PHOTOCATALYTIC DEGRADATION OF AMIDOBLACK-10B USING COPPER HEXACYANOFERRATE (II) AS SEMICONDUCTOR

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ABSTRACT

The photocatalytic degradation of amidoblack-10B has been investigated using copper hexacyanoferrte (II) as semiconductor. Copper hexacyanoferrte(II) was prepared from co-precipitation process. The effect of operational parameters, i.e. pH of solution, amount of semiconductor, conc. of dye solution and effect of light intensities on the rate of photocatalytic process has been examined. A tentative mechanism for the photocatalytic degradation of amidoblack-10B has also been proposed.

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

INTRODUCTION

Water resources are most often affected by various industrial effluents which are generally discharged into water courses either treated or untreated. Most of industries like distilleries, tanneries paper and pulp, textile industries are important source of organic pollution. Dyes are extensively used in the textile industries, due to high conc. of organics in the effluents and higher stability of modern synthetic dyes, conventional biological treatment methods are not sufficient effective for the complete degradation and removal of organic pollutants and dyes. Other conventional methods e.g. coagulation, filtration, adsorption by activated carbon treatment with ozone or H_2O_2, of colour removal from an aqueous medium, have its own advantages and disadvantages.

In recent years, many studies have been focused on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalyst. Various

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semiconductors like oxides[1-5] and sulphides[6,7] of metal ions are used as photocatalyst in degradation of organic pollutants or dyes. Now combination of sulphides of two metals, oxides of two metals are taken as photocatalyst. Gandhi et al.[8,9] used CoS-ZnS (1 : 2) and CoS-ZnS (1 : 10) as semiconductor in the phptocatalytic degradation of azure-B and methylene blue, respectively. Hong et al.[10] reported the synthesis of nano sized TiO_2/SiO_2 particle in the micro emulsion and their photocatalytic activity on the decomposition of p-nitrophenol.

Presently, different transition metal complexes play an important role in photocatalytic degradation of different dye. Jhala et al.[11] studies the photocatalytic degradation of neutral red using potassium trioxalatoferrate (III). The effect of light on trioxalatoferrate (III) was observed by Doberiner[12]. Draper[13] suggested that this kind of system can be used for the purpose of photometry.
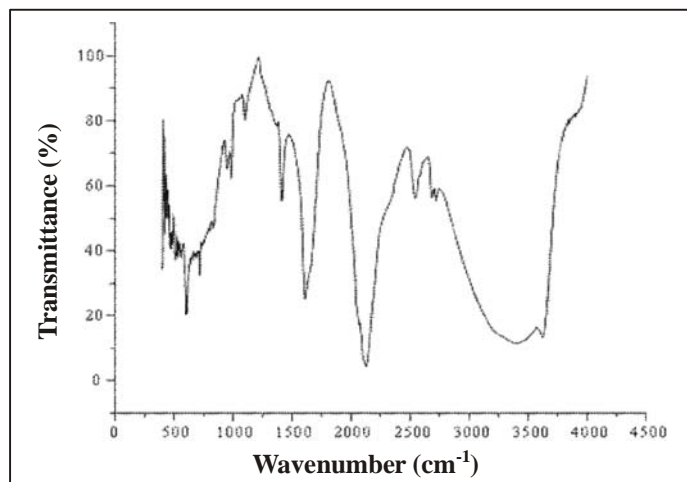
From the literature survey, it is apparent that very little attention has been paid on copper hexacyanoferrate (II) as semiconductor for photocatalytic bleaching of dyes, which is coloured and able to utilize sun light efficiently. In present work, copper hexacyanoferrate (II) is found good SC for the photocatalytic degradation of amidoblack-10B. This is the most important acid wool azo dye for black shades of moderate fastness.

EXPERIMENTAL

Synthesis of copper hexacyanoferrate (II)

For the preparation of copper hexacyanoferrate (II), 0.1 M solution of potassium hexacyanoferrate (Merck) and 0.1 M solution of copper (II) chloride (Qualigens) are prepared. Than added potassium ferrocyanide solution (167 mL, 0.1 M) slowly into copper (II) chloride (500 mL, 0.1 M) solution with constant stirring according to the method used by Kourium et al.[14] The reaction mixture was heated on a water bath at $100^{\circ}C$ about 2-3 hrs. Chocolate brown precipitate is obtained. Then, it was cured for 24 hrs. The reddish brown precipitate obtained was washed and dried at $60^{\circ}C$.

IR Spectral data of copper ferrocyanide shows a broad peak about 3637 cm^{-1}, which is characteristics of OH group and water molecule. Thus some water molecules are associated with this complex, also a peak at around 1619 cm^{-1} is due to HOH bending. A sharp intense peak at 2139 cm^{-1} and a broad peak at 595 cm^{-1} are the characteristics of cyanide coordinated to a metal transition ion[15-17] and Fe-C stretching respectively. A broad band at 500 cm^{-1} is obtained, which may be due to polymerisation of metal nitrogen bond.

Fig. 1: IR Spectra of copper ferrocyanide

Photocatalytic degradation of amidoblack-10B

The stock solution (1.0 x 10^{-3} M) of amidoblack-10B was prepared in doubly distilled water (500 mL) and diluted as and when required. The desired pH of the solution was adjusted by addition previously standardised H_2SO_4 and NaOH solutions and measured by a digital pH meter (Systronics, Model 335). 0.08 g of copper hexacyanoferrate (II) was added to 50.0 mL for 4.2 x 10^{-5} M amidoblack-10B solution. The solution was irradiated by a 200 W tungsten lamp (Philips). The intensity of light was measured by a solarimeter (Surya mapi CEL Model 201). A water filter was used to remove thermal degradation. The optical density of solution was recorded at regular time interval by using Spectrophotometer (Systronics-104). Before measuring OD, copper hexacyanoferrate (II) was removed by the help of centrifuging machine [Remi, Model 1258].

RESULTS AND DISCUSSION

Photocatalytic degradation of amidoblack-10B was observed at λ_{max} = 615 nm. A graph, plotted between exposure time and 1 + log OD is obtained as a straight line, which indicates that photocatalytic degradation of amidoblack-10B follows pseudo first order kinetics. The rate constant k for the reaction was determined using the expression.
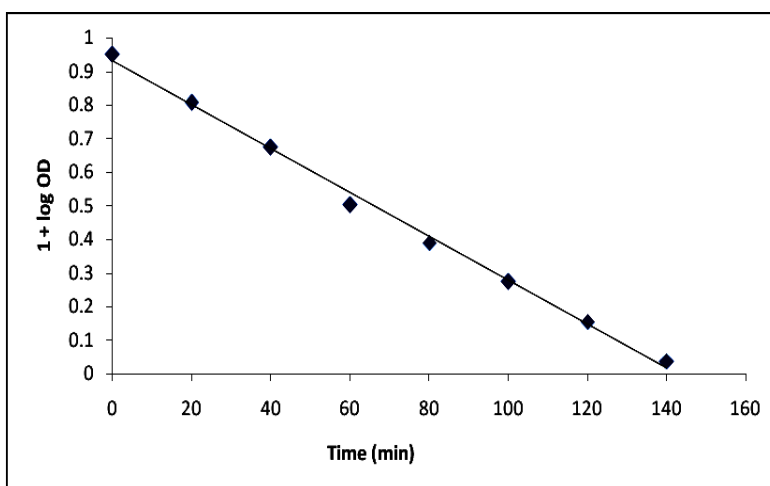
$$k = 2.303 \times Slope$$

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

Table 1: A Typical run

[Amidoblack-10B] = 4.2 x 10^{-5} M   pH = 11.5

Copper hexacyanoferrate (II) = 0.08 g   Light intensity = 51.0 mWcm^{-2}

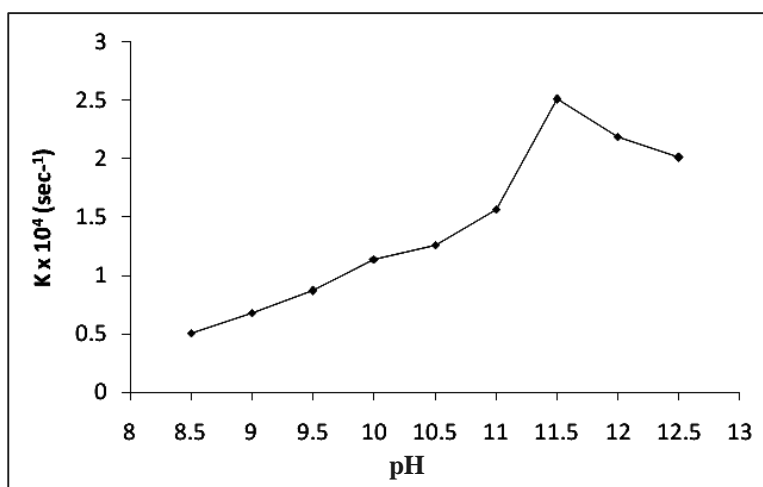| Time (min.)	Optical density (O.D.)	1 + log O.D.
0	0.894	0.9513
20	0.643	0.8082
40	0.472	0.6739
60	0.319	0.5038
80	0.246	0.3909
100	0.188	0.2742
120	0.143	0.1553
140	0.109	0.0374
		k = 2.51 x 10^{-4} sec^{-1}

Fig. 2: A typical run

Effect of pH

The pH of solution is likely to affect the photocatalytic degradation of the dyes and hence, the effect of pH on the rate of dye solution was investigated in the pH range (8.5 to 12.5). The results are represented in the Table 2 and graphically presented in Fig. 3.

Table 2: Effect of pH

[Amidoblack -10B] = 4.2 x 10^{-5} M

Copper hexacynaoferrate (II) = 0.08 g　　Light intensity = 51.0 mWcm^{-2}

pH	k x 10^4 (sec^{-1})
8.5	0.51
9.0	0.68
9.5	0.87
10.0	1.14
10.5	1.26
11.0	1.57
11.5	2.51
12.0	2.19
12.5	2.01

Fig. 3: Effect of pH

　　　　It has been observed that the photocatalytic degradation of amidoblack-10B increases with increase in pH upto pH = 11.5. It is due to more availability of the OH$^-$ ion at higher pH values. These OH$^-$ ions combine with the hole to form $^{\bullet}$OH radicals, thus more OH$^-$ will generate more $^{\bullet}$OH radical. These hydroxyl free radicals are responsible for this photocatalytic degradation. On increasing the pH above pH = 11.5, rate of degradation of dye decreases, as the pH of the solution is increased, more OH$^-$ 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 between two negatively charged species (OH⁻ 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 studies by using different concentration of amidoblack-10B. The results are reported in Table 3 and graphically presented in Fig. 4.
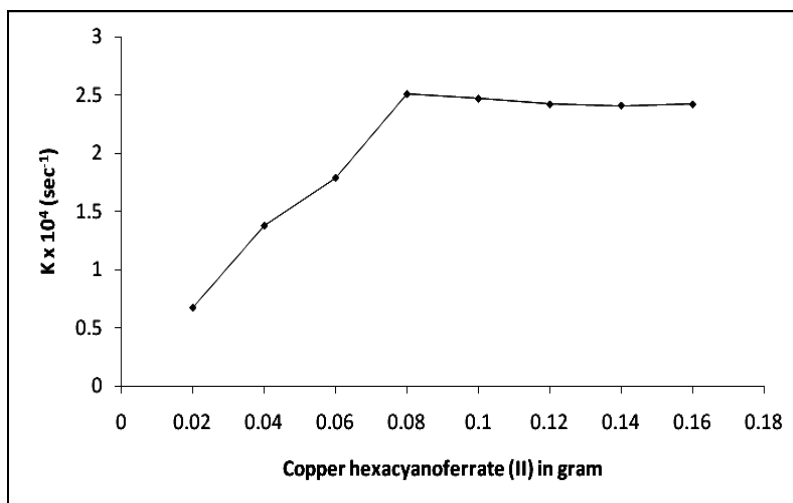
Table 3: Effect of amidoblack-10B concentration

Copper hexacyanoferrate = 0.08 g

Light intensity = 51.0 mWcm^{-2} pH = 11.5

[Amidoblack-10B] x 10^5	k x 10^4 (sec^{-1})
3.2	1.81
3.4	2.12
3.6	2.17
3.8	2.24
4.0	2.31
4.2	2.51
4.4	2.44
4.6	2.02
4.8	1.86

It was observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye up to 4.2 x 10^{-5} M. Further increase in concentration of dye resulted into a decrease in the rate of photocatalytic degradation. 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 for consecutive energy transfer, hence increase in the rate of photocatalytic degradation is observed. But when the concentration of amidoblack-10B is increased above 4.2 x 10^{-5} M, the dye itself will start acting as a 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 degradation of amidoblack-10B is observed.

Fig. 4: Effect dye concentration

Effect of amount of semiconductor

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

Table 4: Effect of amount of semiconductor

[Amidoblack-10B] = 4.2 x 10^{-5} M

Light intensity = 51.0 mWcm^{-2} pH = 11.5

Amount of Copper hexacyanoferrate (II) (g)	k x 10^4 (sec^{-1})
0.02	0.67
0.04	1.38
0.06	1.79
0.08	2.51
0.10	2.47
0.12	2.42
0.14	2.41
0.16	2.42

As indicated from above data, it is observed that rate of photocatalytic degradation of dye increases with increase in the amount of copper hexacyanoferrate (II) up to 0.08 g. But beyond 0.08 g, the rate of reaction becomes virtually constant. This can be explained on the fact that, as the amount of semiconductor is increased exposed surface area of SC will also increased, thus an increase in the rate of reaction is observed. But, after this certain limiting amount of SC (0.08 g), if the amount of SC was further increased. It will not contribute to an increase in the exposed surface area. This will also confirmed by using reaction vessel of different dimensions. Thus, after certain amount of SC, the saturation point like behaviours is observed.

Fig. 5: Effect of amount of semiconductor
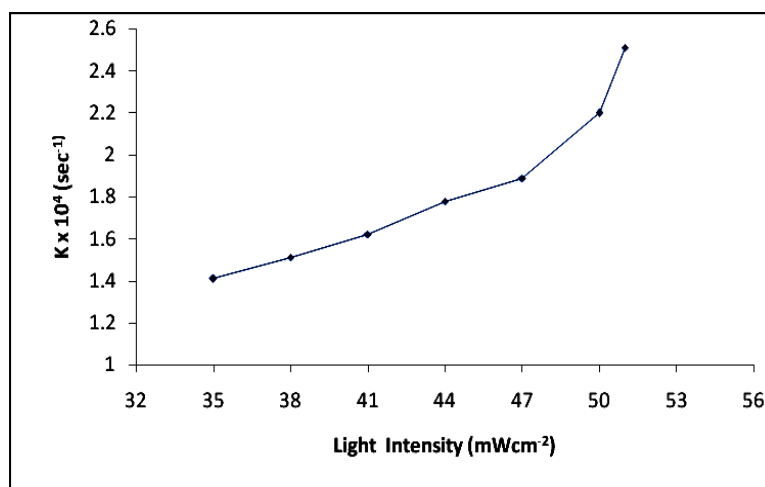
Effect of intensity of light

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

As indicated from the data, it is observed that rate of photocatalytic degradation of amidoblack-10B increases on increasing the intensity of light. It may be explained on the basis that as the light intensity is increased, the number of photon striking per unit area of SC are also increased. Thus increase in the rate of photocatalytic reaction is observed and a linear behaviour between light intensity and rate of reaction is observed. However, higher intensities are avoided due to thermal effect.
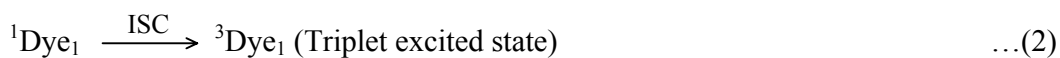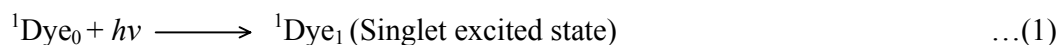
Table 5: Effect of light intensity

[Amidoblack-10B] = 4.2×10^{-5} M

Copper hexacyanoferrate (II) = 0.08 g   pH = 11.5

Light intensity in mWcm^{-2}	k x 10^4 (sec^{-1})
35	1.41
38	1.51
41	1.62
44	1.78
47	1.89
50	2.20
51	2.51

Fig. 6: Effect of light intensity

Mechanism

On the basis of experimental observation, a tentative mechanism has been proposed for degradation of amidoblack-10B by copper hexacyanoferrate (II).

$$^1Dye_0 + h\nu \longrightarrow {}^1Dye_1 \text{ (Singlet excited state)} \qquad \qquad …(1)$$

$$^1Dye_1 \xrightarrow{\text{ISC}} {}^3Dye_1 \text{ (Triplet excited state)} \qquad \qquad …(2)$$

$$SC + h\nu \longrightarrow e^- + h^+ \text{ or } SC^* \qquad \qquad …(3)$$

$$h^+ + OH^- \text{ (from base)} \longrightarrow {}^\bullet OH \qquad \dots(4)$$

$$^3Dye_1 + {}^\bullet OH \longrightarrow Product \qquad \dots(5)$$

When solution of dye was exposed to light in 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^- ions generating ${}^\bullet OH$ free radical. The dye is bleached by this ${}^\bullet OH$ radical. The participation of ${}^\bullet OH$ radical was confirmed by using hydroxyl radical scavenger (2-propanol), which almost stops the degradation.

CONCLUSION

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

ACKNOWLEDGEMENT

REFERENCES

1.   M. Mrowetz and E. Selli, J. Photochem. Photobiol., **180A**, 15 (2006).

2.   C. Karunakaran, S. Senthilvelan and S. Karuthapandian, J. Photochem. Photobiol., **172A**, 207 (2005).

3.   J. Gunlazuardi, W. Andayani and Lindu, J. Photochem. Photobiol., **173A**, 51 (2005).

4.   K. L. Ameta, R. K. Malkani and S. C. Ameta, Int. J. Chem. Sci., **8(3)**, 1658 (2010).

5.   S. S. Kim, J. H. Yun and Y. E. Sung, Photochem. Photobiol., **171A**, 275 (2005).

6.   D. Vaya, R. Vyas, R. Ameta and V. K. Sharma, J. Ind. Chem. Soc., **85**, 1269 (2008).

7.   A. Mills and G. Williams, J. Chem. Soc., Faraday Trans I, **83(8)**, 2647 (1987).

8.   N. Gandhi, V. Sharma, A. Khant and R. C. Khandelwal, Int. J. Chem. Sci., **8(2)**, 857 (2010).

9.   N. Gandhi, V. Sharma, A. Khant and R. C. Khandelwal, Int. J. Chem. Sci., **8(3)**, 1924 (2010).

10.   S. S. Hong, M. S. Lee, S. S. Park and G. D. Lee, Catel. Today, **87**, 99 (2003).

11.   Y. Jhala, A. K. Chittora, K. L. Ameta and P. B. Panjabi., Int. J. Chem. Sci., **8(3)**, 1389 (2010).

12.   J. Dobereiner, Schw. J., **62**, 90 (1831).

13.   J. Draper, Phil. Mag., **51**, 161 (1957).

14.   V. Kourium, J. Raise and B. Millions, J. Inorg. Nucl. Chem., **26**, 1111 (1964).

15.   K. Nakamota, Infrared and Raman Spectra of Inorganic and Coordination Compounds 4th Ed., Willy Interscience, New York (1987).

16.   K. S. Sustick, D. A. Hammertonand and R. E. Cliv, J. Am. Chem. Soc., **108**, 5641 (1986).

17.   S. V. S. Rao, K. B. Lal, S. V. Narasimhan and J. Ahmed, J. Radioanalytical and Nu. Chem., **240(1)**, 269 (1999).