

Use of Barium Chromate Semiconducting Powder in Photocatalytic Degradation of Azure A

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ABSTRACT

The photocatalytic degradation of azure A was carried out in the presence of semiconductor barium chromate. The rate of degradation of dye was observed using UV-Visible spectrophotometer at regular time intervals. The effect of different variables like pH, concentration of dye, amount of semiconductor and light intensity on rate of dye degradation was observed. The optimum conditions were obtained at pH = 9.0, [Azure A] = 3.0×10^{-5} M, amount of BaCrO_4 = 0.06 g, light intensity = 50.0 mW/cm^2 . The rate constant obtained was; $k = 1.70 \times 10^{-4} \text{ sec}^{-1}$. A tentative mechanism for photocatalytic degradation of azure A involving hydroxyl radical as an active oxidizing species has also been proposed.

1. Introduction

A wide variety of organic contaminants are introduced into the water resources from industrial effluents, agricultural run-off and chemical spills. Their toxicity & stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world. Clean and safe water is vital for all known forms of life. It also plays an important role in world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Water gets contaminated due to the presence of dyes in the industrial effluent and the inadequate treatment of industrial effluents for removal of harmful compounds make it unfit for human use particularly for drinking purpose and also effects plants and organisms living in water bodies. Therefore, it is essential to treat waste water so as to make water more acceptable for drinking or for other purposes. Coagulation, flocculation, sedimentation, filtration, disinfection and sludge drying and others have been used traditionally to remove dyes from water bodies, but all such methods have several limitations. Photochemistry is most efficient and cost effective method for waste water treatment. The photodegradation of dyes using photocatalyst is one of the noteworthy treatment processes. This treatment method has sparked a lot of interest because of its efficiency in mineralization, especially towards organic pollutants. Photocatalytic oxidation is also an economically efficient method.

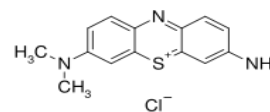
The photocatalytic degradation of methylene blue, crystal violet and malachite green was carried out by Ameta et al. [1] in the presence of semiconducting iron (III) oxide while Houas et al. [2] carried out the degradation of alizarin S, crocein orange G, methyl red, congo red and methylene blue dye by titania under UV radiation. Moura et al. [3] reported ZnO to be an n-type semiconductor that possesses suitable band gap (3.17 eV), large excitation binding energy (60 meV) and high electron mobility. Ong et al. [4] reported the use of immobilized TiO_2 to remove a commercial dye from an aqueous solution and investigated the effectiveness of TiO_2 to remove MB whereas Anwar et al. [5] worked on the anatase form of TiO_2 which has attracted much attention for its potential application in the decomposition of various environmental pollutants in both gases and liquid phase. Fatin et al. [6] worked on immobilized TiO_2 , which is capable in removing MB under the illumination of either UV or sun light. They synthesized and studied the photo luminescence of well dispersible anatase TiO_2 nanoparticles and did a comparative study of photocatalytic degradation of cationic and anionic dyes.

Daheshvar et al. [7] studied the photocatalytic degradation of azo dye acid using ZnO as photocatalyst. Chakrabarti and Dutta [8] have explored the potential of a common semiconductor ZnO as an effective catalyst for the photodegradation of two model dyes; methylene blue and eosin Y. Gajbhiye . [9] has utilized ZnO semiconductor for photocatalytic degradation process for methylene blue under UV & solar irradiation. Kim et al. [10] used ZnO coated TiO_2 nanoparticles for the dye-sensitized solar cells. Benjamin et al. [11] have achieved enhanced photocatalytic activity of ZnO by coating it with some natural pigments. Mansoori et al. [12, 13] used ZnO and PbO as photocatalysts for the photocatalytic bleaching of rhodamine-B and rhodamine-6G. Panwar et al. [14] have investigated the photocatalytic bleaching of methylene blue, malachite green and eriochrome black-T in presence of zirconium phosphate.

Ameta et al. [15] compared the photocatalytic activity of copper oxide and nickel oxide by using rose Bengal as model system. Vaya et al. [16] have studied photocatalytic degradation of eosin Y using doped ZnS by different type of transition metal ions like V (II), Cr (IV), Mn (II), Fe (III), Co (III), Ni (II) and Cu (II). Degradation of various organic pollutants including dyes, pesticides, surfactants, drugs, etc. using semiconductors such as TiO_2 , ZnO, CdS and BaCrO_4 etc. is a promising resolution for waste water treatment, but still remains a great challenge. Most of these photocatalysts work under UV light [17-19]. Colored semiconductors are more useful as they may utilize visible radiation and therefore, in the present work barium chromate, which is yellow in color has been used for the degradation of azure B.

2. Experimental Methods

Azure A dye is an organic compound with the chemical formula $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{S}$ and its IUPAC name is N', N'-dimethylphenothiazin-5-ium-3,7-diamine chloride. It is also called 3-amino-7-(dimethylamino) phenothiazin-5-ium chloride with molecular weight 291.79906 g/mol. It is a light blue to dark blue dye and is soluble in water. It is used in the screening test for mucopoly saccharides.



Structure of Azure A

Exactly 0.0292 g of azure A was dissolved in 100.0 mL doubly distilled water so as to make the concentration of dye solution 1.0×10^{-3} M. It was used as a stock solution. 0.06 g of barium chromate was added and pH was

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adjusted to 9.0 and it was exposed to a light of 50.0 mWcm⁻². The absorbance of azure A solution was determined with the help of a spectrophotometer at $\lambda_{\text{max}} = 630$ nm. The dye solution was divided in four beakers.

- First beaker containing azure A solution was kept in dark.
- Second beaker containing azure A solution was exposed to light.
- 0.06 g barium chromate was added to the third beaker containing azure A solution and was kept in dark.
- 0.06 g barium chromate was added to the fourth beaker containing azure A solution and was exposed to light.

These beakers were kept for 3-4 hours and then the absorbance of each solution was measured with the help of a spectrophotometer (Systronics Model 106). It was observed that the absorbance of solutions of first three beakers remained virtually constant, while the solution of fourth beaker showed reasonable decrease in its initial value. The observation suggests that this reaction requires both; the presence of light as well as semiconductor barium chromate. Therefore, this reaction is a photocatalytic reaction in nature and it is not a chemical (thermal) or photochemical type of reaction.

3. Results and Discussion

A solution of 3.0×10^{-5} M azure A was prepared in doubly distilled water and 0.06 g of barium chromate was added to it. The pH of the reaction mixture was adjusted to 9.0 and then this solution was exposed to a 200 W tungsten lamp at 50.0 mWcm⁻². It was observed that there was a decrease in the absorbance of azure A solution with increasing time of exposure. A plot between $1 + \log A$ vs time was obtained as a linear line, which indicates that the photocatalytic degradation of azure A follows pseudo-first order kinetics. The rate constant for this reaction was measured by the following expression –

$$\text{Rate constant (k)} = 2.303 \times \text{slope}$$

The data of typical run has been presented in Table 1 and graphically in Fig. 1.

Table 1 A typical run ([Azure A] = 3.0×10^{-5} M; pH = 9.0; Light Intensity = 50.0 mWcm⁻²; BaCrO₄ = 0.06 g)

Time (min.)	Absorbance (A)	1 + log A
0.0	0.496	0.695
15.0	0.434	0.637
30.0	0.335	0.525
45.0	0.313	0.495
60.0	0.275	0.439
75.0	0.241	0.382
90.0	0.224	0.350
105.0	0.204	0.309
120.0	0.186	0.269
135.0	0.169	0.227

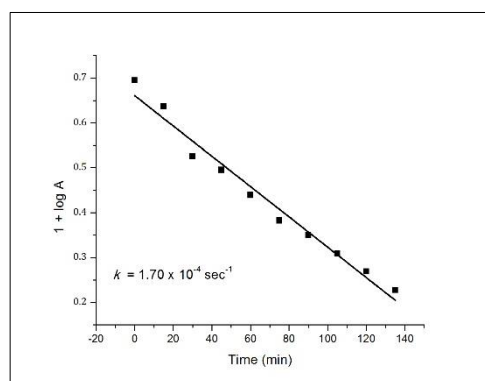


Fig. 1 Typical run

Different rate affecting parameters were studied to get the optimum rate for degradation of dye including pH, concentration of dye, amount of semiconductor and light intensity.

3.1 Effect of pH

The effect of pH on photocatalytic degradation of azure A was in pH range from 5.0 - 10.0. The results are tabulated in Table 2.

Table 2 Effect of pH ([Azure A] = 3.0×10^{-5} M; Light Intensity = 50.0 mWcm⁻²; BaCrO₄ = 0.06 g)

pH	k x 10 ⁴ (s ⁻¹)
5.0	0.24
5.5	0.25
6.0	0.33
6.5	0.42
7.0	0.54
7.5	0.73
8.0	0.90
8.5	1.09
9.0	1.70
9.5	1.23
10.0	1.07

Table 3 Effect of Azure A concentration (Light Intensity = 50.0 mWcm⁻²; pH = 9.0; BaCrO₄ = 0.06 g)

[Azure A] x 10 ⁵ M	k x 10 ⁴ (s ⁻¹)
2.0	1.31
2.2	1.39
2.4	1.45
2.6	1.51
2.8	1.59
3.0	1.70
3.2	1.68
3.4	1.12

It has been observed that the rate of photocatalytic degradation of the dye increases as pH was increased and it attained an optimum value at pH 9.0. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of hydroxyl radicals, which are produced from the reaction between -OH ions and hole (h⁺) in valence band of the semiconductor. With the formation of more •OH radicals, the rate of photocatalytic degradation of the dye increases. Above pH 9.0, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of dye is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to adsorption of -OH ions.

3.2 Effect of Azure A Concentration

The effect of dye concentration was studied by taking different concentrations of azure A. The results are given in Table 3. From the above data, it was observed that the rate of photocatalytic degradation of dye increases with increasing concentration of azure A upto 3.0×10^{-5} M. It may be attributed to the fact that as the concentration of azure A was increased, more dye molecules were available for excitation followed by consecutive energy/electron transfer and hence there was an increase in the rate. The rate of degradation was found to decrease with an increasing concentration of dye above 3.0×10^{-5} M. This may be because of the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel and thus decreasing the rate of photocatalytic degradation of azure A.

3.3 Effect of Amount of Semiconductor

The effect of amount of semiconductor on the rate of photocatalytic degradation of azure A was also observed by taking different amounts of barium chromate. The results are tabulated in Table 4.

Table 4 Effect of amount of barium chromate ([Azure A] = 3.0×10^{-5} M; Light Intensity = 50.0 mWcm⁻²; pH = 9.0)

Amount of Semiconductor (g)	k x 10 ⁴ (s ⁻¹)
0.02	1.27
0.04	1.60
0.06	1.70
0.08	1.37
0.10	1.31
0.12	1.26
0.14	0.76

Table 5 Effect of light intensity ([Azure A] = 3.0×10^{-5} M; pH = 9.0; BaCrO₄ = 0.06 g)

Light Intensity (mW cm ⁻²)	k x 10 ⁴ (s ⁻¹)
20	0.20
30	0.39
40	0.59
50	1.70
60	1.30
70	1.21

It was observed that the rate of reaction was found to increase on increasing the amount of semiconductor, barium chromate. The rate of degradation reached to its optimum value at 0.06 g of the photocatalyst. Beyond 0.06 g, the rate of reaction become almost constant. This may be due to fact that as the amount of semiconductor was increased, the exposed surface area also increases. However, after a particular value (0.06 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

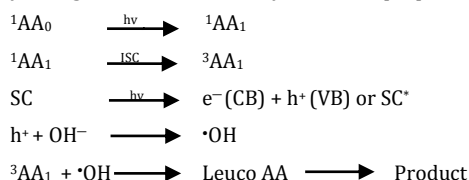
3.4 Effect of light intensity

The effect of variation of light intensity on the photocatalytic degradation of azure A was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are presented in Table 5.

The results indicate that photocatalytic degradation of azure A was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a light decrease in the rate of reaction as the intensity of light was increased beyond 50.0mW cm⁻² due to thermal reaction. Therefore, light intensity of medium order was used throughout the experiments.

3.5 Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of azure A dye has been proposed as follows:



Azure A (AA) absorbs radiations of suitable wavelength and gets excited to its first excited singlet state followed by intersystem crossing (ISC) to give the more stable triplet state. Along with this, the semiconductor barium chromate (SC) also utilizes this energy to excite its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h⁺) present in the valence band of semiconductor generating $\cdot\text{OH}$ radical. This hydroxyl radical will oxidize azure A to its leuco form, which may ultimately degrade to products. It was confirmed that the $\cdot\text{OH}$ radical participates as an active oxidizing species in the degradation of azure A, as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger i.e. 2-propanol.

4. Conclusion

In the present work, a ternary semiconductor i.e. barium chromate is successfully used as a photocatalyst for degradation of azure A, which explore its use for removal of a variety of industrial effluents in future.

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