

Photocatalytic degradation of catechol over ZnO powder the influence of peroxomonosulphate and peroxodisulphate on the reaction rate

M. Maria Berjilia¹, S. Manikandan¹ and K.B. Dhanalakshmi²

¹Department of Chemistry, Government Arts College, Ariyalur- 621 713, Tamil Nadu, India.

²Department of Chemistry, Government Arts College, Musiri - 621 211 Tamil Nadu, India.

Abstract:

The degradation of catechol was carried out under uv-visible light by zinc oxide as photocatalyst. To measure the efficiency of the photocatalyst, the different variables studied included amount of photocatalyst, effect of oxidants peroxomonosulphate (PMS) and peroxodisulphate (PDS) on the photocatalytic oxidation of catechol on illumination ZnO surfaces has been investigated. The efficiencies of these oxidants on photocatalytic degradation of catechol are compared with that of PMS and PDS. The experimental results indicate that these oxidants exhibited enhanced rates of mineralization of catechol. A reaction mechanism, involving the generation of both hydroxyl radicals and sulphate radicals. In conclusion, this investigation indicated high potential of zinc oxide suspension to remove high level concentration of resorcinol under UV irradiation.

Keywords: Photocatalyst ZnO, catechol, PMS, PDS.

1. Introduction

The Pulp and paper industry generates about 175 m³ of wastewater per ton of paper produced [R. Nagarathnamma *et al* 1999]. A large number of organic and inorganic compounds are introduced during the processing of pulp and paper. Among them, phenol and its derivatives are present extensively in the wastewater of papermaking [J. Chen *et al* 1997]. These compounds are quite toxic and degrade slowly in the environment [R.P. Schwarzenbach *et al* 1996]. These substances persist in the environment for a long time and produce number of adverse effects and disorders in human life [P. Pitter *et al* 1990, R. Crompton,

1997]. Therefore it becomes imperative to completely degrade these organic compounds. A number of oxidation systems have been reported that can be used for the treatment of wastewater [G. Chen, 1837]. However most of them have been proved inefficient in the complete degradation of phenol, catechol and their derivatives present in the wastewater. The biological means for degradation of many chlorinated compounds have been a failure because of the fact that these compounds cannot be completely degraded within the stipulated time period [P.H. Howard, 1991, S. Manahan, 1994]. Moreover the complete degradation of the organics by this technique is very costly and energy consuming. To address these problems, heterogeneous photocatalysis method of wastewater degradation is one of the advanced techniques which may prove useful for the degradation of phenol, catechol and its chloro-derivatives. In the present study, the effect of oxidant, PMS and PDS on the photocatalytic degradation of catechol on illuminated ZnO surfaces has been investigated. The photodegradation rate of catechol in presence of these oxidants was found to be more than in the absence of each of these oxidants. The added oxidant enhances the catechol oxidation rate drastically.

2. Experimental Methods

ZnO (>99.99%, Aldrich, USA) semiconductor grade (specific surface area $\sim 4.6 \text{ m}^2 \text{ g}^{-1}$) sample was used as such in this work. The sample of potassium peroxomonosulphate was donated by the E.I. du pont de Nemours and Co. (Inc.), USA, under the trade name OXONE. Potassium peroxodisulphate from Fluka (>99.9%) was used as such. Catechol (E. Merck, Germany) was used after

distillation. All other chemicals used were of the best research grade commercially available. Doubly distilled water was used to prepare all the reagent solutions.

The photocatalytic experiments were carried out in a Pyrex cell of volume 100 ml. In all the experiments, 50 mg of the photocatalyst powders (except the experiments involving variation of catalyst amounts) were suspended in 70 ml of the substrate (resorcinol) solution, stirred magnetically at a constant rate and then irradiated. A 150 W tungsten-halogen lamp (Lewin-Lighting PVT. LTD. Mumbai, India) was used as the light source. Samples for analysis were withdrawn at regular intervals of time. The catalyst was separated from the solution by filtration. The quantitative analysis of catechol was performed by a standard colorimetric method [R.W. Martin *et al* 1963, K.B. Dhanalakshmi *et al* 2008]. The photodegradation of catechol was also confirmed by colorimetric estimation. The percentage of photodegradation was calculated as follows:

$$\text{Photodegradation\%} = 100[(C_0 - C_t)/C_0]$$

Where C_0 = initial concentration of catechol, C_t = concentration of catechol after photo irradiation. All photocatalytic degradation experiments were carried out in duplicate.

3. Results and discussion

3.1 Photocatalytic degradation of catechol

Photodegradation of catechol (1×10^{-3}) in aqueous solutions at natural pH was performed in the presence of ZnO photocatalyst (50 mg). Photocatalyzed disappearance of catechol before and after irradiation and as well as with or without oxidants (PMS and PDS). Were confirmed by colorimetric method. Pyrogallol and Phloroglucinol were the detectable products but they occurred only in low yields. The photodegradation rate of catechol in the presence of oxidants (PMS and PDS) was found to higher than that in the absence of each of these oxidants. The added oxidant enhance of catechol oxidation rate drastically. In order to find the effect of these oxidants on the rate of decomposition of catechol, experiments were carried out at constant concentration of catechol (1×10^{-3} mol dm⁻³), constant catalyst amount (ZnO = 50 mg) and at constant pH (4.0 and 5.2) with various oxidants (PMS and PDS) by colorimetric method.

3.2 Factors influencing photocatalytic oxidation of catechol

3.2.1 Effect of initial concentration of catechol

Experiments were carried out with various initial concentrations of catechol ($1.0 - 6.0 \times 10^{-3}$ mol dm⁻³) at constant catalyst amount TiO₂ (50 mg) and constant concentration of the oxidant ([PMS] or [PDS] = 1×10^{-3} mol dm⁻³). The pH of the solution was maintained constant. The decrease in [catechol] with time was followed by standard colorimetric method. The results obtained for ZnO-PMS-Catechol and for ZnO-PDS-Catechol systems are presented in Table 1. The plots of Log (OD)_t vs time for various initial concentrations of catechol are linear and from the slopes of the plots, the rate constants were calculated and tabulated (Table 1 and Figs.1 and 2). The plots of rate vs [catechol]₀ (Table 1; inset of Figs. 1 and 2) show that catechol degradation increases with increase in [catechol]₀, reaches a maximum and remains almost constant. The effect of [catechol]₀ on rate could be described by the following relation:

$$\text{rate} = \frac{kK [\text{Catechol}]_0}{1 + K [\text{Catechol}]_0}$$

Where k and K are the proportionality and equilibrium constants, respectively. The reciprocal of the above equation gives

$$\frac{1}{\text{rate}} = \frac{1}{kK [\text{Catechol}]_0} + \frac{1}{k}$$

Table 1 Rate constants for the photodegradation of various amounts of catechol in the presence of PMS and PDS

[Resorcinol] ₀ x 10 ³ mol dm ⁻³	With PMS, k ₁ x 10 ⁻³ s ⁻¹	With PDS, k ₁ x 10 ⁻³ s ⁻¹
1	11.75	9.12
2	7.5	7
3	5.87	6.12
4	5	5.5
5	4.3	4.75
6	3.62	4

ZnO = 50 mg/70ml; T = 30°C; [PMS] = [PDS] = 1×10^{-3} mol dm⁻³.

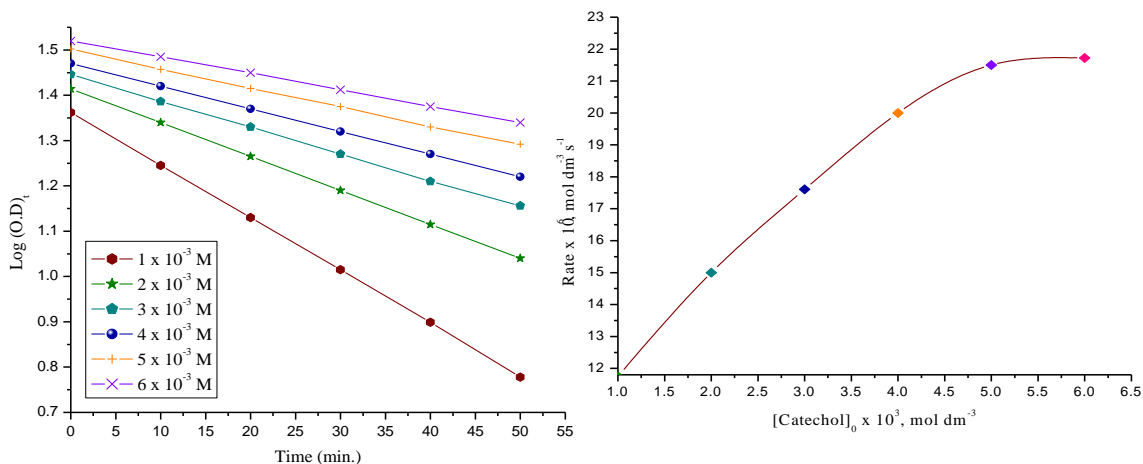


Fig.1 Log (OD)_t vs time plot for the photodegradation of various amount of catechol (1 - 6 x 10⁻³ M). [Catalyst] = 50 mg/70 ml and [PMS] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate for various amounts of catechol.

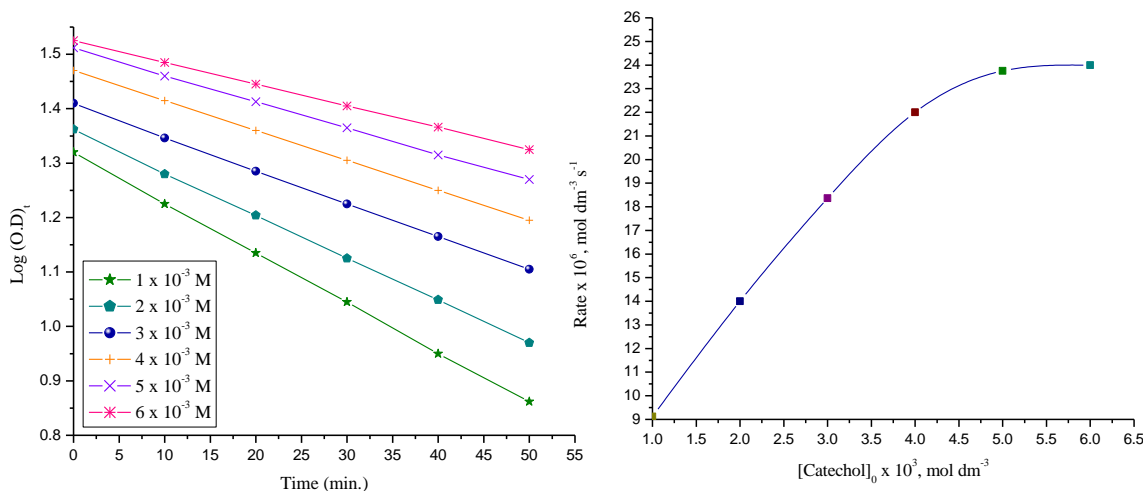


Fig.2 Log (OD)_t vs time plot for the photodegradation of various amounts of catechol (1 - 6 x 10⁻³ M). [Catalyst] = 50 mg/ 70 ml and [PDS] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate for various amounts of catechol.

The plots of 1/rate vs 1/[catechol]₀ are straight lines with intercepts on the ordinate indicating Langmuir kinetics. The values the proportionality constant *k* and equilibrium constant *K* are evaluated (Table 2). For ZnO-PMS-Catechol system the values of *k* and *K* are found to be 9.50 x 10⁻⁶ mol dm⁻³ s⁻¹ and 9.411 dm³ mol⁻¹,

respectively. The values of *k* and *K* for ZnO-PDS-Catechol system are 6.90 x 10³ mol dm⁻³ s⁻¹ and 141.17 x 10³ dm³ mol⁻¹, respectively

3.2.2 Effect of concentration of the oxidant ([PMS] or [PDS])

In order to find the effect of concentration of the oxidant ([PMS] or [PDS]), experiments were carried out with various concentrations of the oxidants (1 - 6 x 10⁻³ mol dm⁻³) at a constant concentration of catechol (1.0 x 10⁻³ mol dm⁻³) and at a constant catalyst amount. The pH of the solution was also maintained constant. Similar

results were obtained for both PMS and PDS systems. But the enhancement in catechol degradation due to PMS addition is higher than that of PDS. The results obtained are presented in Figs. 3 and 4. From the plot of rate vs [oxidant], it is seen that the rate of decomposition of catechol increases linearly with increases in concentration of the oxidant.

Table 2: Evaluation of k and K for the photodegradation of various amounts of catechol

$1/[\text{Catechol}]_0 \times 10^{-3}$ $\text{mol}^{-1} \text{dm}^3$	With PMS, $1/\text{rate}$ $\times 10^6 \text{ mol}^{-1} \text{dm}^3 \text{ s}$	With PDS, $1/\text{rate} \times 10^{-6}$ $\text{mol}^{-1} \text{dm}^3 \text{ s}$
1	8.51	10.96
0.5	6.66	7.14
0.33	5.67	5.44
0.25	5	4.54
0.2	4.65	4.21
0.16	4.59	4.16
$k = (\text{mol dm}^{-3} \text{s}^{-1})$	9.50×10^{-6}	6.90×10^{-6}
$K = (\text{dm}^{-3} \text{mol}^{-1})$	9.411	141.17×10^3

ZnO = 50mg/70ml; T = 30 °C; [PMS] = [PDS] = 1
 $\times 10^{-3} \text{ mol dm}^{-3}$

3.2.3 Effect of catalyst amount

Experiments carried out with various amount of catalyst powders (20 – 100 mg) at constant [catechol] ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) and at constant concentration of oxidant ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) showed similar results for ZnO-PMS-Catechol and ZnO-PDS-Catechol systems (Fig.5 and 6). The rate increases initially with an increases in the catalyst amount and reaches a maximum and then gets decreased. This due to the fact that with increasing catalyst amount, absorption of light by photocatalyst particles also increases. Hence, the rate of degradation of catechol also increases. After a certain limit, there is a decrease in rate observed. This is due to the scattering of light by the catalyst particles, which is responsible for the reduction in the rate.

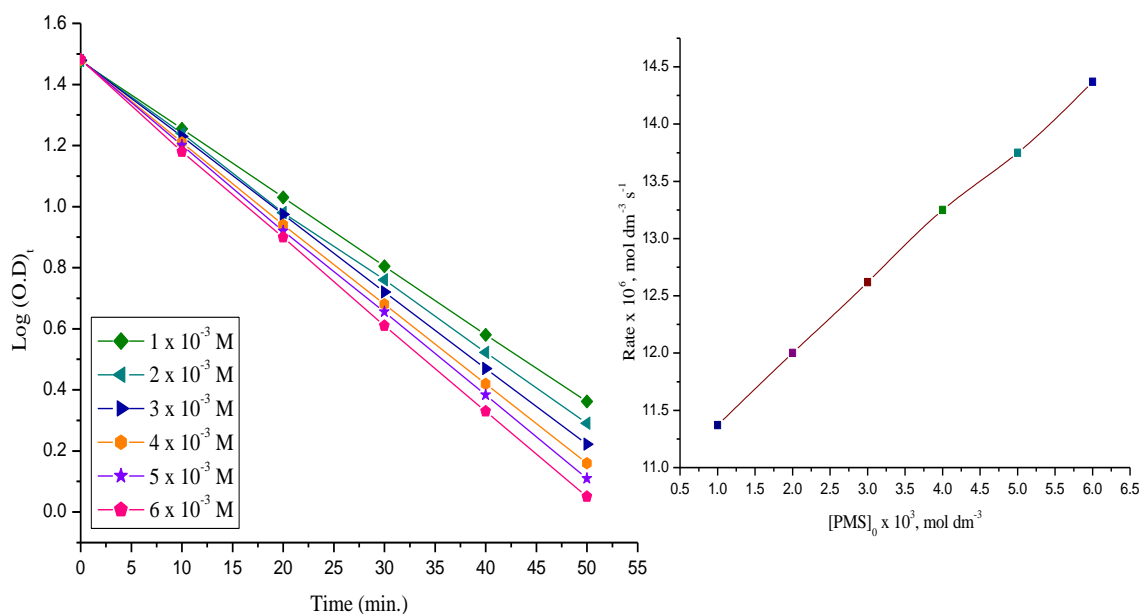


Fig.4 Log (O.D)_t vs time plot for the photodegradation of catechol for various concentrations of PMS (1.0 – 6.0 x 10⁻³M). [Catalyst] = 50 mg/70 ml and [Catechol] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of catechol for various concentrations of PMS.

3.2.4 PMS an effective oxidant for the photocatalytic degradation of catechol

A comparison of the efficiency of the oxidants (PMS and PDS) for the Photocatalyzed degradation of catechol ($1 \times 10^{-3} \text{ mol dm}^{-3}$) was obtained by comparing the results of the experiments carried out under identical conditions but with different oxidants (PMS and PDS, $[\text{Oxidant}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$). Pure ZnO without any oxidants shows 15 % degradation of catechol in 50 min, which is

enhanced to 24 % in the presence of PDS. PMS have similar activity and they enhance the decomposition of catechol up to 95 % and under the same illumination time (Table 3). An enhanced efficiency of PMS over PDS can be rationalized since PMS gets decomposed through e_{CB}^- and h_{VB}^+ of the semiconductor photocatalysts whereas PDS can be decomposed only by e_{CB}^- [P. Maruthamuthu *et al* 1977, J. Madhavan *et al* 2006] and the key reactions are represented below.

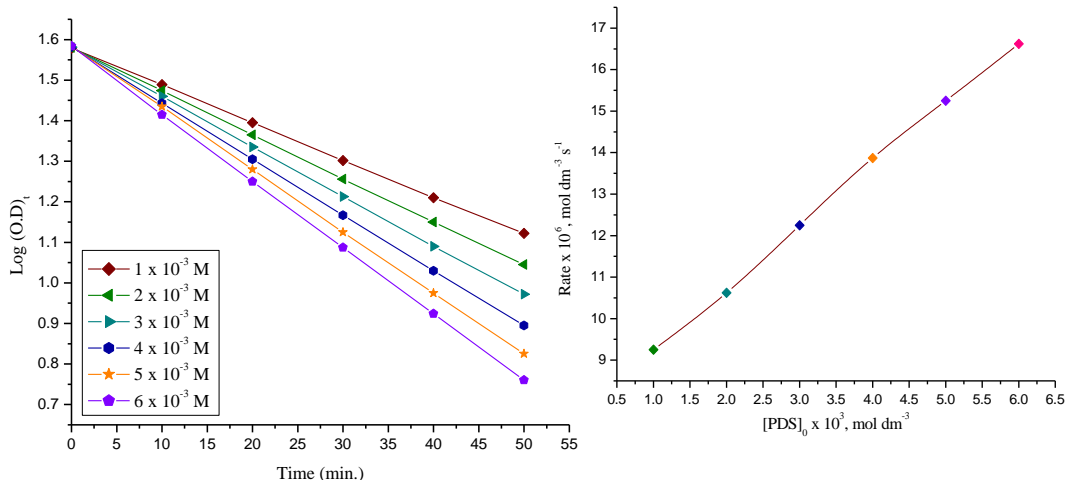


Fig.5 Log (O.D)t vs time plot for the photodegradation of catechol for various concentration of PDS ($1.0 - 6.0 \times 10^{-3} \text{ M}$). $[\text{Catalyzed}] = 50 \text{ mg}/70\text{ml}$ and $[\text{catechol}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset shows plot of photodegradation rate of catechol for various concentrations of PDS.

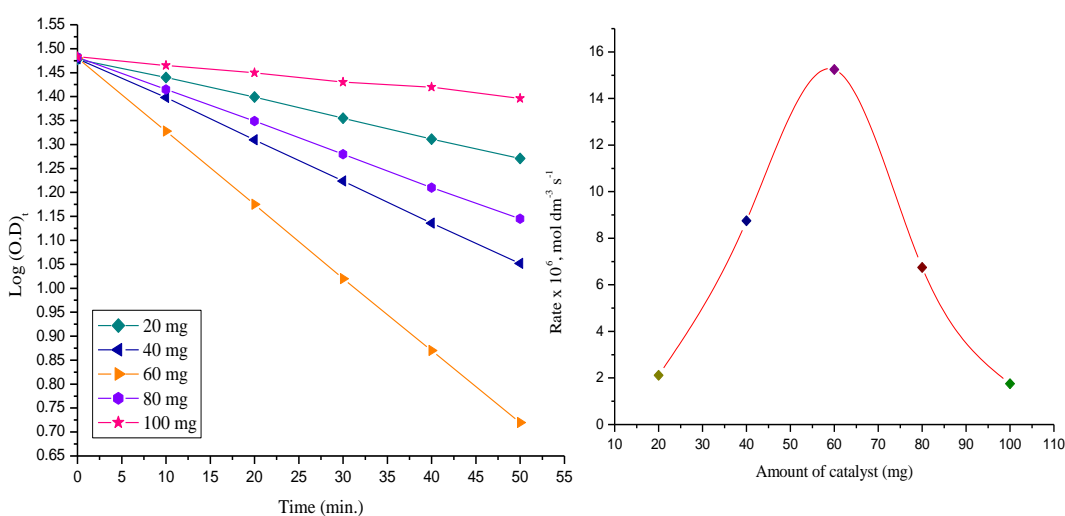


Fig.6 Log (O.D)t vs time plot for the photodegradation of catechol for various concentrations of ZnO (20 - 100 mg). $[\text{PMS}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{catechol}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset shows plot of photodegradation rate of catechol for various concentrations of ZnO.

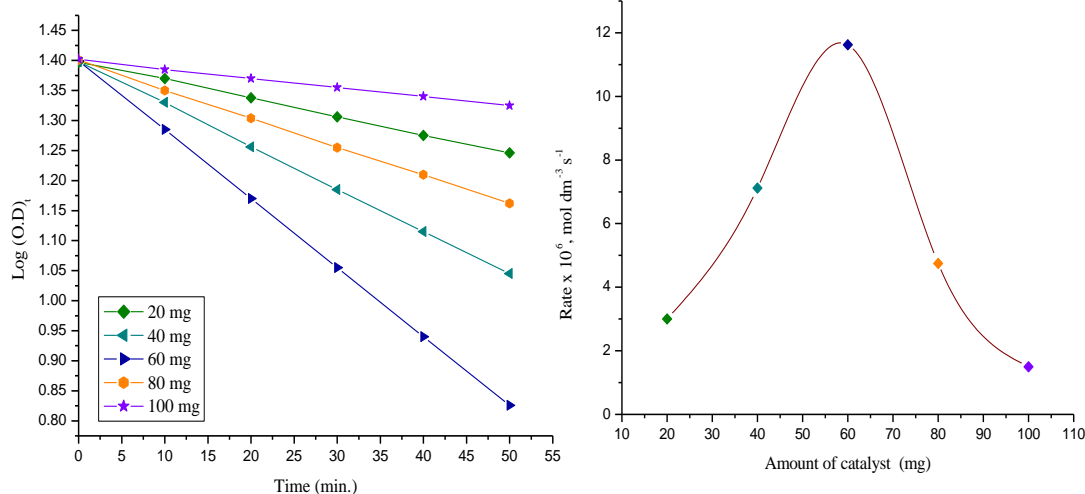


Fig.7 Log (O.D)_i vs time plot for the photodegradation of catechol for various concentration of ZnO (20-100mg). [PDS] = 1 × 10⁻³ mol dm⁻³ and [catechol] = 1 × 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of catechol for various concentration of ZnO.

Table 3: Comparison of photocatalytic efficiencies of PMS, PDS on photocatalytic decomposition of catechol

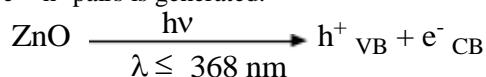
System	k ₁ × 10 ³ s ⁻¹
ZnO-Catechol	5.62
ZnO-PDS-Catechol	9.12
ZnO-PMS-Catechol	11.75

With PDS:



3.2.5 Mechanism

When photons of band gap energy (greater than 3.2 eV) fall on ZnO semiconductor particles, an e⁻ - h⁺ pairs is generated.



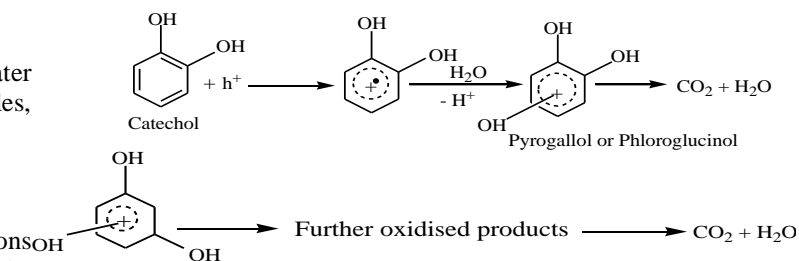
In a oxygenated solution, the following reactions occur: The atmospheric oxygen present in the solution can react with e⁻_{CB} and prevent the recombination of electron-hole pairs [I. Izumi *et al* 1980, M. Fujihira *et al* 1982, I. Izumi *et al* 1984, R.W. Mathews, 1984, J.M. Herrmann *et al* 1980]



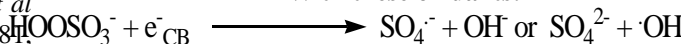
On the other hand, holes react with either H₂O or OH⁻ adsorbed on TiO₂ surface to give hydroxyl radicals.



Hydroxyl radical attacks dihydric phenol catechol molecules to form the trihydroxyl products Pyrogallol (PG) and Phloroglucinol (PG) as follows: Under prolonged irradiation, Pyrogallol and Phloroglucinol may further degrade finally to CO₂ and H₂O [K. Hashimoto *et al* 1984].



With these oxidants:



These radicals enhance the oxidation of resorcinol and hence the rates of disappearance of resorcinol in the presence of these oxidants are more (Table 3) than those in the absence of them.

4. Conclusions

The present study establishes several basic features concerning the performance of photocatalytic degradation of catechol in the presence of oxidants under visible light irradiation. The influence of fundamental parameters such as catalyst amount, concentration of substrate and concentration of oxidants is now established, opening up the way for further development of these systems. A rapid photodegradation rate was observed with PMS as oxidant indicating that PMS is a more efficient oxidant than PDS for the photocatalyzed degradation of catechol.

Acknowledgement

The authors wish to thank the Principal for providing the infrastructural facilities in the Department of Chemistry, Government Arts College, Ariyalur, Tamil Nadu and India.

References:

- [1] R. Nagarathnamma, P. Bajpai, PK. Bajpai., Studies on decolourization, degradation and detoxification of chlorinated lignin compounds in kraft bleaching effluents by ceriporiopsis subvermispora, *Process Biochemistry*, 34(1999)939-948.
- [2] Jian Chen, Wim H.Rulkens, Harry Bruning., Photochemical elimination of phenols and cod in industrial wastewaters., *Water Science and Technology*, 35(4)(1997)231-238.
- [3] R.P. Schwarzenbach, P.M. Gschwend & D.M. Imboden, *Environmental Organic Chemistry* (Wiley, New York), 1996.
- [4] P. Pitter & P. Chudoba, *Biodegradability of Organic Substances in the Aquatic Environment* (CRC Press, Boca Raton, FL), 1990.
- [5] R. Crompton, *Toxicants in the Aqueous Ecosystem* (Wiley, UK), 1997.
- [6] Guohua Chen, Lecheng Lei L & Po-lock Yue., Wet Oxidation of High-Concentration Reactive Dyes, *Ind Eng Chem Res*, 38(5) (1999) 1837-1843.
- [7] Philip H. Howard, *Handbook of Environmental Degradation Rates* (Lewis Publishers, MI), 1991. S. Manahan, *Environmental Science and Technological Connection* (CRC Press, Boca Raton, FL), 1994.
- [8] R.W. Martin., Reaction of dimethylol urea with phenol, *The journal of organic chemistry*, (1952) 17(3): 342-343.
- [9] K.B. Dhanalakshmi, S. Anandan, J. Madhavan, P. Maruthamuthu., Photocatalytic degradation of phenol over TiO₂ powder: The influence of peroxomonosulphate and peroxodisulphate on the reaction rate, *Solar Energy Material and Solar cells* 92, 457-463(2008).
- [10] P. Maruthamuthu, P. Neta, *J. Phys. Chem.* (81) 936(1977).
- [11] J. Madhavan, B. Muthuraman, S. Murugesan, S. Anandan, P. Maruthamuthu., *Sol. Cells*, (2006) (90): 1875.
- [12] Izumi, W.W. Dunn, K.O. Wilbourn, Fran F.-R.F, A.J. Bard., The Heterogeneous Photocatalytic Oxidation of Hydrocarbons on Platinized TiO₂ Powders., *J. Phys. Chem.* (1980) 84:3207.
- [13] M. Fujihira, Y. Satoh, T. Osa., Heterogeneous Photocatalytic Reactions on Semiconductor Materials. III. Effect of pH and Cu²⁺ Ions on the Photo-Fenton Type Reaction., *Bull. Chem. Soc. Japan*, (1982) 55(3): 666-671.
- [14] Izumi, F.F. Fan, A.J. Bard., Heterogeneous photocatalytic decomposition of benzoic acid and adipic acid on platinized titanium dioxide powder. The photo-Kolbe decarboxylative route to the breakdown of the benzene ring and to the production of butane, *J. Phys. Chem.* (1981) 85(3): 218-223.
- [15] R.W. Mathews., Hydroxylation reactions induced by near-ultraviolet photolysis of aqueous titanium dioxide suspensions., *J. Chem. Soc. Faraday Trans. 1*, (1984) (80): 457-471.
- [16] J.M. Herrmann, P. Pichat., Heterogeneous photocatalysis. Oxidation of halide ions by oxygen in ultraviolet irradiated aqueous suspension of titanium dioxide., *J. Chem. Soc. Faraday Trans. 1*, (1980) (76): 1138-1146.
- [17] K. Hashimoto, T. Kawai and T. Sakata., Photocatalytic reactions of hydrocarbons and fossil fuels with water. Hydrogen production and oxidation., *J. Phys. Chem.*, (1984) 88(18): 4083-4088.