Copper Hexacyanoferrate(II) As Photocatalyst:Decolorisation Of Neutral Red Dye

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Abstract: Copper hexacyanoferrate(II) complex was synthesised by the reaction between potassium hexacyanoferrate(II) and copper(II) chloride. The synthesised complex was characterised by IR spectra, X-ray diffraction and cyclic voltammetric measurments. The decolourisation of neutral red dye in presence of UV light radiation and copper hexacyanoferrate(II) as photocatalyst has been studied spectrophotometrically. The effect of variation of different parameters on the rate of photocatalytic degradation like pH and concentration of dye solution, amount of copper hexacyanoferrate(II) and Intensity of light has been studied. The optimum value for each parameter has also been determined. A tentative mechanism for the photocatalytic degradation of dye has also been proposed.
Key words: Photocatalyst, Neutral red dye, Copper hexacyanoferrate(II), Semiconductor (SC), Optical density (OD).

Introduction

To day there are more than 10,000 dyes available commercially[1]. Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, pharmaceutical and food industries. These industries consume large amount of water during the dyeing process. The extensive use of dye often poses pollution problem in the form of coloured wastewater discharged into environmental water bodies, which also interfere with transmission of sunlight into streams, therefore, reduces photosynthetic activity[2]. Dyes used in textile industries are highly toxic, stable, soluble in water and non biodegradable. Since most of the dyes are carcinogenic[3,4] in nature and pose a serious threat to the environment and also have adverse effect on the living organism and humanbeing[5-7]. Some other adverse effect of dyes on human such as skin, lungs and other respiratory disorders, are also reported[8-10]. Thus, decolourisation of effluents from textile dyeing and finishing industry is more important than other organic colourless chemicals[11].

Dyes wastewater has been traditionally treated by as biological, physical and chemical methods[12] including adsorption, membrane filtration, electrolysis, ion exchange, electrokinetics, coagulation etc. But, most of these methods have difficulty in practical use. Recently semiconductor photocatalysis emerged as an alternative to conventional methods. Semiconductors are used as photocatalyst to degrade organic pollutants present in water to less harmful inorganic materials[13]. Several semiconductors such as Titanium dioxide (TiO_2)[14-18], Zinc Oxide (ZnO)[19], Bismuth Oxide(Bi_2O_3)[20], Tin oxide(SnO_2)[21], Iron Oxide (Fe_2O_3)[22,23], Tungsten Oxide(WO_3)[24,25], Cadmium Sulphide(CdS)[26], Zinc sulphide(ZnS)[27] etc are used as photocatalyst in the photocatalytic degradation

of various dyes and organic wastes. The composite semiconductors such as, TiO_2/ZnO[28], ZnO/SnO_2[29], tin doped TiO_2[30], $ZnO/TiO_2/SnO_2$[31] are also used as photocatalyst.

Balazani and Carassiti[32] have reviewed the photochemistry of coordination compounds quite extensively, while the volume edited by Adamson and Fleischaure[33] can be cited as an important mile stone in the evolution of inorganic photochemistry in recent time. Recently, different transition metal complexes are used as photocatalyst in the photocatalytic degradation of various dyes. Jhala et al[34] used potassium trioxalatoferrate(III) as an oxidant for the photocatalytic degradation of neutral red dye. Ammonium phosphomolybdate used as photocatalyst in photocatalytic degradation of Fast Green[35], and Janus Green-B[36]. Potassium hexacyanoferrate(II) was used as semiconductor in the photocatalytic degradation of fuchsin basic and malachite green[37]. Copper ferrocyanide[38] used for the photosensitized oxidation of diphenylamine. Ali et al[39] established the catalytic activity of nickel hexacyanoferrate(II). Copper hexacyanoferrate(II)[40] and Nickel hexacyanoferrate(II)[41] established as semiconductor in photocatalytic degradation of amidoblack-10B.

In the present study copper hexacyanoferrate(II) is used as photocatalyst in the photocatalytic degradation of neutral red dye. Since it is water insoluble complex, thus after treatment of polluted water, it is easy to remove semiconductor. Now, treated water may be recycled in the same factory or reused in other industries in which less quality of water is required.

Materials And Method

Chemicals

Neutral red dye [Loba Chemie], Copper(II) Chloride [Qualigens], Potassium hexacyanoferrate(II) [Merck], Sulphuric acid[BDH] and Sodium hydroxide[Merck] are used in present investigation. Double distilled water was used for the preparation of all solutions.

Apparatus and Instruments

Spectrophotometer (Systronics Model-106), Solarimeter (CEL Model-SM 201), Digital pH meter (Systronics Model-335) and Electronic balance (Citizen Scale Model-CY 204) were used for the measurement of absorbance (OD), light intensity, pH and weight of different substances respectively. 200W tungsten lamp (Philips) was used to irradiate reaction mixture. Infrared spectra of the complex were performed by FTIR (Jasco - 6100, Mumbai, India). X-ray diffraction spectrum of Cu(HCF) were performed by using XRD pro Panalytical system. Cyclic voltammogram of complex were obtained by using a BAS CV 50W electrochemical analyzing system. The metals (copper and Iron) were determined with the help of Perkin Elmer, A Analyst 800 atomic absorption spectrophotometer and the elements carbon, hydrogen and nitrogen were estimated on Elemental Vario (ELHI III, CHNS analyser).

Synthesis and Characterization of Copper Hexacyanoferrate(II)

Copper hexacyanoferrate(II) is the chocolate brown complex. Its colour intensity depends on the number of water molecules associated to the complex. This complex was prepared by using the 0.1M potassium hexacyanoferrate(II) and 0.1M copper(II) chloride solutions. 167mL of 0.1M potassium hexacyanoferrate(II) solution was added slowly into 500 mL of 0.1M copper(II) chloride solution, with constant stirring, according to the method used by Kourim *et al*[42] and also used by Tewari [43]. The reaction mixture was heated on a water bath at 100^0C about 2-3 hrs and kept as such for 24 hrs at room temperature. Chocolate brown precipitate was obtained. This was filtered and washed thoroughly with double distilled water and then dried in an oven at 60^0C. Complex was ground and sieved to (100-150)BSS mesh size.

Copper hexacyanoferrate(II) is fairly stable in acids like HNO_3, HCl, H_2SO_4 etc and bases like NaOH, KOH etc. The percentage of metal copper and iron were determined by AAS where as percentage of carbon, hydrogen and nitrogen were determined by CHNS analyser. Results are shown in Table 1 as-

Table 1: Elemental Analysis of Copper Hexacyanoferrate(II)

Value	Composition (%)				
	C	**H**	**N**	**Fe**	**Cu**
Observed	14.21	3.38	17.33	11.40	26.36
Calculated	14.91	3.34	17.39	11.56	26.30

On the basis of results of elemental analysis, shown in Table 1, the molecular formula of copper hexacyanoferrate(II) was proposed as $Cu_2[Fe(CN)_6].8H_2O$

IR Spectral data of copper hexacyanoferrate(II), shows a broad peak about 3637cm^{-1}, which is characteristics of -OH group and water molecule. Thus suggesting that 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 transition metal ion[44-46] and Fe-C stretching respectively. A broad band at 500cm^{-1} was obtained, which may be due to polymerisation of metal nitrogen bond.

X-ray diffraction measurements have been performed by using Panalytical system having CuK , as a radiation source of wave length   = 1.5406A^0 within the 2theta ranging from10^0 to 79.98^0 (Fig. 1).
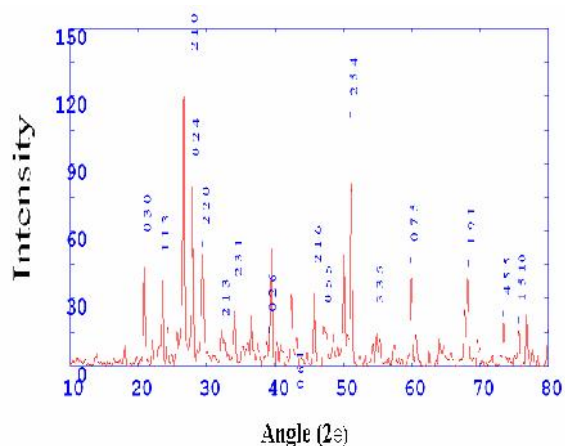
 Fig. 1: XRD of Cu (HCF)

The clarity and sharpness of the X-ray peaks indicate that complex is a highly crystalline in nature. Lattice parameters for this complex were obtained as, a=6.9234, b=12.672, c=14.789 and   =   = = 90^0, thus for this complex crystal system was found as orthorhombic lattice type.

Cyclic voltammetric measurements were carried out using a BAS CV 50W electrochemical analyzing system ($E_{1/2}$ measured to an accuracy of $\pm$ 1.0 mv). Cyclic voltammogram of complex was recorded in ammonia solution. A three electrode configuration composed of Pt-disk working electrode, a pt-wire counter electrode and Ag/AgNO3 reference electrode was used for measurement.
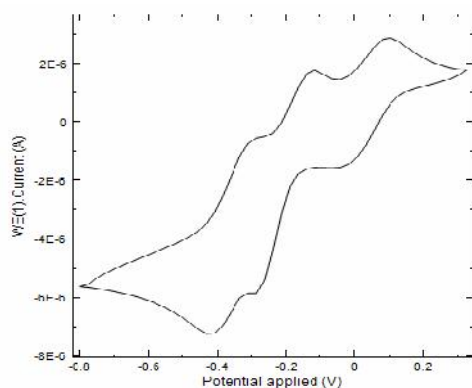
Fig. 2: Cyclic Voltammogram of Cu(HCF) in ammonia solution, Scan rate 100mV/Sec.

In above cyclic voltammogram, in forward scan (potential from -0.8 to 0.4 V) two oxidation peaks were observed having peak potentials (E_p) -0.14084 and 0.1033V. Whereas, in reverse scan (potential from 0.4 to -0.8 V) two reduction peaks were observed at E_p -0.313 and -0.40939 V. These are corresponding to one electron exchange [47,48] between Fe^{+2} and Fe^{+3}. Thus, this complex may be used as oxidant or reductant in photocatalytic reactions depending on the nature of dye and reaction conditions.

Procedure of Photochemical Degradation of Neutral Red Dye

1.0×10^{-3} M Neutral red dye solution was prepared by dissolving 0.2888g of the dye in 1000mL of doubly distilled water and it was used as stock solution and further diluted as and when required. The desired pH of the solution was adjusted by adding previously standardised solutions of H_2SO_4 and NaOH. 0.175g of copper hexacyanoferrate(II) was added to 50.0mL 5.8×10^{-5}M neutral red dye solution. Irradiation was carried by using 200W tungsten lamp. The intensity of light was measured at various distances by using 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 copper hexacyanoferrate(II) was removed with the help of centrifuging machine.

Result And Discussion

Typical Run

In order to examine the photocatalytic activity of copper hexacyanoferrate(II), neutral red dye solution was irradiated in the presence of copper hexacyanoferrate(II) and UV light radiation. The optical density of irradiated reaction mixture was noted at 20min time interval at λ_{max} = 520nm. Experimental results obtained are presented in Table 2.

Table 2 : A Typical Run

Copper hexacyanoferrate(II) = 0.175g, pH = 3.5
Light intensity = 51.0 mWcm^{-2}, [Neutral red] = 5.8×10^{-5}M

Time(min)	OD	1 + logOD
0	1.590	1.2014
20	1.080	1.0334
40	0.688	0.8376
60	0.466	0.6684
80	0.365	0.5623
100	0.203	0.3075
120	0.152	0.1818

From the data presented in the Table 2, it was observed that optical density of neutral red dye solution decreased with increase in time of irradiation i.e. decolourisation of dye take place. A graph plotted, between exposure time and (1+ log OD), is obtained as straight line as presented in Fig. 3.
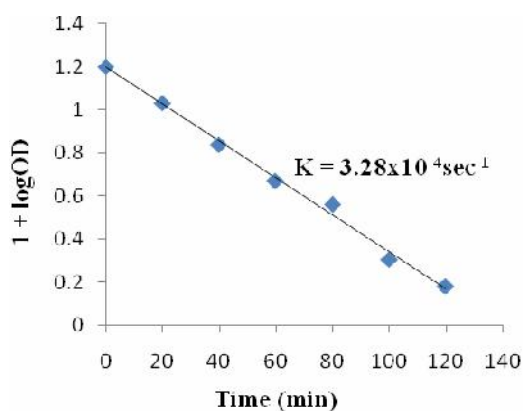
Fig. 3: A Typical run

Linear behaviour of this curve shows that photocatalytic degradation neutral red dye with copper hexacyanoferrate(II) follows pseudo first order kinetics. The degradation rate constant K for the reaction was calculated by the expression-

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

and obtained as $3.28 \times 10^{-4} sec^{-1}$.

Effect of pH

The pH of solution is an important parameter to be studied for the photocatalysis of wastewater. It affects the surface change of SC, hence, it also affects the activity of Cu(HCF). Thus, degradation rate of pollutant may be changed by varying the pH of the solution. The effect of pH on the photocatalytic degradation was studied in the pH range 2.0 to 6.0, keeping all other factors identical. The results are presented in Table 3 and graphically presented in Fig 4.

Table 3 : Effect of pH

[Neutral Red] = 5.8×10^{-5}M,   SC = 0.175g
Light Intensity = 51mW cm^{-2}

pH	K x 10^4 (sec^{-1})
2.0	0.879
2.5	1.50
3.0	2.92
3.5	3.28
4.0	2.87
4.5	2.65
5.0	2.47
5.5	2.09
6.0	1.94

It has been observed from above data that the rate of bleaching of neutral red dye increases with an increase in pH up to pH = 3.5, on further increase in pH above 3.5 rate of bleaching decreases. This effect of pH on rate of bleaching may be explained by the fact that at a higher pH (>3.5) the semiconductor surface became slightly negatively charged and so the anionic dye molecule will experience a force of repulsion causing a decrease in the rate of the reaction. On the other hand at lower pH (<3.5) the surface of the semiconductor becomes slightly positively charged and the dye molecules may become protonated, in the presence of H^+ ions, causing a force of repulsion between the surface of semiconductor and the protonated dye molecules. This will also retard the rate of the reaction.
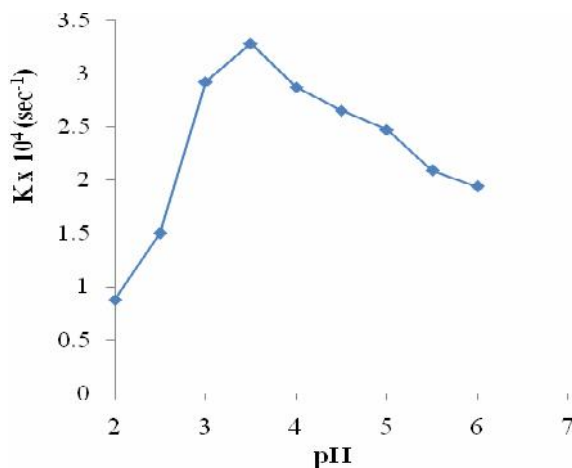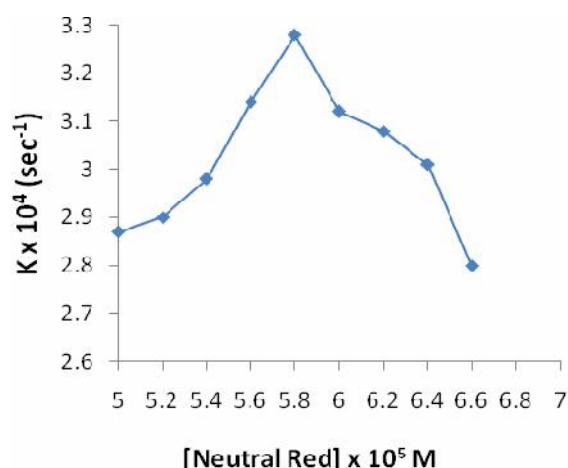

Fig. 4: Effect of pH

Effect of Neutral Red Dye Concentration

The effect of variation of neutral red dye concentration on the rate of reaction was also studied by using different concentration solutions of dye. The results are reported in table: 4 and graphically presented in Fig: 5.

Table 4 : Effect of Neutral Red Concentration

SC = 0.175g   pH = 3.5
Light Intensity = 51mWcm^{-2}

[Neutral red] x 10^5M	$Kx10^4$ (sec^{-1})
5.0	2.87
5.2	2.90
5.4	2.98
5.6	3.14
5.8	3.28
6.0	3.12
6.2	3.08
6.4	3.01
6.6	2.80

Fig. 5: Effect of Dye Concentration

It was observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye up to 5.8×10^{-5}M. It may be explained on the basis of the fact that as the concentration of neutral red dye increased, more dye molecules would be available for excitation and consecutive energy transfer, hence increase in the rate of photochemical degradation was observed. But, as the concentration of neutral red dye was further increased above 5.8×10^{-5}M, the rate of photocatalytic bleaching is decreased. This is probably due to the fact that after certain limits of dye concentration, the dye molecules present in the upper layer of the solution will absorb a major portion of light. This will prevent the incident light radiation to reach the semiconductor surface in the bulk of the solution. Thus, high concentration of dye act as a filter for the incident light and hence, at higher concentration of the dyes, the rate of bleaching decreases.
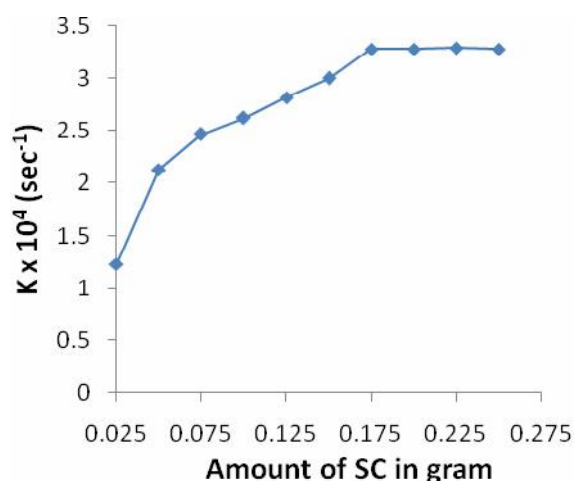
Effect of Amount of Semiconductor

The effect of amount of copper hexacyanoferrrate(II) powder on the rate of photocatalytic bleaching of the neutral red dye was also studied by taking different amount copper hexacyanoferrate(II). The results are reported in Table 5 and graphically presented in Fig 6.

Table 5: Effect of Amount of Semiconductor

[Neutral Red] = 5.8×10^{-5}M   pH = 3.5
Light Intensity = 51mWcm^{-2}

Amount of SC in gram	$Kx10^4(sec^{-1})$
0.025	1.23
0.050	2.13
0.075	2.47
0.100	2.62
0.125	2.82
0.150	3.00
0.175	3.28
0.200	3.28
0.225	3.29
0.250	3.28

Fig. 6: Effect of Amount Semiconductor

From above data, it was observed that rate of photocatalytic degradation of dye increases with increase in the amount of copper hexacyanoferrate(II) up to 0.175g. But beyond 0.175g, the rate of reaction remains almost constant. It may be explained on the fact that, as the amount of semiconductor was increased exposed surface area of SC also increased, thus an increase in the rate of reaction was observed. But, after this optimum amount of SC (0.175g), if the amount of SC was further increased it did not contribute in the exposed surface area. Thus, after certain amount of SC, almost constant degradation rate was observed.

Effect of Light Intensity

In photochemical reactions active species are generated by the absorption of radiations. Thus rate of photocatalytic degradation is also governed by the intensity of radiation.

The effect variation of light intensity on the rate of photocatalytic bleaching of neutral red dye was studied by varying the intensity from $35 mWcm^{-2}$ to $51 mWcm^{-2}$ keeping all other factors identical. The results are reported in Table 6 and graphically presented in Fig 7.
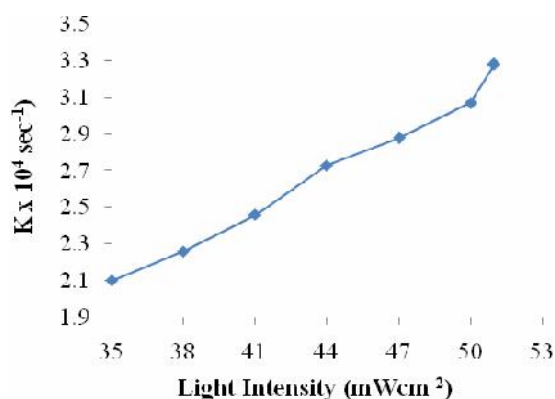
Table 6 : Effect of light intensity
[Neutral red] = 5.8 x 10^{-5}M,   pH = 3.5
SC = 0.175g

Light intensity in mWcm^{-2}	K x 10^4(sec^{-1})
35	2.10
38	2.26
41	2.46
44	2.73
47	2.88
50	3.07
51	3.28

As indicated from the above data, it has been observed that rate of photocatalytic degradation of neutral red dye increases on increasing the intensity of light. It may be explained on the basis that as the light intensity was increased the number of photons striking per unit area of SC will also increased. Thus, increase in the rate of photocatalytic reaction was observed and a linear behaviour between light intensity and rate of reaction was observed. However, higher intensities are avoided due to thermal effect.
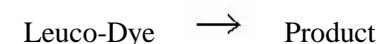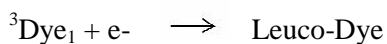
Fig.7: Effect of light intensity

Mechanism

On the basis of experimental observation, a tentative mechanism for photocatalytic bleaching of dye in presence of copper hexacyanoferrate(II) has been proposed as-

$^1Dye_0 + h \longrightarrow$ $^1Dye_1$ (Singlet excited state)

$^1Dye_1 \xrightarrow{ISC}$ $^3Dye_1$ (Triplet excited state)

$SC + h \longrightarrow$ $e^- + h^+$ or SC^+

$^3Dye_1 + e- \longrightarrow$ Leuco-Dye

Leuco-Dye $\longrightarrow$ Product

When solution of dye, Neutral Red, was exposed to light in presence of semiconductor copper hexacyanoferrate(II); initially, the dye molecules, present in singlet ground state($^1Dye_0$), absorb the radiation of suitable wavelength, then excited to their first excited singlet state ($^1Dye_1$). These excited singlet molecules were converted to the triplet excised state through inter system crossing (ISC). Semiconductor also absorb light to excite its electron from valence band to conduction band; thus, leaving behind a hole in the balance band. The electron of the SC will reduce the dye molecule to its colourless Leuco form which is ultimately degraded into final products.

Conclusion

Neutral red dye can be successfully degrading using Copper hexacyanoferrate(II) semiconductor under visible light irradiation. Thus, Coper hexacyanoferrate(II) may act as a photocatalyst quite effectively to photodegrade different dye molecules to colourless less toxic products.

Acknowledgements

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