Use of a new nanosized photocatalyst $BaO_3TiO.SrO_3TiO$ for degradation of Azure B: An eco friendly process

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ABSTRACT

Colours are widely used in different industries like textile, plastic, yarn etc. When not consumed these are excreted in environment polluting it. Efforts in present work are made to remove these pollutants through photo catalytic degradation process using a new semiconductor $BaO_3TiO.SrO_3TiO$. The optimum conditions were extracted by varying pH, concentration of dye, amount of semiconductor, intensity of light etc. The process follows pseudo first order rate law which is confirmed on kinetic parameters. Formation of nontoxic degraded products like NO_2, CO_2, H_2O etc makes the process of immense importance. Participation of OH^* free radical was confirmed by use of scavenger.

Keywords: Photo degradation, Pseudo first order, Azure B, Barium strontium titanate.

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INTRODUCTION

Today most of water resources are polluted. Water pollution is increasing steadily, due to rapid population growth, industrialization, urbanization, increasing living standard and wide sphere of human activities. There are many methods available for removals of various water pollutants, but these are associated with some or the other demerits. One of the most economical and ecofriendly methods is, however, the use of photocatalytic reactions. In last few years, Advanced Oxidation Processes (AOP's) like photocatalysis, photo-Fenton reaction, ozonolysis, sonolysis etc. have emerged as successful techniques in combating the problem of environmental pollution. Coloured solution containing dyes from industrial effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. Dye containing coloured water is of almost no use, but if this coloured solution is leached to give colourless water, then it may be used for washing, cooling, irrigation and cleaning purposes. The photocatalytic bleaching seems to be quite promising and can provide a low cost method to solve this problem.

The field of photocatalysis has been excellently reviewed by Ameta et al.[1]. Photodegradation of direct red 81 by using zinc oxide nanoparticles in acidic pH was carried out by Ebrahimi et al. [2]. An Efficient Photocatalytic Degradation of Methyl Blue Dye by Using Synthesised PbO Nanoparticles was studied by Borhade et al.[3]. Photocatalytic degradation of cetylpyridinium chloride over TiO2 has been reported by Singhal et al.[4]. Similar photocatalytic reaction of xylidine ponceau and orange-G dyes by ZnO powder has been reported by Sharma et al.[5]. Yoneyama et al.[6] studied the photocatalytic reduction of dichromate ions using WO3 powder in acidic range. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins et al.[7]. Photocatalytic degradation of acid blue-62 over CuO/SnO2 nanocomposite photocatalyst under simulated sunlight has been reported by Xia et al.[8]. Photocatalytic degradation of azo dye acid readily in water using ZnO as photocatalytic has been investigated by Daneshvar et al.[9]. TiO2 sol-gel deposited over glass and its application on the photocatalytic phenol degradation was reported by Colon et al.[10] whereas photodegradation of lignin from black liquor using a UV/TiO2 system was investigated by Ksibi et al.[11]. Morwetz and Selli[12] investigated the effect of iron species in photocatalytic degradation of azo dye in TiO2 suspension. Photocatalytic water

decontamination has been reported by Gelover et al.[13]. Photo-induced transformation of some organophosphorous pesticides over TiO2 was investigated by Calza et al.[14]. Reddy et al.[15] showed the photocatalytic activity of Bi_2O_3 for the treatment of phenolic wastes. Degradation of some dyes using zirconium phosphate photocatalyst have been studied by Panwar et al.[16]. Photoreduction of Congo red by ascorbic acid and EDTA over cadmium sulphide as photocatalyst was carried out by Kothari et al.[17]. Sharma et al.[18] used semiconducting bismuth sulfide as a photocatalyst for degradation of rose Bengal.

Although a lot of work has been carried out in the field of photocatalysis, a fewer attention is paid on ternary photocatalysts which are found to be more effective pollutant removers than binary ones. Thus an attempt in present work is made to remove dyes by using a novel nano sized photocatalyst $BaO_3TiO.SrO_3TiO$.

MATERIALS AND METHODS

The stock solution of dye [Azure B 0.0761 g/250ml = 1 x 10^{-3} M (BDH)] was prepared in doubly distilled water and diluted as required. The pH of the solution was measured by pH meter [Hena imported pen type] and was varied using standardized solutions of HCl (BDH) and NaOH (Merck). Solution of dye was taken in a 100ml beaker (borosil), known amount of semiconductor [Barium strontium titanate (Aldrich)] was added and was covered with water filter to avoid the heat reaction. Then the solution was irradiated by a 200 watt tungsten lamp (Philips) and optical density was recorded spectrophotometrically (systronic model 106). The intensity of the lamp was measured by solorimeter (CEL 201).
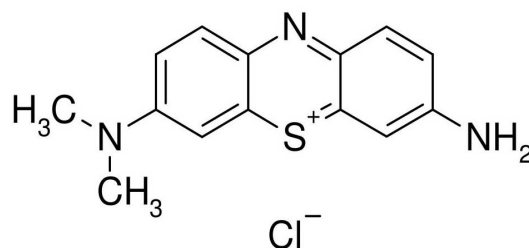

Fig.1. Azure B (Iupac name: 3-(dimethylamino)-7-methlylamino)-phenothiazine-5-ium chloride)

This dye belongs to phenothizine group. It 1s a dark green powder soluble in water. The colour of the dye solution in water is blue. It has λ_{max}=645 nm and is used as a biological stain.

RESULTS AND DISCUSSION

At regular time intervals, an aliquot was drawn from the reaction mixture and the optical density was recorded. The effect of irradiation time is shown in plot of 1+log O.D. v/s time and was found to be straight line suggesting that the reaction follows pseudo first order rate law. Rate constant was calculated by

k = 2.303 x slope

The typical run is given in table 1 and figure 2. The rate slows down with time as the breakdown of C-N is found difficult and so becomes difficult the conversion of nitrogen atom into nitrogen compounds [19,20].

Table 1: Amount of semiconductor=0.16g,light intensity=37mWcm^{-2},[Azure B]=5x10^{-5}M, pH=10.1

Time (min.)	O.D.	1+log O.D.
0.0	0.57	0.7558
5.0	0.45	0.6532
10.0	0.36	0.5563
15.0	0.29	0.4623
20.0	0.22	0.3424
25.0	0.15	0.1760
30.0	0.10	0.0000
35.0	0.00	0.0000

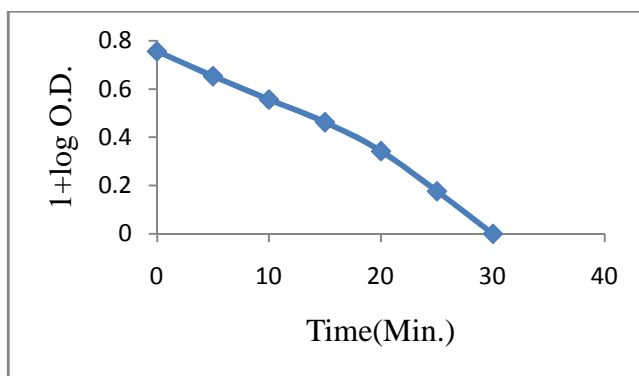*K=7.29x10^{-3} sec^{-1}*

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Figure 2: A typical run
Amount of semiconductor=0.16g,light intensity=37mWcm⁻², [Azure B]=5x10⁻⁵M, pH=10.1

The data show a continuous decrease in optical density. Simultaneously controlled experiments were carried out and no change was observed in the optical density proving the reaction to be a photocatalytic one. Use of scavenger suggested the participation of OH* free radical.

3.1 Effect of pH: Effect of variation of pH (6 to 10.5) was studied with keeping all other factors constant and the data are recorded in Table 2 and figure 3.

Table 2: Effect of variation of different parameters

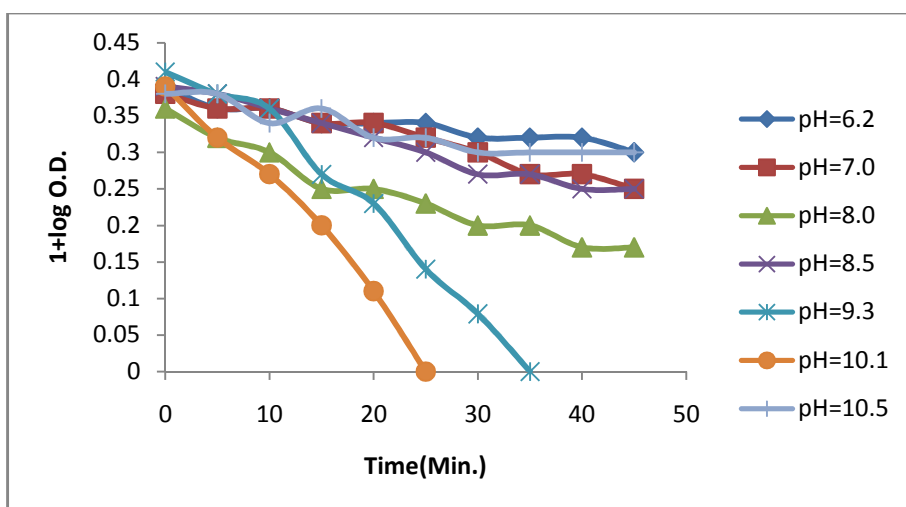| Effect of pH variation		Effect of Azure B concentration variation		Effect of amount of catalyst variation		Effect of light intensity variation	
Dye conc. =5 10⁻⁵M Catalyst = 0.16g Light intensity =37 mW /cm² pH varied	Rate constant × 10³	Catalyst = 0.16g pH=10.1 Light intensity = 37mW/cm² Dye Concentration varied	Rate constant × 10³	Dye conc. =5× 10⁻⁵M pH=10.1 Light intensity = 37 mW /cm² Catalyst varied	Rate constant ×10³	Dye conc. =5× 10⁻⁵M Catalyst = 0.16g pH=10.1 Light intensity mW/cm² Varied	Rate constant ×10³
6.2	1.24	0.8	1.36	0.06	1.32	**37**	**7.29**
7.0	1.40	1.0	1.38	0.08	2.05	34	2.27
7.5	1.52	3.0	2.97	0.12	3.01	30	1.01
8.0	1.67	4.0	3.66	0.14	4.34	27	0.53
9.3	5.79	**5.0**	**7.29**	**0.16**	**7.29**	----	----
10.1	**7.29**	6.0	0.72	0.18	1.69	----	----
10.5	1.02	----	-----	----	----	----	----

Figure 3: Plot of 1+ log O.D. v/s time for pH variation
(Amount of semiconductor=0.16g, light intensity=37mWcm⁻², [Azure B]=5x10⁻⁵M)

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It was found that as pH increases, the rate of reaction increases. It attains a maximum value at 10.1. After this, if pH is raised, the rate decreases. Increase in pH increases the number of OH⁻ ions. Due to irradiation hole is generated at semiconductor surface which abstracts an electron from OH⁻ ion converting it into OH* free radical. This free radical is responsible for the bleaching of dye which is proved by use of scavenger. After this, increase in pH reduces the rate. It is because of more availability of base generating more number of OH⁻ ions. This causes repulsion between negatively charged surface of dye and negatively charged OH⁻. Thus rate reduces.

3.2 Effect of concentration: Keeping all other factors constant, the concentration of dye was varied (0.8×10^{-5} to 6.0×10^{-5}M) and its effect on rate was evaluated. The data are recorded in table 2 and Figure 4.
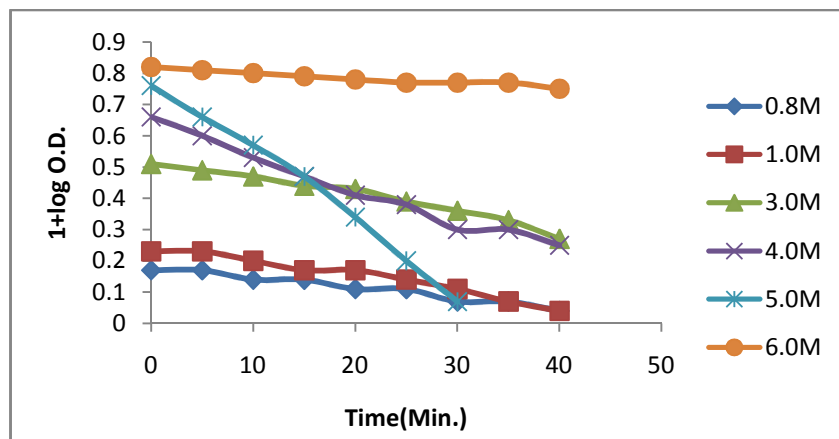

Figure 4: A plot of 1+log O.D. v/s time for variation of concentration of dye
(Amount of semiconductor=0.16g, light intensity=37mWcm⁻², pH=10.1)

The rate of photocatalytic bleaching is found to increase with increase in the concentration. This is because the rate of reaction is directly proportional to the molar concentration. Number of photons striking the surface area of dye molecule increases and thus increases the number of excited molecules. These molecules in their triplet excited state react with OH* free radical and break down in fragments occurs. If more concentration of dye is taken, the rate of reaction decreases. It is due to the fact that more concentration of dye imparts only darker colour to the solution and may act as filter to the incident light reaching the semiconductor surface. As a consequence the pathway of other molecules gaining the light and attaining excited state is interrupted and this results in the decrease in bleaching.

3.3 Effect of amount of semiconductor: Keeping all other parameters constant, amount of semiconductor was varied (0.04g to 0.18g). The data are recorded in table 2 and figure 5.
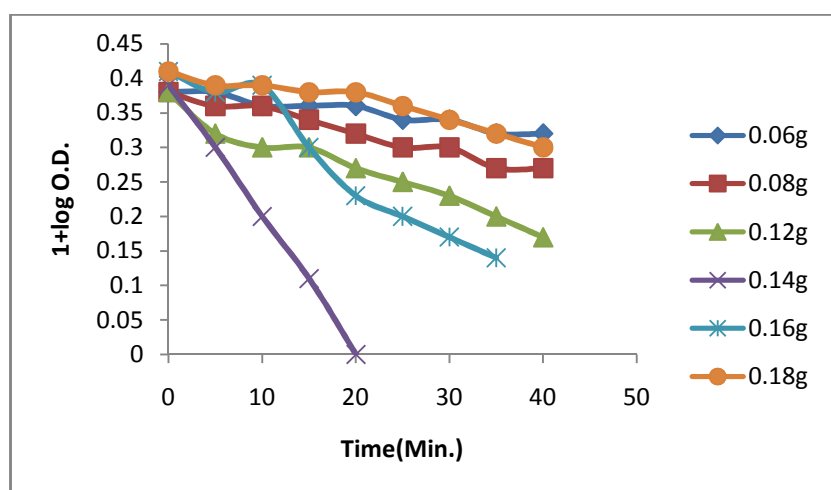

Figure 5: A plot of 1+log O.D. v/s time of variation of amount of semiconductor
(Light intensity=37mWcm⁻²,[Azure B]=5x10⁻⁵M, pH=10.1)

It was found that up to a limited weight of semiconductor (0.16 g), the rate of photo bleaching increases. It may be due to more surface area available of semiconductor to catch hold the photons of light and generate the excited state.

After a limited amount (0.16 g) the rate decreases because the increase in amount of semiconductor increases only the thickness of the layer and not the exposed area. Thus the molecules gaining photons becomes limited. Further, after a limit, substrate molecules are not sufficient to fill the active site of semiconductor and simultaneously increases in turbidity reduces the light intensity reaching the base. Thus further addition of photo catalyst decreases the rate.

3.4 Effect of light intensity: The effect of intensity of light on rate of bleaching was studied by keeping the reaction mixture at different intensity below the lamp and all other factors were kept constant. The data are given in table 2 and figure 6.
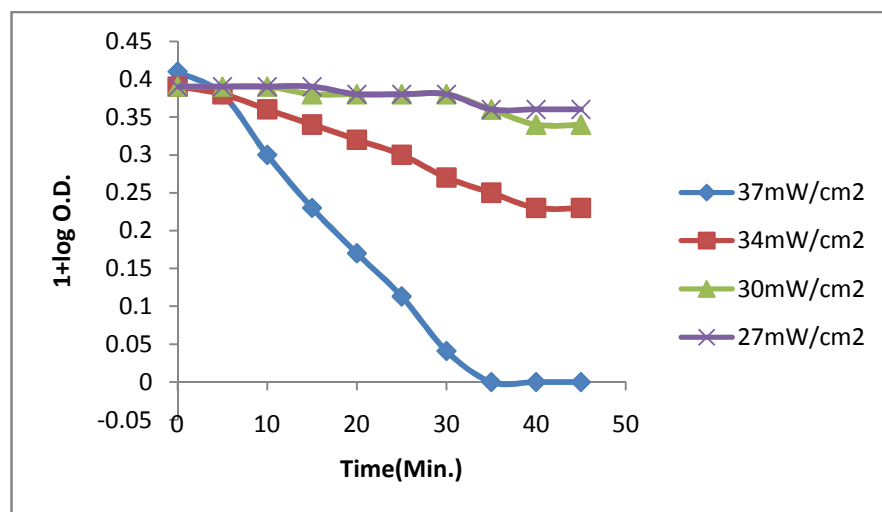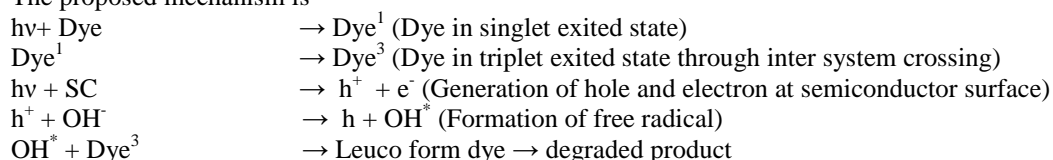

Figure 6: A plot of 1+log O.D. v/s time of variation of intensity of light
(Amount of semiconductor=0.16g,[Azure B]=5x10⁻⁵M, pH=10.1)

The rate of photocatalytic bleaching increases as the intensity of light is increased [21,22]. It may be explained on basis of excited molecule. As more intensity of light falls on semiconductor molecules, more number of molecules get excited which in turn may bleach more dye molecule. Thus the rate of bleaching was found increasing with increase in intensity of light.

The proposed mechanism is

$h\nu$+ Dye $\rightarrow$ Dye^1 (Dye in singlet exited state)

Dye^1 $\rightarrow$ Dye^3 (Dye in triplet exited state through inter system crossing)

$h\nu$ + SC $\rightarrow$ h^+ + e^- (Generation of hole and electron at semiconductor surface)

h^+ + OH^- $\rightarrow$ h + OH^* (Formation of free radical)

OH^* + Dye^3 $\rightarrow$ Leuco form dye $\rightarrow$ degraded product

Here SC is semiconductor or photocatalyst, h^+ is hole generated at the surface of photocatalyst and e^- is electron generated at the surface of photocatalyst.

Controlled experiments have proved the reaction to be a photocatalytic one. Use of scavenger has proved the participation of OH^* free radicals causing photo degradation and various degraded products like NO_2, CO_2, H_2O etc. have been tested which are not harmful to the environment. Thus an eco-friendly, cost effective, trapping the natural resource of energy i.e. solar energy and environmental protecting process may be used to make the planet clean and pollution free.

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