Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(6):2979-2987

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Photocatalytic degradation of amidoblack-10B using nanophotocatalyst

***E K Kirupavasam and G Allen Gnana Raj**

Department of Chemistry and Research Centre, Scott Christian College, (Autonomous)
Nagercoil, Tamil Nadu

ABSTRACT

This study involves the photocatalytic degradation of amidoblack- 10B (AB - 10B) in water using nanosized silver doped TiO_2*, with the use of solar light as the stimulating source. It has been investigated that, when the full range of emitted photons is used, decolourization and complete mineralization of the solution is achieved with satisfactory rates, depending on initial dye concentration. The rate of degradation follows first order kinetics. The photocatalytic degradation of dye depends on concentration of dye, amount of catalyst, silver doped* TiO_2*, pH of the solution. The mechanism of the photodegradation process under visible light illumination involves an electron excitation into the conduction band of the modified* TiO_2 *semiconductor leading to the generation of very active oxygenated species that attack the dye leading to photodegradation Photocatalytic activity of Ag-doped* TiO_2 *was also increased by using* H_2O_2 *as electron scavenger.*

Keywords: Amidoblack-10B, Photodegradation, Ag doped TiO_2, Visible light.

INTRODUCTION

Dye pollutants produced from textile industries are becoming a major source of environmental contamination [1]. Among the different types of dyes used in textile industries, 60-70 % is azo compounds. These dyes have chromophore of N= N unit in their molecular structure and are lost in water during dyeing operation. These soluble azodyes when incorporated into the body are split into corresponding aromatic amines which can cause cancer in human [2-3]. Various physical and chemical processes such as coagulation, adsorption on activated charcoal, reverse osmosis are not destructive, but only transfer the dye from one phase to another. Among the various photo catalysts employed TiO_2 has attracted much interest in recent years for its highly active photocatalytic functions, like the ability to decompose the chemical compounds as well as super hydrophilic and antibacterial properties [4-6]. The only drawback of TiO_2 semiconductor is that it absorbs smaller portion of solar spectrum in the UV region. Therefore modification of TiO_2 photocatalyst for pollutant degradation using visible light is a demanding area of research. Dye sensitization seems to be one of the viable methods for dealing with this issue.

Several studies of photocatalytic degradation of dyes have been reported [4-8]. Dipti Vaya has investigated the effect of transition metal ions such as Mo (VI) doped ZnO for photocatalytic bleaching of eosin Y[9]. Abofarha reported[10] the photocatalytic degradation of monoazo and diazodyes in wastewater on nanometer sized TiO_2. Krishnakumar [11] studied the solar photocatalytic degradation of acid black 1 with ZnO. The photocatalytic bleaching of textile azo dye Reactive Yellow 86 has been carried out in the presence of semiconductor TiO_2 and the progress of reaction was observed spectrophotometrically by Preeti Mehta[12]. The optimum conditions for the photobleaching of (Direct Yellow 12) has been established by Menka Surana[13]. The potential of Polyalthia longifolia (PL) seed powder to adsorb methylene blue (MB) from aqueous solution has been investigated through batch experiments by Mundhe.[14]. Mirkhani investigated that the photocatalytic degradation of azodyes catalyzed by Ag- doped TiO_2 photocatalyst is higher than ordinary TiO_2. In this study surface modified TiO_2 with Ag, (Ag-TiO_2) particles were used for the photocatalytic degradation of amidoblack-10B (AB -10B) using solar light.

EXPERIMENTAL SECTION

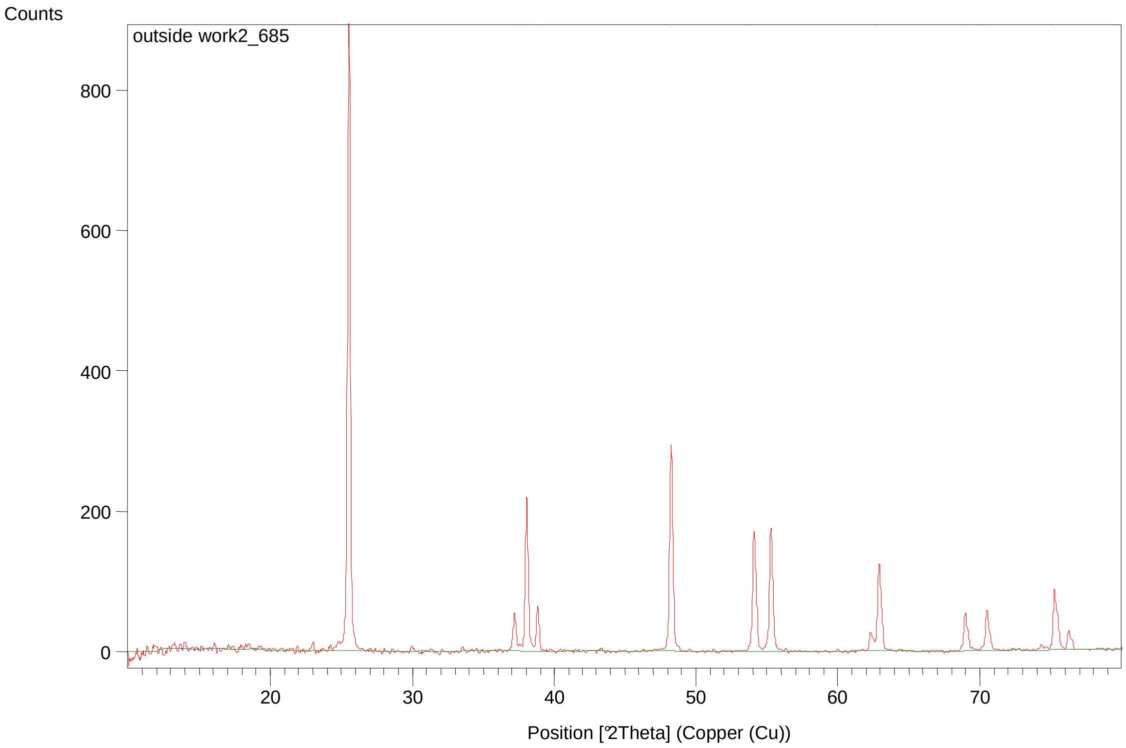
The commercial azodyes amidoblack-10B (80 % of dye) was obtained from sigma and was used without purification (λmax=620nm). TiO_2 powder which was in anatase crystalline form of surface area of about 50 m^2/g was obtained from Merck. The dye solutions were prepared using double distilled water. The pH of the solution was adjusted with diluted HNO_3 or by NaOH. Solvents and other materials such as $AgNO_3$, H_2O_2, and Na_2CO_3 were also purchased from Merck.

The silver doped photocatalyst (Ag-TiO_2) was prepared adding a calculated amount of TiO_2 to a solution of $AgNO_3$ (0.1 M)**.** To this slurry a solution of (1.0 % W/V) sodium carbonate was added and the suspension dried at room temperature and heated at 400°C for 6h [15]. The visible light photo activity of Ag-TiO_2 can be explained by a new energy level produced in the band gap of TiO_2, by the dispersion of metal nanoparticles in the TiO_2 matrix.

The photocatalytic experiments were carried out under similar condition on sunny days between 11 am to 2 pm. An open borosilicate glass beaker of 250 ml capacity was used as the reaction vessel for sunlight exposure in an open atmosphere. The suspensions containing dye and the photocatalyst were magnetically stirred in the dark for 30 minutes to achieve the adsorption equilibrium of AB-10B on the surface of the catalyst. All irradiation experiments were performed under constant stirring. Samples were withdrawn regularly for every 30 minutes and the photocatalyst were removed by centrifuge. Then absorption spectra were recorded and the rate of decolourization was observed in terms of change in intensity at absorption maximum *i.e.,* 620 nm for AB – 10B. The percentage of decolourization was calculated as, % Decolourization $= 100 \times (C_0\text{-}C)/C_0$ Where C_0 represents initial concentration of dye, C_0 - concentration of dye after irradiation.

To measure the structural variation, XRD patters were obtained using an X-ray generator (Shimdazu XD-D1, Shimadzu Corporation, Kyoto, Japan). Fig.1 shows the XRD patterns of silver doped TiO_2.

Fig. 1: XRD Pattern of Ag-TiO_2 Photocatalyst



Crystallite size of nanoparticles can be calculated by Scherer's equation

$$D= 0.9\lambda/\beta\cos\theta$$

Where D is the average crystallite size, 0.9 is the shape factor of the grain. λ is the wavelength of X-ray (0.154051nm) for Cukα radiation and is the FWHM of the diffraction peak, θ is the incident angle of X-ray. By the diffraction data in Fig.1, the particle size of Ag-TiO_2 is about 36 nm. Scanning electron microscopy was used to observe the surface state and structure of the photocatalyst composites. Scanning electron microscopy (SEM, JSM-5200, Joel, and Tokyo, Japan) along with Energy dispersive X-ray spectroscopy (EDX) was also used for elemental analysis of the samples. The SEM image of 1.15At % Ag-TiO_2 nanoparticles is shown in Fig 2.

Fig. 2: SEM Images of Ag-TiO_2 Photocatalyst

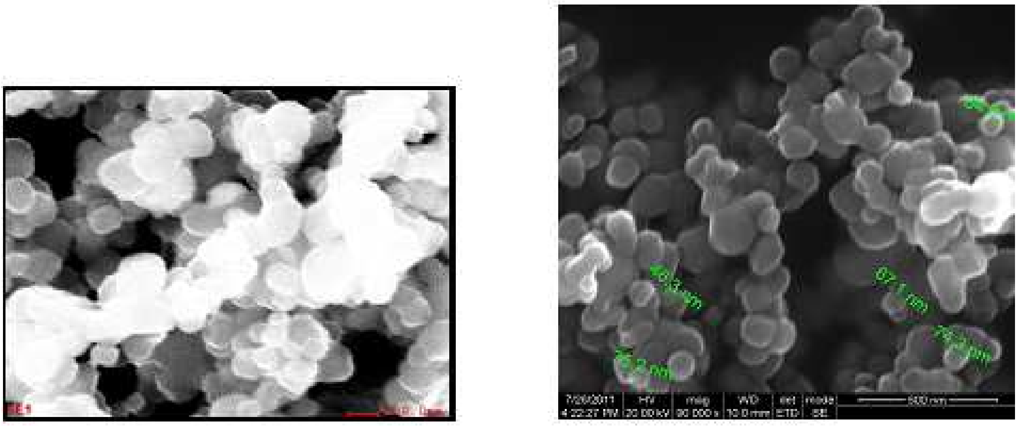


Fig. (a) At 100 nm

Fig. (b) At 500 nm

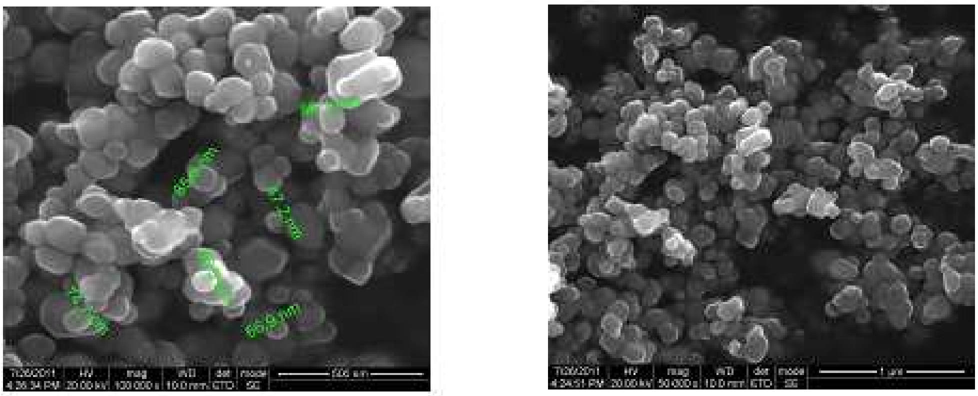
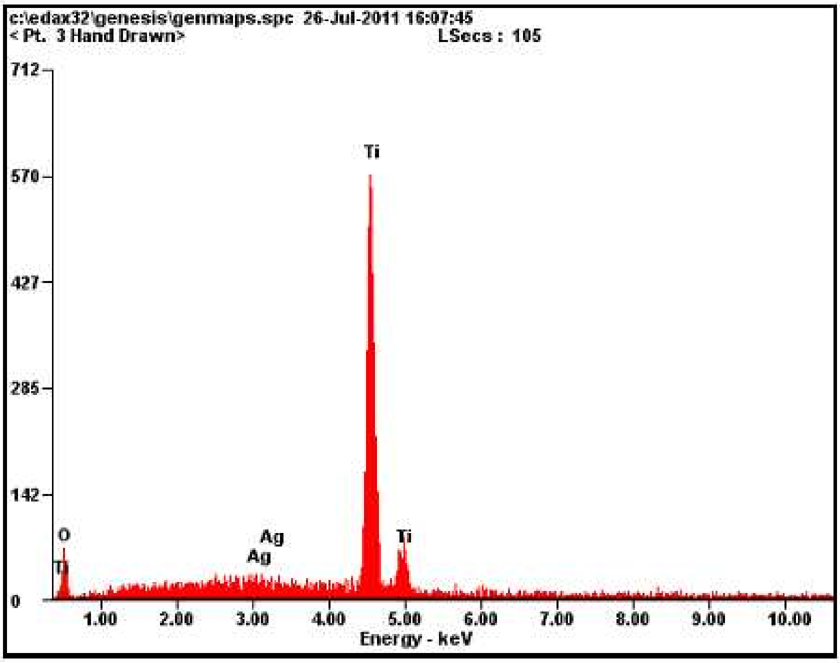


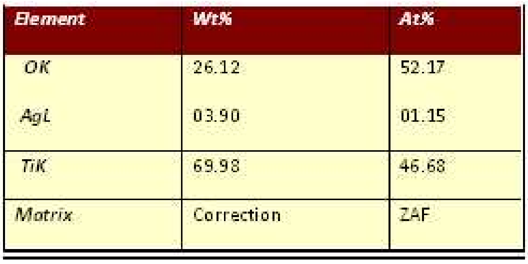
Fig. (c) At 500 nm

Fig. (d) At 1 µm

Some porous surfaces dispersed among cauliflower-like clusters of grains were observed. Fig. 3 shows EDX analysis on 1.15At % Ag-TiO_2 catalyst.

Fig. 3 : EDX Elemental Micro analysis of Ag-TiO_2 Photocatalyst





Element	*Wt%*	*At%*
OK	26.12	52.17
AgL	03.90	01.15
TiK	69.98	46.68
Matrix	Correction	ZAF

The silver signals are found at around 3.00 Kev. Though the peaks of silver are in significant due to its content in TiO_2 matrix; it can be the indicative of the silver particles in the catalyst. Degradation products of dye was confirmed using GC-MS analysis carried out by thermo GC-trace ultraver 5.0, thermo MS DSQ equipment, TR 5-MS capillary standard, non polar column 30 m length, 0.25 mm diameter.

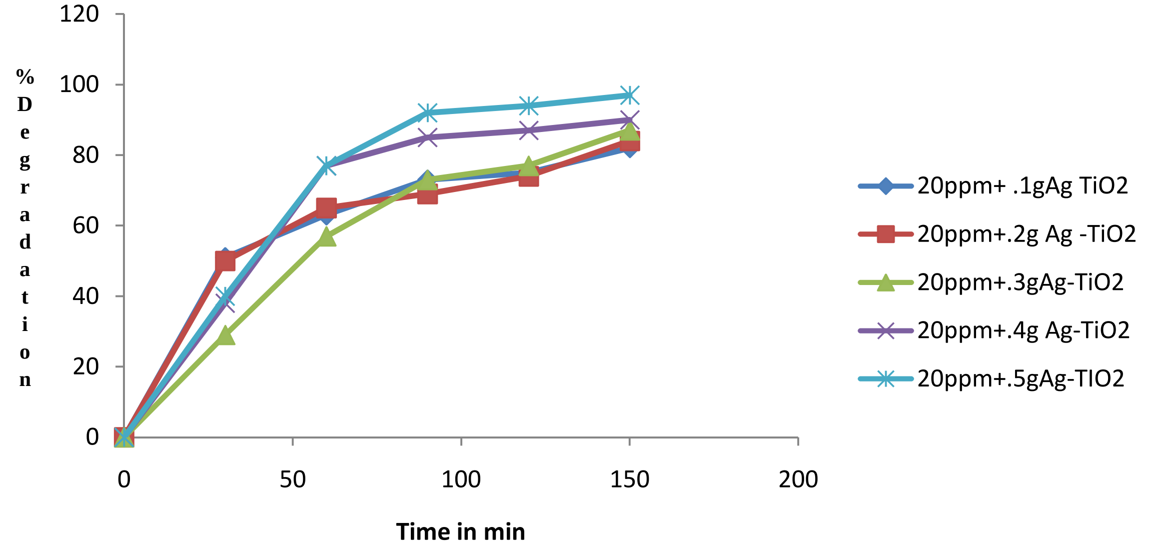
RESULTS AND DISCUSSION

The degradation of AB – 10B catalyzed by modified TiO_2 with Ag metal (1% w/w) in aqueous solution under irradiation with solar light has been investigated. The synthesized Ag – TiO_2 were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and EDX. The effect of various parameters such as amount of photocatalyst, effect of substrate concentration, pH, calcinations temperature and the presence of electron acceptors such as H_2O_2 were carried out. The kinetic of photo degradation of AB –10B using nanosized Ag – Tio_2 was also examined. GC – MS was applied to the analysis of the intermediates coming from the photo catalytic degradation of AB–10B.

Effect of catalyst concentration

An important parameter that can affect the degradation rate is the catalyst concentration. Fig.4 shows the effect of catalyst loading on the degradation of AB - 10B at pH = 4.

Fig 4 Effect ofcatalyst concentration on % degradation of AB-10B

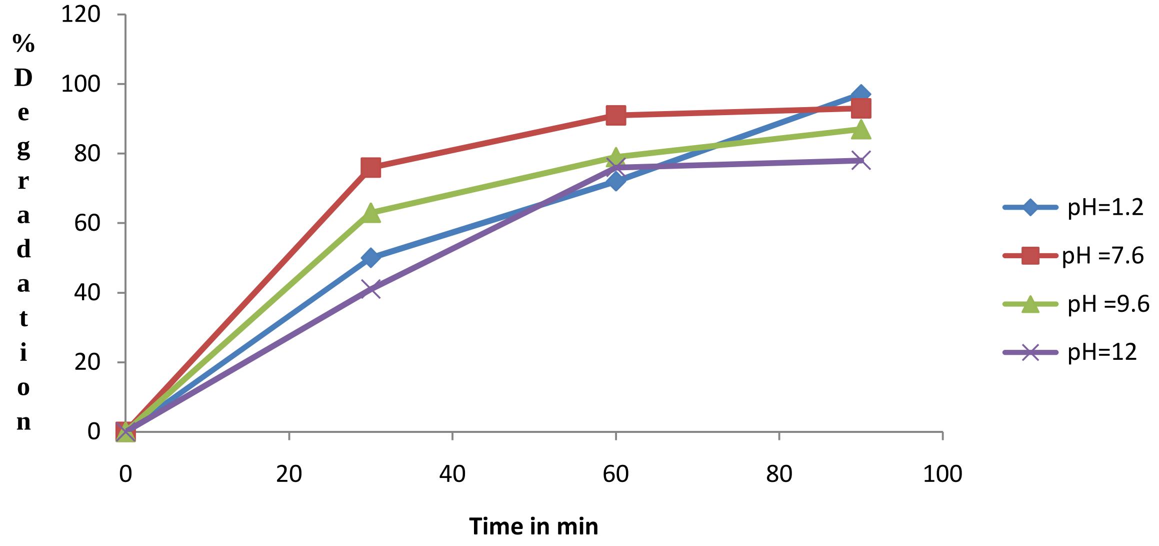


It has been seen that rate of photodegradation increase with catalyst loading (0.1 to 0.5g L^{-1}), above this loading, increase in turbidity of the solution reduces the light transmission through the solution. Many authors have investigated the reaction rate as a function of catalyst loading under different experimental conditions [16]. The enhancement of the removal rate is due to the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed, and the density of particles in the area of illumination [17]. Hence it is concluded that higher dose of catalyst may not be useful both in view of possible aggregation as well as reduced irradiation field due to increase in light scattering. Therefore catalyst dose (0.5 g L^{-1}) was fixed for further studies.

Effect of pH

In order to study the effect of pH on the degradation efficiency, experiments were carried out at various pH values from 1.2-12 for constant dye concentrations (20 mgL^{-1}) and catalyst loading (0.5 g L^{-1}). Fig. 5 shows the color removal efficiency of AB-10B as a function of pH.

Fig 5 Effect of pH on % of degradation



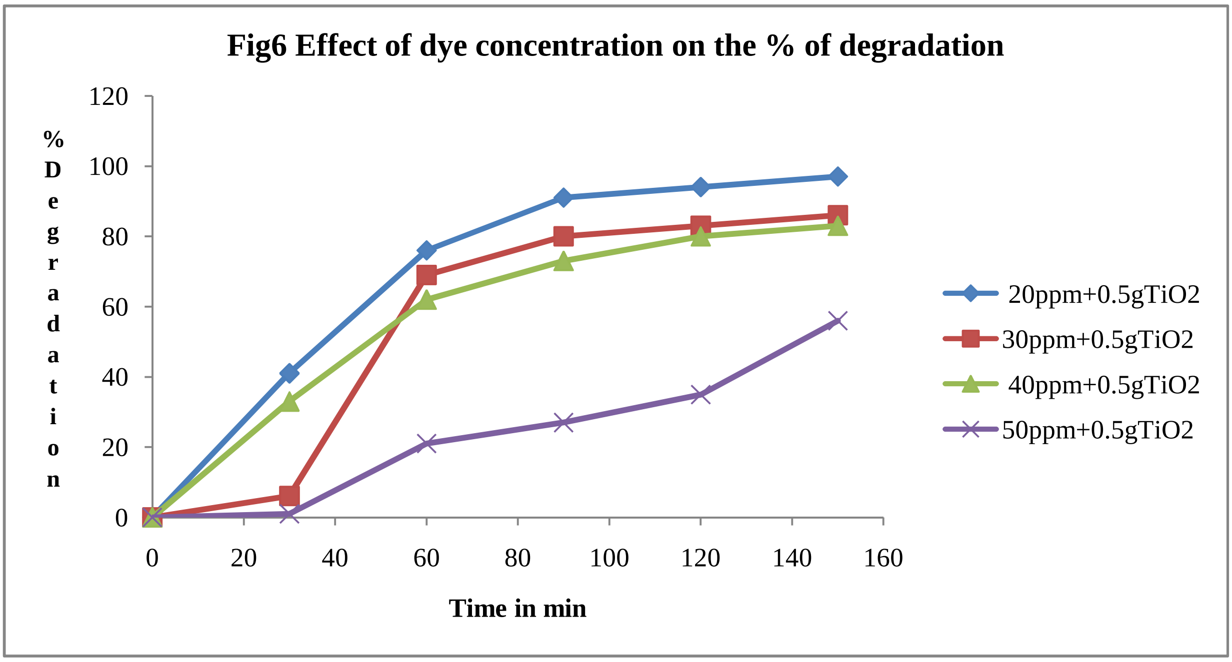
The efficiency of degradation increases with increasing pH exhibiting maximum rate of degradation at pH7.6. Similar behavior was reported for the photocatalytic efficiency of Ag-TiO_2 for degradation of azo dyes. The amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst [18]. Due to the amphoteric behavior of most metal hydroxides the following two equilibria are considered·

$$M - OH + H^+ \longrightarrow M - OH_2^+$$
$$M - OH \longrightarrow MO^- + H^+$$

Photocatalyst surface is positively charged in acidic media, whereas it is negatively charged under alkaline media. Thus for azo dyes with sulphonic acid group in their structures at low pH range, surface adsorption of catalyst is more effective than photocatalytic degradation of dyes.

In the alkaline solution, dyes are not absorbed onto the negative surface of photocatalyst effectively. Hence in the pH range of 1-7.6, the formation of more hydroxyl radical would enhance the photodegradation of dyes [19].

Effect of concentration of dye
After optimizing the experimental conditions, at pH 7.6, Ag-TiO_2 (0.05 mg L^{-1}), the photocatalytic degradation of AB-10B was carried out by varying the initial concentrations of the dye from 20 mg L^{-1}, the rate of photodegradation decrease indicating either to increase the catalyst dose or time span. Fig. 7 clearly shows that for dye solution of 20 mg L^{-1}, 97 % degradation was observed in 150 min, whereas for 30, 40, and 50 mg L^{-1} of dye solution, the degradation efficiency was 86 %, 81 % and 64 % respectively.



The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration[20].

Effect of H_2O_2 concentration
The effect of varying the H_2O_2 concentration was investigated. Increase of H_2O_2 concentration (from 5 mM to 1.5 mM) increased the degradation of AB-10B dye. An increase in H_2O_2 concentration up to 1.5 mM leads to an important rise in the dye degradation rate. The optimum amount of H_2O_2 is (1.5 mM), and the percentage of degradation is increased to 94 % within 90 min. Fig. 7 shows the effect of H_2O_2 concentration on degradation of the AB - 10B.

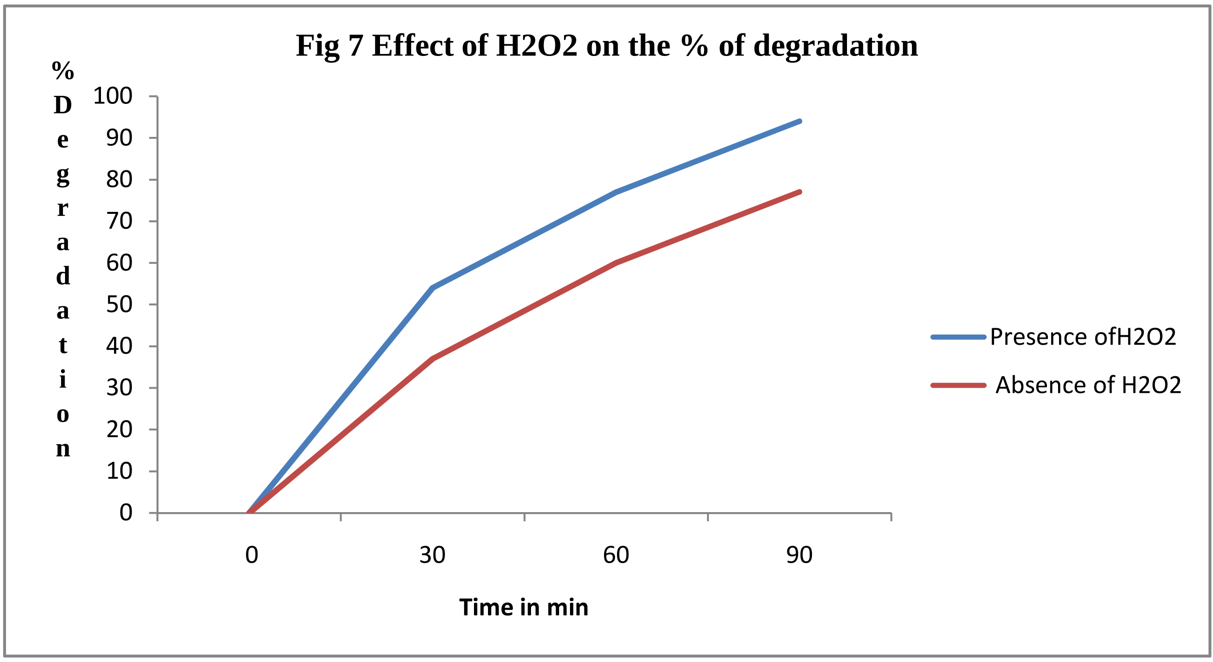


Fig 7 Effect of H2O2 on the % of degradation

This behavior is due to the hydroxyl radicals generated upon photolysis of hydrogen peroxide ^{i}ndicated by the following equation.

$$H_2O_2 + hr \rightarrow 2OH^{\cdot}$$

This radical is a very powerful oxidizer, able to react with inorganic as well with aromatic organic compounds causing the degradation of dye.

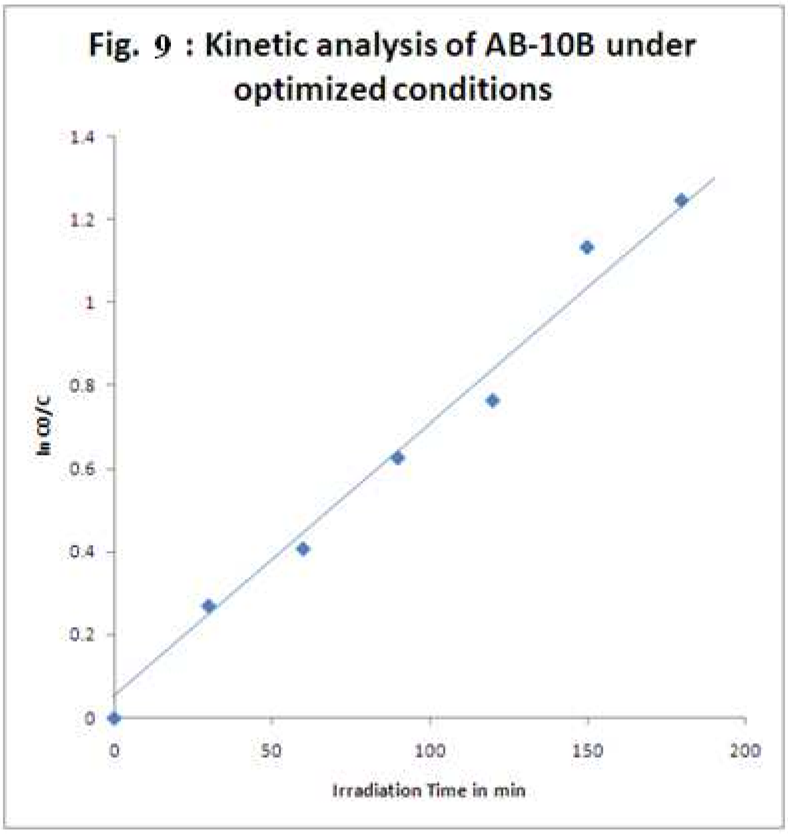


Fig. 9 : Kinetic analysis of AB-10B under optimized conditions

---

Kinetic study

Fig. 8 shows the kinetics of degradation of AB-10B for an initial concentration of 20 mg L^{-1} under optimized conditions for the dyes.

The results show that the photocatalytic degradation of the dye in Ag-TiO_2 can be described by the first-order kinetic model, ln Co/C= kt, where C_o is the initial concentration and C is the concentration at any time t. The semi-logarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be r^2= 0.9976 for AB-10B. The rate constants were calculated to be 0.0072 min^{-1}.

Identification of AB-10B dye degradation intermediates.

For identification of intermediate products, 200 ml of aqueous solution of AB-10B dye containing Ag-TiO_2 (5g L^{-1}) was irradiated with solar light for 2 h and the photocatalyst was removed by filtration. The filtrate was extracted using chloroform and was subsequently dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to get the residual mass, which was analyzed by GC-MS. Irradiation of AB-10B dye using Ag-TiO_2 results in the formation of naphthalene type molecules such as 2-napthol, coumarin, as the primary degradation products obtained by the oxidative cleavage of the dye molecule in the vicinity of azobond along with phthalic acid and benzene dicarboxylic acid as intermediates as reported[21] . This is accompanied by the formation of low molecular acids such as formic acid which eventually decompose to give carbondioxide by photo-kolbe reaction.

Efficiency of the turn over frequency

Photocatalysis is a clean technology, which normally does not involve any waste disposal problem. The catalyst can be recycled. Ag-TiO_2 can be used at least thrice without significant change in the efficiency[22] . The economy of the photocatalytic process depends upon how many times a catalyst can be reused without sacrificing its efficiency and the type of regeneration it requires. The photodegradation efficiency of turn over frequency were examined and it was found that the turn over frequency was found to be 97 % as that obtained with the fresh catalyst under the same experimental conditions. The used catalyst was regenerated to get Ag-1 first by treating with boiling distilled water till a colorless wash liquid was obtained and then drying it in a hot air oven at a temperature of about 100 ºC. The decrease in turn over frequency may be attributed to the deposition of photosensitive hydroxides on the photocatalyst surface blocking its active sites.

CONCLUSION

The results of degradation experiments show that photocatalyst can effectively degrade the dye into nontoxic forms using sunlight. Experimental results indicated that the degradation of dyes is facilitated in the presence of catalyst Ag-TiO_2. The initial rate of photodegradation increased with increase in catalyst dose up to an optimum loading. Further increase in catalyst dose showed no effect. As the initial concentration of dyes was increased, the rate of degradation is decreased. However in the presence of hydrogen peroxide, the degradation efficiency is also increased. The photocatalytic degradation of dye showed pseudo first order kinetics. This method is also one of the cheapest and an ecofriendly method for degradation of dye.

REFERENCES

[1]Yingxuehen;Kangwang; LipingLou; *J. Photochem Photobiol.A:Chem* ., **2004**, 163, 281.
[2] I Arslan;IA Baleioglu; DW Bahnermann; *Dyes and Pigments.*, **2000**, 47**,** 207.
[3]V Mirkhani; S Tangestaninejad; M Moghadam; MH Habibi; A.Rostami-Vartooni., *J. Iran. Chem.Soc.,* **2009**, 3**,** 578.
[4]A Fujishima; TN Rao ; DA Tryk;*J Photochem.Photobiol A :chem***.,** **2000**, 1, 1.
[5]S Al- Qaradawi; SP Salman; *J. Photochem. Photobiol.A: Chem.,* **2002**, 148, 161.
[6]D Chatterjee; S Dasgupta*; J. Photochem. Photobiol. A: chem.,* **2005**, 186,123.
[7]A Syoufian; K Nakashema;*, J. Coll and Inter. Sci.,* **2008**,317, 512.
[8]HY Shu;MC Chang;H Fan; *J. Energy mater sol.Cells.,* **2003**,77,201.
[9]Dipti Vaya; and VK Sharmab ; *J. Chem. Pharm. Res.,* **2010**, 2 ,269-273.
[10] SA Abofarha; *J. of American Science*;**2010,** 6, 11.
[11] Preeti Mehta; Rajeev Mehta; Menka Surana; B V Kabra; *J. Chem. Pharm. Res;* **2010** ,2, 546-557.
[12] Menka Surana; Preeti Mehta; Kavita Pamecha; B V Kabra; *J. Chem. Pharm. Res.*, **2010,** 2,655-662.
[13]K Mundhe; S Gaikwad;RC Torane,NR Deshpande and RV Kashalkar; *J. Chem .Pharm. Res.*,**2012,** 4 ;423-436.
[14]B Krishnakumar; M Swaminathan; *Ind. J .Chem.* **2010**, 49, 1035.
[15]M Kondo; W Jardim;*water Res.*, 1991, 25, 823.
[16]RW Matthews, *Water Res.,* **1990**, 24, 653.
[17]M Murugandham; M Swaminathan; *Dyes and pigments.* **2004**, 62, 269.

[18]S Sakthivel; B Neppolian; MV Shankar; MV Arabindoo; M Palanichamy; V Murugesan;, *Mater. Sol. Cells.*, **2003**, 77, 65.
[19]Z Shourong; H Qigguo; Z Jun;W Bingturn, *J.Photochem.Photobiol A:Chem.*, **1997**,103, 235.
[20]JH Baxendale ; JA Wilson; *Trans. Faraday. Soc.*, **1957**, 53, 344.
[21]ID Mariastylidi; Kondarides; Xenophon.E.Verykios; *I.J of Photoenergy.*, **2003**, 5, 60.
[22]S Chakrabarti;B.K.Dutta; *J.Hazard.Mater.*, **2004**, 156**,** 435
.