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ROLE OF NICKEL VANADATE IN PHOTOCATALYTIC DEGRADATION OF AZURE A

RANJANA RATHORE, RAKSHIT AMETA and SURESH C. AMETA*

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

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ABSTRACT

Photocatalytic degradation of Azure A has been carried out in the presence of nickel vanadate powder. Effect of various parameters like pH, amount of nickel vanadate, concentration of Azure A and light intensity on rate of degradation has been observed. A tentative mechanism for the degradation of Azure A has been proposed involving superoxide anion radical as an active reducing species.

Key words: Photocatalytic, Nickel vanadate, Azure A, Degradation.

INTRODUCTION

Vijay et al.[1] investigated the efficiency of WO_3 for photocatalytic degradation of Azure B dye. Effect of some factors such as catalyst dose, concentration of dye, intensity of light, pH etc., on degradation of the dye was examined. The experimental data proved that the reaction follows pseudo-first order kinetics. Participation of $^{\bullet}OH$ free radical was confirmed by scavenger studies. Optimum conditions (pH 7.8, dye concentration 5×10^{-6} moles/litre, semiconductor amount 0.12 g, light intensity 37.0 $mWcm^{-2}$) were obtained. It was reported that mineralization of dye azure B produced harmless products.

Yadav et al.[2] adopted different methods for the removal and degradation of dyes from effluents of textile, dyeing and printing industries. These methods have their own merits and drawbacks. Lead sulfide has been used as a photocatalyst for the degradation of azure B. The effect of different parameters like the pH, concentration of dye, amount of semiconductor and light intensity on the rate of reaction has been investigated. The reaction follows pseudo-first order kinetics. The optimum conditions were obtained as: [Azure-B] = 3.00×10^{-6} M; PbS = 0.12 g; pH = 8.0, and light intensity = 37.0 $mWcm^{-2}$. The rate constant was 2.50×10^{-3} sec^{-1}. A mechanism has been proposed for the oxidative degradation of Azure B involving hydroxyl radicals.

Ameta and Jhalora[3] observed the photocatalytic degradation of azure B using calcium oxide semiconductor. Effect of various parameters like pH, concentration of dye, amount of semiconductor and light intensity has been studied on the rate of reaction. Various control experiments were carried out, which indicated that semiconductor calcium oxide played a key role in photocatalytic degradation of dye.

Ameta et al.[4] investigated the use of advanced oxidation technology for removal of azure B. They

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*Author for correspondence; E-mail:

discussed different methods for degradation of organic pollutants from effluents of various industries. Out of which, photocatalysis, a part of advanced oxidation technology was considered as a promising technology for waste water treatment. Azure B dye has been degraded using Well-Dowson polyoxometalate, as a photocatalyst. Various rate affecting parameters have been studied. The degradation rate was monitored spectrophotometrically, On the basis of observed data, a tentative mechanism has been proposed. The kinetic study of this system shows that this reaction follows pseudo-first order kinetics.

Khant et al.[5] carried out photocatalytic degradation of azure B using $Ni_2P_2O_7$ as photocatalyst. Effect of various parameters like pH, dye concentration, amount of semiconductor, light intensity etc. were observed to obtain optimum conditions for degradation. Tentative mechanism has been proposed.

Aarthi et al.[6] investigated the dependence of photocatalytic rate on molecular structure of the substrate undergoing degradation. The photocatalytic degradation of azure (A and B) and sudan (III and IV) dyes, having similar structure, but different functional groups, were investigated with two catalysts. The photocatalytic activity of solution combustion synthesized TiO_2 (CS TiO_2) was compared with that of Degussa P-25 for degrading these dyes. The effect of solvents and mixed-solvent system on photodegradation of sudan III was also investigated. The photodegradation rate was found to be higher in solvents with higher polarity. The effect of pH and the presence of metal ions in the form of chloride and nitrate salt, on degradation rate of azure A was also investigated. The metal ions significantly reduced the photocatalysis rates. A detailed Langmuir-Hinshelwood kinetic model has been developed to explain the effect of metal ions on degradation rate of the substrate. This model elucidates the contribution of holes and electrons towards degradation of the dye.

Nihalani et al.[7] reported that colours are widely used in different industries like textile, plastic, yarn etc. When these are consumed and a part of it is left in environment polluting it. Efforts have been made to remove these pollutants through photo catalytic degradation process using a new semiconductor $BaO_3TiO.SrO_3TiO$. The optimum conditions were determined by varying pH, concentration of dye, amount of semiconductor, intensity of light etc. The process follows pseudo-first order rate law, which was confirmed by kinetic parameters. Formation of nontoxic degraded products like NO_2, CO_2, H_2O etc makes this process of immense importance. Participation of $^{\bullet}OH$ free radical was confirmed by use of scavenger.

Sharma et al.[8] used Bi_2O_3 and Bi_2S_3 for photocatalytic degradation of azure B dye. The effect of various parameters, such as the pH, concentration of dye, effect of amount of semiconductor, effect of light intensity, etc. were observed and discussed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum reaction conditions were experimentally determined. The photochemical oxidation of dyes follows pseudo–first order kinetics. The final products of degradation were characterized and a tentative mechanism was proposed for the photochemical oxidation of dyes.

EXPERIMENTAL

0.0291 g of azure A was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This stock solution was further diluted. The absorbance of Azure A solution was determined with the help of spectrophotometer at $\lambda_{max} = 630$ nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing Azure A solution was kept in dark.
- The second beaker containing Azure A solution was exposed to light.
- The third beaker containing Azure A solution and 0.10 g nickel vanadate was kept in dark.
- The fourth beaker containing Azure A solution and 0.10 g nickel vanadate was exposed to light.

After keeping these beakers for 3-4 hrs, the absorbance of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the absorbance of solution of first three beakers remained almost constant, while the solution of fourth beaker had a decrease in initial value of absorbance. From this observation, it is clear that this reaction requires presence of both; the light as well as semiconductor nickel vanadate. Hence, this reaction is a photocatalytic reaction in nature.

A solution of 3.0×10^{-5} M azure A was prepared in doubly distilled water and 0.08 g of nickel vanadate was added to it. The pH of the reaction mixture was adjusted to 8.5 and then this solution was exposed to a 200 W tungsten lamp at 50.0 $mWcm^{-2}$. A decrease in absorbance of azure A solution was observed with increasing time of exposure. A plot of 1+ log A against time was found to be linear, which indicates that the photocatalytic degradation of azure A follows pseudo-first order kinetics. The rate constant was measured with the help of equation (1).

$$k = 2.303 \times \text{slope} \qquad \ldots(1)$$

A typical run has been presented in Table 1.

Table 1: A typical run

pH = 8.5 Nickel vanadate = 0.08 g

[Azure A] = 3.00×10^{-5} M Light intensity = 50.0 $mWcm^{-2}$

Time (min.)	Absorbance (A)	1 + log A
0.0	0.277	0.4424
10.0	0.265	0.4232
20.0	0.256	0.4082
30.0	0.245	0.3891
40.0	0.235	0.3729
50.0	0.230	0.3617
60.0	0.224	0.3502
70.0	0.216	0.3344
80.0	0.206	0.3138
90.0	0.200	0.3010
100.0	0.193	0.2856

Rate constant (k) = 6.02×10^{-5} sec^{-1}

Effect of pH

The pH of the solution is likely to affect the degradation of azure A. The effect of pH on the rate of degradation of azure A was investigated in the pH range 5.0 - 10.5. The results are reported in Table 2.

It has been observed that rate of photocatalytic degradation of azure A was increased as pH was increased and it attained optimum value at pH 8.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that on increasing pH, there was greater probability for the formation of oxygen anion radical ($O_2^{-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the semiconductor. Thus, the rate of photocatalytic degradation of the dye increases.

Above pH 8.5, a decrease in the rate of the photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of azure A is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to the absorption of OH^- ions.

Table 2: Effect of pH

[Azure A] = 3.00×10^{-5} M Light intensity = 50.0 $mWcm^{-2}$
Nickel vanadate = 0.08 g

pH	Rate constant (k) × 10^5 (sec^{-1})
5.0	2.03
5.5	3.16
6.0	3.25
6.5	3.69
7.0	4.25
7.5	4.61
8.0	5.43
8.5	**6.02**
9.0	5.41
9.5	4.68
10.0	4.33

Effect of dye concentration

The effect of dye concentration was studied by taking different concentrations of azure A. The results are tabulated in Table 3.

Table 3: Effect of azure a concentration

pH = 8.5 Light intensity = 50.0 $mWcm^{-2}$
Nickel vanadate = 0.08 g

[Azure A] × 10^5 M	Rate constant (k) × 10^5 (sec^{-1})
2.0	4.61
2.2	4.81
2.4	5.02
2.6	5.42
2.8	5.67
3.0	**6.02**
3.2	4.87
3.4	4.25
3.6	3.87
3.8	2.99

The rate of photocatalytic degradation of dye was found to increase on increasing the concentration of azure A upto 3.0×10^{-5} M. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of dye was observed. A decrease in rate was observed on increasing the concentration of dye above 3.0×10^{-5} M because now, dye will start acting as an internal filter and it will not permit the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel.

Effect of amount of semiconductor

The amount of semiconductor is also likely to affect the degradation of dye and hence, different amounts of photocatalyst were used. The results are reported in Table 4.

Table 4: Effect of amount of nickel vanadate

pH = 8.5 Light intensity = 50.0 $mWcm^{-2}$

[Azure A] = 3.0×10^{-5} M

Nickel vanadate (g)	Rate constant (k) × 10^5 (sec^{-1})
0.02	3.13
0.03	3.30
0.04	4.17
0.05	4.84
0.06	5.47
0.07	5.63
0.08	**6.02**
0.09	6.01
0.10	6.03
0.12	6.00

It was observed that the rate of reaction increases with increase in the amount of semiconductor nickel vanadate. The rate of degradation was optimum at 0.08 g of the photocatalyst. Beyond 0.08 g, the rate constant was virtually constant. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor was also increased. However, after this limiting value (0.08 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not exposed the surface area. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher side for larger vessels, while reverse trends was observed for the smaller vessels.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of azure A, the distance between the light source and the exposed surface area of photocatalyst was varied. The results are summarized in Table 5.

The results indicate that degradation was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder per unit time. However, on increasing the intensity above 50.0 $mWcm^{-2}$, there was a slight decrease in the rate of degradation. This may be due to some side reactions.

Table 5: Effect of light intensity

pH = 8.5 Nickel vanadate = 0.08 g

[Azure A] = 5.00×10^{-5} M

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^5 (sec^{-1})
20.0	2.00
30.0	3.21
40.0	4.62
50.0	**6.02**
60.0	5.53
70.0	5.46

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of Azure A dye is proposed as follows:

$$ {}^{1}AA_{0} \xrightarrow{h\nu} {}^{1}AA_{1} \qquad ...(2)$$

$$ {}^{1}AA_{1} \xrightarrow{ISC} {}^{3}AA_{1} \qquad ...(3)$$

$$ SC \xrightarrow{h\nu} e^{-}(CB) + h^{+}(VB) \qquad ...(4)$$

$$ e^{-} + O_2 \longrightarrow O_2^{-\bullet} \qquad ...(5)$$

$$ O_2^{-\bullet} + {}^{3}AA_{1} \longrightarrow \text{Leuco AA} \qquad ...(6)$$

$$ \text{Leuco AA} \longrightarrow \text{Products} \qquad ...(7)$$

Azure A dye (AA) absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting nickel vanadate also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce the dye Azure A to its leuco form, which may ultimately degrade to products. $^{\bullet}OH$ radical does not participate as an active oxidizing species in this degradation. It was also confirmed that this degradation proceeds through reduction and not oxidation as the rate of degradation was not affected appreciably in presence of hydroxyl radical scavenger (2-propanol).

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