

Photo Degradation of *p*-Nitrophenol in Presence of Semiconductor

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The photocatalytic degradation of *p*-nitrophenol by irradiation in presence of semiconductor ZnO was studied. Kinetics of the reaction were found to be affected by parameters like concentration of substrate, pH, amount of photocatalyst, light intensity, band gap, etc. The effects of radical quencher, sensitizer were also studied. A probable mechanism is also suggested.

Key Words: Degradation, Photocatalytic, *p*-Nitrophenol, Semiconductor.

INTRODUCTION

Photocatalytic reactions in presence of ZnO suspensions have been studied¹. Some photochemical redox reactions at the zinc oxide-water interface in additive free systems have been investigated². The kinetics of the catalytic oxidation of phenol over manganese oxide in super-critical water have also been studied³. Concepts related to the chemistry of semiconductors, the electronic properties of solids and photoelectrochemistry were also discussed recently⁴. A kinetic model for photocatalytic degradation of organic contaminants in a thin film TiO₂ catalyst have been investigated⁵. Photocatalytic properties of cadmium sulfide and cadmium oxide in the reaction of methanol oxidation to formaldehyde have been studied⁶. Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO₂ have been investigated⁷. The photocatalytic and excimer laser photocatalytic studies of the environmentally hazardous compound 4-chlorophenol have been observed⁸. Photocatalytic degradation of *p*-nitroaniline⁹ and *o*-nitroaniline¹⁰ in presence of oxide semiconductor was found to be effective. *p*-Nitrophenol is used in manufacture of many important compounds. Hydroxylation of benzene using titanium dioxide as a semiconductor was studied¹¹.

EXPERIMENTAL

Zinc oxide (Merck) was used and another chemicals were of AR grade. *p*-Nitrophenol was crystallized from hot water and its purity was checked. Double

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distilled water was used throughout. A 10 mL 0.15 mM stock solution of *p*-nitrophenol and 200 mg of semiconductor (zinc oxide powder, 60 mesh) were taken in a 100 mL beaker and its photocatalytic degradation was observed. The solution was then exposed to 500W halogen lamp from the top side of a closed beaker. When a halogen compound is included inside the tungsten bulb, its purpose is to combine with the tungsten evaporated from hot filament. This forms a compound that is electrically attracted back to tungsten filament¹². Thus it prevents evaporated tungsten from condensing on the envelope and darkening it. The tungsten halogen lamps develop a larger amount of ultraviolet radiation than general service lamps¹³. The absorbance was measured at 390 nm using spectrophotometer (Spectronics 20D⁺) in a glass cuvette with path length 1.0 cm and the progress of photocatalytic reaction was observed.

RESULTS AND DISCUSSION

The result of typical run for photocatalytic degradation of *p*-nitrophenol is shown in Table-1 and graphically represented in Fig. 1. A linear least square graph¹⁴ of $2 + \log \text{ABS}$ vs. exposure time was drawn and its slope determined. The rate of this reaction was determined using the expression $K = 2.303 \times \text{slope}$. The photocatalytic degradation of *p*-nitrophenol was found to be a two-step reaction. In the first step hyperchromic shift was observed without change in λ_{max} value. In the second step the actual degradation reaction occurred as shown in Fig. 1.

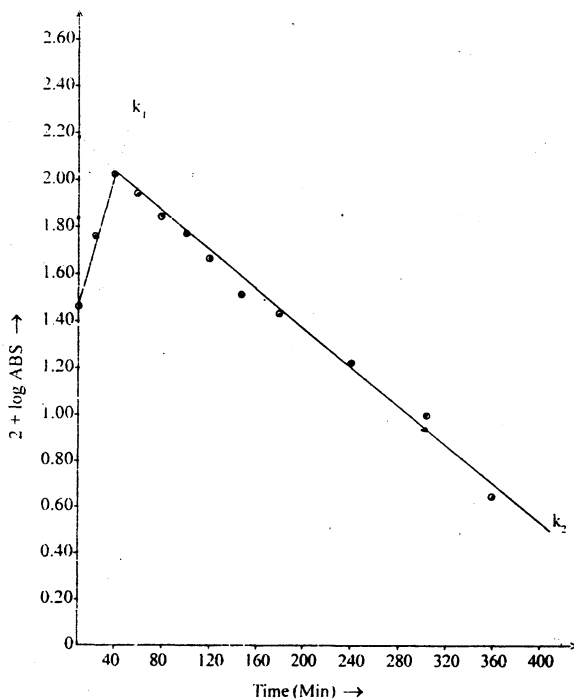


Fig. 1. A typical run

TABLE-1
TYPICAL RUN

Zinc oxide = 200 mg Light intensity = 3.80 mW cm ⁻² [<i>p</i> -NO ₂ C ₆ H ₄ OH] = 0.15 mM		pH = 7.00 Temperature = 306K λ _{max} = 390 nm	
Time (min)	ABS	2 + log ABS	
0	0.278	1.44	
20	0.582	1.76	
40	0.995	2.00	
60	0.827	1.92	
80	0.700	1.85	
100	0.604	1.78	
120	0.470	1.67	
150	0.320	1.51	
180	0.264	1.42	
240	0.167	1.22	
300	0.101	1.00	
360	0.044	0.64	

$$K_1 = 3.28 \times 10^{-2} \text{ min}^{-1}, \quad K_2 = 0.92 \times 10^{-2} \text{ min}^{-1}.$$

Effect of *p*-nitrophenol concentration: The impact of concentration of *p*-nitrophenol upon the rate of degradation was observed. The results are tabulated in Table-2. It is obvious to expect a decrease in reaction rate on increasing the concentration. In the degradation of *p*-nitrophenol the value of K_2 was found to decrease with increase in concentration. However, an unexpected observation was noticed for the value of K_1 which increased as the concentration of substrate increased, but after reaching a certain value (0.200 mM) the value of K_1 decreased.

TABLE-2
EFFECT OF *p*-NITROPHENOL CONCENTRATION

Zinc oxide = 200 mg Light Intensity = 3.80 mW cm ⁻²		pH = 7.00 Temperature = 306 K	
No.	<i>p</i> -nitrophenol concentration (mM)	$K_1 (\text{min}^{-1}) \times 10^2$ λ _{max} = 390 nm	$K_2 (\text{min}^{-1}) \times 10^2$ λ _{max} = 390 nm
1.	0.100	1.67	2.63
2.	0.125	2.99	2.02
3.	0.150	3.28	0.92
4.	0.175	6.91	0.80
5.	0.200	7.14	0.57
6.	0.225	3.33	0.51
7.	0.250	3.11	0.36

Effect of pH variation: pH variation had two types of effects on the degradation of *p*-nitrophenol. When pH was increased the value of K_1 steadily increased; however the value of K_2 decreased (Table-3). It may be possible that the first step is more affected by radicals like OH, which are more likely to be generated with increase in pH of the solution.

TABLE-3
EFFECT OF pH VARIATION

Zinc oxide = 200 mg [<i>p</i> -NO ₂ C ₆ H ₄ OH] = 0.150 mM		Temperature = 306 K Light intensity = 3.80 mW cm ⁻²	
No.	pH	K_1 (min ⁻¹) × 10 ² $\lambda_{\max} = 390$ nm	K_2 (min ⁻¹) × 10 ² $\lambda_{\max} = 390$ nm
1.	6.0	1.79	1.47
2.	6.5	2.59	1.09
3.	7.0	3.28	0.92
4.	7.5	3.57	0.73

Effect of amount of photocatalyst: The effect of variation in the amount of photocatalyst was also observed and the results are tabulated in Table-4. The data indicates that the rate of photocatalytic degradation of *p*-nitrophenol increased with increase in the amount of semiconductor, whereas the value of K_1 is decreased on increasing the amount of photocatalyst.

TABLE-4
EFFECT OF AMOUNT OF PHOTOCATALYST

[<i>p</i> -NO ₂ C ₆ H ₄ OH] = 0.150 mM Light Intensity = 3.80 mW cm ⁻²		pH = 7.00 Temperature = 306 K	
No.	Amount of photocatalyst (mg)	K_1 (min ⁻¹) × 10 ² $\lambda_{\max} = 390$ nm	K_2 (min ⁻¹) × 10 ² $\lambda_{\max} = 390$ nm
1.	50	3.74	0.73
2.	100	3.57	0.78
3.	150	3.34	0.89
4.	200	3.28	0.92
5.	250	3.11	1.03
6.	300	2.99	1.11
7.	350	2.65	1.17

Effect of light intensity: To study the effect of light intensity on the photocatalytic degradation of *p*-nitrophenol, the distance between light source and semiconductor surface was varied. The results obtained are shown in Table-5. It is obvious to expect an increase in reaction rate on increasing light intensity. In the degradation of *p*-nitrophenol the value of K_2 was found to decrease with increase in light intensity, but after reaching a certain intensity (at 3.80 mW cm⁻²), the value of K_2 increased with increase in light intensity. The value of K_1 also

increased with increase in light intensity, but after reaching a certain intensity (at 3.80 mW cm^{-2}), the value of K_1 decreased. The probable reason for this is unknown.

TABLE-5
EFFECT OF LIGHT INTENSITY

Zinc oxide = 200 mg		pH = 7.00	
[<i>p</i> -NO ₂ C ₆ H ₄ OH] = 0.150 mM		Temperature = 306 K	
No.	Light intensity mW cm ⁻²	$K_1 (\text{min}^{-1}) \times 10^2$ $\lambda_{\text{max}} = 390 \text{ nm}$	$K_2 (\text{min}^{-1}) \times 10^2$ $\lambda_{\text{max}} = 390 \text{ nm}$
1.	2.50	1.96	1.62
2.	3.18	2.59	1.54
3.	3.80	3.28	0.92
4.	4.56	1.73	1.61
5.	5.30	1.56	1.67
6.	6.06	1.38	1.73
7.	6.89	1.32	1.89

Effect of sensitizer: Sensitizers are usually known to increase the photocatalytic reaction rate by initially absorbing e.m.r. and then passing the energy to the reaction system. In the present investigation the sensitizers selected were methylene blue, methyl orange, crystal violet and $K_3[\text{Fe}(\text{CN})_6]$. It was observed that all at 10 ppm concentration were not able to enhance the reaction rate.

Impact of free radical quencher: The presence of free radical quenchers (aliphatic alcohol) caused some marked effects on the photocatalytic degradation of *p*-nitrophenol. Alcohols are known to quench free radicals presence. Two sets were studied for this purpose. The two sets contained respectively 2 mL and 3 mL Ethanol which is usually regarded as a good quencher. The results are mentioned in Table-6. It was observed that the first step was found absent in presence of ethanol and the addition of ethanol did not reduce the rate of degradation; on the contrary, the reaction rates were found to increase in the presence of alcohol for both the steps. Hence, it may be more responsible for this degradation reaction. The λ_{max} value showed blue shift of 75 nm.

TABLE-6
EFFECT OF RADICAL QUENCHER

Zinc oxide = 200 mg		pH = 7.00		
Light intensity = 3.80 mW cm^{-2}		Temperature = 306 K		
[<i>p</i> -NO ₂ C ₆ H ₄ OH] = 0.150 mM				
No.	Ethanol (mL)	λ_{max}	$K_1 (\text{min}^{-1}) \times 10^3$	$K_2 (\text{min}^{-1}) \times 10^3$
1.	2	315	—	1.35
2.	3	315	—	1.29
3.	Typical run	390	3.28	0.92

Effect of band gap: The usual excited semiconductor has separated hole and electron pair that induce the photocatalytic reactions, hence the band gap energy has an important role to play¹⁵. In this study four semiconductors with band gap ranging from 0.30 eV to 3.8 eV were taken up. It was observed that when the band gap energy increased from 0.30 eV to 3.2 eV, the values of both K_1 as well as K_2 increased. These values reached a maximum at 3.2 eV (ZnO) and thereafter a fall was observed on increasing the band gap to 3.8 eV value.

TABLE-7
EFFECT OF BAND GAP

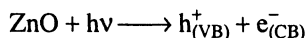
Light intensity = 3.80 mW cm^{-2}
 $[p\text{-NO}_2\text{C}_6\text{H}_4\text{OH}] = 0.150 \text{ mM}$

pH = 7.00
 Temperature = 306 K
 $\lambda_{\text{max}} = 390 \text{ nm}$

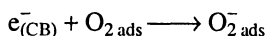
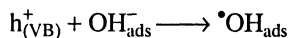
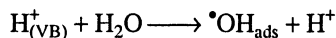
No.	Semiconductor used	Band gap (eV)	$K_1 (\text{min}^{-1}) \times 10^3$	$K_2 (\text{min}^{-1}) \times 10^2$
1.	PbS	0.30	2.72	0.64
2.	CdS	2.50	3.06	0.83
3.	ZnO	3.20	3.28	0.92
4.	ZnS	3.80	1.25	0.62

Mechanism

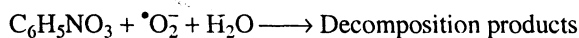
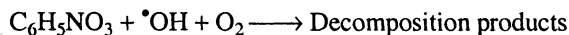
When a semiconductor is irradiated with light having energy ($E = h\nu$) equal to or more than band gap energy, heterogeneous photocatalytic reactions occur at the solid-solution contact surface. The semiconductor forms a pair of valence band (VB) hole and conduction band (CB) electron.



The hole generated is capable of oxidizing the substrate and the electron of CB is capable of reducing the substrates. Furthermore, as per the reactions mentioned below, medium containing species, *e.g.*, $\cdot\text{OH}$, H^+ , $\cdot\text{O}_2^-$, H_2O_2 , $\cdot\text{HO}_2$, O_2 which are due to the semiconductor-light-water-oxygen interactions are also capable of carrying out redox reactions. The generation of super oxide radical anion $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radical can be shown as under



It was observed that the products of photocatalytic degradation of *p*-nitrophenol in presence of ZnO were colourless gases with virtually no solid residue left in the solution. Hence probable reactions are proposed as under.



Conclusion

The photocatalytic degradation of *p*-nitrophenol was found to be a two-step reaction. Concentration of substrate, pH of solution, amount of photocatalyst, light intensity etc. showed their expected impact on the reaction rate. Thus the reaction mechanism is extremely sensitive to some photoactive molecules. This method is useful to degrade *p*-nitrophenol completely into decomposition products other than solids.

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(Received: 26 September 2003; Accepted: 31 December 2003) AJC-3319

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