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Photo Catalytic Degradation of Cobalt Picrate in The Presence of Zinc Oxide

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ABSTRACT

Huge amount of work has been going on in the field of dye, herbicide, insecticide but little work is carried out in the field of metal complexes. Photo catalytic degradation of cobalt picrate was studied in the presence of heterogeneous semiconductor. Various parameters were studied such as effect of concentration, amount of semiconductor, effect of light intensity, effect of pH etc. on solution of cobalt picrate.

Keywords: Photo catalysis, degradation, Zinc oxide, cobalt picrate.

INTRODUCTION

Heavy metals are present in the effluents of different types of industries such as paint, electroplating, lather tanning, agriculture and battery manufacturing [1-3]. In present days treatment of waste water is a big challenge for scientists and researchers. Time to time several methods are developed to remove industrial waste, such as chemical precipitation and biological removal but out of them, advance oxidation process (AOP) has been widely used technology for treatment of waste water in last decades [4-6]. Advance oxidation processes like Fenton and photo-Fenton catalytic, H_2O_2/UV, semiconductor photo catalysis have been studied for the purpose such as decolourization of waste water [7-9]. In recent years, semiconductor is more attractive and important since it has a great competence to contribute to environmental issues [10]. Heterogeneous photo catalysts are widely used to degrade the toxic pollutants to its non-toxic form [11], ZnO has more efficiency to degradation of pollutant rather than TiO_2 in certain conditions [12-15]. Photo catalytic degradation of Rhodamine B dye has been done using hydrothermally prepared ZnO and MoO_3, Cu_2O, V_2O_5 [16-17]. Photo catalytic degradation of acridine orange has been done in the presence of ZnO [18]. ZnO loaded activated carbon has highest activity to degradation of DB53 which was experimentally proved [19]. Photo catalytic degradation of acid red 18 was done by ZnO [20]. Photocatalytic degradation of crystal violet dye has been studied in the presence of doped TiO_2 and $Fe_2Mo_3O_{12}$ [21-22]. Photocatalytic reduction of Cr (VI) has been done by GO/TiO_2, and GO/ZnO [23]. In this present work we have focused on the optimization of degradation of cobalt picrate in the presence of zinc oxide (200 mesh) and various parameters were studied.

MATERIALS AND METHODS

Control experiments: Four beakers were taken to analyze whether the reaction occurs via chemical, thermal, photochemical or photo catalytic routes. It was observed that the reaction occurred only via photo catalytic route.

Cobalt picrate was prepared by reported method [24]. When an aqueous solution of $CoCl_2.6H_2O$ (0.01M) was allowed to react with an aqueous solution of equal volume of silver picrate (0.02 M), precipitation of silver chloride occurred and cobalt picrate remained in solution. Its filtrate was put on sand bath for halving of the volume and cooled to give Co-picrate precipitates.

A 1 x 10^{-3} M cobalt picrate solution was prepared as stock solution, which was then diluted further as required. The absorbance of cobalt picrate was measured in a quartz cuvette with round bottom and path length 10 mm, at λ_{max}= 357 nm by using Shimadzu UV-1800 spectrophotometer.

A 15 mL solution of 4 x 10^{-5} M of cobalt picrate was treated with 250 mg (200 mesh) powder of zinc oxide. The solution was subjected to 500 W halogen lamps. EMR was radiated from the top side of the beaker. The measurement of light intensity was done by Lux meter HTC LX -101. In these experiments, water filter was used to cut off thermal radiation. The pH and conductivity of solution were measured with (μ pH System 361) and (EQ 667) respectively, adjustment of pH was done by HCl and NaOH.

RESULTS AND DISCUSSION

The photo catalytic degradation of cobalt picrate has been studied using ZnO semiconductor. The kinetic study was carried out at the λ_{max} of the solution (357 nm). Typical run of this experiment has been shown in table – 1. As per graph of 2 + log ABS versus exposure time, cobalt picrate degrades in a single step reaction. Its slope was determined and the rate constant of cobalt picrate was determined using the expression, k = 2.303 × slope, the equation for the first order reaction.

Table -1: Typical run of cobalt picrate

Time	Abs	2+log abs
0	1.00	2.00
30	0.91	1.96
60	0.77	1.89
90	0.65	1.81
120	0.52	1.72
150	0.42	1.62
180	0.33	1.52
210	0.25	1.40
240	0.21	1.32

[Co – picrate] = 4 × 10^{-5} M, Zinc oxide = 250 mg (200 mesh), light intensity = 7.61 $mWcm^{-2}$, pH = 5.5, Temperature = 303.6 K, λ_{max} = 357 nm, k= 6.8 × 10^{-3} min^{-1}

Effect of cobalt picrate concentration: The effect of variation of Co - picrate concentration on the rate of photo catalytic degradation was studied by taking different concentrations of Co-picrate solution. The results are tabulated in table 2. It was observed that the rate of photo catalytic degradation of Co-picrate decreases with increase in concentration of Co-picrate. It may be possible that, the substrate is acting as a filter for incident light. The larger concentration of cobalt picrate will not permit the desired light intensity to reach the solution and ZnO contact surface.

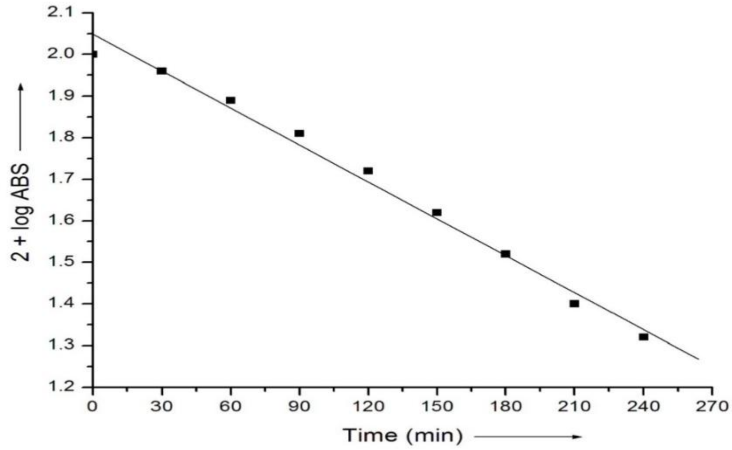

Fig 1. Typical run for Co-picrate

Table 2: Effect of cobalt picrate concentration

No	Concentration × 10^5 M	k × 10^3 (min^{-1})
1	2.0	12.8
2	3.0	8.9
3	4.0	6.8
4	5.0	4.7
5	6.0	3.8
6	7.0	2.9

Zinc oxide = 250 mg (200 mesh), light intensity = 7.61 $mWcm^{-2}$, pH = 5.5, Temperature = 303.6 K, λ_{max} = 357 nm

Effect of amount of semiconductor: The amount of semiconductor has much effect on the photo catalytic degradation rate of Co-picrate. Therefore, different amounts of semiconductor were used in the present investigation. The results are tabulated in table -3. It was observed that the rate of photo catalytic degradation of Co- picrate increased with increase in amount of photo catalyst up to 300 mg but after reaching a certain amount (300 mg) it decreased.

The addition of around 250 mg of ZnO seems to cover the whole surface area and therefore an addition of photo catalyst more than 300 mg does not effectively increase the degradation rate. The 7.48 × 10^{-3} min^{-1} rate (for 300 mg semiconductor) may be possibly due to formation of minute amount of suspended semiconductor particles.

Table- 3: Effect of amount of semiconductor

No	ZnO Semiconductor in Mg	k × 10^3 (min^{-1})
1	100	3.79
2	150	4.35
3	200	5.41

4	250	6.80
5	300	7.48
3	350	6.70

[Co – picrate]= 4 × 10^{-5} M, light intensity = 7.61 $mWcm^{-2}$, pH = 5.5, Temperature = 303.6 K, λ_{max} = 357 nm

Effect of light intensity: To investigate the effect of light intensity on the rate of photo catalytic degradation, different distances between source of light and exposed surface area were kept. The results are reported in table 4. It was evident that rate of photo catalytic degradation increased with increasing light intensity. It is a fact that as light intensity increases, electrons striking per unit area of semiconductor increases and hence the reaction rate has to increase.

Table 4: Effect of light intensity

No	Light intensity $mWcm^{-2}$	$k \times 10^3$ (min^{-1})
1	3.66	2.2
2	5.12	3.2
3	7.61	6.8
4	10.24	9.8
5	14.64	11.0

[Co-picrate] = 4 × 10^{-5} M, Zinc oxide = 250 mg (200 mesh), pH =5.5, Temperature = 303.6 K, λ_{max} = 357 nm

Effect of pH: The pH of solution has profound impact on the rate of photo catalytic degradation of Co-picrate. The effect of pH on rate of photo catalytic degradation of Co-picrate was investigated in the pH range between 2 to 9. The results are reported in table 5. It has been observed that rate of photo catalytic degradation increased with increase in pH up to 5.5. After that, there was a sudden fall in degradation rate at 7.0 pH. Then after, it gradually increased with increase in pH. A probable reason would be different species seem to be responsible for degradation in acidic and alkaline regions.

Table 5: Effect of pH

No	pH	$k \times 10^3$ (min^{-1})
1	2.0	2.98
2	3.0	4.48
3	4.0	5.18
4	5.5	6.80
5	7.0	2.63
6	8.0	4.54
7	9.0	5.93

[Co –picrate] = 4 × 10^{-5} M, Zinc oxide = 250 mg (200 mesh), light intensity = 7.61 $mWcm^{-2}$,
Temperature = 303.6 K, λ_{max} = 357 nm

Effect of band gap: The exited semiconductor has separated hole and electron pair that carry out the photo catalytic reaction hence, band gap energy plays an important role in photo catalysis [25]. The effect of band gap in photo catalytic degradation was studied with semiconductors having different band gap energy. The results are reported in table 6. The results indicated that except ZnO, no other semiconductor (ZnS, CdS, or PbS) underwent photo catalytic reaction with Co-picrate. It seems that along with photo catalysis using ZnO, some sort of other chemical reaction may be occurring and assisting the picrate degradation.

Table 6: Effect of band gap

No	Semiconductor	Band gap (eV)	k × 10^3 (min^{-1})
1	ZnS	3.8	0.0
2	ZnO	3.2	6.8
3	CdS	2.5	0.0
4	PbS	0.3	0.0

[Co –picrate] = 4 × 10^{-5} M, light intensity = 7.61 $mWcm^{-2}$, pH = 5.5, Temperature = 303.6 K, λ_{max} = 357 nm

Effect of radial quencher: Alcohols are used for quenching free radicals. Methanol and ethanol were used in present investigation. It was observed that addition of methanol and ethanol as quencher, successfully stopped the degradation to occur. In both the cases, reaction was totally quenched even in smaller amount (2 ml). The results are tabulated in table 7. It was very clearly indicated that the degradation occurred through free radical intermediates.

Table 7: Effect of radial quencher

No	Quencher	λ_{max} (nm)	k × 10^3 (min^{-1})
1	Typical run	357.0	6.8
2	Methanol (2mL)	357.0	0.0
3	Methanol (4mL)	357.0	0.0
4	Ethanol (2mL)	357.0	0.0
5	Ethanol (4mL)	357.5	0.0

[Co-picrate] = 4 × 10^{-5} M, Zinc oxide = 250 mg (200 mesh), light intensity = 7.61 $mWcm^{-2}$, pH = 5.5, Temperature = 303.6 K

CONCLUSIONS

Cobalt picrate, an industrially useful molecule, was taken for the current study. In dilute aqueous solution it undergoes photo catalytic degradation with all the major characteristics of a typical photo reaction in presence of a semiconductor in heterogeneous phase. The reaction was found to occur via free radical intermediates generated by the irradiated semiconductor.

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