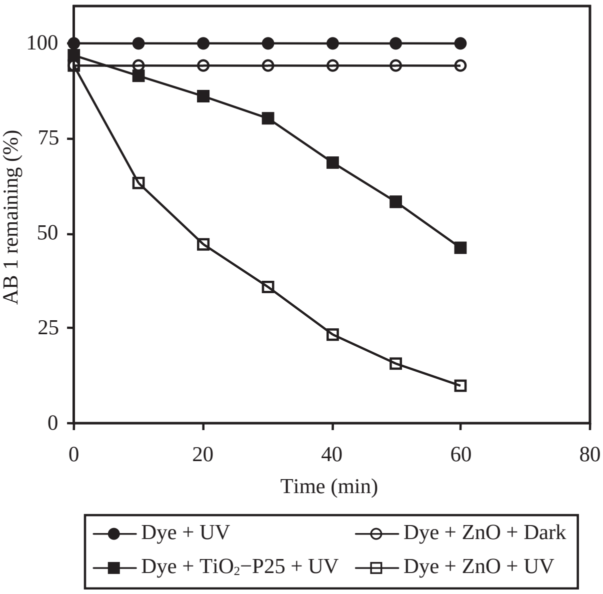


Fig. 4. Photodegradability of AB 1: [AB 1] = 2×10^{-4} M; pH = 7; catalyst suspended = 2 g L^{-1}; airflow rate = 8.1 mL s^{-1}; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

operational parameters had been carried out to find out the optimum conditions.

3.2. Effect of solution pH

The pH is an important parameter in photocatalytic degradation as it is related to the ionization state of the surface of the photocatalyst as well as pollutants [33–36]. pH changes can also influence the adsorption of pollutants on the photocatalyst surface, an important step for the photocatalytic oxidation to take place. The photocatalytic degradation of AB 1 dye containing commercial ZnO obeys pseudo-first-order kinetics. The rate expression is given by

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k[\mathrm{C}], \qquad (2)$$

where k is the pseudo-first-order rate constant. The dye is adsorbed onto the ZnO surface and the adsorption–desorption equilibrium is reached in 30 min. After adsorption, the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (2) gives Eq. (3),

$$\ln(C_0/C) = kt, \qquad (3)$$

where C_0 is the equilibrium concentration of dye and C is the concentration at time 't'. The rate constants (k) were determined from the plot of $\ln(C_0/C)$ vs t. These plots were linear ($R^2 = 0.98 - 0.99$).

The effect of initial pH on AB 1 degradation is shown in Fig. 5. It is pertinent to mention here that the pH of the solution was adjusted before irradiation and it was not maintained throughout the reaction. After 30 min of irradiation the pseudo-first-order rate constants are 0.020, 0.030, 0.034 and 0.021 min^{-1} for ZnO at pH 3, 5, 7, 9 and 11, respectively. It is observed that increase in pH from 3 to 7 increases the removal efficiency of AB 1 with ZnO and above pH 7 the efficiency decreases. The optimum pH for efficient AB 1 removal on ZnO is 7.

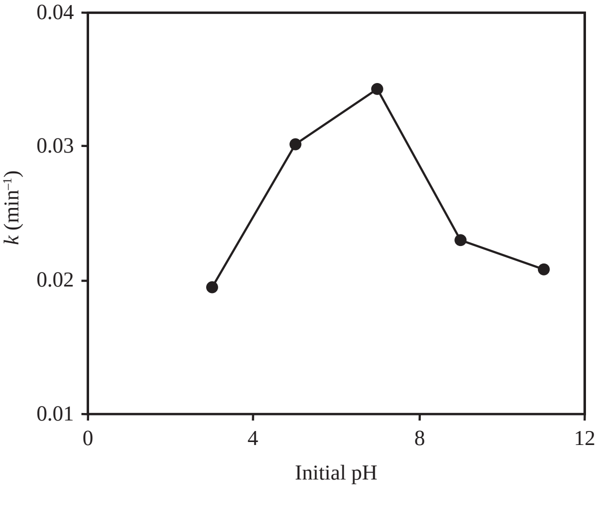


Fig. 5. Effect of pH on photodegradation rate constants: [AB 1] = 2×10^{-4} M; catalyst suspended = 2 g L^{-1}; airflow rate = 8.1 mL s^{-1}; irradiation time = 30 min; $I = 1.381 \times 10^{-3}$ einstein $\mathrm{L}^{-1}\,\mathrm{s}^{-1}$.

The zero-point charge for ZnO is 9.0 and below this value, ZnO surface is positively charged and it is negatively charged above pH 9. Because the dye has two sulfonic acid groups in its structure it exists as negative ions in the pH range 5–7. From pH 5 to 7 the electrostatic attraction between positively charged ZnO and negatively charged dye solution may lead to strong adsorption of dye on ZnO surface. This facilitates the reaction at catalyst surface leading to higher degradation in this pH range.

ZnO is reported to undergo photocorrosion in acidic pH. Hence its leaching was analyzed at different pH. After complete degradation the concentration of Zn^{2+} ions in the solution at different pH was determined using AAS. The amount of Zn^{2+} ions at pH 3, 5, 7, 9 were found to be 10.1, 8.4, 2.6 and 1 ppm, respectively. The leaching is maximum at pH 3 and 5 and it is lowest at pH 9. At the neutral pH 7 the leaching is very less when compared to pH 3 and 5. So the neutral pH 7 can be taken as optimum for the degradation of AB 1. Mixed semiconductor nanocomposites are reported to be stable with small amount of leaching [37].

3.3. Effect of catalyst loading

A series of experiments were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 1 to 6 g L^{-1}. Fig. 6 shows the percentage degradation of AB 1 as a function of catalyst concentration. It is interesting to note that the percentage degradation of AB 1 increases with increase in catalyst concentration from 1 to 5 g $\mathrm{L}^{-1}$and then decreases. Enhancement of removal rate is due to (i) the increase in the amount of catalyst which increases the number of dye molecules adsorbed, (ii) the increase in the density of particles in the area of illumination. The decrease in the removal efficiency of AB 1 at higher concentrations (above 5 g L^{-1}) is due to the enhancement of light reflectance by catalyst particles. Similar results have been reported for the photocatalysis by $\mathrm{TiO_2}$ and ZnO in the degradation of dyes [38–40].

3.4. Effect of initial dye concentration

The effect of various initial dye concentrations on the degradation of AB 1 on ZnO has been investigated.

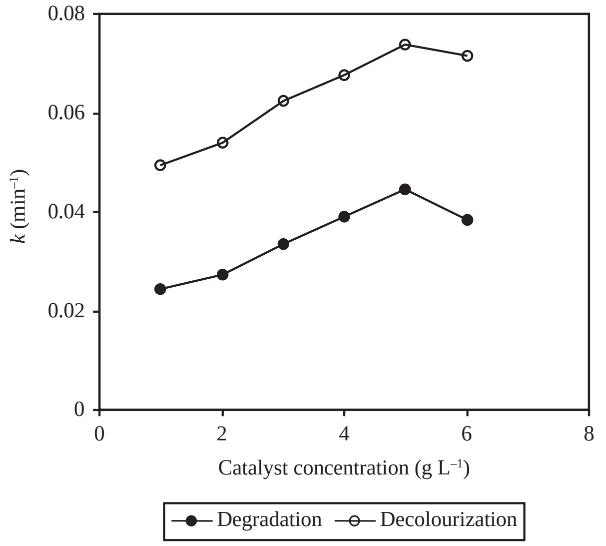


Fig. 6. Effect of photocatalyst dosage on photodegradation: [AB 1] = 2×10^{-4} M; pH = 7; airflow rate = 8.1 mL s^{-1}; irradiation time = 30 min; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

Fig. 7 shows that the increase of dye concentration from 1 to 5 × 10^{-4} M decreases the rate constant from 0.069 to 0.010 min^{-1} for degradation and 0.112 to 0.056 min^{-1} for decolorization in 30 min. The rate of degradation relates to the •OH radical formation on catalyst surface and probability of •OH radical reacting with dye molecule. For all initial dye concentrations, the catalyst amount and UV power are same. Since the generation of hydroxyl radical remains constant, the probability of dye molecule to react with hydroxyl radical decreases. At high initial dye concentrations the path length of photon entering into the solution also decreases.

Many authors [6, 41] have used the Langmuir-Hinshelwood (L-H) kinetic expression to analyze the heterogeneous photocatalytic reaction. The experimental data has been rationalized in terms of the modified form of L-H kinetic model to describe the solid–liquid reaction successfully [42]. The rate of degradation of AB 1 at the surface is proportional to the surface coverage of AB 1 on the ZnO assuming that the adsorption of AB 1 is more on the catalyst surface than the intermediate products [43,44]. The effect of the AB 1 concentration on the rate of degradation is given in the following equation.

$$r = \frac{kKC}{1 + KC}. \tag{4}$$

This equation can be modified as

$$\frac{1}{r} = \frac{1}{kKC} + \frac{1}{k} \tag{5}$$

where C is the initial concentration of AB 1, k is the reaction rate constant and K is the Langmuir adsorption constant. The reaction rate constant, k reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions and K represents the equilibrium constant for adsorption of AB 1 on the illuminated ZnO. The applicability of L-H equation for degradation has been confirmed by the linear plot (correlation coefficient of 0.99), obtained for $1/r$ vs. $1/C$ (Fig. 8). This indicates that the degradation of AB 1 occurred mainly on the surface of ZnO. The

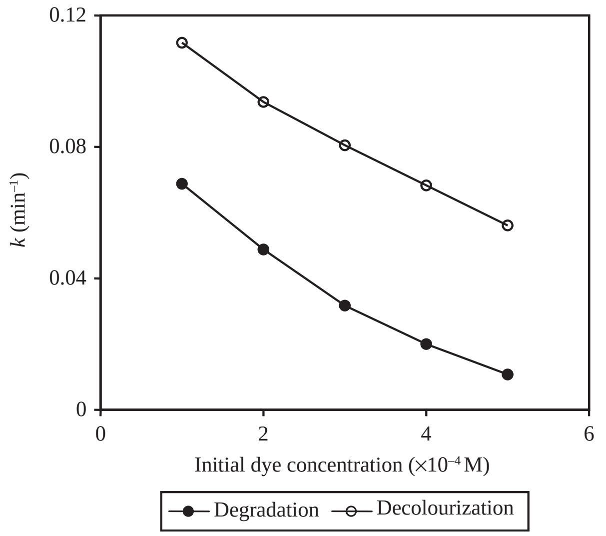


Fig. 7. Effect of initial dye concentration on photodegradation: Catalyst suspended = 5 g L^{-1}; pH = 7; airflow rate = 8.1 mL s^{-1}; irradiation time = 30 min; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

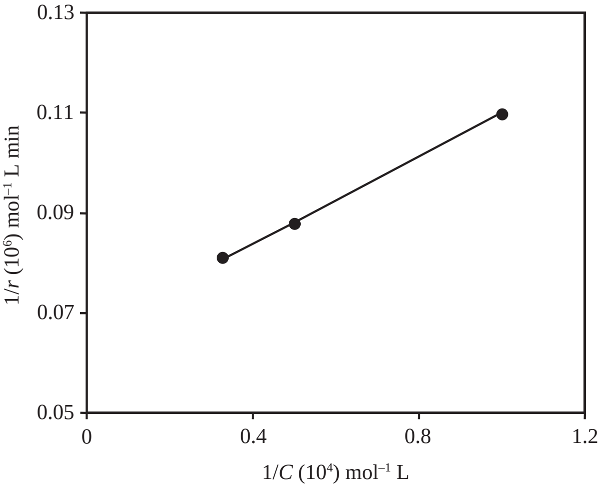


Fig. 8. Linearized reciprocal kinetic plot on the photodegradation of AB 1: catalyst suspended = 5 g L^{-1}; pH = 7; airflow rate = 8.1 mL s^{-1}; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

Table 1
Effect of anions on photodegradation of AB 1 with ZnO by UV light

Anions	Percentage of degradation
Bare ZnO	71.9
Na_2CO_3	41.7
$NaHCO_3$	27.2
NaCl	59.7
$NaNO_3$	52.3
Na_2SO_4	59.7

[Dye] = 2×10^{-4} M; catalyst suspended = 5 g L^{-1}; anions = 0.1 M; irradiation time = 30 min; airflow rate = 8.1 mL s^{-1}; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

values of k and K, determined from the slope and intercept of the plot are 0.0436×10^4 mol L^{-1} min^{-1} and 6.64×10^{-4} L mol^{-1}, respectively.

3.5. *Influence of other factors*

The effect of oxone, KIO_4, KIO_3 and H_2O_2 on the photocatalytic degradation of AB 1 with and without zinc oxide catalyst has been carried out at pH 7. It is observed that oxone enhances the degradation efficiency of ZnO from 72% to 98% in 30 min, whereas KIO_4, H_2O_2, KIO_3 fail to do so. In the presence of oxone alone the photodegradation is 17.5% in 30 min.

The most effective oxidant, oxone is a mono –SO_3^- substituted hydrogen peroxide (HOOH) and has been used in a restricted way as an oxidant in light induced processes. It can liberate one sulfate radical anion ($SO_4^{\bullet-}$) and a hydroxyl radical (Eq. (6)). The sulfate radical anion reacts with water producing hydroxyl radical (Eq. (7)) [45].

$$\mathrm{HSO_5} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{SO_4^{\bullet-}};\ E^0 = 1.82\,e\mathrm{V\ vs.\ NHE} \tag{6}$$

$$\mathrm{SO_4^{\bullet-}} + \mathrm{H_2O} \rightarrow \mathrm{SO_4^{2-}} + {}^{\bullet}\mathrm{OH} + \mathrm{H^+};\ E^0 = 2.60\mathrm{eV\ vs.\ NHE} \tag{7}$$

The influence of added inorganic ions on the degradation of AB 1 is shown in Table 1. The results clearly show that the addition of inorganic anions on the photocatalytic process decreases the degradation rate. After 30 min of irradiation time, 59.7%, 41.7%, 59.7%, 52.3% and 27.2% of degradations occurred by the addition of 0.1 M of Na_2SO_4, Na_2CO_3, NaCl, $NaNO_3$ and $NaHCO_3$, respectively. The order of inhibition of these ions is $HCO_3^- > CO_3^{2-} > NO_3^- > Cl^- \approx SO_4^{2-}$.

The inhibition effect of these ions is due to the reaction of these ions with holes or ${}^{\bullet}OH$ (Eqs. (8)–(12))

Table 2
Effect of transition metal ions on photodegradation of AB 1 with ZnO by UV light

Cations	Percentage of degradation
Bare ZnO	71.9
Ag^+	65.4
Cu^{2+}	74.6
Mg^{2+}	63.0
Fe^{2+}	78.4
Mn^{2+}	26.8

[Dye] = 2×10^{-4} M; catalyst suspended = 5 g L^{-1}; cations = 0.1 M; irradiation time = 30 min; airflow rate = 8.1 mL s^{-1}; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}.

$$\mathrm{SO_4^{2-}} + \mathrm{h_{VB}^+} \rightarrow \mathrm{SO_4^{\bullet-}} \tag{8}$$

$$\mathrm{SO_4^{2-}} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{SO_4^{\bullet-}} + \mathrm{OH^-} \tag{9}$$

$$\mathrm{HCO_3^-} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{CO_3^{\bullet-}} + \mathrm{H_2O} \tag{10}$$

$$\mathrm{CO_3^{2-}} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{OH^-} + \mathrm{CO_3^-} \tag{11}$$

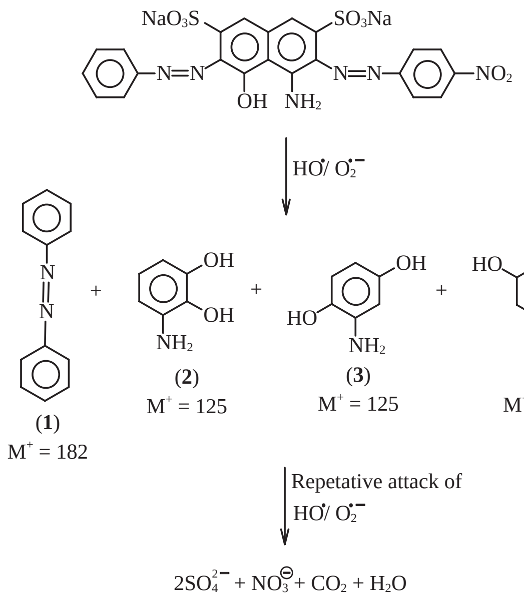
$$\mathrm{Cl^-} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Cl^{\bullet}} + \mathrm{OH^-} \tag{12}$$

The presence of dissolved metal ions is common in industrial wastewater and they can sensibly affect the rate and efficiency of photocatalytic degradation. The effect of added metal ions on photocatalytic degradation of AB 1 is shown in Table 2.

Except Fe^{2+} and Cu^{2+}, other metal ions have not influenced the degradation rate. After 30 min of irradiation time, 65.4%, 74.5%, 63.0%, 78.4% and 26.8% of degradations were observed by the addition of 0.1 M of Ag^+, Cu^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+} ions, respectively. Addition of Fe^{2+} and Cu^{2+} enhances the efficiency of ZnO slightly, whereas addition of Ag^+, Mg^{2+} and Mn^{2+} inhibits the degradation efficiency of ZnO. This retardation effect may be due to blocking of active sites of ZnO by the deposition of these metals on the ZnO surface which decreases the degradation rate. Similar inhibition effect was reported in the photocatalytic and photoelectrolytic degradation of HCOOH on Ag deposited TiO_2 film [46].

3.6. *Mineralization and degradation pathway*

To confirm the complete degradation of AB 1, the degradation was analyzed by COD values. The COD value of 1,344 for 2×10^{-4} M dye concentration decreased to 89.6 (93.3% COD reduction) after one hour irradiation with ZnO. This reveals that the mineralization is almost complete in one hour. Mineralization



Scheme 1. Proposed degradation pathway of AB 1with ZnO.

was also confirmed by the formation of $CaCO_3$ when the evolved gas (carbon dioxide) during degradation was passed into $Ca(OH)_2$ solution.

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the AB 1 through GC-MS analysis of the solution obtained after 15 and 30 min irradiation. We got four predominant peaks with retention times of 14.27, 16.12, 20.05 and 21.76 min. These four products were identified as azobenzene (**1**), 3-aminobenzene-1,2-diol (**2**), 2-aminobenzene-1,4-diol (**3**) and 5-aminobenzene-1,3-diol (**4**) based on their molecular ion and mass spectrometric fragmentation peaks and they are given below. Since the three retention times gave the same molecular ion ($M^+ = 125$) and fragmentation peaks, the compounds **2**, **3** and **4** could not be distinguished. The reaction for the formation of these products is given in Scheme 1.

Compound	Mass spectral data (m/z)
1	182 (M^+), 105, 77, 51
2	125 (M^+), 111, 97, 81, 71, 69, 57, 55
3	125 (M^+), 111, 97, 81, 71, 69, 57, 55
4	125 (M^+), 111, 97, 81, 71, 69, 57, 55.

4. Conclusions

ZnO is found to be more efficient than TiO_2-P25 for degradation of AB 1. The optimum pH and catalyst concentration for efficient removal of dye are found to be 7 and 5 g L^{-1}, respectively. At pH 7 the degradation efficiency is maximum and the leaching of Zn^{2+} due to photocorrosion is also significantly reduced when compared to pH 3 and 5. The increase of initial dye concentration decreases the degradation rate. The applicability of Langmuir-Hinshelwood kinetic equation reveals that the degradation of AB 1 occurs mainly on the surface of the photocatalyst. Addition of oxone increases the catalytic efficiency significantly. Except Cu^{2+} and Fe^{2+}, other metal ions Ag^+, Mg^{2+}, Mn^{2+} inhibit the degradation efficiency of ZnO. The order of inhibition of anions is $HCO_3^- > CO_3^{2-} > NO_3^- > Cl^- \approx SO_4^{2-}$. COD measurements and carbon dioxide formation confirm the mineralization of AB 1 molecule. GC-MS analysis reveals the formation of azobenzene, 3-aminobenzene-1,2-diol, 2-aminobenzene-1,4-diol and 5-aminobenzene-1,3-diol as intermediates.

Acknowledgements

Authors, B. Krishnakumar and K. Selvam are thankful to CSIR, New Delhi, for the award of Senior Research Fellowship. The authors thank the Ministry of Environment and Forests (MOEF), New Delhi, for the financial support through research grant No. 315-F-36, F.No.19/9/2007-RE.

References

[1] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, Chemosphere, 46 (2000) 1173−1181.
[2] M. Saquib and M. Muneer, Dyes Pig., 56 (2003) 37−49.
[3] W.Z. Tang and H. An, Chemosphere, 39 (1995) 4157−4170.
[4] V. Meshko, L. Markovska, M. Mincheva and A.E. Rodrigues, Water Res., 35 (2001) 3357−3366.
[5] W.S. Kuo and P.H. Ho, Chemosphere, 45 (2001) 77−83.
[6] C. Galindo, P. Jacques and A. Kalt, Chemosphere, 45 (2001) 997−1005.
[7] J. Tseng and C.P. Huang, in: Proceedings of the First International Symposium on Chemical Oxidation Technologies for the Nineties, Vanderbilt University, Vol. 1, Nashville, TN, 1991, p. 262.
[8] J.-M. Herrmann, Catal. Today, 53 (1999) 115−129.
[9] R. Andreozzi, V. Caprio, A. Insola and R. Marotta, Catal. Today, 53 (1999) 51−59.
[10] C.G. Silva and J.L. Faria, J. Photochem. Photobiol. A, 155 (2003) 133−143.
[11] C.A. Emilio, M.I. Litter, M. Kunst, M. Bouchard and C. Colbeau-Justin, Langmuir, 22 (2006) 3606–3613.
[12] V. Iliev, J. Photochem. Photobiol. A, 151 (2002) 195–199.
[13] G. Al-Sayyed, J.C. D'Oliveira and P. Pichat, J. Photochem. Photobiol. A, 58 (1991) 99–114.
[14] J. Xie, X. Lu, M. Chen, G. Zhao, Y. Song and S. Lu, Dyes Pig., 77 (2008) 43−47.
[15] W. Xiaohong, Q. Wei, L. Li, G. Yun and X. Zhaoyang, Catal. Commun., 10 (2009) 600–604.
[16] J. Eberl and H. Kisch, Photochem. Photobiol. Sci., 7 (2008) 1400–1406.
[17] A. Hameed, T. Montini and P. Fornasiero, J. Am. Chem. Soc., 130 (2008) 9638–9659.

[18] A.H. Zyoud, N. Zaatar, I. Saadeddin, C. Ali, D. Parkc, G. Campet and H.S. Hilal, J. Hazard. Mater., 173 (2010) 318–325.

[19] S. Liu, L. Yang, S. Xu, S. Luo and Q. Cai, Electrochem. Commun., 11 (2009) 1748–1751.

[20] V. Gombac, L. De Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello and M. Graziani, Chem. Phys., 339 (2007) 111–123.

[21] O. Carp, C.L. Huisman and A. Rellar, Prog. Solid State Chem., 32 (2004) 33–177.

[22] K. Pirkanniemi and M. Sillanpaa, Chemosphere, 48 (2002) 1047−1060.

[23] M.C. Yeber, J. Rodriguez, J. Freer, J. Baeza, N. Duran and H.D. Mansilla, Chemosphere, 39 (1999)1679−1688.

[24] A.A. Khodja, T. Sehili, J.F. Pitichowshi and P. Boule, J. Photochem. Photobiol. A, 141 (2001) 231−239.

[25] G. Marci, V. Augugliaro, M.J.L. Munoz, C. Martin, L. Palmisano, V. Rives, M. Sehhiavello, R.J.D. Tilley and A.M. Venezia, J. Phys. Chem. B, 105 (2001) 1033−1040.

[26] J. Grzechulska and A.W. Morawski, Appl. Catal. B, 36 (2002) 45−51.

[27] H.Y. Shu, M.C. Change and H.J. Fan, Sol. Energy Mater. Sol. Cells, 77 (2003) 201−208.

[28] K. Selvam, M. Muruganandham and M. Swaminathan, Chem. Eng. J., 128 (2007) 51−57.

[29] N. Sobana and M. Swaminathan, Sep. Purif. Technol., 56 (2007) 101−107.

[30] M. Muruganandham, N. Sobana and M. Swaminathan, J. Hazard. Mater., 137 (2006) 1371−1376.

[31] L. Ravichandran, K. Selvam and M. Swaminathan, Aust. J. Chem., 60 (2007) 951−956.

[32] L. Ravichandran, K. Selvam and M. Swaminathan, Sep. Purif. Technol., 56 (2007) 192−198.

[33] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, Sol. Energy Mater. Sol. Cells, 77 (2003) 65−82.

[34] C. Lizama, J. Freer, J. Baeza and H.D. Mansilla, Catal. Today, 76 (2002) 235−246.

[35] C. Guillard, H. Lacheb, A. Houas, M. Ksibi, E. Elaloui and J. Herrmann, J. Photochem. Photobiol. A, 158 (2003) 27–36.

[36] A. Aguedach, S. Brosillons, J. Morvan and E.K. Lhadi, Appl. Catal. B, (2005) 55–62.

[37] A. Hameed, T. Montini, V. Gombac and P. Fornasiero, Photochem. Photobiol. Sci., 8 (2009) 677–682.

[38] M.S.T. Goncalves, A.M.F. Oliveira-Compos, E.M.M.S. Pinto, P.M.S. Plasencia and M.J.R.P. Queiroz, Chemosphere, 39 (1999) 781−786.

[39] J.M. Herrmann, Catal. Today, 53 (1999) 115–129.

[40] O.E. Kartal, M. Erol and H. Oguz, Chem. Eng. Technol., 24 (2001) 645−649.

[41] C. Chen and T.C. Chou, Ind. Eng. Chem. Res., 32 (1993) 1520−1527.

[42] L. Wenhua, L. Hong, C. Suoan, Z. Jianqing and C. Chunan, J. Photochem. Photobiol. A, 131 (2000) 125−132.

[43] H. Al-Ekabi and N. Serpone, J. Phys. Chem., 92 (1988) 5726−5731.

[44] R.W. Matthews, J. Phys. Chem., 91 (1987) 3328−3333.

[45] P. Kanakaraj and P. Maruthamuthu, Int. J. Chem. Kinet., 15 (1983) 1301−1310.

[46] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya, Bull. Chem. Soc. Jpn., 58 (1985) 2015−2022.