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Use Of Cobalt Hexacyanoferrate(II) Semiconductor In Photocatalytic Degradation Of Neutral Red Dye

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Abstract: Cobalt hexacyanoferrate(II) were synthesised by reaction of potassium hexacyanoferrate and cobalt nitrate. The synthesised product was characterised by X-ray diffraction, IR spectra and from cyclic voltammetry. The photocatalytic behaviour of cobalt hexacyanoferrate(II) complex was established spectrophotometrically through decolourisation of neutral red dye in presence of UV light radiation and photocatalyst. The effect of variation of different parameters, like pH of dye solution, amount of cobalt hexacyanoferrate(II), concentration of dye solution and Intensity of light, have been observed on the rate of photocatalytic degradation and optimum condition for each parameter has also been determined. A tentative mechanism for the photocatalytic degradation of dye has been proposed.

Key words: Photocatalyst, Neutral red dye, Cobalt hexacyanoferrate(II), Semiconductor (SC), Optical density (OD).

INTRODUCTION

Excessive and indiscriminate use of dye stuffs has become increasingly a subject of environmental concern. The release of textile industrial waste water in natural environment is very problematic to aquatic life and mutagenic to human. The release of this waste water without treatment into water system is very dangerous. Since most of the dyes are carcinogenic [1,2] in nature and pose a serious threat to the environment[3], as a result an effective purification methods for eliminating dye have been in urgent demand.

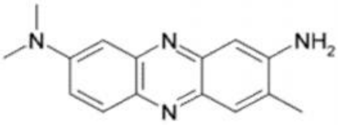
The already existing methods, like chemical method[4], elctrocoagulation[5], electrochemical method[6] or biological treatment[7], appear to have their own drawbacks. But, for the treatment of waste water photocatalysis has become a promising method all over the globe. It is being used for solving the problem of environment. In recent years many studies have been focused on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalyst.

Morwetz et al[8] investigated the effect of Iron species in photocatalytic degradation of azo dye in TiO_2 suspension. Solar photocatalyzed oxidation of aniline on TiO2 studied by Karuakaran et al[9]. Janaki et al [10] compare the efficiency of various semiconductor catalysts for photodegradation of Safranin-T. A comparative study of degradation real textile effluents by photocatalytic reactions involving $UV/Fe^{+2}/H_2O_2$ and $UV/TiO_2/H_2O_2$ system was reported by Garcia et al[11]. Photocatalyst for water decontamination has been reported by Gelover et al[12]. The field of catalysis has been excellently reviewed by Scheavello[13].

Balazani and Carassiti[14] have reviewed the photochemistry of coordination compounds quite extensively. The photochemistry of transition metals has been a matter of interest for a chemist due to their exclusive redox properties. Copper ferrocyanide[15] was used in dehydrogenation of ascorbic acid with methylene blue in the presence of light. Alam et al[16] study the interaction of aniline and p-anisidine with chromium ferrocyanide and found that the outer metal ions of chromium ferrocyanide are responsible for the interaction. The photochromic behaviour of potassium hexacyanoferrate(II)-fuchsin basic and Potassium hexacyanoferrate(II)- malachite green systems was investigated by Taneja[17]. Recently, different transition metal complexes are used as semiconductor in the photocatalytic degradation of various dyes. Jhala et al[18] 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[19] and Janus Green B[20]. Copper hexacyanoferrate(II) was used as semiconductor in the photocatalytic degradation of Rose bengal[21] and Bismarck brown[22]. Ali et al[23] established the catalytic activity of nickel hexacyanoferrate(II). Copper hexacyanoferrate (II)[24] and Nickel hexacyanoferrate(II)[25] are established as semiconductor in photocatalytic degradation of amidoblack-10B.

From the literature survey, it is apparent that very little attention has been paid on Cobalt hexacyanoferrate(II), which is coloured and able to utilize sun light efficiently, as semiconductor for photocatalytic bleaching of dyes. In present study cobalt hexacyanoferrate(II) is found good SC for the photocatalytic degradation of neutral red dye. Since it is water insoluble, thus after treatment of polluted water, it is easy to remove from treated water. Now, treated water may be recycled in the same factory or reused in other applications such as other industries or agriculture, in which less quality of water is required.

Neutral red is a basic dye of the azine series. It is widely used as a biological stain for a variety of purposes including the demonstration of gonococci and other intracellular Gram-negative bacteria, for the supravital staining of blood, differentiation of living and dead cells etc. and it is also used as an indicator(pH 6.8-8.0, pinkish- red-brown- yellow). It is also used for desensitizing photographic emulsions [26].



Neutral red dye

MATERIALS AND METHOD

Chemicals

Neutral red dye [Loba Chemie], Cobalt(II) Nitrate[BDH], 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 solutions.

Apparatus and instruments

Spectrophotometer (Systronics Model-106), Digital pH meter (Systronics Model – 335), and Electronic balance (Citizen Scale Model-CY 204) were used for the measurement of absorbance (OD), pH of dye solution and weight of different substances respectively. 200W tungsten lamp (Philips) was used for irradiation of reaction mixture. Infrared studies of the complex were performed by FTIR (Jasco -6100, Mumbai, India) from Pune University, Maharashtra. X-ray diffraction spectrum of Co(HCF) were performed by using XRD pro Panalytical system. Cyclic voltammogram of complex were obtained by using a BAS CV 50W electrochemical analyzing system.

Synthesis and Characterisation of Cobalt hexacyanoferrate(II)

For the preparation of Cobalt hexacyanoferrate(II), 0.1M solution of Potassium hexacyanoferrate and 0.1M Cobalt nitrate were prepared. Then added potassium hexacyanoferrate (167ml, 0.1M) solution slowly into cobalt nitrate (500ml, 0.1M) solution, with constant stirring according to the method used by Kourim et al[27] and also used by Tanveer et al[28]. The reaction mixture was heated on a water bath at 60^0C about 2-3 hrs and kept as such for 24 hrs at room temperature. The precipitate obtained was filtered and washed thoroughly with doubly distilled water and then dried in an oven at 60^0C.

Cobalt ferrocyanide was characterised by spectral studies. It is fairly stable in acids like HNO_3, HCl, H_2SO_4 etc and base like NaOH, KOH etc. The IR Spectral data of cobalt ferrocyanide shows a broad peak about 3408 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 1605 cm^{-1} is due to HOH bending. A sharp intense peak at 2117 cm^{-1} and a broad peak at 595 cm^{-1} are the characteristics of cyanide coordinated to a metal transition ion [29,30] and Fe-C stretching[31] respectively. A broad band about 500 cm^{-1} is obtained, which may be due to polymerisation of metal nitrogen bond.

The synthesised complex was also examined by XRD. X-ray diffraction measurements have been performed by using Panalytical system having CuKα, as a radiation source of wave length λ = 1.5406A^0 within the 2theta ranging from10^0 to 79.98^0 (Fig. 1).

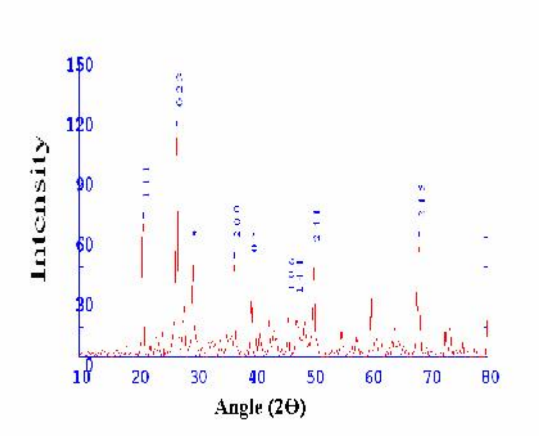


Fig. 1: XRD of Co (HCF)

The clarity and sharpness of the X-ray peaks indicate that complex is a highly crystalline in nature. Lattice parameters for this complex are obtained as, a=4.9168, b=10.987, c=12.891 and $\alpha = \beta = \gamma = 90^0$, thus for this complex crystal system is 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 ± 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.

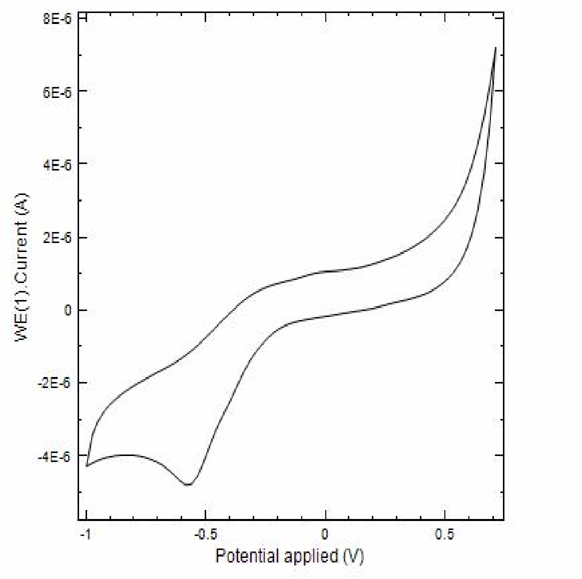


Fig. 2: Cyclic Voltammogram of Co(HCF) in ammonia solution, Scan rate 100mV/Sec.

In the above cyclic voltammogram, in forward scan (from -1.0 to 0.75V) no significant peaks were observed. Where as, in reverse scan (potential from 0.75 to -1.0V) one reduction peak at E_p= -0.56061 was observed. This is corresponding to one electron exchange[32] between Fe^{+2} and Fe^{+3}. Thus, this complex may be used as oxidant or reductant in photochemical reactions depending on the nature of dye and reaction conditions.

Photochatalytic degradation of Neutral red dye

1.0×10^{-3} M neutral red dye solution was prepared by dissolving 0.2888g of neutral red 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 prepared standardised solutions of H_2SO_4 and NaOH. 0.150g of cobalt hexacyanoferrate(II) was added to 50.0mL 5.8×10^{-5}M neutral red dye solution. Irradiation was carried out by using 200W tungsten lamp. The intensity of light was measured at various distances by using solorimeter. 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 Cobalt hexacyanoferrate(II) (SC) was removed with the help of centrifuging machine.

RESULT AND DISCUSSION

Typical Run

In order to examine the photocatalytic activity of cobalt hexacyanoferrate(II), photochetalytic degradation of neutral red dye has been investigated at λ_{max}= 520nm. Optical density of irradiated solution was noted at 20 minute time interval, and graph was plotted between exposure time and 1+logOD, which were obtained as straight line. Linear behaviour of this curve shows that photocatalytic bleaching of neutral red dye with cobalt 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: 3.

Table 1

[Neutral red] = 5.8 x10^{-5}M, Amount of SC = 0.150g
Light intensity = 51.0 mWcm^{-2}, pH = 5.0

Time(min)	OD	1+logOD
0	0.756	0.8785
20	0.617	0.7903
40	0.511	0.7084
60	0.431	0.6345
80	0.372	0.5705
100	0.282	0.4502
120	0.241	0.3820

K=1.582x10^{-4} Sec^{-}

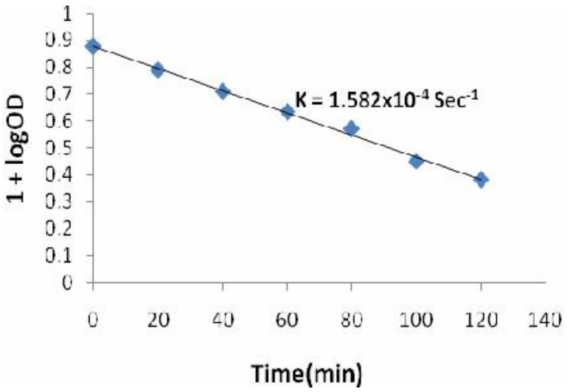


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Fig. 3: A Typical run

Effect of pH

The rate of photocatalytic degradation of dye depends on the pH of solution. To study the effect of pH on the photocatalytic degradation of neutral red dye, dye solutions were prepared in the pH range 2.5 to 6.5, keeping all other factor identical. The results are presented in the table: 2 and graphically presented in Fig: 4.

Table 2: Effect of pH

[Neutral red] = 5.8x10^{-5}M SC=0.150g
Light intensity = 51mW cm^{-1}

pH	**K x 10^4 (Sec^{-1})**
2.5	0.410
3.0	0.734
3.5	1.232
4.0	1.416
4.5	1.509
5.0	1.582
5.5	1.314
6.0	0.832
6.5	0.689

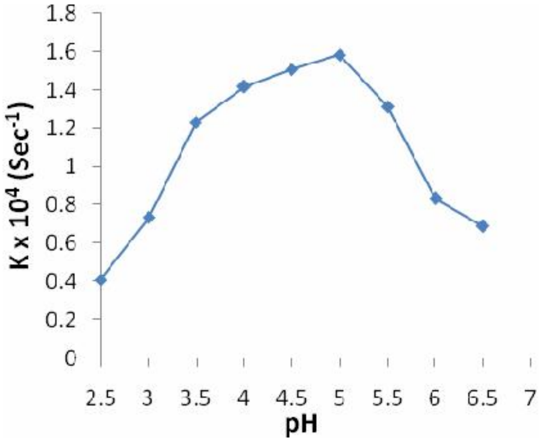

Fig.4: Effect of pH

It has been observed from the above data that the rate of bleaching of neutral red dye with cobalt hexacyanoferrate(II) increased with increase in pH upto 5.0, on further increase in pH above 5.0 rate of bleaching decreases. This behaviour may be explained on the basis that at a higher pH (pH = >5.0) the surface of the semiconductor becomes slightly negatively charged, thus anionic dye molecule experience a force of repulsion with SC, causing a decrease in the rate of reaction. On the other hand at lower pH (pH = <5.0), in the presence of H^+ ions, the surface of SC becomes slightly positively charged and dye molecule become protonated, causing a force of repulsion between the surface of SC and protonated dye molecules, this will also retard the rate of reaction.

Effect of Neutral red dye concentration

The rate of photocatalytic bleaching of dye also depends on the on the concentration of dye solution. To study the effect of concentration, dye solutions were prepared in the concentration range 5.0x10^{-5}M to 6.8x10^{-5}M, keeping all other factor identical. The results are reported in table: 3 and graphically presented in Fig: 5

Table 3: Effect of Neutral red concentration

SC = 0.150g pH = 5.0
Light intensity = 51mWcm^{-2}

[Neutral red] x 10^5M	Kx10^4(Sec^{-1})
5.0	0.922
5.2	1.210
5.4	1.321
5.6	1.444
5.8	1.582
6.0	1.516
6.2	1.458
6.4	1.418
6.6	1.248
6.8	1.219

It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye up to 5.8x10^{-5}M. This behaviour may be explained on the fact that as the concentration of red dye was increased, more dye molecule will be available for excitation and consecutive energy transfer, hence increase in the rate of photochemical bleaching was observed.

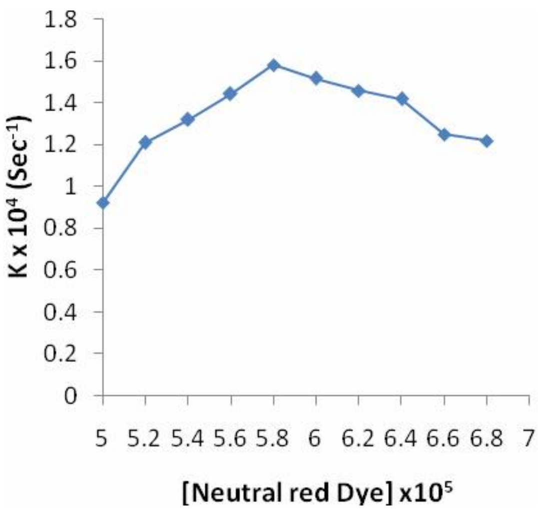

Fig.5: Effect of Dye Concentration

On further increase in the concentration of dye (above 5.8x10^{-5}M), the rate of photochemical bleaching decreases. This is probably due to the fact that after certain limits of dye concentration, dye molecule present in the upper layer of the solution will absorb a major portion of light. This will prevent the incident light to reach SC surface in the bulk of solution. Thus, high concentration of dye acts as a filter for the incident light and hence at higher concentration, the rate of bleaching decreases.

Effect of amount of semiconductor

The amount of SC also affects the rate of photcatalytic bleaching of dye. The effect of amount of SC on the rate of photocatalytic bleaching of dye was studied by taking different amount of cobalt hexacyanoferrate(II) and keeping all other factor identical. The results are reported in table: 4 and graphically presented in Fig: 6.

Table 4:Effect of amount of semiconductor

[Neutral red] = 5.8x10^{-5}M pH=4.5
Light intensity = 51mWcm^{-2}

Amount of SC in gram	Kx10^4(Sec^{-1})
0.050	1.050
0.075	1.138
0.100	1.223
0.125	1.369
0.150	1.582
0.175	1.593
0.200	1.574
0.225	1.599

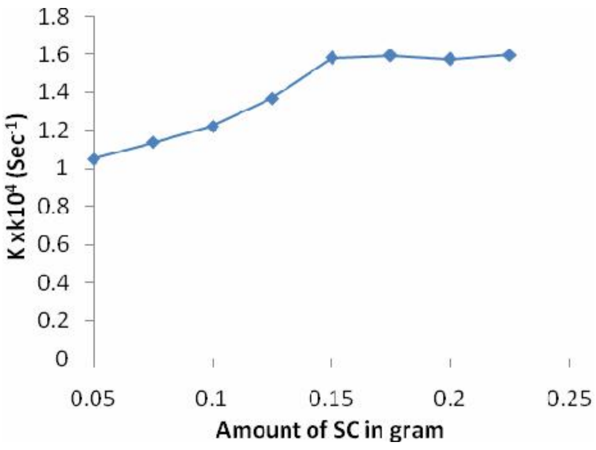

Fig.6: Effect of amount of Semiconductor

From above data, it has been observed that rate of photocatalytic degradation of dye is increases with increase in the amount of Cobalt hexacyanoferrate (II) up to 0.150g. But beyond 0.150g the rate of reaction remains almost constant. It may be explained on the basis of fact the that, as the amount of semiconductor increased, exposed surface area of SC will also be increased, and more radiation will be absorbed by SC, thus an increase in the rate of reaction was 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. It is also confirmed by using reaction vessel of different dimension. Thus, after certain amount of SC, the saturation point like behaviours was observed.

Effect of intensity of light

The effect variation of light intensity on the rate of photocatalytic bleaching of neutral red dye was also observed. The results are reported in table: 5 and graphically presented in Fig: 6.

Table 5: Effect of light intensity

[Neutral red] = 5.8 x 10^{-5}M, pH = 5.0

SC = 0.150g

Light intensity in mWcm^{-2}	K x 10^4 (Sec^{-1})
35	1.007
38	1.056
41	1.131
44	1.195
47	1.319
50	1.441
51	1.582

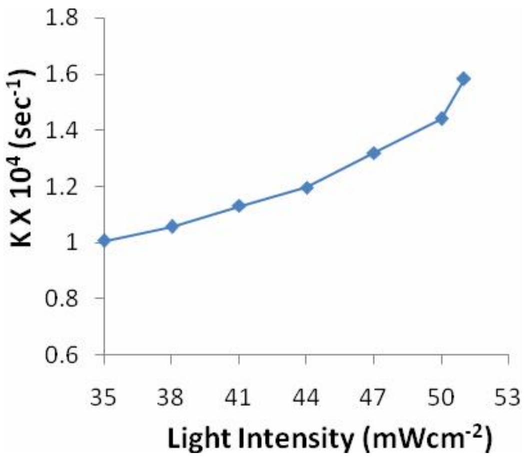

Fig.7: Effect of light Intensity

As indicated from the above data, it is 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 is increased the number of photons striking per unit area of SC will also be increased. This will result in the corresponding increase in rate of photocatalytic bleaching of neutral red dye. However, higher intensities are avoided due to thermal effect.

MECHANISM

On the basis of experimental observation, a tentative mechanism has been proposed for bleaching of neutral red dye with Cobalt hexacyanoferrate(II).

$$^1\text{Dye}_0 + h\nu \longrightarrow {}^1\text{Dye}_1 \text{ (Singlet excited state)}$$

$$^1\text{Dye}_1 \xrightarrow{\text{ISC}} {}^3\text{Dye}_1 \text{ (Triplet excited state)}$$

$$\text{SC} + h\nu \longrightarrow e^- + h^+ \text{ or } \text{SC}^+$$

$$^3\text{Dye}_1 + e^- \longrightarrow \text{Leuco-Dye}$$

$$\text{Leuco-Dye} \longrightarrow \text{Product}$$

When solution of dye, neutral red, was exposed to light in presence of semiconductor Cobalt hexacyanoferrate(II); initially, the dye molecules, present in singlet ground state(^{1}Dye$_0$), absorb the radiation of suitable wavelength, excited to their first excited singlet state(^{1}Dye$_1$). These excited singlet molecules were converted to the triplet excited state through inter system crossing (ISC). Semiconductor also absorb light radiation to excite its electron from valence band to conduction band; thus, leaving behind a hole in the balance band. The electron, released from the SC, will reduce the dye molecule to its colourless Leuco form which is ultimately degraded to colourless final products.

CONCLUSION

The result of this study clearly establish that cobalt hexacyanoferrate(II) semiconductor photocatalysis can be efficiently used for the degradation of the dyes and other organic compounds in dyeing and printing effluents. Cobalt hexacyanoferrate (II) SC may act as a photocatalyst quite effectively to photodegrade neutral dye molecules to colourless less toxic products. Rate of declourisation of dye is effected by pH, conc. of dye solution, amount of semiconductor and intensity of light. The optimum degradation of neutral red dye found at pH=5.0, Concentration of dye =5.8x10^{-5}M and amount of SC = 0.150gram.

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