Research Journal of Recent Sciences ____ ISSN 2277-2502
Vol. **2(ISC-2012),** 82-89 **(2013)** *Res. J. Recent. Sci.*

Influence of Reaction Intermediates on the Oscillation in the Concentration of insitu formed Hydrogen peroxide during the Photocatalytic Degradation of Phenol Pollutant in Water on Semiconductor Oxides

Sindhu Joseph, Jyothi K.P., Suja P. Devipriya, Suguna Yesodharan and Yesodharan E.P.
School of Environmental Studies, Cochin University of Science and Technology, Kochi 682022, INDIA

Available online at: www.isca.in
Received 31th July 2012, revised 29th December 2012, accepted 22nd January 2013

Abstract

Phenols are common pollutants in many petrochemical industry wastewaters. Due to the stability of the aromatic ring their destruction requires extreme conditions. Photocatalysis using semiconductor oxides as catalysts is found to be an effective Advanced Oxidation Process (AOP) for the mineralisation of phenol. The degradation proceeds through the formation of various intermediates which eventually get mineralized to yield CO_2 and H_2O. The intermediates identified are hydroquinone, catechol, and benzoquinone which are formed by the interaction of photogenerated OH radicals with phenol. These intermediates do not accumulate beyond a particular concentration even though the phenol degradation continues unabated. The insitu formed H_2O_2 concentration increases and decreases periodically in a wave like fashion indicating concurrent formation and decomposition. Externally added H_2O_2 enhances the degradation rate of phenol initially due to the generation of more reactive OH radicals by inhibiting the recombination of photogenerated electrons and holes as well as by its own self decomposition. Externally added catechol and hydroquinone inhibit the degradation of phenol initially. However their influence on the fate of H_2O_2 is not quite significant. The study also shows that the formation/decomposition of H_2O_2 is concentration dependent and after the initial build up, the formation or decomposition takes precedence depending on the concentration and composition of the reaction system. Possible reasons for the observed phenomenon are analysed and a mechanism is proposed.

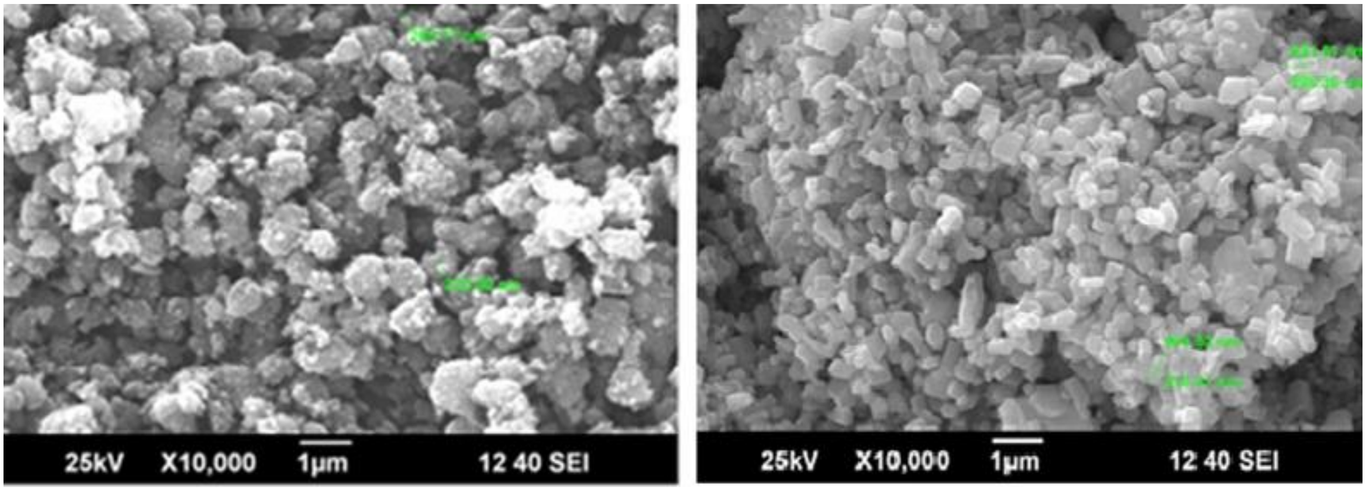
Keywords: Photocatalysis, zinc oxide, titanium dioxide, hydrogen peroxide, phenol, oscillation.

Introduction

Heterogeneous photocatalysis is an Advanced Oxidation Process (AOP), widely investigated for the degradation of organic pollutants in water and air[1-6]. The basic mechanism of photocatalysis involving hydroxyl radicals has also been well established[6]. Some of the major industrial pollutants in water degraded by photocatalysis include dyes, pesticides, petrochemicals etc. Semiconductor oxides such as TiO_2 and ZnO and their modifications by doping, immobilizing, metal deposition etc. are the most widely tested photocatalysts[7-9]. The process involves illumination of the catalyst particles either dispersed as slurry in the contaminated aqueous solution or in immobilized form. Combination of sonolysis and photocatalysis, referred to as sonophotocatalysis is emerging as another AOP in water purification[10]. It is also reported that the sonophotocatalytic degradation of phenol pollutant in water is more than the sum of individual sono and photocatalysed degradation, implying synergy in the combined process[11].

Phenols are common pollutants in many petrochemical industry wastewaters. Photocatalytic degradation of phenols in water has been investigated extensively[2,12-14]. The degradation mechanism involves complexation of OH radicals with the pi (π) system of the aromatic ring forming a pi complex in which the OH groups do not have a specific position in the molecule. The second step corresponds to the formation of a sigma complex between the carbon atom of the aromatic ring and the radical OH. The formation of the sigma complex is usually the rate determining step of the reaction[2,13].

One of the reaction products in all these processes is H_2O_2. However, the concentration of H_2O_2 does not increase beyond a limit, even though the degradation of the pollutant proceeds unhindered. It has been reported from our laboratories that the concentration of insitu formed H_2O_2 undergoes an oscillatory type of behavior resulting in periodic increase and decrease, possibly due to concurrent formation and decomposition[15,16]. Externally added H_2O_2 enhances the degradation rate significantly by inhibiting the rate of recombination of photogenerated electrons and holes, thereby increasing formation of reactive oxygen species and the degradation rate of pollutants[17,18]. However, the attention of researchers was always focused on achieving optimum mineralisation of the pollutant and consequently the fate of concurrently formed H_2O_2 has received much less attention. In the case of phenol, the eventual mineralisation proceeds through a number of intermediates, of which some are fairly stable. These intermediates can influence the overall photocatalytic degradation rate of phenol including the fate of insitu formed H_2O_2. In this paper, we are reporting our findings on the influence of reaction intermediates on the photocatalytic degradation of phenol and the oscillatory behavior of insitu formed and externally added H_2O_2.



a **b**

Figure-1
Typical SEM image of (a) TiO_2 and (b) ZnO

Material and Methods

ZnO and TiO_2 used in the study were supplied by Merck India Limited. In both cases the purity was over 99%. The surface areas of TiO_2 and ZnO, as determined by the BET method were 15 and 12 m^2/g respectively. The average particle size of both ZnO and TiO_2 was approx.10 μm, as determined by Scanning Electron Microscopy (SEM). Typical SEM of ZnO and TiO_2 are shown in figure 1.

Phenol AnalaR Grade (99% purity) from Qualigen (India) was used as such without further purification. All other chemicals were of AnalaR Grade or equivalent. The catalytic reactions were performed as reported earlier[19]. The concentration of phenol left behind was analyzed periodically by Spectrophotometry at 500 nm. The intermediates catechol (CC), hydroquinone (HQ) and benzoquinone (BQ) were monitored by HPLC using UV detector. H_2O_2 was determined by iodometry[16]. Mineralization was identified by the evolution of CO_2.

Results and Discussion

Investigations on the photocatalytic degradation of phenol using ZnO and TiO_2 catalysts under identical conditions showed that no significant degradation took place in the absence of UV light or the catalyst suggesting that both catalyst and light are essential to effect degradation. ZnO is slightly more efficient as a photocatalyst compared to TiO_2. The ultimate reaction products are CO_2 and H_2O formed by the mineralisation of phenol. H_2O_2 is an end- product as well as intermediate which participate in further reactions with phenol and reactive oxygen species resulting in the formation of H_2O and O_2. The reaction intermediates detected are CC, HQ and traces of BQ. The concentration of the intermediates is comparatively small probably because they may be getting transformed into other products and eventually mineralized at the same rate or faster compared to parent phenol (figure 2).

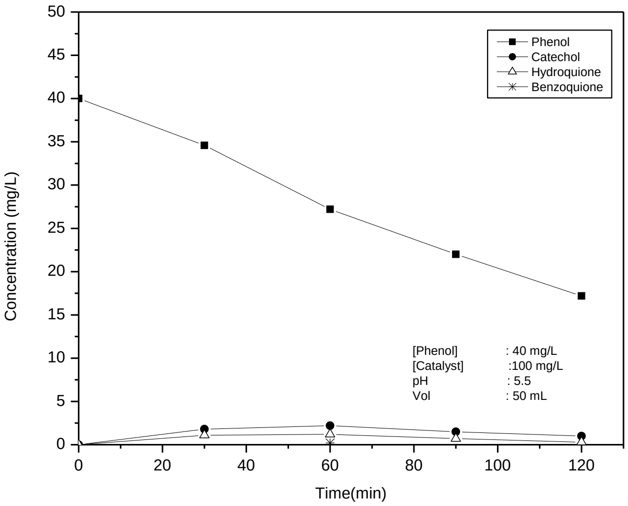


Figure-2
Photocatalytic degradation of phenol and formation of intermediates on ZnO

While there is a clear increase and later stabilization in the degradation of phenol, the concentration of intermediates does not increase correspondingly. The intermediates detected are the same in the case of both ZnO and TiO_2 even though the quantities are slightly different. BQ is not detected in the case of TiO_2 while a very small quantity is detected in one instance in the case of ZnO. Intermediates such as pyrogallol, 2-hydroxy benzoquinone and 1,2,4 benzene triol reported by other authors[2] are not detected in our experiments. The H_2O_2 formed insitu increases initially. However, after reaching a maximum its concentration decreases and reaches a minimum where it starts rising again. This periodic increase and decrease in the concentration of H_2O_2 in a wavelike fashion indicates concurrent formation and decomposition (figure-3).

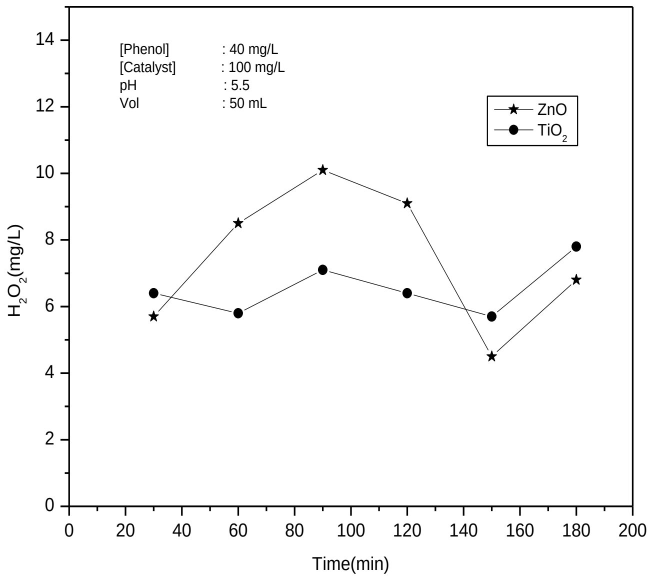


Figure-3
Formation and decomposition of H_2O_2 during the photocatalytic degradation of Phenol

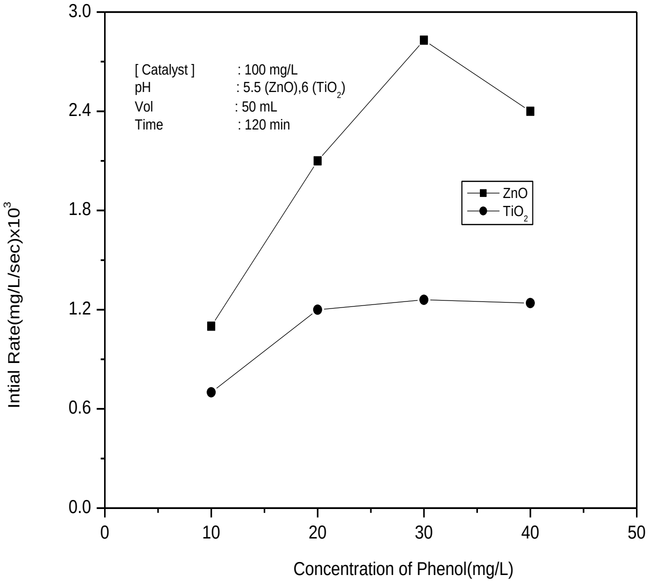


Figure-4
Effect of concentration of Phenol on its photocatalytic degradation on ZnO and TiO_2

One of the most important operating parameters in the photocatalytic degradation of phenol in presence of semiconductors is the pH of the medium because it affects the surface charge or the isoelectric point of the catalyst particles, size of the catalyst aggregates and the positions of the valence and conduction bands. In the case of ZnO and TiO_2, the effect of pH is often correlated with their respective Point of Zero Charge (PZC). When the pH of the medium is less than the PZC of the catalyst the surface of the catalyst becomes positively charged and the neutral or negatively charged contaminant ions can get adsorbed onto the activated catalyst surface leading to enhanced degradation. In the case o both ZnO and TiO_2 acidic pH favours such a situation. The natural pH of water containing small quantities of phenol contaminant is in the acidic range, approx. 5.5 and 6 in ZnO and TiO_2 suspension respectively. Hence all studies in presence of ZnO and TiO_2 were conducted in the natural pH of phenol solution which also happens to be the optimum pH for degradation of phenol[11].

Similarly, the optimum catalyst loading of ZnO and TiO_2 for phenol degradation has been determined experimentally and the values are100 and 250 mg/L respectively. Beyond the optimum loading the light photon absorption coefficient decreases radially. However such a light attenuation over the radial distance does not obey the Beer-Lambert law due to the strong absorption and scattering of light photons by the catalyst particles[20]. Excess catalyst particles lead to screening of light which reduces the effective surface area of the semiconductor being exposed to illumination leading to decreased photocatalytic efficiency. Investigations on the effect of concentration of phenol on its photocatalytic degradation show that the rate of degradation is optimum at 30 mg/L in presence of both ZnO and TiO_2 (figure 4)

All further investigations in this report were carried out using the optimized parameters as above, unless mentioned otherwise.

The effect of addition of major intermediates catechol and hydroquinone at different concentrations on the rate of phenol degradation in presence of ZnO are shown in figures 5 and 6 respectively.

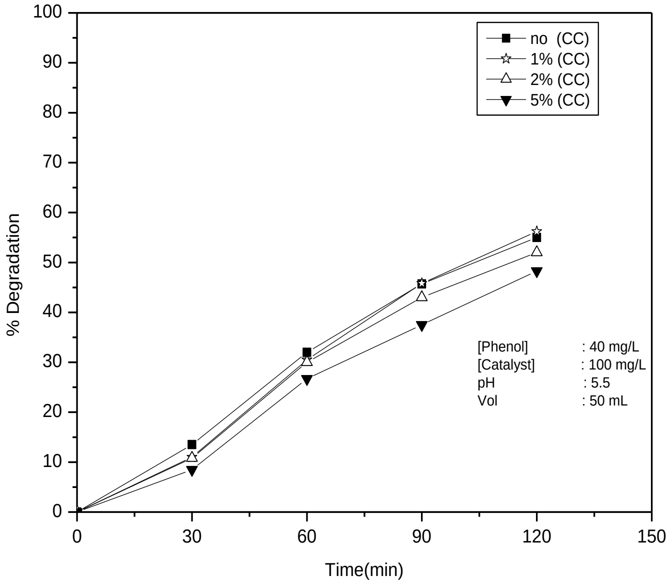


Figure-5
Effect of externally added intermediate Catechol (CC) on the photocatalytic degradation of phenol on ZnO

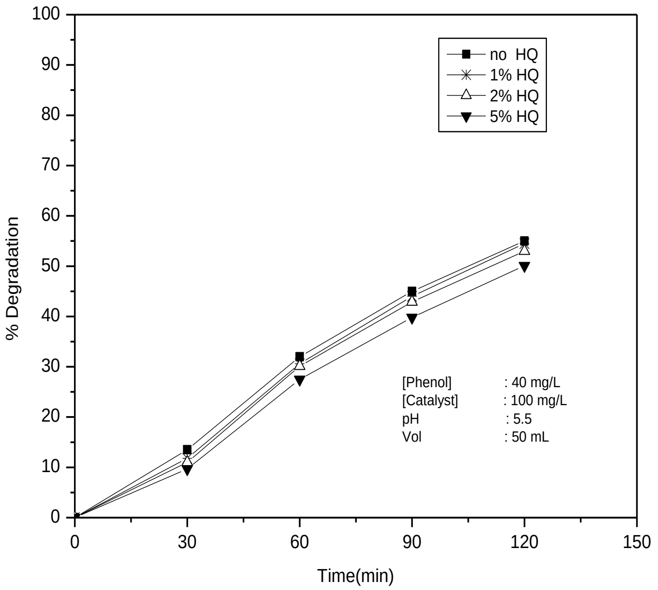


Figure-6
Effect of externally added intermediate Hydroquinone (HQ) on the photocatalytic degradation of phenol on ZnO

The rate of degradation of phenol is retarded slightly, probably because the intermediates are also getting adsorbed on the surface, thereby reducing the surface concentration and consequent activation of phenol molecules. The intermediates are also getting degraded at comparable or even faster rate. Once they are completely removed from the surface, majority of the vacated sites will be occupied by phenol and its degradation proceeds smoothly without any hindrance. The behavior is identical in the case of TiO_2 also. Evaluation of comparative adsorption of phenol, catechol and hydroquinone in equimolar concentrations on ZnO and TiO_2 show that the extent of adsorption is approximately the same. The inhibition of phenol degradation by CC as well as HQ is increasing with increase in their concentration. At higher concentrations the intermediates occupy more surface sites and because of the concentration advantage, at least part of the surface sites vacated by mineralized intermediates will be occupied by fresh molecules of the same. In the absence of externally added intermediates, the concentration of insitu formed intermediates is very small and because they degrade concurrently, the relative concentration of phenol will always be more. Hence the surface will always be preferentially occupied by phenol and influence of the intermediates on the degradation will be negligible.

The effect of the intermediates on the fate of H_2O_2 is plotted in figure 7.

In presence of the added intermediates also the oscillation is sustained. However, the H_2O_2 at the maxima as well as the minima in the oscillation curve is more in presence of the added intermediate. This implies that the rate of formation is enhanced by the intermediate while the rate of decomposition is inhibited. This can be attributed to the relatively faster rate of degradation of catechol or hydroquinone which produces more OH radicals compared to phenol only. This is further verified by investigating the effect of concentration of the intermediates on the oscillation in the concentration of H_2O_2 (figures 8 a,b) in presence of ZnO. The results show that the maxima and minima of H_2O_2 in the oscillation curve are increasing with increase in the concentration of the intermediate.

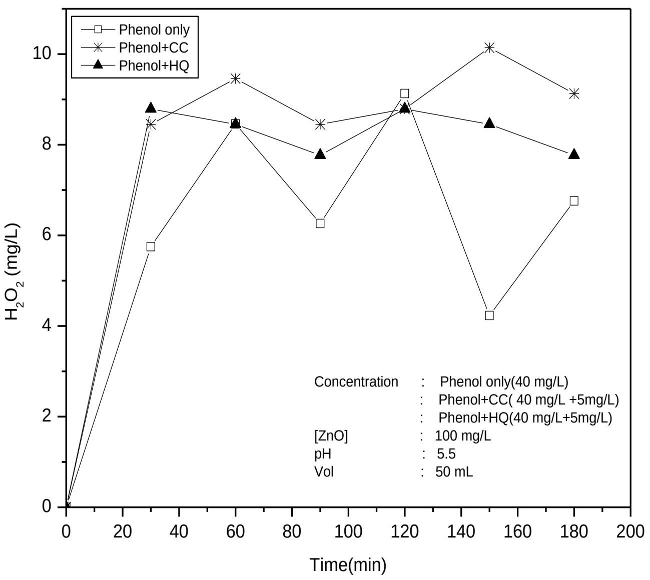


Figure-7
Effect of added intermediate CC and HQ on H_2O_2 formed during the photocatalytic degradation of phenol

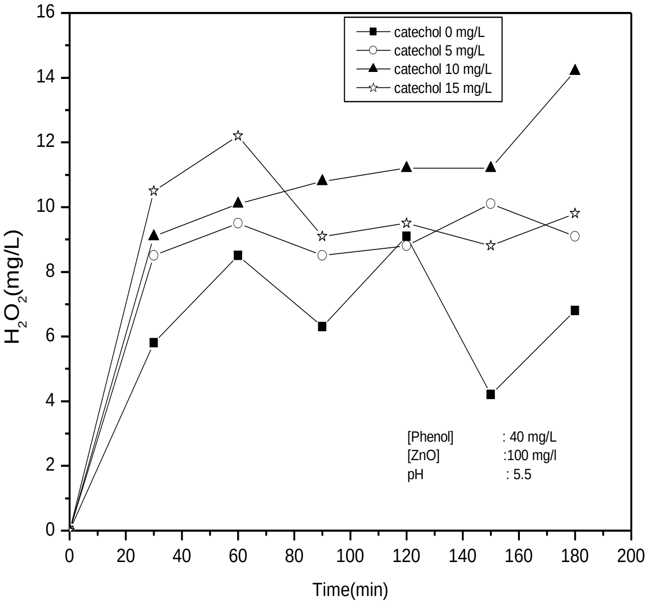


Figure-8 (a)
Effect of intermediate CC at different concentration on H_2O_2 the photocatalytic degradation of phenol in presence of ZnO

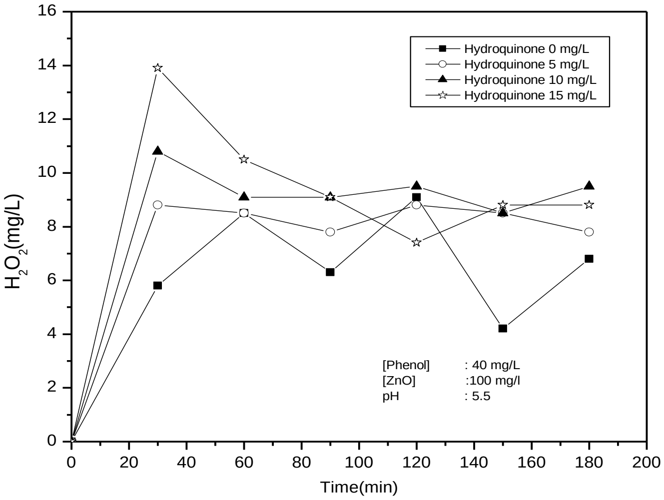


Figure-8 (b)

Effect of added intermediate HQ on H_2O_2 formed during the photocatalytic degradation of phenol in presence of ZnO

The influence of concentration of the intermediate is less pronounced in the case of TiO_2 catalysts (not shown here). The surface composition as well as the composition of the catalyst-bulk interface is more or less the same in presence of the intermediate.

The basic mechanism of the photocatalytic degradation of phenol involves the formation of OH radicals initiated by the activated catalyst surface followed by their interaction with the substrate as well as various intermediates such as catechol, hydroquinone and p-benzoquinone as follows: [2].

$$\text{Semiconductor} + h\nu \rightarrow h^+ + e^- \tag{1}$$

$$h^+ + e^- \rightarrow \text{Heat} \tag{2}$$

$$h^+ + H_2O \rightarrow H^+ + {}^{\cdot}OH \tag{3}$$

$$OH + {}^{\cdot}OH \rightarrow H_2O_2 \tag{4}$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \tag{5}$$

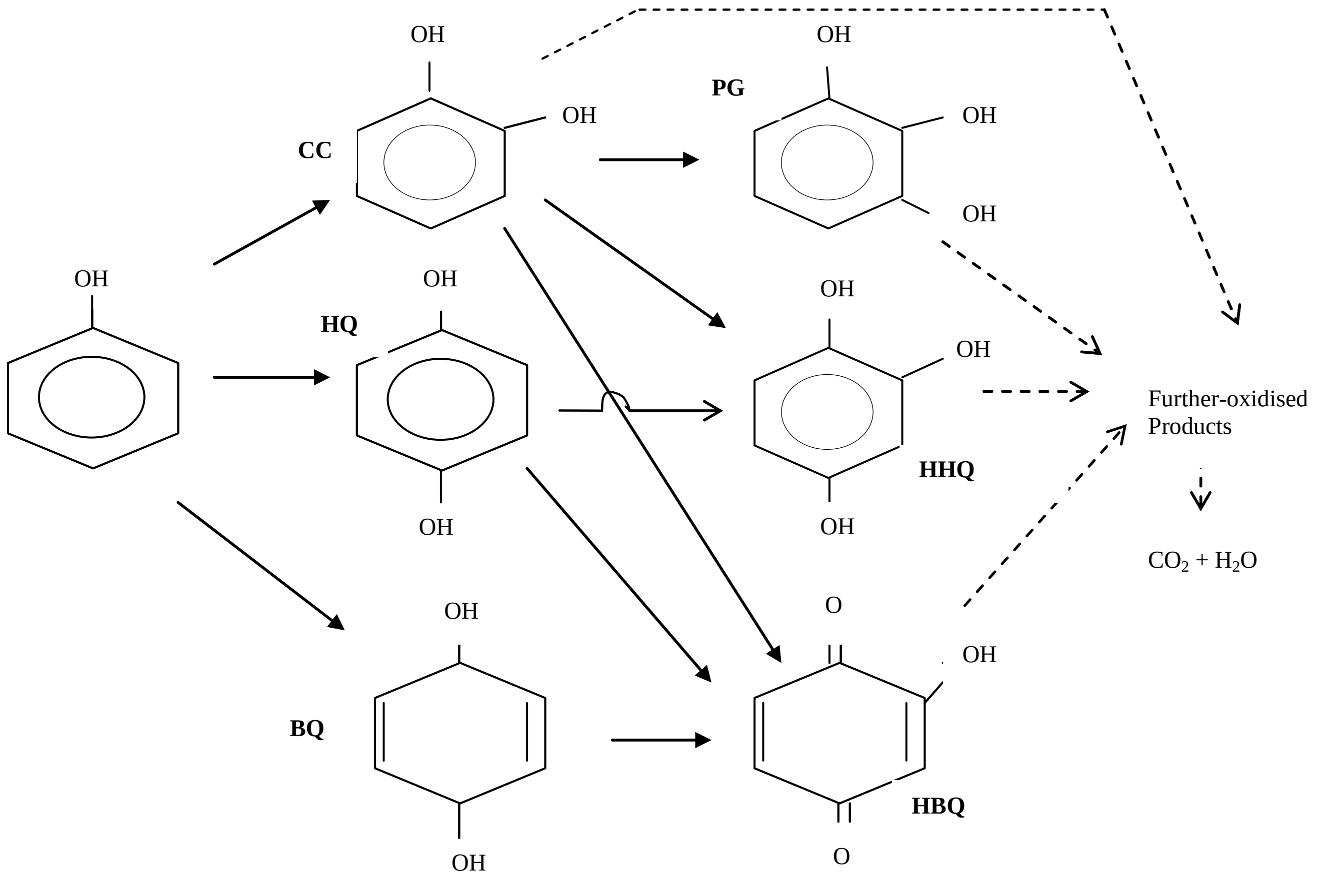
$$O_2^{\cdot -} + H_2O \rightarrow HO_2^{\cdot} + {}^{-}OH \tag{6}$$

$$h^+ + {}^{-}OH \rightarrow {}^{\cdot}OH \tag{7}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 \tag{8}$$

Various reactive oxygen species formed as above will interact with phenol as shown in scheme 1.

$$\text{Reactive oxygen species} + \text{phenol} \rightarrow \text{Intermediates} \rightarrow H_2O + CO_2 \tag{9}$$



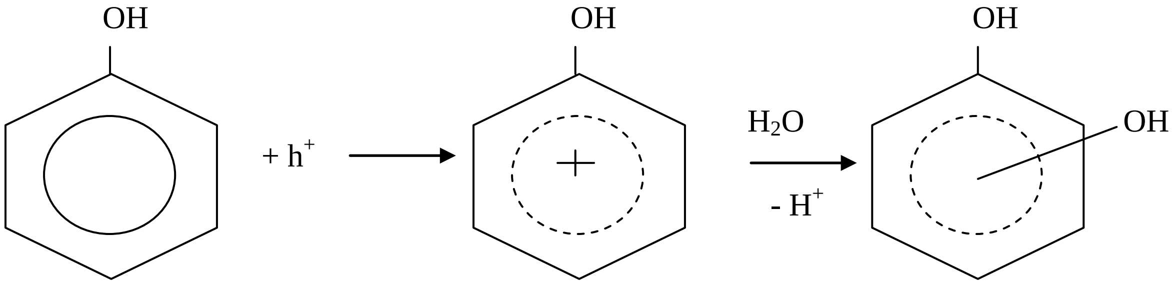
Scheme-1

Mechanism of the photocatalytic mineralisation of phenol on ZnO

It is also possible for the photogenerated holes to react with adsorbed phenol to yield dihydroxycyclohexadienyl radicals via phenol radical cation[2,21]. The energy of holes in the valence band of TiO_2 is approx. -7.5eV which is high enough for the holes to react with H_2O and organic compounds. This would happen if phenol is strongly adsorbed onto the surface. Adsorption studies of very dilute solution of phenol in water (< 30 mg/L) on ZnO and TiO_2 shows that phenol does get adsorbed on to the surface under our reaction conditions, though not very significantly. Hence the possibility of scheme 2 cannot be ruled out.

Based on the observations from the direct photosonochemical degradation of phenol in water, Wu etal[13] suggested that reaction of hydroxyl radical with phenol in presence of oxygen leads to the formation of peroxyl radicals, which form hydroquinone and catechol after eliminating superoxide radicals and rearranging the aromatic system. These compounds degrade to carboxylic acids and eventually to CO_2. However, in the present study carboxylic acid intermediate is not detected probably because of its shorter lifetime or a different mechanism of degradation altogether.

Under mild oxidizing conditions provided by H_2O, direct conversion of phenol to CO_2 and H_2O is not probable. But water can take part in the reaction along with the dissolved oxygen present in the medium to yield hydroxylated intermediates and then the final product[22]. The intermediates formed during the degradation depend on the reaction conditions and the reagents used. Velasco etal[23] reported the presence of hydroquinone and benzoquinone during the photocatalytic degradation of phenol in presence of carbon/titania composite. In the presence of Fenton's reagent, more intermediates such as catechol resorcinol, hydroquinone, p-benzoquinone and o-benzoquinone have been detected[24]. When the degradation was carried out with Fe(II)-Fe(III) green rust, only non-aromatic intermediates were detected[25]. Sivalingam etal[14] reported formation of catechol and hydroquinone when the degradation was carried out in presence of Degussa P-25. Pyrogallol also has been detected during the photocatalytic degradation of phenol by base metal-substituted vanadates[22]. In the present study we could detect the presence of only three intermediates; catechol, hydroquinone and traces of benzoquinone which also disappeared eventually. This indicates that the intermediates also get degraded fast and as time progresses, as the phenol concentration decreases, the rate of degradation of the intermediate becomes even faster. The rates of degradation of phenol, catechol and hydroquinone under identical conditions on ZnO and TiO_2 are given in figure 9 which shows that the rates are comparable.



Scheme-2
Reaction of photogenerated hole with H_2O and phenol

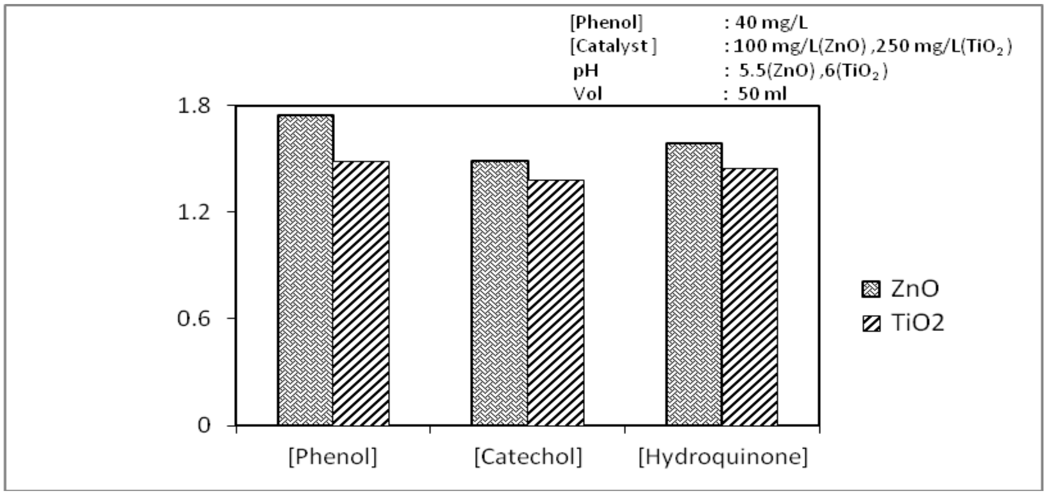


Figure-9
Comparative initial rate of degradation of Phenol, Catechol and Hydroquinone

The present study was carried out at the natural pH of the phenol solution-catalyst suspension, ie 5.6-5.7. Serpone etal [26] have reported that the intermediates depend on the pH conditions in the case of ultrasonic removal of phenol. They reported that the principal intermediates at pH 3 are catechol, hydroquinone and p-benzoquinone while only catechol and hydroquinone were detected at pH 5.4-5.7. No intermediates were observed at pH 12. In the current study, the intermediates are the same in case of both ZnO and TiO_2 indicating that in the case of photocatalysis, pH is the prime factor that determines the mechanism of the reaction.

The periodic change in the concentration of H_2O_2 and the oscillatory behavior suggest that its formation and decomposition takes place simultaneously. The decrease in concentration can be either due to its parallel decomposition into water and oxygen and/or its participation in the degradation of phenol[15,27,28]. At the same time the removal of phenol continues. H_2O_2 formed consequent to reactions (1) to (8) decomposes simultaneously as follows:

$H_2O_2 + h\nu\ (\lambda < 380\ nm) \rightarrow 2\ ^{\cdot}OH$ (10)

$2\ h_{vb}+ + H_2O_2 \rightarrow\ O_2 + 2\ H^+$ (11)

$2\ e_{cb}^- + 2\ H^+ + H_2O_2 \rightarrow 2\ H_2O$ (12)

$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot}$ (13)

$H_2O_2 + HO_2^{\cdot} \rightarrow H_2O + {}^{\cdot}OH + O_2$ (14)

Being a complex free radical system, other interactions leading to the formation and decomposition of H_2O_2 are also possible.

Since both the formation and decomposition are initiated by free radicals and reactive oxygen species, the surface plays an important role. Phenol and various intermediates formed have similarity in the adsorption and photocatalytic behavior. Hence the intermediates are not expected to influence the oscillatory behavior of H_2O_2 significantly, at least in the concentration range of insitu formation. However, the concentrations of H_2O_2 at the maxima and minima of the curve increase in the presence of the added intermediates. This indicates that the intermediates enhance the formation of H_2O_2 and inhibits its decomposition, though slightly. The formation and decomposition of H_2O_2 proceeds in parallel after build up of a critical initial concentration. Depending on the concentration of the substrate and H_2O_2 at any point of time, either of the process will predominate.

Conclusion

Photocatalytic degradation of phenol proceeds through two major intermediates; catechol and hydroquinone. The intermediates do not influence the rate of degradation significantly as they themselves undergo degradation and eventual mineralisation under the experimental conditions. H_2O_2 formed in the process undergoes simultaneous formation and decomposition resulting in oscillation in its concentration. Depending on the relative concentration of the substrate, stable intermediates and H_2O_2, the formation or decomposition will predominate. The degradation of phenol as well as the formation and decomposition of H_2O_2 is initiated by $^{\cdot}OH$ radicals generated at the photo-activated semiconductor oxide surface. The degradation ultimately leads to complete mineralization of phenol. The study provides convincing experimental evidence for the concurrent formation and decomposition of H_2O_2 in photocatalytic systems. Further, it demonstrates that semiconductor mediated photocatalysis can be developed into a viable route for the removal of organic water pollutants.

Acknowledgement

The authors gratefully acknowledge the financial support from the University Grants Commission (UGC)/Dept of Science and Technology (DST), Government of India to SJ (UGC JRF), JKP (UGC JRF) and SPD (DST WOS-A).

References

1. Herrmann J.M., Heterogeneous Photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catal. Today*, **53**, 115-129 **(1999)**

2. Okamoto K., Yamamoto Y., Tanaka H., Tanaka M. and Itaya A., Heterogeneous photocatalytic degradation of phenol over TiO_2 powder, *Bull Chem Soc. Jpn*, **58,** 2015-2022 **(1985)**

3. Devipriya S. and Yesodharan S., Photocatalytic degradation of pesticide pollutants in water, *Solar Energy Mater and Solar Cells*, **86**, 309-348 **(2005)**

4. Sakthivel S., Neppolean B., Shankar M.V., Arabindoo B., Palanichamy M. and Murugesan V., Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO_2, *Solar Energy Materials and Solar Cells*, **77(1),** 65-82 **(2003)**

5. Uchida H., Itoh S. and Yoneyama H., Photocatalytic decomposition of propyzamide using TiO_2supported on activated carbon, *Chemistry Letters*, **22**, 1995-1998 **(1993)**

6. Turchi C.S. and Ollis D.F., Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attacks, *J. Catal*, **122**, 178-192 **(1990)**

7. Wu C.G., Chao C.C. and Kuo F.T., Enhancement of the photocatalytic performance of TiO_2 catalysts via transition metal modification, *Catal. Today*, **97(23),** 103-112 **(2004)**

8. Sakthivel S., Shankar M.V., Palanichamy M., Arabindoo A., Bahnemann D. M. and Murugesan B.V., Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au, and Pd deposited on TiO_2 catalyst, *Wat. Res.*, **38 (130),** 3001-3008 (**2004)**

9. Pellegrin J.Y., Le Pleux L, Blart L.E., Renaud A., Chavilion B., Szuwarski N., Boujitita M., Cario L., Jobic

S., Jacquemin D. and Odobel F., Ruthenium polypyridine complexes as sensitisers in NiO based p-type dye-sensitized solar cells: Effects of the anchoring groups, *J Photochem. Photobiol. A-Chem.*, **219(2)**, 235-242 **(2011)**

10. Joseph C.G., Puma G.L., Bono A., Krishniah D., Sonophotocatalysis in advanced oxidation process: A short review, *Ultrason., Sonochem.* **16**, 583-589 **(2009)**

11. Anju S.G., Suguna Yesodharan and Yesodharan E.P., Sonophotocatalytic degradation of phenol over semiconductor oxides, *Chem Eng. J.*, **189-190(1),** 84-93 **(2012)**

12. Kim S. and Choi W., Visible light induced photocatalytic degradation of 4-chlorophenol and phenolic compounds in aqueous suspension of pure titania: demonstrating the existence of surface complex-mediated path, *Journal of Phys. Chem. B*, **109(11),** 5143-5149 **(2005)**

13. Wu C., Liu X., Wei D., Fan J., Wang L., Photosonochemical degradation of phenol in water, *Wat. Res.* **35(16)** 3927-3933 **(2001)**

14. Sivalingam G., Priya M.H. and Madras G., Effect of substitution on the photocatalytic degradation of phenol using combustion synthesized TiO_2: Mechanism and kinetics, *Appl. Catal. B: Environ*., **51,** 67-76 **(2004)**

15. Anju S.G., Jyothi K.P., Sindhu Joseph, Suguna Yesodharan and Yesodharan E.P., Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comarative efficacy of ZnO, TiO_2 and ZnO-TiO_2, *Res J Rec Sci.,* **1**, 191-201 **(2012)**

16. Kuriacose J.C., Ramakrishnan V. and Yesodharan E.P., Photoinduced catalytic reactions of alcohols on ZnO suspensions in cyclohexane: Oscillation in the concentration of H_2O_2 formed, *Indian J. Chem*., **19A**, 254-256 **(1978)**

17. Pignatello J.J. and Sun Y., Complete oxidation of metolachlor and methyl parathion in water by photoassisted fenton reaction, *Wat Res*., **29**, 1837-1844 **(1995)**

18. Han W., Zhu W., Zhang P., Zhang Y. and Li L., Photocatalytic degradation of phenols in aqueous solutions under irradiation of 254 and 185 nm UV light, Catal. Today, **90**, 319-324 **(2004)**

19. Rabindranathan S., Devipriya S. and SugunaYesodharan, Photocatalytic degradation of phosphamidon on semiconductor oxides, *J. Hazard. Mater.,* **102**, 217-229 **(2003)**

20. Chen C.C., Lu, C.S., Chung and Y.C., Jan, J.L., UV light induced photodegradation of malachite green on TiO_2 nanoparticles, *J. Hazard.Mater.*, **141**, 520-528 **(2007)**

21. Hashimoto K., Kawai T. and Sakata T., *Photocatalytic reactions of hydrocarbons and fossil fuels with water-Hydrogen production and oxidation, J Phys Chem* , **88**, 4083 **(1984)**

22. Desahpande P.A., Madras G., Photocatalytic degradation of phenol by base metal substituted orthovanadates, *Chem. Eng. J.*, **161,** 136-145 **(2010)**

23. Velasco L.F., Parra J.B. and Ania C.O., Role of activated carbon features on the photocatalytic degradation of phenol, *Applied Surf. Sci.* **256,** 5254-5258 **(2010)**

24. Yalfani M.S., Contreras S., Medina F. and Suegras J., Phenol degradation by Fenton's process using catalytic insitu generated hydrogen peroxide, *Appl. Catal. B:Environ*, **89**, 519-526 **(2009)**

25. Hanna K., Kone K. and Ruby T.C., Fenton-like oxidation and mineralization of phenol using synthetic Fe(II)-Fe(III) green rust, *Environ Sci. Poll. Res*., **17**, 124-134 **(2010)**

26. Serpone N., Terzian R., Colarusso P., Minero C., PelizettiE and Hidaka H., *Res. Chem. Int.* **18(2-3),** 183-190 **(1992)**

27. Anju S.G., Jyothi K.P., Sindhu Joseph, Suguna Y.esodharan and Yesodharan E.P., Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comparative efficacy of ZnO, TiO_2 and ZnO-TiO_2, *Res. J. Recent Sci.,* **1**, 191-201 **(2012)**

28. Hartmann J., Bartels P., Mau U., Witter M., Tumpling W.V., Hofmann J., Nietzschmann E., Degradation of the drug diclofenac in water by sonolysis in presence of catalysts, *Chemosphere*, **70**, 453-461 **(2008)**