



The influence of PMS and PDS oxidants on reaction rate of photocatalytic degradation of *p*-cresol over TiO₂ powder - Advanced Oxidation Process

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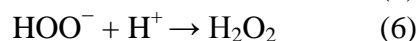
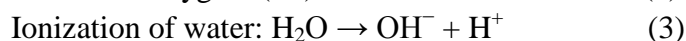
Abstract:

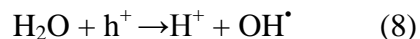
The degradation of *p*-cresol is approved out under UV-visible light by TiO₂ as a photocatalyst. In the direction of determining the efficiency of the photocatalyst, the, unlike variables, studied built-in the amount of photocatalyst, consequence of oxidants peroxomonosulphate (PMS) and peroxodisulphate (PDS) on the photocatalytic oxidation of *p*-cresol on elucidation TiO₂ surface have been investigating. The efficiencies of these oxidants on photocatalytic degradation of *p*-cresol are compared with that of PMS and PDS. The investigational results indicate that these oxidants reveal improved rates of mineralization of *p*-cresol. A response mechanism, linking the production of hydroxyl radicals and sulfate radicals. In conclusion, this investigation indicated a high potential of TiO₂ suspension to remove the high-level concentration of *p*-cresol under UV radiation.

Keywords: Photodegradation, *p*-cresol, PMS, PDS, TiO₂ Catalyst.

1. INTRODUCTION:

Photocatalysis is a subject of interest in view of its prosperous application in pollutant decontamination. Photocatalysis takes the advantage of the ability of semiconductor photocatalyst to generate surface bound hydroxyl radical and trapped hole upon excitation by band gap light [1–3]. Basically, under illumination by suitable light, this process (Equations 1–8) produces hydroxyl radical and hole which are powerful oxidants that can degrade a variety of organic compounds [1,4,5].





Among the several semiconductor photocatalysts used, TiO_2 has been considered the most superior in terms of suitability for application [6,7]. The current interest in ZnO is based on its high spectral response in UV region, which presumably, in some studies, resulted in higher efficiency of photocatalytic degradation well over TiO_2 [8–12]. Based on the aforementioned, ZnO photocatalysis has been proposed as an alternative in the removal of various aqueous pollutants including phenolic compounds [13–19]. *p*-cresol as a phenolic compound has been listed as the priority [20]. Water solubility of *p*-cresol is above 21.5 g/L (25°C) [21]. Therefore, *p*-cresol can be a significant threat to surface water, groundwater sources, or generally the environment [7,22]. The effective removal of *p*-cresol is currently an environmental problem [23,24]. In our previous works, the effect of operational parameters on photocatalytic degradation of *m*-cresol [25] and *o*-cresol [26] was reported by UV and visible/ ZnO process. However, no study has been conducted on aquatic *p*-cresol photocatalytic degradation using ZnO under UV irradiation. We undertake to investigate the effect of operating parameters such as *p*-cresol concentration, amount of photocatalyst and pH on degradation efficiency.

2. Experimental

2.1 Investigational Methods

The photocatalytic experiment be passed out in a Pyrex cell of amount 100 ml. In every one the experiment, 50 mg of the photocatalyst powder (except the experiments involving variation of catalyst amounts) were balanced in 70 ml of the substrate (*p*-cresol) solution, stirred magnetically at a invariable rate, and then irradiated. A 150 W tungsten-halogen lamp was used as the light resource. Samples for analysis were withdrawn at regular intervals of time. The catalyst was divided from the solution by filtration. The quantitative analysis of *p*-cresol was carry out by a standard colorimetric process [27, 28]. The photodegradation of *p*-cresol was also confirmed by colorimetric estimation. The proportion of photodegradation was measured as follows:

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

Where C_0 = initial concentration of *p*-cresol, C_t = concentration of *p*-cresol after photo-irradiation. All photocatalytic degradation experiments be approved out in duplicate.

3. Results and discussion

3.1 Photocatalytic degradation of *m*-chlorophenol

Photodegradation of *p*-cresol (1×10^{-3}) in aqueous solutions at usual pH was perform in the presence of TiO_2 photocatalyst (50 mg). Photocatalyzed disappearance of *p*-cresol before and after irradiation and as well as with or without oxidants (PMS and PDS). The photodegradation rate of *p*-cresol in the attendance of oxidants (PMS and PDS) was found to higher than that in the nonappearance of each of these oxidants. The added oxidant enhance of *p*-cresol oxidation rate drastically. In order to find the effect of these oxidants on the rate of decomposition of *p*-cresol, experiments were carried out at a constant concentration of *p*-cresol ($1 \times 10^{-3} \text{ mol dm}^{-3}$), constant catalyst amount ($\text{TiO}_2 = 50 \text{ mg}$), 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 *p*-cresol

3.2.1 Result of the initial concentration of *p*-cresol

The results obtained for TiO₂-PMS-*m*-Chlorophenol and for TiO₂-PDS-*p*-Cresol system are offered in Table 2. The plots of Log (OD)_t vs time for a range of initial concentrations of *p*-cresol are linear and from the slopes of the plots, the rate constants were calculated and tabulated (Table 2 and Figs.4 and 5). The plots of rate vs [*p*-cresol]₀ (Table 2; inset of Figs. 4 and 5) illustrate that *p*-cresol degradation increases with an increase in [*p*-cresol]₀, reach a maximum, and remains approximately constant. The effect of [*p*-cresol]₀ on rate could be describe by the following relation:

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

Anywhere *k* and *K* are the proportionality and stability constants, respectively. The mutual of the above equation gives

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

Table.2 Rate constants for the photodegradation of a selection of amounts of *p*-cresol in the presence of PMS and PDS

[<i>p</i> -cresol] ₀ x 10 ³ mol dm ⁻³	With PMS, <i>k</i> ₁ x 10 ⁻³ s ⁻¹	With PDS, <i>k</i> ₁ x 10 ⁻³ s ⁻¹
1.0	15.12	11.87
2.0	23.50	12.87
3.0	33.00	14.75
4.0	39.48	15.62
5.0	46.25	16.25
6.0	46.50	17.37

TiO₂ = 50 mg/70ml; T = 30°C; [PMS] = [PDS] = 1 x 10⁻³ mol dm⁻³

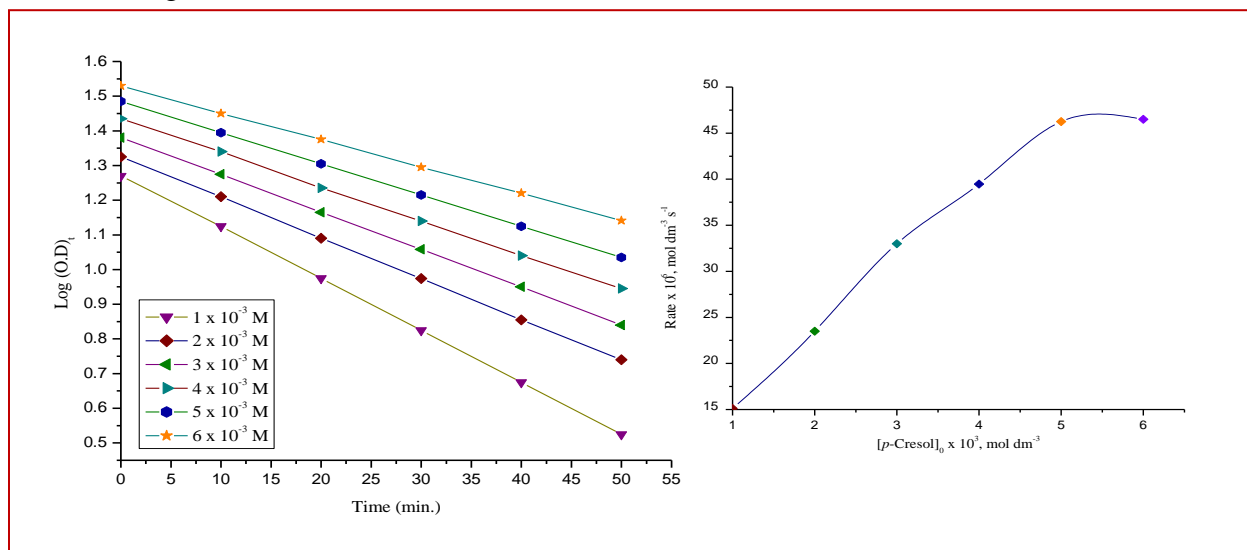


Fig.4 Log (OD)_t vs time plot for the photodegradation of a selection of measure of

p-cresol ($1 - 6 \times 10^{-3} \text{M}$). [Catalyst] = 50 mg/70 ml and [PMS] = $1 \times 10^{-3} \text{mol dm}^{-3}$. Inset show scheme of photodegradation rate for a mixture of amounts of *p*-cresol.

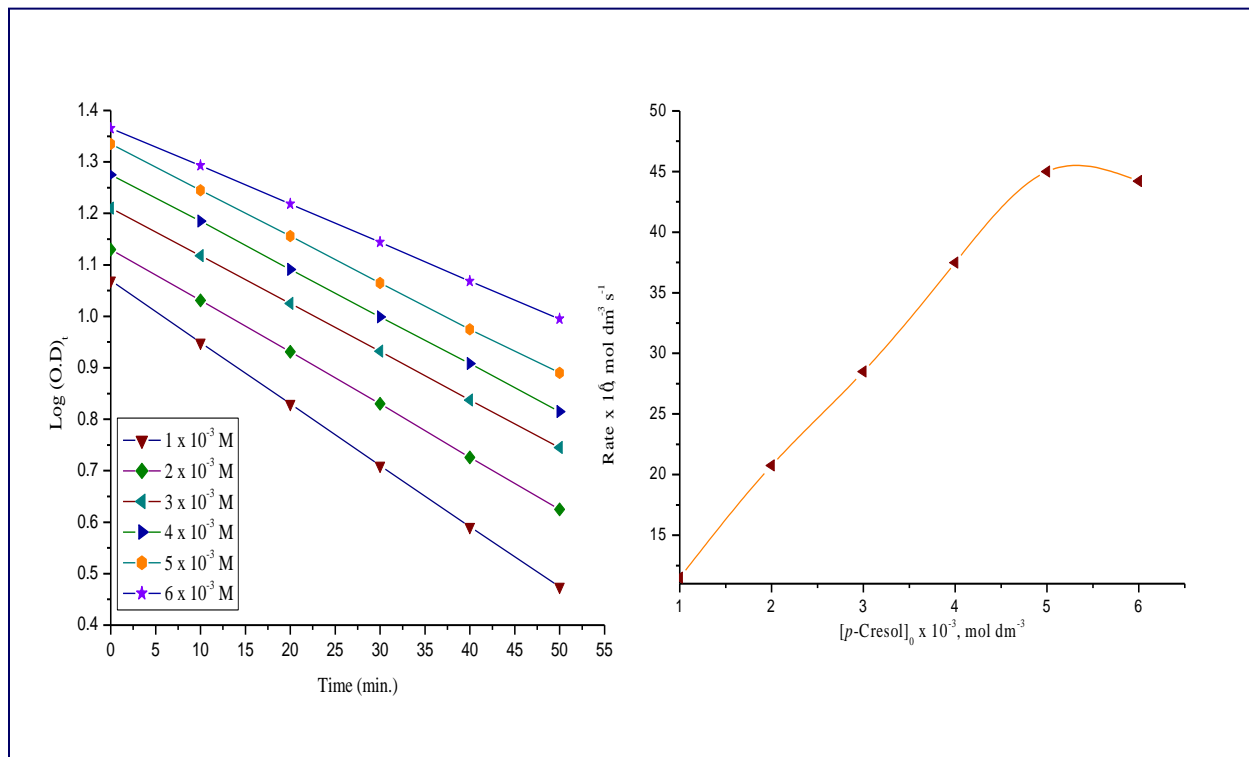


Fig.5 Log (OD)t vs time plot intended for the photodegradation of a choice of amounts of *p*-cresol ($1 - 6 \times 10^{-3} \text{M}$). [Catalyst] = 50 mg/ 70 ml and [PDS] = $1 \times 10^{-3} \text{mol dm}^{-3}$. Inset shows plot of photodegradation rate intended for a variety of amounts of *p*-cresol.

The plots of $1/\text{rate}$ vs $1/[p\text{-cresol}]_0$ are straight lines with intercepts on the ordinate representing Langmuir kinetics. The standards of the proportionality constant k and equilibrium constant K are evaluated (Table 3). For the $\text{TiO}_2\text{-PMS-}p\text{-Cresol}$ system, the values of k and K are found to be $6.20 \times 10^{-6} \text{mol dm}^{-3} \text{s}^{-1}$ and $155.88 \text{dm}^3 \text{mol}^{-1}$, in that order. The standards of k and K for the $\text{TiO}_2\text{-PDS-}p\text{-Cresol}$ classification are $9.10 \times 10^{-6} \text{mol dm}^{-3} \text{s}^{-1}$ and $826.66 \times 10^3 \text{dm}^3 \text{mol}^{-1}$, respectively.

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

The results obtain are to be had in Figs. 6 and 7. From the plot of rate vs [oxidant], it is seen that the rate of decomposition of *p*-cresol increases linearly with increases in the absorption of the oxidant.

Table.3 Valuation of k and K for the photodegradation of a variety of amounts of *p*-cresol $\text{TiO}_2 = 50\text{mg}/70\text{ml}$; $T = 30^\circ \text{C}$; [PMS] = [PDS] = $1 \times 10^{-3} \text{mol dm}^{-3}$

$1/[p\text{-cresol}]_0 \times 10^{-3} \text{mol}^{-1} \text{dm}^3$	With PMS, $1/\text{rate} \times 10^{-6} \text{mol}^{-1} \text{dm}^3 \text{s}$	With PDS, $1/\text{rate} \times 10^{-6} \text{mol}^{-1} \text{dm}^3 \text{s}$
1.00	6.61	8.69
0.50	4.25	4.82

0.33	3.03	3.50
0.25	2.53	2.66
0.20	2.16	2.22
0.16	2.15	2.26
$k = (\text{mol dm}^{-3} \text{s}^{-1})$	2.90×10^{-6}	1.90×10^{-6}
$K = (\text{dm}^{-3} \text{mol}^{-1})$	103.15	153.73

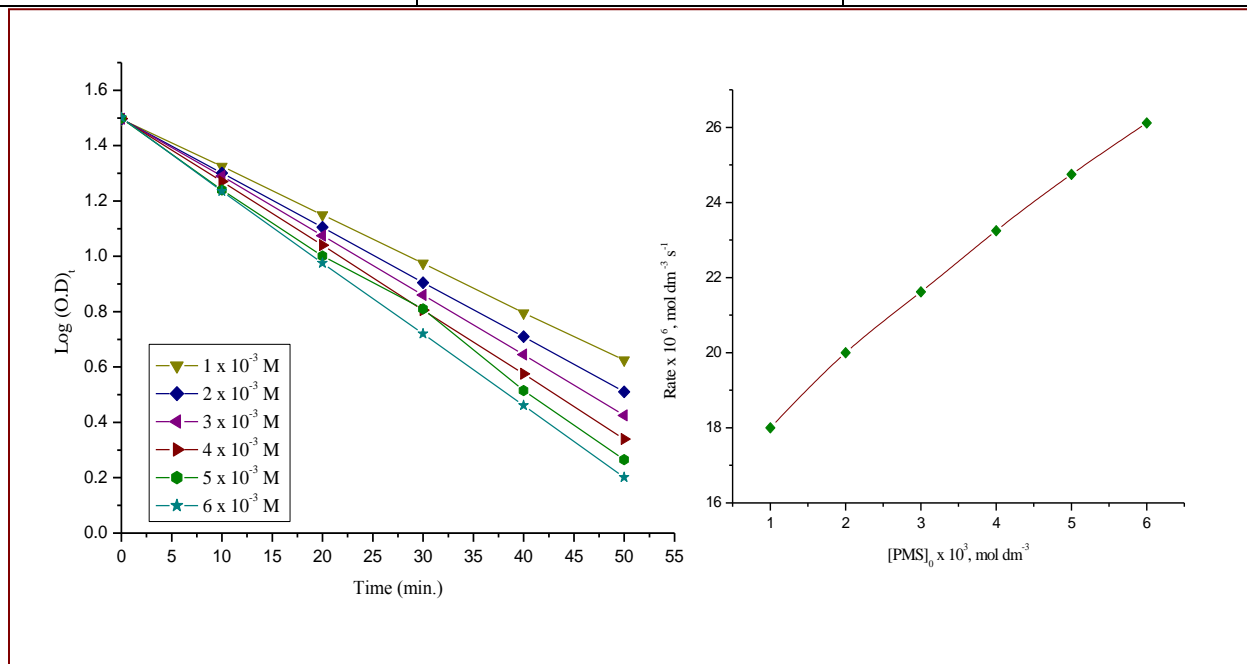


Fig.6 Log (O.D)_t vs time plot for the photodegradation of *p*-cresol for a variety of concentration of PMS ($1.0 - 6.0 \times 10^{-3} \text{M}$). [Catalyst] = 50 mg/70 ml and [*p*-cresol] = $1 \times 10^{-3} \text{mol dm}^{-3}$. Inset show plot of photodegradation rate of *p*-cresol used for a range of concentrations of PMS.

3.2.3 Effect of catalyst amount

The rate increases originally with an increase in the catalyst amount and reach a maximum and then gets decrease (Figs.8 and 9). This due to the fact that with increasing catalyst amount, absorption of light by photocatalyst particles also increases. Therefore, the rate of degradation of *p*-cresol also increases. Subsequent to a certain limit, there is a decrease in the rate experimental. This is due to the allocation of light by the catalyst particles, which is answerable designed for the lessening in the rate.

3.2.4 PMS an effective oxidant for the photocatalytic degradation of *p*-cresol

A calculate approximately of the efficiency of the oxidants (PMS and PDS) for the Photocatalyzed degradation of *p*-cresol ($1 \times 10^{-3} \text{mol dm}^{-3}$) was obtained by compare the results of the experiments carried out under identical conditions but with different oxidants (PMS and PDS [Oxidant] = $1 \times 10^{-3} \text{mol dm}^{-3}$). Pure TiO_2 without any oxidants shows 8 % degradation of *p*-cresol in 40 min, which is enhanced to 80 % in the presence of PDS. PMS have similar activity and they enhance the decomposition of *p*-cresol up to 54 % under the same clarification time (Table 4). An improved effectiveness of PMS over PDS can be modernized as PMS gets

decomposed through e^-_{CB} and h^+_{VB} of the semiconductor photocatalysts whereas PDS can be rotting only by e^-_{CB} [29, 30] and the enter reactions are represented below.

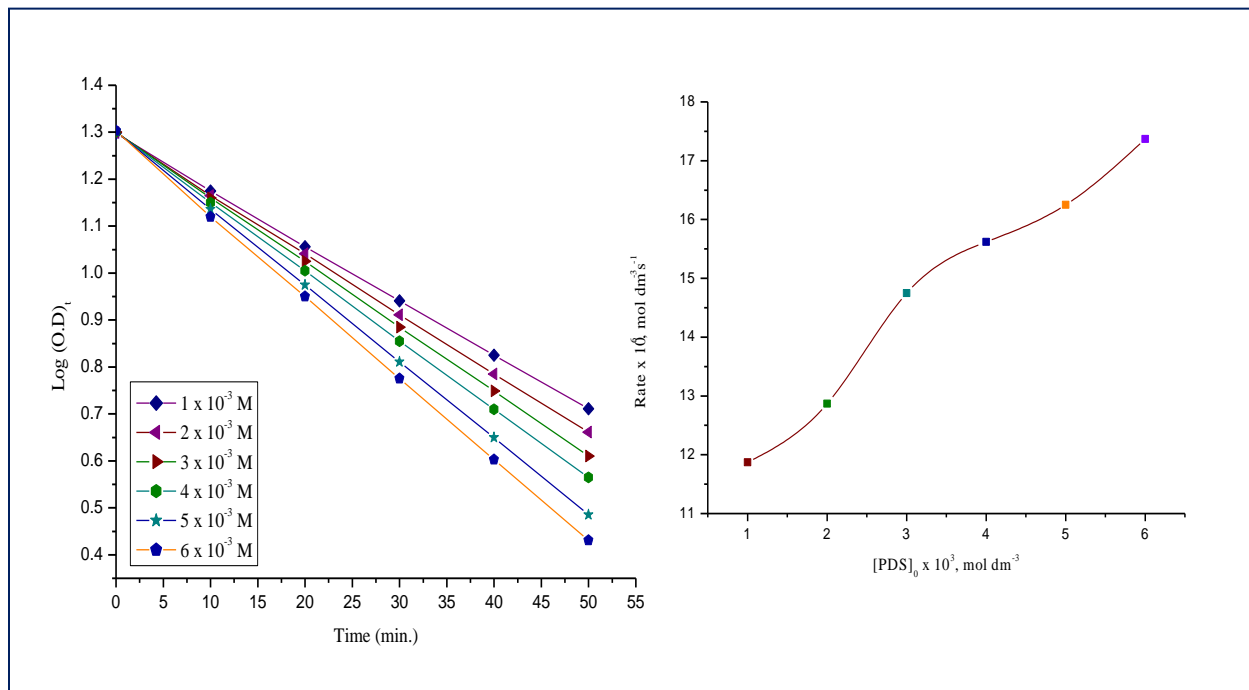


Fig.7 Log (O.D)t vs time plot for the photodegradation of *p*-cresol for a diversity of concentration of PDS ($1.0 - 6.0 \times 10^{-3}$ M). [Catalyzed] = 50 mg/70ml and $[p\text{-cresol}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset shows plot of photodegradation rate of *p*-cresol for a variety of concentrations of PDS.

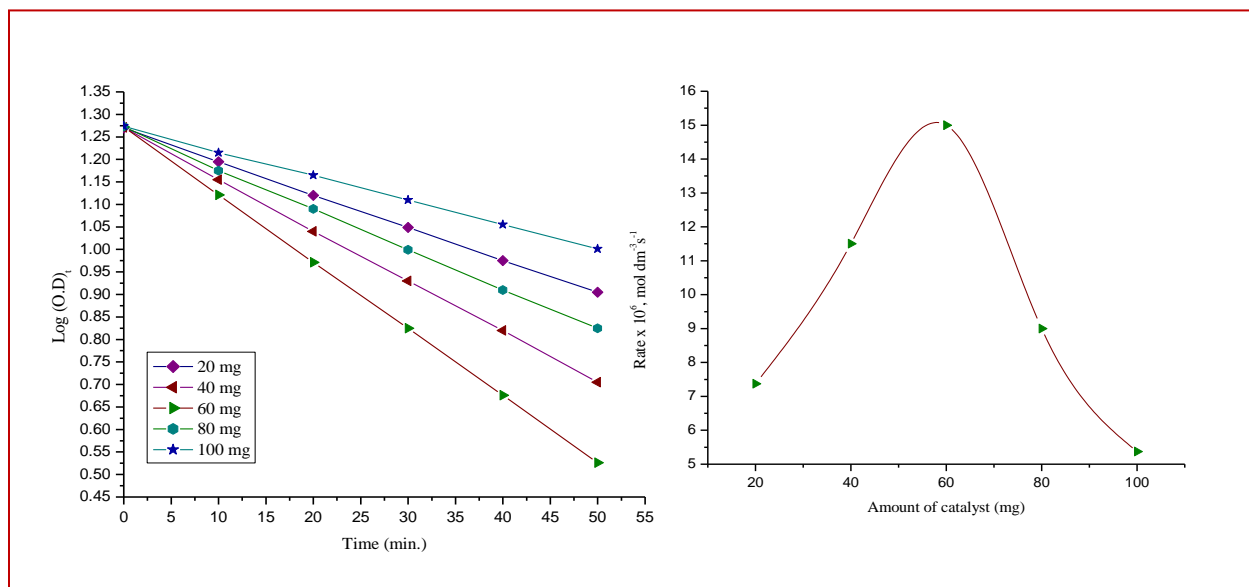


Fig.8 Log (O.D)t vs time plot for the photodegradation of *p*-cresol for a range of concentrations of TiO_2 (20-100 mg). $[\text{PMS}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ and $[p\text{-cresol}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset show plot of photodegradation rate of *p*-cresol used for a range of concentrations of TiO_2 .

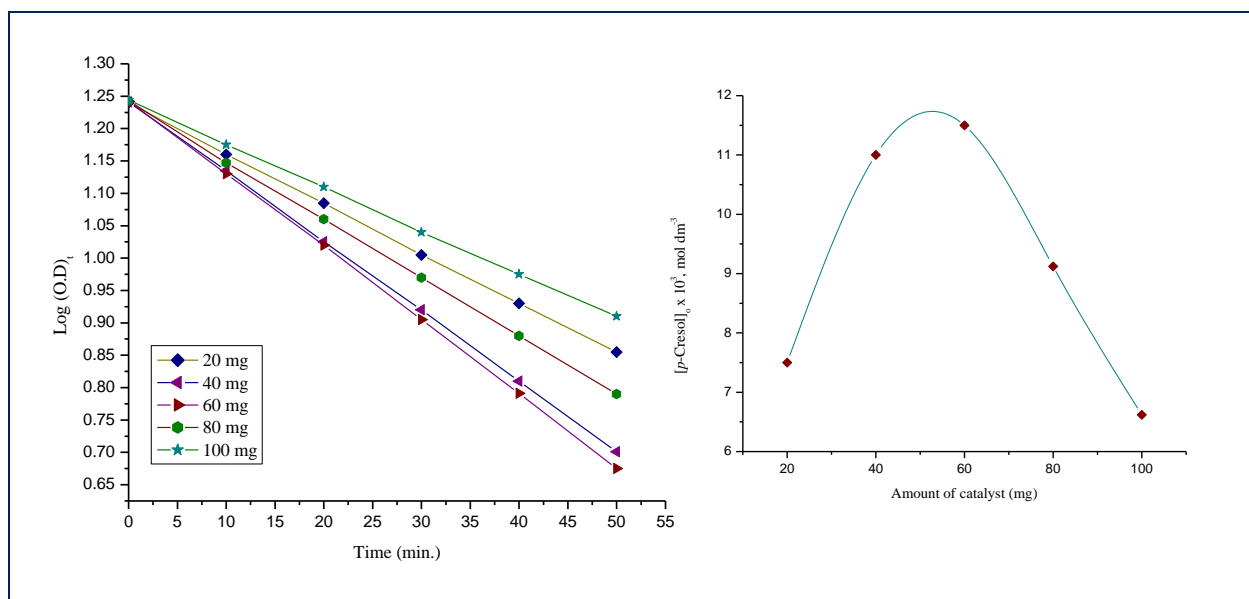


Fig.9 Log (O.D)_t vs time plot for the photodegradation of *p*-cresol for various concentration of TiO₂ (20-100mg). [PDS] = 1 × 10⁻³ mol dm⁻³ and [*p*-cresol] = 1 × 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of *p*-cresol for various concentration of TiO₂.

With PMS:

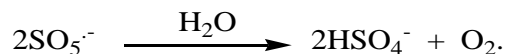
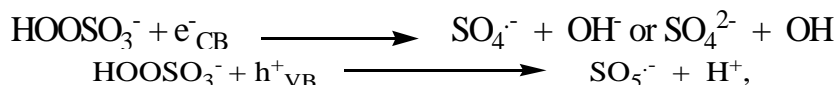


Table.4 Evaluation of photocatalytic efficiencies of PMS and PDS on photocatalytic disintegration of *p*-cresol

System	$k_1 \times 10^3 \text{ s}^{-1}$
TiO ₂ - <i>p</i> -Cresol	5.12
TiO ₂ -PMS- <i>p</i> -Cresol	26.12
TiO ₂ -PDS- <i>p</i> -Cresol	17.37

Table.5 Evaluation of photocatalytic percentage degradation of PMS and PDS on *p*-Cresol

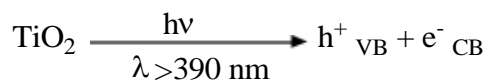
System	% degradation
TiO ₂ - <i>p</i> -Cresol	16.59
TiO ₂ -PMS- <i>p</i> -Cresol	83.79
TiO ₂ -PDS- <i>p</i> -Cresol	61.51

With PDS:



4. Mechanism

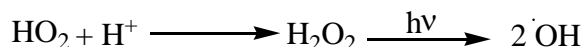
When the photons of the bandgap energy (greater than 3.2 eV) fall on TiO₂ semiconductor particle, an e⁻ - h⁺ pairs are generate.



In an oxygenated solution, the following reactions occur: Oxygen adsorbed on the anatase surface prevents the recombination of electron-hole pairs by trapping the electrons [31-35].



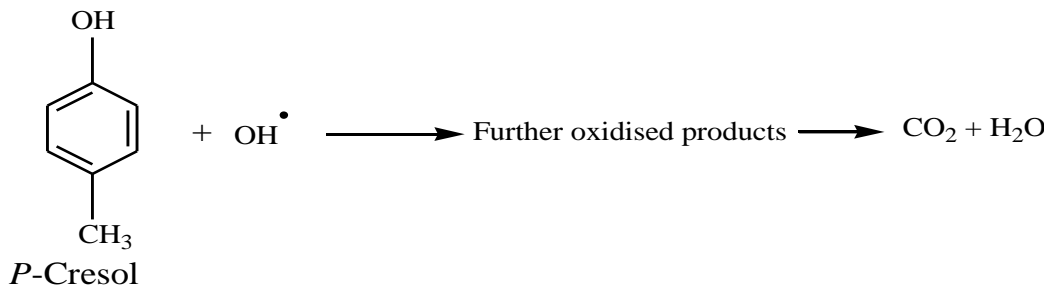
It is likely that H₂O₂ is formed from O₂^{·-} according to the following reaction [33, 35, 36].



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

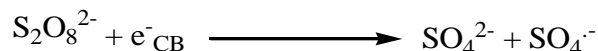
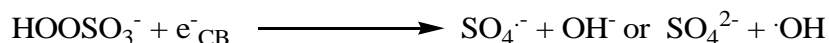


Hydroxyl radical attacks trihydric phenol *p*-cresol to form a product namely is further degraded into carbon dioxide and water.



Under prolonged irradiation, *p*-cresol may additional degrade form to CO₂ and H₂O finally. There remainder the opportunity that photogenerated holes react with *p*-cresol adsorbed on TiO₂ to give *p*-cresol radicals' cations, as has been projected by the photocatalytic oxidation of benzene by Hashimoto *et al.*, [37-55].

The adding together of HOOSO₃⁻ and S₂O₈²⁻ to the response system will produce ·OH and SO₄^{·-} by the reaction of e⁻_{CB} with these oxidants,



These radicals enhance the oxidation of *p*-cresol and hence the rates of disappearance of *p*-cresol in presence of these oxidants are more (Tabs. 4 and 5) than those in the absence of them.

5. Conclusions

The incidence learning develops a number of basic facial appearances regarding the concert of photocatalytic degradation of *p*-cresol in the presence of oxidants when exposed to visible light. The manipulation of elementary parameters such as catalyst amount, the concentration of substrate, and the concentration of oxidants is nowadays conventional, opening the way for the added expansion of these systems. Express photodegradation rates are experimental with PMS as an oxidant, with the aim of PMS being a more well-organized oxidant than PDS for the photocatalyzed degradation of *p*-cresol.

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