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Research Article

PHOTOCATALYTIC DEGRADATION OF AZURE A IN AQUEOUS SOLUTION BY CALCIUM OXIDE

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ABSTRACT

In this work, the photocatalytic degradation of Azure A by heterogeneous photocatalytic process using Calcium oxide (CaO) as semiconductor has been investigated. The effect of various parameters such as catalyst loading, pH, light intensity and concentration of the dye has been studied on the rate of reaction. Kinetic studies reveal that the photocatalytic process follows pseudo-first order kinetics. A tentative mechanism for the photocatalytic degradation of Azure A was proposed.

Keywords: Photocatalytic degradation, Azure B, Calcium oxide.

INTRODUCTION

Industrialization and urbanization are mainly responsible for the environmental pollution. Water pollution due to dyeing industry is the matter of great concern since large quantity of effluent is discharged into the water bodies which are a mixture of dyes, salts, carcinogenic chemicals and heavy metals. According to the World Bank, around 17-20 per cent of all water contamination is caused by colouring and finishing measures. Approximately 72 distinctive poisonous synthetics are available in water only from colouring measures. These effluents are intensely coloured, non-biodegradable and toxic to environment. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra filtration can be used for colour removal from effluents. However, these techniques are non destructive, since they only transfer the non biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment. Recently there has been considerable interest in the utilization of Advanced Oxidation Processes (AOPs) for the complete degradation of dyes used in textile industry. The heterogeneous photocatalytic oxidation process has been extensively used for the degradation of dyes. Photocatalytic treatments are based on generation of highly reactive hydroxyl radicals. These radicals are high oxidant species, they attack the most of organic molecules. Devarahosahalli *et al.,* (2014) used, ecofriendly and economically, viable photocatalyst, that is, calcium oxide, for the degradation of indigo carmine dye and the degradation was close to 100%. The photocatalytic activity of CaO for the degradation of the methylene blue dye in distilled water under natural sunlight was studied by Jaiswal *et al.,* (2021). Photocatalytic degradation of the Methylene Blue dye is studied by Sawant *et al.,* (2014) in distilled water (laboratory conditions) and sea water (field condition) using Indian Edible Chuna (Calcium oxide/hydroxide) as a photocatalyst. CaO NPs were examined by Sree et al.(2020) for photocatalytic dye degradation of two model dyes such as Methylene blue (MB) and Toluidine blue (TB) in aqueous medium and observe that CaO effectively degraded both the dyes within 15 min. Ameta *et al.,* (2014) studied the photocatalytic degradation of methylene blue by heterogeneous photocatalytic process using Calcium oxide (CaO) as semiconductor. Ameta and Jhalora (2014) studied photocatalytic degradation of Azure B using calcium oxide semiconductor. Singh *et al.,* (2021) prepared nanocrystalline cobalt(II) oxide doped with nickel using sol-gel method and employed as a photocatalyst for azure A dye degradation under visible light and observed that approximately 76% and 85% of azure A dye was degraded within 90 min through undoped and Ni-doped CoO, respectively. The photocatalytic activity of strontium chromate ($SrCrO_4$) is for the photodegradation of azure-A dye was studied by Jangid *et al.,* (2018) Hussein *et al.,* (2019) studied the color removal of Azure A dye in aqueous solution by ZnO and hydrogen peroxide under solar irradiation. Soni *et al.,* (2018) reported the oxidation of azure-A dye of thiazine series using a photocatalised reaction and potassium peroxydisulfate as photo oxidant and ferrous sulphate as photocatalyst at normal laboratory temperature and at atmospheric pressure. Photocatalytic degradation of Azure A was carried out in the presence of N-doped zinc oxide by Rathore et al. (2015). To investigate the photocatalytic activity of Nickle Bismuth Iodide, photooxidation of Azure-A and Toluidine blue was comparatively studied by Sharma *et al.,* Alkaykh *et al.,* (2020) observed photocatalytic degradation of methylene blue dye in aqueous solution by $MnTiO_3$ nanoparticles under sunlight irradiation. Rao *et al.,* (2018) studied the photocatalytic degradation of dyes using CuO nanosheets and found that the Methylene Blue (MB) has enhanced adsorption compared to Rhodamine – B (RhB) at the nanocatalysts surface. Taghavi Fardood *et al.,* (2019) studied the photocatalytic degradation of Congo red dye by $ZnMn_2O_4$ nanoparticles. DTG. Crystal violet (CV) and methylene blue (MB) dyes were efficiently removed by Abdelrahman *et al.,* (2019) from aqueous solution by photocatalytic degradation under UV irradiation in the presence of Fe_2O_3 and H_2O_2. Dashairya et al. (2019) reported the photocatalytic degradation of toxic industrial dye, remazol brilliant red (RBR) and remazol brilliant blue (RBB) under visible light irradiation using mixture of tin disulfide (SnS_2) quantum dots (QDs) and nanodiscs (NDs), supported on reduced graphene oxide (RGO) sheets. Chanu *et al.,* (2019) studied the photocatalytic degradation of aqueous solution of methylene blue dye under UV light illumination by using manganese doped ZnO nanoparticles as a photocatalyst.

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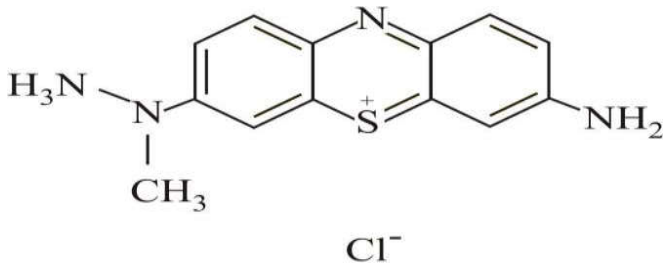
EXPERIMENTAL

Azure A dye was used as a model system to investigate the photocatalytic degradation by CaO. Molecular formula of Azure A is $C_{14}H_{14}ClN_3S$, and its molar mass is 291.80 g/mol. 1.0×10^{-3} M solution of Azure A (0.0292 g Azure A in 100.0 mL water) was prepared in volumetric flask with doubly distilled water and stored as a stock solution.



Structure of Azure A

The optical density of Azure A solution was determined with the help of a spectrophotometer at λmax = 633 nm. The dye solution was placed in equal amounts of four beakers.

- The first beaker containing only dye solution was kept in dark.
- The second beaker containing only dye solution was kept in sunlight.
- 0.30 g of semiconductor calcium oxide was added to the third beaker containing dye solution
- and was kept in dark, and
- 0.30 g of semiconductor calcium oxide was added to the fourth beaker containing dye solution and was exposed to sunlight.

After 4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was observed that the optical density of solutions of first three beakers remained almost same, while the solution of fourth beaker had a decrease in initial value of optical density. The above experiments confirms that the reaction between Azure A and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction. The data for a typical run are presented in Table 1 and graphically presented in Fig. 1. The photocatalytic degradation of Azure A was observed by taking dye solution of 3.0×10^{-5}M and 0.30 g of CaO. Irradiation was carried out keeping the whole assembly exposed to a 200 W tungsten lamp at 60.0 $mWcm^{-2}$. A decrease in optical density of Azure A solution was observed with increasing time of exposure. A plot of 2 + log O.D. against time was found to be linear. The rate constant was measured with the following expression k = 2.303 × slope.

Table 1: A Typical Run

[Azure A] = 3.00×10^{-5} M pH = 6.0

CaO = 0.30 g Light Intensity = 60.0 $mWcm^{-2}$

Temperature = 298 K

Time (min.)	Optical Density (O. D.)	2 + log O. D.
0.0	0.745	1.8722
10.0	0.494	1.6937
20.0	0.346	1.5395
30.0	0.220	1.3424
40.0	0.147	1.1673
50.0	0.098	0.9868
60.0	0.064	0.8062
70.0	0.042	0.6232

Rate constant (k) = 6.82×10^{-4} s^{-1}

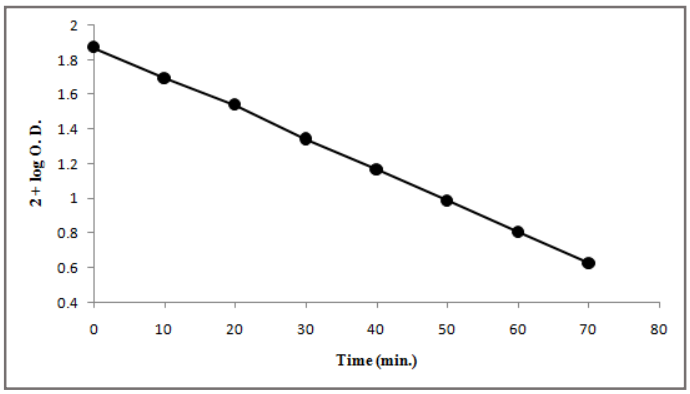


Fig. 1: A typical run

Effect of pH

The effect of pH on photocatalytic degradation was investigated in the range 3.0-8.5. The results are reported in Table 2.

Table 2: Effect of pH

[Azure A] = 3.00×10^{-5} M Light Intensity = 60.0 $mWcm^{-2}$

CaO = 0.30 g Temperature = 298 K

pH	k × 10^4 (s^{-1})
3.0	3.63
3.5	4.84
4.0	5.10
4.5	5.43
5.0	6.37
5.5	6.37
6.0	**6.82**
6.5	6.62
7.0	6.37
7.5	6.02
8.0	5.10
8.5	3.83

It is evident from the data that the degradation rate of Azure A increases with increasing pH of solution upto 6.0 and above this value of pH the rate of photocatalytic degradation of Azure A starts decreasing. It may be explained on the basis that at low pH, the anionic dye was attracted by positively charged surface of photocatalyst, but further increase in pH above 6.0, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that Azure A does not remain in its cationic form and will not experience a force of attraction with negatively charged surface of the semiconductor due to adsorption of more OH^- ions on the surface of photocatalyst.

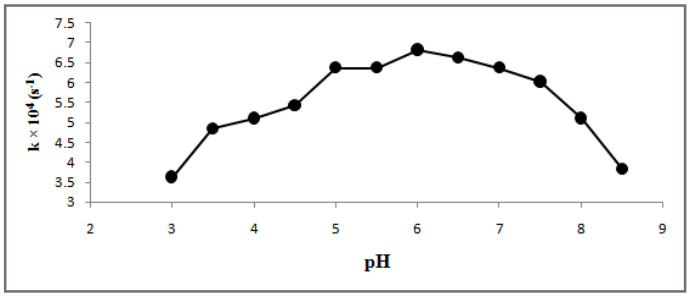


Fig. 2: Effect of pH

Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed by using different concentration of the Azure A solution. The results are given in Table 3.

Table 3: Effect of dye concentration

pH = 6.0 Light Intensity = 60.0 mWcm^{-2}

CaO = 0.30 g Temperature = 298 K

[AA] × 10^5 M	k × 10^4 (s^{-1})
0.50	3.63
1.00	3.83
1.50	4.30
2.00	6.07
2.50	6.37
3.00	**6.82**
3.50	5.83
4.00	4.55

It was observed that the rate of photocatalytic degradation increase in the concentration of the dye upto 3.00 × 10^{-5} M. It may be due to fact that as the dye was increased, more dye molecules were available for excitation and consecutive degradation. Hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye started acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface; thus, a decrease in the rate of photocatalytic degradation was observed.

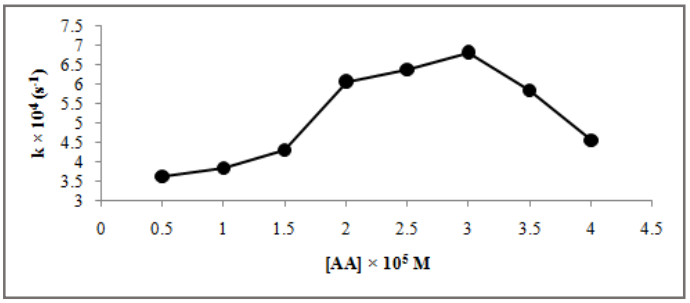


Fig. 3: Effect of dye concentration

Effect of amount of semiconductor

The effect of amount of semiconductor on the rate of photocatalytic degradation of Azure B was also observed. The results are reported in Table 4.

Table 4: Effect of amount of semiconductor

[Azure A] = 3.0 × 10^{-5} M pH = 6.0

Light Intensity = 60.0 mWcm^{-2} Temperature = 298 K

CaO (g)	k × 10^4 (s^{-1})
0.10	5.17
0.20	6.21
0.30	**6.82**
0.40	6.80
0.50	6.78
0.60	6.76
0.70	6.72
0.80	6.70

It was observed that the rate of reaction increases with increase in the amount of semiconductor up to 0.30 g and beyond 0.30 g, the rate of reaction becomes almost constant; however, there is a slight decrease. This may be due to the fact that as the amount of semiconductor was increased in the initial state, the exposed surface area of the semiconductor also increases but after this limiting value (0.30 g) any increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the semiconductor layer. This was also confirmed by using reaction vessels of different dimensions.

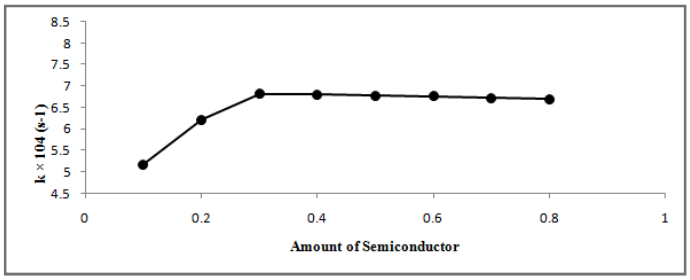


Fig. 4: Effect of amount of semiconductor

Effect of light intensity

The effect of light intensity on the rate of Azure B was also observed. The results are reported in Table 5.

Table 5: Effect of light intensity

[Azure A] = 3.00 × 10^{-5} M pH = 6.0

CaO = 0.30 g Temperature = 298 K

Light intensity (mWcm^{-2})	k × 10^4 (s^{-1})
20.0	3.88
30.0	5.30
40.0	6.19
50.0	6.37
60.0	**6.82**
70.0	6.72
80.0	6.25
90.0	5.96

The data indicate that the degradation action was accelerated as the intensity of light was increased, because any increase in the light intensity increases the number of photons striking per unit time per unit area of the photocatalyst powder. An almost linear behavior between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

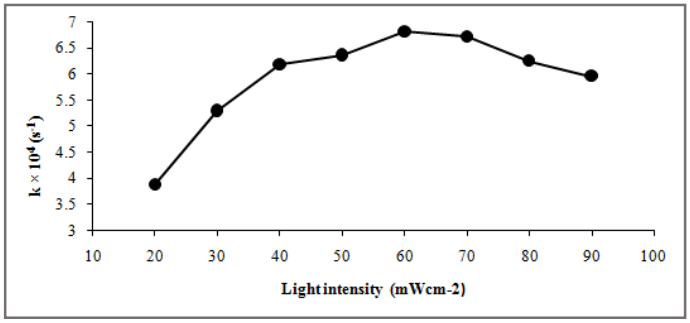


Fig. 5: Effect of light intensity

Tentative mechanism of Azure A photodegradation

On the basis of our experimental observations, a tentative mechanism for photocatalytic degradation of Azure A may be proposed as –

$$^{1}AA_{0}^{-} \xrightarrow{h\nu} {}^{1}AA_{1}^{-} \quad (1)$$

$$^{1}AA_{1}^{-} \xrightarrow{ISC} {}^{3}AA_{1}^{-} \quad (2)$$

$$CaO \xrightarrow{h\nu} CaO[h^{+}(VB) + e^{-}(CB)] \quad (3)$$

$$^{3}AA^{-} + CaO \longrightarrow AA + CaO(e^{-}) \quad (4)$$

$$CaO(e^{-}) + O_2 \longrightarrow CaO + O^{-} \quad (5)$$

$$OH^{-} + CaO(h^{+}) \longrightarrow {}^{\bullet}OH + CaO \quad (6)$$

$$^{3}AA^{-} + {}^{\bullet}OH \longrightarrow \text{Products} \quad (7)$$

When the solution of the dye was exposed to light in presence of CaO, the 1Dye molecules are excited to first excited singlet state (1 Dye*). Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). On the other hand, the semiconductor CaO also absorbs photons and as a result electron-hole pair is generated. The OH^{-} will react with hole of the semiconductor to generate •OH radicals and these radicals will convert the dye molecules into products, which are colourless. The participation of •OH radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of some hydroxyl radical scavengers like 2-propanol, where the rate of degradation was drastically reduced.

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