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PHOTOCATALYTIC DEGRADATION OF ARSENAZO-I BY ZnO IN AQUEOUS SOLUTION

VINOD KUMAR SHARMA, ASHOK KUMAR KAKODIA[a], BHUPENDRA K. SHARMA[a], SUNIL KUMAR PAMECHA and R. C. KHANDELWAL[*]

Department of Chemistry, B. N. (P. G.) College, UDAIPUR – 313004 (Raj.) INDIA
[a]Department of Chemistry, S. G. G. Govt. College, BANSWARA (Raj.) INDIA

ABSTRACT

Photocatalytic degradation of Arsenazo-I dye by ZnO has been investigated in aqueous solution. The effects of different parameters such as pH, amount of ZnO, dye concentration and light intensity on the rate of degradation of dye solution were also studied. A tentative mechanism has also been proposed for this photocatalytic degradation.

Key words: Photocatalytic degradation, ZnO, Arsenazo-I dye.

INTRODUCTION

Textile industries produce large volume of colored dye effluents, which are toxic and non-biodegradable[1]. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the waste water. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents[2-5]. 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[6-8].

Recently, there has been considerable interest in the utilization of advanced oxidation processes (AOP's) for the complete degradation of dyes. AOP's are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively[9,10]. AOP's include photocatalytic systems such as combination of semiconductors and light, and semiconductor and oxidants.

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[*]Author for correspondence; E-mail: bhoopendrasharma@ymail.com, kakodia30@gmail.com, dr.vinodsharma08@gmail.com

Semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band[11]. On irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl radical (oxidation potential 2.8 V) or superoxide radicals[12]. Although, TiO_2 in the anatase form has been used for many environmental applications, ZnO (3.2 eV) may be a suitable alternative to TiO_2 so far as band gap energy is concerned. The quantum efficiency of ZnO powder is also significantly larger than that of TiO_2 powder, and higher catalytic efficiencies have been reported for ZnO[13].

More recently work shows successfully photodegradation of *m*-cresol and p-cresol by ZnO under visible-light irradiation[14,15]. Mansilla and Villasnov[16] investigated the ZnO-catalyzed photodegradation of Kraft-Black liquor, which is an effluent from pulp and paper industries. Photocatalytic reaction of xylidine ponceau dye by ZnO powder has been reported by Sharma et al.[17] Photocatalytic degradation of azo dyes in water using ZnO as photocatalytic has been investigated by Daneshvar et al.[18] Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins et al.[19]

Arsenazo-I (Neothorin) is widely used in textile industries, but it causes great potential of water pollution. As a precaution a proper treatment of waste water is necessary before discharge. Therefore, the aim of the present work is to investigate the potential of ZnO as a photocatalyst under irradiation for the oxidation of Arsenazo-I in aqueous solutions and to evaluate the dependence factors for the color removal rate such as concentration of dye Arsenazo-I, photocatalyst semiconductor ZnO, irradiation intensity and pH of the experimental solutions. These are the major variables governing the efficiency of the process.

EXPERIMENTAL

Materials and methods

In the present work the commercial azo dye Arsenazo-I (C.D.H.) and photocatalyst ZnO (C.D.H., 99%) were used for photocatalytic degradation. For the photobleaching process, 1.0×10^{-3} M stock solution of dye Arsenazo-I was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

The total volume of the reaction mixture was 25 mL. To carry out the photobleaching, the reaction mixture was irradiated by light source (200W Tungsten lamp). Water filter was used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, Model 335). The progress of the reaction was observed at definite time intervals by measuring optical density using UV-Vis. spectrophotometer (Systronics Model 106) at λ_{max} 499 nm. The rate of dye bleaching with the time was monitored continuously.

RESULTS AND DISCUSSION

Control experiments (in absence of ZnO, light) confirm the necessity of ZnO, light to follow the photocatalytic path for the photobleaching of dye. The optimum conditions for the photobleaching of dye were [Dye] = 2.50×10^{-5} M, ZnO = 0.10 g, and pH = 9.50 at λ_{max} 499 nm. The result of photocatalytic bleaching of Arsenazo-I is presented in Table 1. It was observed that optical density (O.D.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between 1 + log O.D. and time was plotted. The linearity of the graph indicates that the photocatalytic bleaching of Arsenazo-I follows a first order kinetics. The rate constant (k) of this photobleaching process was 3.96×10^{-5} sec^{-1}.

Table 1: Typical run

[Arsenazo-I] = 2.50×10^{-5} M pH = 9.50

Light intensity = 80.00 mWcm^{-2} Zinc oxide = 0.10 g

Time (min.)	Optical density (O.D.)	1 + log (O.D.)
0.0	0.424	0.6253
30.0	0.382	0.5821
60.0	0.359	0.5551
90.0	0.351	0.5453
120	0.315	0.4983
150	0.296	0.4713
180	0.271	0.4330
210	0.251	0.3997
240	0.233	0.3766

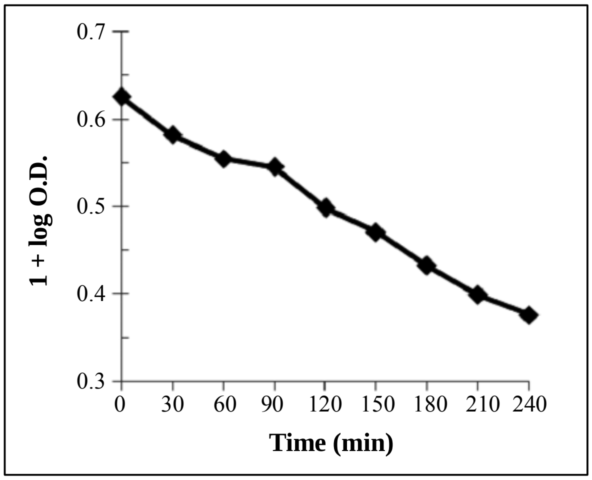

Fig. 1: Typical run of photocatalytic degradation of Arsenazo-I

Effect of pH

The effect of pH on the rate of photocatalytic degradation was studied by keeping all the other experimental conditions constant. The results are given in Table 2.

Table 2: Effect of pH

[Arsenazo-I] = 2.50×10^{-5} M Zinc oxide = 0.10 g

Light intensity = 80.0 $mWcm^{-2}$

pH	$k \times 10^{-4}$ (sec^{-1})
8.0	2.84
8.5	3.11
9.0	3.41
9.5	3.96
10.0	3.19
10.5	2.45

The increase in the rate of photocatalytic bleaching may be due to more availability of the OH^- ions at higher pH values. OH^- ions generates more $^{\cdot}OH$ radicals by combining with the hole of the semiconductor and theses hydroxyl radicals are considered responsible for this photocatalytic bleaching. But after optimum pH (9.50), a further increase in pH of the medium, decrease the rate of photocatalytic bleaching. It may be that the Arsenazo-I does not remain in its cationic form due to greater concentration of hydroxyl ions as such, the force of attraction between dye and negatively charged semiconductor surface decrease. As a consequence, the reaction rate decreases.

Effect of concentration of Arsenazo-I

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentration of Arsenazo-I solution. The results are given in Table 3. The rate of photochemical degradation was found to increase with increase in the concentration of Arsenazo-I upto 2.50 × 10^{-5} M. On further increasing the concentration, a sudden decrease in the rate of degradation was observed. This may be explained on the basis that on increasing the concentration of Arsenazo-I, more molecules of Arsenazo-I are available for degradation. However on increasing the concentration above 2.50 × 10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of Arsenazo-I is increased, it started acting like a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles, thus, a decrease in the rate of photocatalytic degradation of Arsenazo-I was observed.

Table 3: Effect of dye concentration

pH = 9.50 Zinc oxide = 0.10 g
Light intensity = 80.00 mWcm^{-2}

[Arsenazo-I] × 10^5 M	**k × 10^{-4} (sec^{-1})**
1.00	2.04
1.50	2.48
2.00	3.47
2.50	3.96
3.00	3.66
3.50	3.33
4.00	2.39

Effect of amount of semiconductor

The effect of amount of ZnO on the rate of photocatalytic degradation of Arsenazo-I was observed by keeping all other factors constant. The results are given in Table 4. It is clear from the observation that the rate of photodegradation increases on increasing the amount of ZnO upto 0.10 g, while it becomes almost constant after a 0.10 g. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases. After a certain limit (0.10 g) further increase in the amount of ZnO will not increase the exposed surface area of the photocatalyst but it will only increase the thickness of the layer at the bottom of the vessel, once the complete bottom of the reaction vessel is covered by the photocatalyst. It may be considered like a saturation point, above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of Arsenazo-I.

Table: 4. Effect of amount of semiconductor

[Arsenazo-I] = 2.50×10^{-5} M pH = 9.50
Light intensity = 80.0 mWcm^{-2}

Zinc oxide (g)	k × 10^{-4} (sec^{-1})
0.04	1.40
0.06	1.84
0.8	3.16
0.10	3.96
0.12	3.94
0.14	3.92
0.16	3.92

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of Arsenazo-I was also observed. The results are given in Table 5.

Table 5: Effect of light intensity

[Arsenazo-I] = 2.50×10^{-5} M pH = 9.50
ZnO = 0.10 g

Light intensity (mWcm^{-2})	k × 10^{-4} (sec^{-1})
20.0	2.13
40.0	3.04
60.0	3.37
80.0	3.96

A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity increases the rate of reaction. It may be attributed to the fact an increase in the intensity of light will increase the number of photons striking per unit time per square cm of semiconducting powder.

Mechanism

On the basis of the experimental observations, a tentative mechanism for photocatalytic degradation of Arsenazo-I may be proposed as-

$$^{1}AA_0 + h\nu \longrightarrow {}^{1}AA_1 \quad \ldots(1)$$

$$^{1}AA_1 \xrightarrow{ISC} {}^{3}AA_1 \quad \ldots(2)$$

$$^{3}AA_1 + ZnO \longrightarrow AA^{+} + ZnO(e^{-}) \quad ...(3)$$

$$ZnO\ (e^{-}) + O_2 \longrightarrow ZnO + O_2^{-\bullet} \quad ...(4)$$

$$AA^{+} + OH^{-} \longrightarrow AA + {}^{\bullet}OH \quad ...(5)$$

$$AA + {}^{\bullet}OH \longrightarrow \text{Degraded Product} \quad \ldots(6)$$

When the solution of the dye was exposed to light in presence of a semiconductor, initially the Arsenazo-I molecule are excited to singlet state. Then these excited singlet molecules get transformed to the triplet state through inter system crossing (ISC). The triplet state may donate its electrons to the semiconductor and Arsenazo-I becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor thus, regenerating the semiconductor. The positively charged molecules of Arsenazo-I will immediately react with hydroxyl ions to form ${}^{\bullet}OH$ radical and these ${}^{\bullet}OH$ radicals will degrade the Arsenazo-I into colourless end products. The participation of ${}^{\bullet}OH$ radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of hydroxyl ion scavenger (2-propanol) where the reaction rate was drastically retarded.

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