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Kinetic Study of Application of ZnO as a Photocatalyst in Heterogeneous Medium

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Abstract: The photocatalytic degradation of 2,4-dinitrophenol over ZnO was carried out in the presence of light. Control experiments were carried out. The photocatalytic degradation of 2,4-dinitrophenol was observed spectro-photmerically. The various parameters like concentrations of substrate, pH, amounts and band gaps of semiconductor, impact of light intensity, sensitizers and radical quenchers affected the kinetics of the degradation process. A probable mechanism for this process has been proposed.

Keywords: 2,4-Dinitrophenol, Photocatalytic, Degradation, Semiconductor, ZnO.

Introduction

The photocatalytic reactions are carried out in the presence of light and semiconductor. These reactions have been classified into two categories depending upon the nature of reactants and semiconductors, homogeneous and heterogeneous. Homogeneous photocatalysis and the generation of active species *in situ* by light is potentially interesting[1]. The attention has been mainly devoted to the chemistry originated when light observed by a photo redox process has grown enormously in recent years[2] and several physical methods are being adopted for the characterization of the catalyst films, particles and for the study of their reactions[3]. Heterogeneous photo catalysis by semiconductor through particulate systems has become an exciting and rapidly growing area of research in the last few years[4-5]. Lan Z. *et al*. reported the photoinduced hydrogen elimination reaction in phenol via the conical intersections of the dissociative $^1\pi\sigma^*$ state with the $^1\pi\pi^*$ state and the electronic ground state has been investigated by time-dependent quantum wave-packet calculations and described by the $^1\pi\sigma^*$ photochemistry of phenol[6]. Want P. *et al*. studied quinone methide intermediates and have been investigated in organic photochemistry[7]. Shin C.T. *et al*. discovered the quantum efficiency of riboflavin in the presence of phenols that decreased and determined a linear relationship between the Hammett's sigma values and the rate of photodecomposition on the photochemistry of riboflavin[8]. Monti S. *et al.* investigated absorption and induced circular dichroism (ICD) spectra as well as photophysical (fluorescence quantum yield, fluorescence lifetime and triplet-triplet absorption) and photochemical (hydrated electron formation) properties have been measured in aqueous solutions of phenol, p-cresol, 2,6-dimethylphenol 3,5-dimethylphenol, 2,4,6-trimethylphenol, and 3,4,5-trimethylphenol in the presence of 8-cyclodextrin and compared to their behaviors in pure aqueous and ethanolic solutions[9]. Joshi J. D. *et al.* synthesized degradation of *o*-nitro phenol that has been studied in the presence of semiconducting oxide[10]. Ameta S.C. *et al.* studied the photoelectro chemical study of picric acid has been carried out by using ZnO as 'n' type Semiconductor[11]. 2,4-dinitrophenol is volatile with steam and sublimes when carefully heated .It is toxic compound readily absorbed through the intact skin and causes sweating, nausea, vomiting, collapse and may cause death[12].

Experimental

2,4-dinitrophenol and Zinc oxide (Merck) were used in the present investigation. All the chemicals were of AR grade. Stock solution of 2,4-dinitrophenol (2.5×10^{-4} M) was prepared in doubly distilled water.

Photocatalytic degradation of 2,4-dinitrophenol was studied by taking 10 mL solution (2.5×10^{-4} M) in 100 mL beaker and 200 mg of photocatalyst (ZnO, 60 Mesh powder) was added to it. Then this solution was exposed to a 500W halogen lamp from the topside of a closed beaker. The tungsten halogen lamps develop a larger amount of ultraviolet radiation than the other general service lamps[13].

The progress of photocatalytic reaction was observed by measuring absorbance (ABS) at 360nm using spectrophotometer (spectronic-20D$^+$) in a glass cuvette with path length 1 cm. Graphs of 2+log ABS versus exposure time were drawn and their slopes were determined. These graphs were plotted according to the linear least squares method[14].

Results and Discussion

The photocatalytic degradation of 2,4-dinitrophenol was observed at 360 nm. The results for typical run for the photocatalytic degradation of 2, 4-dinitrophenol is shown in Table 1. From the graph of 2+log ABS versus exposure time, its slope was determined. Using expression k = 2.303 x slope, the rate constant was found. The photocatalytic degradation of 2, 4-dinitrophenol was found to be of first order.

Table 1. Typical Run

Zinc Oxide = 200 mg; pH = 6.00; Temperature = 309K; [2,4-dinitrophenol] = 7.0×10^{-5} M
λ_{max} = 360 nm ; Light Intensity = 7.38 mWcm^{-2}

S. No	Time, min	ABS	2+log ABS
1.	00	0.714	1.85
2.	45	0.624	1.79
3.	90	0.598	1.77
4.	135	0.525	1.72
5.	180	0.456	1.65
6.	225	0.417	1.62
7.	270	0.367	1.56
8.	315	0.283	1.45

$k = 2.61 \times 10^{-3}$ min^{-1}

Effect of 2,4-dinitrophenol concentration

The effect of 2,4-dinitrophenol concentration on the rate of its photocatalytic degradation was observed by taking different concentrations of 2,4-dinitrophenol. The results are tabulated in Table 2. It was observed that as the concentrations of 2,4-dinitrophenol were increased, the value of rate constant (k) increased. Within lower concentration range, the reaction rate is proportional to its concentration. This is a normal feature of first order reaction.

Table 2. Effect of 2,4-dinitrophenol concentration.

Zinc Oxide = 200 mg; pH = 6.00; Temperature = 309 K; λ_{max} = 360 nm; Light intensity = 7.38 mWcm^{-2}

S. No	Substrate Concentration M 10^5	k10^3, min^{-1}
1.	5.0	2.12
2.	6.0	2.37
3.	7.0	2.61
4.	8.0	2.97
5.	9.0	3.14

Effect of pH

The effect of pH on the rate of photocatalytic degradation of 2,4-dinitrophenol was investigated in pH range 2 to 8. The results are tabulated in Table 3. In the acidic region, when pH was raised, the rate constant value increased and at pH 6.00, the k value was highest. On still increasing pH in the alkaline region, the k value decreased. It seems that neutral species play an important role in the degradation process.

Table 3. Effect of pH.

Zinc Oxide = 200 mg; Temperature = 309 K; [2,4-dinitrophenol] = 7.0x10^{-5}M; λ_{max} = 360 nm;Light intensity = 7.38 mWcm^{-2}

S. No.	pH	k10^3, min^{-1}
1.	2.00	2.15
2.	4.00	2.29
3.	6.00	2.61
4.	7.00	2.10
5.	8.00	2.03

Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of 2,4-dinitrophenol was observed by taking different amounts of semiconductor keeping all other factors identical. The results are reported in Table 4. As indicated from the data, the photocatalytic degradation of 2,4-dinitrophenol increases with the increase in the amount of semiconductor. Usually an amount of 200 mg covers the whole surface area but an additional quantity is likely to increase floating photcatalyst particles, hence increase in reaction rate is observed.

Effect of light intensity

The effect of light intensity on the rate of photocatalytic degradation of 2,4-dinitrophenol has been observed by varying the distance between the light surface and exposed surface of the semiconductor. The results are given in Table 5. As the intensity of light was increased, more photons would be available for excitation at the semiconductor surface and in turn more electron hole pairs will be generated. Thus this resulted in enhanced rate of photocatalytic degradation. In the degradation of 2,4-dinitrophenol, the value of k was found to increase with the increase in light intensity, a typical characteristic of a photocatalytic reaction.

Table 4. Effect of amount of photocatalyst.

[2,4-dinitrophenol]=7.0x10^{-5} M; pH=6.00; Light intensity= 7.38 mWcm^{-2}
Temperature = 309 K; λ_{max} = 360 nm.

S. No.	Amount of Photocatalyst, mg	k10^{3}min^{-1}
1.	100	2.19
2.	150	2.34
3.	200	2.61
4.	250	3.22
5.	300	4.53

Table 5. Effect of intensity of light.

Zinc Oxide = 200 mg; pH = 6.00; [2,4-dinitrophenol] = 7.0x10^{-5} M; Temperature = 309K
λ_{max} = 360 nm

S. No.	Light intensity mWcm^{-2}	k10^{3}, min^{-1}
1.	4.76	2.19
2.	5.67	2.34
3.	7.38	2.61
4.	8.55	3.66

Effect of band gap of semiconductor

The usual exited semiconductor has separated the hole and electron pairs that induce the photocatalytic reactions and hence the band gap energy has important role to play[15]. The effect of band gap on the photocatalytic degradation was studied in the presence of different semiconductors having different band gap values. It is observed that the value of the rate of photocatalytic degradation (k) increased as the band gap increased up to band gap of ZnO (3.20 ev), but after the band gap (ZnS, 3.80 ev) increased, the value of the rate of photocatalytic degradation (k) decreased. Results are shown in Table 6.

Table 6. Effect of band gap of semiconductor.

Zinc Oxide = 200 mg; pH = 6.00; [2,4-dinitrophenol] = 7.0 x10^{-5} M; Temperature =309 K
Light intensity = 7.38 mWcm^{-2} ; λ_{max} = 360 nm.

S. No.	Semiconductor, 200 mg	Band gap, ev	k 10^{3}, min^{-1}
1.	PbS	0.30	2.21
2.	CdS	2.50	2.25
3.	ZnO	3.20	2.61
4.	ZnS	3.80	1.76

Effect of radical quencher

The presence of free radical quenchers caused marginal effects on the photocatalytic degradation of 2,4-dinitrophenol. Alcohols are known to quench free radicals present. When this photocatalytic reaction was carried out in the presence of free radical quenchers like-methanol, ethanol *etc*., the rate of reaction was found to decrease to a marginal level indicating the active participation of free radicals in the degradation. The results are tabulated in Table 7. Out of the three quenchers selected, the quenching efficiency of isopropanol was found to be highest among all. The free radical quenching efficiency of alcohols is $3^0 > 2^0 > 1^0$ which is observed in these reacting systems.

Table 7. Effect of radical quencher.

Zinc Oxide = 200 mg; pH = 6.00; [2,4-dinitrophenol] = 7.0x10^{-5} M; Temperature =309K
Light intensity = 3.40 mWcm^{-2} ; λ_{max} = 360 nm.

S. No.	Radical Quencher	λ_{max} = 360 nm	k10^3, min^{-1}
1.	Typical Run	360	2.61
2.	Methanol, 1mL	360	2.27
3.	Methanol, 2 mL	360	2.05
4.	Ethanol, 1 mL	360	2.51
5.	Ethanol, 2 mL	360	1.83
6.	Isopropanol, 1 mL	360	2.28
7.	Isopropanol, 2 mL	360	1.76

Effect of sensitizer

Certain dyes or complex compounds show the tendency to increase the rate of degradation by sensitization. In the present investigation, three compounds were taken for study *i.e.* methyl orange, crystal violet (methyl violet), $K_3[Fe(CN)_6]$. The results are tabulated in Table 8. The experimental results show that these compounds were unable to sensitize the reaction rate.

Table 8. Effect of sensitizer.

Zinc Oxide = 200 mg; pH = 6.00; [2,4-dinitrophenol] = 7.0x10^{-5} M; Temperature = 309K
Light intensity = 7.38 mWcm^{-2}; λ_{max} = 360 nm.

S. No.	Sensitizer	k10^3, min^{-1}
1.	Typical Run	2.61
2.	Methyl Orange	2.20
3.	Crystal Violet	2.05
4.	$K_3[Fe(CN)_6]$	1.97

When a semiconductor is irradiated with light having energy (E =hυ) equal to or more than band gap energy, a heterogeneous photocatalytic reaction occurs at the solid solution contact surface. The semiconductor forms a pair of valence band (VB) hole and conduction band (CB) electron.

$$ZnO + h\upsilon \rightarrow h^+(VB) + e^-(CB) \quad (1)$$

The hole generated is capable of oxidizing the substrate and the electron of CB is capable of reducing the substrate. Further more, the solution contains species *e.g.* $^{\cdot}OH$, H^+, $^{\cdot}O^-_2$, $^{\cdot}HO_2$, H_2O_2, O_2, which are due to the semiconductor light-water-oxygen interactions. These species are also capable of carrying out redox reactions. The generation of super oxide radical anion $^{\cdot}O_2^-$ and $^{\cdot}OH$ radical can be shown as under-

$$h^+(VB) + H_2O \rightarrow {}^{\cdot}OH_{ads} + H^+ \quad (2)$$

$$h^+(VB) + OH^-_{ads} \rightarrow {}^{\cdot}OH_{ads} \quad (3)$$

$$e^-(CB) + O_{2\,ads} \rightarrow {}^{\cdot}O_2^- \quad (4)$$

Subscript "ads" refers to species adsorbed on the surface of semiconductor. It was observed that the products of photocatalytic degradation of 2,4-dinitrophenol in presence of ZnO were colorless gases with virtually no solid residue left in the solution after almost complete degradation. Hence, probable reactions proposed are as under.

$$C_7H_7N_3O_3 + {}^{\cdot}OH + O_2 \rightarrow \text{Decomposition Products} \quad (5)$$

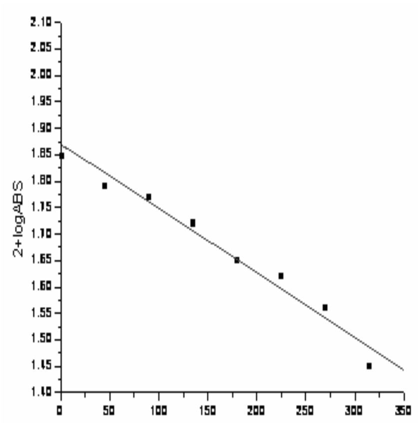

Figure 1. (Typical Run) Degradation of 2,4-dinitrophenol

Conclusion

The photocatalytic degradation of 2,4-dinitrophenol was observed. Concentration of substrate, pH of solution, amount of photocatalyst, light intensity *etc* showed their expected impact on the reaction rate. This method is useful to degrade 2,4-dinitrophenol completely into decomposition products other than solids. Using the kinetic parameters, the rate of reaction can be increased to a faster speed as required.

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