PHOTOCATALYTIC DEGRADATION OF ZINC PICRATE IN PRESENCE OF ZnO

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ABSTRACT

The present study describes the photocatalytic degradation of zinc picrate in the presence of zinc oxide semiconductor. The progress of the reaction was checked by Schimadzu 1600 UV spectrophotometer at different time intervals. Its various parameters like effect of concentration, amount of semiconductor, light intensity and effect of pH on aqueous solution of zinc picrate were studied.

Key words: Zinc picrate, Degradation, ZnO, Heterogeneous photocatalysis.

INTRODUCTION

In recent years, photocatalytic process is mostly used for oxidation of organic molecules and reduction of inorganic species[1-2]. Generally, metal ions are non-degradable, they have eternal lifetime[3]. Photocatalytic process is used for conversion of metal in their nontoxic from[4]. The secondary source of heavy metal is the improper removal of different industrial wastewater. Physical and chemical processes are available to remove heavy metal from waste water like ion exchange, adsorption and membrane process etc. All these methods have their own advantages and disadvantages[5].The influence of photocatalysis is depended on the generation of free radicals. Hydroxyl radical plays an important role for the treatment of waste water[6-8]. Hydroxyl radical is highly reactive and that can oxidize and decompose several toxic inorganic and organic species[9-11]. Photocatalytic reduction of Cr(VI) was studied by using ZnO[12]. Photocatalytic reduction of Hg(II) was done with two commercially available TiO$_2$[13]. Photocatalytic removal of Ag(I) was studied withTiO$_2$ based photocatalyst[14]. Metal complexes of picric acid are used in the field of homeopathy[15]. Photocatalytic reduction of mercuric salt has been studied in the presence of TiO$_2$[16].

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EXPERIMENTAL

Control experiments

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

When an aqueous solution of zinc chloride (0.01 M) was allowed to react with equal volume of an aqueous solution of silver picrate (0.02 M), precipitation of silver chloride occurred and zinc picrate remained in solution. This filtrate was put on sand bath till half of the volume and subsequent cooling gave solid zinc picrate. 1×10^{-3} M stock solution of zinc picrate was prepared in double distilled water.

HTC LX-101A digital lux meter was used to measure light intensity. 15 mL solution was treated with ZnO 250 mg (200 mesh) powder. This setup was irradiated in the presence of 500 W halogen lamp on top side of the glass covered beaker. Absorbance (ABS) of the solution was measured using Schimadzu- 1800 UV spectrophotometer. The solution was taken in a quartz cuvette with round bottom whose path length was 10 mm. Water filter was used for inhibition of thermal radiation[17]. The pH and conductivity of solution were measured by (μ pH System 361) and conductometer (EQ 667) respectively, adjustment of pH was done by HCl and NaOH.

RESULTS AND DISCUSSION

Photocatalytic degradation result of typical run was tabulated in Table 1 and represented graphically in Fig. 1. It was observed that the graph of 2 + log (absorbance) versus time was linear. This graph was plotted according to the linear least squares method[18] and rate constant of the reaction has been calculated by the expression k = 2.303 × slope (First order reaction).

Table 1: Typical run for zinc picrate degradation

Time (min)	ABS	2 + log ABS
0	1.06	2.02
30	0.95	1.98
60	0.80	1.90

Time (min)	ABS	2 + log ABS
90	0.74	1.87
120	0.62	1.79
150	0.53	1.72
180	0.45	1.65
210	0.40	1.60
240	0.32	1.50

[Zinc picrate] = 5×10^{-5} M, Zinc oxide = 250 mg (200 mesh),
Light intensity = 7.61 mWcm^{-2}, pH = 6.08, Temperature = 300.4 K,
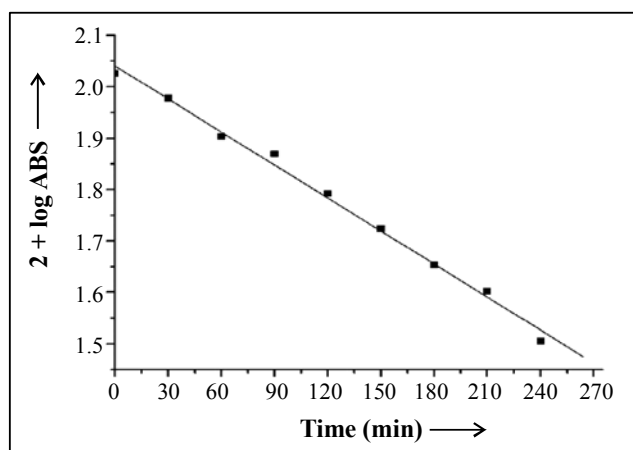λ_{max} = 357 nm, k = 4.9×10^{-3} min^{-1}

Fig. 1: Typical run for Zn-picrate

Effect of zinc picrate concentration

Photocatalytic degradation of zinc picrate was observed at different concentrations and rate constants were tabulated in Table 2. When concentration of zinc picrate increases, corresponding rate constant decreases. The reason for this trend is due to the obstruction of emr by increasing concentration of the substrate.

Effect of amount of zinc oxide

The effect of zinc oxide amount on degradation of zinc picrate solution was studied by taking different amounts of zinc oxide. The results are tabulated in Table 3. It was clearly observed that as the amount of zinc oxide was increased, corresponding rate of reaction

increased upto the amount of 300 mg. After this amount, rate of reaction decreases. The photocatalyst covers more and more surface that is exposed to light when the amount is increased. When the whole surface is covered, there will not be any further increase. The decrease in k for the last case may be due to more suspension of the solid particles.

Table 2: Effect of zinc picrate concentration

[Concentration $\times 10^5$M]	$k \times 10^3$ (min^{-1})
2.0	10.7
3.0	7.8
4.0	6.7
5.0	4.9
6.0	3.5
7.0	2.8

Zinc oxide = 250 mg (200 mesh), Light intensity = 7.61 mWcm^{-2}, pH = 6.08, Temperature = 300.4 K, λ_{max} = 357 nm

Table 3: Effect of amount of photocatalyst

ZnO Photocatalyst in (mg)	$k \times 10^3$ (min^{-1})
100	2.6
150	3.6
200	4.4
250	4.9
300	6.3
350	4.3

[Zn-picrate] = 5×10^{-5} M, Light intensity = 7.61 mWcm^{-2}, pH = 6.08, Temperature = 300.4 K, λ_{max} = 357 nm

Effect of pH

The effect of the pH on the reaction rate was observed between pH range from 3 to 9. It was observed that, as pH of solution was increased rate constant increased upto 6.08 pH and then decreased. Again it increased upto pH 8.0 and then decreased. It may be due to generation of different species at different pH values.

Table 4: Effect of pH

pH	$k \times 10^3$ (min^{-1})
3.00	3.8
4.00	4.4
5.00	3.5
6.08	4.9
7.00	3.9
8.00	4.2
9.00	4.0

[Zn-picrate] = 5×10^{-5} M, Zinc oxide = 250 mg (200 mesh),
Light intensity = 7.61 mWcm^{-2}, Temperature = 300.4 K, λ_{max} = 357 nm

Effect of light intensity

The effect of light intensity on photocatalytic reaction of zinc picrate solution has been observed by change in the distance between the exposed surface of the reaction mixture and source of light. The results are indicated in Table 5. As per the data, on increasing the light intensity, rate constant also increased. This is due to the fact that increase in the light intensity results in more electrons being available for excitation on surface of the semiconductor.

Table 5: Effect of light intensity

Light intensity (mWcm^{-2})	$k \times 10^3$ (min^{-1})
3.6	2.8
5.1	3.3
7.6	4.9
9.5	6.9
12.4	8.0

[Zn-picrate] = 5×10^{-5} M, Zinc oxide = 250 mg (200 mesh), pH = 6.08,
Temperature = 300.4 K, λ_{max} = 357 nm

Effect of band gap

The exited semiconductor has separated hole and electron pair that carry out the photocatalytic reaction hence, band gap energy plays an important role in photocatalysis[19]. The effect of band gap in photocatalytic degradation was studied with different semiconductors having different band gap energy. It was clearly observed that the zinc oxide (3.2 eV) has highest rate constant. All other semiconductors taken, ZnS, CdS and PbS were not able even to start the photocatalytic reaction.

Table 6: Effect of band gap

Photocatalyst	Band gap (eV)	$k \times 10^3$ (min^{-1})
ZnS	3.8	0.0
ZnO	3.2	4.9
CdS	2.5	0.0
PbS	0.3	0.0

[Zn-picrate] = 5×10^{-5} M, light intensity = 7.61 mWcm^{-2}, pH = 6.08,
Temperature = 300.4 K, λ_{max} = 357 nm

Effect of radial quencher

Alcohols were used for quenching free radicals. Methanol and ethanol were used in present investigation. The addition of even a small (2 mL) amount of ethanol or methanol was successful to completely quench the photocatalytic reaction. This observation unambiguously confirmed that this photocatalytic reaction proceeds by free radicals.

Table 7: Effect of radical quencher

Quencher	λ_{max} (nm)	$k \times 10^3$ (min^{-1})
Typical run	357.0	4.9
Methanol (2 mL)	357.0	0.0
Methanol (4 mL)	358.0	0.0
Ethanol (2 mL)	357.6	0.0
Ethanol (4 mL)	357.5	0.0

[Zn-picrate] = 5×10^{-5} M, Zinc oxide = 250 mg (200 mesh),
Light intensity = 7.61 mWcm^{-2}, pH = 6.08, Temperature = 300.4 K

CONCLUSION

Zinc picrate is an industrially important material. It was observed that only ZnO, out of four semiconductors selected, proved to be successful to carry out photocatalytic reaction of zinc picrate. Control experiments proved that ZnO carried out photocatalytic reaction. This first order reaction was found to be affected by parameters like concentration, band gap, amount of photocatalyst, quenchers etc. This degradation reaction was very sensitive to the pH of the solution. The reaction was totally stopped by quencher like alcohol.

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