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RESEARCH ARTICLE

PHOTOCATALYTIC DEGRADATION OF CATECHOL OVER TiO_2 POWDER THE INFLUENCE OF PEROXOMONOSULPHATE AND PEROXODISULPHATE ON THE REACTION RATE

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ABSTRACT

Advanced Oxidation Processes (AOPs) have been developed as an emerging technology for treating hazardous organics in wastewater and groundwater. In the present study, the effect of oxidants peroxomonosulphate and peroxodisulphate on the photocatalytic oxidation of catechol on illuminated TiO_2 surfaces has been investigated. The efficiencies of these oxidants on photocatalytic degradation of catechol are compared with that of peroxomonosulphate and peroxodisulphate. 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, was proposed.

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INTRODUCTION

Today, the whole world is facing a series of environmental problems such as contaminated ground water, hazardous waste effluent coming out of industrial sectors due to advanced industrialization in different fields. Hence various techniques were developed for purification of water, the application of advanced oxidation processes in water and wastewater treatment is the subject of several studies and research topics. In majority of the existing process, the parameter responsible of an efficient degradation is the existence of highly reactive hydroxyl radicals (Achilleos *et al*., 2010). These free radicals are molecules capable of oxidizing numerous organic complex, no chemically oxidizable or compounds difficult to oxidize. Heterogeneous photocatalysis is an alternative method for removing organic pollutants in water, this process can be carried out under ambient conditions of temperature and pressure and may lead a total mineralization of organic carbon to CO_2 (Zayani *et al*., 2009). In the presence of oxygen, the electron may induce reduction and leads to formation of hydroxyl radicals. These radicals are well known to be strong oxidizing agents and react efficiently without any selectivity with most organic substrates (D'Oliveira *et al*., 1990; Okamoto *et al*., 1985; Ollis *et al*., 1989). Titanium dioxide (TiO_2) is widely used as semiconductor photocatalyst, because it is chemically stable, non toxic and low cost material (Herrmann, 1995; Silva *et al*., 2007; Pera-Titus *et al*., 2004). In addition, it has been proposed to solve various environmental problems because of its ability to eliminate microorganisms such as bacteria and viruses, controlling odor and degrading organic pollutants such as pesticides and phenolic compounds (Fujishima *et al*., 1999; Topalov *et al*., 1999). The photocatalytic degradation rate of different organic compounds depends on various parameters. In this paper, we report our investigation of photodegradation of catechol in aqueous solution (Kansal *et al*., 2007), using TiO_2 under UV irradiations, and assess the influence of various parameters such as initial pollutant concentration and oxidant concentration. So, the focus of our investigation is to apply peroxomonosulphate (PMS) and peroxodisulphate (PDS) as oxidant, thereby to enhance the photocatalytic degradation rate of catechol on illuminated TiO_2 powder under visible light and compare the efficiencies of these oxidants PMS and PDS.

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.

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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 (expect the experiments involving variation of catalyst amounts) were suspended in 70 ml of the substrate (catechol) solution, stirred magnetically at a constant rate and then irradiated. A 150W tungsten-halogen lamp (Lewin-Lighiting 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 (Martin, et al., 1949; Dhanalakshmi *et al.*, 2008). The photodegradation of catechol was also confirmed by colorimetric estimation.

RESULTS AND DISCUSSION

Photodegradation of catechol (1 x 10^{-3}) in aqueous solutions at natural pH was performed in the presence of TiO_2 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 x 10^{-3} mol dm^{-3}), concentration of constant catalyst amount (TiO_2 = 50mg) and at constant pH (4.0 and 4.8) with various oxidants (PMS and PDS) by colorimetric method.

Factors influencing photocatalytic oxidation of catechol

Effect of initial concentration of catechol

Experiments were carried out with various initial concentrations of catechol (1.0 – 6.0 x 10^{-3} mol $dm^{-3)}$ at constant catalyst amount (50 mg) and constant concentration of the oxidant ((PMS) or (PDS) = 1 x 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 TiO_2-PMS-Catechol and for TiO_2-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:

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

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

$(Catechol)_0$ 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	13.37	9.12
2.0	10.00	8.12
3.0	9.00	7.37
4.0	8.37	7.12
5.0	7.75	6.75
6.0	6.50	5.62

TiO_2 = 50 mg/70ml; T = 30ºC; (PMS) = (PDS) = 1 x 10^{-3} mol dm^{-3}.

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 TiO_2 - PMS-catechol system the values of k and K are found to be 2.20 x 10^{-6} mol dm^{-3} s^{-1} and 86.66 dm^3 mol^{-1}, respectively. The values of k and K for TiO_2-PDS-catechol system are 1.30 x 10^{-8} mol dm^{-3} s^{-1} and 113.48 x 10^3 dm^3 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 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 TiO_2 = 50 mg/ 70 ml; T = 30 ^{0}C; (PMS) = (PDS) = 1 x 10^{-3} mol dm^{-3}

$1/(catechol)_0$ 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	7.27	10.96
0.50	5.00	6.15
0.33	3.70	4.52
0.25	2.98	3.51
0.20	2.58	2.96
0.16	2.56	2.96
k = (mol $dm^{-3}s^{-1}$)	3.10 x 10^{-6}	2.50 x 10^{-6}
K = (dm^{-3} mol^{-1})	107.95	9.473 x 10^3

Effect of catalyst amount

Experiments carried out with various amount of catalyst powders (20 – 100 mg) at constant (catechol) (1.0 x 10^{-3} mol dm^{-3}) and at constant concentration of oxidant 1.0 x 10^{-3} mol dm^{-3}) showed similar results for TiO_2-PMS-Catechol and TiO_2-PDS-catechol systems (Fig.5 and 6).

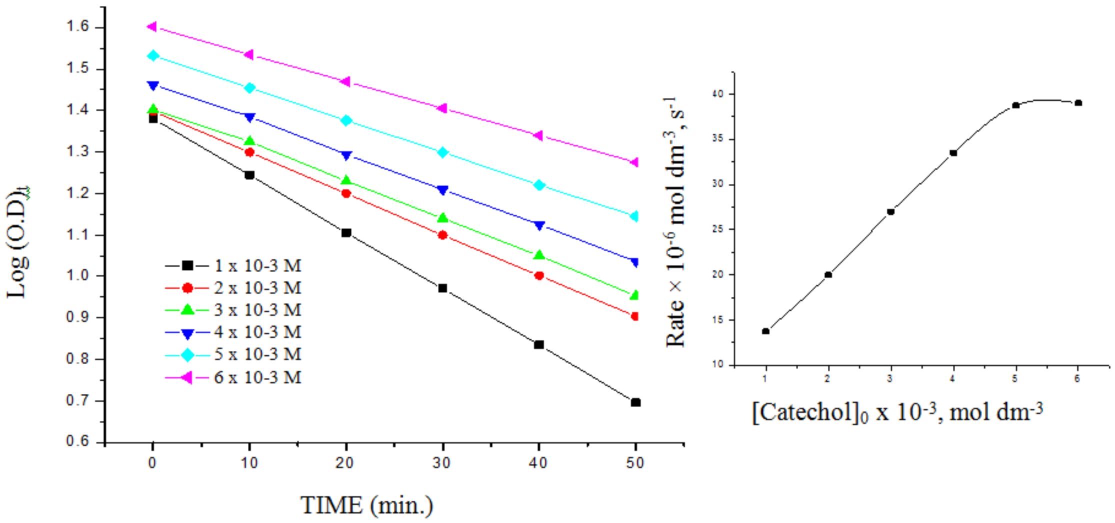


Fig.1. Log $(OD)_t$ vs time plot for the photodegradation of various amount of catechol (1- 6 x 10^{-3}M). (Catalyst) = 50 mg/70 ml and (PMS) = 1 x 10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate for various amounts of catechol

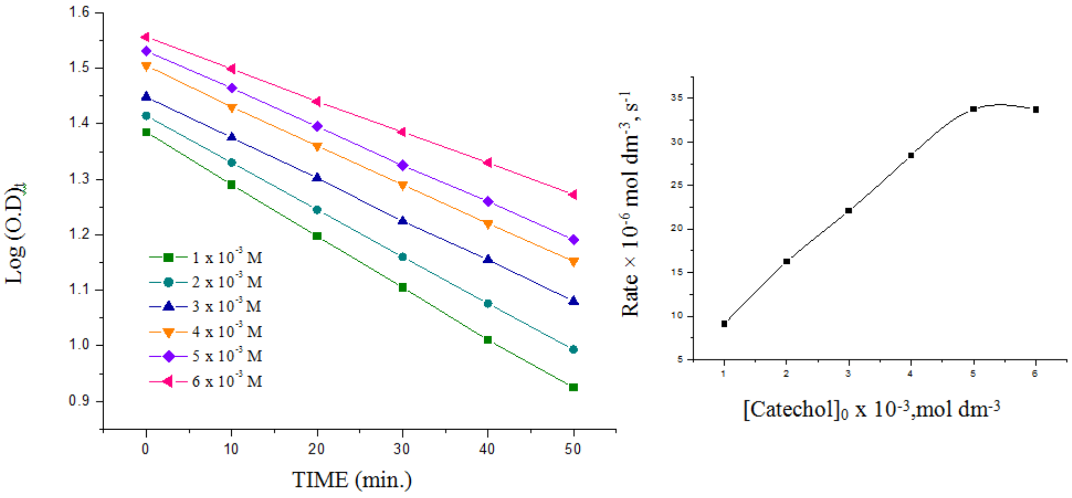


Fig.2. Log (OD)t vs time plot for the photodegradation of various amounts of catechol (1 - 6 x 10^{-3}M). (Catalyst) = 50 mg/ 70 ml and (PDS) = 1 x 10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate for various amounts of catechol

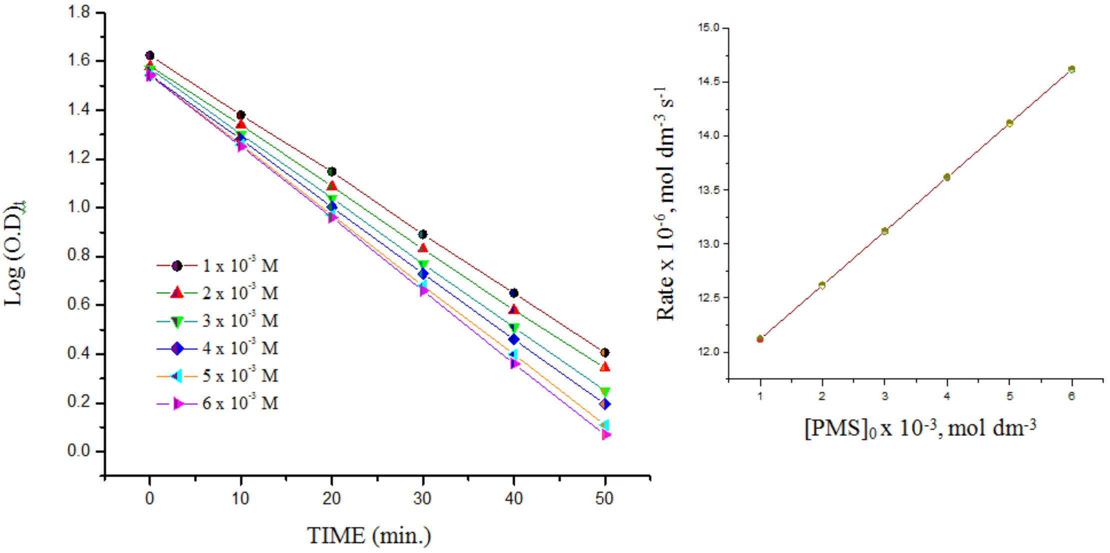


Fig.3. Log $(O.D)_t$ vs time plot for the photodegradation of catechol for various concentrations of PMS (1.0 – 6.0 x 10^{-3}M). (Catalyst) = 50 mg/70 ml and (Catechol) = 1 x 10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate of catechol for various concentrations of PMS

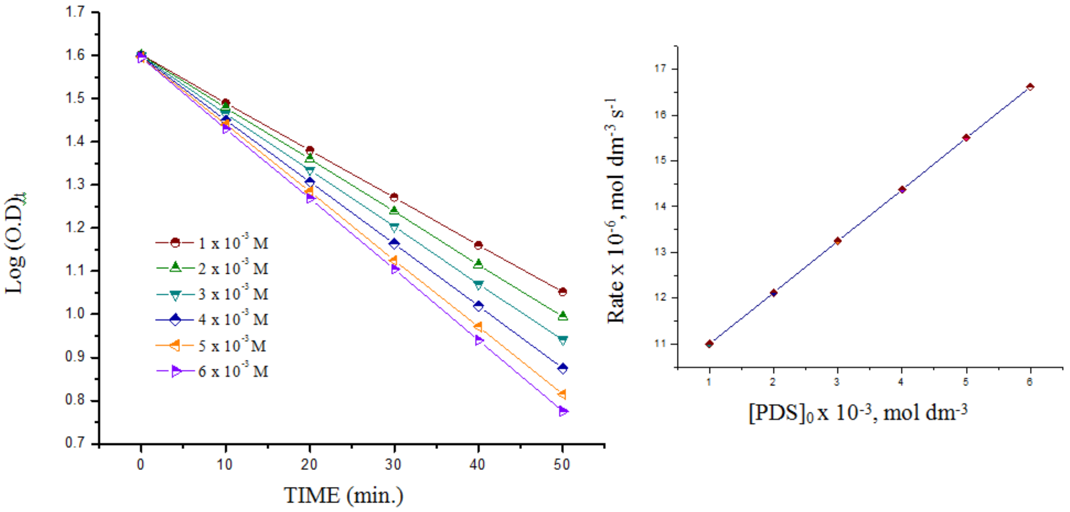


Fig.4. Log (O.D)t vs time plot for the photodegradation of catechol for various concentration of PDS (1.0 – 6.0 x 10^{-3} M). (Catalyzed) = 50 mg/70ml and (catechol) = 1 x10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate of catechol for various concentrations of PDS

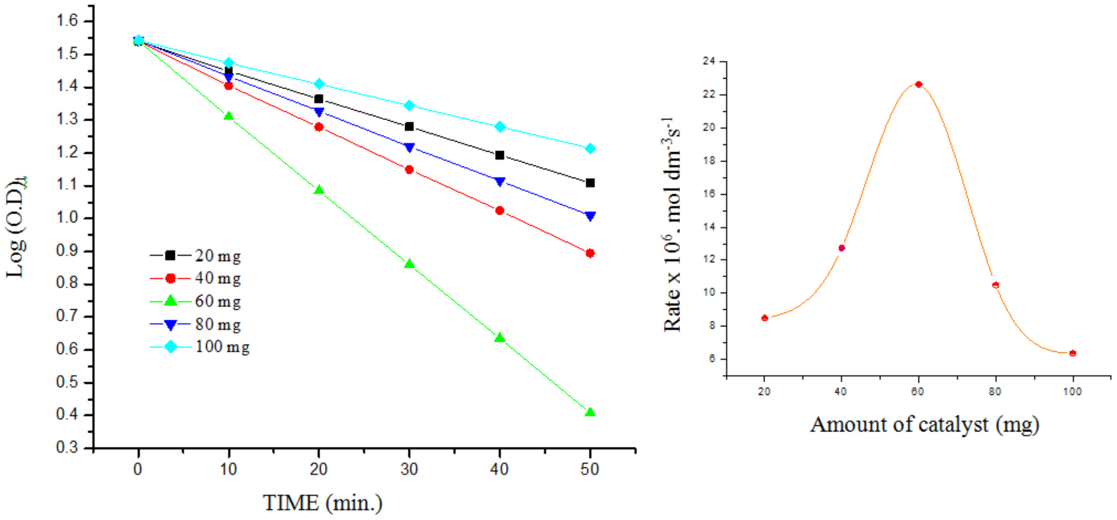


Fig.5. Log $(O.D)_t$ vs time plot for the photodegradation of catechol for various concentrations of TiO_2 (20-100 mg). (PMS) = 1 x 10^{-3} mol dm^{-3} and (catechol) = 1 x 10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate of catechol for various concentrations of TiO_2

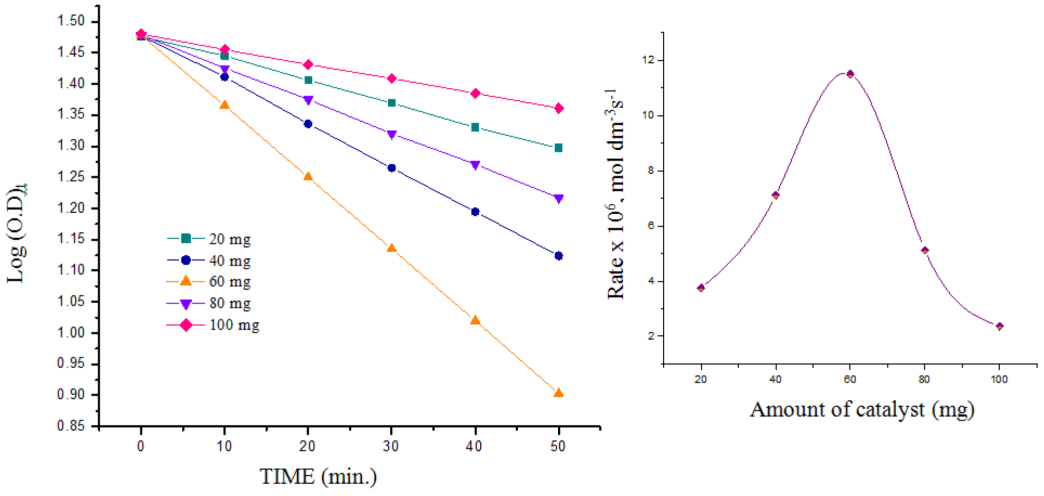


Fig.6. Log $(O.D)_t$ vs time plot for the photodegradation of catechol for various concentration of TiO_2 (20-100 mg). (PDS) = 1 x 10^{-3} mol dm^{-3} and (catechol) = 1 x 10^{-3} mol dm^{-3}. Inset shows plot of photodegradation rate of catechol for various concentration of TiO_2

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.

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 x 10^{-3} mol dm^{-3}) was obtained by comparing the results of the experiments carried out under identical conditions but with different oxidants (PMS and PDS (Oxidant) = 1 x10^{-3} mol dm^{-3}). Pure TiO_2 without any oxidants shows 28% degradation of catechol in 50 min, which is enhanced to 51% in the presence of PDS. PMS enhances the degradation of catechol up to 95% 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} (Dhanalakshmi *et al*., 2008; Maruthamuthu and Neta, 1977; Madhavan *et al*., 2006) and the key reactions are represented below.

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

System	k_1 x 10^3 s^{-1}
TiO_2-catechol	6.62
TiO_2-PDS-catechol	9.12
TiO_2-PMS-catechol	13.75

With PDS

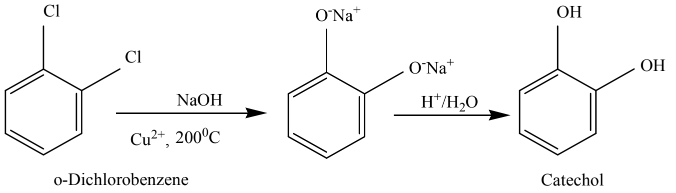
$$HOOSO_3^- + e^-_{CB} \longrightarrow SO_4^{\cdot -} + OH^- \text{ or } SO_4^{2-} + OH$$

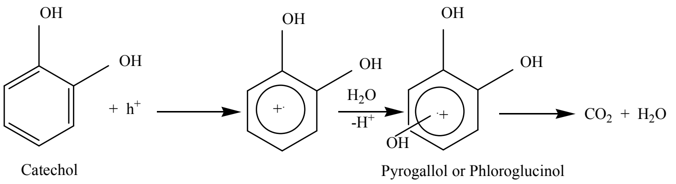
$$HOOSO_3^- + h^+_{VB} \longrightarrow SO_5^{\cdot -} + H^+$$

$$2SO_5^{\cdot -} \xrightarrow{H_2O} 2HSO_4^- + O_2$$

Mechanism

A possible mechanism for the photocatalytic degradation of catechol is as follows. It is obtained by hydrolysis of *o*-dichlorobenzene with dilute sodium hydroxide solution at 200^0C and in the presence of copper sulphate catalyst.





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

$$TiO_2 \xrightarrow[\lambda \geq 390\,nm]{h\upsilon} h^+_{VB} + e^-_{CB}$$

The atmospheric oxygen present in the solution can react with e^-_{CB} and prevent the recombination of electron – hole pairs (Izumi *et al*., 1980; Fujihira *et al*., 1982; Izumi *et al*., 1981):

$$O_2 + e^-_{CB} \longrightarrow O_2^{\cdot -}$$

Hydroxyl radical attacks catechol 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 catechol adsorbed on TiO_2 to give dihydroxycyclohexadienyl radicals via catechol radical cations, as has been proposed for the photocatalytic oxidation of o-Dichlorobenzene (Dhanalakshmi *et al*., 2008).

With these oxidants

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

$$S_2O_8^{2-} + e^-_{CB} \longrightarrow SO_4^{2-} + SO_4^{\cdot -}$$

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

Conclusion

The presence 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 rates were observed with PMS as oxidant indicating that PMS is a more efficient oxidant than PDS for the photocatalysed degradation of catechol.

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