# PHOTODEGRADATION OF m-NITROPHENOL BY IRRADIATED SEMICONDUCTOR IN HETEROGENEOUS PHASE.

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## ABSTRACT

The photocatalytic degradation of m-nitrophenol was carried out by irradiation in presence of ZnO powder. The concentration of substrate, amount of semiconductor, pH, light intensity, sensitizer, band gap, radical quencher, etc. were found to affect the kinetics of the degradation process. A tentative mechanism for the photocatalytic degradation of m-nitrophenol has been suggested.

**Key words :** Zinc oxide, Degradation, Photocatalysis, m-nitrophenol.

## INTRODUCTION

The rate of reaction, which is thermodynamically allowed, is increased by the presence of an irradiated solid in heterogeneous phase. This is due to the creation in these conditions of some new reaction paths involving photo-created species and a decrease of the activation energy. The solid bring into contact, the reactants with electron and/or holes, which are generated within the solid by photons of energy equal or higher than the band gap of the solid. Manys reactions can be driven under favorable conditions in the presence of a photocatalyst. It has opened new avenues of research in the field of photocatalytic reactions.

Photodegradation of dichloromethane, tetrachloroethylene and 1,2-dibromo-3-chloropropane in aqueous suspension of $TiO_2$ with natural, concentrated and simulated sunlight was investigated[1]. Photodegradation of fluorinated aromatics over titania in aqueous media was studied[2]. Degradation of ethyl benzene in $TiO_2$ aqueous suspension was observed by Vidal et al[3]. Photocatalytic degradation of p-toluenesulphonic acid in aqueous system containing powdered and immobilized $TiO_2$ was studied and p-cresol was identified as the main intermediate[4]. Sclafani et al[5]. studied photocatalytic degradation of phenol in aqueous poly crystalline $TiO_2$ dispersion. Photocatalytic dehydrogenation of alcohol in the presence of Pt-CdS was studied[6].

Sobate et al[7]. studied the kinetics of photocatalytic degradation of 3-chlorosalicylic acid over $TiO_2$ membranes supported on glass. Photodegradation of substituted benzoic acid on $TiO_2$ was carried out[8]. Photocatalytic degradation on mixed surfactants and some commercial soap detergent products using suspended $TiO_2$ catalysts has been carried out[9]. The photo catalytic degradation of picric acid in presence of ZnO semiconductor has also been studied[10]. Hydroxylation of benzene using titanium dioxide as a semiconductor has been recently reported[11].

## EXPERIMENTAL

Zinc oxide (Merck) was used and other chemicals were of AR grade. Double distilled water was used throughout. Photocatalytic degradation of m-nitrophenol was studied by taking 10 mL solution (0.200 mM) in 100 mL beaker and 200 mg of semiconductor (ZnO, 60 Mesh powder) was added to it. This solution was exposed to 500 W halogen lamp from the top side of a closed beaker.

When a halogen is present inside the tungsten bulb, its purpose is to combine with tungsten evaporated from hot filament. This forms a compound that is electrically attracted back to tungsten filament[12]. Thus it prevents evaporated tungsten from condensing on the envelop and darkening it. The tungsten halogen lamps develop a larger amount of ultra violet radiation than general service lamps[13]. The absorbance was measured at 355 nm using spectrophotometer (Spectronic 20D) in a glass cuvette with path length of 1 cm and progress of the photocatalytic reaction was observed.

## RESULTS AND DISCUSSION

The results of typical run for photocatalytic degradation of m-nitrophenol is tabulated in Table-1 and graphically represented in Fig. 1. A graph of 2 + log Abs. versus exposure time was drawn and its slope was determined. This graph was plotted according to the linear least squares method[14].The rate constant of this photocatalytic reaction was determined using expression k = 2.303 x slope. The photocatalytic degradation of m-nitrophenol was found to be a two-step reaction.

### Table 1. A TYPICAL RUN

Zinc oxide = 200 mg                                    pH = 7.00
Light Intensity = 4.54 $mWcm^{-2}$                      Temperature =305 K
$[m-NO_2C_6H_4OH]$ = 0.200 mM                          $\lambda_{max}$ = 355 nm

| Time (min) | Abs | 2 + log Abs. |
|:---:|:---:|:---:|
| 00 | 0.204 | 1.31 |
| 20 | 0.250 | 1.40 |
| 40 | 0.232 | 1.37 |

| 60 | 0.211 | 1.32 |
|---|---|---|
| 80 | 0.200 | 1.30 |
| 100 | 0.186 | 1.27 |
| 120 | 0.176 | 1.25 |
| 150 | 0.152 | 1.18 |
| 180 | 0.130 | 1.11 |
| 240 | 0.088 | 0.94 |
| 300 | 0.044 | 0.64 |

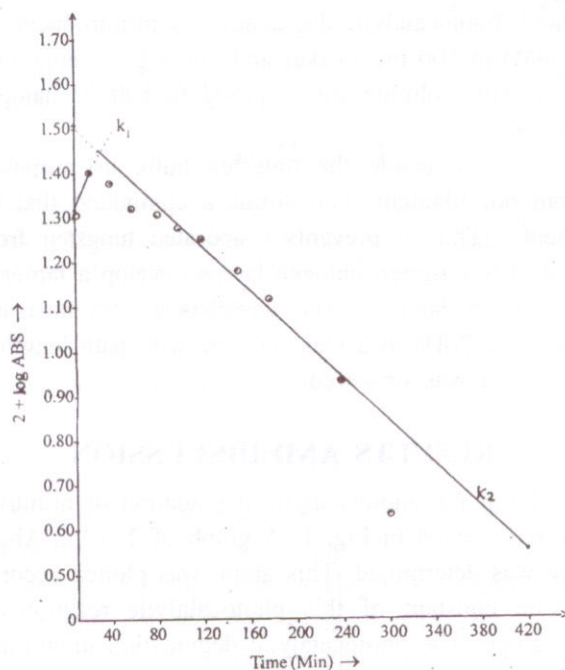$k_1 = 9.21 \times 10^{-3}$ min$-1$          $k_2 = 5.87 \times 10^{-3}$ min$-1$



Figure 1. A Typical Run.

## Effect of m-nitrophenol concentration

The effect of variation of m-nitrophenol concentration on the rate of its photocatalytic degradation was studied taking its different concentrations. The results are tabulated in Table-2. It is obvious to expect a decrease in reaction rate on increasing the concentration. It is evident that as the concentration of m-nitrophenol was increased, the rate of photocatalytic degradation of m-nitrophenol was decreased. However, the value of $k_1$ increased as the concentration of substrate was increased but after reaching a certain value (0.200 mM), the value of $k_1$ was found to decrease.

## Table 2. Effect of m-nitrophenol concentration

Zinc oxide = 200 mg

Light Intensity = 4.54 mWcm$^{-2}$

pH = 7.00

Temperature = 305 K

$\lambda_{max}$ = 355 nm

| [m-nitrophenol] (mM) | $k_1 \times 10^3$ (min$^{-1}$) | $k_2 \times 10^3$ (min$^{-1}$) |
|---|---|---|
| 0.150 | 4.61 | 6.31 |
| 0.175 | 6.91 | 6.08 |
| 0.200 | 9.21 | 5.87 |
| 0.225 | 4.61 | 4.42 |
| 0.250 | 4.61 | 3.62 |

### Effect of pH

The effect of variation of pH on the rate of photocatalytic degradation of m-nitrophenol was investigated by determining the rate at different pH values. The semiconductor dissolves in highly acidic medium and therefore, photocatalytic degradation could not be investigated in lower pH range. The results are shown in Table-3. It was observed that when pH was increased, the value of $k_2$ also increased. However, the value of $k_1$ was also increased but after reaching a certain value of pH (7.00), the values of $k_1$ fell down and became constant. The constancy of $k_1$ in alkaline medium is not understood properly.

## Table 3. Effect of pH

Zinc oxide = 200 mg

Light Intensity = 4.54 mWcm$^{-2}$

[m-NO$_2$C$_6$H$_4$OH] = 0.200 mM

Temperature = 305 K

$\lambda_{max}$ = 355 nm

| pH | $k_1 \times 10^3$ (min$^{-1}$) | $k_2 \times 10^3$ (min$^{-1}$) |
|---|---|---|
| 6.50 | 2.88 | 4.24 |
| 7.00 | 9.21 | 5.87 |
| 7.50 | 1.15 | 6.29 |
| 8.00 | 1.15 | 6.36 |
| 8.50 | 1.15 | 7.05 |

### Effect of amount of photocatalyst

The effect of variation in amount of photocatalyst was observed and the results are tabulated in Table-4. The data indicate that the rate of photocatalytic degradation reaction as well as the value of $k_1$ increased with increase in amount of semiconductor. The normal tendency is to obtain constant values after reaching the total surface area coverage, however a steady increase in both the values of rate constants indicates possibility of some additional pathway.

## Table 4. Effect of amount of photocatalyst

pH = 7.00

Light Intensity = 4.54 mWcm$^{-2}$

[m-NO$_2$C$_6$H$_4$OH] = 0.200 mM

Temperature = 305 K

$\lambda_{max}$ = 355 nm

| Amount of photocatalyst (mg) | $k_1$ x 10$^3$ (min$^{-1}$) | $k_2$ x 10$^3$ (min$^{-1}$) |
|---|---|---|
| 100 | 4.61 | 4.97 |
| 150 | 6.91 | 5.11 |
| 200 | 9.21 | 5.87 |
| 250 | 11.52 | 6.03 |
| 300 | 13.82 | 6.24 |

### Effect of light intensity

To observe the effect of light intensity on the photocatalytic degradation of m-nitrophenol, the distance between light source and exposed surface of the semiconductor was varied. The intensity of light was measured using light meter (Mastech, Taiwan, Model Lux-1). The results are tabulated in Table-5. The data show that in the degradation of m-nitrophenol, the value of $k_2$ was found to increase with increased light intensity. This increase is due to the fact that more photons will be available for excitation on increasing the light intensity and in turn, more electron-hole pairs will be generated in the semiconductor, thus resulting into enhanced rate of photocatalytic degradation. However, the value of $k_1$ was found to be constant with increase in light intensity. This nature of $k_1$ indicates that the first step is almost independent on the value of intensity of light.

## Table 5. Effect of light intensity

Zinc oxide = 200 mg

[m-NO$_2$C$_6$H$_4$OH] = 0.200 mM

pH = 7.00

Temperature = 305 K

$\lambda_{max}$ = 355 nm

| Light intensity (mWcm$^{-2}$) | $k_1$ x 10$^3$ (min$^{-1}$) | $k_2$ (min$^{-1}$) x 10$^3$ (min$^{-1}$) |
|---|---|---|
| 3.03 | 9.21 | 2.76 |
| 3.79 | 9.21 | 3.98 |
| 4.54 | 9.21 | 5.87 |
| 5.30 | 9.21 | 7.14 |
| 6.06 | 9.21 | 7.42 |

### Effect of sensitizers

In the present work, sensitizers selected were $K_3[Fe(CN)_6]$, methylene blue, crystal violet and methyl orange. The results are tabulated in Table-6. 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 case of crystal violet and methyl orange, it was found that either of the degradation reaction could not be observed possibly due to the e.m.r absorption by the dyes. Hence, these two dyes were not found to be useful as sensitizer. In case of $K_3[Fe(CN)_6]$ and methylene blue, it was observed that the reaction rates decreased by their use. Compared to the typical run, these compounds were not found to be useful as sensitizer for the degradation reaction, however the elimination of the first step helped in reduction of the time required to start the actual degradation process.

### Table 6. Effect of sensitizers

Zinc oxide = 200 mg                                                      pH = 7.00
$[m-NO_2C_6H_4OH]$ = 0.200 mM                                Temperature = 305 K
Light Intensity = 4.54 mWcm$^{-2}$                             $\lambda_{max}$ = 355 nm

| Sensitizers | $k_1 \times 10^3$ (min$^{-1}$) | $k_2$ (min$^{-1}$) $\times 10^3$ (min$^{-1}$) |
|---|---|---|
| Typical Run | 9.21 | 5.87 |
| $K_3[Fe(CN)_6]$ | - | 0.93 |
| Methylene blue | - | 2.27 |

### Effect of radical quencher

Alcohol are well known as free radical scavengers. In this work, methanol and ethanol were selected to know the possibility of participation of radicals in this degradation. Ethanol quenched the reaction by reducing the rates of both the steps. When methanol was taken, the reaction rate for the first step decreased however a slight increase in reaction rate of second step was observed. The results are reported in Table-7.

### Table 7. Effect of radical quencher

Zinc oxide = 200 mg                                                      pH = 7.00
$[m-NO_2C_6H_4OH]$ = 0.200 mM                                Temperature = 305 K
Light Intensity = 4.54 mWcm$^{-2}$

| Volume of alcohol | | $\lambda_{max}$ | $k_1 \times 10^3$ (min$^{-1}$) | $k_2 \times 10^3$ (min$^{-1}$) |
|---|---|---|---|---|
| Typical Run | | 355 nm | 9.21 | 5.87 |
| Methanol | 2 mL | 355 nm | 6.91 | 5.92 |
| | 3 mL | 355 nm | 6.91 | 5.94 |
| Ethanol | 2 mL | 355 nm | 2.30 | 5.67 |
| | 3 mL | 355 nm | 2.30 | 5.14 |

**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 play[15]. In this study, four semiconductors with band gap ranging from 0.30 eV to 3.80 eV were taken. It was observed that the value of photocatalytic degradation rate decreased as the band gap was increased. In case of 0.30 eV (PbS) and 3.80 eV (ZnS), the first step was found to be absent. The results are tabulated in Table-8.

**Table 8. Effect of Band gap**

Semiconductor = 200 mg                                           pH = 7.00

$[m-NO_2C_6H_4OH]$ = 0.200 mM                          Temperature = 305 K

Light Intensity = 4.54 mWcm$^{-2}$                          $\lambda_{max}$ = 355 nm

| Semiconductor used | Band gap | $k_1 \times 10^3$ (min$^{-1}$) | $k_2 \times 10^{-3}$ (min$^{-1}$) |
|---|---|---|---|
| PbS | 0.30 eV | - | 13.50 |
| CdS | 2.50 eV | 4.61 | 8.43 |
| ZnO | 3.20 eV | 9.21 | 5.87 |
| ZnS | 3.80 eV | - | 2.88 |

## MECHANISM

Heterogeneous photocatalytic processes typically occurr at solid-solution interface, when sufficient energy equal to the band gap of the semiconductor is provided, the semiconductor forms a pair of valence band hole and conduction band electron.

$$ZnO + h\nu \rightarrow h^+_{(VB)} + e^-_{(CB)}$$
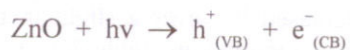
The charge carriers recombine or trapped by a defect site or electron transfer between adsorbed electron donors and acceptor can proceed.

$$h^+_{(VB)} + (Red_2)_{ads} \rightarrow (Ox_2)_{ads}$$

$$e^-_{(CB)} + (Ox_1)_{ads} \rightarrow (Red_1)_{ads}$$
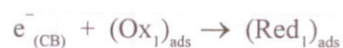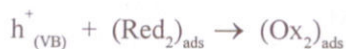
The degradation of m-nitrophenol resulted in virtually all-gaseous products. A probable mechanism may be written as :

$$C_6H_5NO_3 + {}^\bullet OH + O_2 \rightarrow \text{Decomposition products}$$

$$C_6H_5NO_3 + O_2^{\bullet -} + H_2O \rightarrow \text{Decomposition products}$$

Where, $(OX_1)_{ads}$ is compound, reducible by electron to $(Red_1)_{ads}$, and $(Red_2)_{ads}$ is compound, oxidized by the hole of valence band of the semiconductor to $(Ox_2)_{ads}$, both adsorbed on ZnO surface. $Ox_1$ and $Red_2$ may be substrate or its oxidized or reduced form.

## CONCLUSION

The photocatalytic degradation of m-nitrophenol was found to be a two-step process. The concentration of substrate, pH of the solution, amount of photocatalyst, light intensity etc. show appreciable impact on reaction rate. The reaction mechanism is very sensitive to some photoactive molecules like sensitizers and radical quenchers. This method is useful to degrade m-nitrophenol completely into gaseous products.

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