

# Photocatalytic degradation of *o*-cresol over $\text{TiO}_2$ powder the influence of pms and pds on the reaction rate

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## Abstract

In this study, the photocatalytic degradation of *o*-cresol in hazardous organics in wastewater and ground water using ultra violet (UV) irradiation,  $\text{TiO}_2$  as photocatalyst the effect of oxidants peroxomonosulphate [PMS] and peroxodisulphate [PDS] on the photocatalytic oxidation of *o*-cresol on illumination  $\text{TiO}_2$  surfaces has been investigated. The efficiencies of these oxidants on photocatalytic degradation of *o*-cresol are compared with that of PMS and PDS. The experimental results indicate that these oxidants exhibited enhanced rates of mineralization of *o*-cresol. A reaction mechanism, involving the generation of both hydroxyl radicals and sulphate radicals, was proposed.

**Keywords:** Photodegradation, *o*-cresol, PMS and PDS,  $\text{TiO}_2$  photocatalyst.

## 1. Introduction:

Currently,  $\text{TiO}_2$  semiconductor photocatalysis has become increasingly promising technique in environment remediation, due to its optical and electronic properties, low cost, ease of availability, high stability and non-toxicity [H.W. Chen *et al* 2007, C.M. Gomez *et al* 2012]. Phenolic compounds such as *o*-cresol are widely used in manufacturing products, for examples, herbicides, pharmaceuticals and cresol-based resin [N. Shivaraman *et al* 2000]. *o*-Cresol have been planned as one of the main concern pollutants in the USA-EPA list [M. Callahn *et al* 1979]. The water solubility of *o*-cresol is above 24 at 25°C [E. Copper, 1912]. Therefore, in the system of pollution abatement, the effective elimination of

this organic multifarious becomes an essential condition.

Photocatalytic degradation of different toxic organic compounds is an attractive technique for the complete destruction of undesirable contaminants in liquid phase by using reproduction light [H.Q.Zhan *et al* 1998]. On the other hand, the use of UV/vis radiation, alone or in combination with different auxiliary oxidizing agents is the basis of advanced oxidation processes (AOPs) [T. Oppeni Abdollahi, 2003]. Therefore, photocatalytic reaction provides another interesting route to the environmental degradation of many organic pollutants. Since phenolic compounds in *o*-cresol is a major industrial pollutant. Many conventional methods have been proposed to treat solutions containing *o*-cresol [Yadollah Abdollahi, 2011, Yadollah Abdollahi *et al* 2011]. Money authors [Yadollah Abdollahi *et al* 2011, K.B. Dhanalakshmi *et al* 2008, Anh-Thu Nguyen *et al* 2014] have studied the heterogeneous photocatalytic decomposition of *o*-cresol over  $\text{TiO}_2$  powder. With the above information in hand, we decided to undertake a study aiming to clarify different aspects of the mechanisms of direct visible light photodegradation and of  $\text{TiO}_2$  photocatalytic degradation of *o*-cresol in aqueous solution, to give a better understanding of AOPs. So, the focus of our investigation to apply peroxomonosulphate (PMS) and peroxodisulphate (PDS) as oxidants, thereby to enhance the photocatalytic degradation rate of *o*-cresol on illuminated  $\text{TiO}_2$  powder under visible light and compare the efficiencies of these oxidants.

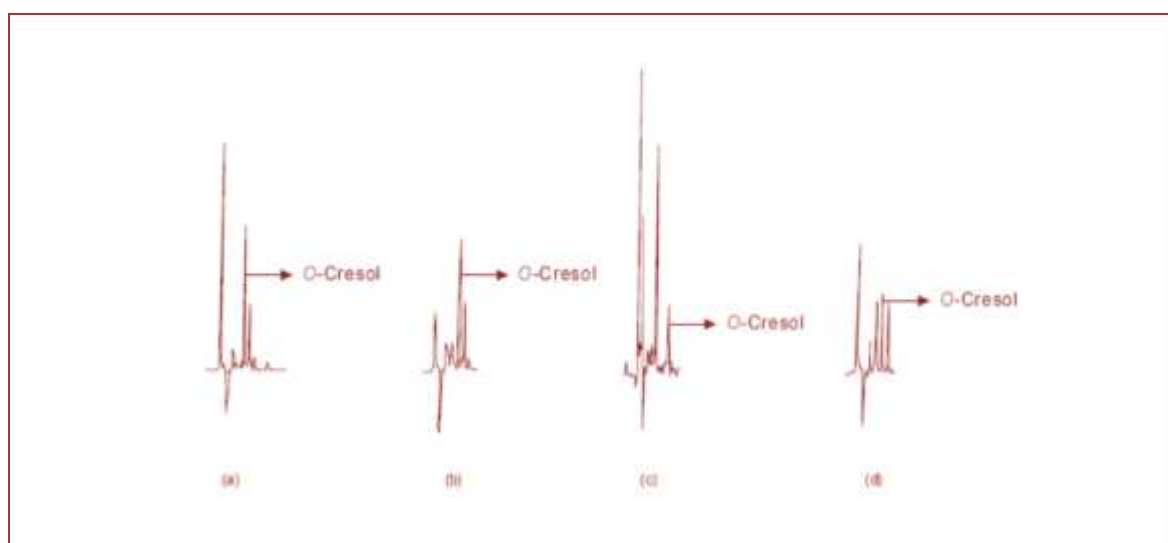
## 2. Experimental methods:

$\text{TiO}_2$  (E. Merck, Germany) semiconductor grade (specific surface area  $55 \text{ m}^2 \text{ g}^{-1}$ ) 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. *o*-Cresol (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 (*o*-cresol) 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 *o*-cresol was performed by a standard colorimetric method [R.W. Martin, 1963, K.B. Dhanalakshmi *et al* 2008]. The photodegradation of *o*-cresol was also confirmed by HPLC analyses Fig.1.



(a)  $10^{-3}$  M *o*-Cresol + TiO<sub>2</sub> (Before Irradiation)

(b)  $10^{-3}$  M *o*-Cresol + TiO<sub>2</sub> (After Irradiation)

(c)  $10^{-3}$  M *o*-Cresol + TiO<sub>2</sub> + PMS (After Irradiation)

(d)  $10^{-3}$  M *o*-Cresol + TiO<sub>2</sub>+ PDS (After Irradiation)

**Fig.1 HPLC Analysis of *o*-Cresol**

### 3. Results and discussion:

#### 3.1 Photocatalytic degradation of *o*-cresol

Photodegradation of *o*-cresol ( $1 \times 10^{-3}$ ) in aqueous solutions at natural pH was performed in the presence of TiO<sub>2</sub> photocatalyst (50 mg). Photocatalyzed disappearance of *o*-cresol before and after irradiation and as well as with or without oxidants (PMS and PDS). Were confirmed by colorimetric method. Hydroxy *o*-cresol were the detectable products but they occurred only in low yields. The photodegradation rate of *o*-cresol 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 *o*-cresol oxidation rate drastically. In order to find the effect of these oxidants on the rate of decomposition of *o*-cresol, experiments were carried out at constant concentration of *o*-cresol ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>), constant catalyst amount (TiO<sub>2</sub> = 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 *o*-cresol

#### 3.2.1 Effect of initial concentration of *o*-cresol

Experiments were carried out with various initial concentrations of *o*-cresol (1.0 – 6.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>) at constant catalyst amount (50 mg) and constant concentration of the oxidant ([PMS] or [PDS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>). The pH of the solution was maintained constant. The decrease in [o-cresol] with time was followed by standard colorimetric method. The results obtained for TiO<sub>2</sub>-PMS-*o*-Cresol and for TiO<sub>2</sub>-PDS-*o*-Cresol systems are presented in Table 1. The plots of Log (OD)<sub>t</sub> vs time for various initial concentrations of *o*-cresol

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 [o-cresol]<sub>0</sub> (Table 1; inset of Figs. 2 and 3) show that *o*-cresol degradation increases with increase in [o-cresol]<sub>0</sub>, reaches a maximum and remains almost constant. The effect of [o-cresol]<sub>0</sub> on rate could be described by the following relation:

$$\text{rate} = \frac{kK [o\text{-Cresol}]_0}{1 + K [o\text{-Cresol}]_0}$$

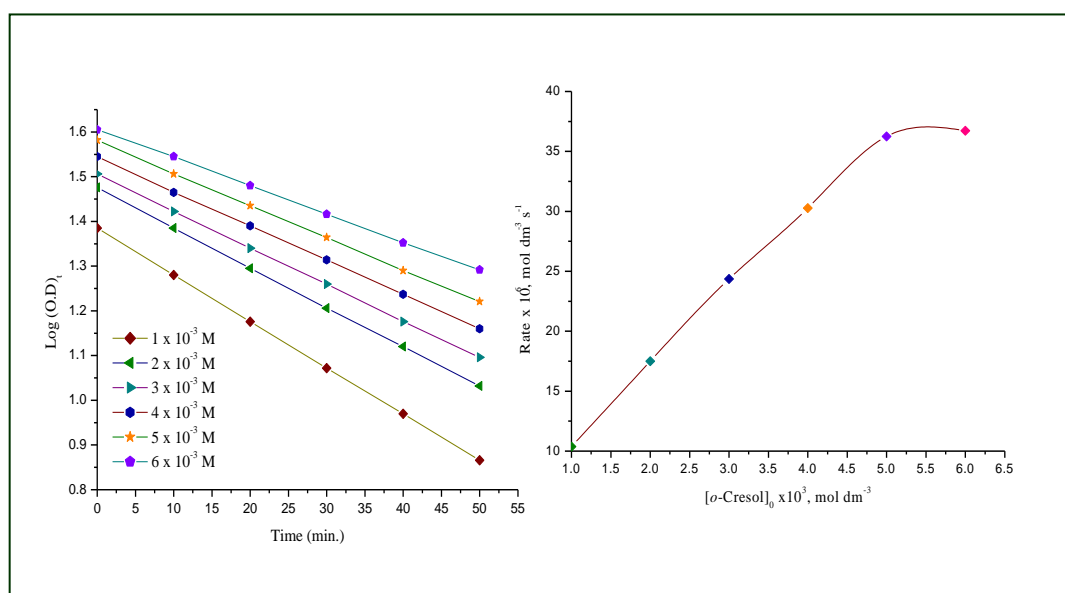
Where k and K are the proportionality and equilibrium constants, respectively. The reciprocal of the above equation gives

$$\frac{1}{\text{rate}} = \frac{1}{kK [o\text{-Cresol}]_0} + \frac{1}{k}$$

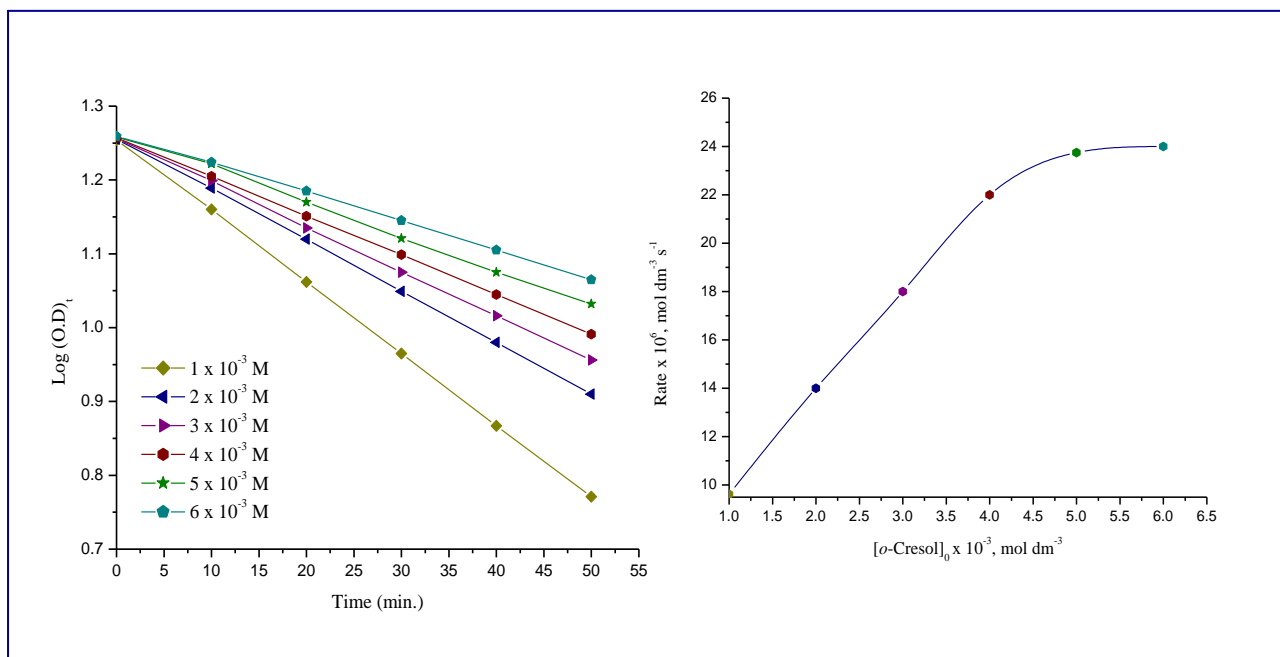
**Table .1:** Rate constants for the photodegradation of various amounts of *o*-cresol in the presence of PMS and PDS

[o-cresol] <sub>0</sub> x 10 <sup>3</sup> mol dm <sup>-3</sup>	With PMS, k <sub>1</sub> x 10 <sup>-3</sup> s <sup>-1</sup>	With PDS, k <sub>1</sub> x 10 <sup>-3</sup> s <sup>-1</sup>
1.0	10.37	9.62
2.0	8.75	7.00
3.0	8.12	6.00
4.0	7.75	5.50
5.0	7.25	4.75
6.0	6.12	4.00

TiO<sub>2</sub> = 50 mg/70ml; T = 30°C; [PMS] = [PDS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>.



**Fig.2** Log (OD)<sub>t</sub> vs time plot for the photodegradation of various amount of *o*-cresol (1- 6 x 10<sup>-3</sup>M). [Catalyst] = 50 mg/70 ml and [PMS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate for various amounts of *o*-cresol.



**Fig.3** Log (OD)t vs time plot for the photodegradation of various amounts of *o*-cresol (1 - 6 x 10<sup>-3</sup>M). [Catalyst] = 50 mg/ 70 ml and [PDS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate for various amounts of *o*-cresol.

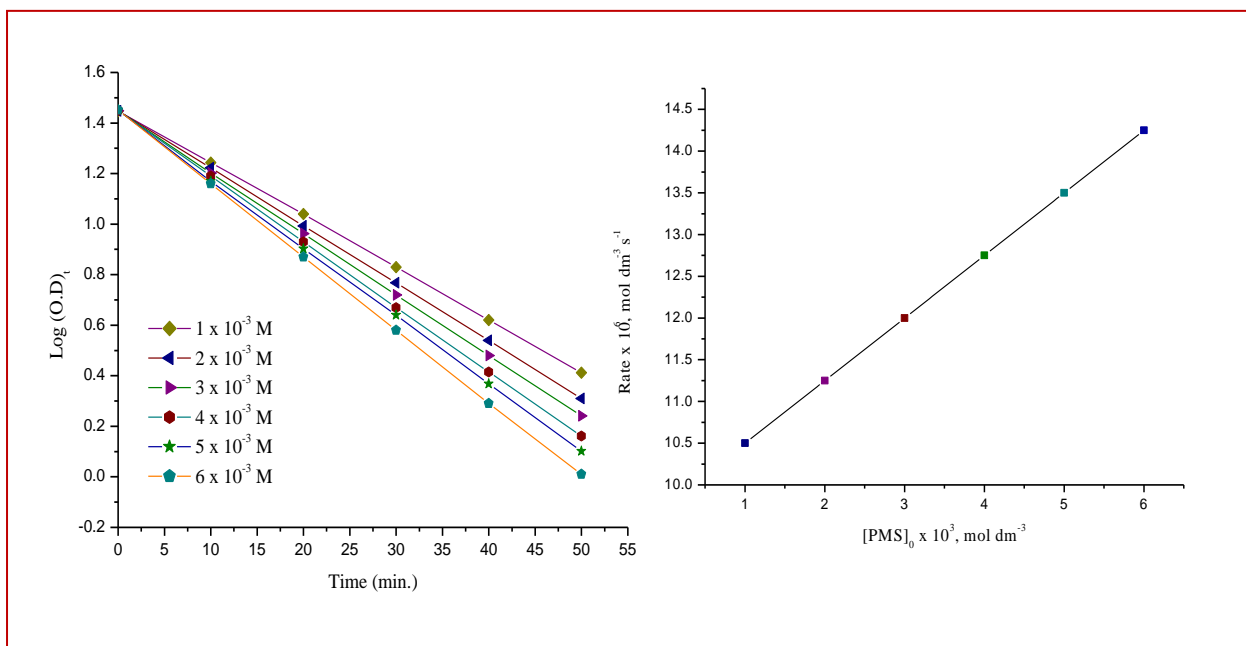
The plots of 1/rate vs 1/[*o*-cresol]<sub>0</sub> are straight lines with intercepts on the ordinate indicating Langmuir kinetics. The values the proportionality constant *k* and equilibrium constant *K* are evaluated (Table 2). For TiO<sub>2</sub> - PMS-*o*-Cresol system the values of *k* and *K* are found to be 3.50 x 10<sup>-6</sup> mol dm<sup>-3</sup> s<sup>-1</sup> and 155.68 dm<sup>3</sup> mol<sup>-1</sup>, respectively. The values of *k* and *K* for TiO<sub>2</sub>-PDS-*o*-Cresol system are 6.40 x 10<sup>-6</sup> mol dm<sup>-3</sup> s<sup>-1</sup> and 13.977 x 10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup>, 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<sup>-3</sup> mol dm<sup>-3</sup>) at a constant concentration of *o*-cresol (1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>) 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 *o*-cresol 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 *o*-cresol increases linearly with increases in concentration of the oxidant.

**Table. 2:** Evaluation of *k* and *K* for the photodegradation of various amounts of *o*-cresol TiO<sub>2</sub> = 50 mg/ 70 ml; T = 30 °C; [PMS] = [PDS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>

1/[ <i>o</i> -cresol] <sub>0</sub> x 10 <sup>-3</sup> mol <sup>-1</sup> dm <sup>3</sup>	With PMS, 1/rate x 10 <sup>-6</sup> mol <sup>-1</sup> dm <sup>3</sup> s	With PDS, 1/rate x 10 <sup>-6</sup> mol <sup>-1</sup> dm <sup>3</sup> s
1.00	9.64	10.39
0.50	5.71	7.14
0.33	4.10	5.55
0.25	3.30	4.54
0.20	2.75	4.21
0.16	2.72	4.16
<i>k</i> = (mol dm <sup>-3</sup> s <sup>-1</sup> )	3.50 x 10 <sup>-6</sup>	6.40 x 10 <sup>-6</sup>
<i>K</i> = (dm <sup>-3</sup> mol <sup>-1</sup> )	155.68	13.977 x 10 <sup>3</sup>



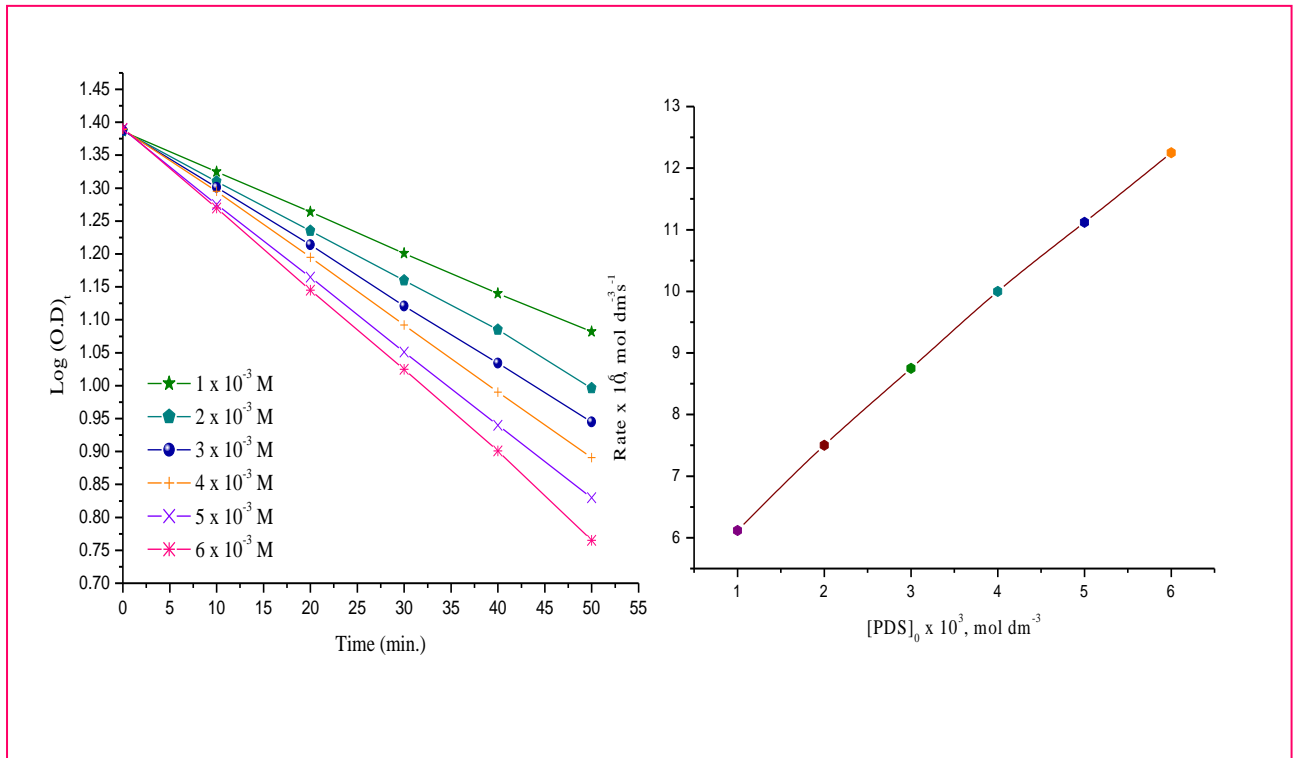
**Fig. 4.** Log (O.D)<sub>t</sub> vs time plot for the photodegradation of *o*-cresol for various concentrations of PMS (1.0 – 6.0 x 10<sup>-3</sup>M). [Catalyst] = 50 mg/70 ml and [*o*-cresol] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate of *o*-cresol for various concentrations of PMS.

### 3.2.3 Effect of catalyst amount

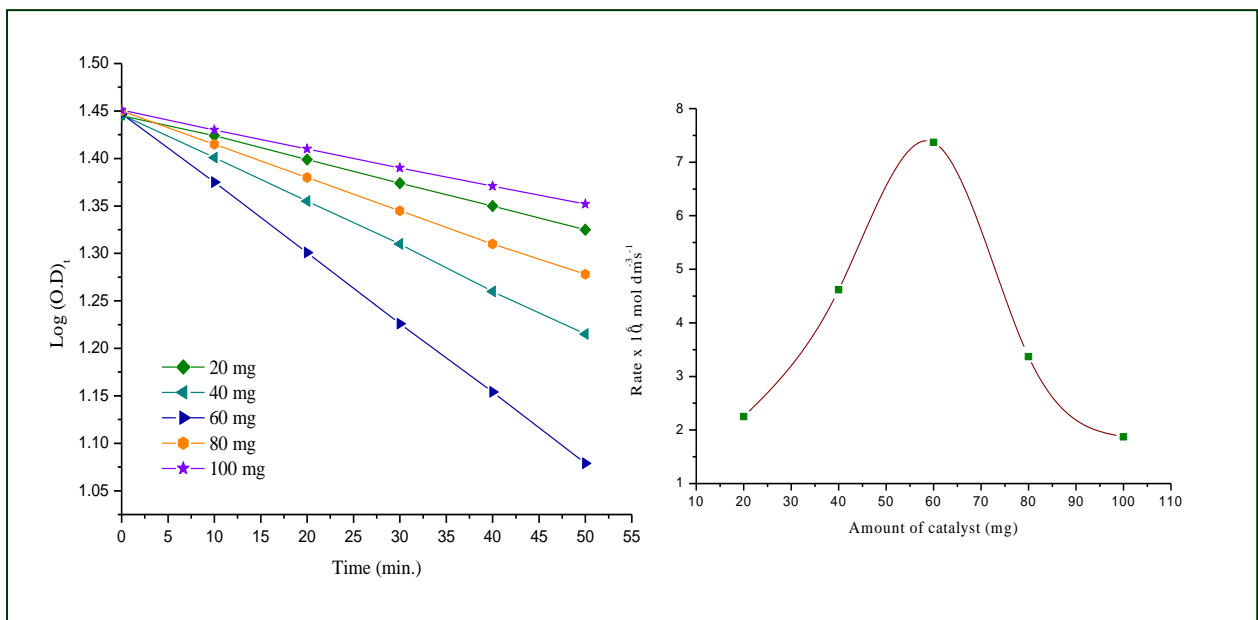
Experiments carried out with various amount of catalyst powders (20 – 100 mg) at constant [*o*-cresol] (1.0 x 10<sup>-3</sup>mol dm<sup>-3</sup>) and at constant concentration of oxidant 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> showed similar results for TiO<sub>2</sub>-PMS-*o*-Cresol and TiO<sub>2</sub>-PDS-*o*-Cresol 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 due to the fact that with increasing catalyst amount, absorption of light by photocatalyst particles also increases. Hence, the rate of degradation of *o*-cresol 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 *o*-cresol

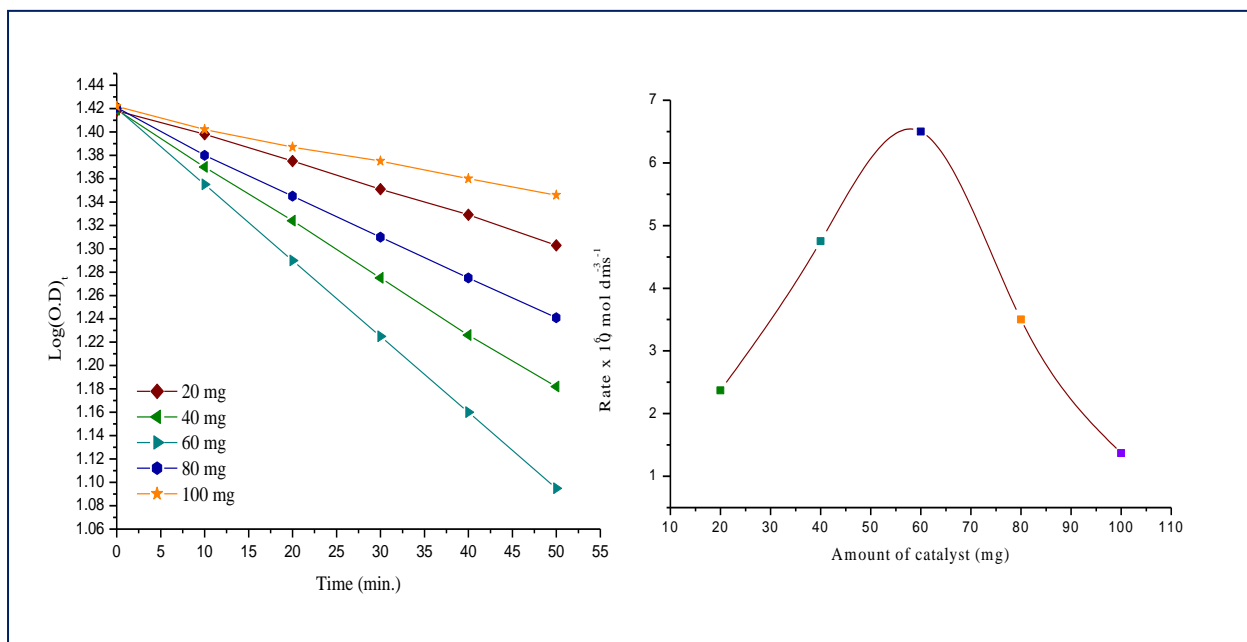
A comparison of the efficiency of the oxidants (PMS and PDS for the photocatalyzed degradation of *o*-cresol (1 x 10<sup>-3</sup> mol dm<sup>-3</sup>) was obtained by comparing the results of the experiments carried out under identical conditions but with different oxidants (PMS and PDS, [Oxidant] = 1 x10<sup>-3</sup> mol dm<sup>-3</sup>). Pure TiO<sub>2</sub> without any oxidants shows 21% degradation of *o*-cresol in 50 min, which is enhanced to 33% in the presence of PDS. PMS have similar activity and they enhance the decomposition of *o*-cresol 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<sup>-</sup><sub>CB</sub> and h<sup>+</sup><sub>VB</sub> of the semiconductor photocatalysts whereas PDS can be decomposed only by e<sup>-</sup><sub>CB</sub> [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 *o*-cresol for various concentration of PDS ( $1.0 - 6.0 \times 10^{-3}$  M). [Catalyzed] = 50 mg/70ml and [*o*-cresol] =  $1 \times 10^{-3}$  mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate of *o*-cresol for various concentrations of PDS.



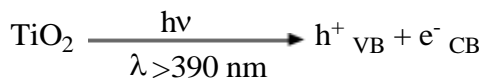
**Fig.6** Log (O.D)t vs time plot for the photodegradation of *o*-cresol for various concentrations of TiO<sub>2</sub> (20-100 mg). [PMS] =  $1 \times 10^{-3}$  mol dm<sup>-3</sup> and [*o*-cresol] =  $1 \times 10^{-3}$  mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate of *o*-cresol for various concentrations of TiO<sub>2</sub>.



**Fig.7** Log (O.D)<sub>t</sub> vs time plot for the photodegradation of *o*-cresol for various concentration of TiO<sub>2</sub> (20-100 mg). [PDS] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> and [*o*-cresol] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>. Inset shows plot of photodegradation rate of *o*-cresol for various concentration of TiO<sub>2</sub>.

**Table. 3:** Comparison of photocatalytic efficiencies of PMS, PDS on photocatalytic decomposition of *o*-cresol

System	k <sub>1</sub> x 10 <sup>3</sup> s <sup>-1</sup>
TiO <sub>2</sub> - <i>o</i> -Cresol	6.12
TiO <sub>2</sub> - PDS - <i>o</i> -Cresol	9.62
TiO <sub>2</sub> - PMS - <i>o</i> -Cresol	10.37

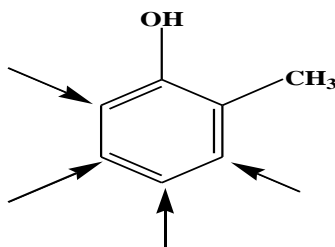


The atmospheric oxygen present in the solution can react with e<sup>-</sup><sub>CB</sub> and prevent the recombination of electron – hole pairs [I. Izumi *et al* 1980, M. Fujihira *et al* 1982, I. Izumi *et al* 1981, R.W. Mathews (1984), J.M. Herrmann *et al* 1980]:



When photons of energy ≥ band gap energy (3.2 eV) fall on TiO<sub>2</sub> semiconductor particles, e<sup>-</sup>h<sup>+</sup> pair is generated:

Hydroxyl radical attacks *o*-cresol molecules to produce the namely hydroxy *o*-cresol as follows [Jian Liao *et al* 2014].









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