



## Solar photocatalytic degradation of resorcinol a model endocrine disrupter in water using zinc oxide

S.K. Pardeshi\*, A.B. Patil

Department of Chemistry, University of Pune, Ganeshkhind, Pune 411007, India

### ARTICLE INFO

#### Article history:

Received 29 January 2008

Received in revised form 20 May 2008

Accepted 27 June 2008

Available online 5 July 2008

#### Keywords:

Photocatalytic degradation

Sunlight

Zinc oxide

Chemical oxygen demand

Resorcinol

### ABSTRACT

Photocatalytic degradation (PCD) of resorcinol a potent endocrine disrupting chemical in aqueous medium was investigated by ZnO under sunlight irradiation in a batch photoreactor. The influence of various parameters such as photocatalyst amount, initial concentration of resorcinol and pH was examined for maximum PCD of resorcinol. A considerable influence of pH upon the chemical oxygen demand (COD) disappearance was observed. In general, neutral or basic pH is favorable for COD removal of resorcinol. PCD intermediates were identified using FTIR and GC/MS. Two of the initial oxidation intermediates detected were 1,2,4-trihydroxy-benzene and 1,2,3-trihydroxy-benzene. FTIR studies revealed 1,2,4-trihydroxy-benzene as the major PCD intermediate. A working photodegradation mechanism is also suggested for PCD of resorcinol. This work envisages the great potential that sunlight mediated photocatalysis has in the removal of resorcinol from waste water.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

The majority of phenols are toxic substances, some have been classified as hazardous wastes, and some are known to be suspected carcinogens [1]. The direct or indirect exposure of some phenolic compounds viz. bisphenol A, 17- $\beta$ -estradiol, ethynylestradiol, alkyl phenols, diethyl stilbestrol, estrone, resorcinol, etc. can affect biological functions of living organisms regulated by endocrine systems. These compounds are listed as endocrine disrupting chemicals (EDCs) [2]. The implication that background level exposures of EDCs lead to an increase in frequency of cancers, reproductive deformities and developmental abnormalities has gained the attention of many groups in US, Europe and Asia [3,4]. Resorcinol is used in the manufacture of adhesives, dyes and as an ingredient in pharmaceutical preparations for the topical treatment of skin conditions. Therefore industrial waste water contains resorcinol as one of the hazardous materials, which needs to be eliminated by employing an effective technique [5]. Extensive studies on degradation of phenol have been reported in literature. However, very less amount of work has been reported on removal of EDCs. Recently it has been found that some microbes can easily consume phenol as sole source of carbon and energy but they cannot consume EDCs [6].

Conventional wastewater treatment methods such as chemical, physical, and biological processes are not always suitable for

treating moderate to high concentration wastewaters. Advanced oxidation processes (AOPs) are alternative techniques for destruction of phenolic compounds and many other organics in wastewater. These processes generally, involve UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub> or UV/Fenton's reagent for the oxidative degradation of contaminants [7]. Semiconductor mediated photocatalysis is a newly developed AOP, which can be conveniently applied for complete destruction of EDCs [8]. The process uses atmospheric oxygen as the oxidant and is carried out under ambient conditions utilizing a semiconductor catalyst. It has several advantages over conventional oxidation processes such as the complete mineralization of the pollutant, the utilization of near-UV light and no addition of chemicals. Metal oxide semiconductors such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, WO<sub>3</sub>, etc. have been attempted for the photocatalytic degradation of a wide variety of environmental contaminants [9]. When TiO<sub>2</sub> or ZnO particles are illuminated with near UV radiation, electron-hole pairs are generated within the metal oxide semiconductor. The valence band hole has an intensive reduction potential and it leads to the generation of •OH radicals that are known to be powerful and non-selective oxidizing agents which are responsible for photocatalytic degradation [10]. Titanium dioxide (TiO<sub>2</sub>) has been extensively investigated as one of the most active semiconductor photocatalysts in UV light. It is used for photocatalytic degradation of various organic compounds. Lam et al. [5] investigated the role of dissolved cupric ions in the photocatalytic oxidation of resorcinol in oxygenated aqueous suspension of Degussa P25 TiO<sub>2</sub> using UV light. Use of ultra violet light in bulk level, for the treatment of huge quantity of industrial effluents is not much feasible and economical. In the countries where ample amount of sunlight is available, photocatalysis involv-

\* Corresponding author. Tel.: +91 20 25601225x514; fax: +91 20 25691728.  
E-mail address: [skpar@chem.unipune.ernet.in](mailto:skpar@chem.unipune.ernet.in) (S.K. Pardeshi).

ing sunlight will be economical and preferable. Therefore, there is a need of effective photocatalyst which undertakes photocatalytic degradation of organic pollutants under sunlight or visible light irradiation. Recent studies have confirmed that zinc oxide exhibits more efficiency than  $\text{TiO}_2$  in visible light photocatalytic degradation of some organic compounds in aqueous solution [11]. Poullos et al. [12] studied photocatalytic degradation of Auramine O in aqueous suspension using ZnO and  $\text{TiO}_2$  separately in a batch reactor. They found that the rate of degradation of pollutants is faster with ZnO than with  $\text{TiO}_2$  (Degussa P25). The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than  $\text{TiO}_2$  [13]. Therefore it is of great interest to use solar light which contains ca. 43% of visible and ca. 4% of UV light, which is free and inexhaustible [14]. The present work focuses on the use of ZnO and solar radiation for effective elimination of resorcinol a model EDC at ambient temperature. Resorcinol is chosen since it exhibits a threat to the endocrine systems, where it has been shown to interfere with tri-iodothyronine (T3) and thyroxin (T4) metabolism, causing disruptions to thyroid activity [15].

## 2. Experimental

### 2.1. Materials

In the present study, zinc oxide (assay 99%), resorcinol (assay 99%), and other required chemicals are of analytical grade, obtained from Merck Limited, Mumbai, India and were used without further purification. The appropriate concentration of resorcinol solutions was prepared by using double distilled water. The pH of the solutions was adjusted to desired values from 4 to 10 by using dilute solution of  $\text{H}_2\text{SO}_4$  (0.01N) and NaOH (0.01N).

### 2.2. Photocatalytic degradation experiments

The solar light assisted photocatalytic degradation (PCD) of resorcinol over ZnO surface was carried out in a slurry form. The PCD of resorcinol was investigated by irradiating the resorcinol solutions with sunlight in the absence and presence of ZnO photocatalyst. All PCD experiments were carried out in duplicate and at ambient temperature. It should also be noted that no external supply of oxygen was employed. Pure resorcinol (Merck, 99%) was dissolved in double distilled water to obtain desired concentration solutions. In all PCD experiments, 100 mL resorcinol solution of appropriate concentration was taken in photocatalytic reactor vessel. A known quantity of photocatalyst was added and mixture was agitated in an ultrasonic bath for 5 min to obtain uniform suspension. Initial pH of suspension was recorded. The whole setup was then placed in sunlight with constant stirring for a specific period of time. When PCD reaction was stopped after the desired time of sunlight irradiation, the whole suspension was centrifuged at a speed of 5000 rpm for 10 min (Remi, India) and then filtered through a 0.45  $\mu\text{m}$  Polytetrafluoro ethylene (PTFE) filter. The liquid portion was used for UV absorbance and COD measurement. The residue (ZnO adsorbed resorcinol and intermediates) was used for FTIR analysis, after drying at 60 °C.

### 2.3. Equipments and light source

Photocatalytic reactions were carried out in batch photoreactor which configures with cylindrical glass vessel (200 mL capacity), condensation tube, quartz cool trap and magnetic stirrer. The extent of PCD at an interval of 1 h sunlight irradiation was primarily checked by means of decrease in absorbance of resorcinol ( $\lambda_{\text{max}} = 274 \text{ nm}$ ) on UV–vis spectrophotometer (UV-1601, Shimadzu). Progress of PCD reaction and identification of

intermediates were examined by FTIR spectra, obtained with Shimadzu FTIR-8400 spectrometer equipped with KBr beam splitter. Existence of PCD intermediates was identified by GC/MS (GCMS-QP5050, Shimadzu) and complete mineralization of resorcinol was ensured by chemical oxygen demand (COD) reduction method. The COD determination tests were performed according to standard dichromate method using COD digester [16]. The PCD efficiency was calculated from the following expression (1)

$$\eta = \frac{\text{COD}_i - \text{COD}_t}{\text{COD}_i} \times 100 \quad (1)$$

where  $\eta$  is the photocatalytic degradation efficiency,  $\text{COD}_i$  the initial chemical oxygen demand, and  $\text{COD}_t$  is the chemical oxygen demand at time  $t$ . pH of suspension was measured with pH meter (EUTECH-pH510)

All PCD experiments were performed under irradiation of sunlight between 9 a.m. and 5 p.m. during summer season (December to March). The intensity of sunlight was periodically checked with ferrioxalate actinometry [17]. The average photon flux calculated for entire duration of irradiation of sunlight was found to be  $1.7 \times 10^{-7} \text{ Einstein s}^{-1} \text{ cm}^{-2}$ .

The reusability of the photocatalyst was evaluated by reclaiming the photocatalyst after PCD reaction in the batch mode, washing, drying in electric oven at 110 °C and using it for resorcinol degradation under similar experimental conditions.

### 2.4. Dark adsorption studies

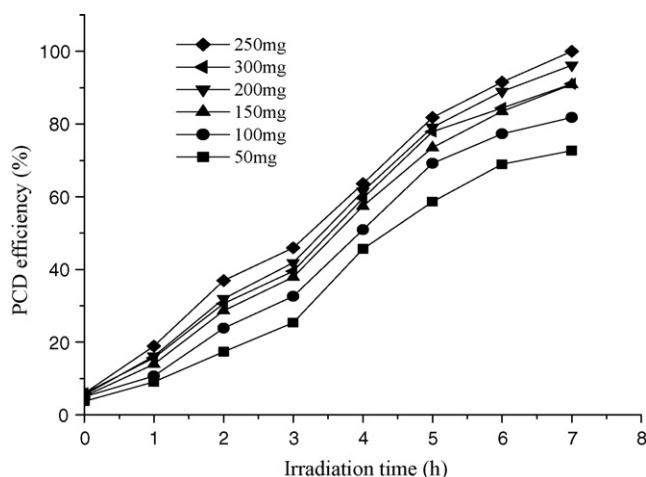
The adsorption of resorcinol in dark on the surface of ZnO was investigated. In typical experiments, 100 mL of resorcinol solution (100 ppm) was taken in batch photoreactor vessel. Natural pH of this solution was 6.8. To this solution 250 mg ZnO was added and resulting suspension was stirred in dark for 7 h. Then the suspension was centrifuged and filtered. Solid was dried at 60 °C and analyzed for FTIR. Filtrate was used for UV–vis absorbance measurement and COD determination.

## 3. Results and discussion

The photocatalytic nature of ZnO, effect of the amount of photocatalyst, substrate concentration, irradiation time and pH on the efficiency of resorcinol degradation were examined and the results are discussed in the following subsections.

### 3.1. Effect of the photocatalyst amount

Blank experiments were carried out without photocatalyst to examine to what extent the resorcinol 'photolyze' if photocatalyst was not used. There was no evidence of PCD of resorcinol in aqueous solution in the absence of ZnO. When aqueous solution of resorcinol containing ZnO was irradiated with sunlight, PCD of resorcinol was observed. The optimum amount of photocatalyst required for maximum PCD of resorcinol was examined in slurry method by varying the photocatalyst amount from 50 to 300 mg in 100 mL resorcinol solution of concentration 50–300 ppm at its natural pH. The PCD of resorcinol was found to increase with increase in amount of ZnO up to 250 mg, further increase in photocatalyst amount showed negative effect. The results obtained are illustrated in Fig. 1. At lower photocatalyst loading level than the optimum amount, photonic absorption controls the efficiency of PCD due to limited surface area of photocatalyst therefore efficiency of PCD increased linearly with increase in photocatalyst loading up to 250 mg (Table 1). The increase in the amount of photocatalyst increased the number of active sites on the photocatalyst surface, which in turn increased the number of hydroxyl, and superoxide radicals (Scheme 1). When



**Fig. 1.** Effect of the amount of photocatalyst on PCD efficiency [resorcinol] = 100 ppm; initial COD = 170.72 ppm; initial pH of suspension = 6.8; intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ .

**Table 1**

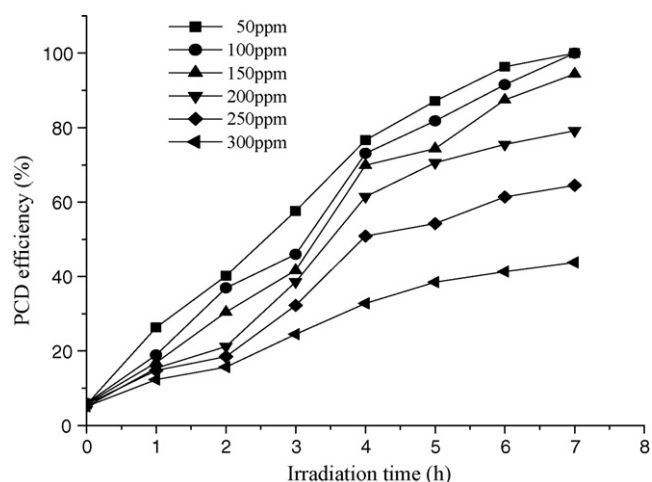
Effect of photocatalyst amount on PCD efficiency ([resorcinol] = 100 ppm; initial COD = 170.72 ppm; initial pH of suspension = 6.8; intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ )

[ZnO] (mg/100 mL)	Sunlight irradiation time (h)							
	0	1	2	3	4	5	6	7
50								
COD <sub>t</sub> <sup>a</sup>	164	155	141	127	93	71	53	46
$\eta^b$ (%)	3.7	09	17.3	25.4	45.7	58.6	69	73
100								
COD <sub>t</sub> <sup>a</sup>	162	153	130	115	84	53	39	31
$\eta^b$ (%)	05	11	24	32.6	51	69	77	82
150								
COD <sub>t</sub> <sup>a</sup>	162	147	122	106	73	45	28	15.5
$\eta^b$ (%)	05	14	29	38	57	73	83.5	91
200								
COD <sub>t</sub> <sup>a</sup>	161	143	116	99	66	36	19	6.5
$\eta^b$ (%)	5.5	16	32	42	61.5	79	88.5	96
250								
COD <sub>t</sub> <sup>a</sup>	161	138	108	92	62	31	14.4	0
$\eta^b$ (%)	06	19	37	46	64	82	91.5	100
300								
COD <sub>t</sub> <sup>a</sup>	160	144	118	103	69	38	27	15
$\eta^b$ (%)	06	16	31	39.5	60	78	84	91

<sup>a</sup> Chemical oxygen demand at time  $t$  (ppm).

<sup>b</sup> PCD efficiency.

the quantity of ZnO was increased above the limiting value, the PCD efficiency decreased. This may be due to an increase in the turbidity of suspension, which affects the penetration of sunlight as a result of increased screening effect and scattering of light [18]. Thus



**Fig. 2.** Effect of concentration of resorcinol on PCD efficiency [ZnO] = 250 mg/100 mL; initial pH of suspension = 6–7 (natural pH); intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ .

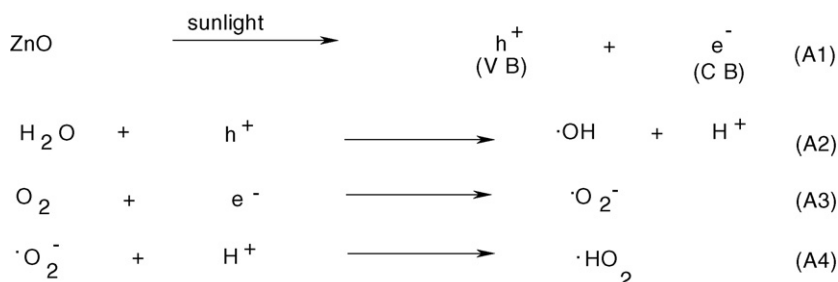
250 mg of ZnO was selected as the optimum amount for the study of other parameters.

### 3.2. Effect of the initial concentration of resorcinol

The PCD of resorcinol at different initial concentrations in the range 50–300 ppm was investigated as a function of sunlight irradiation time at the natural pH of suspension (without adjustment). The results are illustrated in Fig. 2. PCD was found to be inversely affected by concentration of resorcinol (Table 2). This may be due to the fact that as the initial concentration of resorcinol increases, more and more resorcinol molecules are adsorbed on the surface of ZnO, but the number of  $\cdot OH$  and  $\cdot O_2^-$  radicals formed (Scheme 1) on the surface of ZnO and the irradiation time are constant. Therefore relative number of  $\cdot OH$  and  $\cdot O_2^-$  radicals available for attacking the substrate becomes less in comparison to resorcinol molecules. Hence photodegradation decreases. Also, as the concentration of resorcinol increases, the photons get interrupted before they can reach the photocatalyst surface hence absorption of photons by the photocatalyst decreases and consequently the PCD reduces. Hence under given set of conditions, the maximum concentration of resorcinol that could be degraded by 250 mg of ZnO is found to be 100 ppm. Thus 100 ppm resorcinol was selected as optimum concentration for the study of other parameters.

### 3.3. Effect of initial pH

Most of the semiconductor oxides are amphoteric in nature; therefore, the pH of suspension is an important parameter governing the PCD reaction taking place on semiconductor particle



**Scheme 1.**

**Table 2**  
Effect of concentration of resorcinol on PCD efficiency ([ZnO] = 250 mg/100 mL; initial pH of suspension = 6–7 (natural pH); intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ )

[Resorcinol]		Sunlight irradiation time (h)								
(ppm)	COD <sub>t</sub> <sup>a</sup>		0	1	2	3	4	5	6	7
50	86	COD <sub>t</sub> <sup>b</sup>	81	63	51	36.5	20	11	3.2	0
		$\eta^c$ (%)	5.6	26	40	57.6	76.6	87	96	100
100	171	COD <sub>t</sub> <sup>b</sup>	161	138	108	92	62	31	14.4	0
		$\eta^c$ (%)	06	19	37	46	64	82	91.5	100
150	280	COD <sub>t</sub> <sup>b</sup>	263	232	194	163	84	72	35	15.5
		$\eta^c$ (%)	06	17	30.4	41.6	70	74	87.5	94
200	369	COD <sub>t</sub> <sup>b</sup>	350	312	291	227	142	109	90.4	77
		$\eta^c$ (%)	05	15.4	21	38.5	61	70.5	75.5	79
250	482	COD <sub>t</sub> <sup>b</sup>	454	410	392	326	236	220	186	171
		$\eta^c$ (%)	06	14.8	18.5	32	51	54	61.4	64.5
300	553	COD <sub>t</sub> <sup>b</sup>	524	485	466	417	371	340	324	311
		$\eta^c$ (%)	05	12	15.6	24.5	32.8	38.5	41	43.8

<sup>a</sup> Initial chemical oxygen demand (ppm).

<sup>b</sup> Chemical oxygen demand at time *t* (ppm).

<sup>c</sup> PCD efficiency.

surface. It influences surface charge properties of photocatalyst [19]. The effect of initial pH of suspension on PCD efficiency was studied from 4 to 10 with 100 ppm resorcinol solution and 250 mg/100 mL ZnO loading. The pH of the suspension was adjusted before irradiation of sunlight and it was not controlled during the course of reaction. All other parameters were kept constant.

In acidic medium less PCD of resorcinol was observed (Table 3). This may be due to slight dissolution of ZnO at low pH [20]. The extent of PCD of resorcinol was found to increase with increase in initial pH of suspension exhibiting maximum PCD at pH 9. (Fig. 3). It

**Table 3**  
Effect of initial pH on PCD efficiency ([resorcinol] = 100 ppm; initial COD = 170.72 ppm; [ZnO] = 250 mg/100 mL; intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ )

pH	Sunlight irradiation time (h)								
	0	1	2	3	4	5	6	7	
4	COD <sub>t</sub> <sup>a</sup>	161	154.5	144.5	122	106	97	83	67
	$\eta^b$ (%)	5.6	9.5	15.4	28.5	38	43	51.4	61
5	COD <sub>t</sub> <sup>a</sup>	160.8	151	134.4	117.5	102.5	92	77.4	63
	$\eta^b$ (%)	06	11.5	21.3	31.2	40	46.2	54.7	63
6	COD <sub>t</sub> <sup>a</sup>	160.6	148.3	121	102	85.6	71.4	56.2	42
	$\eta^b$ (%)	06	13.2	29	40.4	50	58	67	75.3
6.8 <sup>c</sup>	COD <sub>t</sub> <sup>a</sup>	160.6	138.4	108	92	62	31	14.4	0
	$\eta^b$ (%)	06	19	37	46	64	82	91.6	100
7	COD <sub>t</sub> <sup>a</sup>	160.6	137	107	89.4	60	21	6.4	0
	$\eta^b$ (%)	5.9	19.7	37.3	47.7	64.8	87.6	96.3	100
8	COD <sub>t</sub> <sup>a</sup>	160.6	122	73	62	31.6	14.4	2.4	0
	$\eta^b$ (%)	06	28.5	57.4	63.7	81.5	91.6	98.6	100
9	COD <sub>t</sub> <sup>a</sup>	161	121	69.4	58.8	24.6	6.4	0	0
	$\eta^b$ (%)	06	29	59.4	65.5	85.6	96.4	100	100
10	COD <sub>t</sub> <sup>a</sup>	161	120.4	67.4	57.7	21.4	4.8	0	0
	$\eta^b$ (%)	06	29.5	60.5	66.2	87.5	97.2	100	100

<sup>a</sup> Chemical oxygen demand at time *t* (ppm).

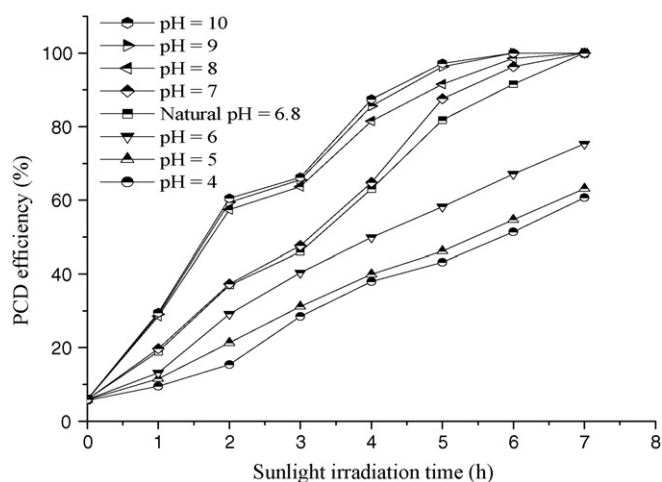
<sup>b</sup> PCD efficiency.

<sup>c</sup> Natural pH of 100 ppm resorcinol solution.

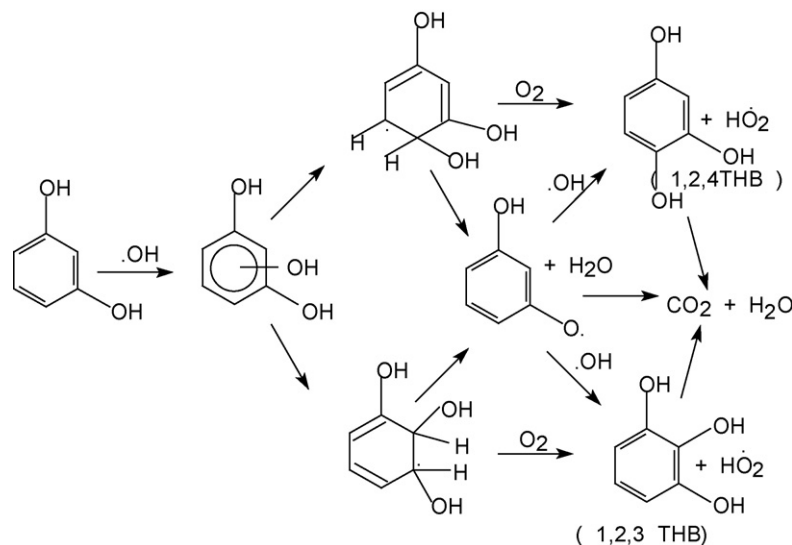
is important to note that, after pH 9 no appreciable change in PCD of resorcinol was observed. Sakthivel et al. [21] have observed a similar trend with ZnO commenting that the acid base property of the metal oxide surface has considerable implications upon the photocatalytic activity. In alkaline medium, excess of hydroxyl anions facilitate photogeneration of  $\bullet OH$  radicals which is accepted as primary oxidizing species responsible for PCD [22,23]. This increases PCD efficiency. The pH at zero point charge (zpc) of ZnO is  $9.0 \pm 0.3$ . When the suspension  $pH > pH_{zpc}$ , the surface of ZnO is negatively charged [18]. As a result, hydroxyl anions may be repelled away from the negatively charged ZnO surface. Therefore PCD efficiency at pH 10 remained nearly same as that at pH 9. The suspension pH up to 9 ( $pH_{zpc}$  of ZnO) is equally favorable for generation of  $\bullet OH$  radicals and adsorption of substrate molecules on the surface of ZnO which attributes to the increase in PCD efficiency. Natural pH of 100 ppm resorcinol is 6.8. This solution has also showed 100% degradation therefore other parameters were studied at natural pH of 100 ppm resorcinol.

### 3.4. Effect of irradiation time

The PCD of 100 ppm resorcinol in sunlight was found to increase with increase in irradiation time and within 7 h there was 100%



**Fig. 3.** Effect of initial pH on PCD efficiency [resorcinol] = 100 ppm; initial COD = 170.72 ppm; [ZnO] = 250 mg/100 mL; intensity of sunlight  $1.7 \times 10^{-7}$  Einstein  $s^{-1} cm^{-2}$ .



Scheme 2.

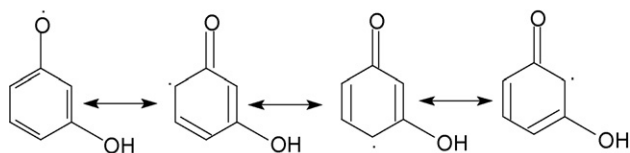
degradation. When 100 ppm resorcinol solution along with ZnO was magnetically stirred for 7 h in the absence of light (dark), negligible (6%) photo degradation was observed (Table 2). For reference it is considered as zero hour irradiation. Thus zinc oxide is an effective photocatalyst in sunlight.

#### 4. Photocatalytic degradation mechanism

When milky white suspension of aqueous solution of resorcinol and ZnO was irradiated with sunlight, the white suspension gradually changed to brown. The intensity of brown color was found to increase up to 4 h irradiation and then it decreased. For the resorcinol solution up to 100 ppm, after 7 h of irradiation white suspension reappeared. The brown color of the photoreaction mixture was probably due to formation of various reaction intermediates viz. 3-hydroxyphenoxyl radical, 1,2,4-trihydroxybenzene (1,2,4-THB), 1,2,3-trihydroxybenzene (1,2,3-THB), etc. (Scheme 2).

The excitation of ZnO by solar energy leads to the formation of an electron-hole pair (Scheme 1, A1). The hole combines with water to form  $\bullet\text{OH}$  radicals while electron converts oxygen to super oxide radical ( $\bullet\text{O}_2^-$ ), a strong oxidizing species (Scheme 1, A2–A4).

When resorcinol molecules are adsorbed on the surface of ZnO particle, there is activation of these molecules by reaction with  $\bullet\text{OH}$  radical, formed during photoexcitation of ZnO. The hydroxyl radical shows electrophilic character and prefers to attack electron rich *ortho* or *para* carbon atoms of resorcinol. It forms trihydroxycyclohexadienyl (TCHD) radicals that undergo further reaction with dissolved oxygen to yield trihydroxy benzenes (THBs) which are colored intermediates, with simultaneous generation of  $\text{HO}_2\bullet$  radical. TCHD radicals are also converted to 3-hydroxyphenoxyl radical as shown in Schemes 2 and 3. The existence of 1,2,3-THB and 1,2,4-THB was confirmed by GC/MS and FTIR which is discussed in following sections.



Scheme 3.

These 3-hydroxyphenoxyl radicals can also react with  $\bullet\text{OH}$  to form THBs. The direct combination of two hydroxyl phenoxyl radicals can lead to intermediates with two aromatic rings attached to each other by a single bond [24].

#### 5. Measurements of spectral changes

After irradiation of sunlight for certain hours, the suspension was immediately centrifuged at 5000 rpm for 10 min, and filtered through a 0.45  $\mu\text{m}$  pore size filter to remove the ZnO particles. The liquid portion was used to check PCD by measuring absorbance and to ensure complete mineralization by measuring COD. The filtered solid was used for FTIR analysis after drying in air at 60 °C. The change in absorption spectra of resorcinol during ZnO mediated photocatalysis of resorcinol at 1 h irradiation intervals is shown in Fig. 4. The decrease in the absorption of resorcinol at  $\lambda_{\text{max}} = 274 \text{ nm}$  indicates a rapid degradation of resorcinol. In order to confirm the role of ZnO and sunlight together, PCD was studied in sunlight irradiation for 7 h in the absence of ZnO and in dark for

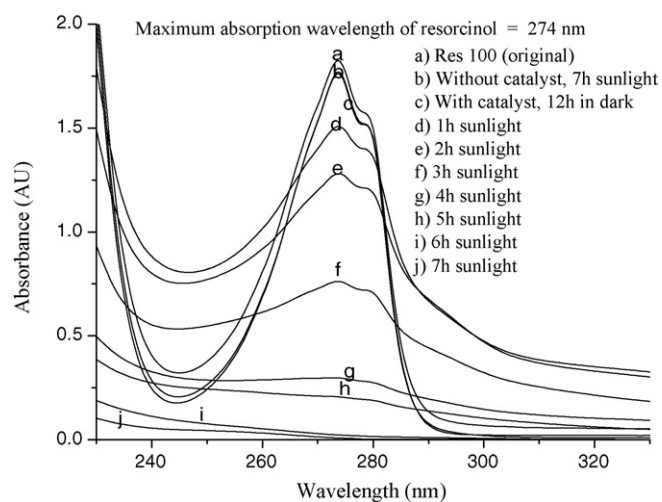
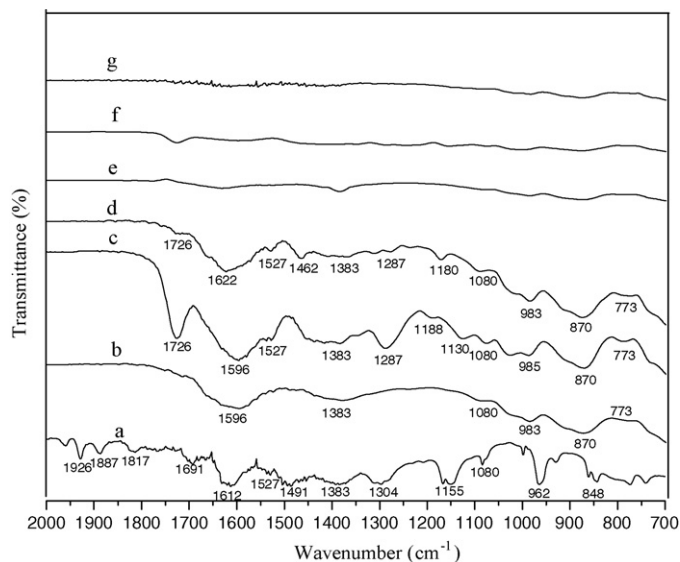


Fig. 4. UV-vis spectral changes recorded during PCD of resorcinol at different irradiation time: [resorcinol]=100 ppm; initial COD=170.72 ppm; [ZnO]=250 mg/100 mL; initial pH of suspension=6.8;  $\lambda_{\text{max}}=274 \text{ nm}$  intensity of sunlight  $1.7 \times 10^{-7} \text{ Einstein s}^{-1} \text{ cm}^{-2}$ .





**Fig. 5.** The FTIR spectra of (a) pure resorcinol; ZnO-adsorbed resorcinol and PCD intermediates after (b) 1 h sunlight irradiation; (c) 3 h sunlight irradiation; (d) 5 h sunlight irradiation; (e) 7 h sunlight irradiation; (f) ZnO-adsorbed resorcinol in dark; (g) pure ZnO.

7 h in presence of ZnO. PCD of these two samples was found to be negligible and absorbance of these samples nearly matches to that of original resorcinol solution (Fig. 4a–c). In the presence of ZnO and sunlight, absorbance at 274 nm decreased with increase in irradiation time and finally become zero at 7 h irradiation (Fig. 4d–j).

The FTIR spectra of pure resorcinol and photocatalyst samples collected after variable time of sunlight irradiation are shown in Fig. 5. Changes were observed in the FTIR spectra with respect to those obtained at  $t = 0$  (Fig. 5a). These spectra reflect the progressive degradation of adsorbed resorcinol molecules and PCD intermediates with time. The intense, broad band near  $3385\text{ cm}^{-1}$  (not shown in figure) represents the hydrogen bonded O–H stretching vibrations of resorcinol. The bands at  $1383$  and  $1190\text{--}1155\text{ cm}^{-1}$  (Fig. 5a–d) are resulting from the interaction between O–H in plane bending and aromatic C–OH stretching vibrations. The strong band near  $1612\text{ cm}^{-1}$  is assigned for C=C conjugation and skeletal vibrations of benzene ring (Fig. 5a–d). The intensity of above mentioned bands decreases with increase in sunlight irradiation time and practically disappears after 7 h irradiation (Fig. 5a–e).

In 3 h sunlight irradiation sample new bands at  $1726$  and  $1287\text{ cm}^{-1}$  appear (Fig. 5c) which are most probably due to 'C=O' stretching vibrations of hydroxyl phenoxy intermediate formed (Scheme 2). The intensity of  $1383$  and  $1190\text{--}1155\text{ cm}^{-1}$  bands decreased in 3 h irradiated sample (Fig. 5c) which may be due to conversion of one of the 'aromatic-OH' group to 'C=O' group. The bands at  $1726$  and  $1287\text{ cm}^{-1}$  are absent in pure resorcinol spectra (Fig. 5a) but then appear in 3 h irradiated sample (Fig. 5c). This supports generation of hydroxyl phenoxy radical as a PCD intermediate during irradiation of sunlight (Scheme 2). The intensity of  $1726$  and  $1287\text{ cm}^{-1}$  bands decreases with increase in irradiation time. The characteristic bands of carbonyl group completely disappear in 7 h irradiated sample (Fig. 5e). The FTIR spectra of 7 h irradiated sample and that of pure ZnO match appreciably (Fig. 5e and g) which indicates that after 7 h irradiation of sunlight there is 100% degradation of resorcinol. An FTIR spectrum of 7 h dark adsorption sample (Fig. 5f) is also nearly similar to that of pure ZnO spectra. This supports negligible adsorption and degradation of resorcinol in dark.

**Table 4**

Reuse of photocatalyst ([Resorcinol] = 100 ppm; initial COD = 170.72 ppm; amount of recovered photocatalyst used = 250 mg/100 mL; initial pH = 6.8; sunlight irradiation time = 7 h)

Photodegradation batch	Photocatalyst <sup>a</sup>	Final COD (ppm)	PCD efficiency ( $\eta$ ) (%)
1	Z	0	100
2	Z <sub>1</sub>	0	100
3	Z <sub>2</sub>	0	100
4	Z <sub>3</sub>	7.1	96.15
5	Z <sub>4</sub>	14.95	91.89

<sup>a</sup> Z is original ZnO (Merck); Z<sub>1</sub>, Z<sub>2</sub>, Z<sub>3</sub> and Z<sub>4</sub> are recovered ZnO photocatalysts obtained after first, second, third and fourth photocatalytic degradation experiments, respectively.

In pure resorcinol, the weak sharp band at  $962\text{ cm}^{-1}$  and medium band at  $848\text{ cm}^{-1}$  are the characteristic bands of 'C–H' in plane bending and 'C–H' out of plane bending vibrations of phenyl ring of resorcinol. The intensity of  $962\text{--}985\text{ cm}^{-1}$  band decreases with irradiation time and disappears after 7 h irradiation of sunlight (Fig. 5a–e).

After 1 h sunlight irradiation a new, strong band appears at  $870\text{ cm}^{-1}$  (Fig. 5b–d) which may be due to C–H out of plane bending vibrations of two adjacent H-atoms of 1,2,4-tri-substituted-benzene ring. This band strongly supports the formation of 1,2,4-trihydroxy-benzene intermediate during PCD reaction (Scheme 2). This was also confirmed by GC–MS. Moreover, the intensity of  $870\text{ cm}^{-1}$  band slightly increases from 1 to 3 h and then decreases with increase in irradiation time and disappears after 7 h irradiation in sunlight (Fig. 5b–d). This indicates that the formation of intermediates is maximum up to 4 h irradiation. From 1 to 5 h sunlight irradiation a band at  $773\text{ cm}^{-1}$  appears with very low intensity (Fig. 5b–d) which is the characteristic band of 'C–H' out of plane bending vibrations for 1,2,3-tri-substituted-benzene ring of 1,2,3-THB. The existence of 1,2,3-THB was confirmed by GC–MS. As compared to  $870\text{ cm}^{-1}$  band the intensity of band at  $773\text{ cm}^{-1}$  is very low which supports the formation of 1,2,4-THB as a major intermediate and 1,2,3-THB as a minor intermediate (Scheme 2). It means para attack of  $\cdot\text{OH}$  radical dominates over *ortho* attack. It also supports the instability of 1,2,3-THB in comparison to 1,2,4-THB.

## 6. Reuse of photocatalyst

At the time of study of effect of various parameters, fresh ZnO (Merck) was used for every photo catalytic degradation experiment. Reuse of ZnO was separately studied, by keeping all other parameters constant. During this study, after sunlight irradiation for 7 h, every photoreaction mixture was centrifuged and filtered. Filtrate was used for COD determination and ZnO residue was washed several times with double distilled water in ultrasonic bath followed by filtration and drying at  $110^\circ\text{C}$  in an electric oven. Recovered ZnO was then reused for new photo degradation batch, without any further treatment such as heating in any kind of furnace. All photocatalytic degradation experiments are carried out in duplicate, under sunlight. Activity of recycled ZnO was found to retain even after fifth photo degradation experiment (Table 4). The reusability of ZnO is due to its stability in neutral solution and negligible photocorrosion [8].

## 7. Conclusions

In the present investigation ZnO was found to be a better photocatalyst in sunlight for degradation of resorcinol.

(1) Zinc oxide photocatalyst was found to be inactive in dark.

- (2) Resorcinol solutions of lower concentration were completely mineralized by photocatalytic degradation on the surface of ZnO under irradiation of sunlight.
- (3) The photocatalytic degradation of resorcinol was favorable in neutral and basic solutions.
- (4) According to FTIR spectral study, 1,2,4-trihydroxy benzene was identified as a major intermediate.
- (5) ZnO can be reused five times as it undergoes photocorrosion only to a negligible extent.
- (6) Higher concentration solutions of phenol may be completely mineralized by modified ZnO, which is the interest of our current research.

## References

- [1] K. Verschuere, Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Co., New York, 1977.
- [2] J.J. Amaral, Mendes, The endocrine disrupters: a major medical challenge, Food Chem. Technol. 40 (2002) 781–788.
- [3] P.T.C. Harrison, P. Holmes, C.D.N. Humfrey, Reproductive health in humans and wildlife: are adverse trends associated with environmental chemical exposure? Sci. Total Environ. 205 (1997) 97–106.
- [4] R.J. Kavlock, Overview of endocrine disruptor research activity in the United States, Chemosphere 39 (8) (1999) 1227–1236.
- [5] S.W. Lam, K. Chiang, T.M. Lim, R. Amal, G.K.-C. Low, Effect of charge trapping species of cupric ions on the photo catalytic oxidation of resorcinol, Appl. Catal. B: Environ. 55 (2005) 123–132.
- [6] A. Fialová, E. Boschke, T. Bley, Rapid monitoring of the biodegradation of phenol-like compounds by the yeast *Candida maltosa* using BOD measurements, Int. Biodeteriorat. Biodegradat. 54 (2004) 69–76.
- [7] G. Chen, L. Lei, P.L. Yue, Wet oxidation of high-concentration reactive dyes, Ind. Eng. Chem. Res. 38 (1999) 1837–1843.
- [8] S. Lathasree, B. Nageswara Rao, V. Sivashankar, K. Sadasivam, Rengaraj, Heterogeneous photocatalytic mineralization of phenols in aqueous solutions, J. Mol. Catal. A: Chem. 223 (2004) 101–105.
- [9] T. Oppenlander, Photochemical Purification of Water and Air, Wiley-VCH, Weinheim, 2003.
- [10] A. Mills, S. LeHunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. 108 (1) (1997) 1–35.
- [11] B. Dindar, S. Icli, Unusual photo reactivity of zinc oxide irradiated by concentrated sunlight, J. Photochem. Photobiol. A: Chem. 140 (2001) 263–268.
- [12] I. Poullos, A. Avranas, E. Rekliti, A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Technol. Biotechnol. 75 (3) (2000) 205–212.
- [13] S. Sakthivel, B. Neppolian, M. Palanichmy, B. Arabindoo, V. Murugesan, Photocatalytic degradation of leather dye Acid green 16 using ZnO in the slurry and thin film forms, Indian J. Chem. Technol. 6 (1999) 161–165.
- [14] S. Sakthivel, H. Kish, Photocatalytic and photo electrochemical properties of nitrogen-doped titanium dioxide, Chem. Phys. Chem. 4 (2003) 487–490.
- [15] S.W. Lam, K. Chiang, T.M. Lim, R. Amal, G.K.-C. Low, The effect of platinum and silver deposits in the photocatalytic oxidation of resorcinol, Appl. Catal. B: Environ. 72 (2007) 363–372.
- [16] J.T. Bellaire, G.A. Parr-Smith, Standard Methods for the Examination of Water and Wastewater, 17th ed., Am Public Health Association, Washington, DC, 1985.
- [17] C.G. Hatchard, C.A. Parker, A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer, Proc. R. Soc. (Lond.) A235 (1956) 518.
- [18] S. Anandan, A. Vinu, N. Venkatachalam, B. Arabindoo, V. Murugesan, Photocatalytic activity of ZnO impregnated H $\beta$  and mechanical mix of ZnO/H $\beta$  in the degradation of monocrotophos in aqueous solution, J. Mol. Catal. A: Chem. 256 (2006) 312–320.
- [19] F. Zhang, J. Zhao, T. Shan, H. Hidaka, E. Pelizzetti, N. Serpone, TiO $_2$ -assisted photodegradation of dye pollutants. II. Adsorption and degradation kinetics of eosin in TiO $_2$  dispersions under visible light irradiation, Appl. Catal. B: Environ. 15 (1998) 147–156.
- [20] M.A. Behnajady, N. Modishahla, R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst, J. Hazard. Mat. B 133 (2006) 226–232.
- [21] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO $_2$  Sol, Energy Mater. Sol. Cells 77 (2003) 65–82.
- [22] M. Muruganandham, M. Swaminathan, Solar photocatalytic degradation of a reactive azo dye in TiO $_2$ -suspension Sol, Energy Mater. Sol. Cells 81 (2004) 439–457.
- [23] A.A. Khodja, T. Sehili, J.-F. Pilichowski, P. Boule, Photocatalytic degradation of 2-phenylphenol on TiO $_2$  and ZnO in aqueous suspensions, J. Photochem. Photobiol. A: Chem. 141 (2001) 231–239.
- [24] A.M. Peiro, J.A. Ayllon, J. Peral, X. Domenech, TiO $_2$ -photocatalyzed degradation of phenol and *ortho*-substituted phenolic compounds, Appl. Catal. B: Environ. 30 (2001) 359–373.