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RESEARCH ARTICLE

PHOTOCATALYTIC DEGRADATION OF RESORCINOL OVER ZnO POWDER THE INFLUENCE OF PEROXOMONOSULPHATE AND PEROXODISULPHATE ON THE REACTION RATE

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Abstract

The degradation of resorcinol 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 resorcinol on illumination ZnO surfaces has been investigated. The efficiencies of these oxidants on photocatalytic degradation of resorcinol are compared with that of PMS and PDS. The experimental results indicate that these oxidants exhibited enhanced rates of mineralization of resorcinol. 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.

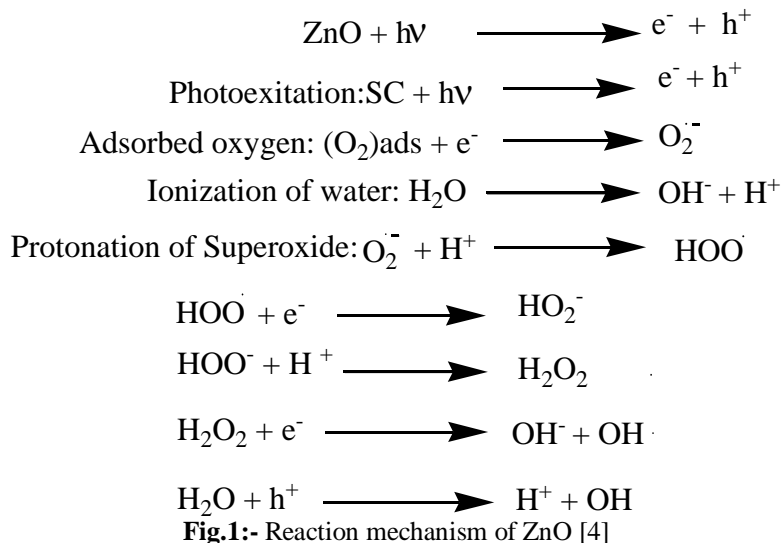
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Introduction:-

Environmental pollution and particularly water pollution on a global scale have drawn scientists' attention to the vital need for environmentally clean and friendly chemical processes. Photocatalysis is the field of current interest given its application in disinfecting drinking water and wastewater [1-2]. Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of a semiconductor photocatalyst [3] to the empty conduction band as the absorbed photon energy, $h\nu$, equals or exceeds the band gap of the photocatalyst. The e^- hole pair (e^-h^+) is generated at the surface of the photoexcited photocatalyst as shown below [4]. The hydroxyl ($\bullet\text{OH}$) radical is a powerful oxidant for degrading non selective organic compounds [5-6]. The most frequently used photocatalysts are TiO_2 , ZnO , ZrO_2 , CdS , and SnO_2 [7-8]. Among these ZnO removed several environmental contaminants under UV irradiation [9-12]. The great advantage of ZnO is its ability to absorb larger fractions of the solar spectrum than the other photocatalysts, removing many organic contaminants in aqueous solution under visible irradiation [13-15]. This work looks at the photodegradation of resorcinol by ZnO (photocatalyst) under UV irradiation.

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Many authors [16-19] have studied the photocatalytic decomposition of resorcinol over ZnO powder. With the above information in hand, we decided to undertake a study aiming to clarify different aspects of the mechanism of direct visible light photodegradation and of ZnO photocatalytic degradation of resorcinol in aqueous solution, to give a better understanding of AOPs. So, the focus of our investigation is to apply peroxomonosulphate (PMS) and peroxydisulphate (PDS) as oxidants, thereby to enhance the photocatalytic degradation rate of resorcinol on illuminated ZnO powder under visible light and compare the efficiencies of these oxidants with PMS and PDS.

Experimental:-

Experimental Methods:-

ZnO (>99.99%, Aldrich, USA) semiconductor grade (specific surface area $4.6 \text{ m}^2 \text{ g}^{-1}$) 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 peroxydisulphate 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 (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 resorcinol was performed by a standard colorimetric method [20, 21]. The photodegradation of resorcinol 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 resorcinol, C_t = concentration of resorcinol after photoirradiation. All photocatalytic degradation experiments were carried out in duplicate.

Results and Discussion:-

Photodegradation of resorcinol (1×10^{-3}) in aqueous solutions at natural pH was performed in the presence of ZnO 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. Pyrogallol and phloroglucinol were 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

($1 \times 10^{-3} \text{ mol dm}^{-3}$), constant catalyst amount (ZnO = 50 mg) and at constant pH (4.0 and 5.2) with various oxidants (PMS and PDS) by colorimetric method.

Factors influencing photocatalytic oxidation of Resorcinol:-

Effect of initial concentration of Resorcinol:-

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

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

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	17.87	5.25
2.0	14.00	6.25
3.0	11.87	6.50
4.0	10.25	7.00
5.0	8.62	7.25
6.0	7.10	6.12

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

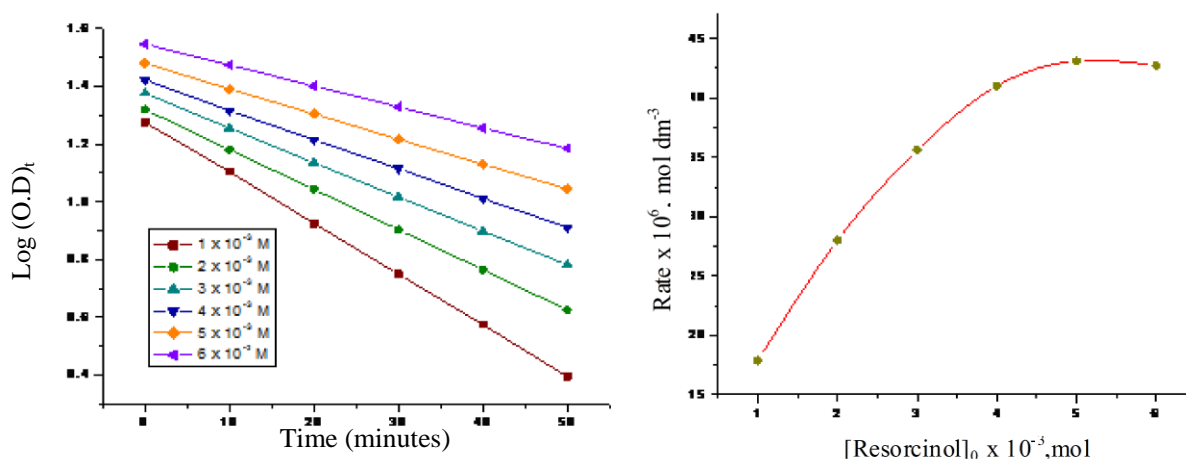


Fig.2 $\text{Log}(\text{OD})_t$ vs time plot for the photodegradation of various amount of resorcinol ($1 - 6 \times 10^{-3} \text{ M}$). [Catalyst] = 50 mg/70 ml and $[\text{PMS}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset shows plot of photodegradation rate for various amounts of resorcinol.

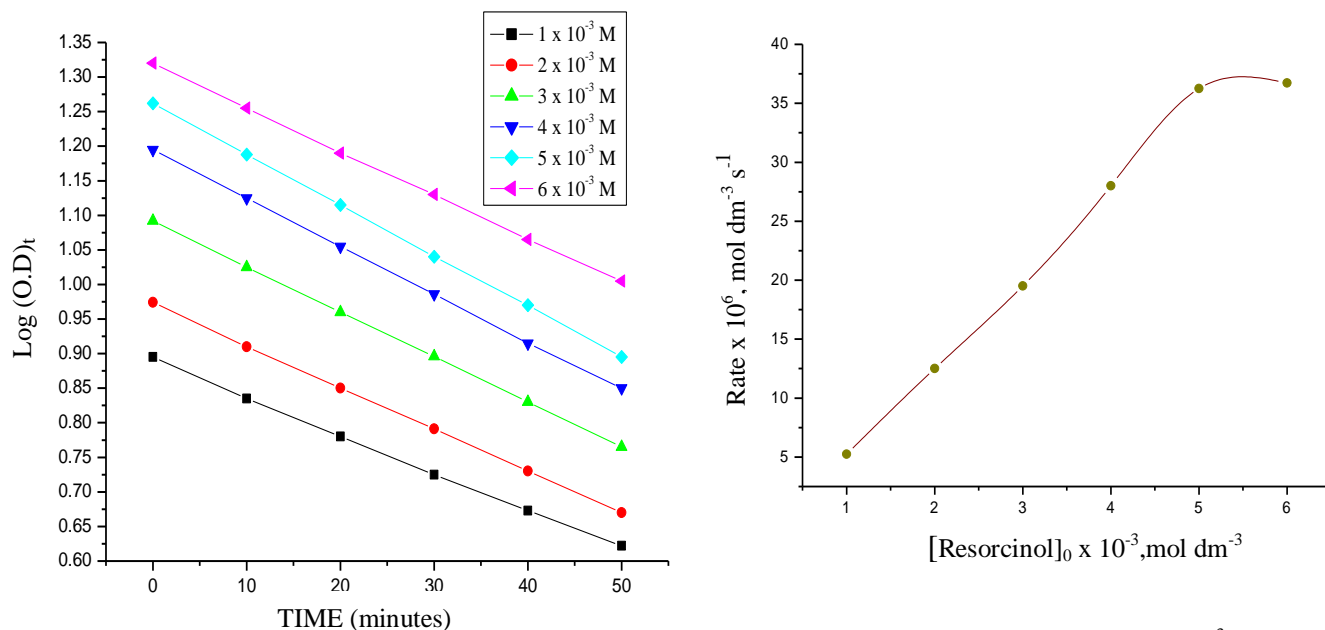


Fig 3:- Log (OD)_t vs TIME (minutes) for photodegradation of various amounts of resorcinol (1 - 6 × 10⁻³ M). [Catalyst] = 50 mg/ 70 ml and [PDS] = 1 × 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate for various amounts of resorcinol.

The plots of 1/rate vs 1/[resorcinol]₀ are straight lines with intercepts on the ordinate indicating Langmuir kinetics. The values of the proportionality constant *k* and equilibrium constant *K* are evaluated (Table 2). For ZnO–PMS–Resorcinol system the values of *k* and *K* are found to be 2.90 × 10⁻⁶ mol dm⁻³ s⁻¹ and 79.01 dm³ mol⁻¹, respectively. The values of *k* and *K* for ZnO–PDS–Resorcinol system are 2.70 × 10⁻⁶ mol dm⁻³ s⁻¹ and 1.38 × 10³ dm³ mol⁻¹, respectively.

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 × 10⁻³ mol dm⁻³) at a constant concentration of resorcinol (1.0 × 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

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

1/[Resorcinol] ₀ × 10 ⁻³ mol ⁻¹ dm ³	With PMS, 1/rate × 10 ⁻⁶ mol ⁻¹ dm ³ s	With PDS, 1/rate × 10 ⁻⁶ mol ⁻¹ dm ³ s
1.00	8.33	19.04
0.50	5.26	8.00
0.33	4.10	5.12
0.25	3.63	3.57
0.20	3.47	2.75
0.16	3.50	2.72
<i>k</i> = (mol dm ⁻³ s ⁻¹)	2.90 × 10 ⁻⁶	2.70 × 10 ⁻⁶
<i>K</i> = (dm ³ mol ⁻¹)	79.012	1.38 × 10 ³

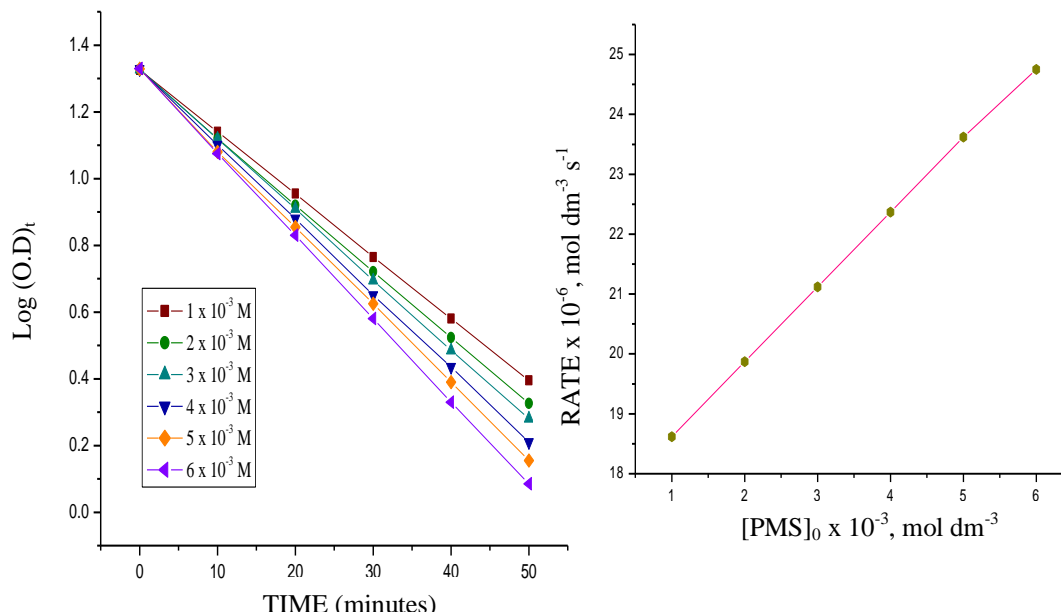


Fig 4:- $\text{Log}(O.D)_t$ vs time plot for the photodegradation of resorcinol for various concentrations of PMS ($1.0 - 6.0 \times 10^{-3} \text{ M}$). [Catalyst] = 50 mg/70 ml and $[\text{Resorcinol}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$. Inset shows plot of photodegradation rate of resorcinol for various concentrations of PMS.

Effect of catalyst amount:-

Experiments carried out with various amount of catalyst powders (20 – 100 mg) at constant $[\text{resorcinol}]$ ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) and at constant concentration of oxidant ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) showed similar results for ZnO-PMS-Resorcinol and ZnO-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 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.

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 ($1 \times 10^{-3} \text{ mol dm}^{-3}$) 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 12 % degradation of resorcinol in 50 min, which is enhanced to 46 % in the presence of PDS. PMS have similar activity and they enhance the decomposition of resorcinol up to 93 % 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}^- [22-23] and the key reactions are represented below.

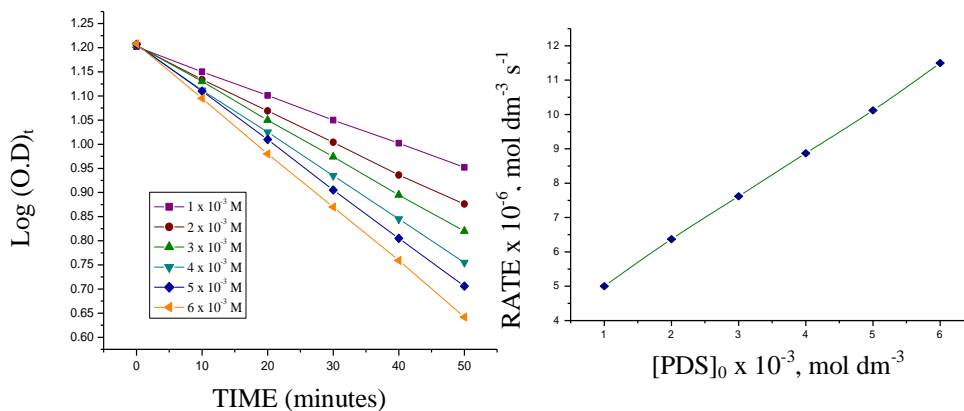


Fig 5:- Log (O.D)_t vs time plot for the photodegradation of resorcinol for various concentration of PDS (1.0 – 6.0 x 10⁻³ M). [Catalysed] = 50 mg/70ml and [resorcinol] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of resorcinol for various concentrations of PDS.

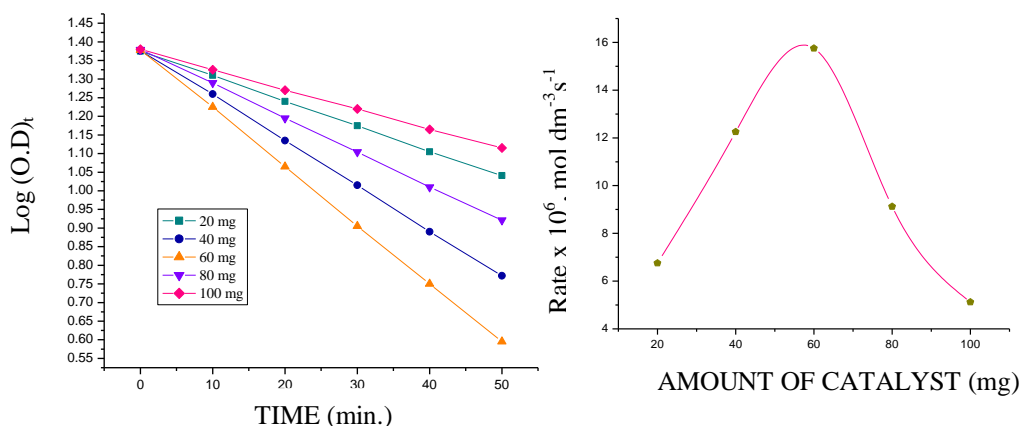


Fig 6:- Log (O.D)_t vs time plot for the photodegradation of resorcinol for various concentrations of ZnO (20 - 100 mg). [PMS] = 1 x 10⁻³ mol dm⁻³ and [resorcinol] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of resorcinol for various concentrations of ZnO.

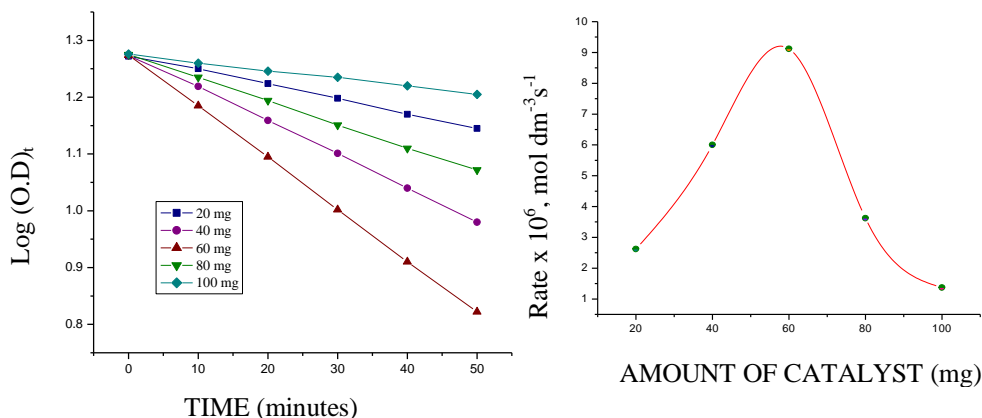


Fig.7 Log (O.D)_t vs time plot for the photodegradation of resorcinol for various concentration of ZnO (20-100mg). [PDS] = 1 x 10⁻³ mol dm⁻³ and [resorcinol] = 1 x 10⁻³ mol dm⁻³. Inset shows plot of photodegradation rate of resorcinol for various concentration of ZnO.

With PMS:

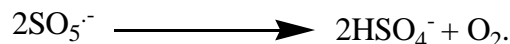
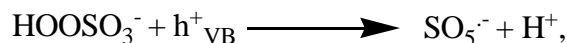
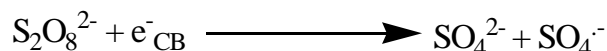


Table 3:- Comparison of photocatalytic efficiencies of PMS, PDS on photocatalytic decomposition of resorcinol

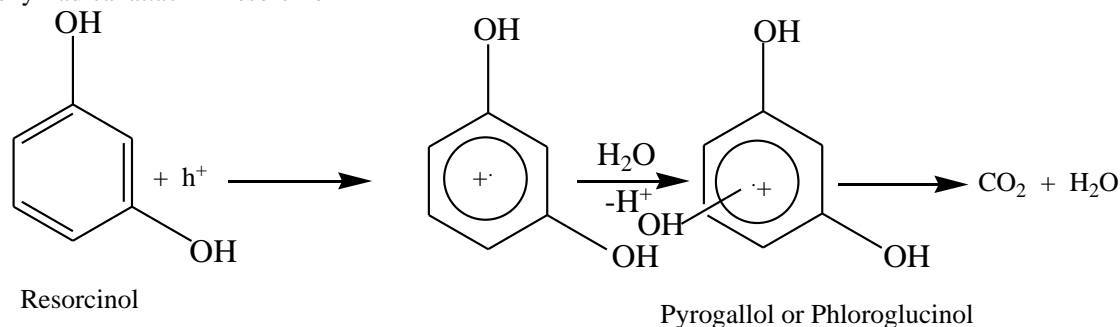
System	$k_1 \times 10^3 \text{ s}^{-1}$
ZnO-Resorcinol	3.37
ZnO-PDS-Resorcinol	5.25
ZnO-PMS-Resorcinol	17.87

With PDS:

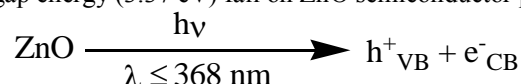


Mechanism:-

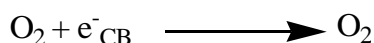
Hydroxyl radical attack in resorcinol



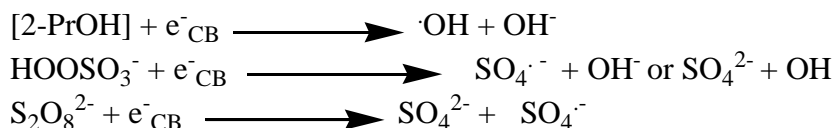
When photons of energy \leq band gap energy (3.37 eV) fall on ZnO semiconductor particles, e^-h^+ pair is generated:



The atmospheric oxygen present in the solution can react with e^-_{CB} and prevent the recombination of electron – hole pairs [24-28]:



Hydroxyl radical attacks resorcinol molecules to form the dihydroxy products-Pyrogallol and phloroglucinol, which under prolonged irradiation, further degrade finally to CO_2 and H_2O . There remains the possibility that photogenerated holes react with resorcinol adsorbed on ZnO to give dihydroxycyclohexadienyl radicals via resorcinol radical cations, as has been proposed for the photocatalytic oxidation of m-Benzenedisulphonicacid [19]

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 their.

Conclusions:-

The present 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 photocatalysed degradation of resorcinol.

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