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ORIGINAL ARTICLE

Photocatalytic decolorization of mercuric picrate in the presence of zinc oxide

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Abstract

Objectives: This study was undertaken to examine the decolorization of mercuric picrate with ZnO as a photocatalyst. **Methodology:** The photo catalytic decolorization of mercuric picrate in the presence of heterogeneous semiconductor in the aqueous solution has been investigated. The progress of the reaction was checked by Shimadzu 1600 UV visible spectrophotometer at different time intervals. The effect of various operational parameters was studied such as the effect of mercuric picrate concentration, amount of photo catalyst, effect of light intensity, effect of band gap and effect of pH on the solution of mercuric picrate. The study on the effect of radial quenchers such as methanol and ethanol were used. **Findings:** The optimum conditions were obtained as pH =5.0, [Hg-picrate] = 6 $\times 10^{-5}$ M, amount of ZnO = 250 mg, light intensity =7.61 $mWcm^{-2}$. The rate constent ontained was k= 7.30 $\times$ 10-3 min^{-1}. The reaction proceeded through oxidation by hrdroxyl radial confirmed by scavenger. Zinc oxide is effective photocatalyst for decolorization of Hg-picrate. Other semiconductors like ZnS, CdS as well as PbS are not capable to carry out photoreaction. A tentative mechanism for this reaction has been proposed. **Novelty:** Mercuric Picrate is a probably explosive toxic substance. Hence a safe way to decompose this molecule into smaller and nonexplosive ways is of crucial importance. Photocatalysis is well established method. However, decomposition of mercuric picrate to a safe level can be achieved by this method.

Keywords: Advanced oxidation processes; decolorization; Zinc oxide; mercuric picrate

1 Introduction

Heavy metals are present in the effluents of different type of industries like paint, lather tanning, electroplating, battery manufacturing and agriculture[1,2]. Generally, metal ions are non-degradable, they have eternal lifetime but the ability to remove metals was found to depend on the standard reduction potential of metals[3–5]. Advanced

oxidation processes (AOPs) have received increasing attention in the research and development of wastewater treatment technologies in the last decades[6]. The efficacy of AOPs depends on the generation of reactive free radicals such as superoxide radical, hydroperoxyl radical, hydroxyl radical and alkoxyl radical, out of them most important is the hydroxyl radical[7–9]. In the recent years, there has been an enormous amount of research and development carried out in the area of heterogeneous photocatalytic for water purification process due to its effectiveness in degrading and mineralizing[10]. Heterogeneous photocatalysis is a process in which the degradation of organic pollutants is governed by the combined action of a semiconductor catalyst, an emitted light and an oxidizing agent[11]. In present study ZnO semiconductor used as a photo catalyst because of its excellent properties, high redox potential, nontoticity, environmentally friendly and low cost as well as wide band gap energy (3.37 eV) and high exciton binding energy (60 meV)[12–15].

2 Experiment

Control experiment

A stock solution of Mercuric picrate was prepared in doubly distilled water and further, it was divided into four different parts.

1. The first beaker contains 30 ml solution and was kept in dark.
2. The second beaker contains 30 ml solution which was exposed to light.
3. The third beaker contains 30 ml of solution and 200 mg zinc oxide semiconductor and it was kept in dark.
4. The fourth beaker contains 30 ml of picrate solution and after adding 200 mg of zinc oxide semiconductor and it was exposed to light.

It was observed that the first three beakers had no change in their color (concentration). While the fourth beaker showed a change in its concentration. It indicated that the decolorization of Mercuric picrate is photocatalytic, it did not proceed through photochemical, chemical or thermal pathway.

Photocatalytic decolorization of Mercuric picrate was studied by taking 30 solutions in 50 ml beaker and 200 mg zinc oxide semiconductor was added. Then the solution was irradiated with 500 W halogen lamp from the topside of the closed beaker. The beaker was closed with 2mm thick glass lid. Water filter was used for inhibition of thermal radiation[5]. The progress of the photocatalytic reaction was observed by measuring the absorbance at 357 nm using Shimadzu UV-1800 spectrophotometer. Quartz cuvette with path length 1cm was used. HTC LX- 101 A digital lux meter was used to measure light intensity.

3 Result and Discussion

Photocatalytic decolorization result of typical run was tabulated in Table 1 and represented graphically in Figure 1. The graph of 2 + log absorbance versus time was drawn and its slope was determined. This graph was plotted according to the linear least squares method[16] and rate constant of the reaction has been calculated by expression k = 2.303 × slope.

Table 1. Typical run of mercuring picrate

Time (min)	ABS	2+log ABS
0	0.78	1.89
30	0.74	1.87
60	0.63	1.80
90	0.52	1.72
120	0.43	1.63
150	0.33	1.52
180	0.25	1.40
210	0.19	1.28
240	0.14	1.15

[Hg-picrate] = 6×10^{-5} M Zinc oxide = 250 mg (200 mesh)
Light intensity = 7.61 $mWcm^{-2}$ pH = 5.0
Temperature = 305.7 K λ_{max} = 356 nm
Hg-picrate k = $7.30 \times 10^{-3} min^{-1}$

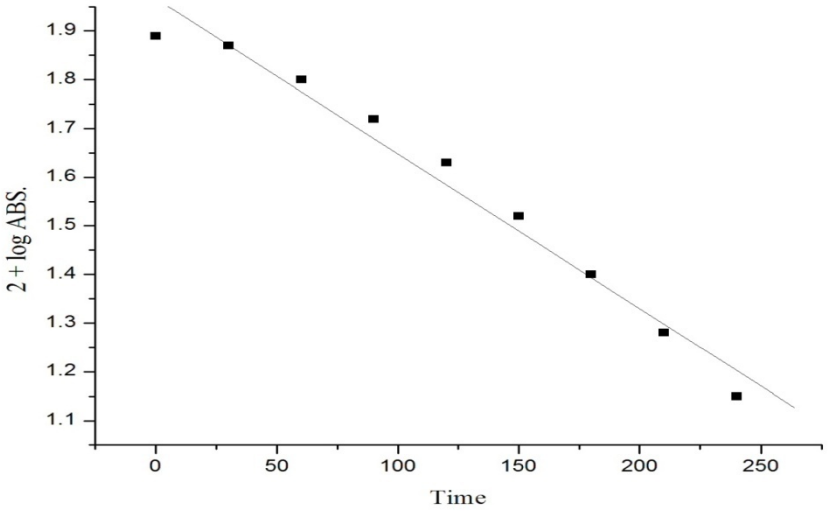

Fig 1. Typical run of mercuric picrate

3.1 Effect of concentration

The effect of concentration on the rate of photocatalytic decolorizationof mercuric picrate was studied with zinc oxide semiconductor. The results are given in Table 2. It has been observed that when the concentration of mercuric picrate was increased rate of photocatalytic degradation of mercuric picrate decreased. The reason for this trend is due to the obstruction of electromagnetic radiation in the solid-liquid interface being absorbed by the substrate. This may also be attributed to the fact that as the concentration of mercuric picture was increased, it may start acting as a filter for the incident light. The larger concentration of Hg-picrate will not permit the desired light intensity to reach the compound in the bulk of the solution [17].

Table 2. Effect of concentration

No.	Concentration $\times 10^5$	k(min^{-1}) $\times 10^3$
1	3	11.3
2	4	9.90
3	5	8.40
4	6	7.30
5	7	6.20
6	8	5.40

Zinc oxide = 250 mg (200 mesh) pH = 5.0
Light intensity = 7.61 $mWcm^{-2}$ λmax = 356 nm
Temperature = 305.7 K

3.2 Amount of semiconductor

Effect of theamount of semiconductor on the rate of photocatalytic decolorization of mercuric picrate was carried out by taking different amounts of semiconductor between 100 mg to 350 mg, keeping all other parameters identical. The results are tabulated in Table 3.

As per the obtained data, it has been observed that rate of reaction increases upto 150 mg addition then after decreased upto at 250 mg value. Beyond that amount, rate of reaction increased upto 350 mg. This type of increase and decrease behaviors may be explained as under. Increase may be due to formation of fine particles of emulsion whereas the decrease may be due to larger floating suspended particles.

Table 3. Amount of photo catalyst

No.	Semiconductor in (mg)	k(min^{-1}) × 10^3
1	100	7.8
2	150	8.6
3	200	8.4
4	250	7.3
5	300	7.8
6	350	8.9

[Hg-picrate] = 6×10^{-5} M pH = 5.0
Light intensity = 7.61 $mWcm^{-2}$ λ_{max} = 356 nm
Temperature = 305.7 K

3.3 Effect of pH variation

The effect of pH on the rate of photocatalytic degradation of mercuric picrate was studied. The results are reported in Table 4. At different pH values, different radicals or ion or radical ions are likely to be generated. These species are largely responsible to carry out the photocatalytic reactions. Furthermore, the proportion of each species may change with pH. It has been observed that the rate of photocatalytic decolorization of mercuric picrate increases initially in acidic medium and rate constant suddenly falls down at pH (8.0), then after it further increased in basic medium. Presumably, generation of different species at different pH may be responsible for increase / decrease behavior.

Table 4. Effect of pH

No.	pH of solution	k(min^{-1}) × 10^3
1	3.0	5.2
2	4.0	6.0
3	5.0	6.5
4	6.1	7.3
5	7.0	5.0
6	8.0	4.3
7	9.0	6.2

[Hg-picrate] = 6×10^{-5} M Zinc oxide = 250 mg (200 mesh)
Light intensity = 7.61 $mWcm^{-2}$ λ_{max}= 356 nm
Temperature = 305.7 K

3.4 Effect of light intensity

The effect of light intensity on the rate of photocatalytic degradation of mercuric picrate has been observed in the present investigation. The distance between light source and exposed surface area are varied and intensity is measured by lux meter. The results are reported in Table 5. The result reported below indicates that rate of the photocatalytic degradation of the mercury picrate increased as the intensity of light was increased. This increases due to the fact that more electron-hole pair are generated in the semiconductor when light intensity passes in the solution, thus resulting in the enhanced rate of photocatalytic degradation. The relation between light intensity and k is roughly linear in the selected range.

[Hg-picrate] = 6×10^{-5} M pH = 5.0
Zinc oxide = 250 mg (200 mesh) λ_{max} = 356 nm
Temperature = 305.7 K

3.5 Effect of band gap energy

Photocatalytic study of mercuric picrate was carried out with the help of different semiconductors which have different band gap energy values. Band gap energy plays an important role in the photocatalytic reaction. The results are tabulated in Table 6.

Table 5. Effect of light intensity

No.	Light intensity mWcm^{-2}	k(min^{-1}) × 10^3
1	02.60	03.1
2	05.12	05.2
3	07.61	07.3
4	10.24	08.4
5	13.44	10.0

This reaction was done by taking four different semiconductors, ZnS, ZnO, CdS as well as PbS and observed that no photocatalytic reaction occurred except with zinc oxide. The photocatalytic reaction of mercuric picrate proceeded only with zinc oxide catalyst. A possible explanation is the occurrence of different species with different photocatalysts.

Table 6. Effect of band gap

No.	Semiconductor	Band gap (eV)	k × 10^3 (min^{-1})
1	PbS	0.3	0.0
2	CdS	2.5	0.0
3	ZnO	3.2	7.3
4	ZnS	3.8	0.0

[Hg-picrate] = 6 × 10^{-5} M pH = 5.0
Light intensity = 7.61 mWcm^{-2} λ_{max} = 356 nm.
Temperature = 305.7 K

3.6 Effect of radical quencher

When the photocatalytic reaction of mercuric picrate was carried out in the presence of a radical quencher, it was observed that photocatalytic reactions of mercuric picrate do not proceed in the presence of radical quenchers like methanol and ethanol. The results are summarized in Table 7. During the photo catalysis, the generated an electron can be abstracted from hydroxyl ion by hole (h+) present in the valence band of semiconductor generating hydroxyl radical. This hydroxyl radical will oxidize Hg-picrate, which may ultimately degrade the products. Gupta et al.[18] reported that hydroxyl radical take part as an active oxidizing species in the degradation of compounds, and observed that in the presence of hydroxyl radial quencher the reaction was appreciably reduced[19]. These reactions were observed by taking different volumes of alcohols (e.g. 1 ml to 2 ml). These photocatalytic reactions are totally stopped due to the addition of small amounts of alcohols (e.g. 1ml). Both alcohols exhibited same quenching efficiency.

Table 7. Effect of radical quencher

No.	Quencher	λ_{max}(nm)	k(min^{-1}) × 10^3
1	Typical run	356.00	7.30
2	Methanol(2ml)	356.50	0.00
3	Methanol(4ml)	356.50	0.00
4	Ethanol(2ml)	357.40	0.00
5	Ethanol(4ml)	357.00	0.00

[Hg-picrate] = 6 × 10^{-5} M Zinc oxide = 250 mg (200 mesh)
Light intensity = 7.61 mWcm^{-2} pH = 5.0
Temperature = 305.7 K

3.7 Tentative mechanism

When the light of energy equal or higher than the band gap energy is irradiated upon the semiconductor, then the semiconductor is excited from valence band (hole) to the conduction band (electron)which are responsible to carry out redox reactions. Heterogeneous photocatalytic system occurs at solid – liquid interface.

$ZnO + hu \longrightarrow h^+(VB) + e^-(CB)$

h^+ (VB) = hole in valence band

e^- (CB)= electron in conduction band

The charge carriers are formed and can be recombined or may be trapped by a defect site or electron transfer with adsorbed electron donors and acceptors may occur.

$h^+(VB) + (Red_2) \longrightarrow$ ads (Ox_2) ads

$e^-(CB) + (Ox_1)$ ads $\longrightarrow (Red_1)$ ads

Where, (Red_2) ads = Oxidizable species adsorbed on the semiconductor surface.

(Ox_2) ads = Oxidation product of (Red_2) ads.

(Ox_1) ads = Oxidation product of (Red_1) ads.

Generally, several species radicals or radical ions such as $HO^{\cdot}$, H_2O_2, O_2, $HO_2^{\cdot}$, $O_2^{\cdot -}$, H^+ etc. are present in the aqueous medium. Out of them, some species play a significant role to carry out reduction and oxidation reactions in the reaction medium. The tentative mechanism of photocatalytic degradation of mercuric picrate in the presence of zinc oxide semiconductor is as under.

$Hg - picrate + HO + O_2 \longrightarrow Decomposition\ products$

$Hg - picrate + O_2^- + H_2O \longrightarrow Decomposition\ products$

4 Conclusion

The Hg-picrate in the solution was decolorization using the semiconducting material ZnO as a photocatalyst. The role of hydroxyl and other radicals, which are responsible for the degradation of Hg-picrate, was confirmed by performing the reaction in the presence of radical quencher like ethanol and methanol. Different kinetic parameters were studied and it was found out that degradation of Hg-picrate was of first order. Zinc oxide is effective photocatalyst for degradation of Hg-picrate. Other semiconductors like ZnS, CdS as well as PbS are not capable to carry out photoreaction.

Financial Disclosure/Conflict of interest

We, the authors declare that there was no financial aid received of the submitted manuscript declare that the work and data present in the manuscript is genuine research carried out by us. The work finally belongs to the institutes. We have not misused the data previously published and have not manipulated the original work.

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