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THE INFLUENCE OF PMS AND PDS OXIDANTS ON REACTION RATE OF PHOTOCATALYTIC DEGRADATION OF RESORCINOL OVER TiO₂POWDER

S. Manikandan[1*], K.B. Dhanalakshmi[2]

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

2. Department of Chemistry, Arignar Anna Government Arts College, Musiri, Tamil Nadu, India.

ABSTRACT: Advanced oxidation processes (AOPs) have been developed as an emerging technology for treating dangerous organics in wastewater and groundwater. In the present study, the effect of oxidants peroxomonosulphate (PMS) and peroxodisulphate (PDS) on the photocatalytic oxidation of resorcinol on illuminated TiO₂ surfaces has been investigated. The efficiencies of these oxidants on photocatalytic degradation of resorcinol are compared with that of peroxomonosulphate and peroxodisulphate. The experimental results designate that these oxidants exhibited enhanced rates of mineralization of resorcinol. A reaction mechanism, involving the production of both hydroxyl radicals and sulphate radicals, was proposed.

KEYWORDS: Photodegradation, resorcinol, PMS and PDS, TiO₂ photocatalyst.

Corresponding Author: Dr. S. Manikandan* Ph.D.

Department of Chemistry, Government Arts College, Ariyalur, Tamil Nadu, India.

Email Address:ssmanik23@gmail.com

1. INTRODUCTION

The discharges of phenolic compounds similar to resorcinol into the atmosphere are from a quantity of anthropogenic sources, including production, processing and shopper uses, in particular from hair dyes and pharmaceuticals. Resorcinol from these sources may result in prevalent contamination of the aquatic ecosystem due to their hazardous and carcinogenic properties [1, 2, 3]. Heterogeneous semiconductor photocatalysis is currently individual considered as a promising technique for water as the substrates and peroxomonosulphate (PMS) and peroxodisulphate (PDS) have been chosen as oxidants. Purification in relationship to other conservative methods [4, 5].This is based on the production of highly immediate hydroxyl radicals by semiconductor materials under UV and visible

light irradiation and utilized to degrade organic compound into carbon dioxide and water[6, 7, 8, 9, 10].The broad application of phenolic compounds in many branches of industries, in the production of disinfectants [11], herbicides and pesticides [12], paints, resins, wood preservatives [13, 14, 15, 16, 17], tooth fillers [12,18] paper and textiles [19,20] is the reason for their rising concentration in water. The hazardous wastewater contains high concentration of phenolic compounds, which must be prevented from entering into the environment [21].Here the nearby learn, the result of oxidant, PMS and PDS on the photocatalytic degradation of resorcinol on illuminate TiO_2 surface have been investigate. The photodegradation rate of resorcinol in the existence of these oxidants was originated to be more than in the absence of all of these oxidants. The additional oxidant enhances the resorcinol, oxidation rate fundamentally. Enhancement of rate of photocatalytic degradation of pollutants on TiO_2 photocatalyst by the addition of oxidants is known as Advanced Oxidation Process (AOP). Pollutants resorcinol has been chosen

2. MATERIALS AND METHODS

TiO_2 (E. Merck, Germany) semiconductor grade (specific surface area ˷ 55 m^2 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. Resorcinol (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 (expect 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 150W 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 resorcinol was performed by a standard colorimetric method [22, 23]. The photodegradation of resorcinol was also confirmed by HPLC analyses Fig.1.
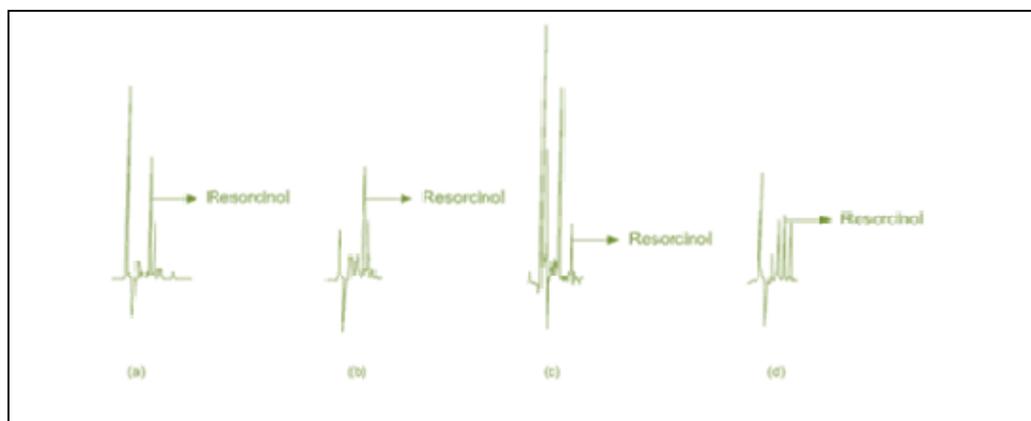
Fig 1: HPLC Analysis of Resorcinol

(a) 10^{-3} M Resorcinol + TiO_2 (Before Irradiation), (b) 10^{-3} M Resorcinol + TiO_2 (After Irradiation)

(c) 10^{-3} M Resorcinol + TiO_2 + PMS (After Irradiation), (d) 10^{-3} M Resorcinol + TiO_2+ PDS (After Irradiation)

3. RESULTS AND DISCUSSION

3.1 Photocatalytic degradation of resorcinol

Photodegradation of resorcinol (1×10^{-3}) in aqueous solutions at natural pH was performed in the presence of TiO_2 photocatalyst (50 mg). Photocatalyzed disappearance of resorcinol before and after irradiation and as well as with or without oxidants (PMS and PDS). Were confirmed by colorimetric method. Hydroxy resorcinol was the detectable products but they occurred only in low yields. The photodegradation rate of resorcinol 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 resorcinol oxidation rate drastically. In order to find the effect of these oxidants on the rate of decomposition of resorcinol, experiments were carried out at constant concentration of resorcinol (1×10^{-3} mol dm^{-3}), constant catalyst amount ($TiO_2 = 50$ mg) and at constant pH (3.0 and 4.0) with various oxidants (PMS and PDS) by colorimetric method.

3.2 Factors influencing photocatalytic oxidation of resorcinol

3.2.1 Effect of initial concentration of resorcinol

Experiments were carried out with various initial concentrations of resorcinol ($1.0 – 6.0 \times 10^{-3}$ mol dm$^{-3)}$ at constant catalyst amount (50 mg) and constant concentration of the oxidant ([PMS] or [PDS] $= 1 \times 10^{-3}$ mol dm^{-3}). The pH of the solution was maintained constant. The decrease in [resorcinol] with time was followed by standard colorimetric method. The results obtained for TiO_2-PMS-Resorcinol and for TiO_2-PDS-Resorcinol systems are presented in Table 1. The plots of Log $(OD)_t$ vs time for various initial concentrations of resorcinol are linear and from the slopes of the plots, the rate constants were calculated and tabulated (Table 1 and Figs.2 and 3). The plots of rate vs [resorcinol]$_0$(Table 1; inset of Figs. 2 and 3) show that resorcinol degradation increases with increase in [resorcinol]$_0$, reaches a maximum and remains almost constant. The effect of [resorcinol]$_0$ on rate could be described by the following relation:

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

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

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

Table 1: Rate constants for the photodegradation of various amounts of resorcinol 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}
1.0	7.50	6.00
2.0	5.00	3.87

3.0	4.12	3.12
4.0	3.62	2.75
5.0	3.25	2.37
6.0	2.75	2.00

$TiO_2 = 50$ mg/70ml; $T = 30^oC$; [PMS] = [PDS] = 1×10^{-3} mol dm^{-3}
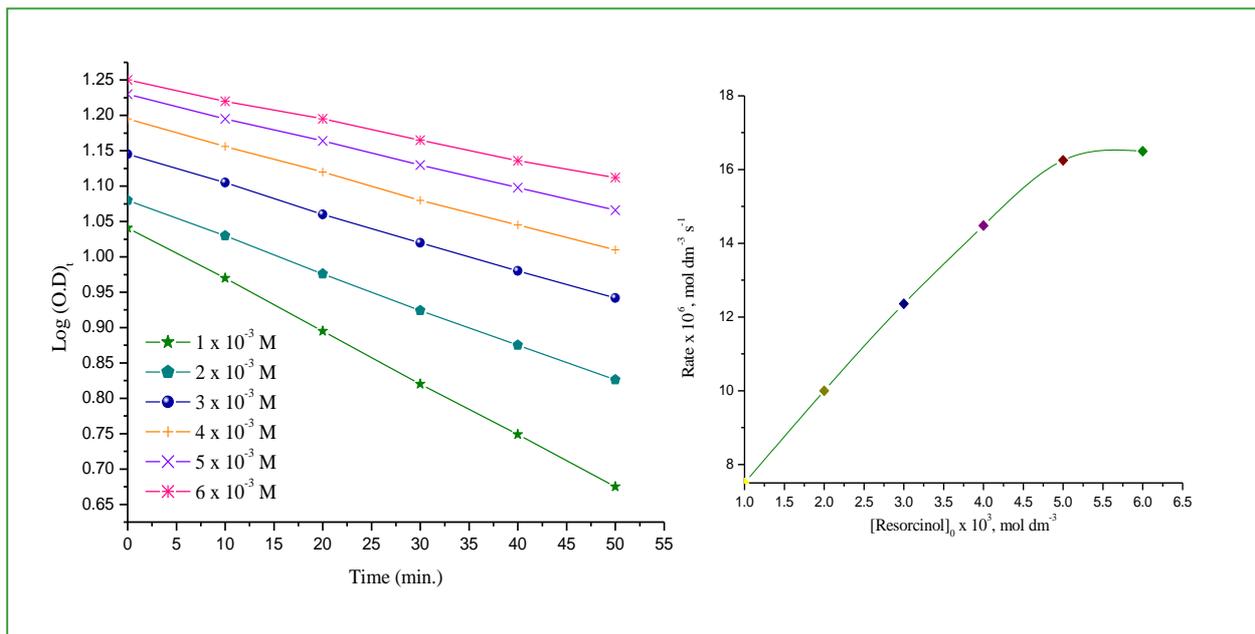
Fig 2: Log (OD)$_t$ vs time plot for the photodegradation of various amount of resorcinol (1- 6 x 10^{-3}M). [Catalyst] = 50 mg/70 ml and [PMS] = 1 x 10^{-3}mol dm^{-3}. Inset shows plot of photodegradation rate for various amounts of resorcinol.
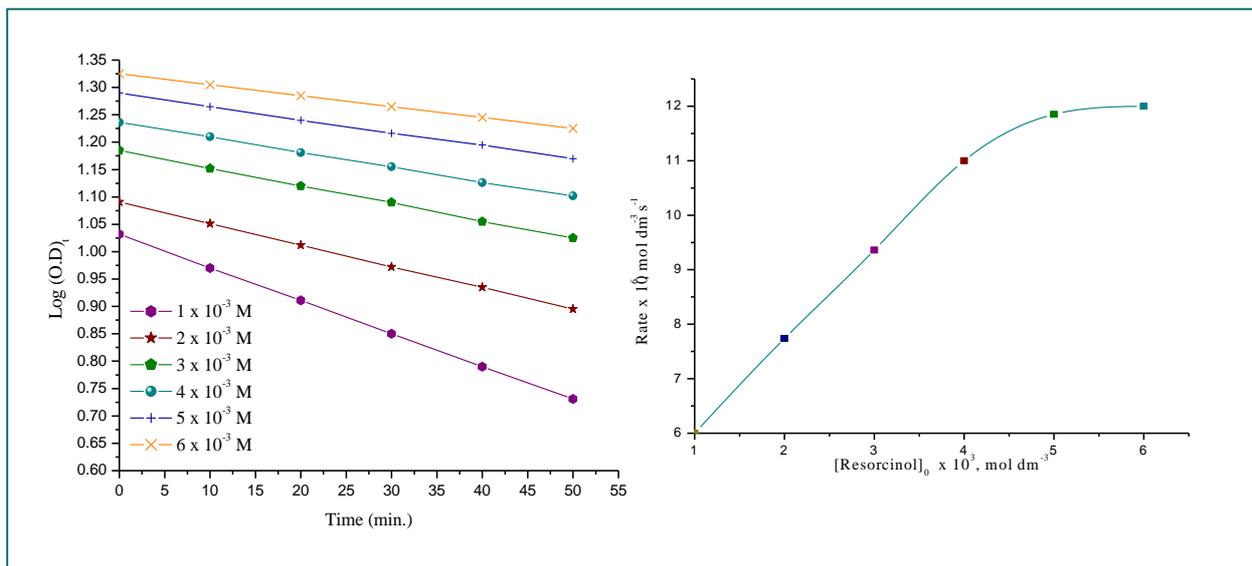
Fig 3: Log (OD)t vs time plot for the photodegradation of various amounts of resorcinol (1 - 6 x 10^{-3}M). [Catalyst] = 50 mg/ 70 ml and [PDS] = 1 x 10^{-3}mol dm^{-3}. Inset shows plot of photodegradation rate for various amounts of resorcinol.

The plots of 1/rate vs 1/ [resorcinol]$_0$ 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 TiO_2 -PMS-Resorcinol system the values of k and K are found tobe4.70 x 10^{-6} mol dm^{-3} s^{-1} and 80.705 dm^3 mol^{-1}, respectively. The values of k and K for TiO_2-PDS-Resorcinol system are 10.80 x 10^{-6}mol dm^{-3} s^{-1} and 284.37 x 10^3 dm^3 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 resorcinol (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 resorcinol degradation due to PMS addition is higher than that of PDS. The results obtained are presented in Figs. 4 and 5. From the plot of rate vs [oxidant], it is seen that the rate of decomposition of resorcinol increases linearly with increases in concentration of the oxidant.

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

TiO_2 = 50 mg/ 70 ml; T = 30 ^{0}C; [PMS] = [PDS] = 1 x 10^{-3}mol dm^{-3}

1/[resorcinol]$_0$ x 10^{-3} mol^{-1} dm^3	With PMS, 1/rate x 10^{-6} mol^{-1} dm^3 s	With PDS, 1/rate x 10^{-6} mol^{-1} dm^3 s
1.00	13.33	16.66
0.50	10.00	12.91
0.33	8.09	10.68
0.25	6.90	9.09
0.20	6.15	8.43
0.16	6.06	8.33
k = (mol dm^{-3}s^{-1})	4.70 x 10^{-6}	10.80 x 10^{-6}
K = (dm^{-3} mol^{-1})	80.705 x 10^3	284.37 x 10^3
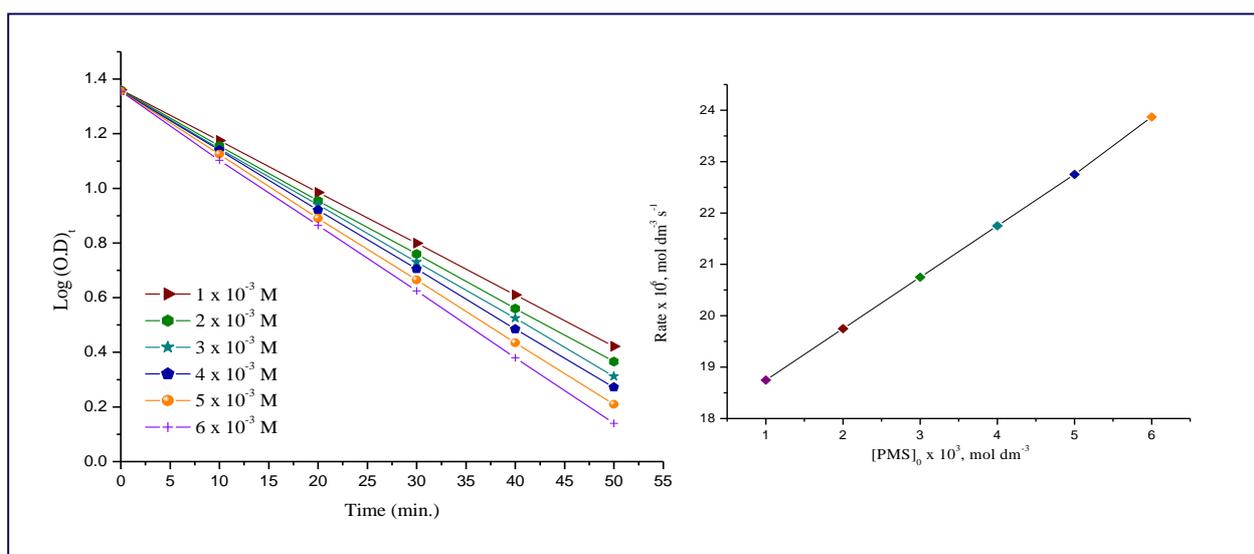
Fig 4: Log (O.D)$_t$ vs time plot for the photodegradation of resorcinol for various concentrations of PMS ($1.0 – 6.0$ x 10^{-3}M). [Catalyst] = 50 mg/70 ml and [resorcinol] = 1 x 10^{-3} mol dm^{-3}. Inset shows

plot of photodegradation rate of resorcinol for various concentrations of PMS.

3.2.3 Effect of catalyst amount

Experiments carried out with various amount of catalyst powders (20 – 100 mg) at constant [resorcinol] (1.0×10^{-3} mol dm^{-3}) and at constant concentration of oxidant 1.0×10^{-3} mol dm^{-3}) showed similar results for TiO$_2$-PMS-Resorcinol and TiO$_2$-PDS-Resorcinol systems (Fig.6 and 7). The rate increases initially with an increases in the catalyst amount and reaches a maximum and then gets decreased. This is due to the fact that with increasing catalyst amount, absorption of light by photocatalyst particles also increases. Hence, the rate of degradation of resorcinol 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.

3.2.4 PMS an effective oxidant for the photocatalytic degradation of resorcinol

A comparison of the efficiency of the oxidants (PMS and PDS for the Photocatalyzed degradation of resorcinol obtained by comparing the results of the experiments carried out under identical conditions but with different oxidants (PMS and PDS, [Oxidant] = 1×10^{-3} mol dm^{-3}). Pure TiO$_2$ without any oxidants shows 21% degradation of resorcinol in 50 min, which is enhanced to 33% in the presence of PDS. PMS have similar activity and they enhance the decomposition of resorcinol up to 99% 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}$ [24, 25] and the key reactions are represented below.

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

Fig 6: Log (O.D)t vs time plot for the photodegradation of resorcinol for various concentrations of TiO$_2$ (20-100 mg). [PMS] = 1 x 10^{-3}mol dm^{-3}and [resorcinol] = 1 x10^{-3}mol dm^{-3}. Inset shows plot of photodegradation rate of resorcinol for various concentrations of TiO$_2$.

Fig 7: Log (O.D)$_t$vs time plot for the photodegradation of resorcinol for various concentration of TiO$_2$ (20-100 mg). [PDS] = 1 x 10^{-3}mol dm^{-3} and [resorcinol] = 1 x 10^{-3}mol dm^{-3}. Inset shows plot of photodegradation rate of resorcinol for various concentration of TiO$_2$.

Table3: Comparison of photocatalytic efficiencies of PMS, PDS on photocatalytic decomposition of resorcinol

System	$k_1 \times 10^3 \ s^{-1}$
TiO_2-Resorcinol	5.62
TiO_2-PDS-Resorcinol	6.00
TiO_2-PMS-Resorcinol	7.50

When photons of energy ≥ band gap energy (3.2 eV) fall on TiO_2 semiconductor particles, $e^-\_h^+$ pair is generated:

$$TiO_2 \xrightarrow[\lambda > 390 \ nm]{h\nu} h^+{}_{VB} + e^-{}_{CB}$$

The atmospheric oxygen present in the solution can react with $e^-{}_{CB}$ and prevent the recombination of electron– hole pairs [26, 27, 28, 29, 30]:

$$O_2 \ (ad.) + e^-{}_{CB} \longrightarrow O_2{}^{\cdot -} \ (superoxide \ ion)$$

Hydroxyl radical attacks dihydric phenol resorcinol to form trihydroxy product namely phloroglucinolas follows [31]. Phloroglucinol is further degraded into carbon dioxide and water.

Resorcinol   Phloroglucinol or Pyrogallol $CO_2 + H_2O$

With these oxidants

The addition of $HOOSO_3{}^-$ and $S_2O_8{}^{2-}$ to the reaction system will generate $\cdot OH$ and $SO_4{}^{\cdot -}$ by the reaction of $e^-{}_{CB}$ with these oxidants,

$$HOOSO_3{}^- + e^-{}_{CB} \longrightarrow SO_4{}^{\cdot -} + OH^- \ or \ SO_4{}^{2-} + \cdot OH$$

$$S_2O_8{}^{2-} + e^-{}_{CB} \longrightarrow SO_4{}^{2-} + SO_4{}^{\cdot -}$$
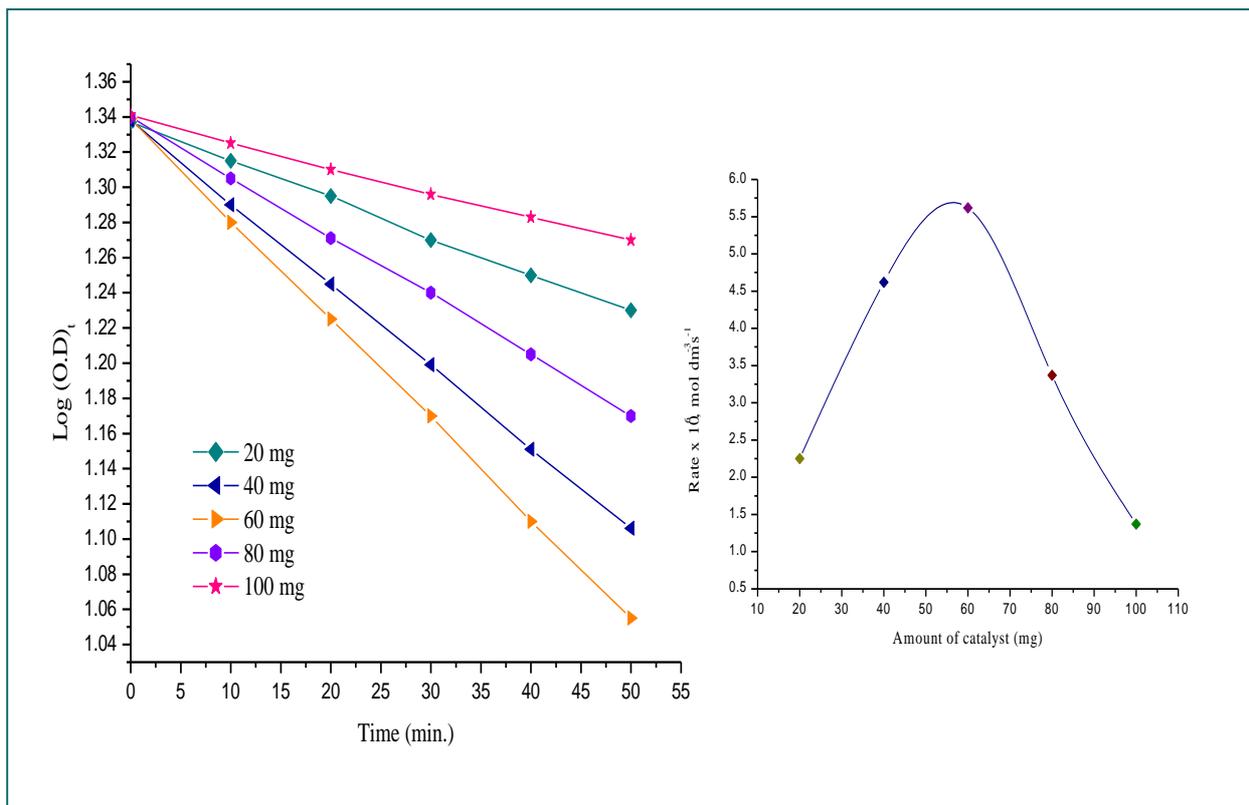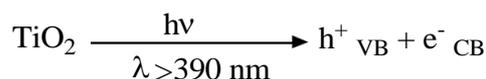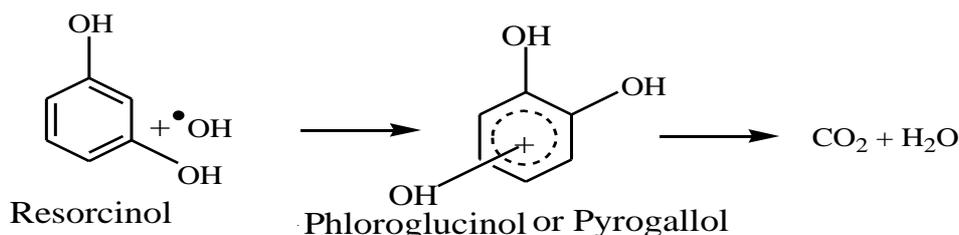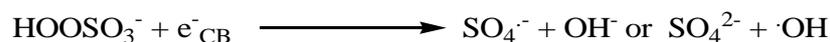
These radicals enhance the oxidation of resorcinol and hence the rates of disappearance of resorcinol in presence of these oxidants are more (Table.3) than those in the absence of them.

4. CONCLUSION

The presence study establishes several basic features concerning the performance of photocatalytic degradation of resorcinol 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 rates were observed with PMS as oxidant indicating that PMS is a more efficient oxidant than PDS for the Photocatalyzed degradation of resorcinol.

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CONFLICT OF INTEREST

No conflict of interest.

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