

## PHOTOCHEMICAL DEGRADATION OF AMIDOBBLACK-10B USING NICKEL HEXACYANOFERRATE (II) AS SEMICONDUCTOR

OMPRAKASH SHARMA\*, MUKESH SHARMA, D.P. UPADHYAY AND M.K. SHARMA<sup>a</sup>

Department of Chemistry, M. S. J. Govt. P.G. College, Bharatpur 321 001 (Raj.), India

**Key words :** Photocatalyst, Amidoblack-10B (AB-10B), Nickel hexacyanoferrate (II), Semiconductor (SC), Photocatalytic degradation, Optical density (OD).

(Received 14 March 2012; accepted 5 May 2012)

### ABSTRACT

---

The Photocatalytic degradation of AmidoBlack-10B is studied using Nickel hexacyanoferrate (II) as semiconductor under visible light irradiation. The rate of Photocatalytic degradation of dye was observed spectrophotometrically. The effects of variation of different parameters like pH, concentration of dye, amount of semiconductor and light intensity, on the rate of photochemical degradation has also been observed. The rate of degradation of dye Amidoblack-10B was found to follow pseudo first order kinetics and optimum conditions for the degradation of this dye are obtained. The tentative mechanism for photocatalytic degradation of AmidoBlack-10B has been proposed.

---

### INTRODUCTION

A number of studies have been concentrated on the degradation of toxic organic compounds in waste water via photo catalysis using various semiconductors like Oxides, Sulphides and Complexes of transition metal ions. The photocatalytic degradation of organic pollutants is having a direct relevance in water remediation treatments. Nanoparticles of TiO<sub>2</sub> are used by Chen *et al.* (2007) in UV light induced photodegradation of malachite green. Sadik (2007) studied the effect of inorganic oxidants in photo decolourization an azo dye Acid Orange -7. Mills *et al.* (1987) used CdS and Vaya *et al.* (2008) used ZnS in photocatalytic degradation of Methyl orange and Eosin-Y respectively. Other Oxides, e.g. TiO<sub>2</sub>/

ZnO (Liao *et al.* 2008), MnO<sub>2</sub> (Chaturvedi *et al.* 2010 and Ameta *et al.* 2010) and Sulphides, e.g. NiS-ZnS (Sharma *et al.* 2010) are also used as photocatalyst.

In these days transition metal complexes are also used as photocatalyst in photocatalytic degradation of various dyes and organic compounds. Jhala *et al.* (2010) used Potassium trioxalatoferrate (III) as an oxidant for the photocatalytic degradation of Neutral red. Copper hexacyanoferrate (II) is used in photocatalytic degradation of Rose Bengal (Tak *et al.* 2009) and Bismark brown (Tak *et al.* 2010). Ali *et al.* (2011) showed the catalytic activity of Nickel hexacyanoferrate (II) in the degradation of Benzyl alcohol. From the literature survey, it is apparent that very little attention has been paid on Nickel hexacyanoferrate (II) as semiconductor for photocatalytic bleaching of dyes, which is coloured, insoluble

\*Corresponding authors email : opsmsj@gmail.com; mks.1122@rediffmail.com

in water and able to utilize sun light efficiently.

In the present study Nickel hexacyanoferrate (II) is used as semiconductor in the photocatalytic degradation of Amidoblack-10B dye. Since it is water insoluble complex, thus after treatment of polluted water, it is easy to remove SC. Amidoblack-10B is the most important acid wool azo dye for black shades of moderate fastness.

EXPERIMENTAL

Material

Amidoblack-10B (CDH), Nickel chloride(Merck) and Potassium ferrocyanide (Merck), are used in the present investigation.

Apparatus

Spectrophotometer (Systronics Model-104), Solarimeter (CEL Model-SM 201) and digital pH meter (Systronics Model- 335) were used for the measurement of absorbance, light intensity and pH respectively. Centrifugal machine(Remi) was used to remove SC for every measurement of OD. 200W tungsten lamp (Philips) was used for irradiation. Infrared studies of the complex were performed by FTIR (Jasco -6100, Mumbai, India) from Pune University, Maharashtra.

Synthesis of Nickel hexacyanoferrate(II)

Nickel hexacyanoferrate(II) was prepared by the solution of potassium ferrocyanide and Nickel (II) chloride. First of all 0.1M Potassium ferrocyanide solution and 0.1M Nickel (II) chloride solution were prepared. Then added Potassium ferrocyanide (167mL, 0.1M) solution slowly into Nickel chloride (500mL, 0.1M) solution, with constant stirring according to the method used by Kourim *et al.* (1964) and also used by Tanveer *et al.* (2000). The reaction mixture was heated on a water bath at 60°C about 2-3 hrs and kept as such for 24 hrs at room temperature. Brownish green precipitate is obtained. The precipitate obtained was filtered and washed thoroughly with water and then dried in an oven at 60 °C.

The prepared Nickel hexacyanoferrate(II) was characterized by IR spectra. IR Spectral data of Nickel ferrocyanide shows a broad peak about 3447 cm<sup>-1</sup>, which is characteristics of OH group and water molecule. Thus some water molecules are associated with this complex, also a peak at around 1637 cm<sup>-1</sup> is due to HOH bending. A sharp intense

peak at 2129 cm<sup>-1</sup> and a broad peak at 519 cm<sup>-1</sup> are the characteristics of cyanide coordinated to a metal transition ion (Ali *et al.* 2011); Nakamota, (1987) and Fe-C stretching respectively. A broad band about 500 cm<sup>-1</sup> is obtained, which may be due to polymerisation of metal nitrogen bond.

Photochemical degradation of Amidoblack-10B

1.0x10<sup>-3</sup>M Amidoblack-10B solution was prepared by dissolving 0.6165g of the dye in 1000mL of doubly distilled water and it was used as stock solution and

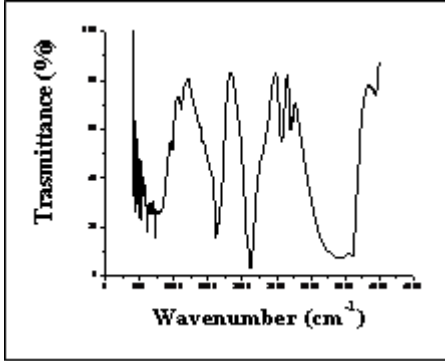


Fig. 1 IR spectra of Ni (HCF)

further diluted as and when required. The desired pH of the solution was adjusted by adding previously prepared standardised solutions of H<sub>2</sub>SO<sub>4</sub> and NaOH and measured by a digital pH meter. 0.150g of Nickel ferrocyanide was added to 50.0mL 3.6 x 10<sup>-5</sup>M Amidoblack-10B solution. The solution was irradiated by a 200W tungsten lamp. The intensity of light was measured by a Solarimeter. A water filter was used to remove thermal degradation. The optical density of this solution was recorded at regular time interval by spectrophotometer. Before measuring OD Nickel hexacyanoferrate (II) was removed with the help of centrifuging machine.

RESULTS AND DISCUSSION

Typical Run

Photocatalytic bleaching of Amidoblack-10B was observed at λ<sub>max</sub> = 615nm. A graph is plotted between exposure time and 1+logOD, which is obtained as straight line, linear behaviour of curve shows that photocatalytic bleaching of Amidoblack-10B with Nickel hexacyanoferrate (II) follows pseudo first order kinetics. The rate constant K for the reaction was determined using the expression

$K = 2.303 \times \text{Slope}$

The results for a typical run are presented in Table 1 and graphically represented in Fig. 2.

Effect of pH

Table 1. A Typical Run

[Amidoblack-10B] = 3.6x10 <sup>-5</sup>		
Light intensity = 51.0mWcm <sup>-2</sup>		
	pH = 11.0	
SC = 0.150g		
Time (min)	OD	1+logOD
0	0.832	0.9201
20	0.634	0.8021
40	0.492	0.6920
60	0.401	0.6031
80	0.325	0.5119
100	0.258	0.4116
120	0.210	0.3222
140	0.174	0.2405

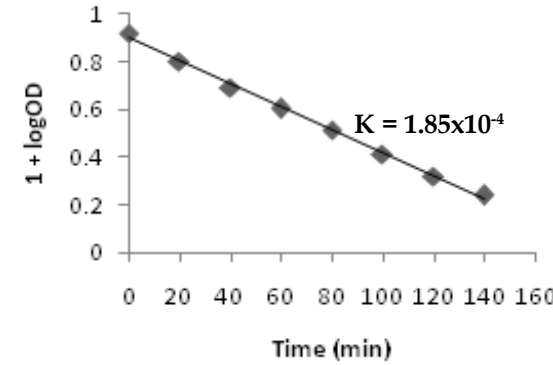


Fig. 2 A typical run

The effect of pH on the photocatalytic degradation of AB-10B was studied in the pH range 9.5 to 12.0, keeping all other factor identical. The results are represented in Table 2 and are graphically presented in Fig. 3.

It is evident from the above data that the rate of photocatalytic bleaching of Amidoblack-10B increases with increase in pH up to pH=11.0. It is due to more availability of the OH<sup>-</sup> ion at higher pH values. These OH<sup>-</sup> ions combine with the hole to form ·OH radicals, thus more OH<sup>-</sup> will generate more ·OH radicals. These hydroxyl free radicals are responsible for this photocatalytic degradation. On increasing the pH above pH=11.0, rate of bleaching of dye decreases, as the pH of the solution is increased, more OH<sup>-</sup> ions will be available and these ions are absorbed on the surface of semiconductor making it negatively charged and as a consequence of repulsive force be-

Table 2. Effect of pH

[Amidoblack-10B]	SC = 0.150g	light intensity
= 3.6x10 <sup>-5</sup>		= 51mWcm <sup>-2</sup>
pH	Kx10 <sup>4</sup> (sec <sup>-1</sup> )	
9.5	0.739	
10.0	1.09	
10.5	1.30	
11.0	1.85	
11.5	1.73	
12.0	1.39	

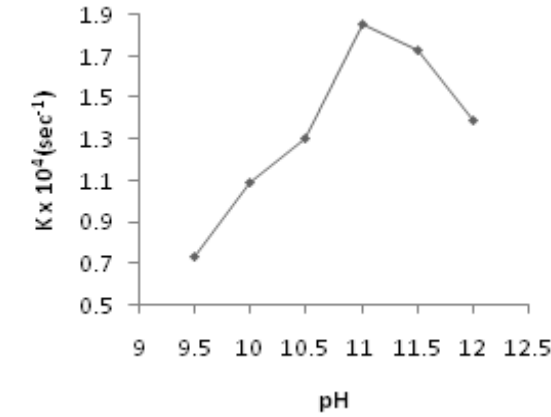


Fig. 3 Effect of pH

tween two negatively charged species (OH<sup>-</sup> ion and electron rich dye), the approach of electron rich dye to the semiconductor surface will be retarded. This will result into a decrease in the rate of photocatalytic degradation of Amidoblack -10B.

Effect of Amidoblack-10B concentration

The effect of variation of Amidoblack-10B concentration on the rate of reaction was also studied by using different concentration solutions of Amidoblack-10B. The results are reported in Table 3 and graphically presented in Fig. 4.

It was observed that the rate of photo catalytic degradation increases with an increase in the concentration of the dye up to 3.6x10<sup>-5</sup>M. Further increase in concentration of dye resulted into a decrease in the rate of photocatalytic bleaching.

It may be explained on the basis of the fact that as the concentration of Amidoblack-10B was increased, more dye molecules will be available for excitation and consecutive energy transfer, hence increase in the rate of photochemical degradation is observed. But as the concentration of Amidoblack-10B is increased above 3.6x10<sup>-5</sup>M, the dye itself will start acting as a

Table 3. Effect of Amidoblack-10B concentration

SC = 0.150g [Amidoblack - 10B] x 10 <sup>5</sup>	pH = 11.0 K x 10 <sup>4</sup> (sec <sup>-1</sup> )	Light intensity = 51mWcm <sup>-2</sup>
3.0	1.47	
3.2	1.64	
3.4	1.71	
3.6	1.85	
3.8	1.72	
4.0	1.67	
4.2	1.59	

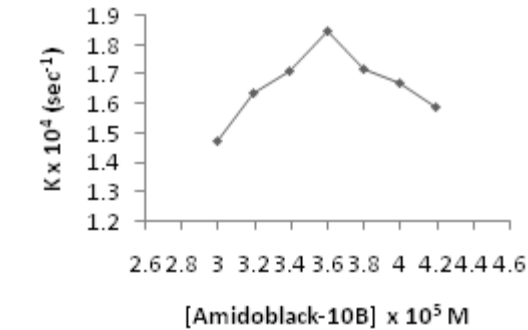


Fig. 4 Effect of Dye Concentration

filter for the incident light. Thus, it will result in a decrease in the desired light intensity to reach the semiconductor surface. Thus, a decrease in the rate of photocatalytic bleaching of Amidoblack-10B is observed.

Effect of amount of semiconductor

The effect of amount of Nickel hexacyanoferrate(II) powder on the rate of photocatalytic bleaching of the Amidoblack-10B was observed. The results are reported in Table 4 and are graphically presented in Fig. 5.

From above data, it is observed that rate of photocatalytic degradation of dye increases with increase in the amount of Nickel hexacyanoferrate (II) up to 0.150g. But beyond 0.150g the rate of reaction remains almost constant. It can be explained on the fact that, as the amount of semiconductor is increased exposed surface area of SC will also increase, thus an increase in the rate of reaction is observed. But, after this certain limiting amount of SC (0.150g), if the amount of SC was further increased it will not contribute in the exposed surface area. This is also confirmed by using reaction vessel of different dimension. Thus, after certain amount of SC, the saturation point like behaviours is observed.

Table 4. Effect of amount of semiconductor

[Amidoblack-10B] =3.6 x 10 <sup>-5</sup> 10 <sup>4</sup> (sec <sup>-1</sup> )	pH=11.0 Kx
Light intensity = 51 mWcm <sup>-2</sup>	
Amount of Nickel hexacyanoferrate(II) in gram	
0.025	1.01
0.050	1.35
0.075	1.45
0.100	1.59
0.125	1.65
0.150	1.85
0.175	1.85
0.200	1.84
0.225	1.84

Table 5. Effect of light intensity

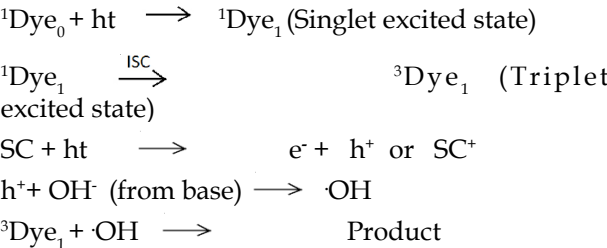
[Amidoblack-10B] = 3.6 x 10 <sup>5</sup> SC = 0.150g Light intensity in mWcm <sup>-2</sup>	pH = 11.0 K x 10 <sup>4</sup> (sec <sup>-1</sup> )
35	0.773
38	0.85
41	0.95
44	1.07
47	1.33
50	1.63
51	1.85

Effect of intensity of light

The effect of variation of light intensity on the rate of photocatalytic bleaching of Amidoblack-10B was also observed. The results are reported in Table 5 and are graphically presented in Fig. 6.

MECHANISM

On the basis of experimental observation, a tentative mechanism has been proposed for bleaching of Amidoblack-10B by Nickel hexacyanoferrate (II).



When solution of dye was exposed to light in the presence of semiconductor; initially, the dye

molecules were excited first to their excited singlet state. These excited singlet molecules were converted to the triplet state through inter system crossing (ISC). Semiconductor also utilize radiant energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole abstracts an electron from OH<sup>-</sup> ions generating ·OH free radicals. The dye is bleached by these ·OH free radicals. The participation of ·OH radical was confirmed by using hydroxyl radical scavenger (2-propanol), which almost stops the degradation.

CONCLUSION

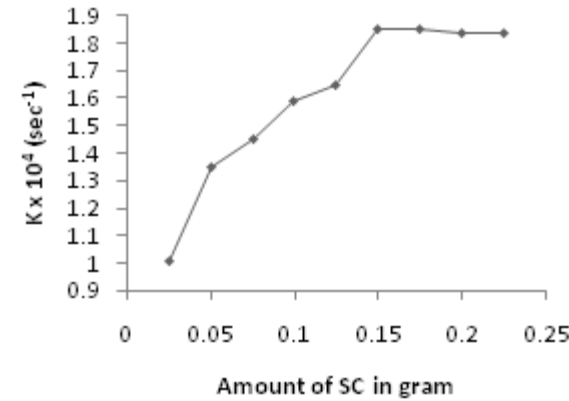


Fig. 5 Effect of Amount of Semiconductor

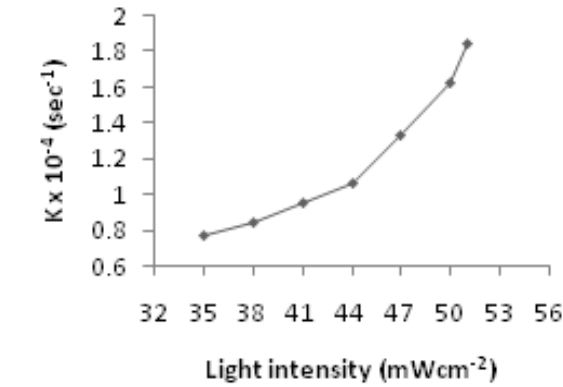


Fig. 6 Effect of light intensity

Amidoblack-10B dye can be successfully degrading using nickel hexacyanoferrate (II) semiconductor under visible light irradiation. Thus, Nickel hexacyanoferrate (II) may act as a photocatalyst quite effectively to photodegrade different dye molecules to colourless less toxic products.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Suresh C. Ameta, Director, Pacific College of Basic and Applied Sciences, Pacific University, Udaipur (Raj.), for helpful discussions and valuable suggestions. Authors are also thankful to the principal, M.S.J. Govt. College, Bharatpur for providing laboratory facilities.

REFERENCES

Alam, Tanveer and Kamaluddin, 2000. Interaction of 2-amino,3-amino and 4-aminopyridines with Nickel and cobalt ferrocyanides. Collids and sufaces A: *Physicochemical and Engineering Aspects* 162 : 89-97.

Ali, S.R., Chandra, P., Latwal, M., Jain, S.K., Bansal, V.K. and Singh, S.P. 2011. Synthesis of Nickel hexacyanoferrate nanoparticles and their potential as hetrogeneous catalysis for the solvent free oxidation of benzyl alcohol. *Chin. Jr. Catal.* 32 (12) : 1-6.

Ameta, K.L., Malkani, R.K. and Ameta, S.C. 2010. Use of semiconducting manganese(IV) oxide particulate system as a photocayalyst: photoassisted bleaching of some dyes. *Int. J. Chem. Sci.* 8 (3) : 1658-1668.

Chaturvedi, N., Sharma, S., Sharma, M.K. and Chaturvedi, R.K. 2010. Decolorization of safranin O in aqueous solution employing manganese dioxie semi-conductor. *Jr. Indus. Pollution Control.* 26 (2) : 161-164.

Chen, C.C., Lu, C.S., Chung, Y.C. and Jan, J.L. 2007. UV light Induced photodegradation of malachite green on TiO<sub>2</sub> nanoparticles. *J. Hazardous Materials.* 141 : 520-528.

Jhala, Y., Chittora, A.K., Ameta, K.L. and Panjabi, P.B. 2010. Photpchemical degradation of neutral red using potassium Trioxalatoferate (III) as an Oxidant. *Int. J. Chem. Sci.* 8 (3) : 1389-1401.

Kourim, V., Raise, J. and Millions, B. 1964, Exchange properties of complex cyanides- I : Ion exchange of Caesium of ferrucyanides. *J. Inorg. Nucl. Chem.* 26 (6) : 1111 -1115.

Liao, D.C., Badour, C.A. and Liao, B.Q. 2008. Preparation of nanosized TiO<sub>2</sub>/ZnO composite catalysis and its photocatalytic activity for degradation of methyl orange. *J. Photochem. Photobiol.* 194A : 11-19.

Mills, A. and Williams, G. 1987. Methyl orange as a probe of the semiconductor-electrolyte interface in CdS suspensions. *J. Chem., Faraday Trans.* 1 83 (8) : 2647-

- 2661.
- Nakamota, K., (4<sup>th</sup>ed) 1987. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Willy Interscience, New York.
- Sadik, W.A. 2007. Effect of inorganic oxidants in photo decolourization of an Azo dye. *J. Photochem. Photobiol.* 191A : 132-137.
- Sharma, V., Gandhi, N., Khant, A. and Khandelwal, R.C. 2010. Role of coprecipitated NiS-ZnS in photocatalytic degradation of Alizarin red S. *Int. J. Chem. Sci.* 8 (2) : 961-968.
- Tak, P., Ameta, R., Sharma, J.C., Jhala, Y. and Panjabi, P.B. 2009. Photocatalytic degradation of Rose Bengal in presence of copper hexacyanoferrate(II). *Int. J. Chem. Sci.* 7 (4) : 2736-2746.
- Tak, P., Ameta, A., Ameta, R., Sharma, V.K. and Punjabi, P.B. 2010. Use of copper hexacyanoferrate(II) as a photocatalyst for photodegradation of Bismark brown. *Int. J. Chem. Sci.* 8 (1) : 351-361.
- Vaya, D., Vyas, R., Ameta, R. and Sharma, V.K. 2008. Use of modified ZnS in photocatalytic bleaching of Eosin-Y. *J. Indian Chem. Soc.* 85 : 1266-1274.
-