



USE OF IRON (III) OXIDE AS A PHOTOCATALYST FOR OXIDATION OF ADIPIC ACID

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ABSTRACT

The photocatalytic oxidation of adipic acid using iron (III) oxide powder as a photocatalyst has been studied. The progress of the reaction was observed volumetrically. The effect of pH, concentration of adipic acid, amount of iron (III) oxide and light intensity etc. has been investigated. A mechanism consistent with experimental data has been suggested.

Key words: Photocatalysis, Adipic acid, Iron (III) oxide

INTRODUCTION

Photocatalysis and related phenomenon are now well recognized. The chemical reactions that occur in the presence of semiconductor and light are collectively termed as photocatalytic reactions. Although a lot of the work has been done on photocatalytic methods for treatments of waste waters, negligible attention has been paid on the use of iron (III) oxide for oxidizing various organic materials. Study of the size effect in the photochemical generation of hydrogen from water by colloidal iron (III) oxide particles was carried out¹. The assessment of photocatalytic activity of Bi_2O_3 , WO_3 and Fe_2O_3 was made by the photodecomposition of peroxomono sulphate in visible radiation². Verma *et al.*³, investigated the photocatalytic removal of nickel (II) from its solution over iron (III) oxide powder. Photocatalytic reduction of nitrite and nitrate ions to ammonia on Ru/TiO_2 , ZnO , ZrO_2 , Fe_2O_3 , $\text{ZnO}_2 - \text{Fe}_2\text{O}_3$ coupled catalysts has been reported⁴. Miyoshi *et al.*⁵ investigated light induced decomposition of saturated carboxylic acids on iron oxide incorporated clay suspended in aqueous solution. Photooxidation of water at $\alpha\text{-Fe}_2\text{O}_3$ electrodes was observed by Kennady and Frese Jr⁶. Tennakone *et al.*⁷ studied oxidation of nitrogen using a composite $\text{ZnO}-\text{Fe}_2\text{O}_3$ catalyst. Preparation and characterization of $\gamma\text{-Fe}_2\text{O}_3$ semiconductor was made by Sharon and Prasad⁸.

A great deal of literature survey reveals that no attention has been paid on the photocatalytic oxidation of adipic acid using iron (III) oxide and therefore, the present work has been undertaken.

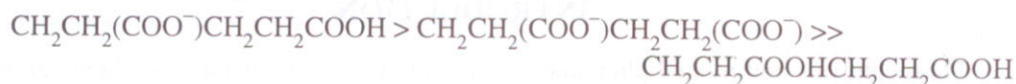
EXPERIMENTAL

0.0182 g of adipic acid was dissolved in 250.0 mL of doubly distilled water so that the concentration of adipic acid was 5.00×10^{-4} M. 50.0 mL of the adipic acid solution was taken out in a beaker and 0.06 g of iron (III) oxide powder (Reidel) was added to it. The pH of the solution was adjusted by addition of previously standardized solution of sodium hydroxide and sulphuric acid, and pH was measured by a digital pH meter (Systronics Model 335). The solution of adipic acid was then exposed to light (intensity – 40.0 mWcm^{-2}). The intensity of light was measured by a solarimeter (Surya Mapi Model CEL 201). After a fixed time interval, 3.0 mL of adipic acid solution was taken out and it was titrated against standardized potassium permanganate (3.0×10^{-4} M) to monitor the progress of the reaction.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the photocatalytic oxidation of adipic acid was investigated and the results are enumerated in the Table 1. It was observed that the rate of reaction increases to an optimum value (at pH 4.5) and then it decreases on increasing the pH of the medium further. The reactivity of different species of adipic acid decreases in the order.



In acidic medium i.e. around pH 4.5, a major fraction of adipic acid may be present in its ionic form $\text{CH}_2\text{CH}_2(\text{COO}^-)\text{CH}_2\text{CH}_2\text{COOH}$ which reacts with the photogenerated hole leading to the formation of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ radicals and CO_2 gas. This explains the increase in the rate of reaction upto pH 4.5. On increasing the pH of the solution above pH 4.5, the rate of the reaction decreases as the fraction of more reactive species $\text{CH}_2\text{CH}_2(\text{COO}^-)\text{CH}_2\text{CH}_2\text{COOH}$ decreases and less reactive $\text{CH}_2\text{CH}_2(\text{COO}^-)\text{CH}_2\text{CH}_2(\text{COO}^-)$ increases.

Table 1. Effect of pH

$[\text{KMnO}_4] = 3.00 \times 10^{-4} \text{ M}$
Light Intensity = 40.0 mWcm^{-2}

$[\text{Adipic Acid}] = 5.00 \times 10^{-4} \text{ M}$
 $\text{Fe}_2\text{O}_3 = 0.06 \text{ g}$

pH	$k \times 10^4 (\text{sec}^{-1})$
2.5	1.04
3.0	1.53
3.5	1.91
4.0	2.43
4.5	2.68

Table 1 Continued...

pH	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
5.0	2.25
5.5	1.87
6.0	1.60
6.5	1.31

Effect of adipic acid concentration

Different concentration of adipic acid were taken and 0.06 g of Fe_2O_3 was added into each beaker, and these solutions were exposed to light at an intensity of 40.0 mWcm^{-2} . The progress of the reaction was observed volumetrically with standardized potassium permanganate solution, whereby; the effect of concentration of adipic acid on the rate of reaction was investigated. The results are tabulated in Table 2. It was observed that the rate of reaction increases with an increase in the concentration up to $5.00 \times 10^{-4} \text{ M}$. This may be due to the fact that as the concentration of the acid was increased, more molecules were available for excitation and consecutive energy transfer. As a result, there was an increase in the rate of reaction. The rate of reaction however decreased on increasing the concentration of adipic acid solution further, after ascertain value. This may be due to the fact that on further increasing the concentration of adipic acid, its movement is likely to be hindered by the molecules themselves and the adipic acid molecules do not reach the semiconductor surface in the desired time limit, and hence a decrease in the rate of the reaction was observed.

Table 2. Effect of adipic acid concentration

[Adipic Acid] $\times 10^4 \text{ M}$	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
3.29	0.70
3.51	1.26
3.80	1.56
4.09	1.88
4.48	2.22
5.00	2.68
5.50	2.28
6.19	1.88
7.11	1.58
8.27	1.34
10.00	1.10

Effect of amount of iron (III) oxide powder

Various amounts of iron (III) oxide powder ranging from 0.02 g to 0.10 g were added into solutions of adipic acid and exposed to light and the effect on the rate of the reaction was observed. Large amounts of iron (III) oxide i.e. above 0.10 g could not be used as slight light yellow color appeared in the acid solution during the reaction. The appearance of light yellow color in the solution of adipic acid might be due to consumption of some iron (III) oxide powder; which creates problems in the measurement of the end point. It was observed that the value of rate constant increases with the amount of iron (III) oxide, which is attributed to the fact as the amount of semiconductor was increased, the exposed surface area also increases, thus increasing the rate of the reaction. The observations are tabulated in Table 3.

Table 3. Effect of amount of iron (III) oxide powder

Amount of iron (III) oxide (g)	k x 10 ⁴ (sec ⁻¹)
0.02	1.61
0.04	2.03
0.06	2.68
0.08	3.27
0.10	4.06

Effect of light intensity

The solution of adipic acid was exposed to different intensities of light ranging from 10.0 mWcm⁻² to 80.0 mWcm⁻². It was observed that, the rate of reaction increases with an increase in the intensity of light. This may be explained by the fact that on increasing the light intensity, the number of photons striking per unit area of iron (III) oxide powder also increases. The results are tabulated in Table 4.

Table 4. Effect of light intensity

Intensity of light (mWcm ⁻²)	k x 10 ⁴ (sec ⁻¹)
10.0	1.27
20.0	1.42
30.0	2.37

Table 4 Continued...

Intensity of light (mWcm ⁻²)	k x 10 ⁴ (sec ⁻¹)
40.0	2.68
50.0	3.10
60.0	3.41
70.0	3.70
80.0	3.70

MECHANISM

On the basis of observations, a tentative mechanism for photocatalytic oxidation of adipic acid has been proposed,



Where SC, SC*, CB, VB and h⁺ represent a semiconductor, an excited semiconductor, a conduction band, a valence band and a hole, respectively.

The amount of carbon dioxide evolved increases with an increase in adipic acid concentration up to a certain limit. Oxygen reacts effectively with photoelectrons forming O₂^{-•} or HO₂ radicals, and it may inhibit the electron-hole recombination.



$\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ free radical formed disappears by reaction with O₂ and $\cdot\text{HO}_2$ radicals are generated.



Ordinarily, recombination of $\cdot\text{HO}_2$ leads of the formation H₂O₂.



But H₂O₂ was not found to be the final product; hence, it may be concluded that H₂O₂ was consumed during photooxidation.

REFERENCES

1. S. Chatterjee, S. Sarkar and S. N. Bhattacharya, J. Photochem, Photobiol., **69A**, 237 (1992)

2. P. Maruthamuthu, K. Gurunathan, E. Subramaniam and M. Ashok Kumar. *Bull. Chem. Soc. Japan.*, **64A**, 1993 (1991).
3. V. Verma, M. Mehta, V. R. Dwivedi and Suresh C. Ameta, *Chem. Environ. Res.*, **9**, 315 (2000).
4. K. T. Ranjit, T. K. Vardarajan and B. Vishwanathan, *Indian J. Chem.*, **35A**, 177 (1996).
5. H. Miyoshi, H. Mori and H. Yoneyama, *Langmuir*, **7**, 503 (1991).
6. J. H. Kennady and K. W. Frese. Jr., *NSEC*, **125**, 709 (1978)
7. K. Tennakone, O. A. Ileperuma, C. T. K. Thamunimulla and J. M. S. Bandara, *J. Photochem. Photobiol.*, **66**, 375, (1992).
8. M. Sharon and B. M. Prasad, *Electrochim. Acta*, **30**, 331, (1985).

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